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Response Surface Optimization of Corn Husk Fiber Mercerization Using NaOH

Julius Mmelikam Chukwuemeka[1,2*], Joseph Tagbo Nwabanne[2] and Victor Ifeanyi Ugonabo[2]

[1]Department of Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University, Uli, Nigeria.
[2]Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria.

Authors' contributions

This work was carried out in collaboration among all authors. Authors CJM and NJT designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors CJM, NJT and UVI managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The optimum mercerization parameters for treatment of corn husk using NaOH were analyzed by response surface methodology (RSM). The surface morphology and chemical structures of the raw and NaOH-treated fibers were studied using scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) to validate the RSM results. The optimum chemical characteristics of corn husk treated with NaOH obtained when 100g of corn husk biomass was mercerized in 2.5Mol/dm^3 NaOH for 8 days were: cellulose -70.51%, hemicellulose -8.99%, lignin -6.54, weight loss – 92.27%, ash content -10.11% and extractive -3.78%. The model summary statistics showed that quadratic model best fitted the optimization analysis. The ANOVA results showed that weight loss, hemicellulose, cellulose and lignin contents of corn husk biomass were affected by retting time, retting concentration and weight of biomass. Cellulose content of corn husk was observed to increase with increment in retting time and retting concentration while the reverse is the case for hemicellulose and lignin contents. The NaOH-treated corn husk has higher cellulose content than the untreated corn husk biomass while the reverse is the case for hemicellulose and lignin. SEM images showed that untreated corn husk

**Corresponding author: Email: julleytex@yahoo.com;*

biomass has irregular cross-section, non-uniform surface and some impurities while NaOH treated is finely packed together. XRD graphs showed that cellulose is the predominant content of the fiber. The FTIR results also indicated a variation of the peaks of the curves after treatment which favors an increase in the cellulose content.

Keywords: Corn husk fiber; sodium hydroxide; optimization; mercerization; characterization.

1. INTRODUCTION

Wood-based biomass is becoming more restricted and expensive for producers of pulp & paper, bio-energy, lumber, and wood-based composite fiberboards. The increasing environmental awareness and concerns of the health of forests, wildlife diversity, biomass productivity, climate, and the biological sink directs research to alternative fiber sources. Agricultural wastes from plants are promising sources for alternative Lignocellulosic fiber composites. Several annual plant fibers such as flax, hemp, jute, kenaf, bagasse, corn, banana and bamboo have been the subject of extensive research for the manufacture of non-wood particle and fiberboards [1]. The agro-straw materials are abundant, inexpensive, and readily available sources of Lignocellulosic fibers. With growing environmental awareness, new rules and legislations; scientists and engineers are forced to seek new materials which are more eco-friendly in nature. Hence, the attention of the research community is focused toward finding an eco-friendly material which can give high performance at affordable costs. The keywords with which the eco-friendly materials focused are “biodegradable,” “recyclable,” “renewable” and “sustainable” [2].

Moreover, increasing concern about global warming and exhausting petroleum reserves have made engineers and fiberboard manufactures to focus more on the use of natural fibers such as Jute, bagasse, coir, sisal, banana waste, corn husk etc. Many researchers have justified the utility and established advantageous features of such natural fibers especially in fiberboard production [3]. This has led to creation of more awareness about the use of natural fibers-based materials mainly composites [3]. In the past there have been many efforts to develop composites to substitute the petroleum and other non-decaying materials-based products. The rich availability of natural fibers gives attention on the development of natural fiber composites primarily to explore value-added application avenues.

Reinforcement with natural fiber in composites has in recent times gained attention due to low cost, easy availability, low density, acceptable specific properties, ease of preparation, renewable, lignocelluloses, enhanced energy recovery, CO_2 neutrality, biodegradability and recyclable in nature [4]. Other several reasons that favor the use of natural fibers instead of any other artificial or synthetic fibers are; they are lightweight materials having superior strength, competitive specific mechanical properties, high specific modulus, and reduced energy consumption [5-6]. Additionally, they are non-toxic and nonhazardous in nature, mostly agricultural waste, naturally recyclable, available in abundance, flexible in usage, less expensive and that allow clean energy recovery, etc. [7]. These natural fibers are basically composed of cellulose, hemicellulose, lignin, pectin, wax, and ash.

Despite wood being one of the most relevant Lignocellulosic components in particle/fiberboards [8], new lignocellulosic particles and fibers (mainly by-products from other industries) have been successfully introduced into these boards, i.e., corncob, sawdust [9] date palm branches [10], sorghum stalk fibers [11,12], almond shell and rice husk [13], etc.

In the development of a composite materials made from natural fibers with significantly improved strength, stiffness, durability, and reliability, there is need for better surface treatment of the fiber and also the manufacturing process technology used to produce the composite. Broad studies on natural fibers such as sisal, jute, pineapple, banana, and oil palm empty fruit bunch fibers with thermoplastic and thermosetting material have been carried out recently by Paul et al [2]. Compared to studies on the other natural fiber reinforced composites, very less efforts and attention have been made towards the optimization of corn husk treatment for fiberboard and composite board production.

This work therefore focuses on the optimum treatment of corn husk using NaOH for fiberboards and composites boards production.

2. MATERIALS AND METHODS

2.1 Material Collection and Preparation

The raw materials used in this research were corn husks biomass. The corn husks were sourced from Mgbakwu market Awka North L.G.A(Lat 6□16'20"N, Long.7□3'22"E). The chemical used was NaOH. The NaOH was purchased from chemical store, Bridge Head Onitsha, Anambra state.

The maize husks were exposed to open air before being cleaned. They were cleaned, pitted, and defibrated by open air retting.

2.2 Corn Husk Treatment Method

The corn husk biomass was treated by open air retting of measured weight of biomass in varied concentration of NaOH. The experiment was repeated for 26 times at varied times (days) and weights of biomass according to the design expert table (Table1).

2.3 Chemical Characterization of Corn Husk Biomass (Raw and NaOH) Treated

The raw and NaOH-treated corn husk were characterized for chemical composition.

2.3.1 Klason lignin

A one-gram sun-dried corn husk fiber was placed in a 150mL beaker. Fifteen mL of cold sulfuric acid (72 percent) was added slowly while stirring and mixed well. The reaction was allowed for two hours with frequent stirring in a water bath maintained at 20°C. After two hours, the fiber was transferred by washing it with 560 mL of distilled water into a 1litres flask, diluting the concentration of the sulfuric acid to three percent. An allihn condenser was attached to the flask. The apparatus was placed in a boiling water bath for four hours. The flask was then removed from the water bath and the insoluble corn husk fiber was allowed to settle. The content of the flask was filtered by vacuum suction into a fritted-glass crucible of known weight. The residue from fiber was washed free of acid with 500 mL of hot tap water and then oven-dried at 103±2°C. Crucible was then cooled in a desiccator and weighed until a constant weight was obtained [14,15]

Equation 1 was used to obtain the lignin content of both corn husk:

$$\text{Klason lignin content in (percent)} = \frac{W_4 - W_3}{100 - W_2} \text{ X } (100 - W_1) \quad (1)$$

Where,

W_1=alcohol-toluene extractive content (percent).
W_2=weight of oven-dried extractive-free corn husk/pumkin stemfibre (grams).
W_3=weight of oven-dried crucible (grams).
W_4=weight of oven-dried residue and crucible (grams). [14,15]

2.3.2 Hemicellulose

A two-gram sample of oven-dried extractive-free corn husk fiber was weighed and placed into a 250 mL flask with a small watch glass cover. The fiber was then treated with 150 mL of distilled water, 0.2 mL of cold glacial acetic acid, and one gram of $NaClO_2$ and placed into a water bath maintained between 70°C -80°C.Every hour for five hours, 0.22mL of cold glacial acetic acid and one gram of $NaClO_2$was added and the contents of the flask were stirred constantly. At the end of five hours, the flask is placed in an ice water bath until the temperature of the flasks was reduced to 10^{o}C.The contents of the flask were filtered into a coarse porosity fritted-glass crucible of known weight. The residue was washed free of ClO2 with 500 mL of cold distilled water and the residue changed color from yellow to white. The crucibles were then oven-dried at 103 ± 2°C, then cooled in desiccators, and weighed until a constant weight was reached.

Equation 2 was used to determine the Hemicellulose content of the fibre.

$$\text{Hemicellulose content (percent)} = \frac{W_4 - W_3}{100 - W_2} \text{ X } (100 - W_1) \quad (2)$$

Where

W_1=alcohol-toluene extractive content (percent).
W_2=weight of oven-dried extractive-free fiber (grams).
W_3=weight of oven-dried crucible (grams).
W_4=weight of oven-dried residue and crucible (grams).

2.3.3 Cellulose

A three -gram oven-dried corn husk was placed in a 250 mL Erlenmeyer flask with a small watch glass cover. The flasks were placed into water bath that was maintained at 20°C. The fiber was then treated with 50 mL of 17.5 percent NaOH and thoroughly mixed for one minute. After the fiber was allowed to react with the solution for 29 minutes, 50 mL of distilled water was added and mixed well for another minute. The reaction continued for five more minutes. The contents of the flask were filtered by aid of vacuum suction into a fritted glass crucible of known weight. The residue was washed first with 50 mL of 8.3 percent NaOH, then with 40 mL of 10 percent acetic acid. The residue was washed free of acid with 1,000 mL of hot tap water. The crucible was oven-dried in an oven at 103±2°C, then cooled in a desiccator, and weighed until a constant weight was reached.

