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Treatment of pharmaceutical wastewater using a composite adsorbent

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ABSTRACT The discharge of industrial effluent usually poses threat to flora and fauna in the water. Commercial adsorbents used for the treatment of the effluents are usually effective but expensive; hence the need to develop adsorbents that are effective, inexpensive and locally available. A composite adsorbent prepared from groundnut shell char and commercial activated carbon has been investigated for the treatment of pharmaceutical wastewater. Groundnut shells were collected washed with water and sun-dried before carbonation and activation. A composite of the groundnut shell char and commercial activated carbon was prepared and was characterized in terms of functional groups, crystalline phase and structure, surface morphology and surface area. The adsorption experiment was designed and analyzed employing Box-Behnken design of response surface methodology. The effluent was treated with the prepared composite adsorbent by varying adsorbent dosage (0.2-1.8 g), contact time (10-110 min) and groundnut shell char fraction (0-1). The adsorbent showed the presence of amines, alkyne, alkene and amides while the XRD revealed a homogeneous and highly crystalline material. The surface morphology of the adsorbent revealed a highly developed irregular pore structure which is due to chemical activation in the activated carbon. The BET surface area, pore volume and pore size were found to be 305.11$m^2.g^{-1}$, 0.27$cm^3.g^{-1}$ and 3.00 nm respectively. The physico-chemical properties of the pharmaceutical wastewater before treatment revealed a pH, EC, TDS, salinity, COD and BOD values of 10.00, 755.50 µS/cm, 528.50 mg/l, 366.50 mg/l, 342.50 mg/l and 44.50 mg/l respectively. The maximum BOD removal efficiency of 97.45 % obtained by the composite adsorbent was achieved using a GSAC fraction of 1 with a mass of 0.20 g and at a contact time of 10.00 mins.

KEYWORDS **Electrical conductivity, optimization, wastewater, adsorbent, composite Introduction**

Introduction

There is need to improve human health conditions to ensure continuity of life. This explains the rationale behind emerging research ideas in environmental sustainability and medicine. Since these studies are only limited to mitigating poisonous emissions arising from their usage, more recent considerations are now given to treatment of pharmaceutical wastewater discharges (Jiang *et al*, 2021). Moreover, pharmaceutical wastewater causes serious pollution to water bodies and sub-chronic or chronic toxicity to aquatic ecosystems and humans (Larsson *et al*, 2007). This is of much concern, because pharmaceutical residues can cause ecotoxic effects and hormonal disruption even when they are in relatively small concentrations (K'oreje *et al* 2016; Blair *et al* 2013). Consequently, the wastewaters coming from pharmaceutical industries are considered environmentally challenging due to their hazardous nature (Dindas *et al* 2020). So, applying several treatment processes has been of interest among researchers. As a result, Jiang *et al* (2021) treated hypersaline pharmaceutical wastewater, using aerobic granular sludge systems. Aerobic granular sludge systems were used despite other methods of membrane filtration, adsorption and biological systems (Barrios-Hernández et al, 2020; Li *et al* 2005; Lotito *et al*, 2012). This was done because organic pollutants, spent solvents and inorganic salts were present in the waste (Zhao *et al*, 2021).

Furthermore, Huang *et al* (2020) investigated the removal of organic contaminants in real pharmaceutical wastewater. This was achieved using iron foam-combined ozonation, which is an advanced oxidation process. Phosphate and nitrogen were removed, and the organic pollutants degraded. Similarly, Mojiri *et al* (2019) removed pharmaceutical micro-pollutants of acetaminophen (ACT) and amoxicillin (AMX) from wastewater using ozone reactor with chitosan/bentonite. Building on this, Dindas *et al* (2020) examined the treatment of pharmaceutical industry wastewater. They basically combined electro-coagulation, electro-fenton and photocatalytic oxidation processes.

Currently, research has reported the use of chitosan-based adsorbents for pharmaceutical wastewater treatment (Karimi-Maleh *et al*, 2021). This is because adsorbents have been introduced as novel materials suitable for the treatment of pharmaceutical wastewaters (Kyzas *et al*, 2015). Examples of these materials include carbons, clays, chitosan, silica, zeolites, graphene, and others. Nonetheless, the use of natural material adsorbents, such as agricultural residues have been scarcely be examined.

For this reason, the aim of this study is to produce commercial activated carbon/groundnut shell char composite for the treatment of pharmaceutical wastewater.

MATERIALS AND METHODS

MATERIALS

Groundnut shells were collected from a waste bin at Uselu and Oluku markets in Benin City, and were pretreated before further use. Commercial activated carbon (CA) was purchased from a local chemical store in Benin City. The pharmaceutical wastewater was obtained from a pharmaceutical company in Lagos State.

METHODS

Collection of Effluent Samples

Pharmaceutical effluent was collected from a pharmaceutical company in Lagos State, Nigeria. The raw effluent was collected from a line feeding the treatment plant using a clean 5L plastic can. The collected effluent samples were placed in a cooler box 4° C and then taken to the laboratory for analysis.

Characterization of the Pharmaceutical Effluent sample

The raw effluent samples were characterized in terms of pH, electrical conductivity (EC), total dissolved solid (TDS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in the Chemical Engineering Laboratory of University of Benin. The sample pH, EC and TDS was determined electronically using Zeal–tech digital pH meter (model 03112, India) for pH, and HACH conductivity/TDS meter (model 44600.00, USA) for EC and TDS. BOD and COD were determined using the APHA standards methods as reported by Kalderis *et al*. (2017)

Preparation of adsorbent Precursor

The groundnut shell was collected from Uselu and Oluku markets in Benin City, washed with water and later sieved to remove sand and stones. This was later sundried for 3hours and followed by oven drying at 100ºC until the mass remained constant, then crushed before carbonization.

