

Process Optimization for the Production of Activated Carbon from Waste Coconut Shells in Trinidad & Tobago

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Abstract

Produced water that is generated from the local oil and gas industry is associated with disposal challenges due to the presence of the pollutant phenol in excess of statutory discharge limits. As Trinidad & Tobago (TT) moves towards achieving sustainable development goals of waste minimization and pollution reduction, produced water treatment and reuse, as well as the indiscriminate disposal of waste coconut shells, are receiving national attention due to adverse environmental impacts. In developing countries, activated carbon (AC) made from cheap and abundantly available coconut shells has been successfully used to remove phenol from water by utilizing a packed bed adsorber. The adoption of the packed bed adsorber technology requires critical technical data on the phenol adsorption capacity of the AC manufactured from the waste coconut shells. Moreover, manufacturing AC involves firstly, carbonizing the coconut shells firstly, and then activating them using an oxidizing agent such as carbon dioxide (CO₂). The objectives of this study were to optimize the carbonization and activation process conditions for the manufacturing of AC from waste coconut shells. The optimized carbonization and activation process conditions were found to be 600°C for 90 mins, and 900°C for 10 mins using a CO₂ flowrate of 0.8 L min⁻¹. A maximum phenol adsorption capacity of 0.013 mg g⁻¹ corresponding to 76% phenol removal at 25°C was obtained. A Brunauer-Emmett-Teller (BET) surface area of 452.9 m² g⁻¹ and an average pore size of 1.79 nm was obtained for the optimized sample, with micropores accounting for 91% of the total pore volume. This study shows that the environmentally hazardous and indiscriminately disposed waste coconut shells in TT can be converted to AC to be utilized in a packed bed adsorber for water treatment. This waste minimization strategy supports the socio-economic transformation plan outlined in TT's Vision 2030 National Development Strategy.

Keywords

Phenol; Pollution; Activated carbon; Waste minimization; Packed bed absorber; Produced water

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1 Introduction

In Trinidad & Tobago (TT), local oil and gas producers are presently facing a global challenge regarding the disposal of large volumes of produced water of more than 75,000 US gal per day. Unpublished compositional analysis reveals that this produced water mainly consists of Total Suspended Solids (TSS), chlorides, ammoniacal nitrogen, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), phenol and oily impurities. Of major concern is the presence of phenol which ranges from 0.5-2 mg L⁻¹ concentration and this exceeds the allowable effluent discharge limit of 0.5 mg L⁻¹ that is stipulated by the TT Environmental Management Authority (EMA)¹. The presence of phenol, even at low concentrations of 3 mg L⁻¹, is associated with harmful effects and is considered toxic to aquatic life².

While targeted reduction of the concentration of the Total Suspended Solids (TSS), chlorides, ammoniacal nitrogen, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and oily impurities can be achieved by relatively inexpensive treatment methods such as multimedia filtration, reverse osmosis, chlorination, hydrogen peroxide chemical treatment, and skim tanks, these techniques cannot be applied to phenol removal. Oil and gas producers in TT cannot reuse the phenol-contaminated water and must contract wastewater collection and disposal companies to handle these large volumes of produced water generated at their production facility, which incurs high disposal costs. If phenol-contaminated water, such as produced water, can be treated on site, the water can be reused within the facility. In addition to being a cost-saving strategy for these companies, the reuse of the treated produced water aligns with the water management and conservation goals of the TT Vision 2030 National Development Strategy³; an initiative in which these producers have expressed great interest.

The technique of Activated Carbon Adsorption has proven to be the most widely used method for phenol removal from water⁴. Although the packed bed

adsorption technology is used in TT, activated carbon (AC) must be imported at high costs using scarce USD foreign exchange, and this presents economic challenges to the industrial users. If the AC can be produced locally and incorporated into the design of a packed bed adsorber, these challenges associated with its use would no longer be significant.

In developing countries, AC is produced from waste materials that are abundantly generated from the agricultural sectors and present disposal challenges^{5,6}. In Small Island Developing States (SIDS) such as TT, progress is slower regarding the recycling of waste materials⁷. However, significant strides have been made on the development of policies that relate to pollution reduction and waste minimization. The National Environmental Policy (NEP)⁸ details concrete actions geared towards environmental sustainability in TT⁸. TT is also a signatory to the Basel Convention Regional Centre for Training and Technology Transfer for the Caribbean Region (BCRC–Caribbean), which is principled in the idea that waste is a resource, and recycling and reusing are techniques to mitigate adverse environmental impacts and stimulate economic development, innovative employment opportunities, and small business entrepreneurs⁹. The utilization of AC made from abundantly available waste material such as coconut shells for the treatment of produced and wastewater therefore represents a sustainable disposal method for this indiscriminately disposed of material.

Literature has shown that in addition to the advantage of being a readily available material in tropical climates¹⁰, coconut shell has a high mechanical strength, abrasion resistance, and pore volume^{6,11}. It also has a high carbon content ranging from 49–52%, low ash content of less than 2%¹², a high volatile matter content, and is environmentally friendly due to low nitrogen and sulphur contents¹⁰, which are desirable characteristics of a precursor for AC production^{6,13}. Of particular interest to TT are the documented studies outlining the success of producing microporous AC from coconut shells, which can be used for effective phenol adsorption and removal

from water. Adsorption capacities of 17.5-205.8 mg g⁻¹ corresponding to phenol removal efficiencies of 54-93% phenol have been reported^{6,14,15}.

