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# SORPTION OF METHYLENE BLUE BY ACTIVATED CARBON PRIMED FROM SUGARCANE BAGASSE

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## ABSTRACT

The utilization of commercially activated carbon (AC) for the synthetic dye uptake even at low concentration is seen as a promising technique with high efficiency and simple operation; however, the cost of its production is too high. Thus, there is the need to focus much attention on the fabrication of AC derived from waste agricultural products. To this end, sugarcane bagasse (SB) was carefully modified via carbonization to formed AC and was subsequently deployed for the uptake of methylene blue (MB) in batch experiments. The prepared adsorbent was characterized using XRD, SEM, FT-IR and TGA. Fourier transformed infrared (FT-IR) revealed that the surface of the biomass contained –OH, –C=C-, -NH$_2$, –C≡N and C-O functional groups as the binding forces in the adsorption of MB, while the microstructure revealed porous nanocrystals morphology. XRD analysis of SB showed a pattern for cellulose type I. Isotherm study showed that equilibrium data fitted well with and governed by Freundlich model. Langmuir isotherm maximum adsorption capacities were 13.350 and 23.340 mg g$^{-1}$ for unmodified sugarcane bagasse (SB) and modified sugarcane bagasse (MSB) respectively. Information from the kinetic investigations suggested that the adsorption of MB by SB followed the pseudo first-order model, while that of the prepared activated carbon was best described by pseudo second-order model. The values of standard enthalpy and the entropy changes obtained in the temperature range of 25–55°C are 34.20 kJmol$^{-1}$ and 14.90 kJmol$^{-1}$K$^{-1}$ for unmodified SB and 65.69 kJmol$^{-1}$ and 2.23 kJmol$^{-1}$K$^{-1}$ for the primed activated carbon respectively. Thus, SB waste can be successfully utilized for the elimination of MB from polluted water.

Keywords: Sugarcane bagasse, methylene blue, sorption, kinetic, isotherms.

## INTRODUCTION

Many ways can pollute ground and surface waters. In municipal areas, the sloppy release of manufacturing wastes and effluents are among the most critical factors accountable for the poor quality of water. Most of the water bodies from these areas in developing countries like Nigeria are at the receiving end of effluents discharged from industries. Synthetic dyes are an integral part of the raw materials used in industries like cosmetics, textiles, paper, plastics, soap, food, detergents to mention but a few (Caparkaya and Cavas, 2008). Effluents from textile and other dye using industries discharge their effluents directly into the water system without proper treatment. The increase in the applications of colours and the

continuous release of dye by-products into waterways has been a significant concern for various governments due to the harmful effects (Choi et al., 20012; Kesarwani et al., 2000). The non-biodegradability, toxicity, and reduction of light penetration are some of the main problems associated with dye contaminated water (Caparkaya and Cavas, 2008). The coloration of water body is highly visible which could occur as a result of the release of even low concentration of dye molecules less than 1 ppm into water system (Oualid and Mahdi, 2007). Aquatic organisms require light to generate energy, but the coloration in water prevents the penetration of light causing an imbalance of ecosystem (Iqbal and Bhatti, 2014). There are documented reports indicating the fact that the photosynthetic activity of water body is mostly affected by the presence of dyes (Ferreira et al., 2014), while other such as the azo dyes had been reported to be

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carcinogenic and toxic which affects not only the aquatic biota but also human health (Crini, 2006).

Although, there exists different treatment methods for the elimination of wastewater among which are chemical precipitation, coagulation, ion-exchange, solvent extraction, membrane processes, filtration, sedimentation and adsorption (Caparkaya and Cavas, 2008; Choi *et al.*, 2012; Veit, 2005; Yan and Viraraghavan, 2001), the use of adsorption has been described as the cheapest and environmentally friendly method (Caparkaya and Cavas, 2008; Azhar *et al.*, 2005; Shaobin *et al.*, 2005). To this end, some agricultural waste products have been successfully used in the treatment of dye contaminated wastewater such as waste prawn (Santhi *et al.*, 2009), coffee grounds (Nakamura *et al.*, 2003), rice bran (Kesarwani *et al.*, 2000), plum kernels and bamboo (Wu *et al.*, 1999a,b). The applicability of these adsorbents is as a result of their complex nature coupled with the presence of lignin and cellulose compounds which are a good source of materials for the uptake of dyes and other contaminants from contaminated water. Another study, Shuhua *et al.* (2012) investigated the potential of tartaric acid modified wheat bran for the adsorption of methyl blue and it was observed that the tartaric acid modification enhanced its adsorption capacity. They reported further that the adsorption capacity of the tartaric acid modified wheat bran was about 1.6 times greater than that of the unmodified wheat bran. Treated and untreated activated carbon was both investigated for the elimination of methylene blue from aqueous solution (Yamin *et al.*, 2007). The results indicated that the treated activated carbon showed better removing ability towards methylene blue when compared with unmodified activated carbon. Although commercial AC is well-liked and widely used adsorbent for the treatment of contaminants, the cost of production of pure and quality activated carbon, (Shuhua *et al.*, 2012) often limit its availability to the ordinary man. The costs of preparation of activated carbon from agricultural waste products are not only cheap when compared to their commercial activated carbon counterpart but also serve as a means of waste recycling, thus adding values to agricultural wastes.

The remains of fibrous residue which is left over after the stalks are crushed for juice production is known as Sugarcane waste. The Sugarcane waste is made up of water, trace amount of soluble solids as well as fibres. Its chemical composition includes about 40-45% of cellulose, 20-30% of lignin, and 30-35% of hemicelluloses (Peng *et al.*, 2009). Report has it that of the many agricultural crop residues, SB is known to be most abundant in lignocellulosic material in tropical countries (Peng *et al.*, 2009), which is widely used in the production of alcohol and sugar. Report has it that about 280 kg of bagasse can be generated by 1 ton of sugarcane (Cerqueira *et al.*, 2007).

Sugarcane farming has been a major source of economic development in many countries like Nigeria as it is used for both human and industrial consumption. Sugarcane is widely consumed in Nigeria, while wastes generated from it are often dumped into public places thereby causing environmental pollution. The waste sugarcane bagasse is of no or little economic value and as such constitutes environmental challenges (Lavarack *et al.*, 2000). It was selected as a source of material in the fabrication of the adsorbent for the sorption of MB dye since it can be obtained in abundance in Nigeria and it is cheap when compared with the cost of purchasing AC or other inorganic materials used as adsorbent. More so, since SB has no or little important industrial value, its conversion into useful materials is desirable. In this study, wastes from sugarcane were sourced as a staring material in the fabrication of activated carbon via carbonization and employed as a sorbent for the sorption of MB via batch adsorption process under different experimental conditions such as MB concentration, time of equilibration, temperature, SB dosage and solution pH which were used to evaluate the adsorption capacity of SB. Characterization of the prepared sorbent was achieved by TGA/DTA, particle size analyzer, SEM, FT-IR and XRD techniques. The kinetics, isothermal and thermodynamic studies were investigated.

## MATERIALS AND METHODS

### Dye Solution Preparation
Methylene blue (MB) (MG, Fluka) was used for the preparation of the adsorbate concentrations without any further purification. The stock solution of the dye solution was made by dissolving 1 g of MB in 1 $dm^3$ of distilled water in a volumetric flask. Different concentrations were later prepared from this stock solution.

### Activated Carbon Preparation
The remaining waste after sugar juice has been extracted from sugarcane was obtained from Papa Lantoro in Ewekoro in Ogun State, Nigeria. The raw sample was treated with hot distilled water, oven dried at $110^oC$ for 6 hours, pulverized and it was labeled as 'unmodified sugarcane bagasse' (SB). The physical modification form of the bagasse was done by calcination of the unmodified SB in a Murflace Furnace at a calcination temperature of $800^oC$ for 4 hrs in three stages. The sample was kept in the airtight bag before analysis, and it was referred to as modified sugarcane bagasse (MSB).

### Adsorption Studies
Briefly, 0.2 g of the bagasse was weighed and 50 mL of the adsorbate solution was added in a 250 mL Erlenmeyer flask and placed on a temperature controlled orbital shaker and equilibrated for 80 mins at a speed of 150 rpm. The value of solution pH was adjusted using 0.1 M HCl or NaOH solutions. The content was removed, filtered

and the filtrate analyzed with the aid of UV-Visible Spectrophotometer. The sorbed amount of the MB in (mg/g) as well as the efficiency of MB removal was estimated as follows:

$$\text{Amount of dye removed} = \frac{C_o - C_e}{m} \times V \quad (1)$$

$$\text{Efficiency of dye removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