Carbonization and Activation of the adsorbent

The carbonization of the groundnut shell was achieved following the method reported by Ajala and Ali (2020) with modification. 100g each of dried groundnut shell was weighed into crucible and placed in the muffle furnace; the temperature of the furnace was set and maintained at 500ºC for 2 hours. This was done according to modified methods of Adebayo and Aluko (2007). The carbonized samples were sieved and impregnated with 1.0 mol/dm^3 KOH solution used as activating agent in a 1:1 of KOH/Groundnut shell char ratio for 24 hours. Then equal molarity of HCl was added to bring the pH to neutral and the paste transferred to an evaporating dish which was placed in a furnace and heated to 300ºC for thirty minutes.

Synthesis of Groundnut shell Char/Commercial Activated Carbon Composite

The preparation of commercial activated carbon (CAC)/groundnut shell activated carbon composite was achieved by Sol gel methods. 20 g of the commercial activated carbon was suspended into 250ml Ethylene glycol in a flask and stirred for 1 hour, and then 20 g of the groundnut shell char was added to the suspension followed by continuous stirring for 3 hours at 100ºC for the solvent to evaporate.

Characterization of Groundnut shell Char/Commercial Activated Carbon Composite

The composite adsorbent produced was characterized in terms of functional groups using Fourier transform infra-red (FTIR) spectroscopy, elemental composition using X-ray fluorescence (XRF), crystalline phase and structure properties using X-ray diffraction (XRD) and surface area and pore sizes using BET surface area analysis.

Treatment of Wastewater

The conical flasks were agitated on an orbital shaker at 150rpm at the various contact times and adsorbent dosage according to the experimental design in Table 1 and then filtered with a Whatmann filter paper into another conical flask. The percentage removal of BOD was determined with Equation (1):

$$\%\ Removal\ of\ BOD = \left(\frac{C_i - C_f}{C_f}\right) * 100 \quad (1)$$

C_i and Cf are initial and final BOD values of wastewater respectively

Design of Experiment

The adsorption of the pharmaceutical waste by the adsorbent composite was analyzed using the Box-Behnken Design (BBD) from RSM. The independent variables considered and the ranges of their values are given in Table 1. The percentage removal of BOD was taken as the response variable.

Table 1: Coded and actual levels of the factors for three factors Box-Behnken Design

Variables	Symbols	Coded and Actual levels		
		-1	0	1
Groundnut shell char fraction	A	0	0.5	1
Adsorbent dose (g)	B	0.2	1	1.8
Contact time (min)	C	10	60	110

The relationship of the independent variables and the responses were calculated by the second-order polynomial equation

$$Y_i = b_o + \sum b_i X_I + \sum b_{ij} X_i X_j + \sum b_{ij} X_i^2 + e_i$$

where Y_i denotes the predicted response; *Xi and Xj* refers to the Coded levels of the input variables; b_0, *bi*, *bii*, and bij are the Regression coefficients (off set term, main, and quadratic, interaction effects); e_i is the experimental error.

3. RESULTS AND DISCUSSION1

CHARACTERIZATION OF ADSORBENT

Figure 1 shows the FTIR spectra of composite activated carbon at a wavelength of 4000 – 650 cm^{-1}. The functional groups in the adsorbent and their characteristics appearance are given in Table 2

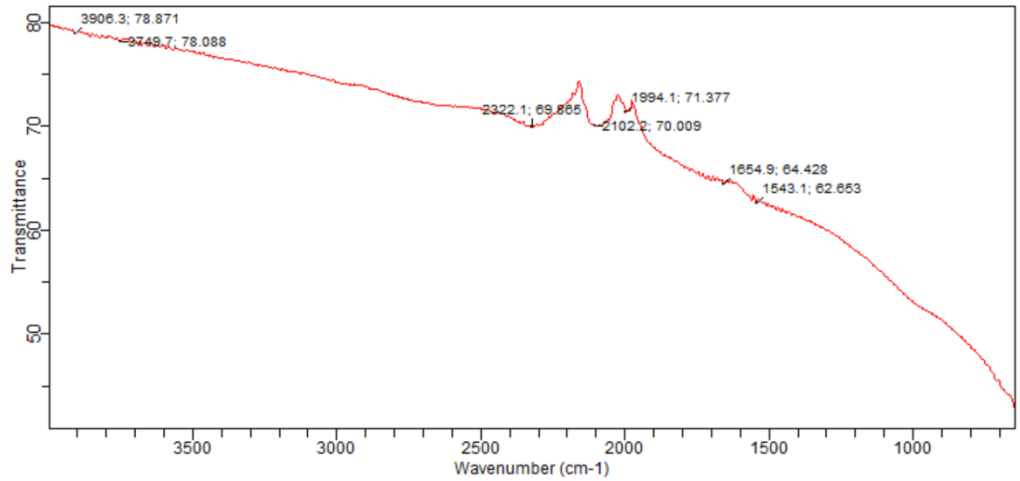


Figure 1: FTIR spectra of composite activated carbon

Table 2: Functional groups in composite activated carbon

Wavelength (cm^{-1})	Appearance	Bonds	Compounds
3906.3	Weak absorption band	N-H stretch	Amines
3749.7	Weak absorption band	N-H stretch	Amines
2102.2	Medium absorption band	C≡C stretch	Alkynes
1654.9	Very weak to medium absorption band	C=C stretch	Alkenes
1543.1	Medium to strong absorption band	N-H bend	Amides

The crystalline structure and phase of the composite adsorbent is shown by the XRD spectra in Figure 2.