It has been shown that the adsorptive performance of AC largely depends on the pore size and volume, and surface functional groups present^{16,17}. Regarding phenol adsorption, the size of the pores is of critical importance. The effective diameter of the phenol molecule is 0.75 nm; therefore, micropores would favour the adsorption of phenol^{4,18}. The development of micropores depends on the manufacturing process, precisely the carbonization temperature, activation time and temperature, and activating agent used⁵.

Researchers have investigated the effect of the carbonization temperature on the adsorptive properties of AC and concluded that the carbonization temperature significantly impacts the micropore and mesopore volumes developed^{19,20}. High carbonization temperature increases the ash content and the fixed carbon content due to the increased release of volatile matter²¹. Above a specific temperature the material will completely change to ash; as such temperature ranging from 200-1100°C have been generally used at this stage²².

The activation conditions were carefully selected and controlled since excess activation leads to excessive burn-off of the char, which negatively impacts the porosity and surface area negatively¹⁶. Researchers determined that for activation times more significant than 1 hour, and temperature that was greater than 900°C, the micropores transition to meso and macropores due to a greater burning away of the pore wall and a greater quantity of ash is generated. They concluded that micropore formation would be achieved at high temperatures of 850-900°C and short activation times (30 min), with micro-porosity development reaching a maximum at 50% burn-off^{5,16}.

The use of carbon dioxide (CO₂) as an activating agent has been shown to favour micro-porosity formation. A comparative study to investigate the effect of both steam and CO₂ on the porosity development of AC prepared from walnut shell was conducted by Gonzalez et al.¹⁶, which concluded that

CO₂ produced highly microporous AC, with broadening of the micro-porosity occurring only at longer activation times. Whereas CO₂ activation for 120 min yielded small pores, further activation to 480 min resulted in the enlargement of these small pores.

The literature has established that the performance of AC largely depends on the raw material composition and the carbonization and activation process conditions, as these factors influence the porosity and surface area developed, thus, influencing the adsorptive capacity. As such, it is imperative that the manufacturing process be optimized, specifically the carbonization and activation conditions, for maximum phenol removal.

A review of the literature showed that information on the manufacture of AC in TT using local raw materials for use in a packed bed adsorber for the removal of phenol and other contaminants needs to be improved. As such, Wahid et al.²³ conducted a preliminary study of the conversion of local waste coconut shells to AC for phenol removal from water and concluded that AC targeting phenol removal from water could be produced from local waste coconut shells. The objective of this study was to optimize the production of the AC from local waste coconut shells, which would allow TT to achieve its sustainable developmental objectives of waste minimization and pollution reduction, while also harnessing the socio-economic benefits of entrepreneurial activity.

2 Materials and Methods

2.1 Preparation of Raw Material

The coconut shell was prepared according to the procedure outlined in previous studies^{24,25}. Brown coconuts that naturally fall from the tree were first sourced and collected from coconut estates. The husks were then removed to yield the coconut shells. The coconut shells obtained were cracked so that the water and the copra could be removed, after which the shells were washed thoroughly with water to remove all traces of oily residue and copra. The shells were then sun-dried for 72 hours, followed by particle

size reduction using a hammer and a 5-mesh sieve to achieve a 2-4 mm particle size range since the intent is to produce a granular AC.

2.2 Process Optimization

As described by Kennedy et al.²⁶ and Fierro et al.²⁷, carbonization of 160 g of coconut shell was conducted using a Carbolite Gero HTR Rotary Reactor Tube Furnace at the Carbon Research Laboratory of the University of the West Indies, St. Augustine Campus, Trinidad at the desired carbonization temperature using a constant nitrogen (N_2) flow of 96 $mL\ min^{-1}$ to maintain the inert environment during pyrolysis. The char was then allowed to cool to room temperature before removal from the furnace. The mass of the char was recorded. The vessel was cleaned with ethanol to remove any oily and sticky residue before the activation stage.

For the activation stage, the method adopted by Gonzalez et al.¹⁶ for physical activation using carbon dioxide (CO_2) was used as CO_2 was readily available, and the literature indicated this as a favoured micropore development. 10 g of the char was placed in the Carbolite Gero HTR Rotary Reactor Tube Furnace and gradually heated to the desired activation temperature utilizing a constant nitrogen flow of 96 $mL\ min^{-1}$. The nitrogen gas was switched to the CO_2 gas flow at the activation temperature. After the activation time ended for each sample, the gas flow was immediately switched from CO_2 to N_2 for the cooling period. The produced AC was then allowed to cool to room temperature. The mass of the product was recorded, after which it was washed repeatedly with de-ionized water until a neutral pH was obtained. It was then dried at 105°C for 24 hours in an oven and double sealed in polyethylene bags¹⁶.

The protocols employed involved the variation of temperature, time and CO_2 flow for the optimization of the carbonization. Activation steps are detailed as shown in Table 1 and Figure 1. The experimental conditions for carbonization and activation

which resulted in an AC product that demonstrated maximum phenol removal from a standard phenol solution, were selected as the optimized conditions.

As outlined in the previous studies^{5,16}, the initial step to determine the optimized activation temperature involved is by using carbonization conditions of 450°C for 90 min, followed by an activation time of 20 min. This optimized activation temperature was then used to determine the optimum activation time. The optimal activation temperature and activation time were determined by the samples that demonstrated the maximum phenol removal. The experimental conditions for determining the phenol removal efficiency of the samples are stated in Table 1; this procedure is further elaborated on in this section.