With $C_o$ (mg/L) and $C_e$ (mg/g) denoting the concentration of MB at beginning and final stage of the reaction respectively, $V$ stands for the volume of the MB taken in L, while the mass of the sugarcane bagasse is denoted as $m$ in g. The schematic diagram for the adsorbent preparation and the adsorption process is as shown in Figure 1.
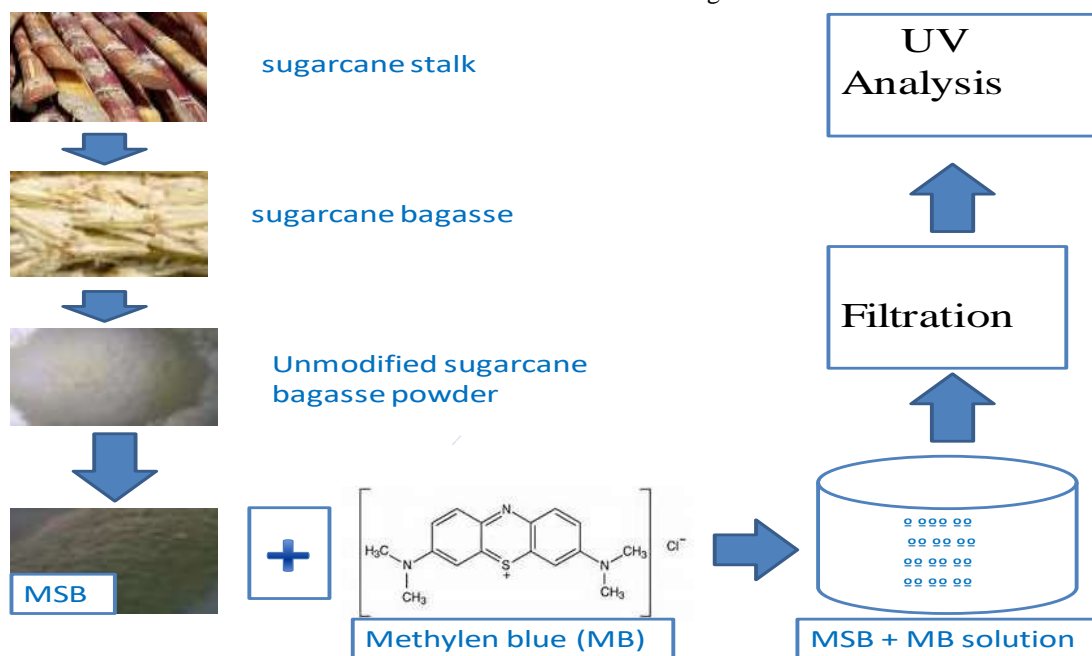


Fig. 1. Schematic representation of adsorbent formation for MB adsorption.

## Characterization Techniques

The micrometre scale particle size of SB was achieved with a Nanotrac equipped with a software of Microtrac FLEX 10.5.2. About 0.2 g of SB was dispersed in 100 mL beaker made up of 50 mL of Millipore water and sonicated for 10 mins so as to reduce the degree of agglomeration of the particle. Information regarding the morphology of SB powder was achieved by using a Hitachi (Japan) S-3000H electron microscope at an accelerating voltage of 15 kV which was performed using carbon tape. The absorption bands of adsorbent (sugarcane bagasse) and adsorbate (MB) were investigated by FT-IR, using the KBr method in which pellet were homogenized by grinding of powder mixture of KBr and MSB, hard-pressed using SHIMADZU MHP-1 hand press. The measurements were recorded in IR range of 400-4000 cm$^{-1}$ with 45 scan, which was done with the aid of SHIMADZU 8400S FT-IR instrument. In order to determine the crystal structure and phase stability of the bagasse sample, X-ray diffraction of SB powder were recorded using Bruker D8 Advance X-ray diffractometer with Cu Kα (λ = 1.5405 A°) radiation at diffraction angle of 2θ between 10 - 45°. Thermal behaviour of MSB was analyzed using SDT Q600 V8.3 Build 101simultaneous DSC-TGA analyzer. Zeta potential analysis was performed using 0.1 g of the bagasse in 20 mL of MB. Adjustment of pH was achieved with 0.1 M HCl or NaOH solution to desired value. A Zetasizer Nano ZS instrument (Malvern, UK) was used for the analysis of the zeta potentials. The percentage abundance of the elemental composition of SB before and after modifications was evaluated using A G. Vario EL analyzer (Germany). A Quantachrome NOVA 2200C (USA) was utilized to compute the pore volume, pore size, and surface area of the prepared sorbent.

## RESULTS AND DISCUSSION

### Characterization

The elemental and physical description of sugarcane bagasse is as listed in Table 1.

Table 1. Chemical Composition and Surface Characterization of SB.

| Parameters | | Unmodified sugarcane bagasse (SB) | Modified sugarcane bagasse (MSB) |
|---|---|---|---|
| Elemental Analysis | %C | 38.40 | 49.30 |
| | %N | 2.10 | 3.20 |
| | %H | 4.70 | 6.80 |
| | %O | 58.40 | 40.70 |
| N$_2$ gas Adsorption Analysis | Surface area (m$^2$/g) | 74.30 | 136.56 |
| | Average pore Size (nm) | 3.41 | 5.63 |
| | Pore volume (cm$^2$/g) | 0.245 | 0.331 |
| Zetal potential | pH$_{ZPC}$ | 4.68 | 5.80 |

It was observed that the elemental composition demonstrated the following distributions: C(38.40, 49.30 %), N(2.10, 3.20%), O(58.40, 40.20 %) and H(4.70, 6.80 %) for SB and MSB, respectively. The percentage abundance of carbon was found to have increased after physical modification which is due to the combustion of the organic contents present in the raw biomass. The pore size, pore volume, and surface area were obtained to be (3.41, 5.63 nm), (0.245, 0.331 cm$^2$/g), and (73.4, 136.56 m$^2$/g) for SB and MSB respectively. It was observed that the physical modification via carbonization enhanced the surface area of the bagasse. The micro structure of SB is as shown in Figure 2. The scanning electron microscope (SEM) of the structure revealed porous nanocrystals morphology, with covered surface after MB adsorption. Changes in the morphology after MB absorption may be associated to the buildup of MB particles onto the empty sites on the sorbent surface. Figure 2c depicts the particle size analysis of modified SB which was found to be in the range of 0.7-0.8 μm. The FT-IR analysis of methylene blue, modified SB before the adsorption of MB and after its uptake is as presented in Figure 3.
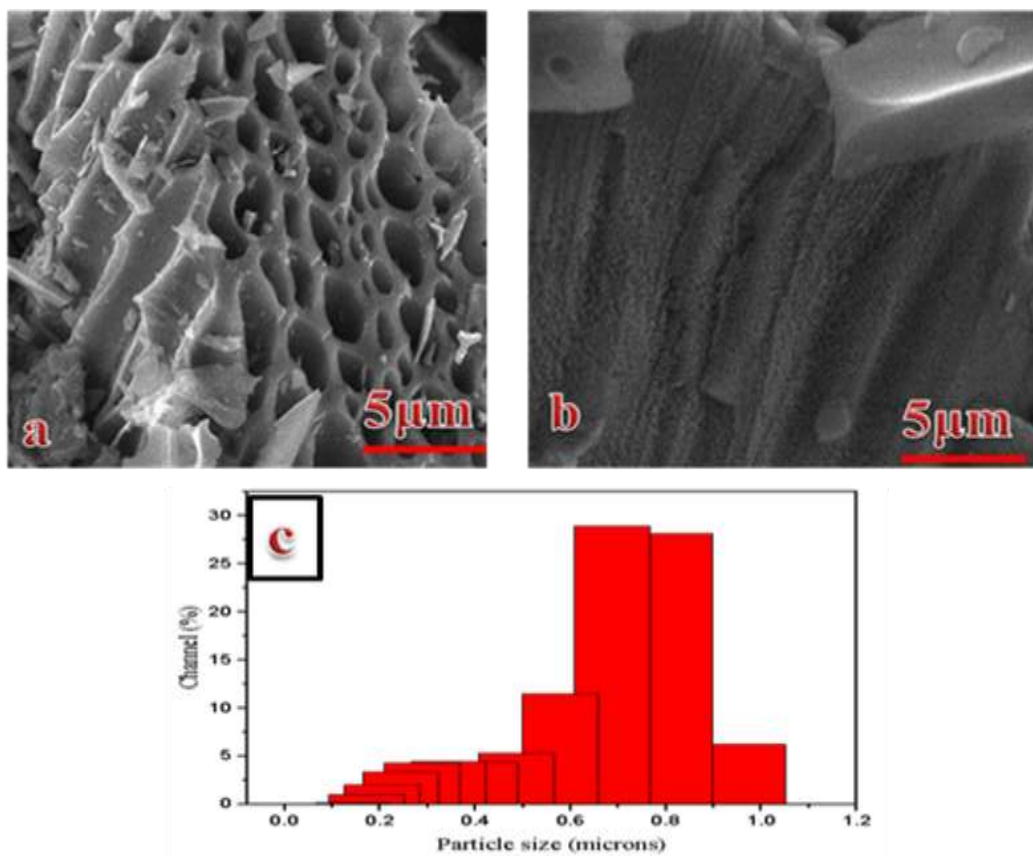