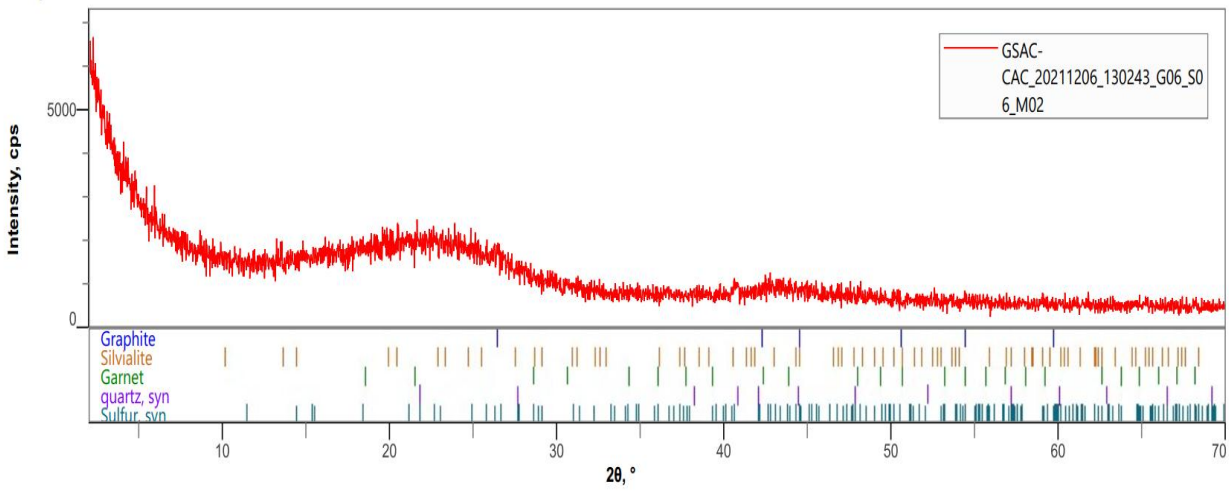
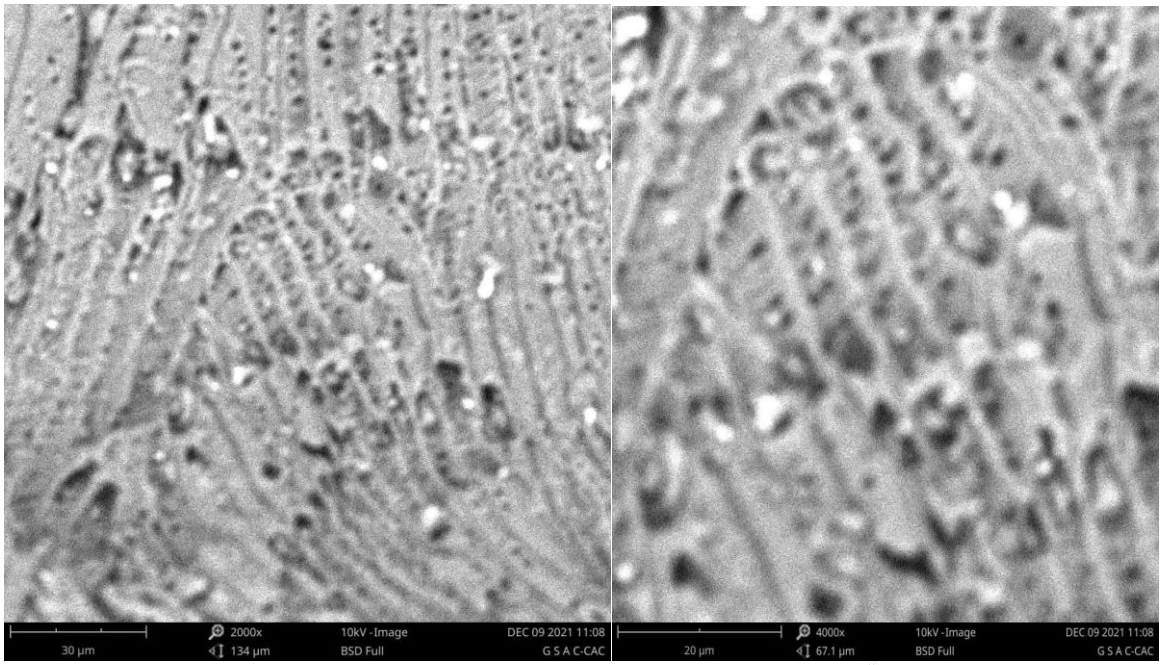


Figure 2: XRD spectra of composite activated carbon

The XRD pattern of the crystalline structure of the composite activated carbon as shown in Figure 2 shows a characteristic reflections of a homogeneous phase material with slightly uniform peaks with little deviation at low 2Θ angles and other uniform peaks at high 2Θ angles. All the reflections are sharp indicative of a highly crystalline homogeneous phase silicate based material. The uniformity of a series of peaks indexed appearing as symmetric line at high 2Θ angle corresponding to basal spacing indicating the presence of an ordered stacking sequence at atomic scale.

Figure 3 (a) and (b) shows the SEM micrographs of the composite adsorbent at 2000 and 500 resolutions respectively.



(a) **(b)**

Figure 3: SEM micrograph of composite activated carbon

It can be seen from the micrograph that the composite activated carbon (Figure 3) has a highly developed irregular pore structure which shows large pore spaces between the particles of composite activated carbon.

The BET surface area is the main indicator for the surface properties of activated carbon/catalyst as described by Chandra *et al*. (2009) and Kalderis *et al*. (2008). The BET surface area, pore volume and pore size of the composite adsorbent as analyzed using BET machine are 301.110$m^2.g^{-1}$, 0.271 $cm^3.g^{-1}$ and 3.000nm respectively. According to the International Union of Pure and Applied Chemistry (IUPAC), the pore development of an activated carbon/catalyst is classified into three groups which are micropores (size < 2 nm), mesopores (2–50 nm) and macropores (size > 50 nm) (Pandolfo and Hollenkamp, 2005; Mohd Iqbaldin *et al*., 2013). The composite adsorbent falls within the mesoporous pore size distribution. Activation leads to significant formation of micropores and/or mesopores due to the reaction between activating agents and carbon and results in the enhancement of specific surface area and total pore volume.

PHYSICO-CHEMICAL PROPERTIES OF PHARMACEUTICAL WATER

The physicochemical properties of the pharmaceutical wastewater and the WHO (2004) and Nigerian Standard for Drinking Water Quality (NSDWQ, 2007) standards of drinking water are given in Table 3.