The carbonization temperature was optimized at the optimum activation conditions and a constant carbonization time of 90 min. The sample determined the optimal carbonization temperature, which demonstrated the maximum phenol removal. The experimental conditions for determining the phenol removal efficiency of the samples are stated in Table 1. The optimized CO_2 flow rate was then determined by using the previously established optimum carbonization and activation conditions. The optimal CO_2 flow rate was determined by the sample, which demonstrated the maximum phenol removal. The experimental conditions for determining the phenol removal efficiency of the samples are stated in Table 1. It must be noted that this process optimization method did not investigate the effect of carbonization time on the phenol removal ability of the AC, specifically its effect on the previously established optimized activation temperature and time. Studies generally focused on the effect of the carbonization temperature on the performance of the AC and concluded that the selection of this carbonization condition is critical to the porosity development in the subsequent activation stage^{5,20,21}.

Table 1. Experimental investigations to determine optimal manufacturing process parameters based on phenol removal efficiency.

Experiment	Carbonization conditions	Activation conditions	Phenol adsorption conditions
Activation temperature ^{5,16}	T = 450°C t = 90 min N ₂ flow = 96 mL min ⁻¹	T = 850-950°C CO ₂ flow = 96 mL min ⁻¹ t = 20 min	T = 25°C t = 120 min C _o = 2 mg L ⁻¹ m = 1.75 g pH = 7
Activation time and AC yield ¹⁶	T = 450°C t = 90 min N ₂ flow = 96 mL min ⁻¹	T = 900°C CO ₂ flow = 96 mL min ⁻¹ t = 10-40 min	-
Activation time and burn-off % ¹⁶	T = 450°C t = 90 min N ₂ flow = 96 mL min ⁻¹	T = 900°C CO ₂ flow = 96 mL min ⁻¹ t = 10-40 min	-
Burn-off % ¹⁶	T = 450°C t = 90 min N ₂ flow = 96 mL min ⁻¹	T = 900°C CO ₂ flow = 96 mL min ⁻¹ t = 10-40 min	T = 25°C t = 120 min C _o = 2 mg L ⁻¹ m = 1.75 g pH = 7
Activation time ^{5,16}	T = 450°C t = 90 min N ₂ flow = 96 mL min ⁻¹	T = 900°C CO ₂ flow = 96 mL min ⁻¹ t = 10-40 min	T = 25°C t = 120 min C _o = 2 mg L ⁻¹ m = 1.75 g pH = 7
Carbonization temperature ^{26,27}	T = 450°C, 600°C, 750°C t = 90 min N ₂ flow = 96 mL min ⁻¹	T = 900°C CO ₂ flow = 96 mL min ⁻¹ t = 10 min	T = 25°C t = 120 min C _o = 2 mg L ⁻¹ m = 5 g pH = 7
Effect of CO ₂ flow ¹⁶	T = 600°C t = 90 min N ₂ flow = 96 mL min ⁻¹	T = 900°C CO ₂ flow = 0.64 L min ⁻¹ - 4 L min ⁻¹ t = 10 min	T = 25°C t = 120 min C _o = 2 mg L ⁻¹ m = 5 g pH = 7

Note: T = Temperature (°C), t = time (min), C_o = initial phenol concentration (mg L⁻¹), m = mass of the AC sample (g)

The phenol removal capacity of each sample was quantified by contacting a fixed mass of the AC product with a 2 mg L⁻¹ phenol solution (C_o) for 2 hours in a water bath at 25°C²⁸, after the sample was filtered and the quantity of phenol in the analyte was determined by using the "US EPA Method 420.1: Phenolics – Direct Photometric Method"²⁹. This method involved diluting the analyte to 100 mL, after 2 mL of ammonium hydroxide buffer solution was added and mixed. 2 mL of 4-Aminoantipyrine solution was then added to the analyte and mixed,

after 2 mL of potassium ferricyanide solution was added, and the analyte was mixed. After 15 min, the analyte samples were tested for phenol concentration using a Hach DR5000 Spectrophotometer. The Phenol Removal Efficiency (%) was calculated by Equation 1.

$$\text{Phenol Removal Efficiency (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

where C_o is the initial phenol concentration (mg L⁻¹) and C_e (mg L⁻¹) is the concentration in the analyte.

