

Kinetic, Isothermal, and Thermodynamic Studies of the Biosorption of Methylene Blue from Synthetic Wastewater using Cow Hooves

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ABSTRACT

Aims: To investigate the feasibility and the kinetic of using cow hooves (CH) as a low-cost adsorbent for the removal of methylene blue (MB) from synthetic wastewater.

Place and Duration of Study: Chemistry Laboratory, Afe Babalola University, Ado-Ekiti, Nigeria, from October 2012 to January 2013.

Methodology: This study was conducted through batch process. The influence of initial pH, contact time, CH dosage and temperature on the adsorption property of CH was investigated using pH ranging from 2–11, contact time of 5–180 minutes, biomass dosage of 0.15–1.0 g and temperature of 298–318 K. The isothermal studies were carried out by using MB concentration ranging from 10–125 mgL⁻¹ at 298 and 308 K and the experimental data obtained were analysed and modelled using Langmuir and Freundlich isotherm models.

Results: Our results indicated that a time of 1hour 30 minutes was required for equilibrium to be attained. The pH for maximum removal of MB was 11. The isotherm data were better fitted by Freundlich model. The kinetics modelling of the experimental data agreed perfectly with the pseudo-second-order model suggesting that chemisorption was the rate determining step. The values of the thermodynamic parameters (ΔG^0 , ΔH^0 and ΔS^0) revealed the adsorption process to be spontaneous, feasible and endothermic.

Conclusion: Cow hoof could be a promising low-cost adsorbent for the removal of methylene blue from wastewater and this could be best achieved at high MB pH and within a period of one and half hours.

Keywords: Adsorption isotherm, cow hooves, methylene blue, wastewater

1. INTRODUCTION

A pure sample of water is said to be colourless. The moment water is coloured its purity and suitability to sustain healthy life is doubtful. Colours can be imparted to water bodies through oil spillage, untreated wastewater from chemical, paint and dye producing industries, etc. Dyes are used extensively in many industries such as textiles, paper, rubber, plastics, cosmetics and food, to colour their products [1]. These dyes are left in the industrial wastes and consequently discharged into the water bodies. Dyes, even in low concentrations, are visually detected [2] in water. Colour is the first contaminant to be recognized in wastewater.

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28 The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is
29 highly visible and undesirable [2]. It has been pointed out that over 100,000 commercial dyes
30 with rough estimated annual production rate of 7×10^5 - 1×10^6 tonnes exist in the world [3]
31 and 10–20% of the dyes are lost during manufacturing and dyeing processes [3]. This
32 implies that great amount of dyes is released into the environment annually.

33 The presence of dyes in the aquatic environment is of great concern because of their
34 adverse effects on human's health and the imbalance created on the ecosystem [4]. Many of
35 these dyes have mutagenic, carcinogenic and teratogenic effects either when inhaled or
36 when in contact with the skin [5, 6]. Also, photosynthetic activity and growth of bacteria are
37 hampered as a result of coloured effluents acquired by water bodies [7, 8, 9].

38 Therefore, the need to remove dyes from wastewater before being emptied into the
39 environment becomes extremely important. The conventional methods employed for dye
40 removal from industrial effluents include: precipitation, oxidation, membrane processes,
41 coagulation and flotation and ion exchange [8]. But most of these methods are associated
42 with inherent limitations such as high running cost, generation of secondary waste,
43 incomplete/ inefficient dye removal. Adsorption techniques have proved to be an effective
44 and attractive process for the removal of non-biodegradable pollutants (including dyes) from
45 wastewater [9, 10]. Most commercial systems use activated carbon as adsorbent to remove
46 dyes in wastewater because of its excellent adsorption ability. But its widespread use is
47 limited due to high costs of manufacturing and regeneration. Many low cost adsorbents,
48 including natural materials, biosorbents, and waste materials from industry and agriculture,
49 have been proposed by several authors [11]. MB is a thiazine (cationic) dye, which is most
50 commonly used for colouring paper, dyeing cottons, wools, etc. Several reports have been
51 published on the use of low-cost biomaterials for the removal of methylene blue from
52 aqueous solution. These include rejected tea [12], rice husk [13], spent cotton seed husk
53 [14], *streptomyces rimosus* [15], chaff [16] sewage sludges [17], rose wood sawdust [18] and
54 *Spirodela polyrrhiza* [19]. Most of these biomaterials earlier published on biosorption of MB
55 are of plant origin. This is one of the reasons that necessitated the use of cow hooves in this
56 study. Besides this CH is made up of insoluble protein called keratin [20] which contains
57 some functional groups such as amino and carboxyl, which may likely enhance biosorption
58 processes.

59 In Nigeria, hills of cow hoofs, horns and bones in many abattoirs have become an eyesore
60 and are environmentally unfriendly due to their non-biodegradation. Many a times, the
61 environment is got rid of this junk by burning. But burning itself generates gases which
62 contribute to the depletion of the ozone layer.

