

Coconut shell-based activated carbon preparation and its adsorption efficacy in reducing BOD from The Real Wastewater from Kitchen Restaurant (RWKR): Characteristics, Sorption Capacity, and Isotherm Model

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Abstract

Real Wastewater from Kitchen Restaurant (RWKR) contains high concentrations of Biochemical Oxygen Demand (BOD) pollutants to pollute the environment. One of the processing alternatives to reduce BOD is the adsorption method using activated carbon from coconut shells. This study aims to determine coconut shell-activated carbon as an adsorbent for the adsorption of organic matter to reduce BOD in RWKR. The method begins with making adsorbents that are activated with activators on HCl 3 M, NaOH 3 M, and H₃PO₄ M, then a preliminary adsorption test is carried out to select the best activator on coconut shell activated carbon to reduce BOD in RWKR. Determining the optimum conditions for adsorption was carried out by varying pH 3, 4, 5, 6, 7, and 8. Variation of contact time with a stirring speed of 250 rpm, then determined the isotherm model. The remaining organic matter in the wastewater will be measured using a DO meter based on SNI 6989.72: 2009 concerning the method of testing for biochemical oxygen demand (BOD). The results showed that the appropriate activator for coconut shell activated carbon was H₃PO₄ 3 M with an average percentage value of uptake of 89.690%. The adsorption process's optimum pH is at pH 3 with an absorption percentage value of 88.626%. The optimum contact time is at 10 minutes and the adsorption isotherm model used is the Freundlich isotherm with a regression value of $R^2 = 0.8864$.

Keywords: wastewater, BOD, activated carbon, adsorption, isotherm model

1. Introduction

Environmental pollution has always been a problem; decreasing water, soil, and air quality impact environmental degradation and human health. One of the crucial issues on environmental degradation is wastewater; wastewater is water with pollutant contamination such as heavy metals ion, organic dyes, low pH, high chemical oxygen demand (COD), high biological oxygen demand (BOD), phosphor, phosphate, and so on (Leiviskä *et al.*, 2008; Naswir *et al.*, 2019; Wibowo & Sadikin, 2019). These parameters reported impact human health such as cancer, skin disease, negative impact on blood, eyes, hair, etc. A recent study reported that managed water use can cause antibiotic resistance in soil bacteria, plants, animals, and humans (Sorinolu *et al.*, 2021). Wastewater is a problem in each city in the world; in Hong Kong, more than 90 % of surface water has been polluted by microplastic (Fok & Cheung, 2015), in Canada, plastic debris was found and impacted the marine ecosystem (Mallory *et al.*,

2006). In Shedu River, China, a recent study informed that the Shedu River in China had been polluted by COD and $\text{NH}_4\text{-N}$ (Fu et al., 2020), every place has its pollution characteristics.

Indonesia is one of a country with a unique characteristic of wastewater, as the big country with more than 2.5 million population, Indonesia has much of a restaurant. Due to the bigger population, Indonesia has more than 7.680 units (BPS-Statistics Indonesia, 2020). Restaurants have different characteristics in their wastewater; one of the high parameters in RWKR is BOD (Zulaikha et al., 2014). BOD is a water and wastewater parameter; BOD is the dissolved oxygen (DO) amount needed by a microorganism (aerobic) to break down the organic material. Several studies informed that BOD give negative impacts on the environment, especially for biota and microorganisms. Due to BOD contamination's negative impacts, many researchers developed methods to solve BOD contamination in wastewater. The methods used in BOD removal from wastewater are bioremediation, electrocoagulation, aeration, filtration, and adsorption, the more economical and efficient method is adsorption. This method is a simple method due to the low-cost of creating the adsorbent materials. A recent study informed that activated carbon chitosan-coated successfully decreased BOD in real wastewater until 99.5% at pH 6 (Lasindrang et al., 2015).

Although several studies have informed methods for dealing with BOD in wastewater, BOD is still a wastewater treatment problem. Competitive absorption, unique characteristics of wastewater, and other external factors still have to be developed and researched. Every single place, source, and external factor always be a problem to solve this parameter. For example, the BOD value on mining has different value with restaurant, Palm Oil Mill Effluent, etc. Besides, the material used to solve BOD in wastewater also give an impact on BOD removal. Several recent studies have reported reducing BOD by more than 90%, a recent study reported successfully reduce more than 90% BOD from a dissolved air flotation unit treating refinery wastewater (Hami et al., 2007). However, this study needs high-cost, high-technologies, and reliable human resources. Unfortunately, as a developing country, Indonesia has limitations on these various resources. Thus, we need to develop a low-cost material to solve the BOD from RWKR.

Due to technology limitations, reliable human resources, and finances, we need to create a low-cost material using abundant and unused resources. Coconut shell is one of abundant and unused material, this resource is abundant in Indonesia. Several studies have also reported that activated carbon derived from coconut shells has better characteristics than other ingredients and is always the leading choice in making activated carbon. Our material is a different activated carbon based on time and chemical process; we used a high concentration of chemical activation (3 M) to generate the better pores. Thus, this study created an activated carbon derived from coconut shell to solve the BOD from RWKR. The Novelty in this research is we have found the isotherm model from the BOD sorption; several studies reported the isotherm model of heavy metals sorption. This study also explains the activated carbon preparation, characteristics of the material, dye sorption, and isotherm model. This research is very appropriate and can be applied to RKWK waste worldwide, especially in developing countries with limited technology, human resources, and finance.