Fig. 2. Secondary electron image of MSB before (a) and after (b) adsorption of MB and (c) particle size of MSB before adsorption.
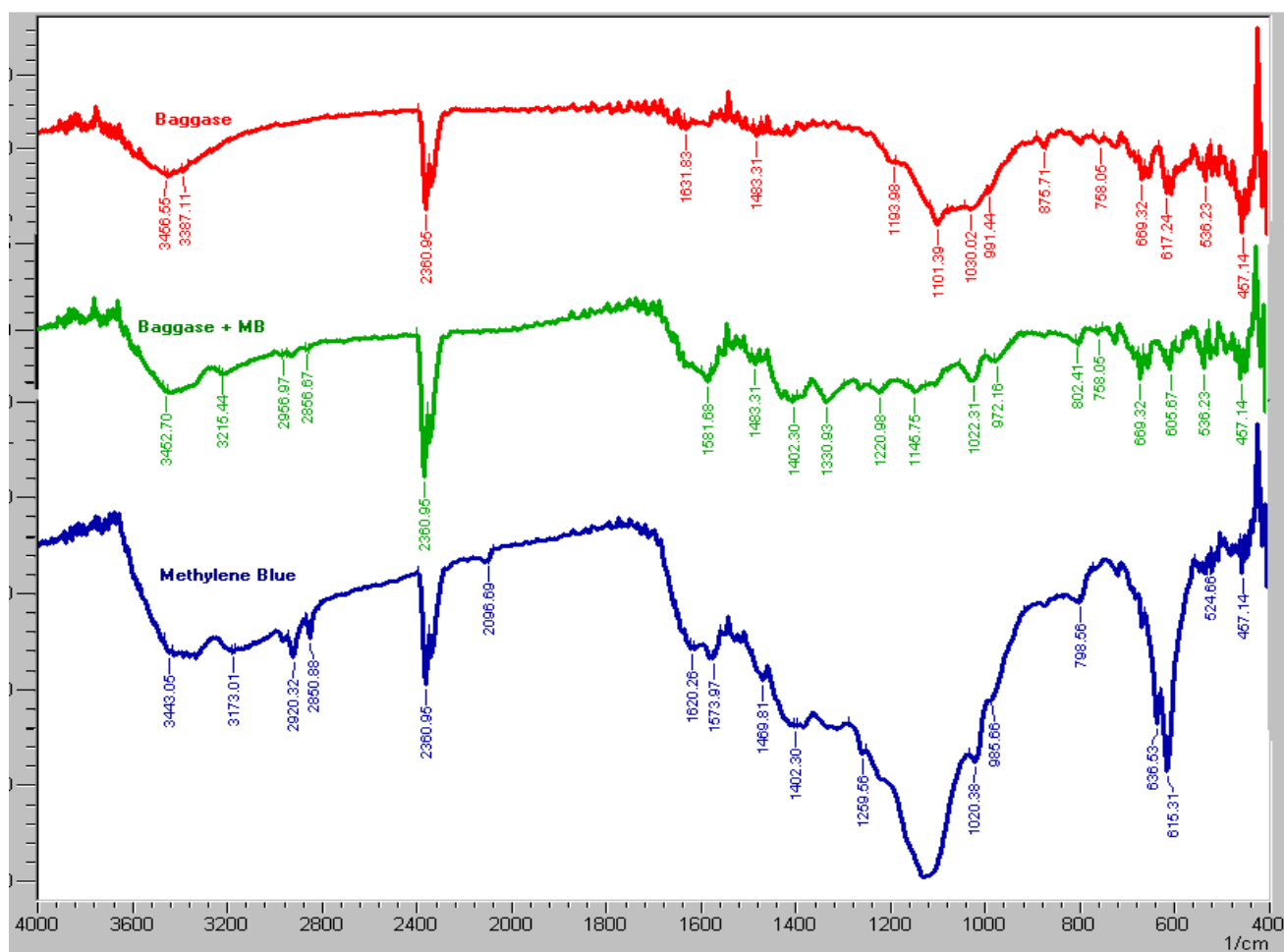
Fig. 3. FT-IR spectra of MSB, MSB +MB and methylene blue alone.

The FT-IR investigation revealed the existence and participation of negatively charged functional groups such as carbonyl, amino, hydroxyl and cyano on the adsorbent surface of the carbonized SB. The broad bands at 3466 and 3389 $cm^{-1}$ were assigned to –OH and –NH stretch respectively, while those peak at 1631-1697 $cm^{-1}$ were assigned to C=C and C=O stretch, while the band at 1485 $cm^{-1}$ was attributed to the symmetric stretching in $CH_2$. The band between 1146 to 1193 $cm^{-1}$ corresponds to C-O stretch, while that between 1022-1030 $cm^{-1}$ was allotted to –CN vibration. Bands at 800-400 $cm^{-1}$ are attributed to C-H in aromatic rings (Ofudje *et al.*, 2014). Reductions in peaks at 3466, 3389, 1631, 1193, 1030, 991 and 876 $cm^{-1}$ in the raw SB as against 3452, 3215, 1581, 1146, 1022, 972 and 802 $cm^{-1}$ in the SB loaded with MB was observed which suggests the contribution of –OH, -$NH_2$, -CN, C-O, and C=C functional groups in the sorption of MB. XRD patterns of SB showed a pattern for cellulose type I with main peaks at about $2\theta = 16.1°$, $18.2°$ and $23.2°$ as shown

in Figure 4. The appearance of the diffraction peak at $2\theta = 23.2°$ correspond to (002) crystallographic planes for cellulose (Xianhong *et al.*, 2015; Paulo *et al.*, 2011). The only small decrease in peaks intensities was observed after MB uptake by the biomass. The distributions of TGA analysis of raw sugarcane bagasse are displayed in Figure 5. The first weight loss which occurred at 94.53 °C is associated with water of vaporization due to heat in the sample (Paulo *et al.*, 2011). The second weight loss was observed at 445.33°C is due to the breaking down of the cellulose components in the sample. The final weight loss which is due to lignin degradation was observed at 717.23°C. Earlier studies Yang *et al.* (2007) and Chen *et al.* (2012) reported that the temperatures at which hemicellulose, cellulose, and lignin will break down is in the range of 200–315, 315–400, and 160–900°C, respectively. The residual weight of the SB biomass after physical activation was 82.01 %.
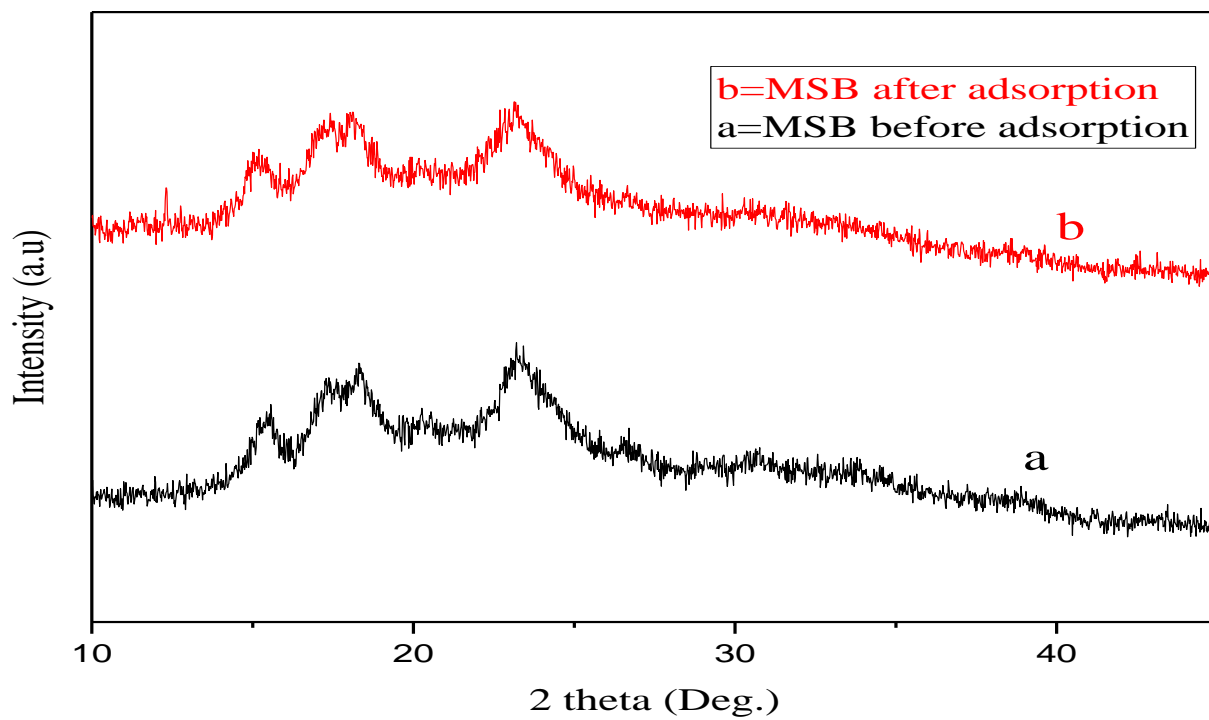
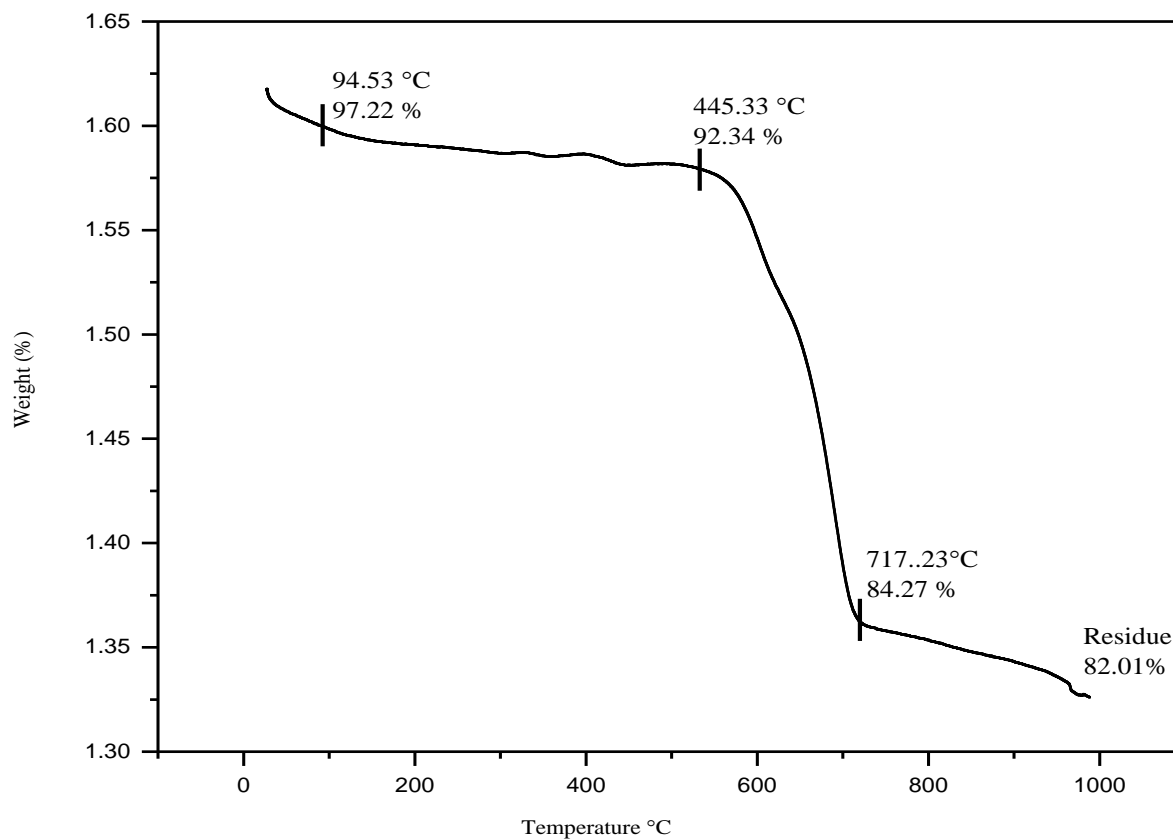Fig. 4. XRD patterns of SB and MSB +MB.



