
Canarium Odontophyllum Waste-Based Activated Carbon for COD Reductions In Textile Wastewater

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Abstract: It has been successfully studied how to synthesize activated carbons from the seeds of *Canarium odontophyllum* (COAC) via physicochemical activation. Carbon dioxide (CO₂) gasification and potassium hydroxide (KOH) impregnation were used to do physicochemical activation. The reduction of COD in industrial textile effluent was used to assess the COAC's adsorption efficacy. Using an experimental methodology, the findings showed that the adsorption performance for all pollutants was significantly influenced by the activation temperature, activation time, and KOH impregnation ratio (IR). The ideal COAC preparation parameters were 798°C for activation temperature, 1.16 hours for activation time, and 2.65 for IR. COAC resulted in a 64.10% decrease in COD. The Langmuir model provided the best fit for the adsorption of the adsorbate onto COAC.

Keywords: *Activated carbon, textile wastewater, physicochemical activation, textile wastewater*

1.0 Introduction

Malaysia is one of many nations whose economies have benefited from the textile industry. There are roughly 1500 textile manufacturers in Malaysia overall, and this number is constantly rising due to the demand for textile goods (Ismail et al., 2015a). Many textile businesses deal with several processing steps, including the production of fibres, spinning and processing, yarn preparation, fabric manufacture, bleaching, dyeing, printing, and finishing (Hayat et al., 2015). Nonetheless, every step results in outputs that call for the proper remedies. In actuality, the textile industry uses a variety of chemicals and solvents in wet processes across the entire production line.

As a result, wastewater from the textile sector has significant concentrations of salts, dyes, chemical oxygen demand (COD), nutrients (phosphorus and nitrogen), and hazardous substances (Ahmad et al., 2015). The textile sector is likewise subject to ongoing demands for durability, quality, and innovation. To meet market demand, this leads to an additional rise in the use of chemicals. Textile manufacturers are looking for quick, quick, and long-lasting chemical products to match the market supply due to the ongoing need for quality, innovation, and durability. As a result, more chemicals are being used to meet market demand, which has resulted in an excess of wastewater that needs to be effectively treated.

Because textile wastewater is hazardous to both the environment and living things, it may pose a concern to water bodies if it is dumped directly into the environment (Freitas et al., 2015). As a result, before being released into the environment, these wastes must be treated.

According to the Environmental Quality Regulation 1989, wastewater containing colours is categorized as scheduled waste in Malaysia (Ismail et al., 2015b). The Environmental Quality Act of Malaysia's strict regulations on discharge quality further restrict the industry's ability to comply. Therefore, ongoing research and study on the treatment of textile wastewater is necessary for a sustainable ecosystem.

2.0 Literature Reviews

2.1 Chemical Oxygen Demand (COD)

An indirect indicator of the quantity of organic molecules in water or wastewater is the chemical oxygen demand, or COD. COD is an essential instrument for characterizing water quality since it can identify the quantity of organic contaminants present in surface water. The mass of oxygen consumed per liter of solution is represented in milligrams per liter (mg/L) or parts per million (ppm) (Yadav et al., 2013). To put it another way, the COD assesses the amount of potential total oxygen in a wastewater sample, which includes the oxidizable elements that the BOD analysis did not eliminate (Zhen et al., 2013).

Because of their hue, untreated wastewater from yarn printing, fabric processing, and dye coloring poses a threat to the environment. Although the biological treatment method is typically effective in removing suspended particles and BOD₅, its low reaction rate and low efficiency make it unsatisfactory. Approximately 90% of BOD₅, 40–50% of COD, and 10–30% of color are often removed using various activated sludge treatment techniques (Yadav et al., 2013).

On the other hand, textile wastewater is typically treated with lime or ferrous sulphate for color and COD removal, which is highly successful at 70–90% and 50–60%, respectively (Pang et al., 2013). Fenton's oxidation and the ozone process are further treatments that remove COD in ranges of 33% and 59%, respectively, whereas color removal is 91% and 89% (Ismail, et al., 2015a).

