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Evaluation of Loofah as a Sorbent in the Decolorization of Basic Dye Contaminated Aqueous System

N. A. Oladoja,* C. O. Aboluwoye, and A. O. Akinkugbe

Department of Chemistry, Adekunle Ajasin University, Akungba Akoko, Nigeria

The hard fibrovascular network of the fruit of *Luffa cylindrica*, loofah, was used in a batch sorption system to remove methylene blue (MB) from aqueous solution. The effects of pH on the sorption of MB by loofah were studied using equilibrium isotherm experiment. The Langmuir sorption capacity (q_m , mg/g) of the loofah increased with increase in pH. The Freundlich isotherm models favored the prediction of the theoretical sorption capacity more than the Langmuir isotherm models. The kinetics of the sorption process was studied at varying initial MB concentrations using pseudo-first-order and pseudo-second-order kinetic models. The pseudo-second-order kinetic model was found to fit the experimental data for the entire sorption period with high coefficient of determination (r^2). The prospects of regenerating the loofah was studied using four different eluting solvents in batch desorption studies. The results of the batch desorption studies showed that both chemisorption and ion-exchange played prominent role in the sorption process. The elution curve obtained from the continuous desorption studies showed that the elution rate was very fast and high elution efficiency could be obtained with 0.1 M HCl as an eluting solvent. The IR analysis confirmed the presence of polar functional groups and established interactions between the MB molecules and these functional groups.

1. Introduction

Dyes are aromatic organic compounds with structures including aryl rings which have delocalized electron systems.¹ Synthetic dyes exhibit considerable structural diversity.² Because of their commercial importance, the impurities, the impact,³ and toxicity^{4,5} of dyes that are released in the environment have been extensively studied.^{6,7} Traditional wastewater treatment technologies have continued to be markedly ineffective for handling wastewater of synthetic dyes because of the chemical stability of these pollutants.²

Dyeing operations require plenitude of water and hence a large quantity of wastewater is usually generated. The generated wastewater is highly colored and repugnant. In order to abate the negative impact of this wastewater on the environment, different treatment technologies are being developed and perfected by scientists and engineers (e.g., Fenton's reagent, ozonation, cucurbituril, photochemical and electrochemical destruction, membrane filtration, electrochemical coagulation, irradiation, etc). Some of these methods have been found to be very effective but adaptation to real-life situations is limited by high installation and operational costs, high energy consumptions, and management of sludge generated from the operations.

The present trends in the technology of water/wastewater treatment are in the development of high performance, low cost, and eco-friendly technologies. This has prompted different studies on the use of sorbents of biological origin (biosorbents) in adsorption process. Adsorption is a unit process commonly used in the tertiary treatment stage of water/wastewater treatment. It is used to polish already treated water to an acceptable standard. The conventional sorbent is activated carbon. However, it is expensive and the process of regeneration for reuse is tedious. The majority of biosorbents are complex materials containing lignin and cellulose as major constituents. Chemical sorption can occur via the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids, phenolics, and ethers, as chemical bonding,⁸ and through ion exchange.⁹

Different binding mechanisms have been proposed to be the mechanisms of biosorption. Such mechanisms include chemisorptions, physisorption, microprecipitation, and oxidation/reduction reactions. It is possible that some of these mechanisms act simultaneously to varying degrees, depending on the biosorbents and the chemical environment.

Litanies of biosorbents have been investigated to remove dyes from aqueous solutions. These include cotton waste, rice husk, bark,¹⁰ palm fruit bunch,¹¹ jack fruit peel,¹² castor seed shell,¹³ wood,¹⁴ orange peel,¹⁵ and mansonias sawdust.¹⁶ The use of some of these sorbents was found to be simple, efficient, and cheap. Consequent upon these, interest in the search for more economical and effective biosorbents has continued to grow.

