



Lapai Journal of Science and Technology, Vol. 10, No. 1 (2024)

REDUCTION OF TOTAL ORGANIC CARBON AND BIOCHEMICAL OXYGEN DEMAND USING MODIFIED AND UNMODIFIED *Hibiscus sabdiriffa* AND *Hibiscus esculentus* STALKS: KINETIC AND ISOTHERM STUDY

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ABSTRACT

Treatment of dye effluent could become a great move towards environmental protection and sustainability. Hence, this research was aimed at studying the use of *Hibiscus esculentus* and *Hibiscus sabdiriffa* Stalks for the reduction of Total Organic Carbon (TOC) and Biochemical Oxygen Demand (BOD). *Hibiscus esculentus* and *Hibiscus sabdiriffa* stalks were collected, modified with Cetyltrimethylammonium Bromide and characterised by various techniques: High Resolution Scanning Electron Microscopy (HRSEM), Electron Dispersive Spectrometer (EDS), and Fourier Transform Infra Ray (FTIR). The adsorption studies of *Hibiscus esculentus* and *Hibiscus sabdiriffa* unmodified and modified for TOC and BOD reduction in wastewater collected from a dyeing pit at Kofar Mata Dye site in Kano, Nigeria were evaluated at different contact times, and dosage of adsorbents. The HRSEM results revealed surface morphology for unmodified *Hibiscus sabdiriffa* and *Hibiscus esculentus* were without defined pores, ridges, and defects, whereas for modified *Hibiscus sabdiriffa* and *Hibiscus esculentus* were textural and morphological changes. EDS studies showed evidence of the increment in carbon into the matrix of the modified *Hibiscus sabdiriffa* and *Hibiscus esculentus* activated carbon: 99.39 % and 98.21 % resp. Reduction of TOC from the wastewater increased with time and attained equilibrium at average of 94.35 % for modified *Hibiscus sabdiriffa* and *Hibiscus esculentus* activated carbon respectively and average of 80.10 % for unmodified *Hibiscus sabdiriffa* and *Hibiscus esculentus* respectively. Reduction of BOD from the wastewater, equilibrium was attained at average of 90.10 %, for modified *Hibiscus sabdiriffa* and *Hibiscus esculentus* activated carbon respectively and 85.10 % for unmodified *Hibiscus sabdiriffa* and *Hibiscus esculentus* activated carbon respectively. Isotherms data evaluated revealed Langmuir isotherm best fitted the equilibrium data. The kinetic data for all the adsorption experiments fitted to the pseudo- second-order model. Surfactant modified *Hibiscus sabdiriffa* and *Hibiscus esculentus* had good performance on TOC and BOD reduction of the textile wastewater than unmodified *Hibiscus sabdiriffa* and *Hibiscus esculentus* stalks.



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Keywords: Activated carbon, BOD, Dye wastewater, *Hibiscus esculentus* stalks, *Hibiscus sabdiriffa*

INTRODUCTION

The growing rate of water consumption necessitates wastewater reuse, therefore being able to recover dye wastewater is a significant step towards sustainability and overall environmental preservation. In addition to their colour, which is an aesthetic pollution or eutrophication and disturbs aquatic life. The elimination of dye-containing wastewater into the water environment is unethical because it reduces photosynthetic activity and interferes with the transmission of sunlight into the stream. Many of these released aromatic dyes such as azo dye and the breakdown products of these dyes are also toxics, carcinogenics, or mutagenics to life (Suteu et al., 2009; Zaharia et al., 2011; Ghaly et al., 2014). Since dyes are organic compounds that are refractory and resistant to aerobic digestion, as well as resilient to light, heat, and oxidising agents, treating effluent containing dyes may be quite challenging (Rangabhashiyam et al., 2013). According to Sasaki et al. (2014), adsorption is a surface occurrence in which a combination of fluid (gas or liquid) components is bonded to the exterior of a solid adsorbent by a chemical or physical connection. Carbonaceous materials having a wider internal surface area and a highly developed porous structure during high temperature reactions are referred to as activated carbon (Romanos, 2012). Numerous methods, such as ozonation, electrochemical oxidation, advanced chemical oxidation, nano-filtration, electrokinetic coagulation, liquid-liquid extraction adsorption, and biological process, have been used to remove dyes from dye wastewater (Regina et al., 2008; Ahmadpour et al., 2009). Because it is so easy to use, activated carbon adsorption has shown to be one of the most successful, widely utilized, and promising techniques. Since commercial activated carbons are expensive, there has been increase in the search for suitable and less expensive adsorbent from locally available plant materials. Stalks from *Hibiscus esculentus* and *Hibiscus sabdiriffa* are widely available, which qualifies them as alternate sources of potent and environmentally acceptable adsorbents for the removal of colours from effluent.