Table 3: Physico-chemical properties of pharmaceutical wastewater before treatment

Parameter	Value	WHO MPL	NSDWQ MPL
pH	10		6.5-8.5
EC(µS/cm)	755.5	500	1000
TDS **(mg/l)**	528.5	-	500
Salinity**(mg/l)**	366.5	-	-
COD **(mg/l)**	342.5	160	-
BOD **(mg/l)**	44.5	30	-

*MPL = Maximum permissible limit

According to the World Health Organization standard (WHO, 2004) and Nigerian Standard for Drinking Water Quality (NSDWQ, 2007), the permissible range of pH for drinking water is 6.5 to 8.5. If the pH of water is less than 6.5, it discontinues the making of vitamins and minerals in the human body. A pH value higher than 8.5 makes the water taste salty, and further results in eye irritation and skin disorder when it is above 11 (Nollet & De Gelder, 2014). The pH of the pharmaceutical wastewater was determined to be 10.00 before treatment which indicates the wastewater is alkaline and above WHO and NSDWQ standards. After treatment with the composite adsorbent, considering several conditions, the pH of the pharmaceutical wastewater ranged from 8.90 to 9.90, which indicate that the different treatment conditions had little effect on the pH of the water. The highest pH value of 8.90 was attained using 1.80 g of adsorbent dose (with

no fraction of GSAC) for 60 mins of contact time with the composite activated carbon. The pharmaceutical wastewater may be harmful when used for domestic purposes.

Electrical conductivity (EC) is a measure of the saltiness of the water and is measured on a scale from 0 to 50,000 µS/cm. Conductivity in itself is a property of little interest but it is an invaluable indicator of the range of hardness, alkalinity and the dissolved solids content of the water (Chindo, 2013). Freshwater is usually between 0 and 1,500 µS/cm and typical seawater has a conductivity value of about 50,000 µS/cm. Low levels of salts are found naturally in waterways and are important for plants and animals to grow. When salts reach high levels in freshwater it can cause problems for aquatic ecosystems and complicated human uses (Water Quality Salinity Standards, 2013). The EC value of the pharmaceutical wastewater was determined to be 755.50 uS/cm before treatment (Table 3) which was above the WHO standard but below the NSDWQ standard. After treatment with the composite activated carbon using different conditions, the EC remaining ranged from 199.00 to 724.52µS/cm. The highest EC uptake (199.00µS/cm remaining) was achieved using a GSAC fraction of 1, adsorbent dose of 0.20 g for a contact time of 60 mins. These values indicate that the pharmaceutical wastewater is safe for discharge into water bodies and consumption following the NSDWQ standard.

TDS is determined by measuring the amount of solid materials dissolved in the water. High TDS values cause harmful effects to public health such as the central nervous system, provoking paralysis of the tongue, lips, face, irritability, dizziness (Gupta *et al*., 2017). The TDS of pharmaceutical wastewater from Table 3 was determined to be 528.00 before treatment and above the NSDWQ standard. The TDS remaining in the pharmaceutical wastewater ranged from 139.00 to 457.00 mg/L after treatment with the composite activated carbon at different conditions. The highest uptake of TDS was observed using a GSAC fraction of 0.5, an adsorbent dose of 1.00 g for a contact time of 60 mins. The TDS values were determined to be below the permissible limit of 500 mg/L by NSDWQ after treatment.

Salinity is a measure of the amount of salts in the water. Because dissolved ions increase salinity as well as conductivity, the two measures are related. The salinity of the pharmaceutical wastewater was determined to be 366.50 mg/L before treatment. The salinity values ranged from 98.00 to 348.00 mg/L after treatment of the pharmaceutical wastewater with the composite activated carbon as given in Table 3. The highest uptake of salinity was observed using a GSAC fraction of 1, adsorbent dose of 1.80 g for a contact time of 60 mins.

COD is an important water quality parameter as it provides an index to assess the effect of discharged wastewater will have on the receiving environment. Higher COD levels represent the presence of a greater amount of oxidizable organic material in the sample, the degradation of which will again lead to hypoxic conditions in the water body. From Table 3, the COD of the pharmaceutical wastewater was determined to be 342.50 mg/L before treatment and above the WHO standard of 160 mg/L and indicates that the pharmaceutical wastewater is low in oxidizable organic matter. The COD however ranged from 109.00 to 482.00 mg/L with the highest uptake (COD remaining of 109.00 mg/L) is within the WHO standard. The highest uptake of COD was observed using a GSAC fraction of 0.5, an adsorbent dose of 1.00 g for a contact time of 60 mins.

BOD is a measure of the amount of oxygen required by micro-organisms to break down organic matter in 1 litre of water. It is used to determine the pollution strength of wastewater. The BOD of the pharmaceutical wastewater before treatment was determined to be 44.50 mg/L which was above the WHO standard of 30 mg/L and indicates that the pharmaceutical wastewater is polluted as given in Table 3. After treatment with the composite activated carbon, the BOD remaining in the pharmaceutical wastewater ranged from 3.20 to 14.70mg/L which indicate less pollution after treatment and show that the composite activated carbon was highly effective for BOD uptake from pharmaceutical wastewater. The highest uptake (3.20 mg/L remaining) was achieved using a GSAC fraction of 1, 0.20 g of adsorbent in contact with the composite activated carbon for 60 mins.

REMOVAL EFFICIENCY OF BOD BY COMPOSITE ADSORBENT

Equation (3) gives the empirical model showing the relationship between the independent variables considered and the response (BOD removal efficiency).

$$Y = 69.03 + 3.49A + 2.27B + 0.20C - 5.45AB - 4.50AC + 2.75BC + 11.55A^2 + 4.08B^2 - 0.92C^2 \quad (3)$$

From Equation (3), it can be observed that all three independent variables have positive effect on the BOD removal efficiency. The interactions between GSAC fraction and adsorbent dose (AB), GSAC fraction and contact time (AC) have negative effect on the BOD removal efficiency, while the interaction between adsorbent dose and contact time (BC) had positive effects on the BOD removal efficiency. Among the quadratic terms, only A^2 and B^2 had positive effects, while C^2 had negative effect on the BOD removal efficiency. Groundnut shell char fraction had the highest significant effect on the BOD removal efficiency while contact time had the least effect among the main factors.