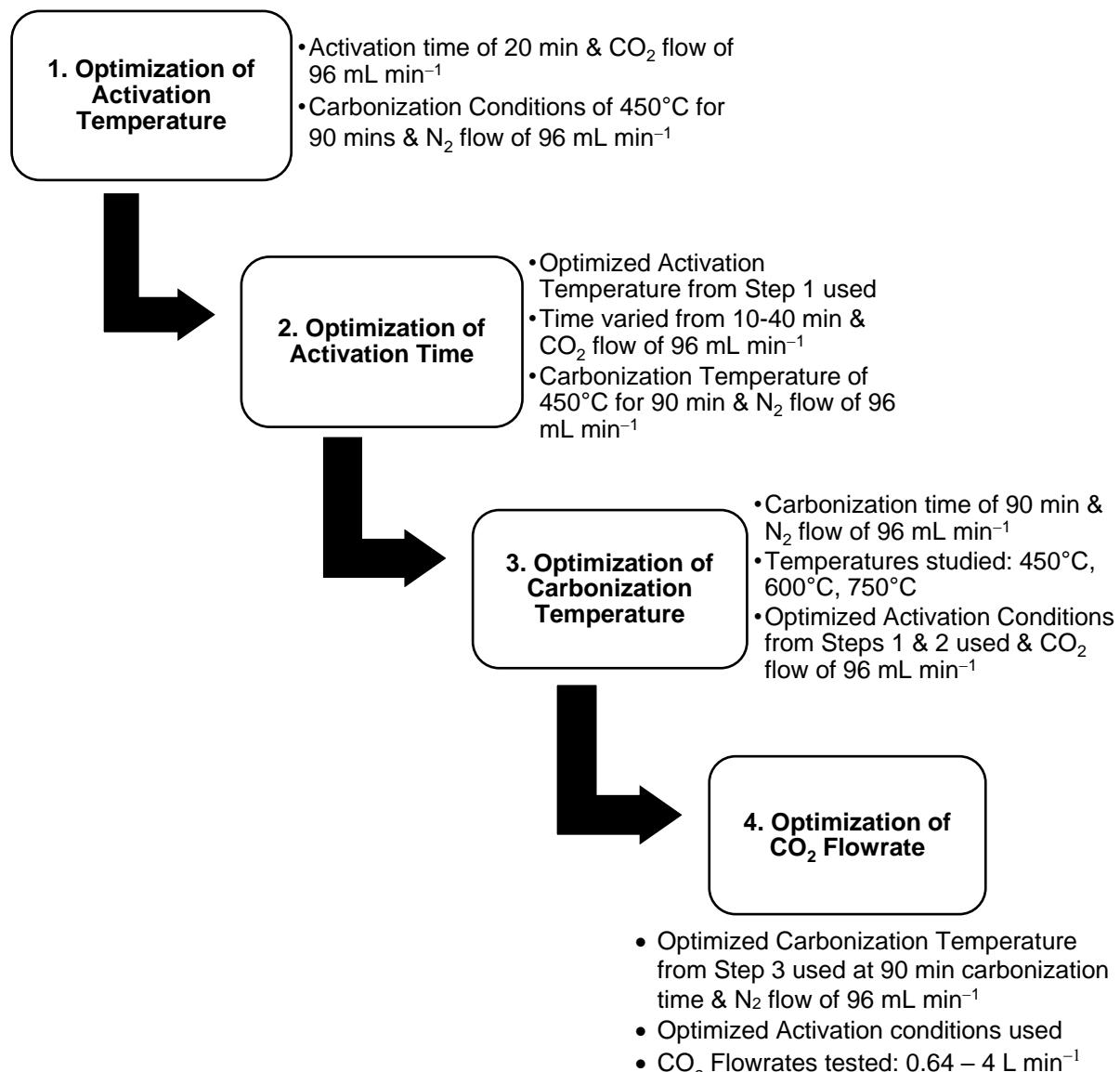


Figure 1. Flowchart showing the procedure for the optimization of process parameters.

A 2 mg L^{-1} phenol solution was used as this value represents the maximum concentration of phenol obtained in produced water in Trinidad & Tobago, and it was prepared in accordance with the "US EPA Method 420.1: Phenolics – Direct Photometric Method"²⁹. A stock phenol solution was prepared by dissolving 1.0 g of phenol in freshly boiled and cooled distilled water followed by a dilution to 1 litre to obtain a solution concentration of 1 mg mL^{-1} phenol. Working Solution A was then prepared by diluting 10 mL of the stock phenol solution to 1 litre with distilled water to obtain a solution concentration of

0.01 mg mL^{-1} phenol. 20 mL of Working Solution A was then pipetted into a 100 mL graduated cylinder and diluted to 100 mL with distilled water to obtain a solution phenol concentration of 2 mg L^{-1} .

In order to determine the adsorption capacity of the optimized product i.e., the effect of the adsorbent dosage on the quantity of phenol removed, varying masses of AC were contacted with a fixed concentration of phenol solution of 2 mg L^{-1} and placed in a water bath at a temperature of 25°C for an equilibration time of 2 hours²⁸. The pH of adsorption was maintained at 3, as preliminary investigations

into the most effective pH for phenol adsorption using non-optimized AC samples determined that maximum phenol removal occurred at a strongly acidic pH, which was similar to the findings obtained by Kennedy et al.²⁶.

For the optimized sample, physical characteristics such as the Brunauer-Emmett-Teller (BET) surface area, pore size and volume were characterized using the conventional nitrogen adsorption isotherms at -196°C (77 K) by a Quantachrome Nova 10.0 Series Gas Sorption System Instrument. 0.1 g of AC was first outgassed for 3 hours at 300°C under a vacuum pressure to clean the surfaces and remove any adsorbed gas. The sample tube was immersed in liquid nitrogen at 77 K to maintain a constant temperature. Gaseous nitrogen was used to dose the sample to obtain the isotherms. The isotherms were evaluated by the NOVAWin2 software to determine the BET surface area, total pore volume and micropore volume, and the average pore diameter²⁷.

Scanning Electron Microscopy (SEM) was used to provide three-dimensional images of the surface morphology of the AC, specifically porosity development. The SEM samples were prepared by depositing a small mass of approximately 50 mg of the AC sample onto an aluminium stub (which is specially designed with conductive, adhesive carbon tapes) and then coated with gold for 1 minute to prevent any charging during observation in the high-vacuum mode^{6,16}. A 30 kV electron emission potential was used to give high resolution images.

3 Results and Discussion

3.1 The Effect of Activation Temperature on Phenol Removal

Figure 2 shows the effect of the activation temperature on the quantity of

phenol adsorbed by the locally produced AC.

For the three AC samples produced at the three temperatures studied, maximum phenol removal of 58% was obtained for the sample produced at 900°C. There was a 53 % increase in phenol adsorption when the activation temperature increased from 850 to 900°C, followed by a 10% decrease when the temperature increased to 950°C. These results are consistent with the findings of Gonzalez et al.¹⁶, in which the optimum conditions to achieve a microporous product were high temperatures of 850-900°C at short activation times of less than 30 min.

McDougall⁵ also found that if activation continued beyond these conditions, there would be a total conversion of micropores to mesopores due to a greater degree of burning away of the pore walls, leading to reduced absorptive performance⁵.