2. Material and Method

2.1 Material

This study's materials are 100 mesh sieves, Stir rod, Suction Ball, Spray bottle, Porcelain Cup, Glass funnel, Desiccator, DO meter, Erlenmeyer, Furnace, Cup glass, Measuring cup, Hot plate. Filter paper, Volumetric flask, Magnetic stirrer, Mortar and alum, Oven, PH meter, Drop pipette, Measuring pipette, Shaker, Spatula, Digital scales, Vacuum filter, RWKR, Distilled water, $\text{Ca}(\text{OH})_2$, HCl, H_3PO_4 , NaOH, Coconut shell

2.2 Activated Carbon Preparation

The dry coconut shell is heated again in the furnace to make a charcoal or carbonization process. Carbonization was carried out at 500 ° C for 2 hours. The carbonized coconut shell will be cooled in a desiccator. After the carbonization process was carried out followed by the activation process, the coconut shell carbon was soaked with an activator solution, namely 3 M HCl, 3 M NaOH, and 3 M H₃PO₄ using a ratio of 1: 4, then stirred with a magnetic stirrer for 2 hours and soaked for 24 hours. Furthermore, the mixture is filtered and the cake is washed with distilled water until the pH is close to neutral to ensure that the activated carbon from the coconut shell does not contain any more water, then it is dried again in an oven at 110 ° C until its weight is constant and will be cooled in a desiccator. The resulting carbon will be mashed using a mortar and sieved using a 100-mesh sieve, the activated carbon is ready for use.

2.3 RWKR

The method to collect RWKR refers to the Indonesian National Standard (SNI) 6989.59: 2008 concerning sampling wastewater. The sampling location point is in the initial reservoir for wastewater because the initial reservoir is high-turbulent to mix well, namely when the wastewater flows at the end of the production process. The method of sampling wastewater will be carried out in six stages:

- a. Prepared a RWKR sampling device.
- b. First, rinse the wastewater sampling tool with restaurant wastewater three times.
- c. Samples of RWKR were taken according to the allotment of analysis and mixed in one temporary container (gallon), then homogenized.
- d. Filtered samples of RWKR using filter paper.
- e. RWKR samples were preserved for parameter testing in the laboratory; RWKR preservation with BOD parameters was carried out by cooling at a temperature of 2-4 °C.
- f. Put in the container according to the purpose of the analysis.

2.4 BOD Measurement

The measurement of BOD is based on SNI 6989.72: 2009 on how to test for biochemical oxygen demand (BOD), which will be carried out in six stages, namely:

- a. 2 DO bottles marked with the notation BOD₀ and BOD were prepared.
- b. Entered the sample of RWKR into each bottle of BOD₀ and BOD until it overflowed, then closed each bottle carefully.
- c. Shaking it several times, then adding mineral-free water around the DO mouth that has been closed.
- d. Stored BOD bottles in an incubator at 20 ° C in a dark room for 5 days.
- e. Dissolved oxygen measurements were carried out on samples of RWKR in bottles of BOD₀ using a calibrated DO meter. The measurement result is the zero-day dissolved oxygen value (BOD₀).
- f. The BOD measurements were repeated from items e) to f) for BOD bottles that had been incubated for 5 days. The measurement results obtained are the value of 5 days dissolved oxygen (BOD).

2.5 Activators selection

The process of selecting the best activator is by testing the adsorption of coconut shell activated carbon using HCl, NaOH, and H₃PO₄ activators in RWKR, which is carried out in nine stages:

- a. 9 250 ml of Erlenmeyer were prepared.
- b. Added 1 gram of activated carbon, which 3 M HCl activated into 3 250 ml Erlenmeyer.
- c. Adding the RWKR with a solution volume of 250 ml each.
- d. Stir the mixture using an orbital shaker for 60 minutes.
- e. Let the mixture sit until it settles.
- f. Filtered the mixture.

- g. The process of selecting the best activator from point c) to g) is repeated using activated carbon activated by 3 M NaOH.
- h. The process of selecting the best activator from point c) to g) is repeated using activated carbon activated H₃PO₄ 3 M.
- i. Wastewater has been filtered, measured, and analyzed BOD from each activator, the most significant reduction in BOD shows the best activator to be used in the adsorption process for the next experiment. The amount of BOD reduction in RWKR is calculated using the equation:

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

qe = The amount of BOD lost from the solution due to the adsorption process in an equilibrium state (mg/g), Co = initial BOD concentration before the adsorption process (mg/L), Ce = BOD concentration after treatment with activated carbon (mg/L), V = Volume of sample (L), M = Mass of adsorbent (gr).

2.6 Material Characterization

Analysis of the quality of coconut shell activated carbon which has been known to be the best activator used, then carried out a characterization test which includes analysis of water content, ash content, FTIR Shimadzu - Prestige 21, and SEM SU3500.

2.6.1 Determination of Water and Ash Content (SNI No. 06-3730-1995)

A total of 1 gram of activated carbon is weighed in a porcelain dish which has been weighed. The porcelain cup with activated carbon was put in an oven at 110 ° C for 3 hours. Then, it is cooled in a desiccator, then weighed to find out the water and ash content

$$\text{water/ash content(\%)} = \frac{W_2 - W_3}{W_2 - W_1} \times 100\% \quad (2)$$

Information about the symbols is W₁ = Weight of empty cup (gr), W₂ = Weight of plate + sample (gr) W₃ = weight of plate + sample after heating (g)

2.6.2 Determination of Functional Groups Using FTIR

Characterization using FTIR in this study is to see the functional groups present in carbon before and after activation. Determination of functional groups can be seen from the resulting wave numbers; then the wavenumbers are adjusted to the table below (Takeuchi, 2006)

Table 1. Functional cluster areas on IR

| Cluster | Types of Compounds | Wavenumber (cm ⁻¹) |
|-----------------|--|--------------------------------|
| C-H | Alkanes (stretching) | 2850-2960, 1350-1470 |
| C-H | Alkenes (stretching out) | 3020-3080, 675-1000 |
| C-H | Aromatic (stretching) | 3000-3100, 675-870 |
| C-H | Alkuna (stretching) | 3300 |
| C=C | Alkenes | 1640-1680 |
| C≡C | Alkuna (stretching) | 2100-2260 |
| C=C | Aromatic (ring) | 1500-1601 |
| C-O | Alcohols, ethers, carboxylic acids, esters | 1080-1300 |
| C=O | Aldehydes, ketones, carboxylic acids, esters | 1690-1760 |
| O-H | Alcohol, phenol (monomers) | 3610-3641 |
| O-H | Alcohol, phenol (H bond) | 200-3600 |
| O-H | Carboxylic acid | 500-3000 |
| N-H | Amine | 3310-3501 |
| C-N | Amine | 1180-1361 |
| NO ₂ | Nitro | 1515-1560, 1345-1386 |

2.6.3 SEM Characterization

Activated carbon before and after activation is characterized using SEM to see the surface's morphology in activated carbon before and after activation.