Fig. 5. TGA plot of SB powder.

**Effect of initial concentrations of MB and contact time**

An investigation into the role of equilibration time on the sorption capacity of the prepared adsorbent at different concentrations of MB is as shown in Figure 6. When unmodified SB was used, the sorbed amount of MB onto the surface of SB increased from 0.62 to 2.46 mg/g at 25 mg/L and from 5.0 to 14.18 mg/g at 150 mg/L of MB when the contact time was adjusted from 5 to 80 mins. Upon modification of the biomass, the sorbed amount of MB increased enormously from 1.45 to 11.27 mg/g at 25 mg/L and from 3.92 to 23.13 mg/g at 150 mg/L when the equilibration time was raised from 5 to 80 mins. Equilibrium was reached at a contact time of 80 mins and after this time, there was no further appreciable increase in the amount of MB adsorbed. Thus, equilibration time of 80 mins was picked for subsequent studies. The sorption of MB by activated SB was fast at the early period of agitation time and thereafter, slows down as the

adsorption process approached equilibrium stage. This is as a result of the fact that at the early stage of the reaction, there exist on the surface of the biomass unoccupied sites, but as the reaction proceeds, these vacant sites become filled up with MB which slows down the adsorption process. Similar reports had also been reported in the literature (Oualid and Mahdi, 2007; Yamin *et al.*, 2007; Pooja *et al.*, 2012). According to Ibrahim *et al.* (2014) equilibrium time obtained depends on the nature of the dyes and also on the type of sorbent. An increased in the concentration of the dye solution provides a formidable strength to force the mass transfer from the aqueous and solid phase and as such, there is an increased in the sorbed amount of MB with pollutant concentrations (Lijuan and Jian, 2013). The results agree well with the findings of Oualid and Mahdi (2007), Saiful *et al.* (2005) and Adeogun *et al.* (2013).
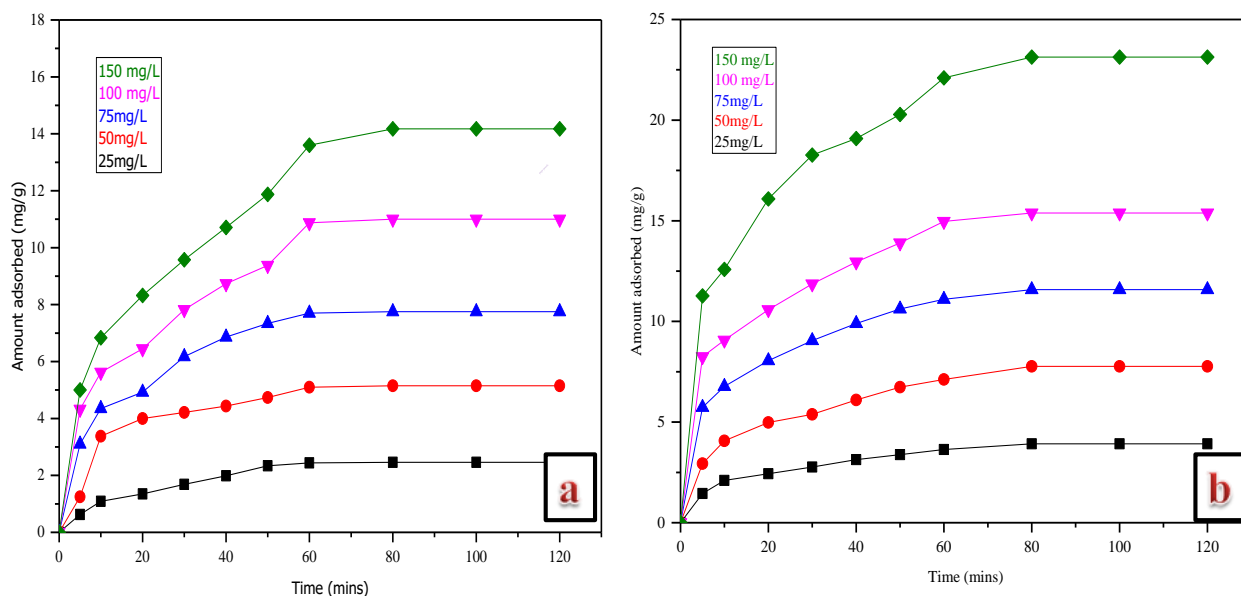


Fig. 6. Effect of contact time on the adsorption of MB at different initial concentration of MB at pH of 6, biomass concentration of 0.2 g, and temperature of 50 °C (a) before and (b) after modification.

**Effect of biomass concentration**

Different biomass concentrations (0.1, 0.15, 0.2, 0.25 and 0.3 g) were selected to evaluate the role of biomass concentration as presented in Figure 7a. The percentage uptake of MB increases with the adsorbent concentration. It was noted that the sorption percentage increased from 46.7 to 76.8% when unmodified SB was used and from 60.93 to 88.9% when the modified biomass was utilized on raising the concentration of the adsorbent from 0.1 to 0.2 g and above this no further appreciable adsorption was observed and a biomass dosage of 0.2 g was chosen for succeeding experiments. The sharp adsorption of the contaminant observed at the early period of the reaction

could be due to the availability of sorption sites owning to large surface area provided by on the surface of the adsorbent, however at increase concentrations of the adsorbent to solute concentration, there is a rapid uptake of MB onto the biomass surface which resulted in reduced concentration of the solute solution when there is lower concentration of adsorbent to solute ratio (Oualid and Mahdi, 2007). As more and more of MB is sorbed onto the active surface of the adsorbent, a point will be reached when saturation will occur and subsequently reduced the sorption efficiency as observed at higher adsorbent concentration (Ofudje *et al.*, 2013).
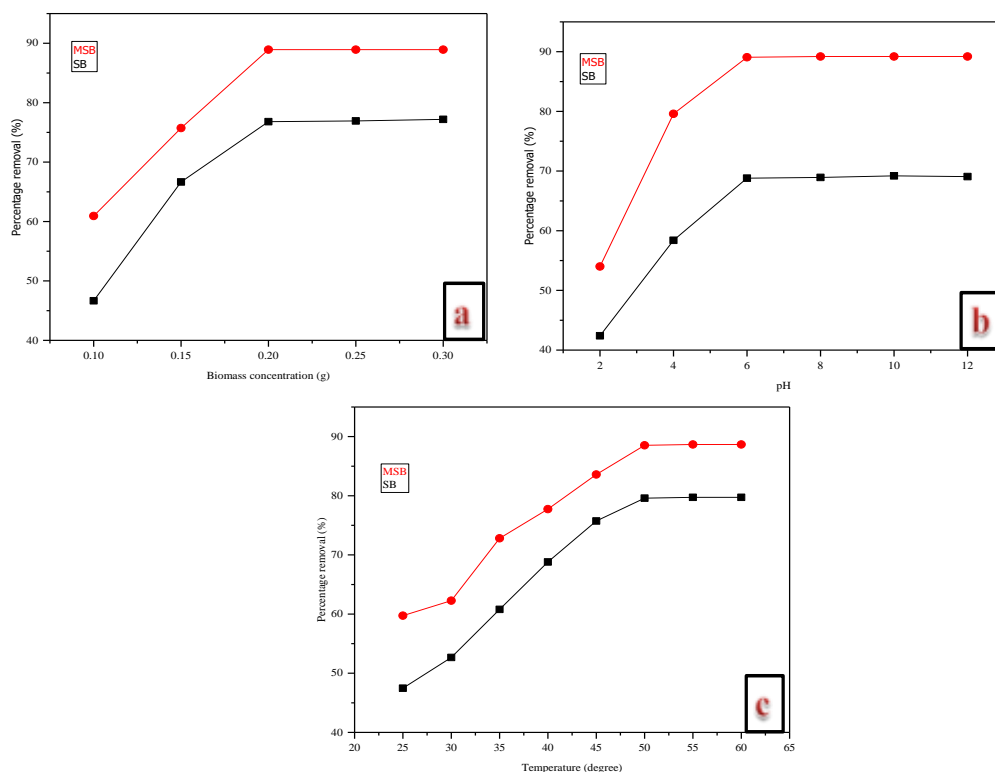
Fig. 7. Effect of (a) biomass concentration, (b) solution pH and (c) temperature on adsorption of MB.

