



Original Research Article

Optimisation of Microporous Biochar Synthesis from Guariuba Sawdust

*Omoruwou, F. and Uzomba, T.P.

Department of Chemical Engineering, College of Engineering and Technology, Federal University of Petroleum Resources Effurun, PMB 1221, Delta State, Nigeria.

*omoruwou.felix@fupre.ng; uzombatochukwu@yahoo.com

<http://doi.org/10.5281/zenodo.14565707>

ARTICLE INFORMATION

Article history:

Received 12 Sep. 2024

Revised 12 Oct. 2024

Accepted 28 Oct. 2024

Available online 30 Dec. 2024

Keywords:

Optimisation

Guariuba

Biochar

Pyrolysis

Porosity

ABSTRACT

This study was carried out to optimise microporous biochar from sawdust. Biochar was prepared by conducting fast pyrolysis of Guariuba wood sawdust derived from saw timber. The pyrolysis process was carried out at a temperature range of 300–700 °C and a time of 10–60 minutes. Chemical activation of Guariuba wood biochar was carried out using potassium hydroxide (KOH) as the activating agent for adsorption studies. The influence of pyrolysis temperature on the biochar pore was investigated by using Brunauer-Emmett-Teller (BET) surface analysis and scanning electron microscopy energy dispersive x-ray spectroscopy (SEM-EDX). It was found that the maximum BET surface area and pore volume were 112.664 m²/g and 0.130 cc/g respectively for biochar pyrolysis at 350 °C. The effects of two variables, including temperature and time, were investigated for maximal porosity by utilising response surface methodology (RSM) with central composite design (CCD). Through the variance of ANOVA, the linear model was established by experimental data with a high R² value (R² = 0.9280), small F-value, and p-value indicating that the proposed model is statistically significant. The estimated optimal conditions were validated by confirmation experiments. It was revealed that the porosity reached 86.0016% at the following optimal conditions; temperature = 640.924 °C and time = 50.171 minutes. These results show that Guariuba wood can be used as an effective adsorbent for wastewater treatment and also highlighted the effect of pyrolysis temperature on biochar pores that are associated with soil fertility and nutrient retention in soil, which could be beneficial to the agricultural industries.

© 2024 RJEES. All rights reserved.

1. INTRODUCTION

Biomass-derived char also known as biochar is a carbon-rich product that is different from charcoal or activated carbon and related materials in that it is produced through the thermochemical conversion of biomass in an “oxygen-limited environment” and derived from a variety of feedstock including wood

biomass, animal manure, crop leftovers, and solid waste (Sohi *et al.*, 2010; Tsai and Chen, 2013). This process of producing biochar from biomass is called pyrolysis, which involves heating organic matter in the absence of oxygen or using a wide range of temperatures (300 to 1,000 °C) for the thermal decomposition of biomass in an oxygen-depleted environment (Novotny *et al.*, 2015). It has gained significant attention in recent years due to its potential applications in agriculture, environmental remediation, and carbon sequestration. Having the qualities of a large specific surface area, porous structure, enriched surface functional groups, and mineral composition in these applications, it can be employed as a good adsorbent for the elimination of contaminants in aqueous solutions (Tan *et al.*, 2015).

The study on the optimisation of microporous biochar synthesis from sawdust typically involves a combination of experimental investigations and optimisation techniques. Researchers explore various parameters that can influence the properties of the resulting biochar, such as pyrolysis temperature, heating rate, residence time, feedstock characteristics, and the use of catalysts or additives (Jin *et al.*, 2021). This involves maximizing the surface area, pore volume, and pore size distribution of the biochar to enhance its adsorption capacity and other desirable properties. Researchers utilise characterisation techniques such as scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR) to evaluate the structural and chemical properties of the biochar (Yaashikaa *et al.*, 2020). In recent years, utilization of the RSM has increased for the optimisation of the preparation of adsorbents. This is because it allows researchers to systematically analyse multiple variables and their interactions to determine the optimal conditions for their synthesis. In most cases, the correlation of these multiple variables is very difficult to understand except for the applications of RSM. By optimising pyrolysis parameters and feedstock characteristics, biochar can be tailored to meet specific application requirements. The optimisation of the biochar production process is therefore a necessity, and statistical methods such as RSM or factorial design can be used effectively to achieve high microporosity, adsorption capacity, and stability which have also been applied by many researchers (Saadat *et al.*, 2018; Sawood *et al.*, 2021; Zubair *et al.*, 2022). These methods can help improve the overall performance and applicability of biochar in various environmental and agricultural applications.

Therefore, in this research work, the interaction of two factors (heating temperature and heating time) during the preparation of biochar was considered using the response surface methodology (RSM) for the optimisation and improvement of the products to suit its applicability in adsorption processes.

2. MATERIALS AND METHODS

2.1. Sample Pre-Treatment and Preparation of Adsorbent

The sawdust used for this investigation was collected from a sawmill in Uselu-Lagos Road, Benin City, Nigeria. The collected sawdust was sun-dried for 24 hours to remove moisture, after which it was sieved to a size of 500 µm using an ASTM test sieve. The dried sawdust sample (500 µm particle size) was placed in a crucible cup in a muffle furnace and was used for the production of the biochar. A specific amount (5 g) of the sawdust was measured into crucibles and weighed on a weighing balance. The weighed samples were kept in a muffle furnace, and pyrolysis was carried out at different temperatures and time rates as specified in the experimental design. The experimental temperature was varied between 300 °C and 700 °C, with the resident time varying between 10 minutes and 60 minutes. The resulting Guariuba Wood Biochar (GWBC) was kept in a desiccator to prevent the absorption of moisture before further analysis (Moradi *et al.*, 2016).