63 It is therefore necessary to find a way of turning this waste into a useful material. Though
64 report has it that keratin extracted from cow hooves has been exploited in making a special
65 fire extinguishing foam used by airport fire and rescue teams across the UK [21]. The
66 present study was conducted to investigate the possible utilization of powdered cow hooves
67 as adsorbent for the removal of MB from aqueous solution as another way of putting cow
68 hooves into a significant use.

69 2. MATERIALS AND METHODS

70

71 2.1 Adsorbent and Methylene Blue (MB) Solution

72 The cow hooves were obtained from an abattoir along Ekiti State University Road Ado-Ekiti,
73 Nigeria. The hooves were thoroughly washed with distilled water and sun dried for a month.

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After drying, the hooves were washed again with distilled water, dried in an oven, ground and sieved using sieve of mesh size 425 μm . A stock solution containing 1000 mg/L of MB was prepared by dissolving 1.0 g of analytical grade MB in distilled water. Standard solutions of different concentrations as might be required were prepared (by dilution) from this stock solution.

2.2 Biosorption Studies

The adsorption experiments were carried out by batch process. 0.25 g of cow hoof powder was placed in Erlenmeyer flasks with 100 mL MB solution of desired concentration. The mixture was equilibrated for a desired period of time at 120 rpm using a thermostatic water bath shaker. The mixture of the biosorbent and the solution was centrifuged after expiration of the agitation time and the concentration of MB present in the liquid phase (supernatant) was determined spectrophotometrically using UV/VIS spectrophotometer model 752. The absorbance of the colour was measured at 661nm where the maximum absorption peak exists. Calibration curve of absorbance versus concentration of the dye solution was plotted. The amount of MB adsorbed per unit mass of biosorbent was determined according to the following equation:

$$q_e = \frac{(C_o - C_f)V}{m} \quad (1)$$

Where, m is the mass of adsorbent (g), V is the volume of the solution (L), C_o is the initial concentration of MB (mgL^{-1}), C_f is the final MB concentration in the liquid phase (mgL^{-1}) and q is the amount of MB adsorbed. The percentage MB removal (%R), was calculated using the following expression:

$$\%R = \frac{(C_o - (C_f)) \times 100}{C_o} \quad (2)$$

2.3 Experimental Conditions

The effect of pH on the sorption of MB was studied by measuring 150 mL of 25 mgL^{-1} MB solution into 250 mL beakers. The pH of the solution in each beaker was adjusted by adding dilute HCl or dilute NaOH. The pH range used was between pH 2 and pH 11. Then, 100 mL of these solutions was taken into properly corked 250 mL Erlenmeyer flasks and agitated with 0.25 g of CH at 298 K. The pH of maximum adsorption was used for other experiments. The effect of contact time on the adsorption process was also conducted through batch studies. This was done at different contact times ranging from 5-180 minutes with initial MB concentration of 25 mgL^{-1} , and biosorbent mass of 0.25 g in 100 mL solution, at 298 K. Experiments to determine the effect of sorbent mass were carried out using 100 mL of 25 mgL^{-1} of methylene blue. The sorbent mass was varied from 0.15- 1.0 g and the flasks were agitated for 90 minutes. After equilibration, the final concentration of MB was determined and the percentage of MB adsorbed was calculated.

2.4 Equilibrium Studies

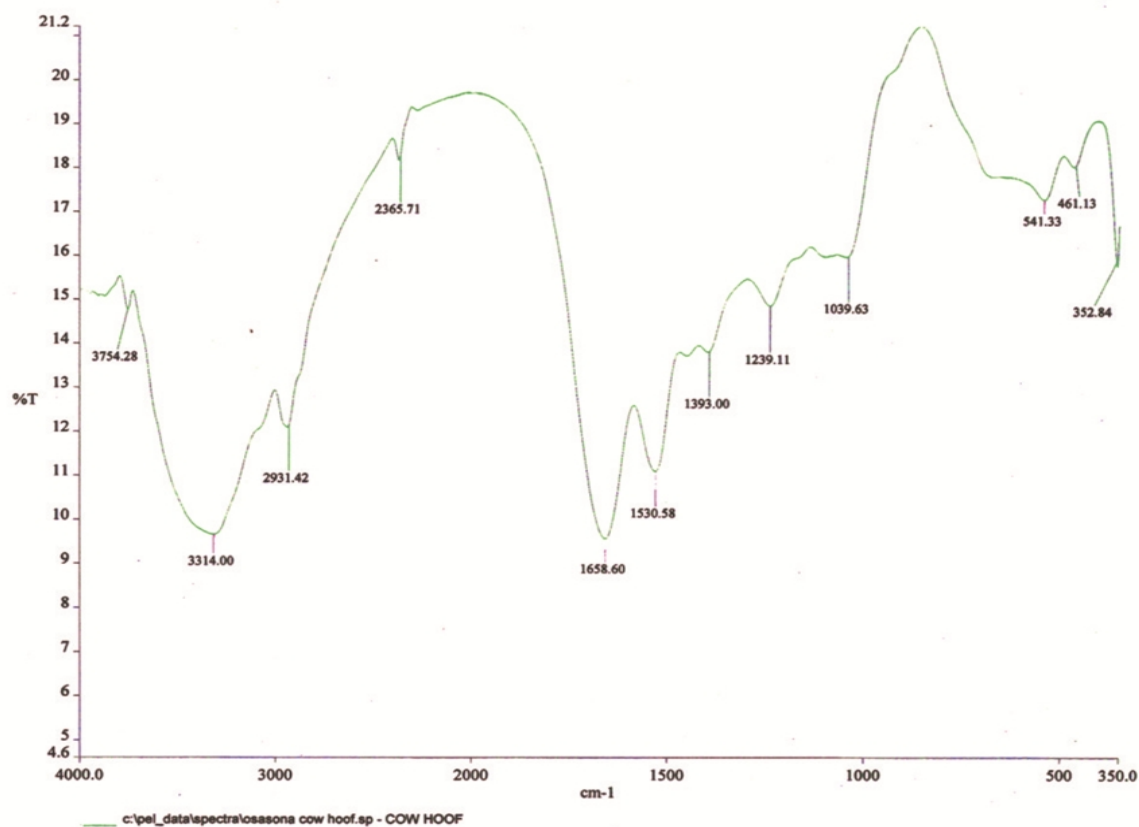
Equilibrium studies were conducted by contacting fixed amount of CH (0.25 g) with 100 mL of MB solution of different initial MB concentrations ranging from 10-125 mgL^{-1} at two