Based on this optimum activation temperature of 900 °C, all activations for this study were conducted at this temperature.

3.2 The Effect of Activation Time on Product Yield, Burn-off and Phenol Removal

The yield of char from the carbonization stage ranged from 27.5-29.0%. This was obtained from a simple calculation of the difference in masses of the raw material to be carbonized and the char obtained, as a percentage of the mass of the raw material. When the char was subjected to five different activation times, the results indicated that as the time increased from 10 to 40 min, the AC product yield decreased by approximately 15% as shown in Figure 3. Activation time that was below 10 min was not investigated because of the minimum time required for the furnace to achieve equilibrium temperature conditions.

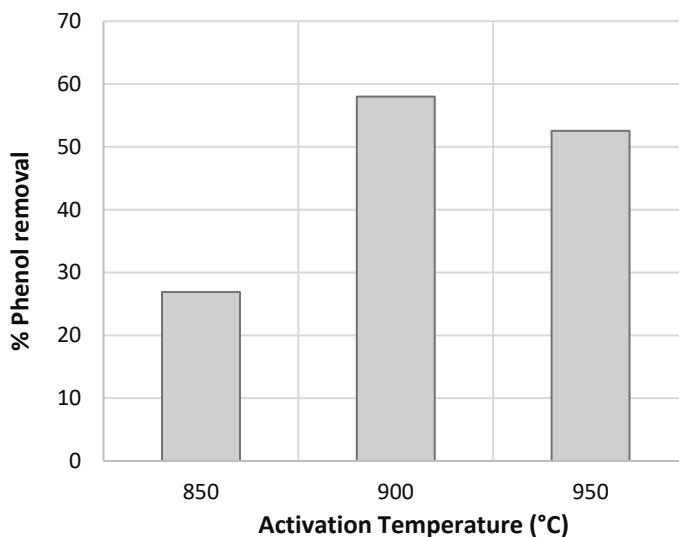


Figure 2. % Phenol removal vs. activation temperature (°C) at $t = 20$ min, $C_o = 2 \text{ mg L}^{-1}$, $m = 1.75 \text{ g}$ and $T = 25^\circ\text{C}$ at constant pressure.

As heating time increases, the burning away of the char, specifically the pore structure, increases. This degree of burning, known as the burn-off, is calculated as shown in Equation 2 below^{5,16}.

$$\% \text{ Burn-off} = \frac{w_i - w_f}{w_i} \times 100 \quad (2)$$

where w_i is the initial mass of the char (g) and w_f is the final mass of the char (g).

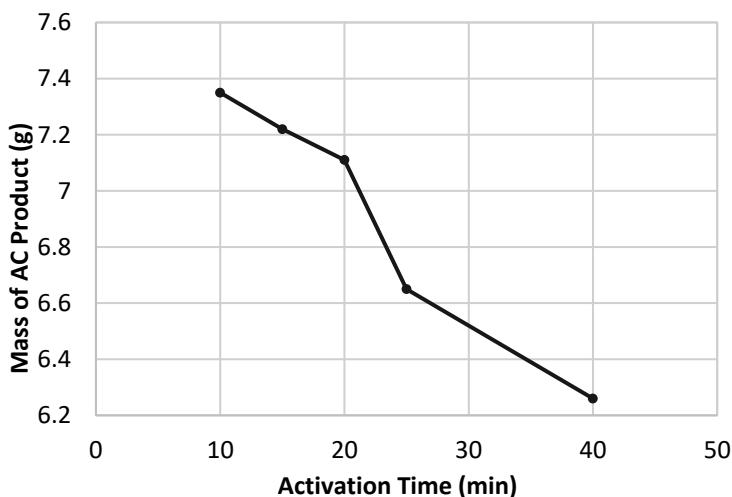


Figure 3. Graph of yield of AC product (g) vs activation time (min) at activation temperature of 900°C at constant pressure.

Excess activation (due to higher temperature or longer activation time) increased the burn-off, resulting in the release of more volatile matter content, which decreasing the product yield. The results obtained are consistent with theory and the findings by Buah and Kuma³⁰ who reported a 60% decrease in the yield of the product after 3 hours of activation time.

However, the relationship between burn-off and product yield is not as critical as understanding the effect of burn-off on the performance of the AC, specifically, the quantity of phenol adsorbed by the AC. Figure 4 shows the relationship between burn-off and phenol removal for four AC samples produced at four activation times of 10 min, 20 min, 30 min, and 40 min.

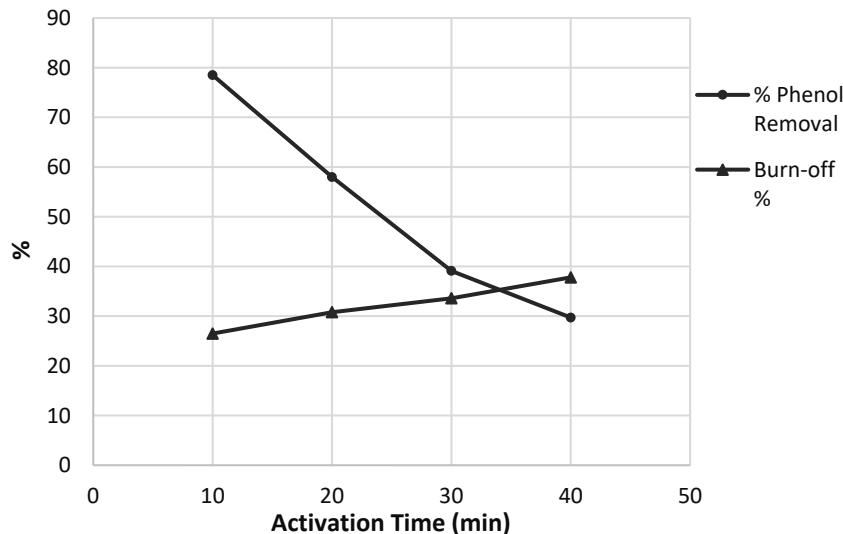


Figure 4. Graph of % phenol removal and burn-off % vs activation time (min) at activation temperature of 900 °C at constant pressure.