2.7 Sorption Test

The process of adsorption of activated carbon to the RWKR will be carried out in four stages, namely:

2.7.1 Optimum pH (pH Variation)

The steps that will be taken in determining the optimum pH adsorption are: Prepared 6 pieces of Erlenmeyer size 250 ml, put 1 gram of activated carbon into each Erlenmeyer, added RWKR with a volume of 250 ml into each Erlenmeyer, set the pH of the solution to 3, 4, 5, 6, 7 and 8 using HCl 1 M solution and Ca(OH)₂ 1 M solution by drip drop by drop until the desired pH is achieved (pH measurement using digital pH meter), stir the mixture using an orbital shaker at a speed of 250 rpm for 60 minutes, silence the mixture until it settles, filtered mixture, wastewater that has been filtered, measured and analyzed BOD from each pH variation, the largest decrease in BOD indicates the optimum pH adsorption. The magnitude of the decrease in BOD in the RWKR is calculated using Eq. 1.

2.7.2 Time Contact

The steps that will be taken in determining the optimum adsorption contact time are: Prepared 6 pieces of Erlenmeyer size 250 ml, denter 1 gram of activated carbon into each Erlenmeyer, Added RWKR with a volume of 250 ml into each Erlenmeyer, Set the pH of RWKR of the restaurant to be equal to the optimum pH obtained from previous experiments (optimum pH / pH variation), Stirred mixture using an orbital shaker with a speed of 250 rpm, Varied stirring time is 5, 10, 20, 25, 30 and 60 minutes, Once the stirring time is reached, it is silenced until it settles. Filtered mixture. Wastewater that has been filtered, measured, and analyzed BOD from each variation in contact time, the most significant decrease in BOD indicates the optimum contact time adsorption. The magnitude of the decrease in BOD in the RWKR is calculated using equation 1.

2.8 Isotherm Model

This determination aims to find out the relationship between the amount of substances desorption by adsorbents and the concentration in the liquid phase at equilibrium. Isotherm determination to lower BOD in the RWKR is carried out at a variation in the active carbon mass of 0.2 gr; 0.4 gr; 0.7 gr; 0.8 gr; 0.9 gr; 1 gr and 2 gr. This adsorption is done from the results obtained in the determination of optimum pH and optimum contact time that has been obtained from previous experiments, then filtered and the RWKR that has been desorption measured with DO Meter to find out the magnitude of the decrease in BOD due to the adsorption process in a balanced state. Next will be specified the appropriate isotherm model between Langmuir isotherm and Freundlich in BOD drop due to the adsorption process.

Determination of adsorption isotherm model is data obtained plotted to a comparison curve based on each model isotherm Freundlich and Langmuir, then determined linearity (R_2). Freundlich adsorption modeling tests were conducted by creating a q_e log curve against C_e logs while testing Langmuir isotherm models by creating a C_e/q_e curve against C_e . The adsorption pattern is determined by comparing the level of curve linearity shown by the R^2 value closest to the number 1, which means that the resulting x and y variables have a very close/linear relationship so that the resulting model is accurate.

2.9 Statistical Test for Isotherm Model

Average Relative Error (ARE) is used as a statistical model as a correction to find the best isotherm model.

$$ARE = \frac{100}{n} \sum \frac{|q_e - q_e^m|}{q_e} \quad (3)$$

Note: q_e is the amount of BOD lost in the solution due to the adsorption process in an equilibrium state (mg/g), q_e^m is the amount of BOD lost in the solution calculated from the isotherm model (mg / g), n is the amount of data.

3. Result and Discussion

3.1 Activators Selection

Selection of the best activators on activated carbon using several activators, namely HCl 3 M, NaOH 3 M, and H₃PO₄ 3 M. Testing conducted in the form of preliminary adsorption testing conducted on activated carbon using several activators. Each activated carbon different activators weighed as much as 1 gram then put in Erlenmeyer and RWKR as much as 250 mL, stirring time for 60 minutes using a shaker with speed 250 rpm. Then filtered using filter paper, the filtrate is ready to be tested using the DO Meter tool to determine the highest BOD decreased by activated carbon different activators. The test results in selecting the best activators on the activated carbon of coconut shells to lower BOD in The RWKR can be seen in the table below.

Table 2. Sorption abilities in different activators

| No. | Chemical activators | Repetition | C _o (mg/L) | C _e (mg/L) | q _e (mg/gr) |
|-----|------------------------------------|------------|-----------------------|-----------------------|------------------------|
| 1. | HCl 3 M | 1 | 826,8 | 175,69 | 162,7775 |
| 2. | | 2 | | 87,25 | 184,8875 |
| 3. | | 3 | | 180,01 | 161,6975 |
| 4. | NaOH 3 M | 1 | | 91,26 | 183,885 |
| 5. | | 2 | | 83,44 | 185,84 |
| 6. | | 3 | | 84,60 | 185,55 |
| 7. | H ₃ PO ₄ 3 M | 1 | | 85,37 | 185,3575 |
| 8. | | 2 | | 90,56 | 184,06 |
| 9. | | 3 | | 79,81 | 186,7475 |

Based on the data in Table 2, the initial BOD concentration in RWKR is 826.8 mg / L. Then RWKR is treated by activated carbons. The BOD value from RWKR has been reducing due to the adsorption process. process in an equilibrium that can be seen in the q_e value calculated using a safe 1, the calculation step is:

$$q_e = \frac{(C_o - C_e) \times V}{M}$$

$$q_e = \frac{(826,8 \text{ mg/L} - 79,81 \text{ mg/L}) \times 0,25 \text{ L}}{1 \text{ gr}} = 186,7475 \text{ mg/gr}$$

The average repetition of adsorption testing in selecting the best activators obtained the highest q_e on activated carbon with H₃PO₄ 3M activators of 185,388 mg /gr.