Luffa cylindrica is a herbaceous annual climber or trailer to 6 mm or more long. It is a cultivated plant but naturalized in all kinds of vegetation, where rainfall is high enough, in all countries. The plant is native of the old world tropics and is of such ancient cultivation that its original home, whether in Africa or in Asia, cannot now be determined. The fruit is the source of the loofah or vegetable sponge which is the hard fibrovascular network found within the ripe fruit after the intervening tissue has been rotted away. Commercial grade loofah is light uniform in color, clean and free of seeds and extraneous matter and preferably over 35 cm long. Aside from its use as a washing sponge, the fiber has commercial uses in hat manufacture, shoe soles, car wipers, marine engine filters, pot holders, table mats, door and bath mats, gloves, etc.

The present studies are aimed at the use of loofah as a low cost sorbent in the abstraction of methylene blue (MB) from aqueous solution. In order to achieve this, batch sorption experiments shall be conducted. The effects of solution pH on the MB uptake shall be studied via isotherm experiment, and the effect of initial MB concentration on the rate of sorption shall be investigated with two widely used kinetic models. The prospects of loofah regeneration shall be examined in different eluting solvents (deionized water, HCl, NaOH, and CH₃COOH), using batch method. The solvent that gave optimum MB

* Corresponding author. E-mail: bioladoja@yahoo.com.

desorption shall be used in fixed-bed desorption, to obtain a desorption curve, from which relevant information shall be generated.

2. Materials and Methods

2.1. Loofah. The loofah was obtained locally, from the plant *Luffa cylindrica*, from the university town (Akungba-Akoko, Nigeria). The loofah was dehusked and the intervening tissue was removed. The hard fibrovascular network (i.e., the loofah) was shredded, steeped in deionized water, washed thoroughly until the washings became clear, and dried in the oven. The dried loofah was ground and screened through a set of sieves to obtain particles of size 100 μm .

2.2. Dye Solution. MB, the sorbate used, is a monovalent cationic dye. It is classified as C.I. Basic blue 9, C.I. solvent blue 8, C.I.52015. It has a molecular weight of 373.90. The MB used was of analytical grade and so it was used without further purification. A stock solution, 1000 mg/L, was prepared by dissolving an appropriate quantity of MB in a liter of deionized water. The working solutions were prepared by diluting the stock solution with deionized water to give the appropriate concentrations of the working solutions.

2.3. Dye Quantification. The MB concentrations in the aqueous solutions were quantified by the determination of the absorbance at the characteristic wavelength using a double beam UV/visible spectrophotometer. Standard solutions of the dye were taken, and the absorbances were determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to the maximum absorbance ($\lambda_{\text{max}} = 661 \text{ nm}$), as determined from this plot, was noted and the wavelength was used for the preparation of the calibration curve used in the present studies.

2.4. Physicochemical Characteristics of Loofah. The proximate physicochemical characteristics of the loofah were determined using the Association of Official Analytical Chemist (AOAC) methods.¹⁷

The point of zero charge (PZC) of the loofah was determined by solid addition method,¹⁸ viz., to a series of 100 mL conical flasks, 45 mL of 0.1 M KNO_3 solution was transferred. The pH_0 values of the solution were roughly adjusted from 2 to 12 by adding either 0.1 N HNO_3 or NaOH . The total volume of the solution in each flask was made exactly to 50 mL by adding the KNO_3 solution. The pH_0 of the solutions were then accurately noted. Loofah (1 g) was added to each flask and securely capped immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($\Delta\text{pH} = \text{pH}_0 - \text{pH}_f$) was plotted against the pH_0 . The point of intersection of the resulting curve at which $\Delta\text{pH} = 0$ gave the PZC.

Surface functional groups determination was based on the Boehm titration method.^{19,20} Solutions of NaHCO_3 (0.1M), Na_2CO_3 (0.05M), NaOH (0.1M), and HCl (0.1M) were prepared with deionized water. A volume of 50 mL of these solutions was added to vials containing 1 g of dry loofah and shaken (100 rpm) until equilibrium (24 h) and then filtered. Five solution blanks (without the loofah) were prepared. The excess of base or acid was then determined by back-titration using NaOH (0.1M) and HCl (0.1M) solutions. The IR spectra of the MB loaded loofah and unloaded loofah were recorded using KBr wafers in conjunction with a Perking-Elmer infrared spectrophotometer (IR spectrophotometer).