Equation 3 was used to obtain the cellulose content in corn husk/pumpkin stem fiber

$$\text{Cellulose (percent)} = \frac{W_4 - W_3}{100 - W_2} \text{ X } (100 - W_1)\frac{W_4 - W_3}{100 - W_2} \text{ x } W_1 \quad (3)$$

Where,

W_1=Holocellulose content (percent).
W_2=weight of oven-dried holocellulose sample (grams).
W_3=weight of oven-dried crucible (grams).
W_4=weight of oven-dried residue and crucible (grams).

2.3.4 Moisture content

Moisture determination is critically referred to a dry basis according to [16]. Initially, the corn husk fiber lignocellulosic material was weighed, around 2 g, the sample was subsequently oven dried at 105ºC for 24 h, and afterwards the sample was left to cool down in a desiccator and weighed to determine its dry mass. The procedure was then repeated every hour until the dry mass of the sample is stable.

Moisture content, of the sample is calculated with equation 4.

$$\frac{M_2 - M_3}{M_2 - M_1} \text{ x } 100 \quad (4)$$

Where:

M_1: Crucible weight, in g
M_2: Crucible plus humid sample weight, in g
M_3: Crucible plus dry banana fiber weight, in g

2.3.5 Ash content

This text was carried out according to ASTM D1102-84. Ashes are the remaining solid after the combustion of lignocellulosic material at 575 ºC for 3 h or more. This method measures the amount of inorganic compounds present in the lignocellulosic material. Crucibles were first treated without corn husk fiber at 575ºC for 1h to remove any organic residue, and then 2 to 5 g of lignocellulosic material was placed in the crucible and left in the oven for the combustion at 575 ± 25ºC for at least 3 h. Crucibles were retrieved from the furnace when the temperature is around 200ºC and left to cool down in a desiccator under vacuum. The whole, crucible plus ashes, were weighed after reaching environmental temperature until mass measure was stable.

Ash content of the sample is referred to its dry basis and is calculated using equation 5

$$\frac{M_2 - M_3}{(M_2 - M_1).\frac{1-H}{100}} \text{ x } 100 \quad (5)$$

Where:

M_1: Crucible weight, in g,
M_2: Crucible plus humid corn husk/pumpkin stem fibre weight, in g,
M_3: Crucible plus ashes weight, in g
H: Relative humidity of fibre

2.4 Instrumental Characterization of Corn Husk Biomass (Raw and NaOH) Treated

2.4.1 Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX)

The morphology of corn husk fiber was investigated by using a JEOL JSM-6510LV scanning electron microscope with electron bean acceleration of 15kV in vacuum mode. The EDX was also studied to identify the elements present on the surface of the fibers as well as their elemental composition. For sample preparation, the fiber was cut into longitudinal and transversal sections and were affixed on metal support stubs using carbon tape.

2.4.2 X-ray diffraction (XRD) analysis

XRD spectroscopy is commonly used in assessing the degree of cellulose's crystallinity. The crystallinity of cellulose is expressed as the ratio of the crystalline cellulose amount to the sample material total amount.

X-ray diffraction patterns of corn husk sample was recorded with a Rigadu Miniflex diffractometer at room temperature from 5 to 40 C, using CuK irradiation (1.54 Å) at 40 kV and 30 mA. Different approaches have been used to measure the crystallinity index. As a consequence, different results were observed even if the sample was the same. In this study, the crystallinity index was calculated by the deconvolution method, which separates amorphous and crystalline contributions from the diffraction spectrum. This procedure was performed by using a curve-fitting process (Fityk 0.9.8 software). The peak function used was Gaussian and the crystallinity index were calculated by dividing the crystalline peaks' area by the total scattering area.

2.4.3 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is an analytical technique used to identify mainly organic materials. FTIR analysis results in absorption spectra which provide information about the chemical bonds and molecular structure of a material. The FTIR spectrum is equivalent to the ''fingerprint'' of the material and can be compared with catalogued FTIR spectra to identify the material. In this study, NaOH-treated corn husk and raw corn husk were determined using Spectrum RX I FT-IR System (Perkin Elmer India Pvt Ltd, Bengaluru, India). The fibers were ground into powder and mixed with potassium bromide powder (ratio 1:10) then formed into a pellet for analysis. The graph was plotted between the percentage of transmitted IR light and the wave number (4000–500 cm−1) [17].

2.5 ANOVA

ANOVA was used to analyze the result and validate the treatment model. It tests the significance of the model suggested including the significance of the individual terms [18,19]. The detailed ANOVA results were presented in Table 3 (section 3.2.2).

3. RESULTS AND DISCUSSION

3.1 Response Surface Methodology Results for NaOH-Treated Corn Husk

The corn husk biomass- NaOH mercerization was performed according to Table 1 below.

From Table 1, the standard order of 16 gave the highest cellulose content of 70.51% for 92.27% weight loss at 8 days of retting using 100grams of corn husk biomass immersed in 2.50 Mol/dm^3 of NaOH.

This is similar to the result obtained by Pandecha et al [20] when corn husk was subjected to mercerization in 10% NaOH for 60 minutes. In Khwanthipha Pandecha's experiment, the untreated corn husk contains 47% cellulose,43.96% hemicellulose,4.13% lignin and 2.93% ash. However, after treatment, it was observed that the cellulose and ash contents increased to 61.37% and 12.48% respectively while the hemicellulose and lignin decreased to 19.93% and 2.23% respectively.

Hence, in run 16, the 70.51% cellulose indicates that the cellulose content of the corn husk increases with increment in retting time and retting concentration while the hemicellulose and lignin contents decrease with increase in retting time and retting concentration. This could be as a result of the leaching of the lignocellulose biomass which increases with increment in retting time and retting concentration. As reported by Arul Marcel Moshi et al [21], fiber source with high cellulose content has good properties for fiberboard production.

The generated data were analyzed using design expert version 11 software, USA and then interpreted. RSM is a statistical technique for the study of the combined effects of independent process variables on a response [22]. A plot of the predicted versus actual values in Fig. 1 a,b,c and d indicated a correlation between the designs predicted points and the actual points. The closer correlation coefficient is to unity, the better the model predicts the response [23]. The plots converge within the boundary lines which further suggest that the predictions using the model equations could give accurate designs.

Table 1. Response surface methodology result for corn husk treated with NaOH

Std Run	Retting time(min)	Retting Conc (mol/dm^3)	Weight of Biomass (g)	%weight Loss	% Hemicellulose Content	% Cellulose Content	% Lignin Content	% Extractive	% Ash Content
1	4	0.91	70	91.32	16.23	63.10	11.17	3.01	6.92
2	12	0.91	70	93.15	12.26	67.75	7.07	3.92	9.30
3	4	2.09	70	98.46	11.42	67.56	8.41	3.64	8.78
4	12	2.09	70	96.90	7.47	72.25	4.64	4.67	10.89
5	4	0.91	130	81.13	17.40	61.21	12.77	2.62	6.01
6	12	0.91	130	86.82	12.67	66.33	9.15	3.59	8.25
7	4	2.09	130	90.34	17.65	61.55	11.83	2.72	6.24
8	12	2.09	130	92.67	11.94	67.17	7.79	3.88	8.63
9	4	0.91	70	92.72	16.89	64.14	11.44	3.81	7.12
10	12	0.91	70	93.75	12.69	69.15	7.87	4.02	9.77
11	4	2.09	130	92.55	18.05	62.35	12.13	2.52	6.87
12	12	2.09	130	93.97	12.04	68.07	7.98	3.58	8.90
13	1	1.50	100	94.85	15.62	61.68	14.05	2.62	6.03
14	15	1.50	100	98.88	8.40	68.98	6.67	4.54	10.30
15	8	0.50	100	81.67	15.00	64.40	9.86	3.26	7.86
16	8	2.50	100	92.27	8.99	70.51	6.54	3.78	10.11
17	8	1.50	50	92.01	13.20	67.33	6.68	3.92	8.90
18	8	1.50	150	80.04	17.40	62.41	10.57	2.92	6.70
19	8	1.50	100	85.07	10.80	67.30	9.64	3.72	8.54
20	8	1.50	100	81.48	12.60	64.31	9.26	3.69	8.84
21	8	1.50	100	83.74	13.80	64.59	10.96	3.23	7.42
22	8	1.50	100	81.28	12.00	66.75	9.19	3.66	8.40
23	8	1.50	100	82.12	14.40	64.96	9.55	3.36	7.72
24	8	1.50	100	84.51	12.10	67.43	8.69	3.79	8.70
25	8	1.50	100	83.42	14.90	63.16	10.05	3.16	7.92
26	8	1.50	100	84.81	11.98	65.93	9.19	3.85	8.56