Table 4: BBD experimental design matrix for BOD adsorption

Run	Factors			BOD Removal efficiency (%)		
	GSAC fraction	Adsorbent dose (g)	Contact time (mins)	Actual	Predicted	Absolute Error
1	0	1.0	10	73.23	71.47	1.76
2	1	1.8	60	85.73	84.98	0.75
3	0.5	1.8	110	78.43	77.42	1.01
4	0.5	1.0	60	67.19	69.03	1.84

5	0.5	1.0	60	71.24	69.03	2.21
6	0.5	1.0	60	66.97	69.03	2.06
7	0.5	0.2	110	67.64	67.37	0.27
8	0	1.8	60	87.42	88.90	1.48
9	0.5	0.2	10	71.46	72.47	1.01
10	0	1.0	110	81.35	80.87	0.48
11	1	1.0	10	86.97	87.44	0.47
12	1	1.0	110	77.10	78.86	1.76
13	0.5	1.8	10	71.24	71.51	0.27
14	0	0.2	60	72.70	73.45	0.75
15	0.5	1.0	60	69.66	69.03	0.63
16	0.5	1.0	60	70.11	69.03	1.08
17	1	0.2	60	92.81	91.33	1.48

From Table 4, the actual response values and the simulataed values of the response using Design expert were observed to be consistently close. The absolute errors between the actual and simulated values range from 0 .27 to 2.21. The small absolute error values between the actual and the simulated response values is indicative of the goodness of the simulation to predict the response.

The fit of the statistical model for the BOD removal efficiency from the pharmaceutical wastewater by the composite adsorbent was assessed by carrying out analysis of variance (ANOVA) and the results are presented in Tables 5 and 6.

Table 5: ANOVA for quadratic model

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**
Model	1023.53	9	113.73	28.03	0.0001*
A – GSC Fraction	97.38	1	97.38	24.00	0.0018*
B – Adsorbent dosage	41.40	1	41.40	10.20	0.0152*
C – Contact time	0.3292	1	0.3292	0.0811	0.7840
AB	118.75	1	118.75	29.27	0.0010*
AC	80.86	1	80.86	19.93	0.0029*
BC	30.31	1	30.31	7.47	0.0292*
A^2	561.70	1	561.70	138.43	< 0.0001*
B^2	70.09	1	70.09	17.27	0.0043*
C^2	3.58	1	3.58	0.8833	0.3786
Residual	28.40	7	4.06		
Lack of Fit	14.32	3	4.77	1.36	0.3756
Pure Error	14.08	4	3.52		
Cor. Total	1051.94	16			

***=significant**

Table 6: Fit statistics of regression model

Parameters	**Values**
Standard deviation (%)	2.01
Mean (%)	75.95
Coefficient of variation, C.V (%)	2.65
R^2	0.9730
Adjusted R^2	0.9383
Predicted R^2	0.7612
Adequate precision	15.51

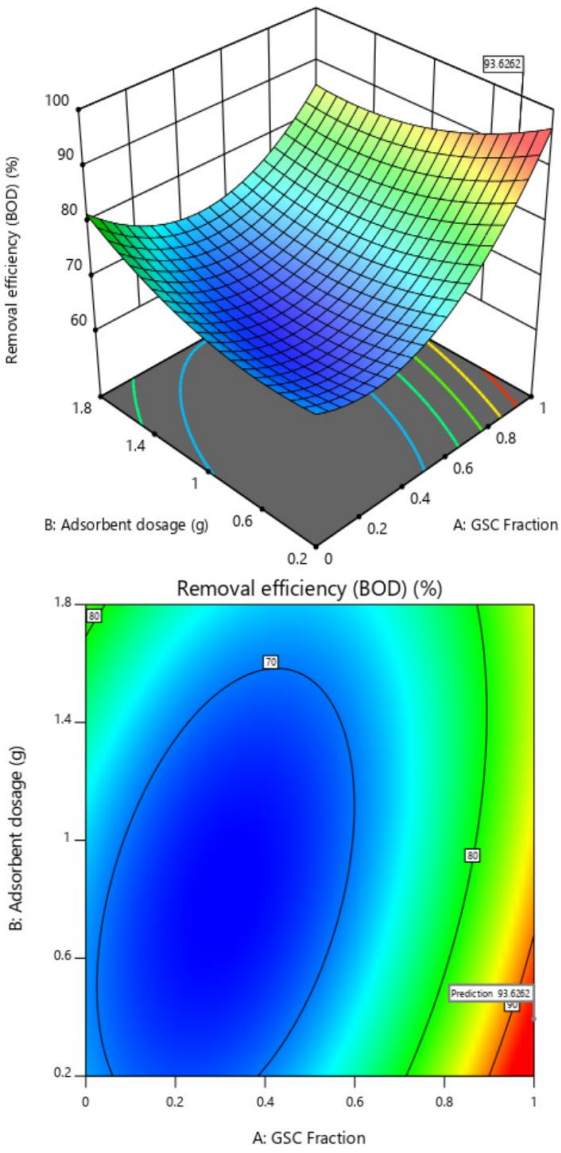
Table 5 gives the tabulated ANOVA results for the BOD uptake from pharmaceutical wastewater using composite adsorbent. A high model F-value of was 28.03 and low p-value of 0.0001 showed that model term is highly significant. Also, in the present study, the model terms; A, B, AB, AC, BC, A^2 and B^2 were highly significant parameters, while C and C^2 do not have any significant impact on the BOD removal efficiency from the pharmaceutical wastewater. The "Lack of Fit" F value of 1.36 and a p-value of 0.3756 (p> 0.05) implies that there was insignificant lack of fit, and this implies that the model has a good fit for predicting BOD removal efficiency from the pharmaceutical wastewater. A good fit

means that the generated model adequately explains the data variation.