2.5. Effect of pH. The effects of pH on the sorption of MB on loofah were studied by determining the adsorption isotherms

over a pH range of 2–10. The initial concentration was varied from 25 to 200 mg/L. Samples were withdrawn at a predetermined equilibrium time and analyzed for residual MB and the amount of MB sorbed per unit mass of the loofah (q in mg/g) was calculated using the following mass balance equation:

$$q_t = \frac{v(c_0 - c_t)}{m} \quad (1)$$

2.6. Effect of Initial Concentration on Sorption Kinetics. The effects of initial MB concentrations on the sorption process were studied using a range of MB concentrations (25–200 mg/L). A typical experimental procedure was conducted by measuring, accurately, a liter of the MB solution of known concentration; 2 g of loofah was added and agitated (at 200 rpm) for 120 min, based on the results obtained from the equilibrium time studies carried out as a preliminary study (results not shown for brevity). Samples were withdrawn at fixed time intervals and centrifuged, and the supernatant was analyzed for residual MB concentration using UV/visible spectrophotometer. The amount of MB sorbed per unit mass of the loofah (q in mg/g), at fixed time intervals, was calculated using the mass balance procedure (eq 1).

2.7. Batch Desorption Studies. The loofah (1 g) was loaded with the MB (200 mg/L) and dried in the oven at 60 °C overnight. This biomass was then placed in Erlenmeyer flasks containing 50 mL of the desorbing agent solution. The sample was agitated for 120 min and then the loofah was filtered. The desorbed MB concentration was quantified using UV/visible spectrophotometer. Four different eluting solvents were used: deionized water, HCl (0.1 M), NaOH (0.1 M), and CH_3COOH (0.1 M).

2.8. Continuous Desorption Studies. The continuous desorption studies were carried out in a fixed bed of MB-loaded loofah in a glass column (40 \times 1 cm). The glass column was packed with a known weight of MB-loaded loofah. The MB-loaded loofah was regenerated using the best eluting solvent, obtained from the batch desorption studies (section 2.7). The effluent was collected at fixed time intervals until the MB concentration in the effluent was less than 0.02 mg L^{-1} .

3. Theory

3.1. Equilibrium Isotherm Studies. Adsorption isotherms are basic requirements to understand the mechanism of adsorption. The monolayer coverage of the sorbate on a sorbent surface at constant temperature is represented by the Langmuir isotherm. The Langmuir isotherm hints toward surface homogeneity. The linearized form of the equation can be represented thus:

$$c_e/q_e = \frac{1}{K_L q_m} + \left[\frac{1}{q_m} \right] c_e \quad (2)$$

where c_e is the concentration of the sorbate at equilibrium (mg/L), q_e is the amount of MB adsorbed at equilibrium per unit mass of loofah (mg/g), q_m is the monolayer capacity (mg/g), and K_L (L/mg) is the adsorption equilibrium constant.

The monolayer coverage can be obtained from a plot of c_e/q_e versus c_e , which should give a straight line. The values of q_m and K_L are derived from the slope and the intercept of this line.

The Freundlich equation for adsorption isotherm indicates the surface heterogeneity of the sorbent. The linearized form of the isotherm is expressed thus:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln c_e \quad (3)$$

where k_f (the measure of the sorption capacity) and n (the sorption intensity) are Freundlich coefficients, obtainable from the plots of $\ln q_e$ versus $\ln c_e$, q_e is the amount of MB adsorbed per specified amount of loofah (mg/g), and c_e is the equilibrium concentration (mg/L).

3.2. Kinetic Studies. In order to prevent arbitrary assumption of mechanism of sorption of solute from solution by an adsorbent, a plethora of kinetic models have been proposed and applied to different sorption processes. In the present studies the mechanism of adsorption of MB on loofah was elucidated by employing two widely used kinetic models (pseudo first order and pseudo second order) to test the data obtained from the kinetic studies.