2.2 The Seeds of *Canarium Odontophyllum* Waste-Based Activated Carbon (COAC)

The potential for sustainable solutions in textile wastewater treatment is demonstrated using activated carbon made from agricultural waste, such as *Canarium Odontophyllum* seeds, for COD removal. This method gives value to underutilized resources while also addressing environmental issues through the repurposing of waste materials.

2.3 Preparation Method of *Canarium Odontophyllum* Waste-Based Activated Carbon (COAC)

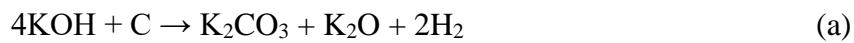
Both single-step and two-step pyrolysis can be used to create activated carbon. Carbonization and activation occur simultaneously in single-step pyrolysis, while activation occurs after carbonization in the latter (Djilani et al., 2015).

A non-oxidized thermal process called carbonization turns raw materials into solid char. This procedure gives the char its first porosity and increases its carbon concentration. Typically, the carbonization temperature falls between 400 and 850°C. Agricultural waste's hemicelluloses, cellulose, and lignin would undergo a dehydration reaction and linkage breaking to produce solid char during the carbonization process.

The process of activation increases the porosity of char and gets rid of tar that is obstructing the pores. Char can be activated in three different ways: chemically, physiochemically, and physically. In physical activation, gases like oxygen (O₂), carbon dioxide (CO₂), and steam are used to pyrolyze the char at a high temperature in an oxidizing atmosphere. Since CO₂ is simple to handle and clean, it is preferred. To maintain a high response rate, the activation temperature is typically set higher than 900 °C. Pores are created and existing pores are enlarged by the reaction between the carbon atom and the oxidizing gas (Njoku et al., 2014).

Conversely, chemical activation often involves impregnating char with chemical activating agents such ZnCl₂, KOH, H₃PO₄, K₂CO₃, and NaCO₃ (Nowicki et al, 2015). Chemical activation is superior to physical activation since it may be carried out in shorter amounts of time and at lower temperatures (between 450 and 900 degrees Celsius). The weight ratio of the char sample to the chemical utilized determines the impregnation ratio (IR). The growth of the adsorbent's porous structure, especially its surface area, depends on optimal IR. Large surface area and strong adsorption capacity are the results. KOH's selectiveness in the

activation process makes it an efficient activating agent. The following is the chemical reaction between carbon material and KOH.



On the other hand, too much infrared radiation can create a layer of insulation on the adsorbent that blocks pores. According to Yadav et al. (2013), the existence of K_2O and K_2CO_3 or K residues collected on the porous surface was suggested by the appearance of white spheres and fluffy materials at very high IR of KOH. Therefore, to obtain a highly porous characterization of AC, optimal IR is necessary.

Physical and chemical treatment are also components of physicochemical activation. Before undergoing CO_2 activation to create AC, the sample was first impregnated with a chemical agent akin to the chemical activation approach. During the activation phase, this molecule hinders the pyrolytic breakdown and delays the creation of tars. In addition to CO_2 gasification, the presence of chemical increases the pore size and porosity of AC (Ismail et al., 2015a). Chemicals could enhance pore growth at lower activation temperatures, between 600 and 900 degrees Celsius, when combined with physical treatment (Hameed et al., 2009). As a result, it will lower energy usage by using chemical treatment to produce AC.

2.4 Adsorption Isotherm

The amount of adsorbate that isothermally settles onto the adsorbent versus pressure (for gas) or concentration (for liquid) is typically used to characterize adsorption. The distribution of adsorbed molecules between the liquid and solid phases at equilibrium is described by the isotherm. To build the adsorption system, the most suitable adsorption isotherm for each adsorbent system must be determined (Ismail et al., 2015b).

The adsorption data are interpreted using popular isotherm models like Freundlich and Langmuir. The experimental equilibrium data are fitted using the isotherm models. The isotherm parameters were estimated using the linear regression approach. The coefficient of determination, or R^2 , was used to analyze how well the isotherm suited the experimental data. The values range from 0 to 1, and the parameter that best correlates the adsorption behavior is the one with the closest R^2 to unity and the lowest percentage error (Ismail et al., 2015a).