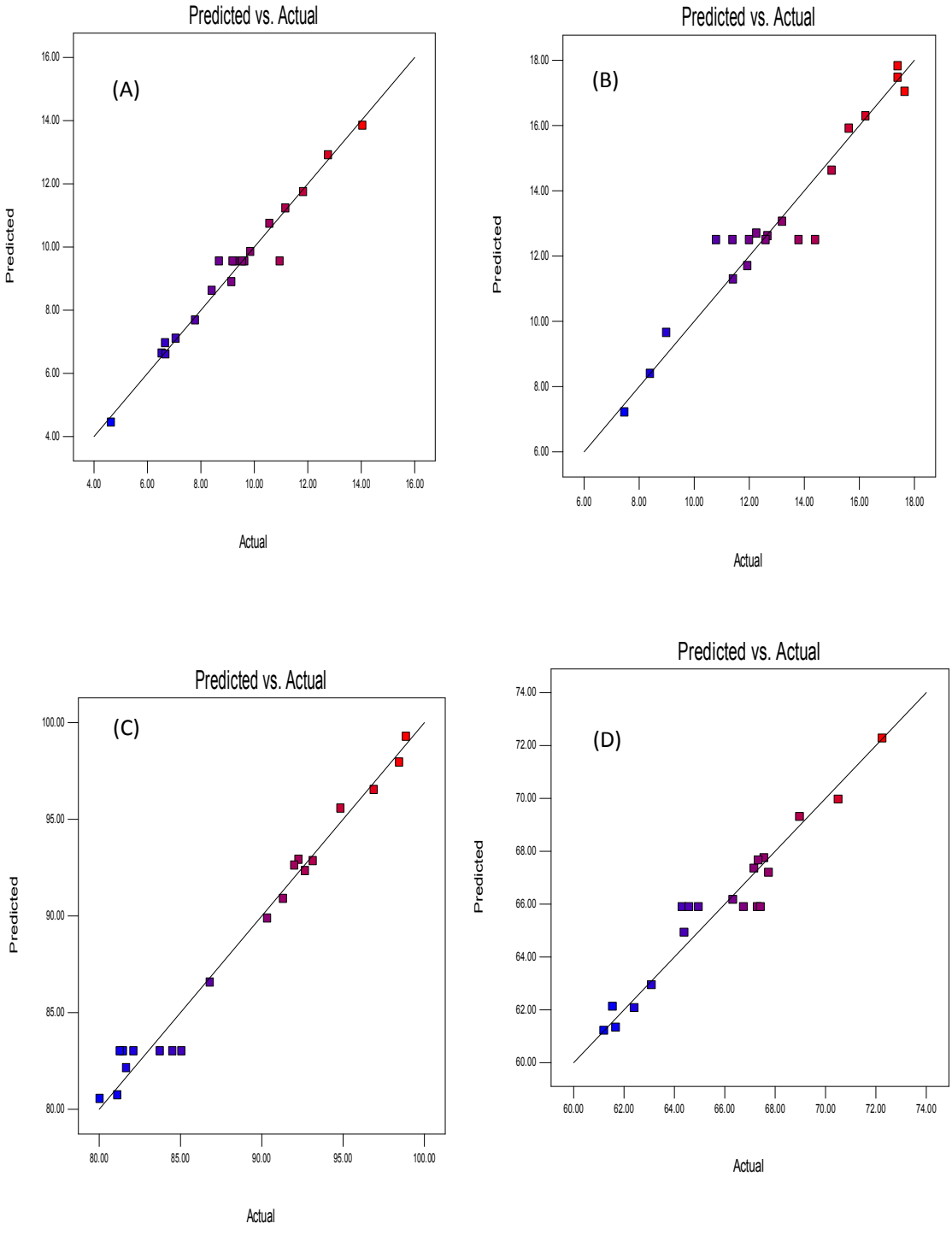


Fig. 1. Predicted versus actual interactive plot for A(Weight loss); B(Hemicellulose); C(Cellulose); and D(Lignin)

3.2 Modeling, Optimization and Statistical Analysis of Corn Husk-NaOH Treated Fiber

3.2.1 Model fitting for corn husk-NaOH fiber treatment

The Model summary is presented in Table 2. It was used to evaluate the adequacy of the experimental results on different models such as linear, two factor interaction (2FI), quadratic or cubic models. Design-Expert version 11 was used to analyze the results. The Fit summary, Sequential fit summary and Model summary all indicated that a quadratic model best fitted the optimization analysis and hence it was suggested.

The coefficient of regression, R^2, was used to validate the fitness of the model equation. The closer the R^2 value to 1, the more model is significant and satisfies all terms of the ANOVA [24]. Also, if the value of the R^2 is in reasonable agreement with the value of the adjusted R^2; that is, if the difference is less than 0.2, there is no problem with either the data or the model.

The weight loss, hemicellulose, cellulose and lignin were all modelled by quadratic models with 97.86%, 93.19%, 93.09% and 96.72% variability in responses respectively. This implies that the prediction of experimental data is quite satisfactory. However, if the regression coefficient (R^2) of the modeling process is low (< 70%), then the mathematical model is not good.

3.2.2 ANOVA for corn husk-NaOH treatment

The ANOVA summary is presented in Table 3. A confidence level of 95% was used hence the significance level is 5%. This implies that P-values greater than 0.05 are considered insignificant while those at 0.05 or less indicate the model terms that are significant [25]. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The P-values check the significance of the factors and equally help to understand the pattern of the mutual interactions between the test variables [25].The result shows that for weight loss, hemicellulose, cellulose and lignin content of the corn husk biomass are affected by retting time, retting concentration and Weight of biomass.

Biomass weight loss and Lignin are affected by retting time, retting concentration and weight of the corn husk biomass [26]. Lignin is the bond (glue) that exists in fibrous or woody material which are often affected by alkaline solution. While Cellulose and Hemicellulose which are interwoven in fiber matrices are affected severally by time required for the retting and the mass of the corn husk biomass in the solution. This simply indicates that the range of 0.9 - 2.5 mol concentration of NaOH used for the mercerization do not have adverse effect on the retting but the soaking time and mass of the biomass could affect the fiber yield adversely.

Final Equation in Terms of Actual Factors

Let X_1 = A = Retting Time (mins), X_2 = B = Retting Concentration (mol), X_3 = C = Weight of Corn Biomass (g)

$$\text{Weight loss} = 136.30812 - 5.1026X1 - 8.27542X2 - 0.51603X3 - 0.35492\,X1X2 + 8.14944E-003X1X3 + 0.029508\,X2\,X3 + 0.31849\,X1\text{^}2 + 4.51843\,X2\text{^}2 + 1.42937E-003X3\text{^}2 \quad (6)$$

Final Equation after removing the insignificant terms as indicated in Table 4

$$\text{Weight loss} = 136.30812 - 5.1026X1 - 8.27542X2 - 0.51603X3 + 0.31849\,X1\text{^}2 + 4.51843\,X2\text{^}2 + 1.42937E-003X3\text{^}2 \quad (7)$$

$$\text{Hemicellulose} = 33.35116 - 0.095080X_1 - 7.45568X_2 - 0.2634X_3 - 0.050769\,X_1X_2 - 2.65513E\text{-}003X_1X_3 + 0.064531\,X_2X_3 - 7.60256E\text{-}003\,X_1^2 - 0.35905\,X_2^2 + 1.17758E\text{-}003X_3^2 \quad (8)$$

Final Equation after removing the insignificant terms as indicated in Table 4.

$$\text{Hemicellulose} = 33.35116 - 0.095080X_1 - 7.45568X_2 - 0.2634X_3 + 0.064531\,X_2X_3 - 7.60256E\text{-}003 + 1.17758E\text{-}003X_3\text{^}2 \quad (9)$$

$$\text{cellulose} = 54.78323 + 0.60584X_1 + 3.14691\,X_2 + 0.097216\,X_3 + 0.028319\,X_1X_2 + 1.47254E\text{-}003X_1\,X_3 - 0.055082X_2\,X_3 - 0.012701X_1\text{^}2 + 1.55067\,X_2\text{^} - 4.11269E\text{-}004\,X_3\text{^}2 \quad (10)$$

Final Equation after removing the insignificant terms as indicated in Table 4.

$$\text{cellulose} = 54.78323 + 0.60584X_1 + 3.14691\,X_2 + 0.097216\,X_3 - 0.055082X_2X_3 \quad (11)$$

Table 2. Model summary statistics for responses

Responses	Model source	Standard deviation	Actual R^2	Adjusted R^2	Predicted R^2	P-value	P>f value
	Linear	5.18	0.4365	0.3308	0.1459	0.0239	0.0043
Weight Loss	2FI	5.65	0.4567	0.2059	-0.3549	0.9207	0.0024
	Quadratic	1.28	0.9786	0.9594	0.9439	< 0.0001	0.9281
	Cubic	1.64	0.9788	0.9328	0.0969	0.9997	0.3316
	Linear	1.57	0.7602	0.7152	0.6091	< 0.0001	0.3723
Hemicellulose	2FI	1.47	o.8289	0.7499	0.6787	0.2084	0.4389
	Quadratic	1.06	0.9319	0.8707	0.8424	0.0220	0.9662
	Cubic	1.28	0.9403	0.811	0.6674	0.9234	0.7690
	Linear	1.31	0.8412	0.8114	0.7505	< 0.0001	0.6659
Cellulose	2FI	1.22	0.8869	0.8347	0.8097	0.2065	0.7667
	Quadratic	1.09	0.9309	0.8687	0.8368	0.1609	0.9605
	Cubic	1.30	0.9412	0.8138	0.9137	0.8915	0.9804
	Linear	0.81	0.8960	0.8765	0.8357	< 0.0001	0.4634
Lignin	2FI	0.85	0.9064	0.8632	0.8371	0.7007	0.3775
	Quadratic	0.58	0.9672	0.9376	0.9295	0.0121	0.9809
	Cubic	0.70	0.9706	0.9069	0.9217	0.9433	0.8734