### Effect of solution pH

The behaviour of the prepared adsorbent coupled with that of the adsorbate varies with the pH of the medium and this makes hydrogen ion concentration an essential parameter while investigating adsorption reactions occurring in aqueous solution medium involving the uptake of adsorbate and in this case, methylene blue. Several studies were done to assess the role of varying the pH of the reacting medium (2.0 to 12) as indicated in Figure 7b. When unmodified SB was tested, adsorption efficiency increased from 42.4 to 68.9% on raising the pH of the reacting medium from 2.0 to 6. Similarly, upon modification of SB, the sorption efficiency increases from 54.0 to 89.2% when the pH of the solution was elevated from 2.0 to 6. Utmost uptake of MB was attained in acidic region of pH of 6.0 after which there was no much increase in the amount of MB adsorbed. In order to properly comprehend the significance of pH on the adsorption mechanism, the determination of the point of zero charges also known as the zeta potential ($pH_{ZPC}$) becomes imperative. From Table 1, the zeta potential of SB and MSB were found to be 4.68 and 5.80 respectively. Above these values, the surface of the biomass is expected to be negatively charged, while below it, the surface will be positively charged (Li and Bai, 2005). Since MB is a cationic dye, an increase in the pH of the reacting medium will enhance the adsorption process onto the surface of the bagasse due to an increase in the electrostatic attraction between the biomass surface which

was revealed by FTIR analysis to be negatively charged and the positively charged methylene blue dye solution (Ofudje *et al.*, 2015). At low pH, there is competition between protons (from the aqueous solution) and the vacant sites of SB on the surface of the biomass which resulted in the reduced adsorption of MB, however, with a rise in the pH of the reacting medium, the active sites of SB becomes protonated, leading to reduction in the competitions between proton and MB for the vacant sites which enhanced the sorption of molecules of MB on the adsorbent surface due to due to electrostatic attractions (Yamin and Faujan, 2007; Lijuan and Jian, 2013).

### Effect of temperature

The significance of temperature on the adsorption process of MB by both unmodified and modified SB is presented in Figure 7c which revealed the sorption of MB by SB was a function of temperature as there was an increase in sorption efficiency with temperature. Utmost sorption capacity was accomplished at a temperature of 50 C; while no further considerable increase in the sorption capacity was noticed at a temperature above 50°C. The rise in the adsorption efficiency with temperature infers that the sorption of MB by SB is endothermic (Ofudje *et al.*, 2015). This can be explained on the following assumptions. First, on increasing the temperature, the molecules of MB acquires more kinetic energy which enhances the mobility of the molecules of the dye onto the adsorbent surface which improved the adsorption ability

of the biomass. Secondly, a raise in temperature will cause swelling effect within the structure of the sorbent to occur and as such, enhanced the penetration of the dye particles onto the surface of the biomass across the boundary layer (Kumar *et al.*, 2005; Yongze and Guilan, 2012). The findings from this present study are in agreement with the observations of Oualid and Mahdi (2007) and that of Turgay *et al.* (2012).

## Kinetics Studies

The kinetic study is significant in understanding and predicting the mechanism involved during the adsorbate and adsorbent interaction. Three kinetic models were employed which are Largergren pseudo-first-order, intraparticle diffusion kinetic, and Ho's pseudo-second-order models. The non-linear expression of the first-order is given as (Langergen and Svenska, 1898):

$$Q_t = Q_e(1 - e^{-k_1 t}) \qquad (3)$$

With $Q_e$ and $Q_t$ (mg/g) representing the adsorbed amount of MB at equilibrium and at time $t$, while $k_1$ (mins$^{-1}$) stands for the rate constants of pseudo-first-order. The values of first-order constants were obtained from the least square fit of $Q_t$ versus $t$ under diverse solutes concentrations as presented in Figure 8a and 9a, while the physical parameters are as listed in Tables 2 and 3 for SB and MSB, respectively.

The non-linear representation of the Ho's pseudo-second-order is given as follows (Ho and Mckay, 1999):

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \qquad (4)$$

Where the rate constant of pseudo-second order is represented as $k_2$ in gmg$^{-1}$min$^{-1}$, $Q_e$ and $Q_t$ are as previously defined. The physical parameters of the second-order model were estimated from the plot of the least square fit of $Q_t$ versus $t$ at different solutes concentrations and the results are as represented in Figure 8b and 9b, while the values are as presented in Tables 2 and 3 for SB and MSB, respectively.

Intraparticle diffusion kinetic equation can be represented as (Mall *et al.*, 2005):

$$Q_t = k_p t^{0.5} + I \qquad (5)$$

Where $k_p$ is defined as the rate constant of intraparticle diffusion model in mgg$^{-1}$min$^{-0.5}$ and $I$ gives an idea about the boundary layer thickness (Mall *et al.*, 2005). Plots of the intraparticle is as shown in Figure 8c and 9c, while the values of the constants obtained are as listed in Tables 2 and 3 for SB and MSB, respectively.
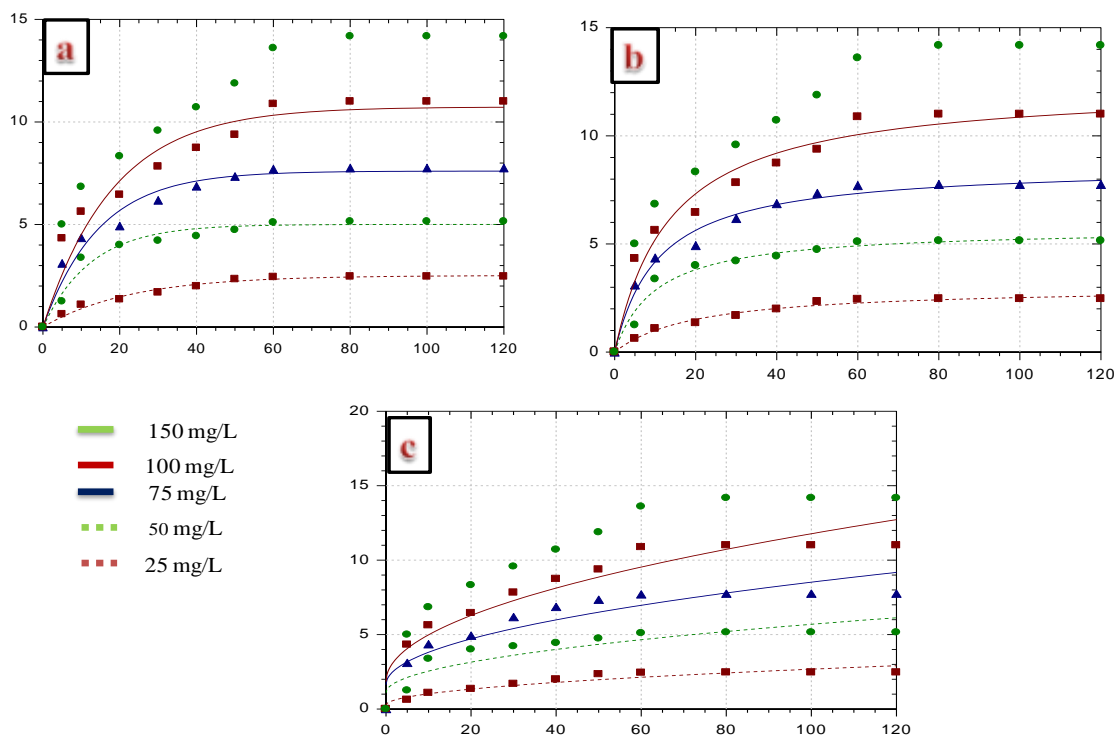


Fig. 8. Plots of (a) Pseudo-first order, (b) pseudo-second order and (c) intraparticle kinetic models for the sorption of MB by SB and MSB at varied initial dye concentrations of 150 mg/L and pH of 6.0 and temperature of 50°C by unmodified biomass.
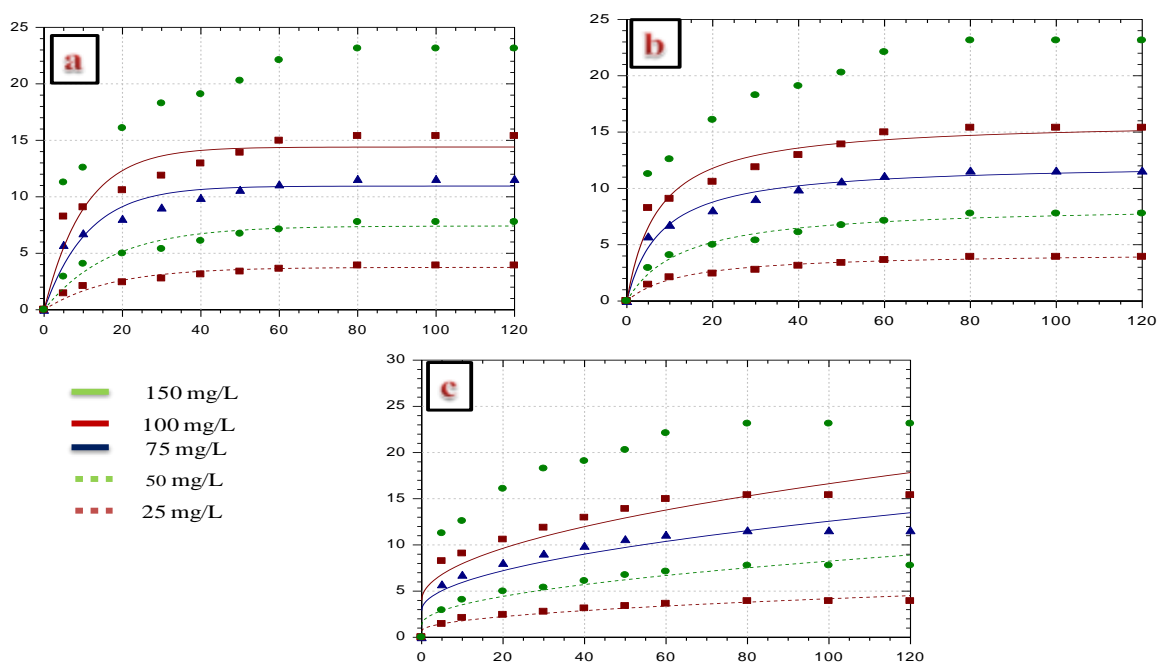
Fig. 9. Plots of (a) Pseudo-first order, (b) pseudo-second order and (c) intraparticle kinetic models for the sorption of MB by SB and MSB at varied initial dye concentrations of 150 mg/L and pH of 6.0 and temperature of 50°C by modified biomass.