2.2. Preparation of Potassium Hydroxide (KOH) for Activation

The potassium hydroxide (KOH) used as an activating agent in this research work was prepared by weighing 14 grammes of potassium hydroxide (KOH) pellets (purity: 98%, molar mass: 56.11 g/mol, specific gravity: 1.0824) in a beaker using a weighing balance and dissolving them in 500 ml of deionized water. The solution was stirred continuously until the pellets were thoroughly dissolved,

resulting in a clear and colourless potassium hydroxide solution ready for further use in the experiment (Hui and Zaini, 2015).

2.4. Preparation of the Adsorbate

Methyl Orange (molecular formula = $C_{14}H_{14}N_3NaO_3S$, molecular weight = 327.33; purity = 95%, absorbance maximum = 464 μm) was purchased from a local dye supplier. A stock solution was prepared by dissolving 20g of Methyl orange dye in 1000 ml of deionised water to obtain a concentration of 200 mg/L. A standard concentration of 50 mg/L was prepared by adding 20 ml of the stock solution into 80 ml of deionised water.

2.5. Chemical Activation of Carbon Produced from Guariuba Wood

The carbonized adsorbent material was weighed and transferred into the crucibles and was placed in a muffle furnace heated at 800 °C for about 2 hours and thereafter allowed to cool at room temperature. After cooling, five grams (5 g) of the cooled biochar was weighed and added to the already prepared KOH solution in a round bottom flask. The solution was stirred for about 5 minutes and placed in a heating mantle to boil for 1 hour. The activated sample from Guariuba wood was cooled at room temperature and the supernatant basic solution was decanted. It was repeatedly washed with deionised water until the washing was free from the base (pH is 6-7) for which the test for pH was done using the standard pH test method. The resulting biochar was filtered, dried and again activated thermally in a hot air oven at 110 °C for two hours according to the modified method of Turap *et al.* (2017). The final product was stored in a plastic container and kept inside the desiccators for further use as an adsorbent.

2.6. Physico-chemical Characterization of Adsorbent

The physio-chemical characterization such as pH, bulk density, moisture content, ash content, and bulk density was evaluated according to standard methods found in the literature. The proximate analysis was analysed by using the American Society for Testing and Materials ASTM (D1762-84) method which is proposed by the International Biochar Initiative (IBI) (Aller *et al.*, 2017). The ultimate or elemental compositions of the biochar sample prepared are shown in Table 2. Energy Dispersive X-ray analysis (EDX) is an X-ray technique which is used to identify the elemental composition of biochar.

2.7. Determination of Bulk Density

A known weight of sawdust samples of 5g each was prepared. The bulk density was determined using the core sampler method (Solgi *et al.*, 2018). The bulk density is the mass of the sample divided by the total volume of the sample as shown in Equation 1.

$$\text{Bulk Density} = \frac{M_s}{V_t} \quad (1)$$

Where M_s = mass of oven-dried sawdust (g) and V_t = total sawdust volume (cm^3) assumed to be equal to the volume of a cylinder

2.8. Determination of Ash Content

The ash content is the residue after a sawdust sample has been burnt. This was measured according to the ASTM D-5142 procedure as recommended by Debdoubi *et al.* (2005) and reported by Elehinafe *et al.* (2019). The pre-weighed samples were burnt in a muffle furnace at 500 °C for 4 hours. They were removed and allowed to cool in a desiccator to obtain the weight of the ash. The final weights of the samples were taken with the aid of OHAUS AV264 Adventurer Pro Analytical balance. The ash contents were calculated using Equation 2.

$$\text{Ash Content (\%)} = \frac{D}{B} \times 100 \quad (2)$$

Where B = sample in grams (after burning) and D = residues in grams (before burning)

2.9. Determination of moisture content

The moisture content was obtained by measuring the weight reduction of the sample when the samples were subjected to drying. The initial weights of the samples were measured and thereafter, an experimental investigation was made on the samples when it was subjected to drying at ambient temperature ranging from 15 °C to 37 °C (Fridh *et al.*, 2014; Nielsen, 2003). The difference in sample weight before and after drying gives exact information on the moisture content. The moisture content was thereafter calculated on a dry basis using this expression:

$$\text{Moisture (\%)} = \frac{(W_w - W_d)}{(W_w - W_c)} \times 100 \quad (3)$$

Where W_c = Weight of container (g), W_w = Weight of container plus wet sample (g) and W_d = Weight of container plus sample after drying (g)

2.10. Determination of pH

The pH of GWABC was determined using the standard method as described by US EPA, (2002). This was done by weighing 5 g of the adsorbent into 20 ml of deionised water and the resulting suspension mixture was agitated for 1 hour in an orbital shaker for proper mixing. Thereafter, the solution was filtered and the temperature of the filtrate was then measured, and the temperature on the dial of the pH meter was set to match the measured temperature. The pH meter probe was rinsed with deionized water and blot-dried. The pH meter was calibrated (using buffers, 4.00, 7.00 and 10.00). The pH meter probe was placed in the filtrate whose pH is to be measured and the value was taken after attaining a steady state.