The linearized form of the pseudo-first-order equation of Lagergren is generally expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - \left[\frac{k_1}{2.303} \right] t \quad (4)$$

where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mg/g). k_1 is the rate constant of pseudo-first-order adsorption.

The plot of $\log(q_e - q_t)$ versus t should give a linear relationship if the sorption process is described by pseudo-first-order kinetics model. The pseudo-first-order parameters k_1 and q_e are calculated from the slope and intercept of the plot, respectively.

The pseudo-second-order kinetic model is represented by the linear equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where q_e , q_t , and t have the same meaning as explained above. k_2 is the overall rate constants of pseudo-second-order sorption (g/mg/min). If pseudo-second-order kinetics is applicable, the plot of t/q_t against t of eq 5 should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot.

If the initial sorption rate is

$$h = k_2 q_e^2 \quad (6)$$

then eq 5 becomes

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (7)$$

3.3. Diffusion Mechanisms. Several steps are involved in the sorption of sorbate by a sorbent. These involve transport of the solute molecules from the aqueous phase to the surface of the solid particulates and diffusion of the solute molecules into the interior of the sorbent pores, which is usually a slow process. The intraparticle diffusion rate constant (k_{id}) is given by the equation formulated by Weber and Morris:²⁷

$$q_t = k_{id} t^{0.5} + C \quad (8)$$

When intraparticle diffusion plays a significant role in controlling the kinetics of the sorption process, the plot of q_t versus $t^{0.5}$ yields a straight line passing through the origin, C , and the slope gives the rate constant, k_{id} .

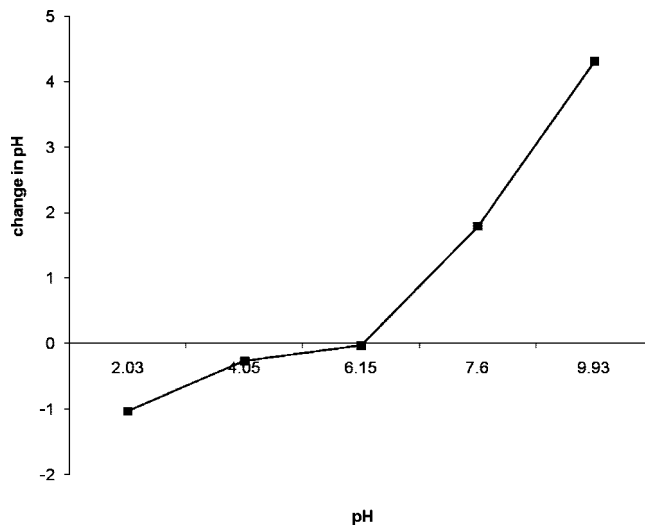


Figure 1. Point zero charge (ΔpH versus pH).

However, when the transport of the solute molecules from the liquid phase up to the solid phase boundary plays the most significant role in adsorption, the liquid film diffusion model may be applied:

$$\ln(1 - F) = -k_{id} t \quad (9)$$

where F is the fractional attainment of equilibrium ($F = q_t/q_e$) and k_{id} is the adsorption rate constant. A linear plot of $\ln(1 - F)$ versus t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid film surrounding the solid sorbent.

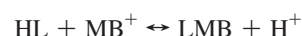
4. Results and Discussion

4.1. Proximate Physicochemical Characteristics of Loofah. The results obtained from the proximate physicochemical characterization showed that the loofah contained (in % dry weight): protein 4.20%; lipid 1.08%; ash 1.04%; fiber 55.78%; and carbohydrate 37.81%. The bulk density of the loofah used was 489.71 kg/m³. The results of the particle size analysis showed that the loofah used for the present study was made up of the following particle sizes (μm): >90 (58.68%); 90–63 (56.92%); and <63 (4.10%).