The most popular sorption isotherm for the sorption of a solute from a liquid solution is the Langmuir adsorption isotherm. This model helps anticipate the presence of monolayer

coverage of the adsorbate on the outer surface of the adsorbent by assuming that intermolecular forces rapidly diminish with distance. The expression for the Langmuir model is:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (1)$$

The linear form of Langmuir isotherm equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_e \quad (2)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_0 is the maximum monolayer adsorption capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant related to the free energy adsorption (L/mg). The constant value can be evaluated from intercept and slope of the linear plot of experimental data of (C_e/q_e) versus C_e . The essential characteristics of Langmuir equation can be expressed in terms of dimensionless separation factor, R_L , defined as:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (3)$$

Where C_0 is the highest initial solute concentration whereas R_L value implies the adsorption to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Ismail *et al.*, 2015a).

2.5 Freundlich Isotherm

The adsorption of heterogeneous surfaces or surface supporting sites with different affinities is the basis for the empirical equation known as the Freundlich model. The stronger binding sites are thought to be occupied initially, and as site occupation increases, the binding strength is thought to diminish. The expression for the Freundlich isotherm is:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where q_e is amount of adsorbate adsorbed per unit mass of adsorbent (mg/g); k_f is Freundlich isotherm constant (mg/g).(L/mg)^{1/n}; which indicate the relative adsorption capacity of the adsorbent related to the bonding energy; C_e is equilibrium concentration of the adsorbate (mg/L) and n_F is the heterogeneity factor representing the deviation from linearity of adsorption

and is also known as Freundlich coefficient. The equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (5)$$

A plot of $(\log q_e)$ against $(\log C_e)$ yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constant can be obtained from the slope $(1/n)$ and intercept $(\log K_f)$ of the linear plot of experimental data. The n_F parameter indicates whether the adsorption is linear ($n_F = 1$), chemical process ($n_F < 1$) or physical process ($n_F > 1$). The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity, becoming more heterogeneous as its value gets closer to zero (Hameed *et al.*, 2009).

3.0 Methodology

3.1 Analytical Methods

The COD test was conducted for high range concentrations (20-1500 mg/L) using Method 8000 (Program number 435). HACH provided the COD reagent. The COD vial was first filled with 2.5 mL of sample and heated to 150 °C for two hours on a reactor before being measured. A benchtop pH meter PC 2700 (Thermo Scientific, USA) was used to measure the pH of the textile wastewater while the wavelength was set at 620 nm.

3.2 Activated Carbon Preparation

Figure 1.0 depicts the experimental setup used to make the activated carbon (AC). The vertical tube reactor made of stainless steel (SS) with a programmable temperature controller makes up the AC preparation rig. The N_2 and CO_2 flow rates fed to the reactor were managed by the gas flow meter. The piping system was mainly made of Teflon and SS fittings and pipes. The carbonization and activation operations were carried out using a vertical stainless-steel reactor that measured 150 mm in length and 25 mm in inner diameter. To keep the sample intact, an SS wire mesh was placed at the bottom of the tubular reactor.

The reactor was set up on a pedestal within a vertical tubular furnace that had a programmable controller (Model Carbolite, USA). The furnace measured 500 mm in length and 82 mm in inner diameter. The temperature of the sample inside the reactor was measured

using a K-type thermocouple. The thermocouple has a maximum tolerance of 1000 °C. A condenser received the extra flue gas.