2.11. Characterisation of Guariuba Wood Activated Biochar (GWABC)

The surface morphology, structure, and surface area of the GWABC were determined using SEM with EDX capability to investigate the localised carbon content on the biochar produced and BET analysis by an automated nitrogen multilayer absorption system. SEM is a characterisation technique that provides high-resolution images to the adsorbent surface which can help to identify the adsorption ability of the adsorbent. For this research, SEM was used to analyse the surface of the activated GWABC. SEM images will show the surface morphology of the adsorbent. Scanning electron microscopy along with Energy dispersive X-ray spectroscopy (EDX) is utilized for examining the elemental composition of biochar. The numerous elements present on the surface of biochar can be determined using SEM-EDX.

2.12. Adsorption Performance of GWABC

The adsorptive performance of activated GWABC towards Methyl orange dye solution was evaluated by batch mode adsorption studies. The experiment was conducted in a series of 250 ml Erlenmeyer flasks containing 25 ml of Methyl orange solution as well as different amounts of GWABC were weighed and added to the various flasks. The flasks were agitated in an orbital shaker with a fixed shaking speed of 195 rpm. The effect of adsorbent dose and pH (2–9) on the adsorption process is studied to determine the optimum conditions for the removal of Methyl orange dye by GWABC. The experiment was conducted with duplicate under the same conditions and studies were undergone about the removal efficiency of an adsorbent which also involved the determination of the absorbance of each of samples at 580µm.

2.13. Design of Experiment

To avoid the traditional experiments (one factor at a time) along with optimising a process through the individual and interactive effects of independent variables simultaneously, the optimised design of experiments can be used to solve this problem. The design expert software (Design Expert 13.0) was used for the experimental runs and the modelling of experimental data. Thirteen (13) runs of the experiment were generated with CCD (Central Composite Design) which was employed to optimize

the GWABC preparation parameters of heating time and heating temperature. The variables were optimized within the studied range to investigate the combined effect of these two independent variables using the response surface methodology (RSM). The Response Surface Methodology (RSM) is a set of statistical and mathematical techniques that are helpful for modelling and analysing situations where multiple independent variables affect an interest response variable (Taiwo *et al.*, 2019). In this study, RSM was used to optimise the preparation conditions of GWABC. The process data for the experimental design is presented in Table 1.

Table 1: Treatment combination: range of factors for GWABC porosity determination

Variables	Unit	Symbol	Variable levels	
			Low level	High level
Temperature	°C	A	300	700
Time	week	B	10	60

3. RESULTS AND DISCUSSION

3.1. Physical and Chemical Analysis of GWABC

The results obtained from the physiochemical analysis of the precursor are shown in Table 2. The proximate analysis result of Guariuba wood biochar has a pH value of 7 which indicates the neutrality of the sample. Contrary to common notions, the pH result indicates that its application has no negative impact on soil pH (Jeffery *et al.*, 2011). The result also revealed that the sample has a far lower moisture content percentage (%MC) of 0.382% compared to those of Nigerian Coal Species which have a % MC of between 32.5% to 42.7% (Elehinafe *et al.*, 2019). According to Shojaeiarani *et al.* (2019), moisture content is a very significant property which can adversely affect the burning characteristics of solid biomass. Ungureanu *et al.* (2018), also reported that moisture content is one of the main parameters determining the total energy needed to bring the biomass up to pyrolytic temperature. This is because moisture acts as a heat sink making transmission of heat difficult, requiring additional energy to evaporate before the biomass can begin to thermally degrade.

Table 2: Showing the Physiochemical Properties of GWABC

Properties Measured	Values Obtained
Proximate Analysis	wt. % dry basis
Ash content	2.743
Moisture content	0.382
Ultimate Analysis	wt. % dry basis
Carbon	96.18
Calcium	0.83
Phosphorus	0.37
Sulphur	0.22
Sodium	0.25
Bulk Density	1.5 g/cm ³
Moisture Content	0.382%
pH	7.0
Total Surface Area	1038m ² /g
Particle Size	<250µm

Sun-drying of the identified samples before the determination of their percentage moisture content could make them fall under the category of low moisture biomass which can also indicate that hardwood contains less moisture content than soft and semi-soft wood. The result also shows an ash content of 2.743% which is higher compared to the average percentage of ash content in sawdust from different wood species as reported by Oyebanji *et al.* (2021). Mitchual (2014) opined that ash is an impurity that will not burn, therefore hardwood of high level of ash content concentration could be more effective if used as activated carbon in a water treatment mechanism. In terms of the effect of particle size on

cellulose content and lignin content, various researchers have reported that cellulose content for hardwood species falls within the range of 40 to 47 % (Joshua *et al.*, 2016). The larger the particle size the higher the lignin content for the range of particle size considered. The sawdust sample particle size is about $<250\mu\text{m}$. Bulk Density is one of the properties of adsorbents. The bulk density of the sawdust sample is $1.51\text{g}/\text{cm}^3$. The variation in the bulk density of different biomass can be attributed to the variation in the physiochemical properties of the wood (Cai *et al.*, 2017; Ikenyiri *et al.*, 2019). The total surface area of the sawdust shows a high value which indicates a large number of pores and a high degree of porosity which makes the sawdust an excellent adsorbent material. It can also be attributed to the presence of lignocellulose materials which have a complex structure consisting of cellulose, hemicellulose, and lignin making it favourable for water treatment as this is in agreement with the report of Roa *et al.* (2021).