different temperatures of 298 and 308 K. The samples were then centrifuged and analysed as described earlier.

3. RESULTS AND DISCUSSION

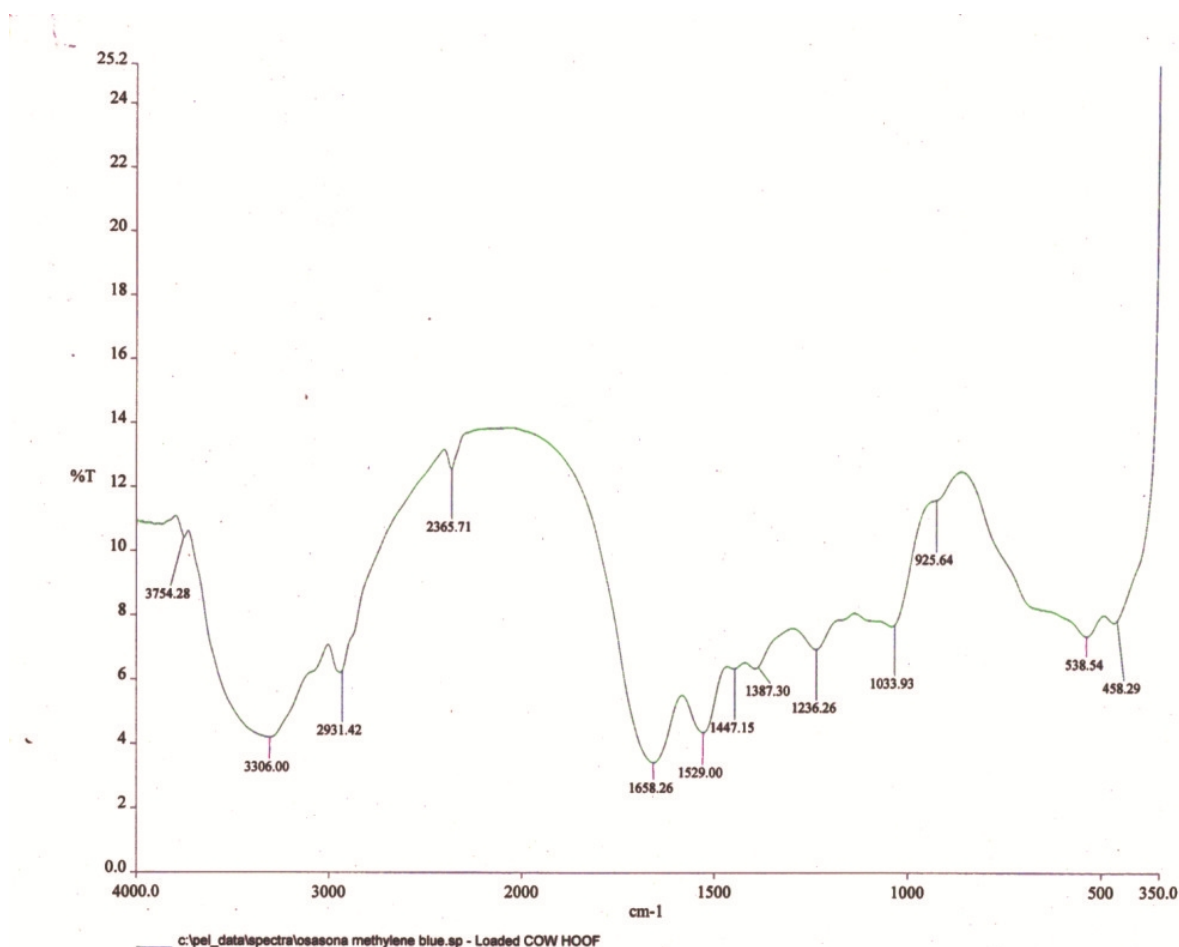
3.1 IR Spectra of CH Surface

The IR spectra of the unloaded and MB loaded CH were taken to ascertain the possible involvement of the functional groups on the CH surface in the sorption of MB. The broad band at 3314 cm^{-1} is attributed to --OH stretching vibration while the band at 2931.42 cm^{-1} and 2365.71 cm^{-1} can be assigned to the --CH and --SH stretching vibrations respectively. The peaks at 1658.6 cm^{-1} , 1530.58 cm^{-1} and 1393 cm^{-1} may be attributed C=O stretching, --NH bending and --CN vibrations of amides respectively. The bands at 1239.11 cm^{-1} and 1039.63 cm^{-1} can be linked to C--O stretching. Figure 1 reveals that some new bands appeared, some retained and some were shifted after MB sorption. The bands at 3314 , 1658.6 , 1530.58 , 1393 , 1239.11 and 1039.63 cm^{-1} were shifted to 3306 , 1658.26 , 1529 , 1387.30 , 1236.26 , 1033.93 cm^{-1} after MB biosorption. This is an indication that --OH , --C=O , --CO and --NH group could be involved in the adsorption of MB onto CH.



(a)

132



133

134 (b)