The results show that as burn-off increased (due to increasing activation time), the amount of phenol removed decreased, i.e., for a 30% increase in burn-off, there was a 62% decrease in phenol adsorption. These results were expected and consistent with the findings of Gonzalez et al.¹⁶ who reported that longer activation time, significantly greater than 60 min, led to increased meso and macropore development due to a greater degree of

burning away of the pore walls which led to impaired micro-porosity development and thus reduced adsorptive capability. As shown in Figure 4, a 26.5 % burn-off occurred at the maximum phenol removal (78.5%) and the shortest activation time (10 min). This finding is consistent with the results obtained by Gonzalez et al.¹⁶ who determined that 20-30% burn-off values favour micropore development.

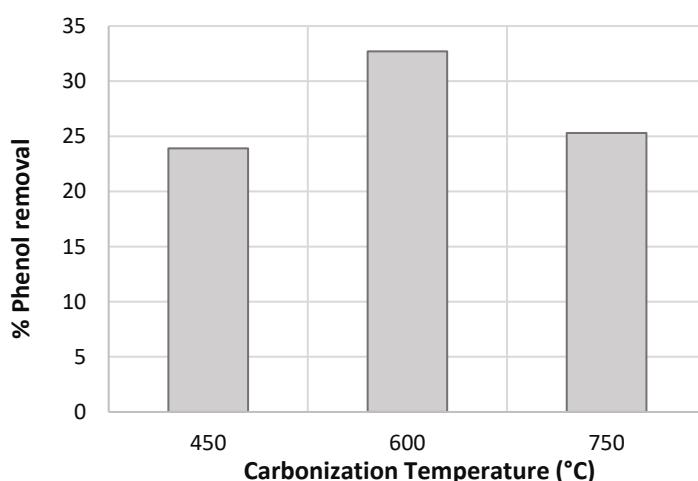


Figure 5. % Phenol removal vs carbonization temperature at $C_0 = 2 \text{ mg L}^{-1}$, $m = 5 \text{ g}$, Activation time = 10 min, Activation temperature = 900 °C at constant pressure.

3.3 The Effect of Carbonization Temperature on Phenol Removal

The carbonization temperature has also been shown to influence the porosity

development of the AC as mentioned previously. Figure 5 shows the effect of carbonization temperature on phenol adsorption.

For the three samples produced, maximum phenol removal was achieved for the sample produced at a carbonization temperature of 600°C. This represented a 27% increase in phenol adsorption from the temperature of 450°C. As the carbonization temperature increased to 750°C, the phenol removal decreased by 23%. These results are consistent with reported results by Sanni et al.³¹, where at 575°C, adsorptive capacity was highest as compared to lower carbonization temperatures, but as the temperature increased, adsorptive capacity decreased. Katesa et al.¹⁹ also reported that the porous properties and surface area of the AC decreased as the carbonization temperature increased.

3.4 The Effect of Carbon Dioxide Flow on Phenol Removal

In physical activation, the quantity of activating agent used plays a critical role in the pore volume and porosity developed. Gonzalez et al.¹⁶ determined that 20-30% burn-off values favour micropore development.

In their study to determine the effect of CO₂ flow on the pore volume, surface area and adsorption properties, Herawan et al.³² varied the CO₂ flowrate from 150-600 mL min⁻¹ and found that at 300 mL min⁻¹, maximum pore volume, surface area and methylene blue adsorption was achieved. They also concluded that excessive flow rates result in thinning of the pore walls, thereby leading to weakness and reduced porosity development³².

Therefore, a preliminary investigation was conducted to determine if there was any significant effect on phenol adsorption by varying the CO₂ flow to produce three AC samples, the results are shown in Figure 6.

Evidently, an increase in the CO₂ flow rate resulted in the increase in phenol adsorption. Therefore, optimization of the

CO₂ flow was necessary, whereby five different CO₂ flow rates were investigated to produce five AC samples, the results of which are presented in Figure 7.

A maximum phenol removal of 55% was achieved when the CO₂ flowrate was 0.8 L min⁻¹. This corresponded to a burn-off of 12%. Further increases in the flowrate resulted in a decrease in phenol adsorption, as much as 34% reduction when the flowrate increased to 4 L min⁻¹. Flowrates between 1.2 L min⁻¹ and 3.2 L min⁻¹ were not studied because once the optimum flowrate was achieved at 0.8 L min⁻¹ and there was a decrease in phenol adsorption at 1.2 L min⁻¹, the maximum flowrates achievable by the flowmeter were studied. Even though the burn-off values at the higher flow range did not significantly change, the phenol removal ability of the AC was impacted, largely because of the pore wall thinning and weakening, which caused the reduced micropore development and hence led to the reduce of phenol adsorption³².

3.5 The Effect of Adsorbent Dosage on Phenol Removal

The adsorption capacity (mg g⁻¹) of the adsorbent is a critical parameter for the adsorber design as the total mass of adsorbent (loading) required to remove at least 75% of the phenol from the water needs to be determined.