3.2. Scanning Electron Microscopy Energy Dispersive X-ray spectroscopy (SEM-EDX) of GWABC

Scanning electron microscopic (SEM) image of sample GWABC is presented in Figure 1. SEM monographs of GWABC illustrate the highly porous structure and surface morphology of biochar. The xylem structure and biochar surface porosity were clearly shown in the biochar sample (as represented in the image in Figure 1). The working distance of these images was approximately 8.0 mm and resolution power (μm) varies at different scales. In the SEM images of GWABC, one can observe mesopores along with micropores. Similarly, the cylindrical micro and mesoporous channels could also be seen. Besides this, a large number of pores are also obvious on the surface which is anticipated to be responsible for the high surface area of this sample. Generally, biochar retains the biomass cell wall structure, which changes with feedstock type and production conditions. The presence of porosities in biochar is relevant to the movement of roots through the soil and serves as a habitat for varieties of microbes in the soil (Atkinson *et al.*, 2010; Wong and Ogbonnaya, 2021).

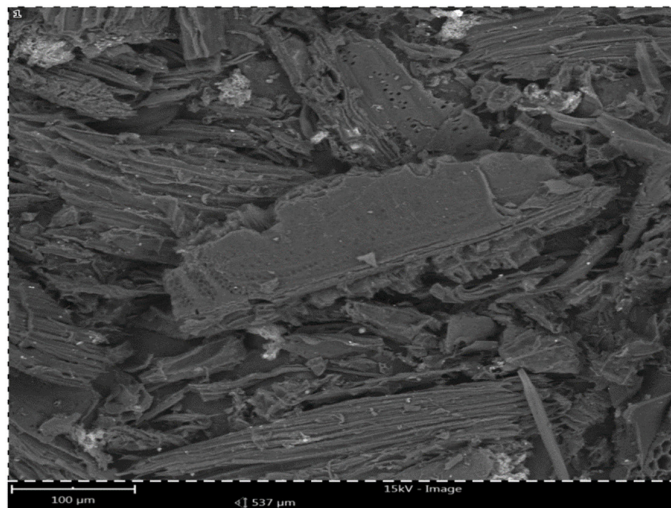


Figure 1: SEM micrograph of pyrolysed sawdust

3.3. Energy Dispersive X-ray Spectroscopy (EDX) Analysis

The data obtained by EDX analysis consists of a spectrum which highlights the distribution of various elements present in the sample and the same can be analysed by coloured peaks. The maximum carbon content observed in Guariuba wood biochar is 96.18%. Other constituents like S, K, Na and P are shown in Table 3. The values of other parameters like total Si, Al, Mg, and Ca were seen in the biochar sample analysed by EDX. Furthermore, the smallest amount of Cl was detected.

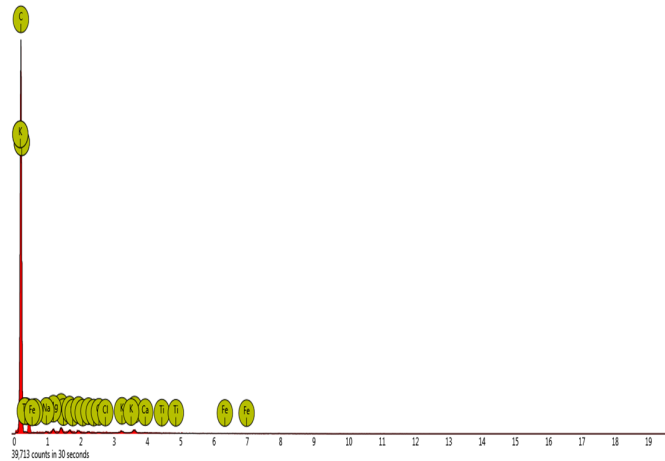


Figure 2: Elemental composition of GWABC by energy dispersive x-ray spectroscopy (EDX)

Table 3: Elements compositions of GWABC

Element number	Element symbol	Element name	Atomic conc. (wt %)	Weight conc. (wt %)
6	C	Carbon	98.46	96.18
20	Ca	Calcium	0.25	0.83
13	Al	Aluminium	0.33	0.72
12	Mg	Magnesium	0.25	0.49
19	K	Potassium	0.13	0.41
15	P	Phosphorus	0.15	0.37
14	Si	Silicon	0.16	0.36
11	Na	Sodium	0.13	0.25
16	S	Sulphur	0.09	0.22
17	Cl	Chlorine	0.06	0.16
22	Ti	Titanium	0.00	0.00
26	Fe	Iron	0.00	0.00

3.4 Brunauer-Emmett-Teller Analysis (BET) of GWABC

The BET analysis was used to ascertain the surface area, pore diameter, and total pore volume of the biochar. Hence, the surface area of GWABC is 112.664 m²/g. A study conducted by Shaaban *et al.* (2013) revealed that there was not a significant rise in BET surface area observed with pyrolysis temperature increases of 300°C to 500 °C. Nevertheless, a considerable increase in BET surface area was observed upon raising the temperature to 700 degrees Celsius. This is probably due to the lower temperatures at which the reactants were partially carbonised. Also, an increase in temperature to 700°C has been shown to increase the volatilities of organic compounds and create more pores, which contribute to a larger surface area. The higher surface area is preferable because it helps to improve the soil structure and increase total water retention in soil (Downie *et al.*, 2009). As expressed before, the particle size of the sawdust was limited to 500 µm. The particle size directly affects the surface area; therefore, a reduction in the particle size can lead to an increase in the surface area. Total pores volume increases proportionally with pore diameter and reported the highest value of 0.130 cc/g with a pore size of 2.647 nm. The presence of micropores may help to improve the moisture content in soil. The average pore diameter denotes the pores are mostly micropores and mesopores (Galarneau *et al.*, 2018). Mesopores are useful for liquid-solid adsorption (Al-Degs *et al.*, 2005).