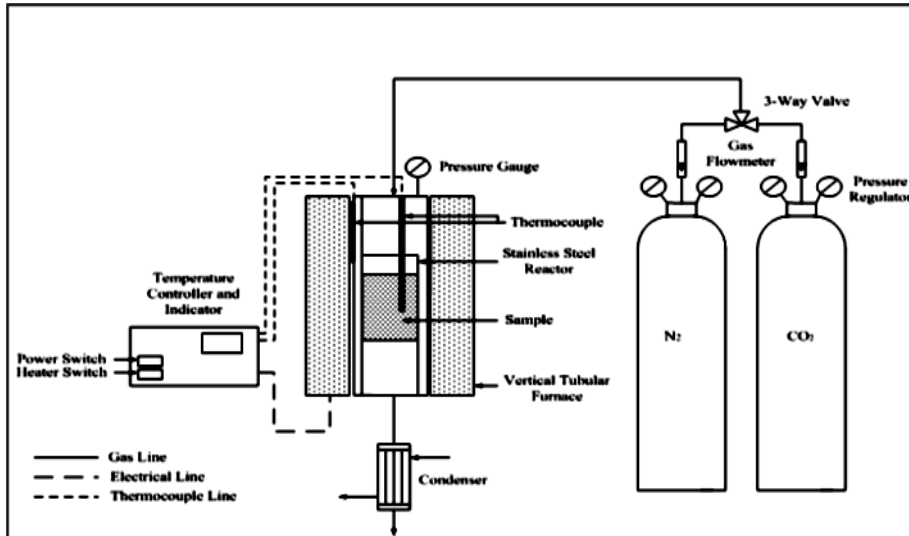


Figure 1.0: Schematic diagram of the experimental setup for activated carbon production

3.3 Precursor Preparation

The dabai (*Canarium Odontophyllum*) seeds were used as a precursor in the production of AC. The pioneer originated in Sibul, Sarawak.

3.3.1 Activated Carbon Synthesis

The activated carbon preparation procedures were divided into three main stages consists of:

- i. Carbonization of the precursors
- ii. KOH impregnation of char
- iii. CO₂ gasification of the KOH-impregnated chars

3.3.1(a) Carbonization

A thirty gram (30 g) of precursor was put inside a vertical reactor continuously purged with nitrogen gas at 150 mL/min. The reactor temperature was ramped to 400 °C and held for 2 h.

After that, the char produced was cooled down to room temperature. Then they were stored inside a dessicator for about 2 h for further treatment.

3.3.2(b) KOH Impregnation

The impregnation of char in powder form (250 μm) with potassium hydroxide (KOH) was done in various impregnation ratio (IR) calculated in Eq. 3.2;
$$\text{IR} = \frac{w_{\text{KOH}}}{w_{\text{char}}} \quad (3.2)$$

where w_{KOH} is the dry weight (g) of KOH pellet and w_{char} is the dry weight (g) of char. A specific amount of char and KOH pellet (depending on the IR) was mixed with deionized water in a 250 mL beaker. The mixture was stirred thoroughly until completely dissolved and have been put in the oven overnight at a temperature of 105 °C for dehydration.

3.3.2(c) Carbon Dioxide Gasification

After that, a constant nitrogen flow at 150 mL/min was used to heat-treat the KOH-impregnated char. The necessary temperature was raised at a rate of 10 °C per minute. After reaching the target activation temperature, the nitrogen was replaced with carbon dioxide (CO₂) at a rate of 150 mL/min and maintained for the time recommended by the Response Surface Methodology (RSM) study. The sample was allowed to cool to ambient temperature for one hour after the CO₂ was replaced with N₂. After that, the AC was cleaned with hydrochloric acid and deionized water to achieve a neutral pH. A pH meter (Model Delta 320, Mettler Toledo, China) was used to measure it. The AC was dried for twenty-four hours at 105 °C in an oven. The dried AC was stored in a dessicator for characterization and further adsorption studies.

3.3.2(d) Experimental Design

This study utilized response surface methodology (RSM) with central composite design (CCD) analysis to optimize the studied parameters. The independent variables include.