The uptake of phenol or adsorption capacity, q_e (mg g⁻¹) is calculated by Equation 3.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where m is the mass of the AC (mg) and V is the volume of solution (liters)¹⁵. The effect of AC dosage on phenol removal at the three temperatures studied is presented in Figure 8 below.

For each temperature, eight varying masses of AC are tested for phenol removal.

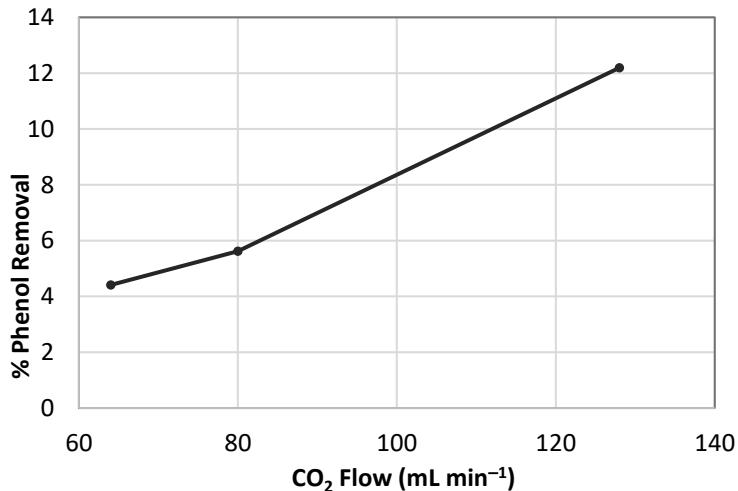


Figure 6. Graph of % Phenol removal vs CO₂ flow (mL min⁻¹) for C₀ = 2 mg L⁻¹, m = 1.75 g, T = 25°C, Activation time = 10 min, Activation temperature = 900°C at constant pressure.

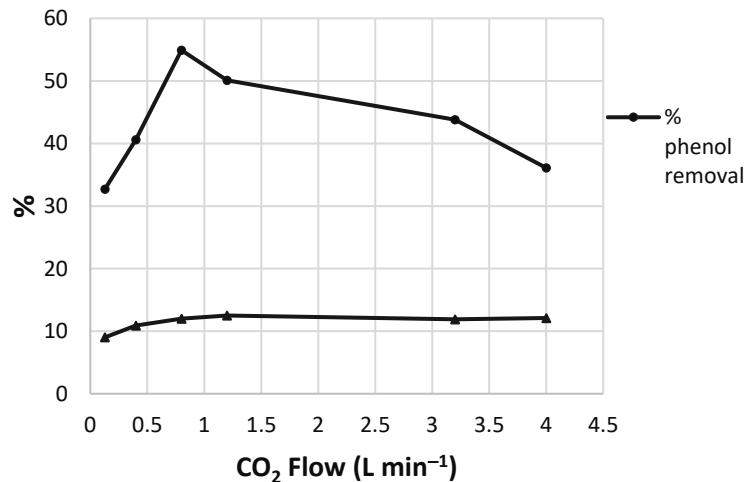


Figure 7. Graph of % Phenol removal vs CO₂ flow (L min⁻¹) and burn-off % at activation time = 10 min, Activation temperature = 900°C at constant pressure.

As shown in Figure 8, as the adsorbent dosage increased, the uptake of phenol by the AC increased. The maximum removal of phenol at 25°C was approximately 76% at an adsorbent dosage of 12 g. The maximum adsorption capacity was determined to be 0.013 mg g⁻¹ AC. At 85°C, the maximum adsorption capacity was found to be 0.011 mg g⁻¹ AC, corresponding to 65.5% phenol removal. The maximum phenol removal attained at 5°C was 29.8% for an adsorption capacity of 0.005 mg g⁻¹ at 5°C. The adsorption capacity is lower than

comparative studies by Desmiarti et al.¹⁵ and Din et al.⁶. They reported a maximum phenol adsorption capacity of 17.54 mg g⁻¹ AC and 205.8 mg g⁻¹, respectively^{6,15} for AC prepared from coconut shells. In both studies, chemical activations were performed, which yielded products with relatively high adsorption capacities. A comparative study on the chemical and physical activation of coconut shells by Prauchner et al.³³ concluded that chemical activation yielded an AC with a significantly higher volumetric adsorption capacity than physical activation³³.

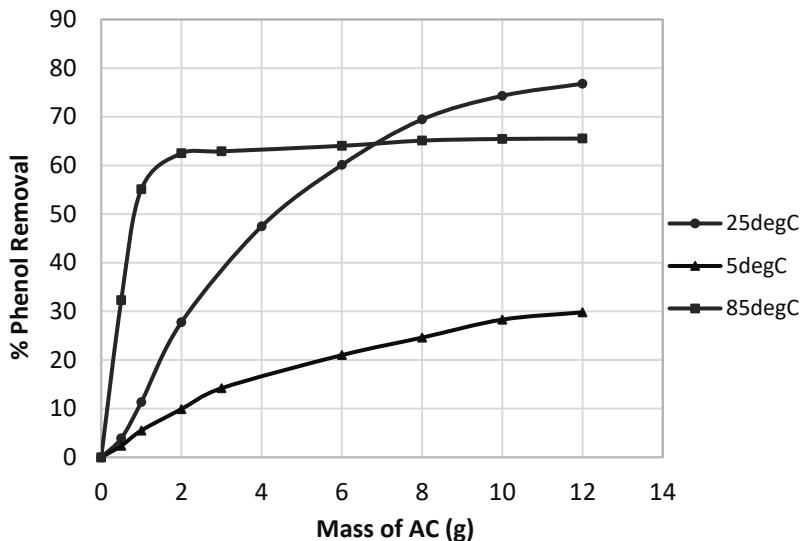


Figure 8. Graph of % Phenol removal vs mass of AC (g) at pH = 3, T = 5°C, 25°C, 85°C at constant pressure.