3.5. Optimisation of the Process Parameters Using Response Surface Methodology

3.5.1. Statistical analysis and the model fitting

The porosity of the Guariuba wood-activated biochar (GWABC) was determined by thirteen (13) experimental runs. The experimental values were obtained using central composite design (CCD) with two adsorption parameters considered: contact time and temperature.

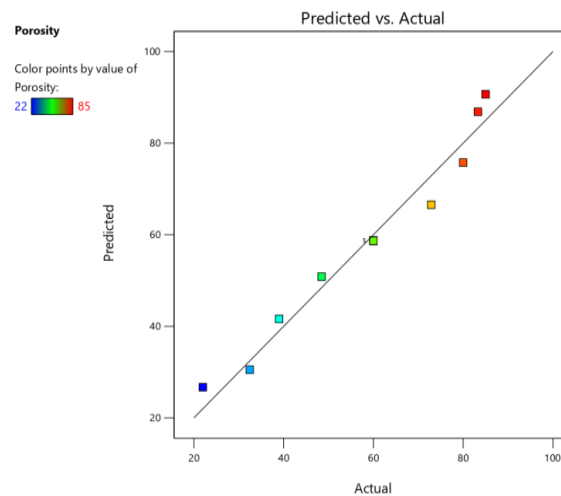


Figure 3: The parity plot of predicted data versus the experimental actual data of the porosity of guariuba wood-activated biochar (GWABC)

Table 4: Central composite design values for the porosity of GWABC

Runs	Factor 1	Factor 2	Porosity (%)	
	A: Temperature (°C)	B: Time (min)	Actual	Predicted
1	358.58	17.32	32.46	30.54
2	641.42	52.68	83.30	83.07
3	500.00	35.00	60.00	61.63
4	500.00	35.00	60.00	61.63
5	500.00	35.00	60.00	61.63
6	500.00	60.00	72.90	69.47
7	700.00	35.00	85.00	84.11
8	300.00	35.00	22.00	26.72
9	358.579	52.68	39.00	41.63
10	500.00	35.00	60.00	61.63
11	500.00	35.00	60.00	61.63
12	500.00	10.00	48.47	53.78
13	641.42	17.32	80.00	71.98

The best model is the one that maximises the adjusted and predicted R^2 values. The linear model with an R^2 value of 0.9280 is higher than the quadratic and two-factor interaction (2FI) R^2 values; hence, it is considered the best model for the porosity of Guariuba wood-activated biochar (GWABC). The data were analysed to correlate the experimental and predicted porosity, as shown in Figure 3, with the porosity of the Guariuba wood-activated biochar (GWABC). As can be seen, the data points were well distributed close to a straight line, which suggested an excellent relationship between the experimental and predicted values of the response, and the underlying assumptions of the above analysis were appropriate. The difference between the adjusted and predicted values of less than 0.2 also indicated that the selected linear model is adequate in assuming the response variables for the experimental data. The response and the test variables were related by the following linear equation:

$$E = +58.70 + 22.62A - 5.55B \quad (4)$$

Where E is porosity, A is temperature, and B is contact time.

The equation in terms of coded factors can be used to make predictions about the response at given levels of each factor. By default, the high levels of the factors are coded as +1, and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. The negative coefficient values indicate that the contact time has a negative effect on the response. In other words, the response gets smaller as time increases. In this equation, the temperature has a positive effect (Porosity increases as temperature increases), but time has a negative effect (Porosity decreases as time increases) in the tested range. The fit summary table is shown in Table 5.

Table 5: Fit summary

Sources	Sequential p-value	Adjusted R ²	Predicted R ²	
Linear	<0.0001	0.9598	0.9280	Suggested
2FI	0.6985	0.9561	0.9002	
Quadratic	0.1296	0.9685	0.8695	
Cubic	0.0010	0.9973	0.9272	Aliased

3.5.2. Analysis of variance (ANOVA)

The analysis of variance (ANOVA) results for the linear equation of GWABC porosity is tabulated in Table 6. The ANOVA indicates that the equation and actual relationship between the response and significant variables represented by the equation is accurate. The values of F and p determine the significance of the coefficient term, and the larger the value of F and the smaller the value of p, the more significant the variable is (Liu *et al.*, 2010). From the analysis, the Model F-value of 144.33 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. The Lack of Fit F-value by statistical interpretation is 25.05. The P-values were used as a tool to check the significance of each of the coefficients, which in turn were necessary to understand the pattern of the mutual interactions between the test variables (Thiese *et al.*, 2016). The Predicted R² of 0.9280 is in reasonable agreement with the Adjusted R² of 0.9598 with a difference of less than 0.2 which indicates that the model was a good fit for the data and explained 95% of the variation in the data. This suggests that the model is an accurate representation of the data. Therefore, the higher the F-test value and the smaller the P-values, the higher the significance of the corresponding coefficient (Thiese *et al.*, 2016).

Table 6: ANOVA values, the sum of squares, df, mean square, f-value, the p-value for the porosity of Guariuba wood activated biochar (GWABC)

Source	Sum of squares	Df	Mean square	F-value	P-value	
Model	4338.51	2	2169.25	144.33	<0.0001	Significant
A -Temperature	4092.20	1	4092.20	272.28	<0.0001	
B – Time	246.30	1	246.30	16.39	0.0023	
Residual	150.30	10	15.03			
Lack of Fit	150.30	6	25.05			
Pure Error	0.0000	4	0.0000			
Cor Total	4488.80	12				

3.5.3. Coefficients in terms of coded factors

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor

settings. When the factors are orthogonal the variance inflation factors (VIF) are 1; VIFs greater than 1 indicate multi-colinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable.