3.2 Material Characteristics

3.2.1 Ash and Water content

Ash content is assumed to be the remaining mineral left behind at the time of carbonization because natural materials as the basis for making activated carbon contain carbon compounds and contain some minerals, some of which have been lost at the time of carbonization and activation. Some are estimated to remain in activated carbon. Determination of ash content in activated carbon aims to

determine the number of materials and minerals present in activated carbon. Ash content obtained from this study amounted to 0.71%, and the results have met SNI 06-3730-1995 that the maximum ash content is 10%. Lower ash levels can increase the ability of activated carbon rapidness due to the lack of clogging of pores so that the surface area of the activated carbon becomes increased (Mall et al., 2005).

Table 3. Ash and water content of activated carbon

| No | Ash content (%) | Water content (%) |
|----|-----------------|-------------------|
| 1 | 0.71 | 5.38 |

3.2.2 FT-IR Analysis

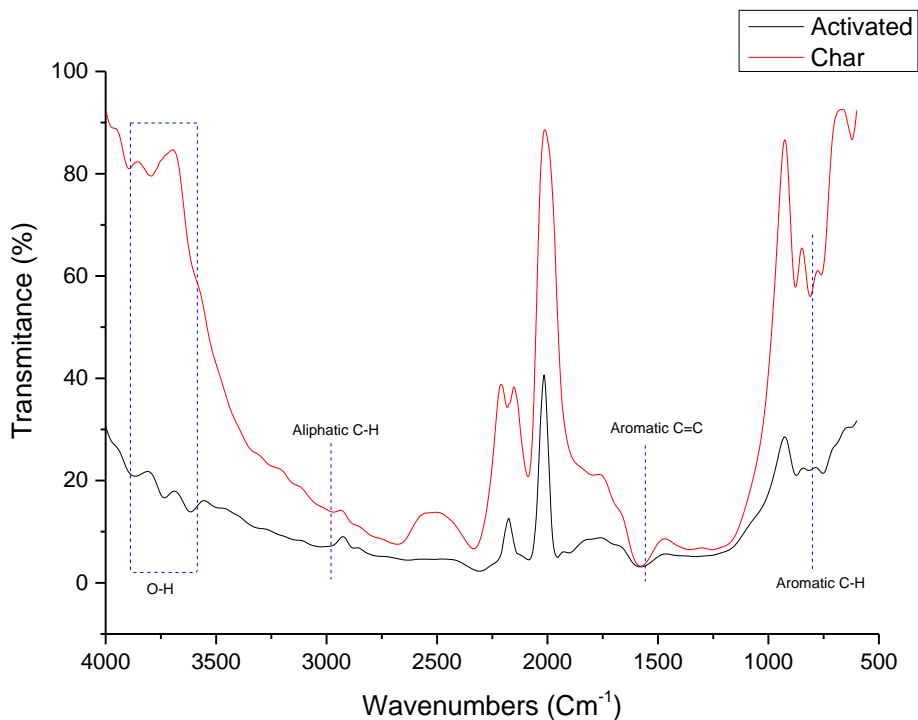


Figure 1. FT-IR characteristic of activated carbon and char

The FTIR spectrum in Figure 1, which is carbon before activation, appears the absorption band at the number 2969.10 cm^{-1} , which is indicated as an aliphatic C-H vibration group (stretching) alkane. The absorption band at 2678.37 cm^{-1} indicates the presence of carboxylic acid O-H group (stall). The absorption band at 1578.14 cm^{-1} indicates the cluster C=C of aromatic carbon (ring). The absorption band at 877.45 cm^{-1} indicates the presence of the C-H alkene cluster. The absorption band at 811.08 cm^{-1} indicates the presence of aromatic C-H groups.

Based on Figure 1 which is carbon after activation appears absorption band at the number 3614.10 cm^{-1} which indicates the O-H alcohol group's presence. The absorption band at 3025.02 cm^{-1} indicates the presence of aromatic C-H groups. The absorption band at 2630.91 cm^{-1} indicates the presence of carboxylic acid O-H group. The absorption band at 1579.98 cm^{-1} indicates the presence of aromatic carbon group C=C. The absorption band at 874.16 cm^{-1} indicates the presence of C-H alcohol (stretched) group. Absorption bands at numbers 816.81 cm^{-1} and 753.79 cm^{-1} indicate the presence of aromatic C-H groups.

The function group produced in Figure 1 shows that the peaks have barely undergone significant absorption intensity changes, namely at the peak of the range of 3614.10 cm^{-1} -2969.10 cm^{-1} , showing the hydroxyl function group C-H. The peak of the range of 2678.37 cm^{-1} - 2630.91 cm^{-1} indicates

the presence of carboxylic acid O-H group. A large number of O-H (hydroxyl) function groups indicate strong hydrogen bonds (from carboxyl, phenol, or alcohol). The peak of the range of 1579.98 cm⁻¹–1578.14cm⁻¹ indicates the presence of aromatic C=C clusters. The existence of the C=C group is a group of carbon with a high amount of purity, in addition to the double carbon bond also indicates the purity of the carbon element produced. The peak of the range of 877.45 cm⁻¹– 874.16cm⁻¹ indicates the presence of the C-H alkene cluster. C-H alkenes have stronger properties than C-H alkane bonds because they have double bonds, the stronger the bond, the harder it is to bond and requires higher energy. The peak of the range of 816.81 cm⁻¹– 811.08cm⁻¹ indicates the presence of aromatic C-H groups. The many appearances of aromatic compounds indicate that the compound is a constituent of the hexagonal structure of activated carbon that is a C atom at each angle has been activated after the activation process so that it has a lot of pores (Takeuchi, 2006).