Adsorbent prepared from agricultural waste has been used to absorb dye. By covering the mucilage of okra on the surfaces of biochar, Nath et al., 2021 created an adsorbent that successfully absorbed methylene blue from water. According to their findings, the ideal parameters for methylene blue adsorption on biochars was an initial methylene blue concentration of $100 \text{ mg}\cdot\text{L}^{-1}$, a pH of about 8.1, and an adsorbent dosage of $1 \text{ g}\cdot\text{L}^{-1}$. Biochars



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methylene blue adsorption capabilities rose as pH rose, reaching their maximum adsorption in the pH range of 8.1–8.7. The potential of *Hibiscus Sabdariffa* seeds in the adsorption-coagulation process for treating greywater was reported by Ahmad et al. in 2023. According to their research, the adsorption procedure yielded the maximum turbidity and chemical oxygen demand (COD) removal at 98.60 % and 61.60 %, respectively, at pH 2 and 3g of adsorbent dose. Ahmad & Associates (2019) reported that Methyl red (MR) dye may be removed from aqueous solutions using lemongrass leaf-based activated carbon (LGLAC), with larger starting concentrations of greywater dye, longer contact times, and higher solution temperatures all contributing to enhanced adsorption. The Langmuir model was found to be the optimal adsorption technique, and Üner et al. (2017) effectively produced activated carbon from okra wastes with a large surface area. The maximal adsorption capacity for Rhodamine B was predicted to be 321.50 mg/g at 25 °C. The okro activated carbon curve was also discovered to align to a pseudo-second order model; at 25 °C, the values of Gibbs free energy, enthalpy, and entropy were -27.87 kJ/mol, 13.03 kJ/mol, and 0.15 kJ/mol K, respectively. Agricultural waste *Hibiscus esculentus* and *Hibiscus sabdariffa* stalks have not, however, been used to reduce Total Organic Carbon (TOC) and Biological Oxygen Demand (BOD) in textile waste water. Thus, the researchers report on the use of both modified and unmodified *Hibiscus esculentus* and *Hibiscus sabdariffa* stalks to reduce TOC and BOD in real dye waste water.

MATERIALS AND METHODS

Materials

Reagents utilized for the analysis were of analytical grade (Analar) and were used without further treatment. The following reagents were used: Cetyltrimethylammonium Bromide CTAB($C_{16}H_{33}N(CH_3)_3Br$) (Sigma-aldrich), Hydrochloric acid (BDH), Nitric acid (BDH). Solvent used includes distilled water

Methods

Samples collection

Plant samples (*Hibiscus esculentus* and *Hibiscus sabdariffa*) stalks were randomly collected from different locations in Paiko Local Government Area, Niger State. The obtained plant samples were separated and thoroughly washed with distilled water. The samples were sun dried, and then milled into powder. A 250 μ m mesh size sieve was used to extract fine powder from the powdered samples.



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Sampling and sample pre-treatment of dyeing wastewater

At the Kofar Mata Dye site in Kano state, 500ml of dyeing effluent, was collected and kept in pristine plastic bottles. The bottles were completely cleansed with de-ionized water and cleaned with 10 % nitric acid prior to sample collection. The local dyeing effluent physico-chemical characteristics were determined using standard procedures (AOAC, 2006). During the storage period, the effluent was kept at 4 °C to prevent any changes to its properties.

Preparation of Activated Carbon

Approximately 2.0 g of the powdered *Hibiscus esculentus* and *Hibiscus sabdiriffa* stalks were weighed individually and subsequently introduced into muffle furnace. The samples were carbonized at 400 °C for 5 min and quenched immediately in an ice bath; the surplus water was removed. The carbonized samples were washed using 0.1 M HCl to eliminate surface ashes, followed by hot and distilled water wash to eliminate remaining acid (Rahman et al., 2005). Chemical activation of the obtained activated carbon was carried out by treating 5 g of activated carbon with 100 ml solution utilizing CTAB ($C_{16}H_{33}N(CH_3)_3Br$) at corresponding 0.5 Critical Micelle Concentrations (CMCs). All the samples were put in a temperature controlled orbital shakers utilizing a stirring speed of 150 rpm, at 80 ± 0.5 °C for 360 min and allowed to obtain the ambient conditions. The samples were filtered by Whatman-42 without washing, then dried in an oven overnight at 110 °C and subsequently kept in a sample vial for future analysis (Nadeem et al., 2006).

Physical Measurements

The percent (%) yield of activated carbons was determined as described by Yulu *et al.* (2001). Determination of bulk density and ash content were done following the AOAC (2006) method. The procedure for pH and conductivity measurements were based on the approach adopted by Okiemen *et al.* (2004). The volatile matter determination was done according to the method of Ioannidou and Zabaniotou (2006). Moisture content was determined according to AOAC (2006) method. The infrared spectra of the as pressed KBr disc, were recorded on the Perkin Elmer 100 model infrared spectrophotometer in the region $4000-400\text{cm}^{-1}$. The prepared adsorbents were characterised for their surface morphology and elemental composition by a HRSEM/EDS micrograph (Zeiss Auriga HRSEM) respectively. The surface area was determined by N_2 adsorption isotherm with relationship using NOVA 1200 (Quantachrome Corp.). Some of the physical measurements were done



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in the Department of Chemistry, Federal University of Technology Minna, Nigeria, others were at University of Western Cape South-Africa.