Table 7: Shows the coefficients in terms of coded factors

Factors	Coefficient estimate	Df	Standard error	95% Low	CI High	VIF
Intercept	58.70	1	1.08	56.31	61.10	
A-Temperature	22.62	1	1.37	19.56	25.67	1.0000
B-Time	5.55	1	1.37	2.49	8.60	1.0000

3.6. Effect of Process Variables

Two important porosity factors which are temperature and contact time were examined to determine the Porosity of guariuba wood-activated biochar (GWABC). The relation between different factors and responses using the three-dimensional (3D) response surface is very helpful as a function of two factors. The effective interaction between temperature and contact time is shown in Figure 4. The results show that as the temperature increased, the porosity also increased, but at a faster rate once the temperature reached 358.579 °C. At this point, the porosity began to increase rapidly until it reached a maximum value of 641.421 °C. This means the initial increase in adsorption efficiency is because the heat supplied acts as activation energy. The stagnancy or decrease afterwards is due to the exothermic nature of adsorption equilibrium. The results also show that there was a slow increase in porosity from 22% - 40% with an increase in time from 17.3223 minutes – 52.6777 minutes. This indicates that a longer contact time favours the reaction towards attaining higher porosity.

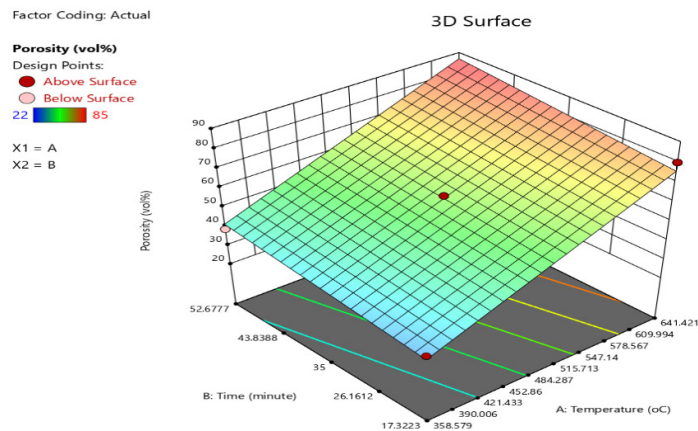


Figure 4: The 3D response surface plot for the interaction of time and temperature

3.7. Process Optimisation

Using numerical optimisation, from the analysis of the effect of the variables explained above, the best maximum porosity was found to be at a temperature of 629.979 °C, time of 52.616 minutes, porosity of 85.0186 % and desirability of 1.000. The desirability ramp for the numerical optimisation of three goals is shown in Figure 5.

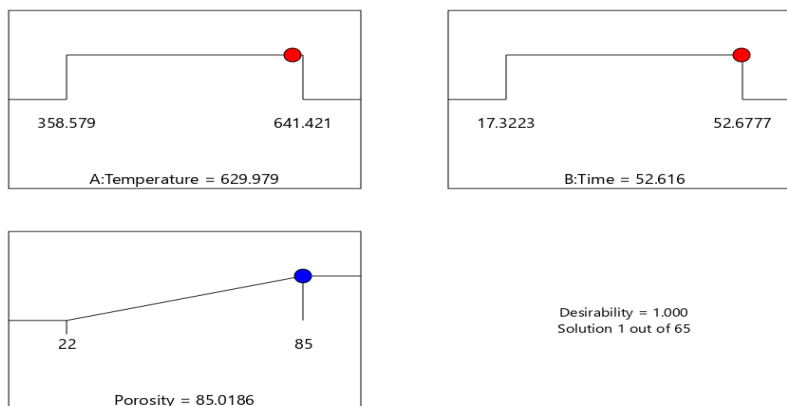


Figure 5: The desirability ramp of the numerical optimisation of the porosity of GWABC

4. CONCLUSION

An experimental study of the porosity of activated carbon from GWABC was investigated for the optimisation of microporous biochar synthesis. Biochar can be synthesized from a wide range of different pyrolysis conditions. The physical characterization of biochar helped to identify the basic structural and elemental composition of the biochar. Biochar consists of cellulose, hemicellulose and lignin content, most of the cellulose and hemicellulose are broken down during pyrolysis. From the SEM image, it has been concluded that the porous surface formation was a consequence of pyrolysis at very high temperatures and time. The proximate analysis indicates that the sawdust precursor is suitable for preparing activated carbon. Chemical activation of GWABC was implored using Potassium Hydroxide as the activating agent that led to an increase in porosity and surface area of the biochar, done by removing some of the carbon atoms from the structure of the biochar, which leaves behind pores. Adsorption studies carried out on GWABC showed its dye removal efficiency using methyl orange dye and it was concluded that an increase in the adsorbent dosage will increase the dye removal efficiency. A linear equation model was suggested using central composite design (CCD) to best describe the model of the experiment. The optimal porosity from the statistical interpretation is (85.0186 %), with a temperature of 629.979 °C and a time of 52.616 minutes. The optimised results show that increasing the temperature and time can increase the porosity of the material. This could be useful in applications where porosity is desired, such as in the production of filters or membranes.

5. ACKNOWLEDGMENT

The authors wish to acknowledge the assistance and contributions of the laboratory staff of the Department of Chemical Engineering, Federal University of Petroleum Resources, Effurun, Delta State, Nigeria, and that of Luco Scientific Laboratory, Benin City, Edo State, Nigeria, toward the success of this work.