Different things that happen to carbon after activation have a greater absorption intensity, with the O-H function group's emergence at 3614.10cm⁻¹ and the C-H function group at 753.79cm⁻¹. The cluster's emergence makes the function group on carbon after activation becomes more numerous than carbon before activation. A recent study informed the FTIR test on rice husk carbon before and after activation using H₃PO₄ after activation has a greater absorption intensity, indicating active groups in rice husks after activation becomes more its bond with other inorganic and organic compounds has been severed due to the activation process.

3.2.3 Surface Morphology

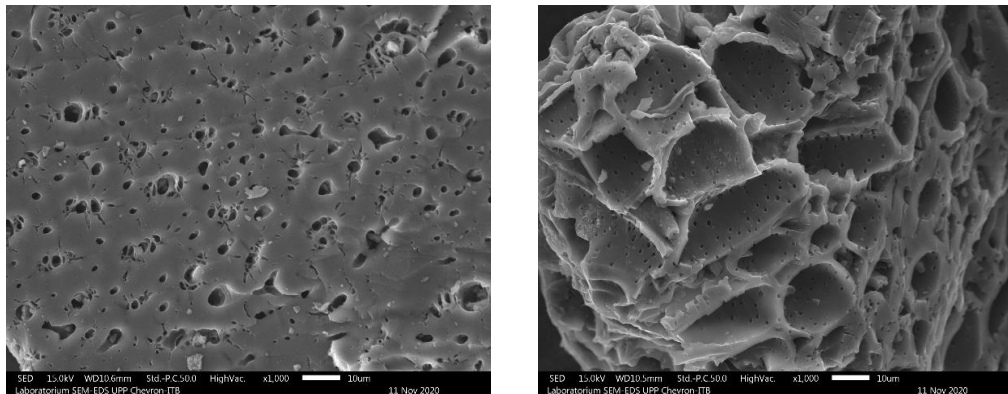


Figure. 2. Surface and pores characteristic of coconut shell (a) and activated carbon (b)

Morphological analysis of coconut shell charcoal pores before and after activation was conducted using Scanning Electron Microscope with a magnification of 1000 times that can be seen in Figure 2. there are differences in the structure of carbon pores before activation and after activation. In carbon after activation (b) pores are formed more and form pore cavities with a greater depth when compared to carbon before activation (a), so activated carbon provides more space for adsorbate to stick. Charcoal pores before activation are still covered mainly by hydrogen, tar, and other organic compounds whose components consist of ash, water, nitrogen, and others. Charcoal pores after greater activation are caused by the dissolving of impurities or the breakdown of hydrocarbon bonds by chemical activators so that carbon changes i.e., the surface area increases and affects adsorption power.

Coconut shell carbon already has pores, but still with a small size, while carbon shells that have been chemically activated coconut have seen the distribution of more irregular pores with a more significant number of pores. Several studies informed that activated carbon after activation of H₃PO₄ has a more significant pore morphology than carbon before activation, the morphology of coconut shell carbon after activation looks more expansive due to the reaction with H₃PO₄ (Naswir *et al.*, 2020). This phenomenon happened because coconut shell carbon activated using H₃PO₄ activator can dissolve the

impurities so that more pores are formed, and adsorbate trapping capability by the active carbon of coconut shell becomes more maximal than carbon before activation. The size of pores on the surface of activated carbon greatly affects the adsorption process. The more pores that open on the surface of activated carbon, the adsorption process will take place well, and the more adsorbates are deposited in the adsorbent pores

3.3 Percent Removal

Furthermore, it is determined the percentage of adsorbates that are intercepted by different activator bents can be seen in the table below.

Table 4. BOD removal using different activators

| Activators | The initial concentration of BOD (mg/L) | Final Concentration (mg/L) | BOD removal | % Removal |
|------------|---|----------------------------|-------------|-----------|
| HCl 3 M | 826,8 | 175,69 | 651,110 | 78,751 |
| | | 87,25 | 739,550 | 89,447 |
| | | 180,01 | 646,790 | 78,228 |
| NaOH 3 M | 826,8 | 91,26 | 735,540 | 88,962 |
| | | 83,44 | 743,360 | 89,908 |
| | | 84,60 | 742,200 | 89,768 |
| H3PO4 3 M | 826,8 | 85,37 | 741,430 | 89,675 |
| | | 90,56 | 736,240 | 89,047 |
| | | 79,81 | 746,990 | 90,347 |

Calculation of the percentage of removal of BOD in the RWKR using equation 1, the calculation steps are:

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100\%$$

$$\% \text{ Removal} = \frac{826,8 - 79,81}{826,8} \times 100\% = 90,347\%$$

Based on Figure 5, reduction of BOD by activated carbon with activator HCl 3 M, NaOH 3 M, and H₃PO₄ 3 M using 3 times repetition of treatment on each different activator, to ensure an utterly appropriate activator on coconut shell carbon to lower BOD in the RWKR. The average repetition obtained the highest decrease in BOD is activated carbon using H₃PO₄ (3 M) with a percentage of 89.69%. This result is better than research done using activated carbon and various other materials such as blanks, active carbon, activaated alumina, steel slag, and limestone aggregate, which can only reduce BOD up to 46.17% (Mortula & Shabani, 2012)

3.4 pH Effect on BOD Sorption

pH is one of the essential physical parameters in wastewater control. In the adsorption process, the pH value can affect the chemical equilibrium of adsorbates and adsorbents. The analysis of pH influence in the adsorption process, the treatment is done by varying the pH values that vary. Optimum pH conditions are determined based on the highest percentage in the highest adsorption process using coconut shell activated carbon to lower BOD in the RWKR. Testing to determine the optimum pH was conducted with the addition of 1 gr of activated carbon measuring 100 mesh into RWKR that has been prepared as much as 250 ml, with the determination of pH variations of 3, 4, 5, 6, 7, and 8 then conducted stirring using shakers for 60 minutes at a speed of 250 rpm. After that, filtered using filter paper, and then the filtrate is ready to be tested using the DO Meter tool.