RESULTS AND DISCUSSION

Physicochemical Features of the Unmodified and Surfactant-Modified *Hibiscus sabdariffa* and *Hibiscus esculentus* Stalks

Four different activated carbons were prepared from *Hibiscus sabdariffa* and *Hibiscus esculentus* Stalks. Two were modified using CTAB: *Hibiscus sabdariffa* activated carbon (AC2) and *Hibiscus esculentus* activated carbon (AC4) and two were unmodified: *Hibiscus sabdariffa* activated carbon AC1 and *Hibiscus esculentus* activated carbon (AC3)

Based on the moisture and ash content findings presented in Table 1. The outcomes showed that the values for AC1 and AC2 were 1.08 and 3.25 %, respectively, and for AC3 and AC4, 2.14 and 3.47 %. Therefore, the results were satisfactory since they fell between the standard (<5%) (Belkebir, 2007). The highest figure of 3.37 % for the percentage of ash contents for AC1–AC4 represents the inorganic residue that remains after the organic component has been burned up. However, it varies according to the plant and the carbon source (FAO, 2005).

In Table 1, the volatile matter percentages for AC1–AC4 were 28.24, 23.43, 33.52, and 29.41%, respectively. These values were much lower than their equivalent fixed carbon content (%), which were 68.61, 69.95, 62.85, and 65.24 respectively. This explains why *Hibiscus esculentus* and *Hibiscus sabdariffa* stalks were used for the activated carbon manufacturing process (Ajifack et al., 2015). As shown in Table 1, the bulk densities of the AC1–AC4 stalks were determined and greater volume activity was produced by higher density, which also often denotes higher quality adsorbent. The carbonized sample pH was measured and in every instance, the value was discovered to be almost neutral, which will be useful for treating all dye wastewater situations and may also be used to purify potable drinking water (Baseri et al., 2012).



Table 1: Physicochemical Features of the Activated Carbons

Data	AC1	AC2	AC3	AC4
Moistures (%)	1.08	3.25	2.14	3.47
Ashes (%)	2.03	3.37	1.58	1.85
Volatile materials (%)	28.24	23.43	33.52	29.41
Fixed carbons (%)	68.61	69.95	62.85	65.24
Bulk densities (g/cm ³)	0.89	0.83	0.46	0.34
pH	6.76	8.11	6.44	7.98
Percentage yields (%)	66.80	64.70	58.65	57.91

Brunauer Emmet Teller (BET)

The surface areas and porosity of the prepared AC1-AC4 are significant parameters in determining its adsorption capacity as well as its adsorption performance (El-Geundi *et al.*, 2005). The adsorption isotherms obtained were analyzed by the conventional BET equations.

Table 2: BET Surface Area and Structural Characterization of Activated Carbons

Data	BET surface areas (m ² /g)	Pore diameters (nm)	Pore volumes (cm ³ /g)
AC 1	348.42	2.10	0.22
AC 2	392.33	2.43	0.23
AC 3	341.72	2.12	0.22
AC 4	361.66	2.41	0.21

The findings given in Table 2 indicate that the surfactant-modified adsorbents displayed considerably greater surface areas, pore dimensions, and specific pore diameters compared to the unmodified activated carbon. AC4 had increased surface area, pore width, and volume compared to AC1, indicating that the presence of the cationic (CTAB) surfactant improved the surface properties of the adsorbent. This is obvious from the FTIR and HRSEM data presented in Figures 1-2 and Plates I-II. This happened because of the cationic molecule attached to the empty site on the unmodified activated carbons. The increase may be attributed to the usual property of micelle generation, adsorption, wetting, and solubilization given by the surfactant-modified surfaces. Due to their amphipathic nature, both AC2 and



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AC4 feature hydrophilic and hydrophobic portions, enabling them to offer wetting qualities for both water and oil.

High Resolution Scanning Electron Microscope (HSEM) analysis

The HSEM utilized to analyse the morphology of the different produced adsorbent AC1-AC4. Plates I and II demonstrate the HRSEM micrographs of the unmodified and surfactant-modified activated carbons.