Table 3. Analysis of variance for the corn husk biomass treatment with NaOH

	Weight loss	Hemicellulose	Cellulose	Lignin
Model	< 0.0001	0.0001	0.0001	< 0.0001
A-Retting time	0.0496	< 0.0001	< 0.0001	< 0.0001
B-Retting Conc	< 0.0001	0.0004	0.0005	0.0001
C-weight of Biomass(corn Husk)	< 0.0001	0.0006	0.0002	< 0.0001
AB	0.0911	0.7538	0.8649	0.9538
AC	0.0574	0.419	0.6596	0.8973
BC	0.2749	0.0124	0.0302	0.1065
A^2	< 0.0001	0.6722	0.4958	0.0737
B^2	0.0008	0.659	0.0856	0.0123
C^2	0.0038	0.0039	0.2348	0.0679
Lack of Fit	0.9281	0.9662	0.9605	0.9809

$$\text{Lignin} = 9.85914 - 0.82916\,X_1 + 0.31035\,X_2 + 0.079085\,X_3 - 5.08149E\text{-}003\,X_1X_2 + 2.26340E\text{-}004\,X_1X_3 + 0.020405\,X_2X_3 + 0.018911\,X_1^2 - 1.30571\,X_2^2 - 3.50831E\text{-}004\,X_3^2 \quad (12)$$

Final Equation after removing the insignificant terms as indicated in Table 4.

$$\text{Lignin} = 9.85914 - 0.82916\,X_1 + 0.31035\,X_2 + 0.079085\,X_3 - 1.30571\,X_2^2 \quad (13)$$

Equations 6 to 13 can be used to make predictions about the response for given levels of each factor, the equation can be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor.

3.2.3 Three-dimensional (3D) surface plots for corn husk-naoh treatment

The three-dimensional (3D) surface plots were used to visualize the relationship between the experimental variables and the responses. It was also used to study the single and interaction effects of all the factors. The response surface and interaction plots were generated from the quadratic model. They illustrate the response of different experimental variables and can be used to identify the major interactions between the variables.

From Figs. 2 to 3, it could be observed that increasing the retting time while increasing the retting concentration and Weight of Biomass leads to increase in the weight loss of the

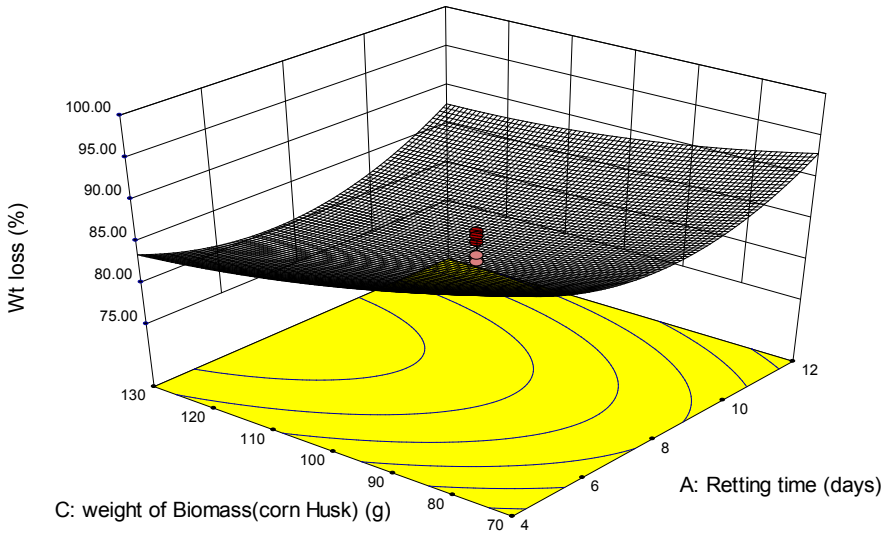


Fig. 2. Effect of retting time and biomass weight on weight loss

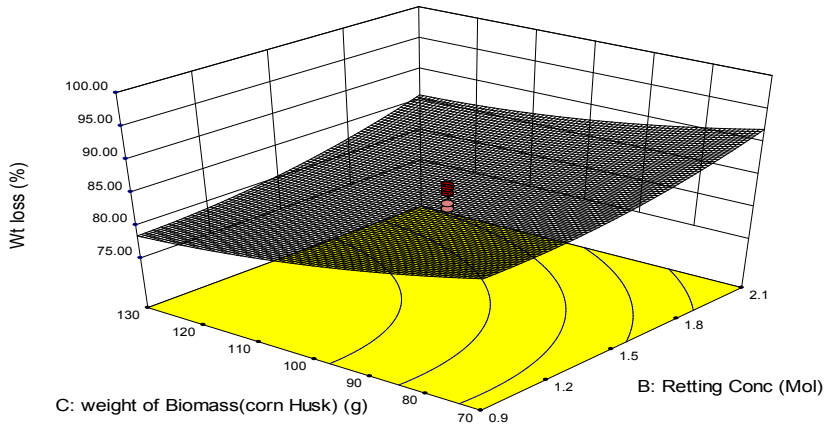


Fig. 3. Effect of retting concentration and weight of biomass on biomass weight loss

biomass. A similar result was reported by Hashim et al [27] when kenaf fiber was subjected to NaOH mercerization. The increase in weight loss of the corn biomass was due to the effect of molar concentration of the NaOH as retting days increased. This could be to the break of wood structure bond (hemicellulose and Lignin).

From Fig 4 to Fig 5 increasing the retting time and concentration results to decrease in the Hemicellulose as the biomass weight increased. It was expected that in mercerization that the walls of the woody structure will break to release fibrous material. Mercerization was aimed to reduce the biomass bond (hemicellulose and lignin) which tend make fiber to be hydrophilic and a bad property for better composite.

From Figs 6 to 7, it was observed that increasing the retting time and retting concentration leads to increase in cellulose. The goal of mercerization is to produce fiber that could have a property similar to the binder (polymer). In wood structure, the lignin and hemicellulose cover the cellulose wall (fibrous). The trend was expected.

In Figs 8 and 9, the reduction of lignin content as time and concentration increase was due to the effect of the NaOH on the lignin cell walls of the woody material (Corn husk). It was the reduction was aimed to improve the fiber for better composite material.

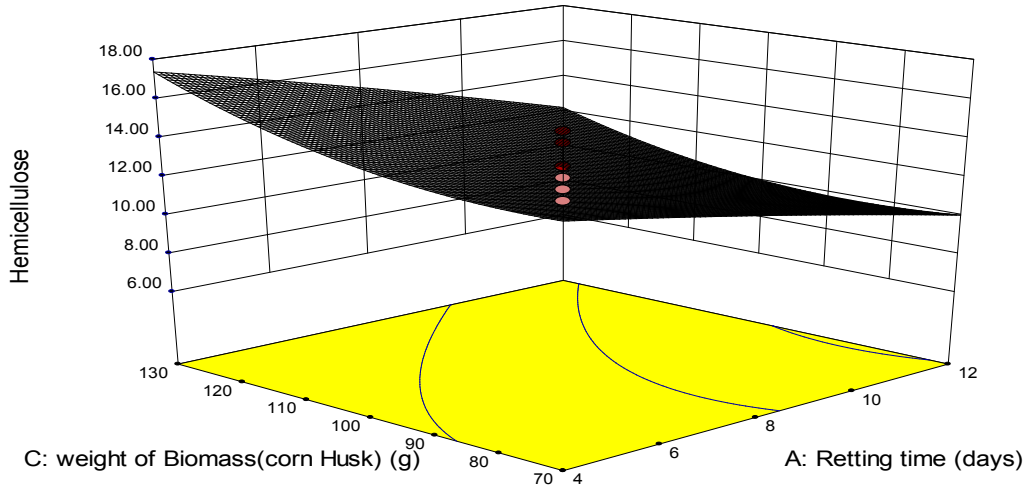


Fig. 4. Effect of retting time and weight of biomass on hemicellulose yiel

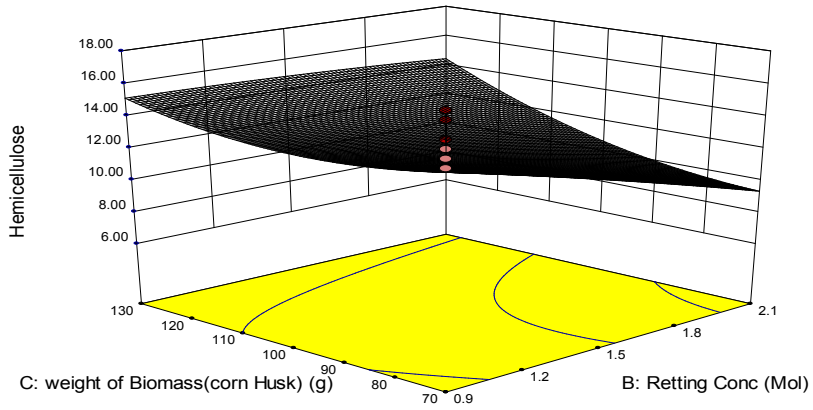


Fig. 5. Effect of retting concentration and weight of biomass on hemicellulose yield