Table 2. Kinetic parameters of the adsorption of MB by SB powder.

| | | $C_o$ (mg/L) | 25 | 50 | 75 | 100 | 150 |
|---|---|---|---|---|---|---|---|
| | Pseudo First order | $Q_e$(exp) (mg/g) | 2.460 | 5.150 | 7.780 | 11.000 | 14.180 |
| | | $Q_e$(cal)(mg/g) | 2.500 | 5.000 | 7.600 | 10.730 | 13.870 |
| | | $k_1$ (mins$^{-1}$) | 0.044 | 0.080 | 0.069 | 0.055 | 0.049 |
| | | $R^2$ | 0.983 | 0.970 | 0.967 | 0.942 | 0.950 |
| | | % SSE | 0.007 | 0.009 | 0.006 | 0.008 | 0.007 |
| | Pseudo Second order | $Q_e$(cal) | 3.024 | 5.735 | 8.644 | 12.354 | 16.211 |
| | | $k_2$ (g/mg/min) | 0.015 | 0.018 | 0.012 | 0.006 | 0.004 |
| | | $R^2$ | 0.982 | 0.972 | 0.985 | 0.970 | 0.975 |
| | | % SSE | 0.076 | 0.038 | 0.038 | 0.041 | 0.048 |
| Intra particle diffusion | | $K_{id}$ (mg/g/mins$^{1/2}$) | 0.242 | 0.461 | 0.689 | 0.993 | 1.302 |
| | | C (mg/g) | 0.253 | 1.093 | 1.635 | 1.845 | 2.003 |
| | | $R^2$ | 0.984 | 0.971 | 0.980 | 0.987 | 0.990 |

Table 3. Kinetic parameters of the adsorption of MB by modified SB powder.

| | | $C_o$ (mg/L) | 25 | 50 | 75 | 100 | 150 |
|---|---|---|---|---|---|---|---|
| | Pseudo First order | $Q_e$(exp) (mg/g) | 3.930 | 7.770 | 11.580 | 15.380 | 23.130 |
| | | $Q_e$(cal)(mg/g) | 4.756 | 8.417 | 10.949 | 14.405 | 21.793 |
| | | $k_1$ (mins$^{-1}$) | 0.059 | 0.059 | 0.089 | 0.097 | 0.084 |
| | | $R^2$ | 0.950 | 0.946 | 0.939 | 0.915 | 0.937 |
| | | % SSE | 0.070 | 0.028 | 0.018 | 0.021 | 0.019 |
| | Pseudo Second order | $Q_e$(cal) | 4.319 | 7.529 | 11.241 | 15.027 | 24.499 |
| | | $k_2$ (g/mg/min) | 0.018 | 0.009 | 0.010 | 0.009 | 0.005 |
| | | $R^2$ | 0.982 | 0.980 | 0.981 | 0.967 | 0.979 |
| | | % SSE | 0.033 | 0.010 | 0.010 | 0.008 | 0.020 |
| Intra particle diffusion | | $K_{id}$ (mg/g/mins$^{1/2}$) | 0.679 | 1.347 | 2.887 | 3.979 | 5.424 |
| | | C (mg/g) | 0.345 | 0.689 | 0.967 | 1.265 | 1.949 |
| | | $R^2$ | 0.919 | 0.921 | 0.959 | 0.952 | 0.973 |

## Fitness of Kinetics Models

In order to determine the best fit from the various kinetics models used, the sum of error squares (SEE, %) given by (Adeogun *et al.*, 2012):

$$\% \quad SSE \quad = \quad \sqrt{\frac{((Q_{(exp)} - Q_{(Cal)})/Q_{exp})^2}{N-1}} \times 100$$ (6)

Given that N stands for different data points. Smaller values of %SSE and higher values of $R^2$, the better the fitting.

Taking the values of $R^2$ as basis for comparison, the Pseudo second-order kinetic model showed better fit than what was observed for Pseudo first-order kinetic model for the unmodified biomass. However, the experimental adsorption capacity ($q_{eexp}$.) of the Pseudo first-order kinetic model demostrated closeness with the calculated adsorption capacity ($q_{ecal}$) than those of second-order model as listed in Table 2. Furthermore, smaller values of % SSE analysis from the first-order kinetic model, inferred that the sorption of MB onto the surface of unmodified SB can be better expressed using Pseudo-first-order model, which implies that the rate determining step is physisorption. However, when modified SB was used, the kinetic data were best explained by Pseudo second-order model; suggesting chemisorptions through a chemical exchange of electrons or a chemical reaction between adsorbent and adsorbate (Mohammadi *et al.*, 2014). This was arrived at following the agreement between the $q_{eexp}$. and those of the $q_{ecal}$ of the second-order kinetic model which was also corroborated by the smaller values observed from % SSE analysis (see Table 3). This finding differs from that of Osuntoki *et al.* (2013). Besides, the linear fitting results of the MB adsorption process conformed to the intraparticle diffusion equation as inferred from the values of $R^2$ in the range of 0.990 to 0.971 and 0.919 to 0.973 for unmodified SB and modified SB respectively. Thus the adsorption mechanism of dye onto the adsorbent could be described by three stages which includes: (1) boundary film transfer onto the biomass surface, (2) mass movement from the exterior of the adsorbent surface to the pores in the interior portion of the adsorbent via intraparticle diffusion or diffusion mechanism and (3) adsorbate molecules diffusion to vacant sites through robust surface diffusion process or by pore diffusion mechanism (Lijuan and Jian, 2013; Witek-Krowiak, 2011).

## Equilibrium Studies

Equilibrium information from the sorption of MB by sugarcane bagasse were evaluated by Freundlich, Langmuir, and Temkin iostherms. The Langmuir isotherm in its non-linear form can be given as (Langmuir, 1916):

$$Q_e = \frac{Q_o b C_e}{1 + b C_e}$$ (7)

Where the sorbed amount of MB at equilibrium in mg/g is given as $Q_e$, the equilibrium concentration of MB in mg/L is represented as $C_e$. To find out whether the uptake of MB by biomass is favourable or not, the Langmuir separation factor $R_L$ was estimated using:

$$R_L = \frac{1}{(1 + b C_o)}$$ (8)

With $b$ standing for the Langmuir constant which was used to predict the favourability of the adsorption process. If $R_L$ is $> 1$, the process is unfavourable but if it lies between 0 and 1; it is favourable.

The Freundlich isotherm in its non-linear form can be described as (Freundlich, 1906):

$$Q_{eq} = K_F C_e^{1/n}$$ (9)

Where the adsorption capacity is represented by $K_F$, while *n* stands for the intensity of the adsorption process. Tempkin adsorption model presumes that the sorption coverage reduces linearly with the heat of adsorption and is due to the relationship between the adsorbate and adsorbent and can be represented by equation 10 below (Temkin and Pyzhev, 1940):

$$Q_e = \frac{RT}{b_T} In a_T C_e$$ (10)

While the linear representation of the Tempkin model is given as:

$$q_e = \frac{RT}{bT} In \alpha_T + \frac{RT}{bT} In C_e$$ (11)