The mass of 12 g of the locally produced AC, which achieved 76% phenol removal was 60 times more than the mass that was used by Din et al.⁶ to achieve approximately 75% phenol removal, which occurred at 83.2 mg g⁻¹ adsorption capacity for an initial phenol concentration of 100 mg L⁻¹. The authors⁶ reported that the adsorption capacity increased to a maximum of 205.8 mg g⁻¹ when the phenol concentration increased to 500 mg L⁻¹. In order to compensate for the low adsorption capacity of the locally produced AC, a greater mass would have to be used for phenol removal.

The results also show that further increases in adsorbent dosage beyond 12 g will not have a significant effect on the removal of phenol. This finding is greatly influenced by the type of pores developed³⁴ as well as the surface chemistry¹⁷. High activation temperature (> 850°C) for a long duration (> 30 min) leads to a pore transition from micro to meso and macro^{5,6}. Lorenc-Grabowska et al.³⁴ found that the adsorption capacity increased with an increasing volume of pores that were less than 1.4 nm in size. This is because phenol is preferentially adsorbed in pores smaller than 1.4 nm (ultra-micropores) as the effective diameter of the phenol molecule is 0.75 nm.

The higher temperature favour phenol adsorption; there was a 61.5% increase in the adsorption capacity when the temperature increased from 5°C to 25°C. Interestingly, even though a minimum of 75% phenol removal could not be achieved at the highest temperature of 85°C, the maximum phenol adsorption of approximately 65% at this temperature was achieved by less than 6 g of the adsorbent, which is almost half of the mass required for 77% removal of phenol. Further studies on the kinetics and thermodynamics of the phenol-AC interaction would need to be conducted to understand this behaviour.

3.6 BET Surface Area and Pore Characteristics

The results obtained from the Quantachrome Nova 10.0 Series Gas Sorption System instrument are shown in Table 2.

Table 2. BET surface area and pore characteristics.

BET surface area (m ² g ⁻¹)	452.9
Average pore diameter (nm)	1.79
Total pore volume (cm ³ g ⁻¹)	0.203
Total micropore volume (cm ³ g ⁻¹)	0.185

The BET surface area of 452.9 m² g⁻¹ is comparable to the findings of other authors

i.e., $494\text{-}2000 \text{ m}^2 \text{ g}^{-1}$ ^{6,15}. This relatively low surface area corresponds to the low adsorption capacity obtained. The total pore volume checks well with the findings from other researchers who obtained volumes ranging from $0.08\text{-}0.58 \text{ cm}^3 \text{ g}^{-1}$ ^{6,15}. The micropore volume accounts for 91% of the total volume, hence, the reason the average pore diameter corresponds to a microporous size. This finding also checks well with other authors' work⁶ and clearly shows that micropores were dominant.

3.7 SEM Analysis

Figure 9 is the SEM image obtained for the sample corresponding to the CO_2 flowrate of 0.128 L min^{-1} and shows the development of a porous structure on the surface of the AC.

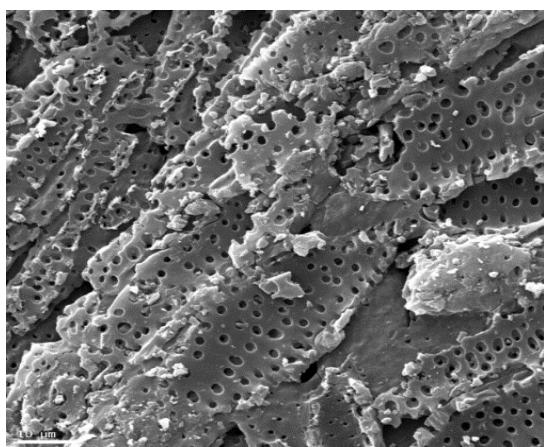


Figure 9. SEM image of the sample produced at 0.128 L min^{-1} CO_2 flow rate (30 kV, X1360, 10 μm)

4 Conclusion

This study demonstrated that AC produced from the locally abundant waste coconut shell removed more than 75% of phenol from phenol-contaminated water. This means that it may be possible to remove sufficient phenol from a contaminated water source (up to 2 mg L^{-1} phenol) such as produced water to an acceptable concentration (0.5 mg L^{-1}) as outlined by the Environmental Management Authority¹.

The optimum process conditions for AC production were established to be a

carbonization temperature of 600°C and time of 90 min, an activation temperature of 900°C and time of 10 min, and a CO_2 flow rate of 0.8 L min^{-1} . The optimum burn-off was 12%.

The performance of the AC as an adsorbent for the contaminant phenol i.e. the adsorptive capacity, at the optimum manufacturing conditions, was established to be 0.013 mg g^{-1} at a temperature of 25°C , and also found to be temperature dependent.

A low BET surface area of $452.9 \text{ m}^2 \text{ g}^{-1}$ corresponded to the low adsorption capacity of 0.013 mg g^{-1} . Importantly, microporosity was the dominant porosity developed, accounting for 91% of the total volume of pores. However, the number of micropores was limited by the relatively low surface area developed; if the surface area for adsorption increases, the number of micropores would be increased, thereby leading to increased phenol removal and improved adsorptive capacity.

Future work involves the design of a packed bed adsorber that utilizes this locally manufactured AC. The phenol removal efficiency of this locally produced AC will be further verified by a comparative study with a commercial AC in the packed bed adsorber.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Formal analysis: Wahid, S.
Visualisation: Not applicable
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