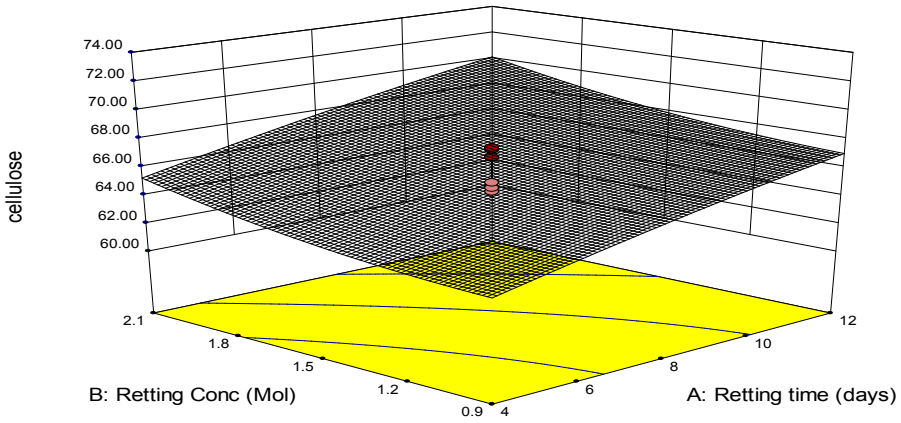


Fig. 6. Effect of retting time and retting concentration on cellulose

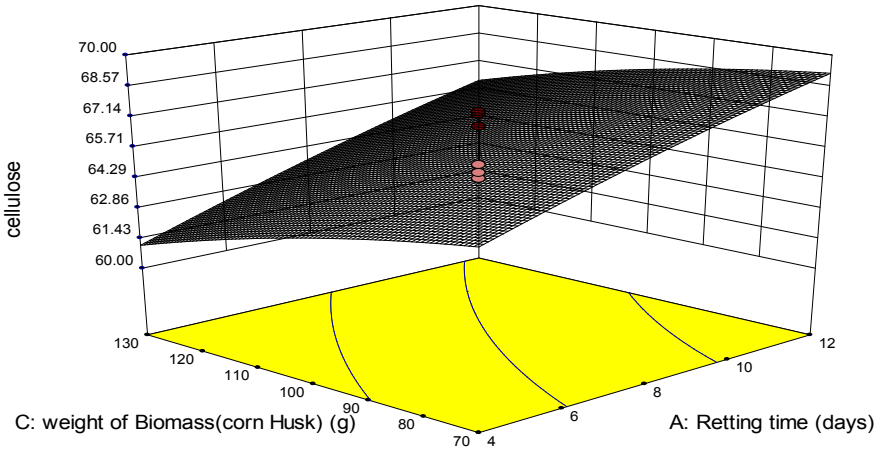


Fig. 7. Effect of retting time and weight of biomass on cellulose

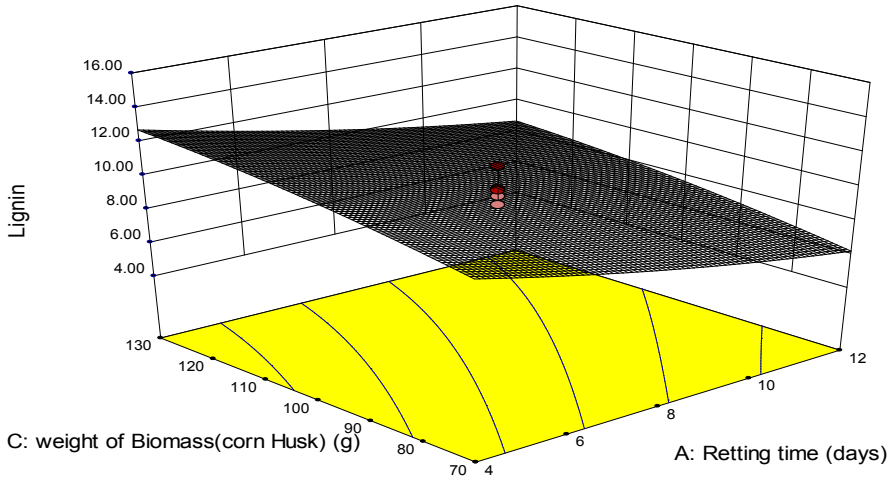


Fig. 8. Effect of retting time and weight of biomass on lignin

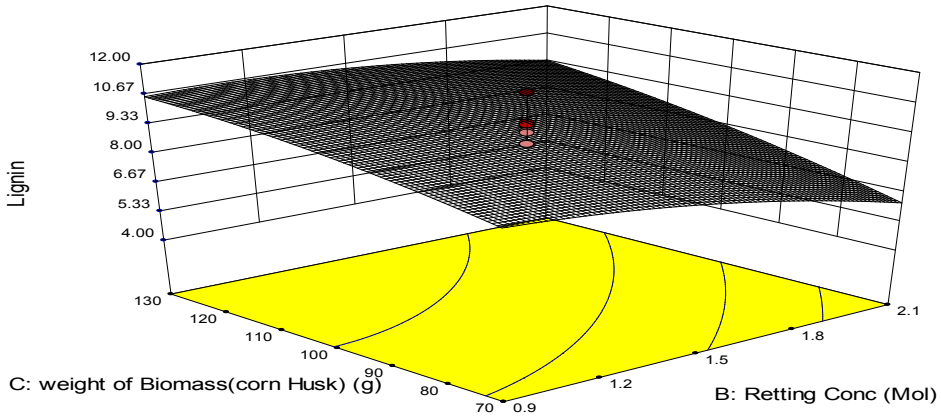


Fig. 9. Effect of retting concentration and weight of biomass on lignin

3.2.4 Optimization of corn husk-naoh fibre produced

From Table 4, the goal was to achieve a greater cellulose yield (fiber) as the retting time is reduced. The Hemicellulose and Lignin were set at minimize because lower percentages of these properties further enhanced better fiber yield.

From Table 5, cellulose content of 67.47 % was achieved after mercerization of the cornhusk biomass at 8 days retting, 1.5% NaOH concentration at weight of biomass of approximately 70g. This also represented a 70% loss of the biomass weight. The result obtained is in agreement with work done by Pandecha et al[16] when corn husk was pretreated with 10% NaOH.

3.3 Characterization of Raw and Treated Biomasses

3.3.1 Physio-chemical characterization of raw and naoh-treated corn husk biomass

The characterization results show that the physio-chemical properties (hemicellulose, acid lignin, moisture absorption, ash content and density) of the untreated fiber are higher than

that of NaOH treatment. The reverse is the case for the cellulose. NaOH mercerization of the biomass yield the highest cellulose content. NaOH-corn husk treatment was found to be effective in modifying the natural fiber-matrix interface thereby making it plasticized by modifying the hydrophilic nature of fiber to hydrophobic [28].

3.3.2 Instrumental characteristics of raw and naoh-treated corn husk

The instrumental characteristics of raw and treated biomasses were further analyzed as follows:

3.3.2.1 Sem results for the untreated and treated biomass

Morphology of the biomass was analyzed by SEM for cellulose, as shown in Fig 10 a and b below. Large number of micro fibrils randomly distributed (white arrows), uneven and wrapped by non cellulose substances were observed in the untreated fiber. The SEM images confirm that the untreated biomass has an irregular cross-section, non-uniform surface, a significant number of short micro fibrils, lumens (vessel structures) and some impurities on the surface, which are typical of raw natural fibers. This is similar to the result obtained by Oliveira et al [29] when acai seeds biomass was treated with NaOH by SEM, XRD and FTIR. The amount and the size of lumens, which are correlated to the voids in the structure, affect the fiber Mechanical strength and also responsible for its hydrophilic nature [30]. The more pronounced the lumens as seen in Fig 10a, the lower the fiber's tensile strength, which is not desirable for use in composite. The impurities can disturb the fiber and polymer adhesion. Therefore, the treated biomass shows a better interfacial adhesion, after mercerization with Alkali solution [30,31]. The SEM analysis also indicated carbon as the most occurring element found in the biomass (see Table 7). Due to the higher carbon atomic concentration, cellulosic fibers are considered carbonaceous in nature; so, the result is expected.