The point of zero charge (PZC) was obtained at pH value of 6.2 (Figure 1). The surface functional group analysis determined by the Boehm titration method showed that the surface functional groups were predominantly acidic; viz., strongly acidic (carboxylic group) 0.52 mequiv/g; weakly acidic (carboxylic, lactonic, and enolic) 0.53 mequiv/g; and phenolic 0.88 mequiv/g. The magnitude of the basic functional groups, determined using 0.1 M of HCl, was low (0.13 mequiv/g). The predominance of the acidic functional groups on the surface of the loofah is an indication that the MB can interact chemically with the polar functional groups of these acidic functional groups as chemical bonding and ion exchange; viz.



or



where L^- and HL are the polar sites on the loofah surface and MB^+ is the methylene blue ion in aqueous medium.

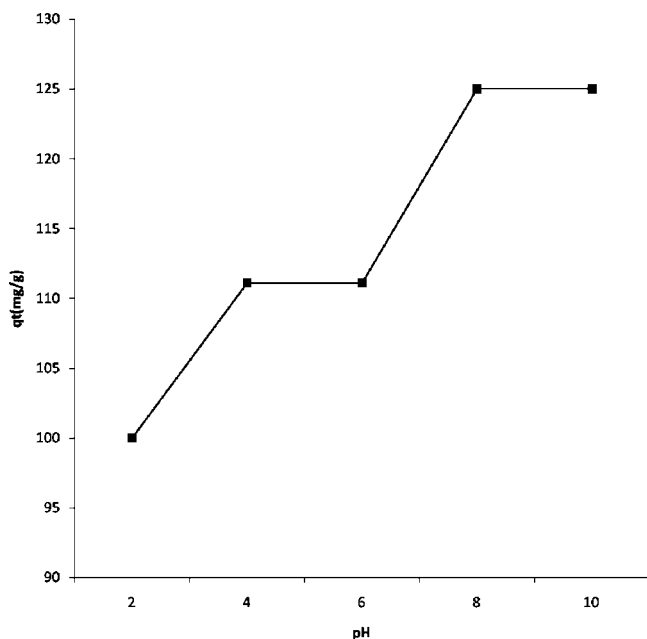
Table 1. Equilibrium Isotherm Parameters of Sorption of MB on Loofah

parameters	Langmuir isotherm parameters			Freundlich isotherm parameters		
	q_m (mg/g)	K_L (L/mg)	r^2	K_f (L/g)	$1/n$	r^2
pH 2	100.00	0.1905	0.806	21.80	0.440	0.913
pH 4	111.11	0.2571	0.881	23.17	0.493	0.950
pH 6	111.11	0.3000	0.965	24.68	0.524	0.967
pH 8	125.00	0.2963	0.967	25.84	0.540	0.973
pH 10	125.00	0.4000	0.915	29.82	0.609	0.935

4.2. Effect of Solution pH. The pH of the medium of interaction between the sorbent and the sorbate is an important parameter in any adsorption process. This is because the pH of the solution affects the surface charge of the adsorbent and the degree of ionization of the sorbate present in the solution. The change of pH affects the adsorptive processes via the dissociation of functional groups on the active sites of the adsorbent. This subsequently leads to a shift in the reaction kinetics and equilibrium characteristics of the adsorption process.²¹ It has been observed that biosorbent surfaces adsorb anions favorably at lower pH due to the presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH due to the deposition of OH^- . In order to understand the effect of solution pH on the uptake of MB by loofah, isotherm experiments were conducted at different pH values (2, 4, 6, 8, and 10). Two classical equilibrium isotherm models were employed to test the data obtained from this study and the results obtained are presented in Table 1.

The monolayer sorption capacities (q_m mg/g), obtained from the Langmuir plot of the data obtained at varying pH values were plotted against pH (Figure 2) to understand the effect of pH on the sorption capacity of the loofah. The q_m value increased with increase in pH value. The trend in the increase in the value of q_m with pH showed that the magnitude of the increase in the q_m value from pH 6 to 8 was greater (111–125 mg/g) than the increase observed (100–111 mg/g) from pH 2 to 4. A similar result has been reported by Ofomaja¹⁶ in the study of sorption of MB onto mansonia wood sawdust.