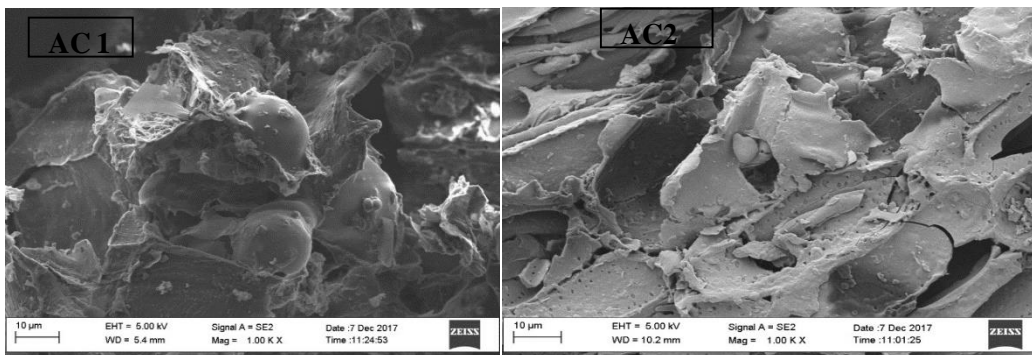


Plate I: HRSEM of AC 1 and AC 2

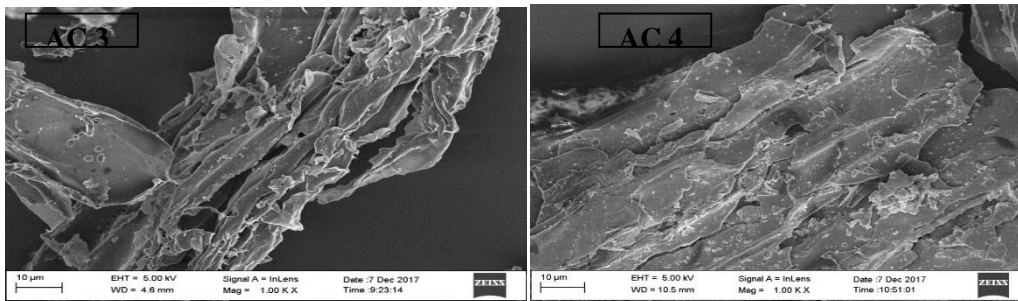


Plate II: HRSEM AC 3 and AC 4

The surface, as shown in AC1, was found to have few flaws (cracks, cavities, and ridges) and to be rather fluffy and smooth. However, this structure was changed when CTAB ($C_{16}H_{33}N(CH_3)_3Br$) was introduced. As plate AC2 indicates, the intensive contact between the activated carbons and the $C_{16}H_{33}N(CH_3)_3^+$ cationic micelles resulted in morphological and textural modifications on the surface of the modified activated carbon. The adsorbent surface produced well-developed flaws such ridges, cavities, and fractures that might serve as an active site for adsorption (Demirbas et al., 2004). When comparing the surface of



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unmodified activated carbon for AC3 to that of modified CTAB ($C_{16}H_{33}N(CH_3)_3Br$), just a little morphological organization change was seen.

Elemental analysis

Table 3.0 presents the elemental composition of the various surfactant-modified and unmodified adsorbent from *Hibiscus esculentus* and *Hibiscus sabdariffa* stalks.

Table 3: Elemental Compositions AC1- AC4

Elements	AC 1	AC 2	AC 3	AC 4
Carbon	98.31	99.38	74.01	98.22
Oxygen	-	-	18.71	-
Magnesium	-	-	1.53	0.64
Silicon	-	-	0.82	-
Calcium	0.64	0.24	1.06	0.39
Bromine			0.78	-
Potassium	1.07	0.20	1.06	0.77
Sulphur	-	0.07	-	-

Table 3.0 shows a significant increase in elemental carbon following modification with CTAB ($C_{16}H_{33}N(CH_3)_3Br$). This increase might be due to the ions $C_{16}H_{33}N(CH_3)_3^+$ micelles fixing into the fabrics of the activated carbons. However, washing and filtration processes during the modification process caused calcium and potassium to decrease from 0.64 and 1.07 % to 0.24 and 0.2 % for *Hibiscus sabdariffa* and from 1.06 and 1.05% to 0.39 and 0.78% for *Hibiscus esculentus*. (Al-Latief et al., 2015). While all other ions, particularly oxygen, have been totally eliminated by a mix of chemical reactions between scavenging atoms in solution and physical procedures like washing and filtering.

Fourier transforms infrared spectrometer (FTIR)

The functional groups on the adsorbent surface that facilitate the adsorption of dye molecules were identified using FTIR spectroscopy.

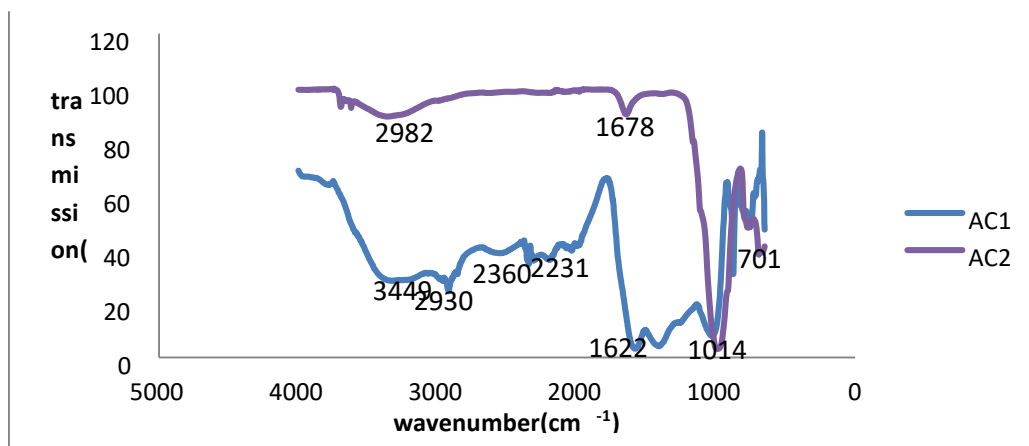


Figure 1: FTIR Spectra AC1 and AC2

The broad peaks detected at 3371 and 3390 cm^{-1} in AC 1 and AC 2 were attributed to the stretch of the hydroxyl group, which occurs owing to the inter- and intramolecular coupling of polymeric compounds, such as alcohols, phenols, and carboxylic acids. Ajifack et al. (2015) concluded that the presence of carboxylic acid hydroxyl groups may be inferred from the extensive range of the O-H band. Following the replacement of the adsorbent with CTAB, the medium peaks seen at 2931, 2561, and 2230 cm^{-1} , which were associated with the symmetric stretching vibrations of C-H, O-H of -COOH, and C-C, respectively, diminished, resulting in the presence of very weak or no peaks in their stead. In addition, after modification, the peak at 1606, 1031, and 741 moved to an increased wavenumber, which corresponds to the stretch vibrations of the C-Br group, C-O-C asymmetrical group, and C=C aromatics (Okeke, 2017).