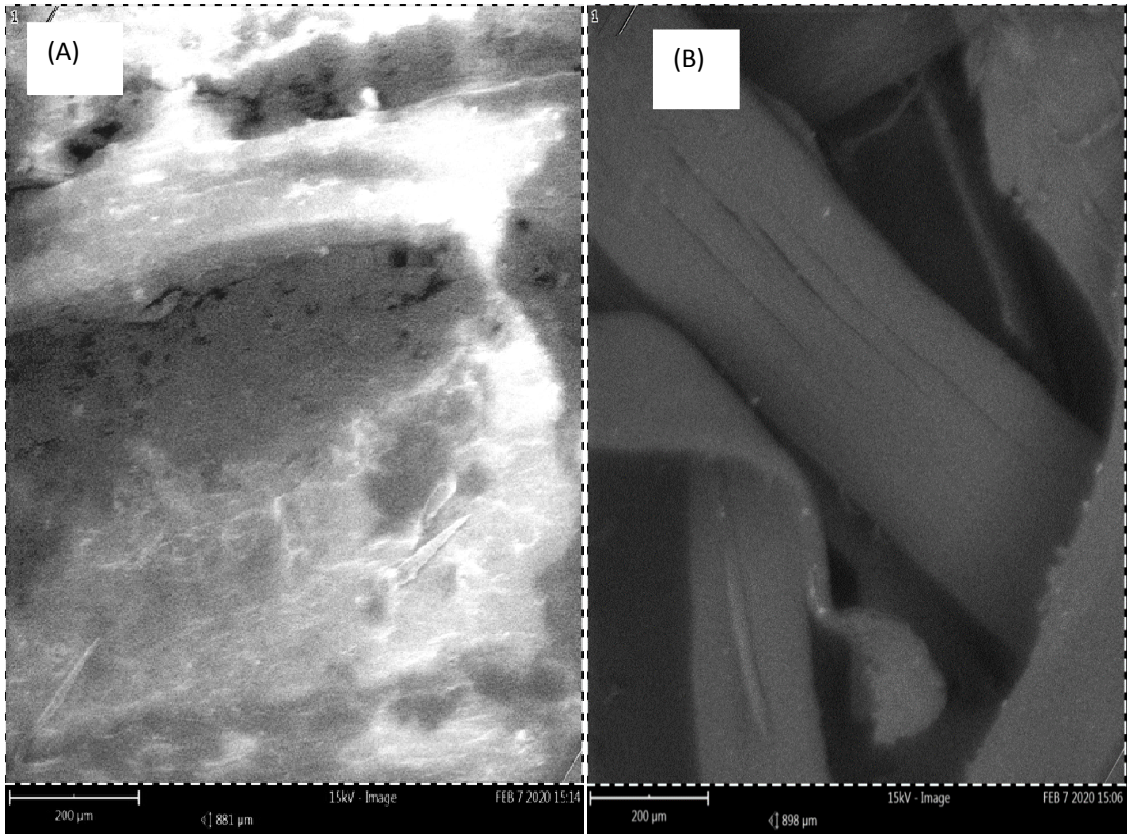


Fig. 10. a & b SEM images for untreated (CUTF) and treated corn husk biomass (CTF)

Table 4. Constraints for corn husk-NaOH fiber

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A:Retting time	Minimize	4	12	1	1	3
B:Retting Conc	Minimize	0.905396	2.0946	1	1	3
C:weight of Biomass(corn Husk)	is in range	70.2698	129.73	1	1	3
Wt loss	is in range	80.04	98.88	1	1	3
Hemicellulose	Minimize	7.47	17.652	1	1	3
Cellulose	Maximize	61.2055	72.2549	1	1	3
Lignin	Minimize	4.64348	14.05	1	1	3
Extractive	is in range	2.61755	4.67	1	1	3
Ash content	is in range	6.01098	10.8896	1	1	3

Table 5. Optimized solution of corn husk- NaOH fibre

S/No	Retting time (days)	Retting Conc (Mol/dm^3)	weight of Biomass (corn Husk)	Wt loss	Hemi Cellulose	cellulose	Lignin	Extractive	Ash content	Desirability
1	8.0	1.5	70	88.10	11.86	67.44	7.86	3.86	8.94	0.544
2	8.1	1.5	70	88.07	11.88	67.43	7.86	3.86	8.93	0.544
3	8.1	1.6	70	88.10	11.84	67.46	7.83	3.86	8.95	0.544
4	8.1	1.5	70	88.08	11.86	67.45	7.84	3.86	8.94	0.544
5	8.0	1.6	70	88.12	11.85	67.45	7.86	3.86	8.94	0.544
6	8.0	1.6	70	88.16	11.81	67.49	7.84	3.86	8.95	0.544
7	8.1	1.5	70	88.01	11.91	67.40	7.86	3.86	8.93	0.544
8	8.0	1.6	70	88.19	11.79	67.50	7.83	3.86	8.96	0.544
9	8.2	1.5	70	88.05	11.85	67.46	7.81	3.87	8.96	0.544
10	7.9	1.5	70	88.08	11.97	67.32	7.96	3.83	8.88	0.544

Table 6. Result of characterization of raw and treated corn husk biomass

S/No	Test	Untreated fiber	NaOH treated
1	Cellulose (%w/w)	34.10	65.20
2	Lignin (Acid) (%w/w)	24.22	7.98
3	Hemicellulose (%w/w)	44.10	11.43
4	Moisture absorption (%)	10.45	4.09
6	Ash content (%)	1.29	0.84
7	Density g/m^3	1.46	0.97

Table 7. SEM-EDX analysis for the untreated and treated corn husk

			Raw corn husk		NaOH-treated corn husk	
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.	Atomic Conc.	Weight Conc.
6	C	Carbon	55.66	31.29	53.7	25.8
7	N	Nitrogen	2.07	1.36	-	-
8	O	Oxygen	3.96	2.97	-	-
11	Na	Sodium	1.96	2.11	1.72	1.58
12	Mg	Magnesium	4.58	5.21	4.61	4.48
13	Al	Aluminum	5.96	7.53	4.75	5.12
14	Si	Silicon	4.73	6.21	5.67	6.37
15	P	Phosphorus	1.97	2.86	2.53	3.14
16	S	Sulfur	4.04	6.07	5.71	7.32
17	Cl	Chlorine	5.64	9.37	4.42	6.27
19	K	Potassium	2.54	4.64	2.39	3.74
20	Ca	Calcium	1.46	2.74	4.8	7.69
30	Zn	Zinc	4.49	13.74	6.41	16.76
39	Y	Yttrium	0.94	3.9	3.3	11.72

3.3.2.2XRD results for the untreated and treated biomasses

Crystallinity index is used to describe XRD. Usually in biomass, cellulose is the prominent component that is attributed to Crystallinity, hemicellulose and lignin are usually characterized as the amorphous parts with a little portion of imperfect crystallites that also contribute to the amorphous content in lignocellulosic biomass. Four crystalline peaks of the crystal polymorph I of cellulose (101, 10i, 002 and 040) are used to calculate the Crystallinity index. However, as shown in the XRD diffraction spectra of the biomass samples (Fig. 11 a and b), these peaks are not well resolved, and only one peak at 16.8^0 to 35.2^0 are clearly observed. These could be linked to (110, 002, 004) crystallographic plane of cellulose I Structure. The Cellulose structure of NaOH - treated corn husk biomass was maintained even after the treatment with NaOH solution as could be observed from Fig11 as hemicellulose and lignin were seen to be removed.

The Crystallinity was evaluated using the seqal method (equation 14) using the maximum intensity of the diffraction from the 002 plane (I_{002}), and the maximum intensity between the 002 and 110 peak (I_{am})

$$Cr\ (\%) = 100\ X\ (I_{002} - I_{am})/\ I_{002} \quad (14)$$

The Crystallinity index of untreated corn husk biomass was 35.5% when compared to 46.6% of the treated corn husk biomass and 10% of Untreated Pumpkin and 35.76% treated Pumpkin. The increase could be attributed to the removal of large amount of hemicellulose, lignin ad other impurities during mercerization with NaOH solutions.

3.3.2.3 Fourier transform infrared spectroscopy (ftir) results for the untreated and treated biomasses

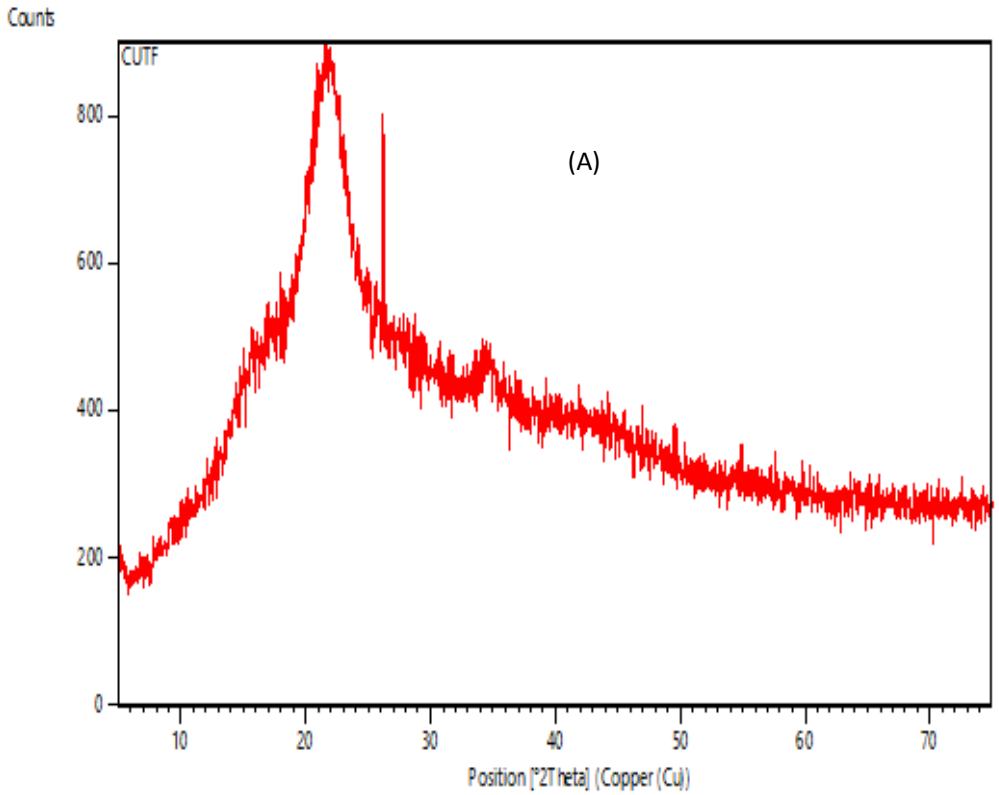
From Fig. 12 a and b, FTIR spectra were used for the analysis of the biomass. The peak centered around 3200 - 3500 cm^{-1} the -OH attitude to water. The 704 -895 cm^{-1} indicated B-glycosidic between glucose units in cellulose. It disappeared after treatment which could be to the removal of glucose during the treatment. 1100 - 1155 cm^{-1} is the glycosidic ether bond in