135 Figure 1: IR spectra of (a) unloaded CH and (b) MB loaded CH.

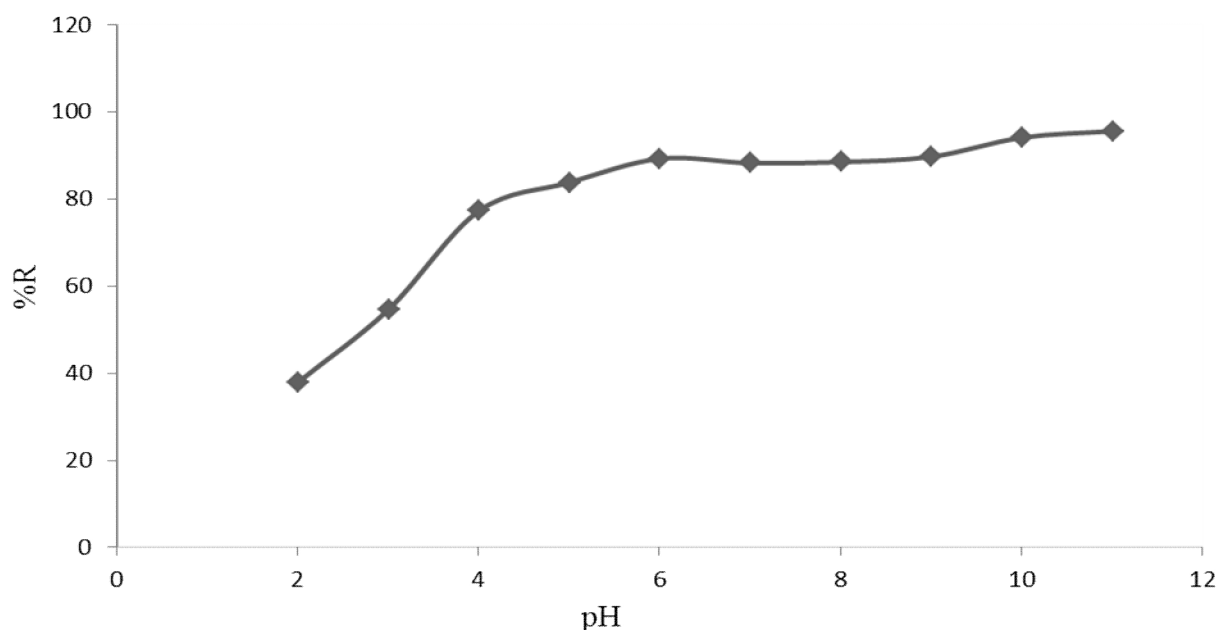
136 3.2 Effect of pH

137 The effect of pH on the adsorption of MB onto CH is depicted in Figure 2. The figure
 138 reveals that variation in MB pH had a significant influence on the biosorption process. The
 139 result shows that the adsorption of MB onto CH increases with increase in solution pH. It
 140 was observed that the percentage removal of MB increased from 38.05 to 95.67% when the
 141 pH was increased from 2 to 11. The maximum adsorption of MB took place at pH 11. The
 142 influence of the solution pH on the dye uptake can be explained on the basis of the zero
 143 point charge or isoelectric point of the biosorbent [22]. The zero point charge (pH_{PZC}) of the
 144 cow hoof was determined by the solid addition method [23]. Fifty five millilitres (55 mL) of
 145 KNO_3 solution of known strength was transferred to a series of 100 mL beakers. The pH_i
 146 values of the solution were adjusted from 2 to 12 by adding either 0.1 M HNO_3 or 0.1 M
 147 NaOH. Then 50 mL of each solution was transferred into a 100 mL conical flask and 0.1 g of
 148 cow hoof was added to each flask. The suspensions were then manually shaken and