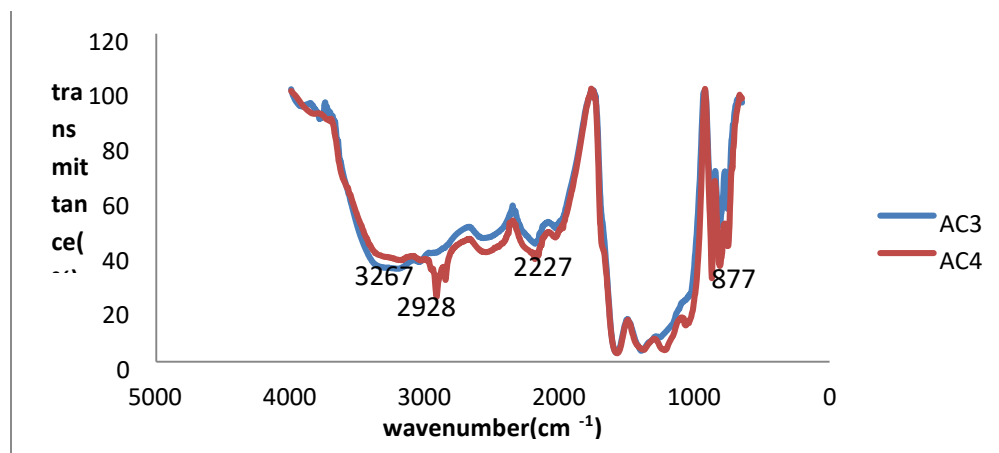


Figure 2: FTIR Spectra AC3 and AC4

The FTIR spectra of AC3 and AC4 shows a large peak at 3324 and 3263 cm^{-1} , respectively, showing the existence of aromatic C-H and the N-H vibration mode of OH groups (Dağdelen et al., 2014). After functionalization, only CTAB-modified adsorbents showed bands at 2928, 2865, 1270, and 1134 cm^{-1} , which indicate an existence of new functional groups due to asymmetric C-H stretching of CH_2 , C-N stretching in aliphatic amines, or C-H wag and C-O stretching in alcohols and carboxylic acids, respectively (Mohan et al., 2012). Following adjustment, the bands at 1612 and 1446 cm^{-1} , which indicate olefinic C-C stretching and C-O stretch in alcohols, esters, ethers, and carboxylic acids, did not change (Yu et al., 2014).

On the other hand, upon alteration, a vibration band was displaced from 3371 to 3390 cm^{-1} , indicating that the O-H stretching or H-bonded amines were replaced by N-H stretching amines. The extra shift from 652 to 697 cm^{-1} suggests that C-C bonding is present. The presence of such functional groups indicates that the precursor and surfactant are bound together, since the cationic surfactant under study is made up of carbon chain and amine (Umpuch and Jutarat, 2013). Additionally, the study of the AC4 spectra revealed a distinct band shift between 3324 and 3263 cm^{-1} , and the band's subsequent decline in strength may have been caused by the participation of the OH group. The compounds' mechanism of action could involve the O-H group forming hydrogen bonds with the active centers of dye constituents, leading to the adsorption of the dyes (adsorbates) onto the adsorbents.



Effect of Contact Time

The impact of contact time on the removal of TOC and BOD by AC 1-AC 4 from textile dyeing wastewater are given in Figures 3 to 4.

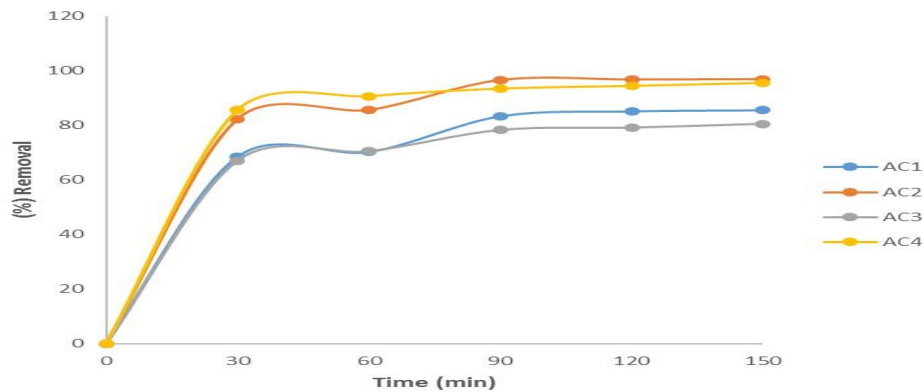


Figure 3: Effect of Contact Time on the Removal of TOCAC1-AC4 (Stirring velocity - 150 rpm, Dosage – 0.8 g, Temp – 25⁰C, pH -7)

Figure 3 shows that the influence of contact time rises with increasing contact time on the reduction of TOC from dye wastewater.