Table 5. pH effect on BOD sorption

| No. | pH | Co (mg/L) | Ce (mg/L) | qe (mg/gr) |
|-----|----|-----------|-----------|------------|
| 1. | 3 | 4715,37 | 536,32 | 1044,76 |
| 2. | 4 | | 838,62 | 969,188 |
| 3. | 5 | | 978,41 | 934,24 |
| 4. | 6 | | 947,65 | 941,93 |
| 5. | 7 | | 1195,88 | 879,873 |
| 6. | 8 | | 832,53 | 970,71 |

The initial BOD concentration in the RWKR before treatment with activated carbon is 4715.37 mg / L. Then treatment with activated carbon in each variation of the pH of the RWKR, after treatment, there is a decrease in BOD in the RWKR because the adsorption process in a balanced state that can be seen in the qe value calculated using equation 1. In the pH variation of the RWKR, the highest qe occurred at pH 3, which is 1044,762 mg/gr with a final concentration of BOD of 536.32 mg/L. The smaller the concentration value (Ce) the more significant the BOD lost from a solution. Furthermore, the percentage of adsorbates that are adsorbed by adsorbents calculated using equation 1 can be seen in Figure 3.

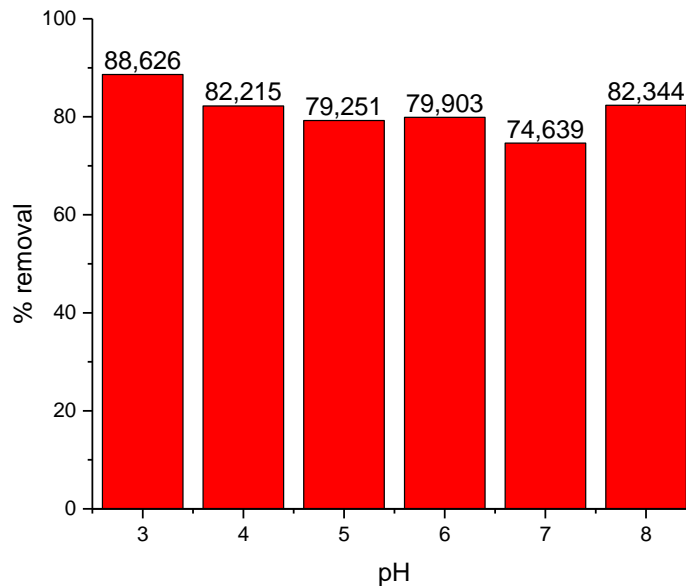


Figure 3. Percent removal of BOD from wastewater

3.5 Time contact

Contact time is one of the most decisive things in the adsorption process, where the contact time is the length of time it takes during the moving process between activated carbon as an adsorbent to lower BOD in the RWKR. The longer the contact time, the possibility of the adsorption process is also increasing, but when the balanced condition has been achieved adsorbent tends to release (desorption) adsorbate because the pores of the adsorbent have been saturated by adsorbates so that the percentage of adsorbs becomes reduced, this indicates that activated carbon is experiencing optimum conditions. Optimum conditions are achieved when the increase in the number of substances intercepted reaches the largest adsorption capacity and then no longer significant or constant as contact time increases.

Optimum contact timing aims to find out how long activated carbon takes to effectively degrade BOD and know the optimum condition of contact time that needs to be done to obtain optimum adsorption capacity. Using the best results from the optimum pH testing of BOD reduction

that has been done in the previous stage and it is known that the optimum active carbon absorption capability occurs at pH 3 with an active carbon mass of 1 g.

Table 6. BOD removal effect on contact time

| No. | Contact times (Minute) | Co (mg/L) | Ce (mg/L) | qe (mg/gr) |
|-----|------------------------|-----------|-----------|------------|
| 1. | 5 | 3269,78 | 1907,1 | 340,67 |
| 2. | 10 | | 1824,99 | 361,198 |
| 3. | 20 | | 1863,76 | 351,505 |
| 4. | 25 | | 1888,08 | 345,425 |
| 5. | 30 | | 1931,54 | 334,56 |
| 6. | 60 | | 1955,5 | 328,57 |

Based on the data in table 6, the initial BOD concentration in RWKR before treatment with activated carbon is 3269.78mg / L. Then, it is done with activated carbon in each by varying the length of the contact time of time stirring RWKR. There is a decrease in BOD in the RWKR because of the process of adsorption in a balanced state that can be seen in the q_e value calculated using a safe 1. In the contact time variation, the highest q_e occurred at a time of 10 minutes which was 361.1975mg/gr with a final concentration of BOD of 1824.99mg/L. Furthermore, the percentage of adsorbates that are adsorbent when the contact time variation is calculated using equation 2 can be seen in Figure 4.