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149 allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the
150 supernatant liquid were noted. The difference between the initial pH (pH_i) and final pH (pH_f)
151 values ($\Delta pH = pH_i - pH_f$) was plotted against the pH_i . The point of intersection of the resulting
152 curve at which ΔpH is zero gave the pH_{PZC} . The procedure was repeated for different
153 concentrations of KNO_3 . The point of zero charge for CH was determined to be 7.7. It has
154 been reported that adsorption of cations is favoured at $pH > pH_{PZC}$, while the adsorption of
155 anions is favoured at $pH < pH_{PZC}$ [23]. This is because at the $pH > pH_{PZC}$, the surface of the
156 biosorbent is negatively charged thereby supporting the uptake of more MB due to
157 electrostatic force of attraction [22] between the negatively charged biosorbent surface and
158 the positively charged MB. At lower pH ($pH < pH_{PZC}$), the H^+ ions compete effectively with
159 the cationic dye. The adsorption of MB seemed to be uniform between pH 6 and 8. This
160 observation could be linked to the fact that the pH_{PZC} (7.7) falls within this region; the
161 surface of the adsorbent has a charge of zero thereby bringing about insignificant adsorption
162 at this region. The percentage removal of MB picked up at pH higher than this region (Figure
163 2).

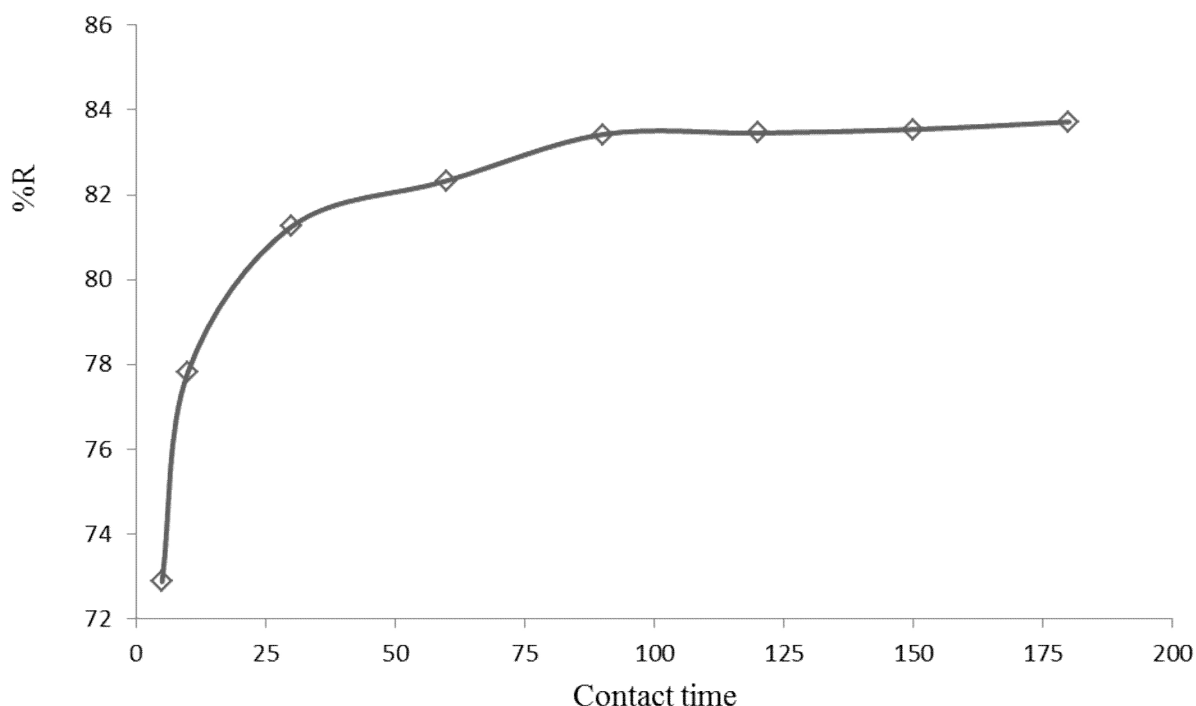


164
165 Figure 2: Effect of pH on the sorption of MB onto CH
166

167 3.3 Effect of Contact Time

168 Contact time is an important factor that affects uptake efficiency in batch adsorption
169 processes. Figure 3 reveals that the maximum adsorption of MB occurred after 90 minutes
170 of equilibration with percentage removal of 83.42%. The rate of the biosorption process
171 increased rapidly in the first 30 minutes and then became reduced as the agitation time
172 increased beyond 30 minutes. The rate of adsorption seemed to be insignificant from the
173 agitation time of 90 minutes. This implies that the adsorption process nearly reached
174 equilibrium within the first 90 minutes of agitation. This observation is similar to the literature
175 report on the adsorption of MB onto *Aspergillus fumigatus* [24]. The initial rapid rate of

adsorption may be due to an increase in the number of vacant sites available at the initial stage of adsorption before the adsorbent surface reached saturation [24].