From Table 6, it seen that the coefficient of variation (C.V) of 2.65% is within acceptable range, since CV is an expression of standard deviation as a percentage of the mean, the small values of CV gives better reproducibility. In general, a high CV indicates that variation in the mean value is high and does not satisfactorily develop an adequate response model (Liyana-Pathirana and Shahidi, 2005). The coefficient of regression (R^2 value) is a statistical measure that represents the proportion of the variance for a dependent variable that's explained by an independent variable or variables. The R^2 value provides a measure of how variability in the observed response values could be explained by the experimental factors and their interactions (Ying *et al*., 2011).Table 6 gives a high R^2 value of 0.9961, which shows that over 99.61% of the variability in the BOD removal efficiency by the composite adsorbent by the variables considered can be explained by the model. There is also a reasonable agreement between the adjusted R^2 and the predicted R^2 values of 0.9479 and 0.9911 respectively since the difference between them is less than 0.2. This also shows that the model reasonably predicted the BOD removal efficiency. Adequate precision gives an indication of the signal to noise ratio, and a value greater than 4 is generally desired (Cao *et al*., 2009). The value of 15.51 obtained therefore indicates an adequate signal and that the model can be used to navigate the design space.

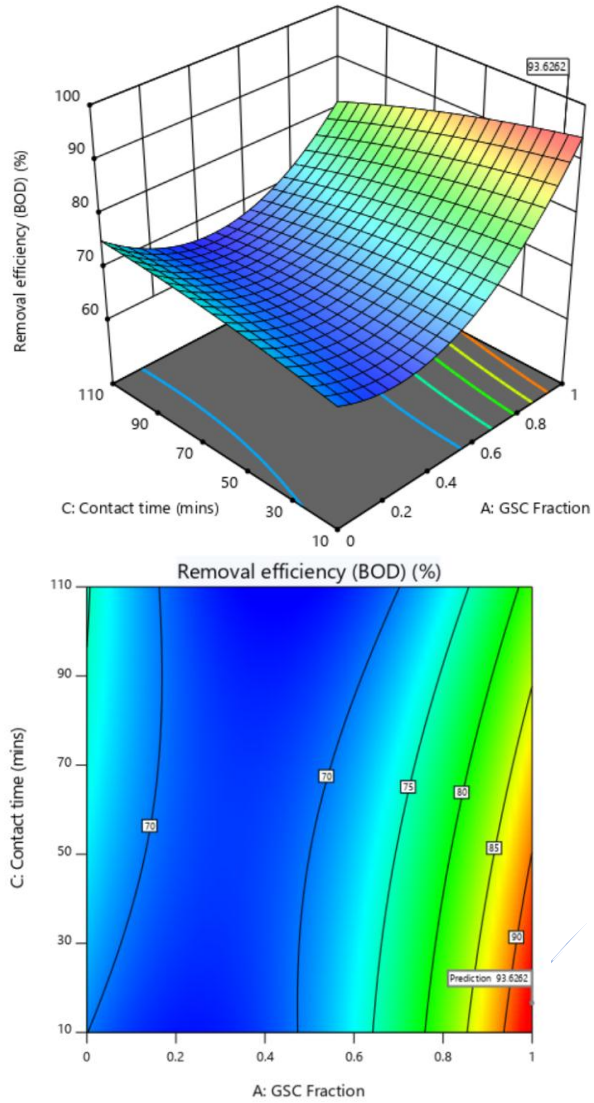
Effects of Interaction of Process Variables on BOD Removal Efficiency

The effects of interactions among the independent variables on the BOD removal efficiency have been visualized through a three-dimensional response surface plots shown in Figures 4-6.



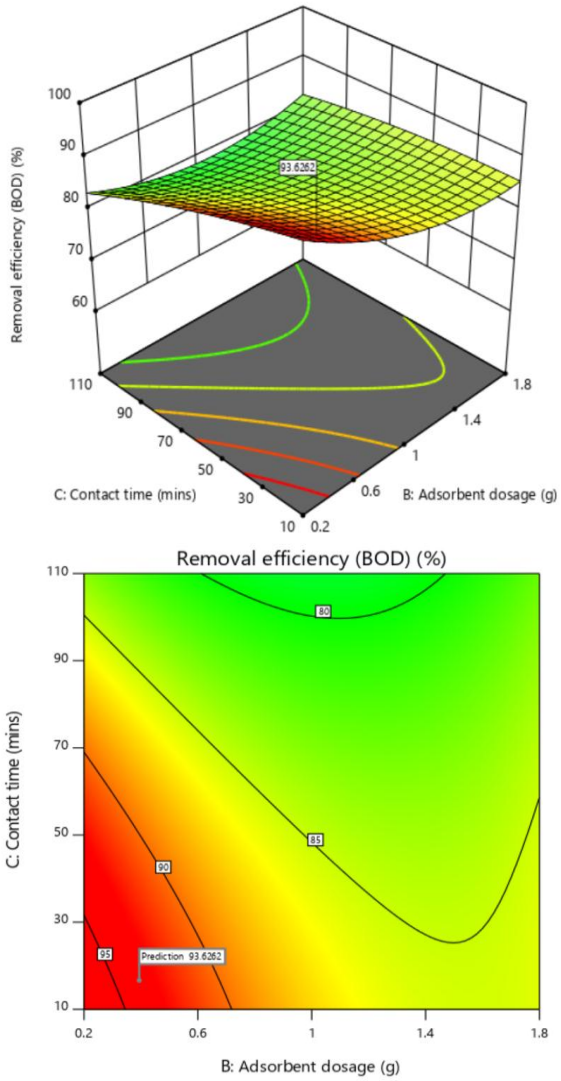
(a) (b)