6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

REFERENCES

- Al-Degs, Y. S., El-Barghouthi, M. I., Khraisheh, M. A., Ahmad, M. N., and Allen, S. J. (2005). Effect of Surface Area, Micropores, Secondary Micropores, and Mesopores Volumes of Activated Carbons on Reactive Dyes Adsorption from Solution. *Separation Science and Technology*, 39(1), pp. 97–111. <https://doi.org/10.1081/ss-120027403>
- Aller, D., Bakshi, S., and Laird, D. A. (2017). Modified method for proximate analysis of biochars. *Journal of Analytical and Applied Pyrolysis*, 124(Vm), pp. 335–342. <https://doi.org/10.1016/j.jaap.2017.01.012>

- Cai, J., He, Y., Yu, X., Banks, S. W., Yang, Y., Zhang, X., Yu, Y., Liu, R., and Bridgwater, A. V. (2017). Review of physicochemical properties and analytical characterization of lignocellulosic biomass. *Renewable and Sustainable Energy Reviews*, 76, 309–322. <https://doi.org/10.1016/j.rser.2017.03.072>
- Debdoubi, A., El Amarti, A., and Colacio, E. (2005). Production of fuel briquettes from esparto partially pyrolyzed. *Energy Conversion and Management*, 46(11), pp. 1877–1884. <https://doi.org/10.1016/j.enconman.2004.09.005>
- Elehinafe, F. B., Okedere, O. B., Odunlami, O. A., Mamudu, A. O., and Bamidele, S. F. (2019). Proximate Analysis of the Properties of Some Southwestern Nigeria Sawdust of Different Wood Species. *International Journal of Civil Engineering and Technology*, 10(3), pp. 51–59.
<http://www.iaeme.com/ijmet/issues.asp?JType=IJCIET&VType=10&IType=3>
<http://www.iaeme.com/IJCIET/index.asp52http://www.iaeme.com/IJCIET/issues.asp?JType=IJCIET&VType=10&IType=3>
- Fridh, L., Volpé, S., and Eliasson, L. (2014). An accurate and fast method for moisture content determination. *International Journal of Forest Engineering*, 25(3), pp. 222–228. <https://doi.org/10.1080/14942119.2014.974882>
- Galarneau, A., Mehlhorn, D., Guenneau, F., Coasne, B., Villemot, F., Minoux, D., Aquino, C., and Dath, J. P. (2018). Specific Surface Area Determination for Microporous/Mesoporous Materials: The Case of Mesoporous FAU-Y Zeolites. *Langmuir*, 34(47), pp. 14134–14142. <https://doi.org/10.1021/acs.langmuir.8b02144>
- Hui, T. S., and Zaini, M. A. A. (2015). Potassium hydroxide activation of activated carbon: A commentary. *Carbon Letters*, 16(4), pp. 275–280. <https://doi.org/10.5714/CL.2015.16.4.275>
- Ikenyiri, P. N., Millionaire, F., Abowei, N., Ukpaka, C. P., and Amadi, S. A. (2019). Characterization_and_physicochemical_pro (1). *Chemistry International*, 5(3), pp. 190–197. <https://doi.org/10.5281/zenodo.2002187>
- Jeffery, S., Verheijen, F. G. A., van der Velde, M., and Bastos, A. C. (2011). A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agriculture, Ecosystems and Environment*, 144(1), pp. 175–187. <https://doi.org/10.1016/j.agee.2011.08.015>
- Jin, C., Sun, J., Chen, Y., Guo, Y., Han, D., Wang, R., and Zhao, C. (2021). Sawdust wastes-derived porous carbons for CO₂ adsorption. Part I. Optimization preparation via orthogonal experiment. *Separation and Purification Technology*, 276, 119270. <https://doi.org/10.1016/j.seppur.2021.119270>
- Joshua, J. A., Ahiekpor, J. C., Kuyea, A., and Kuye, A. (2016). Nigerian Hardwood (*Nesogordonia papaverifera*) Sawdust Characterization: Proximate Analysis, Cellulose and Lignin Contents. *Lignocellulose*, 5(1), pp. 50–58.
- Liu, Y., Zheng, Y., and Wang, A. (2010). Response surface methodology for optimizing adsorption process parameters for methylene blue removal by a hydrogel composite. *Adsorption Science and Technology*, 28(10), pp. 913–922. <https://doi.org/10.1260/0263-6174.28.10.913>
- Mitchual, S. J. (2014). *Densification of Sawdust of Tropical Hardwoods and Maize Cobs at Room Temperature Using Low Compacting Pressure Without a Binder*. Kwame Nkrumah University of Science and Technology.
- Moradi, M., Fazlzadehdavil, M., Pirsahab, M., Mansouri, Y., Khosravi, T., and Sharafi, K. (2016). Response surface methodology (RSM) and its application for optimization of ammonium ions removal from aqueous solutions by pumice as a natural and low cost adsorbent. *Archives of Environmental Protection*, 42(2), pp. 33–43. <https://doi.org/10.1515/aep-2016-0018>
- Nielsen, S. S. (2003). Determination of Moisture Content. In : *Nielsen, S.S. (eds) Food Analysis Laboratory Manual. Food Science Texts Series*. pp. 13–22. https://doi.org/10.1007/978-1-4757-5250-2_3
- Novotny, E. H., Maia, C. M. B. de F., Carvalho, M. T. de M., and Madari, B. E. (2015). Biochar: Carbono pirogênico para uso agrícola - Uma revisão crítica. *Revista Brasileira de Ciencia Do Solo*, 39(2), pp. 321–344. <https://doi.org/10.1590/01000683rbc20140818>
- Oyebanji, J. A., Okekunle, P. O., Oyedepo, S. O., and Fayomi, O. S. I. (2021). Physicochemical Properties of Wood Sawdust: A Preliminary Study. *IOP Conference Series: Materials Science and Engineering*, 1107(1), 012125. <https://doi.org/10.1088/1757-899x/1107/1/012125>
- Roa, K., Oyarce, E., Boulett, A., ALSamman, M., Oyarzún, D., Pizarro, G. D. C., and Sánchez, J. (2021). Lignocellulose-based materials and their application in the removal of dyes from water: A review. *Sustainable Materials and Technologies*, 29, pp. 1-17. <https://doi.org/10.1016/j.susmat.2021.e00320>
- Saadat, S., Raei, E., and Talebbeydokhti, N. (2018). Enhanced removal of phosphate from aqueous solutions using a modified sludge derived biochar: Comparative study of various modifying cations and RSM based optimization of pyrolysis parameters. *Journal of Environmental Management*, 225(April), pp. 75–83. <https://doi.org/10.1016/j.jenvman.2018.07.037>