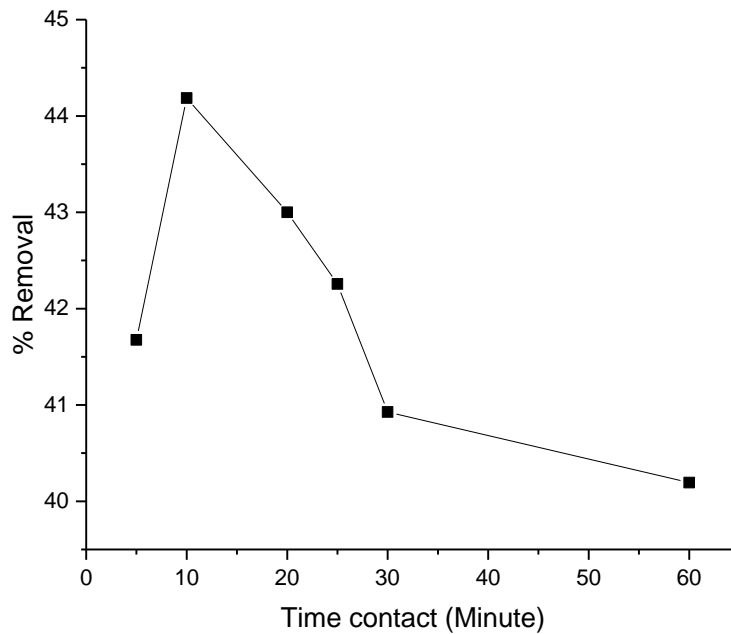


Figure. 4. Time contact on removal percent of BOD

Based on Figure 4 shows at the beginning of the contact time (5 minutes) there are still many adsorbent pores that have not been filled adsorbate so that at the time of adding contact time, the adsorption process can still increase and reach the optimum contact time of 10 minutes with an adsorption capacity of 44.19%. The calculation step is attached to appendix 2 (point h). The percentage decrease in BOD in the RWKR using activated carbon coconut shell decreased the percentage of trapping after obtaining contact time in the 20th to 60th minutes. Based on the adsorption process at a contact time of 10 minutes, the adsorption runs quite well or significantly, but when the addition of contact time of more than 10 minutes occurs, the process of desorption is the release of adsorbate from the surface of the adsorbent. The activated carbon that causes this phenomenon has been saturated by the adsorbate that is intercepted so that percent of the absorption in the contact time is more than 10 minutes, there is a decrease in the absorption by adsorbents (Malik *et al.*, 2006).

When contact time has been obtained with a high percentage of plunder, and when the increase in contact time occurs a decrease in the percentage of ingestion is because activated carbon has been saturated by molecules that are absorbed into the active carbon pore. When the contact time of activated carbon to wastewater is extended, it does not increase the number of exposed adsorbates. This phenomenon caused by the adsorbent surface that has been filled adsorbate has been completely closed so that when the contact time is extended, there is no accessible adsorbent surface so that the adsorbate will be released back into the wastewater. The sorption model of BOD is similar to metals ion sorption; the BOD fill the pores of activated carbon in several times and will be decreased when the pores are entire. Another study informed that time contact effects the sorption ability (Naswir et al., 2020)

3.6 Isotherm Model

Determining the adsorption isotherm model aims to determine how much adsorbent mass is needed to reduce the concentration of a parameter to be reduced to the desired limit. The types of adsorption isotherms that are commonly used are Freundlich isotherms and Langmuir isotherms. Testing the Freundlich adsorption isotherm pattern is done by making a log qe curve against log Ce, testing the Langmuir isotherm pattern is done by making a Ce/qe curve against Ce the adsorption pattern is determined by comparing the level of linearity of the curve shown by the R2 value.