Figure 4: 3D surface plot (a) and the corresponding contour plot (b) for the effect of interaction of groundnut shell char fraction and adsorbent dosage on BOD removal efficiency



(a) (b)

Figure 5: 3D surface plot (a) and the corresponding contour plot (b) for the effect of interaction of contact time and groundnut shell char fraction on BOD removal efficiency



(a) (b)

Figure 6: 3D surface plot (a) and the corresponding contour plot (b) for the effect of contact time and adsorbent dosage on BOD removal efficiency

The effect of the interaction of GSAC fraction and adsorbent dosage on the removal efficiency of composite activated carbon for BOD uptake from pharmaceutical wastewater is shown by the three-dimensional response surface and two-dimensional contour plots in Figure 4. From the plot, it can be observed that at constant contact time, the concurrent increase in GSC fraction and adsorbent dosage lead to an increase in BOD removal efficiency. The converse case of a concurrent decrease in GSC fraction and adsorbent dosage also lead to a decrease in the BOD removal efficiency. The effect of the interaction of GSAC fraction and contact time on the removal efficiency of composite activated carbon for BOD removal efficiency from pharmaceutical wastewater is shown by the three-dimensional response surface and two-dimensional contour plots in Figures 5 (a) and (b) respectively. From the plot, it can be observed that at constant adsorbent dose, the concurrent increase in GSC and contact time also lead to an increase in the BOD removal efficiency. It was also observed that the concurrent decrease in GSC fraction and contact time also lead to a decrease in the BOD removal efficiency. The

effect of the interaction of adsorbent dose and contact time on the removal efficiency of composite activated carbon for BOD uptake from pharmaceutical wastewater is shown by the three-dimensional response surface and two-dimensional contour plots in Figures 6 (a) and (b) respectively. It can be observed that there was an initial increase in BOD removal efficiency when both adsorbent dose and contact time increased from 0 to 0.2 g and 0 to 10 min respectively. Subsequently, the concurrent increase in adsorbent dose and contact time only resulted in a decrease in BOD removal efficiency.

Optimization conditions

The variable settings with maximum desirability are considered to be the optimal parameter conditions. The achieved maximum desirability of 0.923 means that it is possible to reach maximum removal efficiency target. The maximum removal efficiency of 97.45% obtained for BOD removal from pharmaceutical wastewater by the composite adsorbent was achieved using aGSAC fraction of 1 in 0.20 g of the composite activated carbon for a contact time of 10.00 mins. The desirability ramp showing the optimal conditions is given in Figure 7.

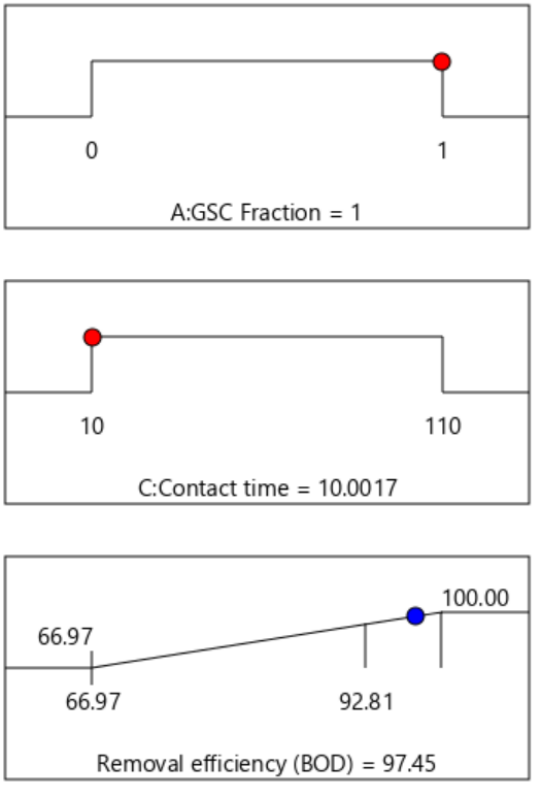


Figure 7: Desirability ramp showing optimal conditions of BOD uptake in pharmaceutical wastewater

Validation of Statistical Model

To ascertain the validity of the statistical model developed, confirmatory experiments in triplicate sets were performed at the obtained optimal parameter values representing the maximum BOD removal efficiency. Experiments conducted at the optimal conditions showed that there was no significant deviation between the actual BOD removal efficiency of 97.80 % and the predicted BOD removal efficiency of 97.45 % by RSM model, as this gave a relative error value of 0.00358. The high positive correlation of the predicted yields and values obtained from actual experiments shows the validity of the statistical model.

CONCLUSIONS

The following conclusions have been made on this study: The functional group showed the presence of amines, alkyne, alkene and amides while the XRD revealed a homogeneous and highly crystalline material. The surface morphology of the adsorbent blend as revealed by the SEM micrograph showed a highly developed irregular pore structure which is due to chemical activation in the activated carbon. The high BET surface elucidates the high adsorptive capacity of the composite adsorbent.

The composite adsorbent is very effective for the reduction of BOD as it gave a maximum removal efficiency of 97.45% . This high BOD removal efficiency is an indication that this adsorbent is a promising material for the effective treatment of wastewater from paint factories.

REFERENCES

Ajala LO & Ali EE 2020. Preparation and characterization of groundnut shell-based activated charcoal. *J. Appl. Sci. Environ. Manag.*, *24*(12):2139-2146.

Barrios-Hernández ML, Pronk M, Garcia H, Boersma A, Brdjanovic D, van Loosdrecht MC & Hooijmans C M 2020. Removal of bacterial and viral indicator organisms in full-scale aerobic granular sludge and conventional activated sludge systems. *Water Res.X*, *6*, 100040. https://doi.org/10.1016/j.wroa.2019.100040.