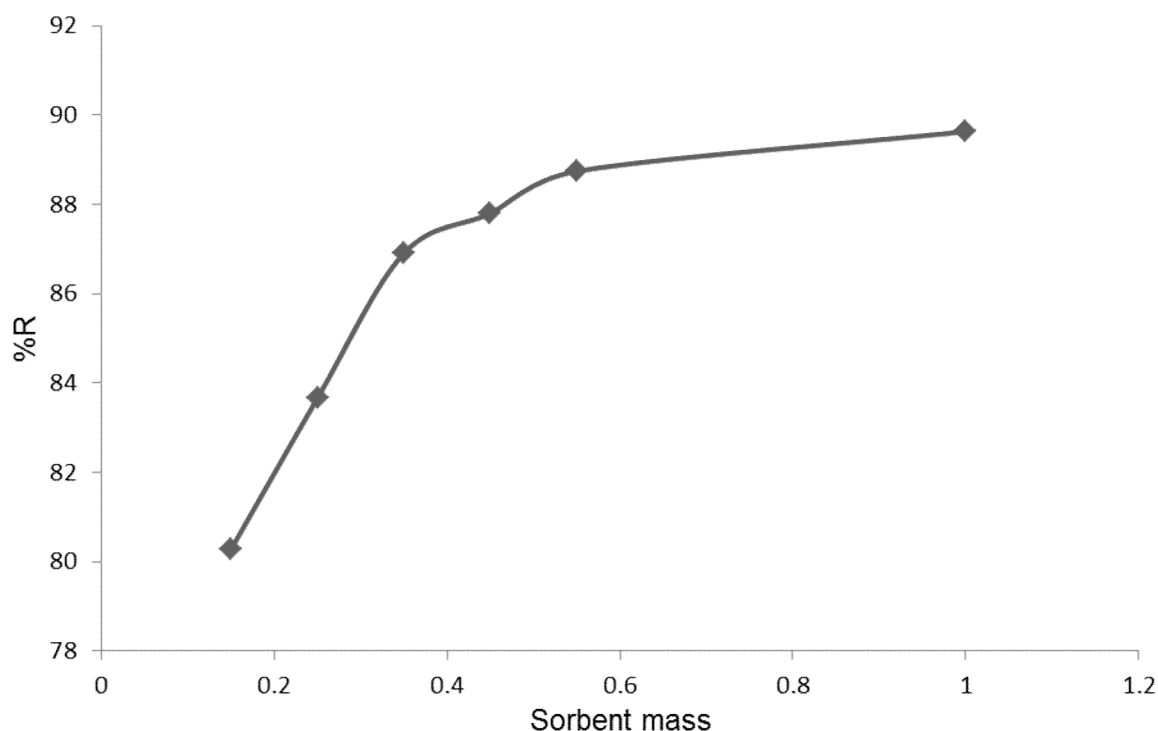


178

179 Figure 3: Effect of contact time on the sorption of MB onto CH

180 3.4 Effect of Sorbent Mass

181 The effect of sorbent mass on the adsorption study is shown in Figure 4. The figure reveals
 182 that percentage MB removal (%R) is highly a function of the mass of the biosorbent used.
 183 The percentage of MB adsorbed increased with increase in the mass of the sorbent dosed.
 184 Increase in the percentage of dye removal with adsorbent mass can be attributed to increase
 185 in the adsorbent surface area, which invariably increases the number of adsorption sites
 186 available for adsorption. The percentage removal of MB increased from 80.27 to 89.63% as
 187 the sorbent mass was raised from 0.15 – 1.0 g. It can also be observed from the figure that
 188 the amount of MB sorbed per gram of CH (q_e) decreased by 11.14 mg g^{-1} as the mass of
 189 sorbent added increased from 0.15 – 1.0 g.