During the first 90 minutes of the process, the dye molecules adsorption onto the adsorbent rises progressively until equilibrium is reached. Because AC2 had higher surface area, pore diameter, and pore volume than AC3, the AC2 eliminated 96.60 % of the TOC during the optimal contact time (90 min) compared to 92.09 %. For AC3, the decrease percentages are 75 and 80.78%, respectively.

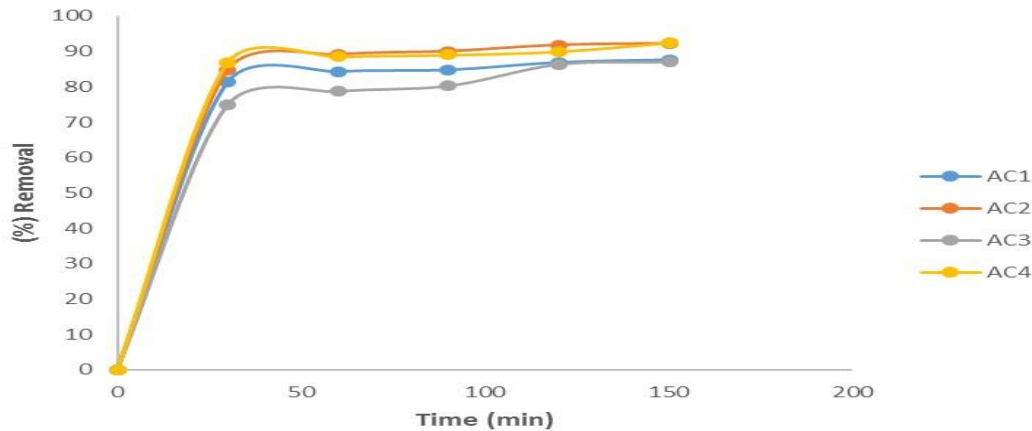


Figure 4: Effect of Contact Time on the Reduction of BOD AC1-AC4 (Stirring velocity – 150 rpm, Dosage – 0.8 g, Temp – 25⁰C, pH -7)

The effect of contact time on BOD reduction by AC 1–AC 4 was also presented in Figure 4, where equilibrium was attained for AC2 and AC1 after 120 minutes, with elimination rates of 91.77 and 86.87 %, respectively. Both AC 4 and AC 3 achieved equilibrium after 120 minutes, with similar BOD removal efficiencies of 89.98 and 86.40 %, respectively. The BOD removal efficiency increased as follows: 91.77 > 89.98 > 86.87 > 86.40. This finding typically demonstrated that the presence of active sites at the beginning of the reaction was the cause of the fast adsorption prior to equilibrium (Igwegbe et al., 2016). Due to the dye molecules diffusing into the adsorbent interior since they had previously occupied its outside, even after equilibrium was reached, the TOC and BOD removal efficiency remained unchanged (Umpunch and Juturat, 2013). Higher surface area and electrostatic interaction between the dye molecules and the activated carbon were credited with the cationic surfactant modified adsorbents' increased adsorption capabilities as compared to the unmodified activated carbons.

Effect of Dosage

The effect of adsorbent dosage on the elimination of TOC from dyeing effluent was tested by increasing dose from 0.2 to 1.0 g. The findings gotten with AC 1- AC 4 are reported in Figures 5 and 6.

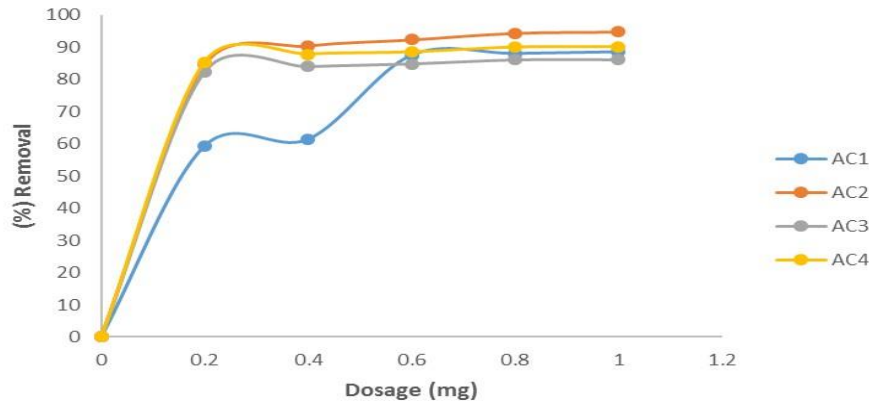


Figure 5: Effect of Dosage on the Reduction of TOCAC1-AC4 (Stirring velocity – 150 rpm, Dosage – 0.8 g, Temp – 25⁰C, pH -7)

As the adsorbent dosage increased, Figures 5 to 6 demonstrate a rise in the reduction of BOD and TOC. For both AC1 and AC2, the best dosage was found to be 0.6 g in Figure 5, with TOC removal efficiencies of 87.5 and 96.6 % at 90 minutes, respectively. It is obvious that following CTAB functionalization, the ideal removal efficiency improved from 87.5% to 96.6 %, and AC3 and AC4 were generated by applying 0.8 g, yielding removal percentages of 86.13 % and 90.01 %, respectively, with the order being AC 2>AC 4>AC 1>AC 3.