- Sawood, G. M., Mishra, A., and Gupta, S. K. (2021). Optimization of Arsenate Adsorption over Aluminum-Impregnated Tea Waste Biochar Using RSM–Central Composite Design and Adsorption Mechanism. *Journal of Hazardous, Toxic, and Radioactive Waste*, 25(2), pp. 1–19. [https://doi.org/10.1061/\(asce\)hz.2153-5515.0000581](https://doi.org/10.1061/(asce)hz.2153-5515.0000581)
- Shaaban, A., Se, S. M., Mitan, N. M. M., and Dimin, M. F. (2013). Characterization of biochar derived from rubber wood sawdust through slow pyrolysis on surface porosities and functional groups. *Procedia Engineering*, 68, pp. 365–371. <https://doi.org/10.1016/j.proeng.2013.12.193>
- Shojaeiarani, J., Bajwa, D. S., & Bajwa, S. G. (2019). Properties of densified solid biofuels in relation to chemical composition, moisture content, and bulk density of the biomass. *BioResources*, 14(2), 4996–5015. <https://doi.org/10.15376/biores.14.2.Shojaeiarani>
- Sohi, S. P., Krull, E., Lopez-Capel, E., & Bol, R. (2010). A review of biochar and its use and function in soil. In *Advances in Agronomy* 105, pp. 47–82. [https://doi.org/10.1016/S0065-2113\(10\)05002-9](https://doi.org/10.1016/S0065-2113(10)05002-9)
- Solgi, A., Naghdi, R., Labelle, E. R., Tsioras, P. A., and Salehi, A. (2018). Comparison of sampling methods used to evaluate forest soil bulk density. *Croatian Journal of Forest Engineering*, 39(2), pp. 247–254.
- Taiwo, A. I., Agboluaje, S. A., and Lamidi, W. A. (2019). Application of Response Surface Method (RSM) and Central Composite Design (CCD) for Optimization of Cassava Yield. *Interdisciplinary Research Review*, 14(6), pp. 62–69. <https://doi.org/10.14456/jtir.2019.60>
- Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., and Yang, Z. (2015). Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere*, 125, pp. 70–85. <https://doi.org/10.1016/j.chemosphere.2014.12.058>
- Thiese, M. S., Ronna, B., and Ott, U. (2016). P value interpretations and considerations. *Journal of Thoracic Disease*, 8(9), pp. 928–931. <https://doi.org/10.21037/jtd.2016.08.16>
- Tsai, W. T., and Chen, H. R. (2013). Adsorption kinetics of herbicide paraquat in aqueous solution onto a low-cost adsorbent, swine-manure-derived biochar. *International Journal of Environmental Science and Technology*, 10(6), pp. 1349–1356. <https://doi.org/10.1007/s13762-012-0174-z>
- Turap, T., Merupakan, T. B., Lebih, T. B., and Turap, T. D. (2017). *Microwave Heating with Potassium Hydroxide Activation for Converting Water Hyacinth into Activated Carbon*. Chulalongkorn University.
- Ungureanu, N., Vladut, V., Voicu, G., Dinca, M. N., and Zabava, B. S. (2018). Influence of biomass moisture content on pellet properties - Review. *Engineering for Rural Development*, 17(May), pp. 1876–1883. <https://doi.org/10.22616/ERDev2018.17.N449>
- US EPA. (2002). *Scientific Engineering Response and Analytical Services Soil pH Determination Operating Procedure*. pp. 1–6.
- Wong, J. W. C., and Ogbonnaya, U. O. (2021). Biochar porosity: a nature-based dependent parameter to deliver microorganisms to soils for land restoration. *Environmental Science and Pollution Research*, 28(34), pp. 46894–46909. <https://doi.org/10.1007/s11356-021-14803-8>
- Yaashikaa, P. R., Kumar, P. S., Varjani, S., & Saravanan, A. (2020). A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy. *Biotechnology Reports*, 28, e00570. <https://doi.org/10.1016/j.btre.2020.e00570>
- Zubair, M., Aziz, H. A., Ihsanullah, I., Ahmad, M. A., and Al-Harthi, M. A. (2022). Enhanced removal of Eriochrome Black T from water using biochar/layered double hydroxide/chitosan hybrid composite: Performance evaluation and optimization using BBD-RSM approach. *Environmental Research*, 209, 112861. <https://doi.org/10.1016/j.envres.2022.112861>.