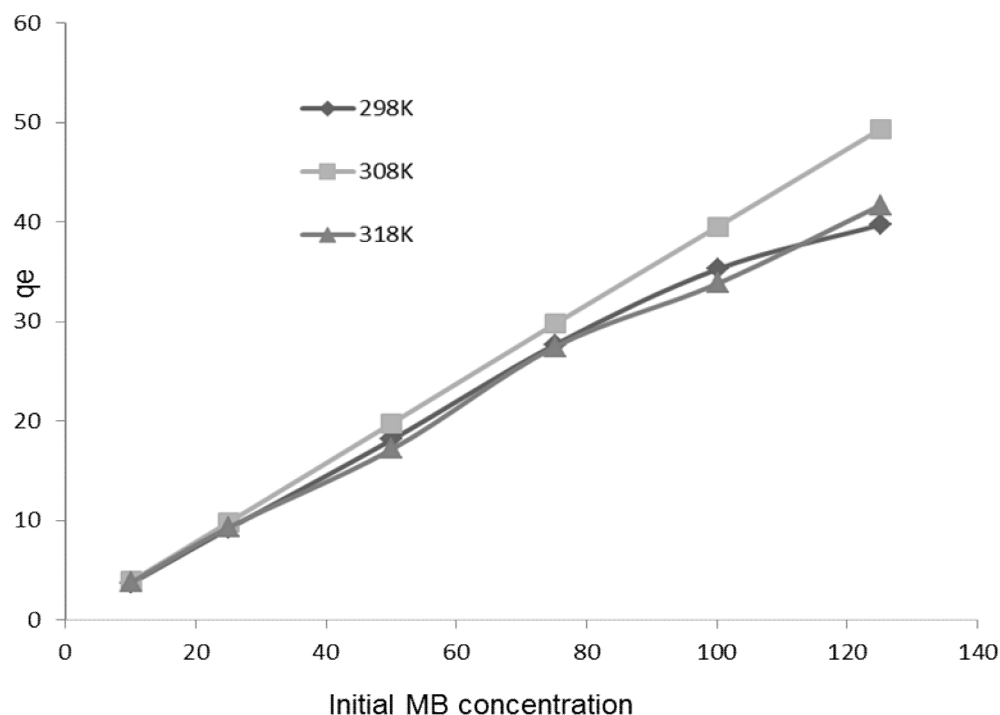


190

191 Figure 4: Effect of sorbent mass on the sorption of MB onto CH

192 3.5 Effect of initial MB Concentration and Temperature

193 The effect of temperature on the adsorption rate of MB on CH was investigated at three
 194 different temperatures (298, 308, and 318 K) using initial MB concentration of 10–125 mgL⁻¹
 195 (Figure 5). As elucidated by Figure 5, there is increase in the equilibrium uptake of MB with
 196 increase in the initial MB concentrations at all temperatures considered. It can be observed
 197 from the figure that the equilibrium uptake of MB adsorption increased rapidly when the
 198 temperature was increased from 298 to 308 K. The maximum adsorption of MB took place at
 199 308 K and it appears that desorption of MB began to take place when the temperature was
 200 increased to 318 K looking at the merging of the 298 and 318K lines (Figure 4). It is a known
 201 fact that temperature affects the diffusion rate of adsorbate molecules and internal pores of
 202 the adsorbent particle [12]. It can be interpreted from this study that the rate of diffusion of
 203 MB molecules increases rapidly across the solvent and the solvent-sorbent interface to CH
 204 surface when the temperature is increased from 298 K to 308 K and conversely decreases
 205 as the temperature increases to 318 K. It could also be that increase in temperature from
 206 308 K to 318 K could cause a great increase in collisions among the adsorbed molecules
 207 and eventually lead to desorption of some of the adsorbed MB molecules from the sorbent
 208 surface.



209

210 Figure 5: Effect of temperature and initial MB concentration on the removal of MB by CH

211 3.6 Adsorption Isotherms

212

213 Many adsorption isotherm models are used to describe equilibrium data but in this study,
 214 Langmuir and Freundlich models were employed to describe the relationship between the
 215 amount of MB adsorbed on CH and its equilibrium concentration at two different
 216 temperatures. The correlation coefficient R^2 value of each plot was used to describe the
 217 applicability of the isotherm models. Langmuir model assumes a monolayer adsorption of
 218 adsorbates on a homogeneous surface without any interaction between the adsorbed
 219 molecules. The model takes the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

220
 221 Where, q_m (mgg^{-1}) is the maximum adsorption capacity, K_L (Lmg^{-1}) is a constant related to
 222 the affinity of binding sites or bonding energy. The values of q_m and K_L can be estimated
 223 from the slope and intercept of the linear plot of C_e/q_e versus C_e respectively. The Freundlich
 224 isotherm model is based on adsorption on a heterogeneous surface. It can be expressed
 225 linearly as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

226
 227 where K_f and n are Freundlich costants which are related to sorption capacity and intensity
 228 respectively. The values of K_f and $1/n$ can be obtained from the slope and intercept of the
 229 linear plot of $\log q_e$ against $\log C_e$. The isotherm parameters for both models are presented
 230 in Table 1. It can be seen from the correlation coefficient values, that the Freundlich isotherm
 231 model exhibited better fit than the Langmuir model.