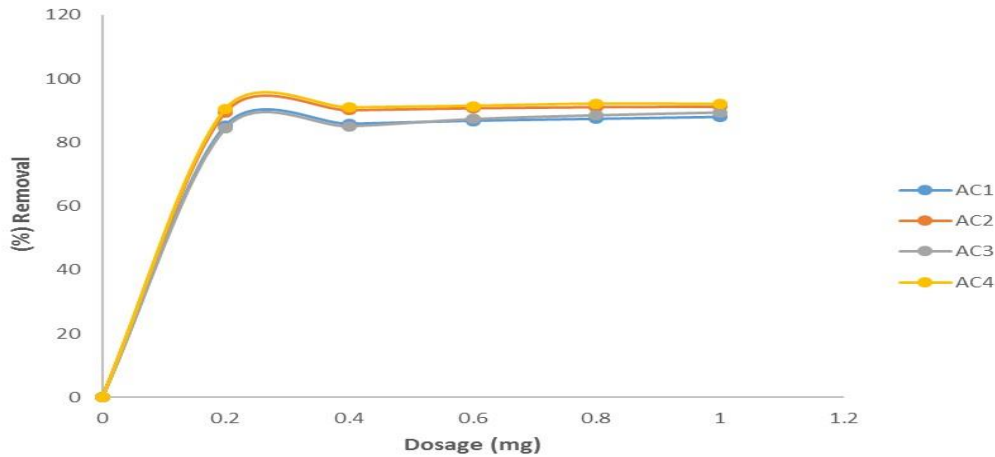


Figure 6: Effect of Dosage on the Reduction of BOD AC1-AC4 (Stirring velocity - 150 rpm, Dosage – 0.8 g, Temp – 25°C, pH -7)

Figure 6 indicates that for AC1 and AC2, an optimal dosage of 0.8 g was identified, with comparable BOD elimination efficacy of 87.35 % and 91.10 %, respectively. Similarly, for AC3 and AC4, the equivalent decreasing efficiency was 88.54 % and 92.12 %, respectively, following the same trend. Because there were more active sites accessible, the percentage reduction of TOC and BOD rose with the adsorbent dosage. This behaviour may also be explained by the influence of pore structure modifications on the adsorption of organic adsorbates onto the exterior of CTAB-modified adsorbent (Xu et al., 2017). The creation of holes, fissures, and ridges within the exfoliated adsorbent particles made the exfoliation volume of the CTAB-modified adsorbent to grow. As a consequence, the AC2 adsorbent's adsorption potential for lowering TOC and BOD in surrounding dyeing wastewater grew with increasing volume. However, the efficiency of chemisorption is larger than physical binding of dye with adsorbent, consequently improved adsorption capacity was reported for surfactant modification when compared to the unmodified adsorbent ($90.1 > 86.13$) for TOC data and ($92.12 > 88.54$) for BOD data.

Adsorption Isotherms

The concentration of the dye in the liquid phases and the dyes in the adsorbent at a certain temperature were compared to determine the equilibrium isotherm relationship. The results are presented in Tables 4 and 4.1 and were obtained using the Langmuir, Freundlich, and Tempkin isotherms to examine the parameters.



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Table 4: Langmuir, Freundlich, and Tempkin Isotherms for Activated Carbon from *Hibiscus sabdiriffa* for TOC and BOD Removal

Isotherms	TOC AC 1	TOC AC 2	BOD AC 1	BOD AC 2
Langmuir				
q_m (mg/g)	47.632	52.619	40.000	40.022
K_L (mg/g) (L/mg) ^{1/n}	0.801	0.868	0.424	0.781
R_L	0.0311	0.0332	0.0615	0.034
R^2	0.996	0.998	0.958	0.999
Freundlich				
$1/n$	0.154	0.125	0.382	0.116
K_f	32.809	34.119	12.303	26.002
R^2	0.709	0.680	0.701	0.919
Tempkin				
b_T	317.271	405.031	117.143	524.687
K_T	45.079	180.138	0.328	125.815
R^2	0.642	0.930	0.664	0.897



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Table 5: Langmuir, Freundlich, and Tempkin Isotherms for Activated Carbon from *Hibiscus esculentus* Stalks for TOC and BOD Removal

Isotherms	TOC AC 3	TOC AC 4	BOD AC 3	BOD AC 4
Langmuir				
q_m (mg/g)	35.586	36.764	40.018	42.982
K_L (mg/g) (L/mg) ^{1/n}	0.987	1.278	0.398	0.426
R_L	0.023	0.028	0.062	0.064
R^2	0.995	0.998	0.998	0.997
Freundlich				
1/n	0.257	0.527	0.514	0.106
K_f	1.192	1.536	1.168	7.295
R^2	0.958	0.738	0.726	0.864
Tempkin				
b_T	2056.077	6401.996	1607.768	7724.414
K_T	3.218	43.047	1.266	237.907
R^2	0.975	0.858	0.908	0.847