Where the Tempkin constant relating to binding energy is given as $\alpha_T$ (L/g), $b_T$ (Jmol$^{-1}$) represents the heat of adsorption, the ideal molar gas constant in Jmol$^{-1}$K$^{-1}$ is represented as *R* and T is the temperature in Kelvin. The plots of $Q_e$ versus $C_e$ were used to estimate the various parameters as shown in Figure 10 and 11 respectively, while their values are as presented in Table 4. The correlation coefficient ($R^2$) of Langmuir, Freundlich and Tempkin isotherms are $R^2$ = 0.948, 0.993, 0.961 and 0.986, 0.989, 0.898 for unmodified and modified biomass respectively. Thus, based on the information obtained fron the evaluation of correlation coefficient ($R^2$), Freundlich isotherm gave best values of fitting. This suggests that the sorption of MB onto the cell walls of the bagasse assume different surface energies as proposed by Freundlich model. Since 1/n < 1, indicates that MB was successfully adsorbed onto SB and MSB surface (Dajana *et al.*, 2012). Langmuir isotherm parameters revealed that the monolayer maximum adsorption capacities of SB and MSB for MB adsorption are 13.450 and 23.340 mg g$^{-1}$

respectively. Also, the values of $R_L$ in this study were found to be less than unity, indicating that the sorption of MB by the biomasses is favourable. Furthermore, the correlation coefficients for Tempkin isotherm model were equally close to unity, suggesting the applicability of this isotherm to explain the adsorption behaviour of the prepared adsorbent. Utmost capacity of adsorption as obtained in this work showed that the sugarcane bagasse adsorbent competes favorably with others as documented in the literature as shown in Table 5.
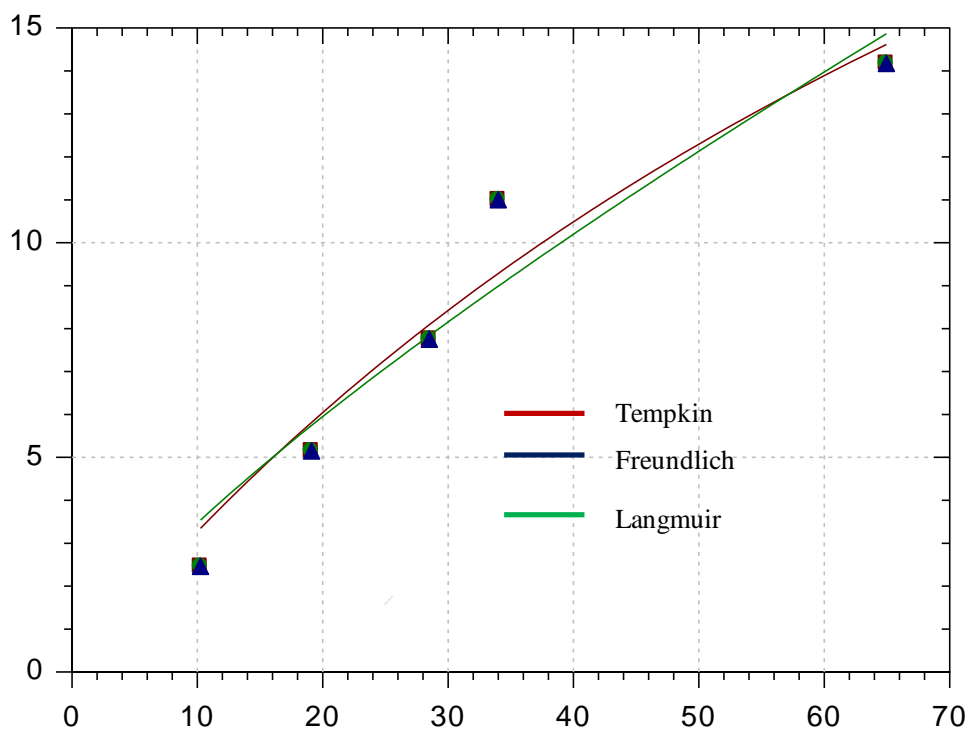


Fig. 10. Plots of Langmuir, Freundlich and Tempkin adsorption isotherms for the adsorption of MB by SB at initial dye concentration of 150 mg/L, pH of 6 and temperature of 50°C.
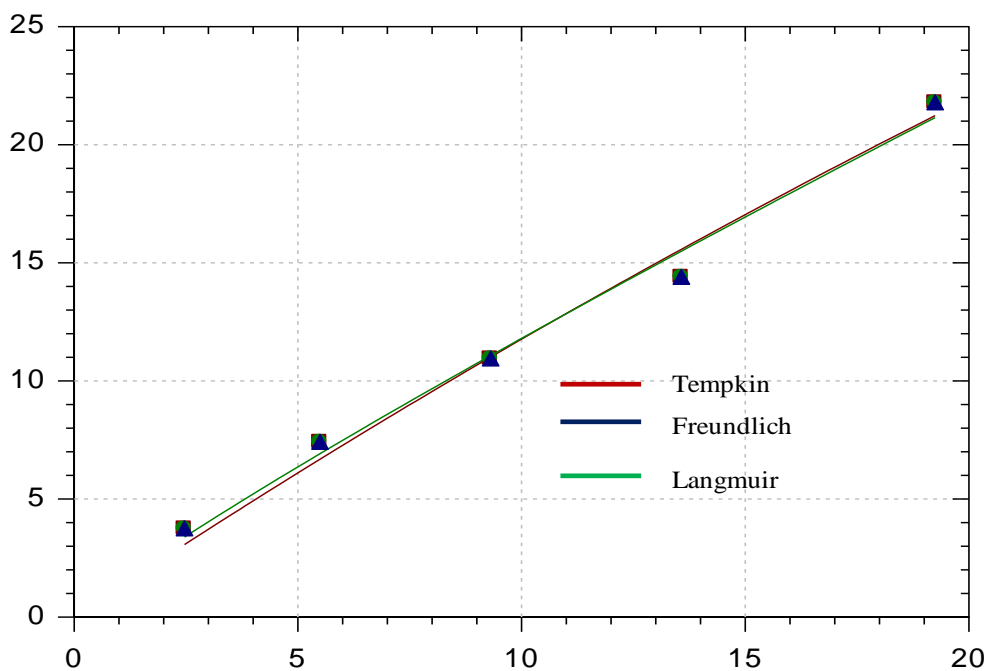


Fig. 11. Plots of Langmuir, Freundlich and Tempkin adsorption isotherms for the adsorption of MB by MSB at initial dye concentration of 150 mg/L, pH of 6 and temperature of 50°C.

Table 4. Physical Isotherm Parameters of MB dye Adsorption on SB and MSB.

| | | | SB | MSB |
|---|---|---|---|---|
| Langmuir | | $Q_{max}$ (mg/g) | 13.350 | 23.340 |
| | | $R_L$ | 0.009 | 0.008 |
| | | b (mg/L) | 12.234 | 7.423 |
| | | $R^2$ | 0.948 | 0.986 |
| | Freundlich | $K_F$ (mg/g)(mg/L)$^{-1/2}$ | 0.579 | 1.515 |
| | | n | 1.286 | 1.122 |
| | | $R^2$ | 0.993 | 0.989 |
| | Temkin | $\alpha_T$ (L/g) | 0.130 | 0.524 |
| | | $b_T$ (J/mol) | 373.970 | 304.807 |
| | | $R^2$ | 0.961 | 0.898 |

**Impact of Carbonization on the Adsorption Property of Sugarcane Bagasse**

Carbonization weakens the chemically combined bonds, leaving behind micropores and caverns when released (Pei-Hsing *et al.*, 2014). It has been reported that such materials which are carbon-based are thermally and chemical stable which demonstrate excellent adsorption ability (Namasivayam and Kadirvelu, 1999). Pei-Hsing *et al.* (2014) reported that since the specific surface area enhances the adsorption potentials of an adsorbent, an improvement in the surface area of the adsorbent symbolizes a rise in the number of empty active sites on the surface of biomass. As shown in Table 1, the pore volume and surface area of the bagasse improved after carbonization. This study revealed that the sorption potential of the carbonized adsorbent was superior when compared with unmodified biomass due to higher porous contents as well as surface area. In one of our previous work, it was demonstrated that carbonized sugarcane showed better adsorption properties when compared with raw and chemically modified biomass for Cr(VI) ions uptake from aqueous medium (Ofudje *et al.*, 2014). It's assumed that the hydrophobic nature of many activated carbon products renders them as excellent sorbent materials for the elimination of organic pollutants from wastewater (O'Connel *et al.*, 2008).

Table 5. Comparison of various maximum adsorption capacities by different biomaterials for the adsorption of methylene blue.

| Biomaterials | Activating Agent | Maximum Adsorption capacity (mg/g) | References |
|---|---|---|---|
| Soybean oil cake | Chemical-KOH | 278 | Turgay *et al.* [36] |
| Coffee beans press cake | Physical | 14.9 | Nunes *et al.* [48] |
| Sunflower oil cake | Chemical-$H_2SO_4$ | 16.4 | Karagoz *et al.* [49] |
| Shea cake | Chemical-$H_3PO_4$ | 32.27 | Ibrahim *et al.* [27] |
| Cotton cake | Chemical-$H_3PO_4$ | 32.33 | Ibrahim *et al.* [27] |
| Crofton weed stalk | - | 28 | Lijuan and Jian, [28] |
| Sugarcane baggase | Physical | 14.177 | This study |

Table 6. Physical parameters of the thermodynamic study of the adsorption of MB by SB.

| Temperature (K) | Unmodified SB | | | | Modified SB | | | |
|---|---|---|---|---|---|---|---|---|
| | $K_c$ | $\Delta G$ (kJmol$^{-1}$) | $\Delta H$ (kJmol$^{-1}$) | $\Delta S$ (kJmol$^{-1}$) | $K_c$ | $\Delta G$ (kJmol$^{-1}$) | $\Delta H$ (kJmol$^{-1}$) | $\Delta S$ (kJmol$^{-1}$) |
| 298 | 5.72 | -4405.95 | | | 1.21 | -472.28 | | |
| 303 | 4.33 | -691.97 | | | 1.28 | -621.88 | | |
| 308 | 3.57 | -3258.67 | 34.20 | 14.90 | 1.37 | -806.14 | 65.69 | 2.23 |
| 313 | 2.48 | -2363.54 | | | 1.65 | -1303.16 | | |
| 323 | 1.88 | -1695.23 | | | 1.62 | -1296.14 | | |