232

233 Table 1: Isotherm parameters for the removal of MB by CH

Isotherm	Parameter	Temperature (K)	
		298	308
Langmuir	q_m (mgg ⁻¹)	54.05	13.7
	K_L (Lmg ⁻¹)	0.124	1.44
	R^2	0.9657	0.9677
Freundlich	K_f (L ^{1/n} g ⁻¹ mg ^{-1/n})	5.365	101.88
	n	1.2145	0.598
	$1/n$	0.8234	1.7862
	R^2	0.9800	0.9911

234

235

236 3.7 Adsorption Kinetics

237 The pseudo-first-order and pseudo-second order kinetic models were used to evaluate the
 238 kinetic parameters for the sorption process. The pseudo-first-order equation can be
 239 expressed as

$$240 \quad \text{Log } (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

241 Where k_1 = the rate constant for pseudo-first-order equation (min⁻¹) and q_e = amount of
 242 metal sorbed at equilibrium (mgg⁻¹). A plot of $\log (q_e - q_t)$ against t gave a straight line. The
 243 values of q_e and k_1 (Table 2) were computed from the slope and intercept of the plot.

$$244 \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

245 where k_2 is the pseudo-second-order sorption rate constant (gmg⁻¹ min⁻¹). The values of q_e
 246 and k_2 can be evaluated from the slope and intercept of the plot of t/q_t against t respectively.
 247 The $q_{e(\text{cal})}$ from pseudo-second-order kinetics model closely agrees with $q_{e(\text{exp})}$ value while the
 248 corresponding value from pseudo-first-order kinetics model does not. This implies that the
 249 sorption mechanism of MB on CH is better described by pseudo-second-order kinetics. This
 250 is further confirmed by the correlation coefficient (R^2) for pseudo-second-order kinetics
 251 (Table 2). This observation could make one suggest that chemisorption might be the rate-
 252 limiting step that controlled the adsorption of MB onto CH.

253

254

255

256

Table 2: Kinetics parameters for the adsorption of MB on CH at 298K

	$q_{e(\text{exp})} (\text{mgg}^{-1})$	$q_{e(\text{cal})} (\text{mgg}^{-1})$	$k_1 (\text{min}^{-1})$	$k_2 (\text{gmg}^{-1} \text{min}^{-1})$	R^2
Pseudo-first-order	8.37	0.906	0.0129	-	0.9274
Pseudo-second-order	8.37	8.41	-	0.128	1

3.8 Thermodynamic Parameters of MB Biosorption onto CH

Thermodynamic studies were done by carrying out equilibrium studies at different temperatures to obtain corresponding values of C_{Ae} and C_e [26]. The equilibrium constant K_e can be calculated from C_{Ae} and C_e values using

$$K_e = \frac{C_{Ae}}{C_e} \quad (7)$$

where, C_{Ae} represents adsorption in mgL^{-1} at equilibrium; and C_e is the equilibrium concentration of the metal in mgL^{-1} . The value of K_e can be obtained from the lowest experimental MB concentration [11]. Vant Hoff's equation is a useful expression that links ΔH^0 and ΔS^0 with the equilibrium constant (K_e) as shown below [26]:

$$\ln K_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

where, T is temperature in Kelvin and R is the gas constant ($\text{kJmol}^{-1}\text{K}^{-1}$). The values of the standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) can be calculated from the slope and intercept of the plot of $\ln K_e$ against $1/T$ while the values of ΔG^0 at different temperatures can be obtained using the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

The values for the thermodynamic parameters are shown in Table 3. The sorption of MB on CH can be described as endothermic, feasible and spontaneous judging from the positive ΔH^0 and negative Gibb's free energy (ΔG^0) values for all temperatures. The low value of ΔS^0 indicates that no remarkable change on entropy is associated with the biosorption process [14, 27] and the positive ΔS^0 value reflects the affinity of the adsorbent for MB [14].

Table 3: Thermodynamic constants for the adsorption of MB on CH at different temperatures

T (K)	$\Delta G^0 (\text{kJ mol}^{-1})$	$\Delta H^0 (\text{kJ mol}^{-1})$	$\Delta S^0 (\text{kJ mol}^{-1})$	$R (\text{kJ mol}^{-1} \text{K}^{-1})$
298	-7.497	18.25	0.0864	8.314×10^{-3}
308	-8.362			8.314×10^{-3}
318	-9.225			8.314×10^{-3}

285 4. CONCLUSION

286 The adsorptive removal of MB from synthetic wastewater by CH was observed to be
 287 influenced by the solution pH, contact time, sorbent dosage and MB initial concentration.
 288 The equilibrium data fitted well with Freundlich isotherm model while the kinetic modelling of
 289 adsorption of MB onto CH perfectly followed the pseudo-second-order rate kinetic model.
 290 The thermodynamic studies showed that the biosorption process was feasible, spontaneous
 291 and endothermic.

292 COMPETING INTERESTS

293 There are no competing interests.

294 295 AUTHORS' CONTRIBUTIONS

296
 297 This work was carried out in collaboration between authors. Author IO designed the study,
 298 performed the statistical analysis, wrote the protocol, and wrote the first draft of the
 299 manuscript. Authors OI and AOO managed the analyses of the study. Author OLF managed
 300 the literature searches. All authors read and approved the final manuscript.
 301

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