cellulose which was present in both untreated and treated. 1310 - 1390 cm^{-1} is the polysaccharide aromatic group, 1446 - 1500 cm^{-1} indicates the presence of lignin which disappeared in the treated biomasses. The FTIR spectra indicate a variation of the peaks after treatment which favors formation of cellulose group.

Table 8. Fourier transform infrared spectroscopy (FTIR) results

Peaks (cm^{-1})	Functional group	CUTF	CTF	References
704 - 895	C = C bending	*	x	[32]
1017 - 1077	C-O in carboxylic acid	*	*	[32]
1100 - 1155	S = O Stretching	*	*	[32]
1200 - 1275	C - O stretching	*	*	[32]
1310 - 1390	C -H bending	*	*	[32]
1408 - 1430	C-H Asymmetric bending	*	*	[32]
1446 - 1500	C-H deformation	*	x	[32]
1617 - 1651	C=C stretching	*	x	[32]
1982 - 2012	C=C=C stretching vibration	*	*	[32]
2068 - 2113	C-C stretching	*	*	[32]
2068 - 2113	O-H	x	x	[32]
2449 - 2993	Functional group	*	*	[32]
3000 -3500	-OH	*	*	[32]

** = presence of functional group; x = absence of functional group*



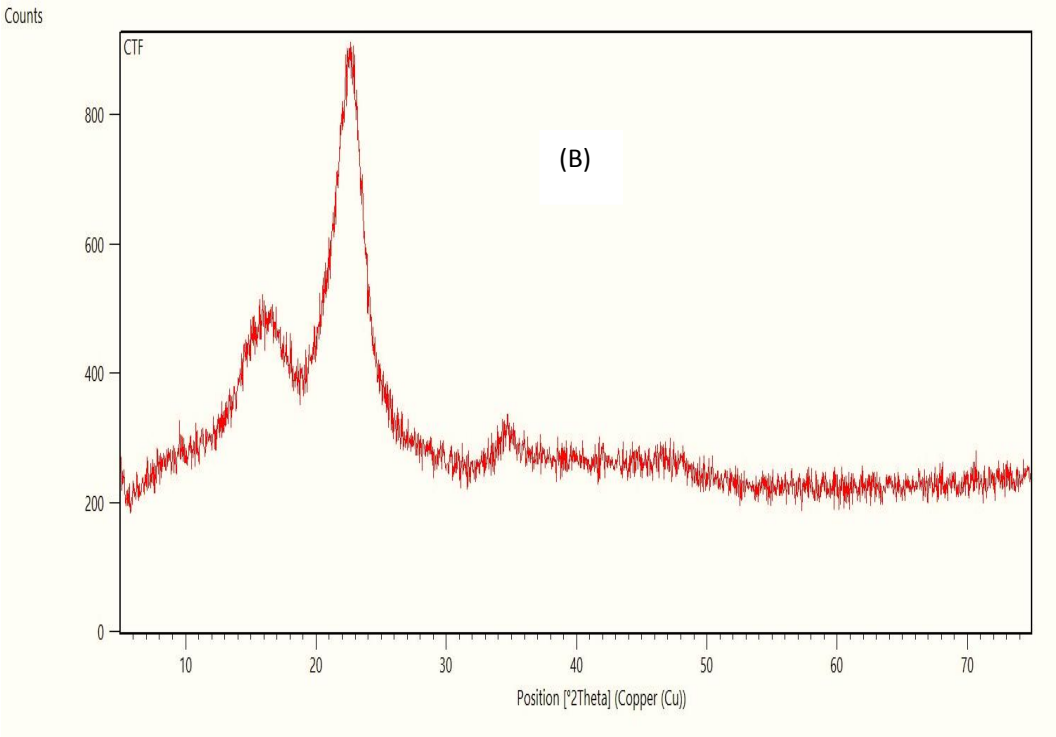
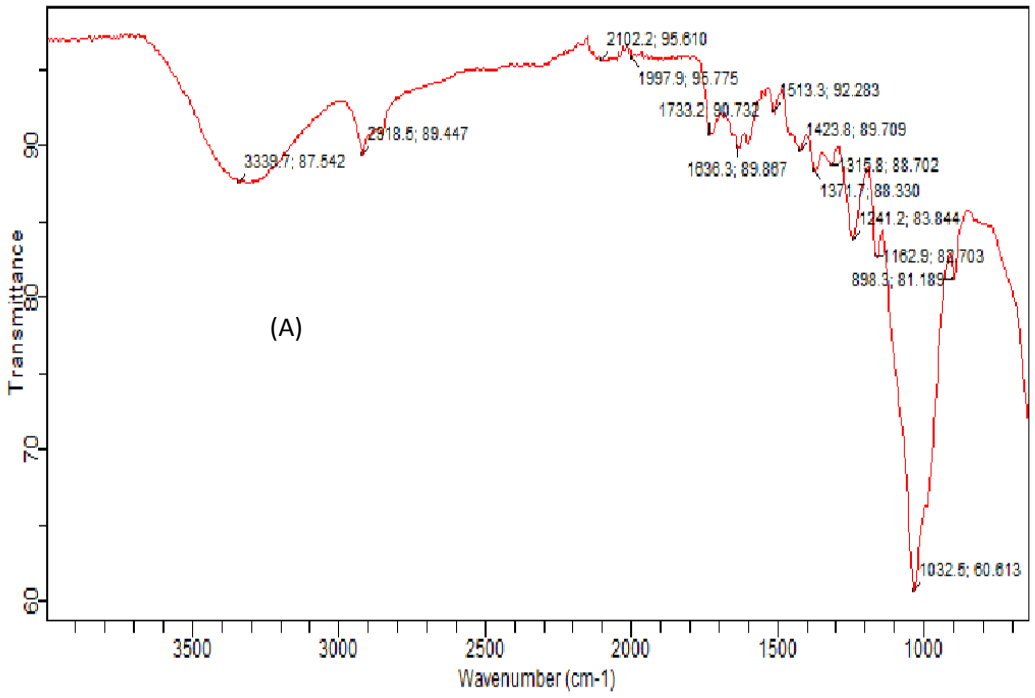


Fig. 11. a & b XRD graphs for CUTF and CTF



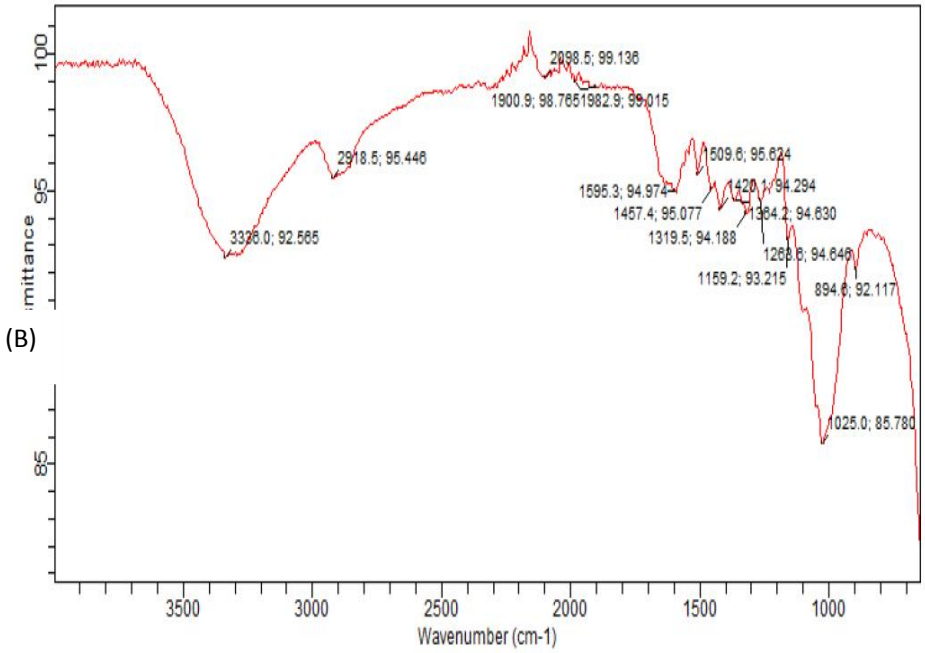


Fig. 12. a & b FTIR images for CUTF and CTF

4. CONCLUSIONS

Based on the experiments conducted, results obtained and the discussions, the following conclusions were made:

- The cellulose content of corn husk biomass increases with an increment in retting time and retting concentration.
- The optimum cellulose yield for NaOH corn husk biomass mercerization is 70.51% for 92.27% weight loss at 8days of retting using 100grams of corn husk biomass in 2.50mol/dm3 solution of NaOH.
- Hemicellulose and lignin contents decreases with increment in retting time and retting concentration.
- The weight loss, hemicellulose, cellulose and lignin of NaOH- corn husk mercerization were modeled by quadratic models.
- Equations 7, 9, 11 and 13 can satisfactorily be used to evaluate the weight loss, hemicellulose, cellulose and lignin contents of NaOH- corn husk mercerization respectively.
- The physio-chemical properties (hemicellulose, lignin, moisture absorption ash content and density) of untreated corn husk biomass are higher than that of NaOH- treated corn husk biomass.
- The FTIR indicated a variation of the peaks after treatment which favors formation of cellulose group.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Rowell RM. Performance driven composites from lignocellulosic resources. International Conference on Science and Technology of Composite Materials. 2001;29-32.
2. Paul SA, Joseph K, Mathew GDG, Pothena LA, Thomasd S. Influence of

polarity parameters on the mechanical properties of composites from polypropylene fiber and short banana fiber. Composites Part A: Applied Science and Manufacturing. 2010;34(9):982-1021.
3. Reddy H, M S, Kodli B, Chikmeti RB. Experimental investigation of mechanical properties of sisal fiber and rice husk reinforced polymer composite. IOSR Journal of Mechanical and Civil Engineering. 201411(4):05–11. Available:https://doi.org/10.9790/1684-11450511
4. Verma D, Gope PC, Shandilya A, Gupta A, Maheshwari MK. Coir fibre reinforcement and application in polymer composites: A review. Journal of Materials and Environmental Science. 2013;4(2):263–276.
5. Vijay R, Singaravelu DL, Vinod A, Sanjay MR, Siengchin S, Jawaid M. International Journal of Biological Macromolecules Characterization of raw and alkali treated new natural cellulosic fi bers from Tridax procumbens. International Journal of Biological Macromolecules. 2019;125:99–108. Available:https://doi.org/10.1016/j.ijbiomac.2018.12.056
6. Indran S, Raj RE, Sreenivasan VS. Characterization of new natural cellulosic fiber from Cissus quadrangularis root. Carbohydrate Polymers. 2014;110:423–429. https://doi.org/10.1016/j.carbpol.2014.04.051
7. Hassan MM, Wagner MH, Zaman HU, Khan MA. Study on the performance of hybrid jute/betel nut fiber reinforced polypropylene composites. Journal of Adhesion Science and Technology. 2010;25(6–7):615–626. Available:https://doi.org/10.1163/016942410X525858
8. Sommerhuber PF, Welling J, Krause A. Substitution potentials of recycled hdpe and wood particles from post-consumer packaging waste in wood-plastic composites. Waste Management. 2015;46:76–85.
9. Akinyemi AB, Afolayan JO, Oluwatobi EO. Some properties of composite corn cob and sawdust particle boards. Construction Building Materials. 2016;127:436–441.
10. Ghofrani M, Ashori A, Mehrabi R. Mechanical and acoustical properties of particleboards made with date palm branches and vermiculite. Polymer Test. 2017;60:153–159.
11. Kusumah SS, Massijaya SY, Prasetyo KW, Sutiawan J, Lubis MAR, Hermawan D. Surface modification of eco-friendly particleboard made from sorghum bagasse and citric acid sucrose adhesive. IOP Conference Series: Materials Science and Engineering. 2020;935(1). Available:https://doi.org/10.1088/1757-899X/935/1/012054
12. Khazaeian A, Ashori A, Dizaj MY. Suitability of sorghum stalk fibers for production of particleboard. Carbohydrate Polymer. 2015;120:15–21.
13. Sabbatini A, Lanari S, Santulli C, Pettinari C. Use of almond shells and rice husk as fillers of poly(methyl methacrylate) (PMMA). *Composites Materials*. 2017;10:872.
14. Hassan MZ, Sapuan SM, Roslan SA, Aziz SA, Sarip S. Optimization of tensile behavior of banana pseudo-stem (Musa acuminate) fiber reinforced epoxy composites using response surface methodology. Journal of Materials Research and Technology. 2019;8(4):3517–3528. Available:https://doi.org/10.1016/j.jmrt.2019.06.026
15. Venkatachalam N. et al. Effect of pretreatment methods on properties on natural composites: A Review. Polymers & Polymer Composites. 2016;24:7.
16. ASTM D1348-94(2008), Standard test methods for moisture in cellulose (Withdrawn 2017), ASTM international, West Conshohocken, PA; 2008. Available:www.astm.org
17. Senthamaraikannan P, Kathiresan M. Characterization of raw and alkali treated new natural cellulosic fi ber from Coccinia grandis . L. Carbohydrate Polymers. 2018;186:332–343. Available:https://doi.org/10.1016/j.carbpol.2018.01.072
18. Chijioke O, Philomena KI, Joseph TN, Charles ON, Paschal EO. Arti fi cial Intelligence in Agriculture Evaluation of optimization techniques in predicting optimum moisture content reduction in drying potato slices. Artificial Intelligence in Agriculture. 2020;4:39–47. Available:https://doi.org/10.1016/j.aiia.2020.04.001
19. Elijah C, Nwabanne JT, Ohale PE, Asadu CO. South African Journal of Chemical

Engineering Comparative analysis of RSM , ANN and ANFIS and the mechanistic modeling in eriochrome black-T dye adsorption using modified clay. South African Journal of Chemical Engineering. 2021;36:24–42.
Available:https://doi.org/10.1016/j.sajce.2020.12.003

20. Pandecha K, Pongtornkulpanich A, Sukchai S. Thermal properties of corn husk fiber as insulation for flat plate solar collector. 2015;10(1):27–36.
21. Arul Marcel Moshi A, Ravindran D, Sundara Bharathi SR, Suganthan V, Kennady Shaju Singh, G. Characterization of New Natural Cellulosic Fibers-A Comprehensive Review. IOP Conference Series: Materials Science and Engineering. 2019;574(1).
Available:https://doi.org/10.1088/1757-899X/574/1/012013
22. Gupta A, Balomajumder C. Statistical optimization of process parameters for the simultaneous adsorption of Cr(VI) and phenol onto Fe-treated tea waste biomass. Applied Water Science. 2017;7:4361-4.
23. Dawood AS, Li Y. Modelling and optimization of new floculant dosage and PH for flocculation: Removal of pollutant from wastewater. Water. 20135(2):342-355
24. Tetteh EK, Rathilal S, Chollom MN. Treatment of industrial mineral oil wastewater - optimisation of coagulation flotation process using Response Surface Methodology (RSM). International Journal of Applied Engineering Research. 2017; 12(23):13084–13091.
ISSN: 0973-4562
25. Igwegbe CA, Onukwuli OD, Onyechi PC. Optimal route for turbidity removal from aquaculture wastewater by electrocoagulation-flocculation process. Journal of Engineering and Applied Sciences. 2019;15(1):99–108.
26. Jain A, Rastogi D, Chanana B, Parmar MS, Dhama A. Extraction of cornhusk fibres for textile usages. 2017;4(1):85–90.
Available:https://doi.org/10.9790/019X-04012934
27. Hashim MY, Amin AM, Marwah OMF, Othman MH, Yunus MRM, Chuan Huat N. The effect of alkali treatment under various conditions on physical properties of kenaf fiber. Journal of Physics: Conference Series. 2017;914(1).
Available:https://doi.org/10.1088/1742-6596/914/1/012030
28. Ali A. et al. Hydrophobic treatment of natural fibers and their composites—A review. Journal of Industrial Textiles. 2018;47:2153–2183.
29. Oliveira JAR, Komesu A, Martins LHS, Filho RM. Evaluation of microstructure of açaí seeds biomass untreated and treated with H2SO4 and NaOH by SEM. RDX and FTIR. Chemical Engineering Transactions. 2016;50:379–384.
Available:https://doi.org/10.3303/CET1650064
30. Wang X, Chang L, Shi X, Wang L. Effect of hot-alkali treatment on the structure composition of jute fabrics and mechanical; 2019.
31. Hossen J, Begum HA, Uddin M, Islam MT, Islam M. Investigating the physical properties of treated and untreated jute fibre-polyester composites; 2018.
Available:https://doi.org/10.3923/ajt.2018.13.21
32. Stuart B. Infrared spectroscopy: fundamentals and applications analytical techniques in the sciences; 2004.

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