According to Tables 4 and 5, the Langmuir isotherm model was deemed to be the most closely matched model for TOC and BOD adsorption onto AC1–AC4. This is because its correlation coefficient (R^2) values were closest to 1 (in the range of 0.996 – 0.999). Furthermore, for the TOC and BOD parameters tested, separation factors (R_L) for AC1–AC4 were determined to be between 0 and 1, suggesting that the removal of TOC and BOD by the unmodified and surfactant-modified adsorbent was advantageous (Malekbala et al., 2015). The data showed that the combination of cationic surfactant had a beneficial impact on the removal of TOC and BOD, as the adsorption abilities at 90 and 120 minutes for TOC-AC2, BOD-AC2, TOC-AC4, and BOD-AC4 were found to be 53.3, 76.9, 54.0, and 75.4 mg/g, respectively. In addition to the Langmuir model (R^2) values, the Freundlich and Temkin models R^2 values were and quite near to 1. Multilayer adsorption with a non-uniform distribution of affinities was proposed by the Freundlich model in Tables 4 and 4.1 as well (Foo and Hameed, 2010). The adsorbent-adsorbate system's K_F and $1/n$ parameters,



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which provide information on adsorption favorability and heterogeneity (the lower $1/n$, the more predicted heterogeneity), were the features of the system. The surface heterogeneity and adsorption intensity ($1/n$) values from Tables 4 and 4.1, respectively, ranged from 0.1053-0.2564, at room temperature. This demonstrates that the dye's adsorption was beneficial since the values are between 0 and 1.

Adsorption Kinetics

Table 6: Pseudo First, Second, Elovich and Intra-Particle Diffusion Kinetic Models for Activated Carbon from *Hibiscus sabdiriffa* Stalk for TOC and BOD Removal

Models	TOC AC1	TOC AC2	BOD AC1	BOD AC2
Pseudo first order q_{exp}				
(mg/g)	43.41	53.31	71.01	75.41
q_{cal} (mg/g)	10.9872	13.3098	5.5835	4.9094
K_1	0.0223	0.0288	0.0181	0.0161
R^2	0.801	0.895	0.956	0.854
Pseudo second order				
q_{cal} (mg/g)	46.6571	55.7632	75.0189.	78.9452
K_2	0.0026	0.0032	0.0037	0.0038
R^2	0.997	0.998	0.998	0.998
Elovich model				
a (mg/g/min)	1.4×10^{-6}	1.04×10^{-13}	4.88×10^{-25}	1.318×10^{-25}
b (g/min)	6.5793	5.1818	3.6587	4.2472
R^2	0.437	0.642	0.758	0.828
Intra-particle diffusion model				
K_i ($mg^{-1}min^{-0.5}$)	1.013	0.962	0.771	0.914
C_i	32.423	42.812	64.112	66.594
R^2	0.928	0.965	0.885	0.895



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Table 7: Pseudo First, Second, Elovich and Intra-particle Diffusion Kinetic Models for Activated Carbon from *Hibiscus esculentus* Stalk for TOC and BOD Removal

Models	TOC AC3	TOC AC4	BOD AC3	BODAC4
Pseudo first order				
q_{exp} (mg/g)	41.91	53.81	67.38	74.11
q_{cal} (mg/g)	6.128	5.901	8.240	4.005
K_1	0.0231	0.0183	0.0273	0.0147
R^2	0.951	0.937	0.920	0.835
Pseudo second order				
q_{cal} (mg/g)	49.59	56.60	77.13	77.92
K_2	0.0016	0.0036	0.0013	0.0041
R^2	0.994	1.001	0.996	0.998
Elovich model				
a (mg/g/min)	1.51×10^{-6}	2.12×10^{-6}	1.08×10^{-14}	4.61×10^{-27}
b (g/min)	6.8572	4.0354	8.4790	3.4275
R^2	0.544	0.751	0.604	0.595
Intra-particle diffusion model				
K_i (mg ⁻¹ min ^{-0.5})	1.213	0.834	1.574	0.617
C_i	31.4851	45.2724	53.8701	69.2241
R^2	0.902	0.944	0.945	0.848

The kinetic parameter for the elimination of TOC and BOD at 25°C using unmodified and surfactant-activated carbon were presented in Tables 6 and 7. In contrast to other models, which had correlation coefficients (R^2) ranging from 0.438 to 0.966, the pseudo second-order model values were quite close to unity, between 0.995 and 1. According to this data, the kinetic model fit the pseudo second-order model, the best out of all the models examined, and the chemisorption process—which involves the exchange or sharing of electrons between activated carbons and dyes in solution played a major influence in the TOC and BOD adsorption rate (Ho and McKay, 2002). This implies that the dosage of activated carbon and the concentration of dye molecules in the effluent determine how rapidly TOC and BOD are decreased.



CONCLUSION

Hibiscus sabdariffa and *Hibiscus esculentus* adsorbents were characterized by different techniques including HRSEM, EDS and FTIR. With a dosage of 0.6 g of adsorbent, the equilibrium time to reach the optimum decrease of TOC (96.60%) for the modified activated carbon produced from *Hibiscus sabdariffa* stalks was 90 min. BOD, on the other hand, took longer time to attain equilibrium; about 120 minutes to complete 91.77% BOD elimination using surfactant *Hibiscus sabdariffa* stalk at an adsorbent dosage of 0.8 g. From the result it is clear that Langmuir isotherm gave the greatest match for the equilibrium information. All of the adsorption tests kinetic data, however, matched the pseudo-second-order model adequately, suggesting that chemisorption was the main phenomenon affecting the reaction.

Acknowledgements

This article has been completed under the mentorship of the last two authors who directed the research design and methodology.

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