- i. x_1 , Activation temperature (°C)
- ii. x_2 , Activation time (h)
- iii. x_3 , KOH: char (IR)

These variables and their respective ranges were selected based on the literature and the results obtained from the preliminary studies. As a matter of facts, this analysis used Design

Expert software version 7.1.5 (STAT-EASE Inc., Minneapolis, USA) to develop regression model and evaluate the significance of responses. Table 1.0 shows the range levels of each factor (variable) studied

Table 1.0: Independent variables and their coded levels for the CCD

Variables (factors)	Coded variables level				
	$-\alpha$	-1	0	+1	$+\alpha$
Activation temperature ($^{\circ}\text{C}$)	514	600	725	850	935
Activation time (hour)	0.32	1.00	2.00	3.00	3.68
IR	0.07	0.75	1.75	2.75	3.43

In this study, The Seeds of *Canarium Odontophyllum* were successfully used to produce COAC using the physiochemical activation method. The optimum preparation conditions of COAC were 794 $^{\circ}\text{C}$, 1.19 h, and 2.75 for activation temperature, activation time, and IR, respectively.

4.0 Data Analysis and Findings

4.1 Adsorption of Equilibrium for Textile Wastewater

The impact of contact time on COD reduction from textile effluent is depicted in Figure 2.0. The COAC COD maximum removal was determined to be 61.10%. The type of adsorbent and adsorbate utilized affected the adsorption effectiveness at various concentrations. In this instance, the adsorption performance is influenced by the properties of the ACs.

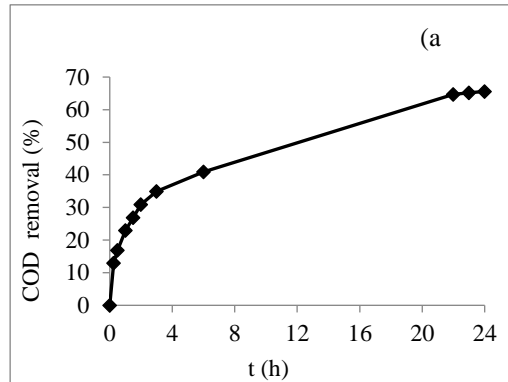


Figure 2.0: COD percent removal versus adsorption time at 30°C for COAC

4.2 Adsorption Isotherms for Textile Wastewater

Industrial wastewater adsorption isotherm data for COD isotherms at the different adsorbents were fitted with the Langmuir and the Freundlich models. Table 2.0 showed that the isotherms model was well fitted to the experimental data for the removal of COD on COAC. The Langmuir isotherm gave slightly closer fittings than other models as it was obvious from a comparison of the coefficient of determination ($R^2 > 0.98$) within the range of adsorbent doses considered. The well fitted isotherm data by the Langmuir suggested that monolayer coverage of COD on COAC. Value of $1/n$ and K_F with R^2 values calculated using linear equation. The value of $1/n$ was found below 1.0 for COAC, suggesting that the adsorption condition was favourable.

Table 2.0
 Isotherm parameters for COAC (COD) at temperature 30°C

Sample	Langmuir			Freundlich		
	Q_m	K_L	R^2	$1/n_F$	K_F	R^2
COAC	64.34	0.0268	0.997	0.724	0.19	0.994

A study of the coefficient of determination ($R^2 > 0.98$) throughout the range of adsorbent dosages taken into consideration made it clear that the Langmuir isotherm provided somewhat closer fits than other models for actual textile effluent. The Langmuir's well-fitting isothermal data indicated that COD was covered in a monolayer. Higher R^2 values indicated that chemisorptions involving valency forces or electron exchange between the adsorbent and adsorbate were responsible for controlling the rate-limiting phase.

Regeneration of activated carbon is strongly advised in terms of financial gain. Because of the decreased adsorbent weight from washing and drying losses, which have an impact on the adsorption capacity and desorption percentage for both activated carbons, the ethanol regenerability results showed that the pollutant removal decreased from the first cycle to the third.

5.0 Discussion and Conclusions

In conclusion, the physiochemical activation approach was successfully employed to create COAC from the seeds of *Canarium Odontophyllum*. For COAC, the ideal activation temperature, activation duration, and IR were 798°C , 1.16 hours, and 2.65, respectively. COAC provided a 64.10% COD decrease. As the starting concentration and contact time of the adsorbates grew, so did the COAC's adsorption uptakes. The Langmuir isotherm model was followed by the equilibrium of adsorption.

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