Blair BD, Crago JP, Hedman CJ & Klaper RD 2013. Pharmaceuticals and personal care products found in the Great Lakes above concentrations of environmental concern. *Chemosphere*, 93(9): 2116-2123

Cao G, Ren N, Wang A, Lee DJ, Guo W, Liu B, Feng Y & Zhao Q 2009. Acid hydrolysis of corn stover for biohydrogen production using Thermoanaerobacterium thermosaccharolyticum W16. *Int. J. Hydrog. Energy*, 34 (17): 7182-7188.

Chandra TC, Mirna MM, Sunarso J, Sudaryanto Y & Ismadji S 2009. Activated carbon from durian shell: Preparation and characterization. *J. Taiwan Inst. Chem. Eng.*, 40: 457-462.

Chindo IY, Karu E, Ziyok I & Amanki ED 2013. Physicochemical Analysis of Ground Water of Selected Areas of Dass and Ganjuwa Local Government Areas, Bauchi State, Nigeria. *World J. Anal. Chem.*,1 (4): 73-79.

Dindaş GB, Çalışkan Y, Çelebi EE, Tekbaş M, Bektaş N & Yatmaz HC 2020. Treatment of pharmaceutical wastewater by combination of electrocoagulation, electro-fenton and photocatalytic oxidation processes. *J. Environ. Chem. Eng.*, **8 (3)** https://doi.org/10.1016/j.jece.2020.103777

Gupta N, Pandey P & Hussain J 2017. Effect of physicochemical and biological parameters on the quality of river water of Narmada, Madhya Pradesh, India. *Water Sci.*, 31 (1):11-23.

Huang Y, Jiang J, Ma L, Wang Y, Liang M, Zhang Z & Li

L 2020. Iron foam combined ozonation for enhanced treatment of pharmaceutical wastewater. *Environ. Res.*, *183*, 109205.

Jiang Y, Shi X & Ng HY 2021. Aerobic granular sludge systems for treating hypersaline pharmaceutical wastewater: Start-up, long-term performances and metabolic function. *J. Hazard. Mater.*, 412, 125229. https://doi.org/10.1016/j.jhazmat.2021.125229.

Kalderis D, Kayan B, Akay S, Kulaksız E & Gözmen B 2017. Adsorption of 2,4-dichlorophenol on paper sludge/wheat husk biochar: Process optimization and comparison with biochars prepared from wood chips, sewage sludge and hog fuel/demolition waste. *J. Environ. Chem. Eng.*, 5(3): 2222-2231,

Kalderis D, Bethanis S, Paraskeva P & Daimadopulos E 2008. Production of activated carbon from bagasse and rice husk by single-stage chemical activation method at low retention times. *Bioresour. Technol.*, 99:6809-6816.

Karimi-Maleh H, Ayati A, Davoodi R, Tanhaei B, Karimi F, Malekmohammadi S & Sillanpää M 2021. Recent advances in using of chitosan-based adsorbents for removal of pharmaceutical contaminants: A review. *J. Clean. Prod.*, *291*, 125880. https://doi.org/10.1016/j.jclepro.2021.125880

K'oreje KO, Vergeynst L & Ombaka DP 2016. Occurrence patterns of pharmaceutical residues in wastewater, surface water and groundwater of Nairobi and Kisumu city, Kenya. *Chemosphere*, 149:238-244.

Kyzas GZ, Fu J, Lazaridis NK, Bikiaris DN & Matis KA 2015. New approaches on the removal of pharmaceuticals from wastewaters with adsorbent materials. *J. Mol. Liq.*, 209: 87-93,

Li X, Gao F, Hua Z, Du G & Chen J 2005. Treatment of synthetic wastewater by a novel MBR with granular sludge developed for controlling membrane fouling. *Sep. Purif. Technol.*, *46*(1-2): 19-25.

Lotito AM, Fratino U, Mancini A, Bergna G & Di Iaconi C 2012. Effective aerobic granular sludge treatment of a real dyeing textile wastewater. *Int. Biodeterior. Biodegr.*, 69: 62-68.

Larsson DGJ, de Pedro C, & Paxeus N 2007. Effluent from Drug Manufactures Contains Extremely High Levels of Pharmaceuticals. *J. Hazard. Mater.*, 148:751–755.

Liyana-Pathirana C & Shahidi F 2005. Optimization of extraction of phenolic compounds from wheat using response surface methodology. *Food Chem.*, 93: 47–56.

Mohd Iqbaldin MN, Khudzir MI, Azlan M, Zaidi AG, Surani B & Zubri Z 2013. Properties of coconut shell activated carbon. *J. Trop. For. Sci.*, 25(4): 497–503.

Mojiri A, Vakili M, Farraji H & Aziz SQ 2019. Combined ozone oxidation process and adsorption methods for the removal of acetaminophen and amoxicillin from aqueous solution; kinetic and optimisation. *Environ. Technol. Innov. 15*, 100404.

Nigerian Standard for Drinking Water Quality (NSDQW) (2007), Standards Organization of Nigeria (SON) Reports, pp.15-17

Nollet LML & De Gelder LSP 2014. Handbook of Water Analysis, 3rd edn. CRC Press, Florida, pp 45-48

Pandolfo AG & Hollenkamp AF 2005. Carbon properties and their role in supercapacitors. *J. Power Sources*, 157: 11–27.

World Health Organization. (2004). Guidelines for drinking water quality. WHO Water Series. 3rd edn. Geneva, pp. 67-69

Ying F, Gao BY, Zhang YF, Zhang XY & Shi N 2011. Organic modifier of poly-silicic-ferric coagulant: Characterization, treatment of dyeing wastewater and floc change during coagulation. *Desalination*, 277: 67-73.

Zhao Z, Xu W, Wang Z, Qin W, Lei J, Guo X & Long J. (2021) Investigation of organic impurity and its occurrence in industrial waste salt produced by physicochemical process. *PLoS ONE*, 16(8): e0256101. https://doi.org/10.1371/journal.pone.0256101.