**Thermodynamic Investigations**

The enthalpy changes (ΔH), entropy change (ΔS) and free energy change (ΔG) during the sorption process were evaluated and presented in Table 6. Thermodynamic analysis was performed using the Van't Hoff equation which can be described as (Adeogun *et al*., 2013):

$$InK_C = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (12)$$

Where the equilibrium constant ($K_C$) described the relationship between the equilibrium concentration ($C_e$) in mg/L and the amount adsorbed ($q_e$) in mg/g, the molar gas constant is given as *R*. The equilibrium constant is given as (Adeogun *et al*., 2013):

$$K_C = \frac{q_e}{C_e} \qquad (13)$$

*ΔH* and *ΔS* were estimated using the linear plots of *InK_C* against the inverse of temperature which is represented in Figure 12, while that of *ΔG* were evaluated from the relation:

$$\Delta G = -RTInK_C \qquad (14)$$

The feasibility and spontaneity of the uptake of MB by the prepared adsorbent was informed by the negative values of free energy change (ΔG) obtained. The negative value of (ΔG) rises with temperature, suggesting the fact that more MB was sorbed onto the biomass surface at the higher temperature. The values of enthalpy and entropy changes in the temperature range of 25–55 °C were 34.20 kJmol$^{-1}$ and 14.90 kJmol$^{-1}$K$^{-1}$ for unmodified SB and 65.69 kJmol$^{-1}$ and 2.23 kJmol$^{-1}$K$^{-1}$ for modified SB respectively. Positive value of ΔH indicates endothermic process of the adsorption of MB by the prepared AC (Ünal *et al*., 2013). Furthermore, the positive value of ΔS reveals an increase in the randomness of the adsorption medium interface and solid-solution during the course of reaction.
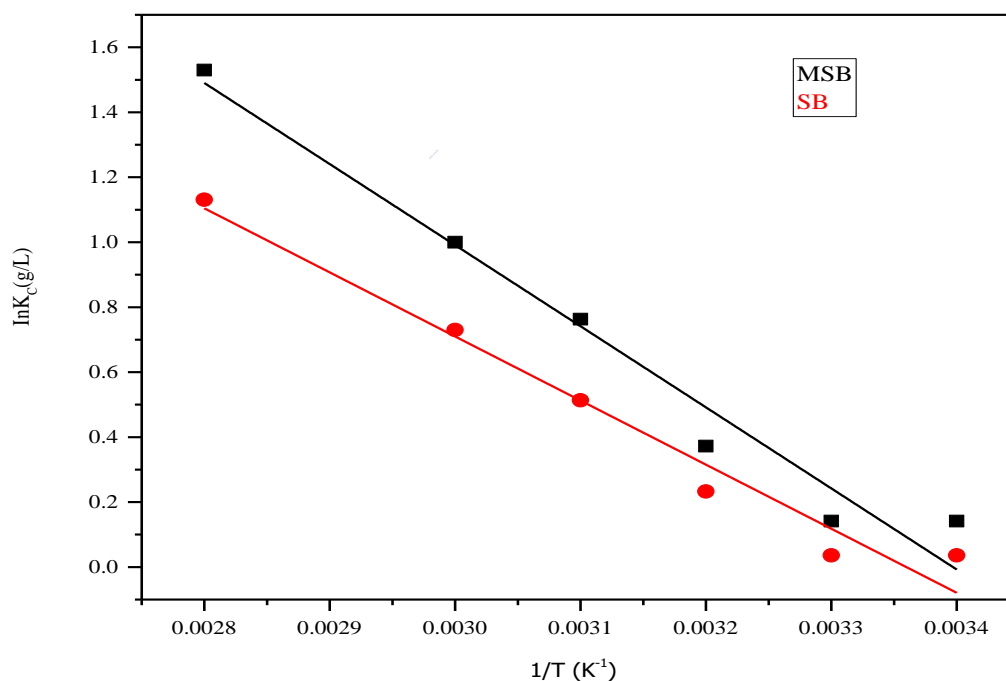


Fig. 12. Plots of *InKc* against 1/T for the adsorption of MB by SB and MSB.

**Desorption Study**

The desorption of methylene blue dye from the adsorbent surface was carried out by the treatment of the adsobate-loaded adsorbent with 0.5M aqueous solution of acetic acid under continuous stirring for 120 mins at a speed of 150 rpm. The content was filtered and the filtrate was analyzed for adsorbate content. The desorption percentage was estimated using the following equation:

$$\%d_e = \frac{Cd_{de}}{Cd_{ad}} \times 100 \qquad (15)$$

Where $d_e$ is desorption, $Cd_{de}$ and $Cd_{ad}$ are the amount of methylene blue dye desorbed and adsorbed in mg/g respectively. The feasibility of the synthesized adsorbent for possible regeneration was evaluated and the results are as presented in Figure 13. The percentages desorption of MB from unmodified SB and thermally modified SB was observed to have decreased from 72.3 to 51.3% and from 82.3 to 64.7%, respectively as the number of reuse of the adsorbent increases. This suggests the reusability of the adsorbent and that acetic acid can be used to extract the various pollutants from the exhausted biomass.
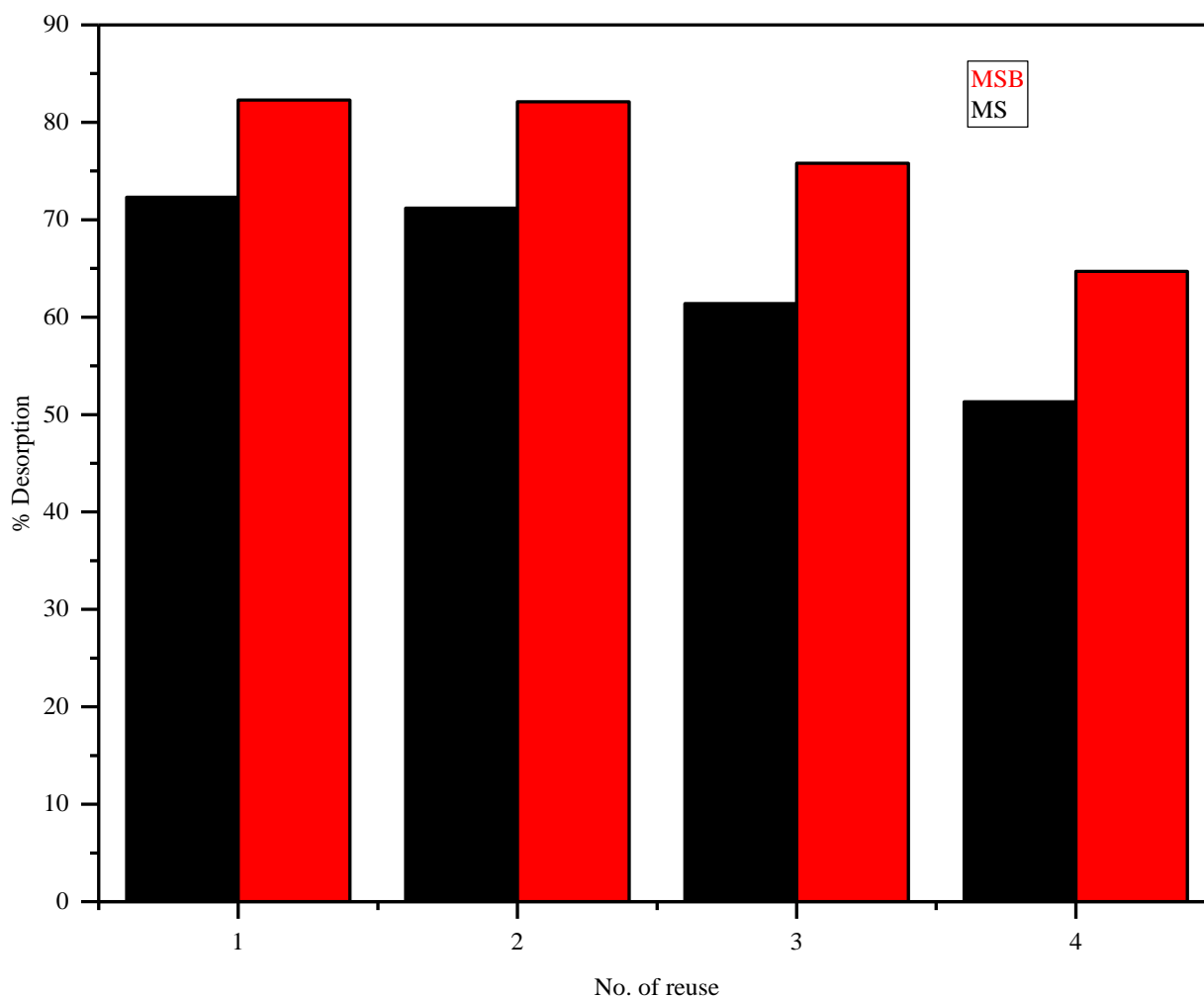
Fig. 13. Recycling efficiency of SB and MSB for the desorption of MB.

## CONCLUSION

The use of activated carbon was primed from waste agricultural by-products of sugarcane bagasse via carbonization and characterized using different analytical techniques such as FTIR, XRD, SEM and TGA. The adsorption potential of the as prepared adsorbent was investigated for the uptake of methylene blue (MB) dye under various conditions among which are equilibration time, pH, initial concentration of MB, temperature and biomass concentration. Adsorption kinetics for the unmodified adsorbent followed the Pseudo first-order model; while that of the modified adsorbent obeyed the Pseudo second-order model. Freundlich, Langmuir, and Tempkin isotherms were used to explain the equilibrium data. The monolayer sorption capacity of the Langmuir isotherm was found to be 13.350 mg/g for SB and 23.340 mg/g for MSB respectively. Thermodynamic properties such as free energy change, enthalpy change and entropy change were equally investigated. Owning to the fact that

sugarcane bagasse is a waste agricultural product with little or no economic value, its application as a sorbent for the treatment of wastewater will not only serve as source of starting material for the preparation of activated carbon but also, as a way of resolving the environmental issues with sugarcane bagasse wastes.

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