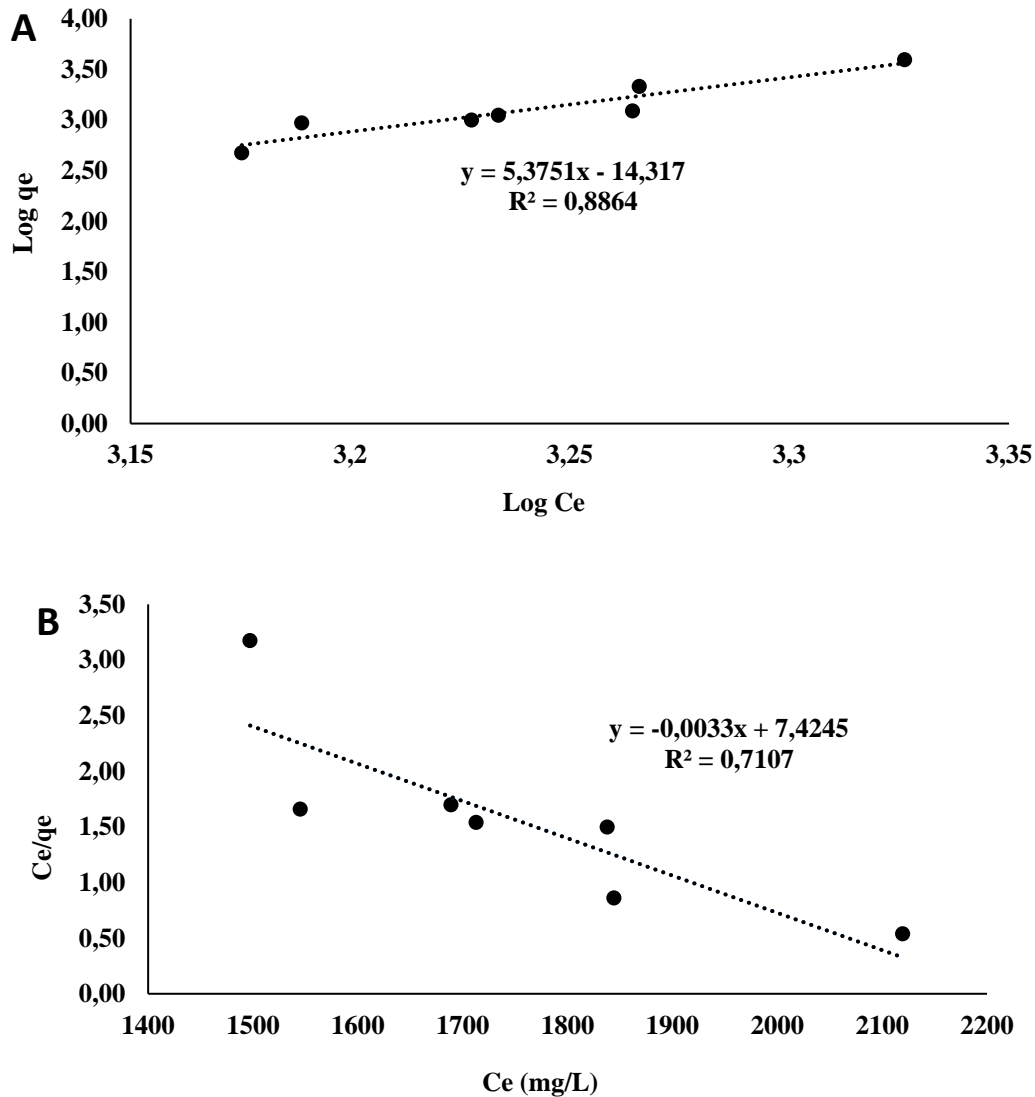


Figure 5. Isotherm model of freundlich (a) and langmuir (b)

The results obtained in the determination of isotherm Freundlich or Langmuir seen a considerable difference, but to strengthen the comparison of linearity data, the calculation of the average relative error (ARE) as another criterion to strengthen the interpretation in determining and which isotherm to be used in this study. The corresponding adsorption isotherm model can be seen by comparing the R^2 line values that are close to one. Figure 5 informed that the RWKR reduce fits the Freundlich model; this can be seen from the Freundlich isotherm chart with linearity (R_2) with the most significant value (close to 1), which is 0.8864, while in isotherm Langmuir obtained R^2 of 0.7107. Linearity values close to 1 or equal to 1 indicate a strong relationship between variables x and y, so that values close to 1 have a perfect sense of conformity, the model is getting true and accurate.

The results obtained in the determination of isotherm Freundlich or Langmuir seen a considerable difference, but to strengthen the comparison of linearity data, the calculation of the average relative error (ARE) as another criterion to strengthen the interpretation in determining and which isotherm to be used in this study. The results of our calculation can be seen in the table below

Table 7. ARE for langmuir isotherm model

| Co (mg/L) | Ce (mg/L) | KL | q max | qe (mg/g) | qe' m | ARE |
|------------|-----------|----------|----------|-----------|----------|---------------|
| | 2119,58 | -0,00044 | -303,030 | 3940,963 | 4930,563 | 0,251 |
| | 1844,21 | -0,00044 | -303,030 | 2142,588 | 1377,708 | 0,356 |
| | 1837,81 | -0,00044 | -303,030 | 1226,621 | 1351,602 | 0,101 |
| | 1712,93 | -0,00044 | -303,030 | 1112,319 | 966,757 | 0,130 |
| | 1688,97 | -0,00044 | -303,030 | 995,383 | 912,513 | 0,083 |
| | 1545,16 | -0,00044 | -303,030 | 931,798 | 664,450 | 0,286 |
| 5272,35 | 1497,23 | -0,00044 | -303,030 | 471,890 | 602,837 | 0,277 |
| ARE | | | | | | 21,264 |

Table 8. ARE for freundlich isotherm model

| Co (mg/L) | Ce (mg/L) | n | KF | qe (mg/g) | qe'm | ARE |
|------------|-----------|-------|---------|-----------|----------|---------------|
| | 2119,58 | 0,186 | 4,8E-15 | 3940,963 | 3646,913 | 0,074 |
| | 1844,21 | 0,186 | 4,8E-15 | 2142,588 | 1726,066 | 0,194 |
| 5272,35 | 1837,81 | 0,186 | 4,8E-15 | 1226,621 | 1694,112 | 0,381 |
| | 1712,93 | 0,186 | 4,8E-15 | 1112,319 | 1160,577 | 0,043 |
| | 1688,97 | 0,186 | 4,8E-15 | 995,383 | 1075,946 | 0,080 |
| | 1545,16 | 0,186 | 4,8E-15 | 931,798 | 666,885 | 0,284 |
| | 1497,23 | 0,186 | 4,8E-15 | 471,890 | 562,980 | 0,193 |
| ARE | | | | | | 17,882 |

The average error result data is relatively comparable from both adsorption isotherm models between Freundlich and Langmuir. The Freundlich model's adsorption isotherm's average relative error is smaller at 17,883, while Langmuir's isotherm is 21,264. The relative error average values of both isotherm models indicate that the Freundlich isotherm model was the appropriate and appropriate isotherm model in this study as it resulted in the most minor relative error average. Freundlich's isotherm model shows that the adsorbate layer formed on the adsorbent surface is multilayer. The same as physical adsorption characteristics, namely, where adsorption can occur in many layers.

4. Conclusions

RWKR is one of the polluted waters. This polluted water will pollute the environment if management is not carried out. One of the materials that can lower pollutant parameters in restaurant liquid waste is activated carbon. Activated carbon has been successfully created using coconut shells to lower BOD parameters in wastewater. Variations of activator, pH, and contact time have been performed. This study informed that the best activator on the activated carbon of coconut shell to lower BOD in the RWKR is to use H_3PO_4 activator with an average percentage of 89.69%. The optimum contact time to lower BOD in the RWKR using activated carbon from the coconut shell was at 10 minutes with a percentage value of 44.186% and the corresponding adsorption isotherm model on the decrease of BOD in the RWKR using activated carbon from the coconut shell that follows the isotherm Freundlich pattern.

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