The observed increase in the value of the q_m obtained from pH 6 could be ascribed to the value of the pH_{PZC} of the loofah

**Figure 2.** Effect of pH on the sorption of MB by loofah.**Table 2. Comparison of the Langmuir Sorption Capacity (q_m , mg/g) of Different Sorbents for MB**

adsorbent	q_m (mg/g)	references
loofah	125.00	present studies
cereal chaff	20.30	Han et al. ²⁸
rice husk	40.60	Vadivelan and Kumar ²⁹
mansonia sawdust	28.89	Ofomaja ¹⁶
castor seed shell	158.73	Oladoja et al. ¹³
raw beech sawdust	9.78	Batzias and Sidiras ³⁰
carbonized spent bleaching earth	94.5	Low et al. ³¹
coconut husk	99	Low and Lee ³¹

surface. Since the PZC was obtained at pH value of 6.2, the interaction of cation (MB^+) with the surface of the loofah is favored at $pH > PZC$ while the interaction of anions is favored at $pH < PZC$. For pH closer to the pH_{PZC} , adsorption seems to be due to both electrostatic and chemical interactions.

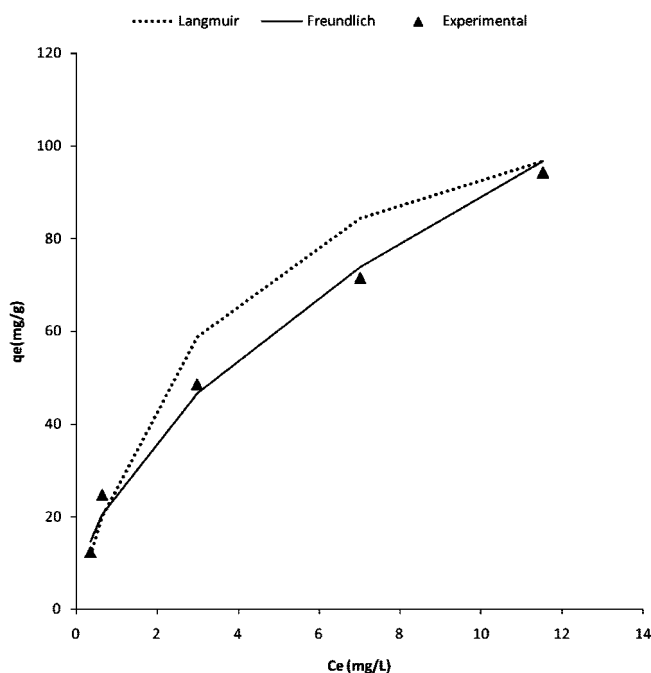
The corresponding linear plots of the values of q_m and K_L against pH were regressed to derive a mathematical relationship with a relatively low coefficients of determination (0.899 and 0.904, respectively). Therefore q_m and K_L can be expressed as a function of pH as follows:

$$q_m = 95.27pH^{3.194}$$

$$K_L = 0.151pH^{0.022}$$

The linear correlation values (r^2) obtained from the fitting of the data with these two isotherm models (Table 2) revealed that MB sorption by loofah took place more on heterogeneous surface, with a uniform distribution of heat of adsorption over the surface, than monolayer coverage.

The equilibrium adsorption plots, relating solid and liquid phase concentrations, for the two isotherms at the different pH values under study are presented below, and the comparative fits of the two isotherms with the equilibrium data plotted as q_e versus C_e at pH 8, the pH at which the optimum sorption capacity of the loofah was obtained, are presented in Figure 3.

**Figure 3.** Comparison of the experimental and predicted adsorption isotherm for the sorption of MB by loofah at the optimum pH.

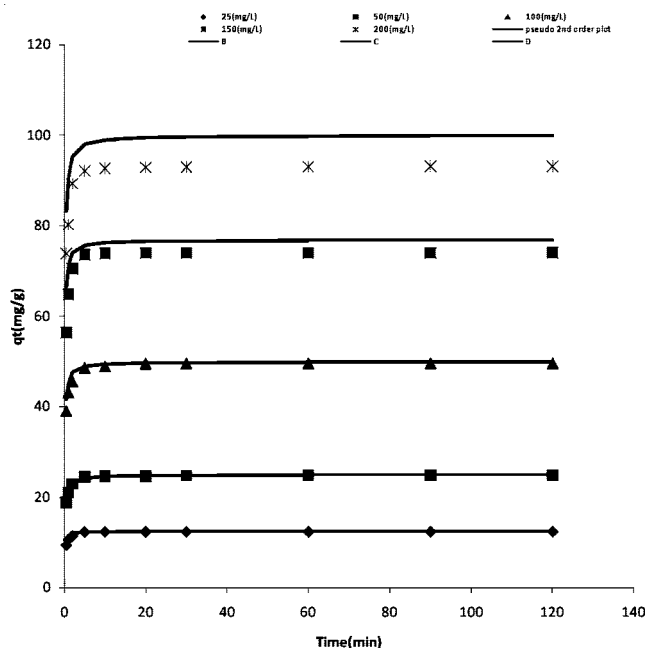


Figure 4. Effect of initial concentration on the sorption of MB by loofah.

Langmuir:

$$\text{pH 2: } q_e (\text{mg/g}) = \frac{19.05C_e}{1 + 0.19.05C_e} \quad (10)$$

$$\text{pH 4: } q_e (\text{mg/g}) = \frac{28.57C_e}{1 + 0.2571C_e} \quad (11)$$

$$\text{pH 6: } q_e (\text{mg/g}) = \frac{33.33C_e}{1 + 0.300C_e} \quad (12)$$

$$\text{pH 8: } q_e (\text{mg/g}) = \frac{37.04C_e}{1 + 0.2963C_e} \quad (13)$$

$$\text{pH 10: } q_e (\text{mg/g}) = \frac{50.11C_e}{1 + 0.400C_e} \quad (14)$$

Freundlich:

$$\text{pH 2: } q_e (\text{mg/g}) = 21.80C_e^{0.440} \quad (15)$$

$$\text{pH 4: } q_e (\text{mg/g}) = 23.17C_e^{0.493} \quad (16)$$

$$\text{pH 6: } q_e (\text{mg/g}) = 24.68C_e^{0.524} \quad (17)$$

$$\text{pH 8: } q_e (\text{mg/g}) = 25.84C_e^{0.640} \quad (18)$$

$$\text{pH 10: } q_e (\text{mg/g}) = 29.82C_e^{0.609} \quad (19)$$

The predicted Freundlich isotherm, q_e , fitted the experimental data better than the Langmuir isotherm models predicted q_e . The Freundlich isotherm is an empirical equation that encompasses the heterogeneity of sites and the exponential distribution of sites and their energies. The results presented in Table 2 give a comparison of the adsorption capacity of MB on different biosorbents taken from the literature.

4.3. Kinetic Studies. 4.3.1. Effect of Initial Concentration on Sorption Kinetics. The results presented in Figure 4

Table 3. Kinetic Parameters for the Sorption of MB on Loofah at Different Initial MB Concentration (mg/L)^a

init concn (mg/L)	pseudo-first-order parameters			pseudo-second-order parameters			
	q_{e1}	k_1	R^2	q_{e2}	k_2	h	R^2
25	4.20	4.836×10^{-2}	0.410	12.50	0.9143	142.81	1.0000
50	1.27	3.685×10^{-2}	0.568	25.00	0.2286	143.13	1.0000
100	2.14	7.139×10^{-2}	0.755	50.00	0.2000	500.00	1.0000
150	1.79	4.376×10^{-2}	0.448	76.92	0.1690	999.92	1.0000
200	3.61	6.679×10^{-2}	0.781	100.00	0.1000	1000.00	1.0000

^a $k_1 = \text{min}^{-1}$; $q_{e1} = \text{mg/g}$; $k_2 = \text{g mg}^{-1} \text{min}^{-1}$; $h = \text{g mg}^{-1} \text{min}^{-1}$.

show the effects of initial concentration on the time—concentration profile of MB adsorption on loofah. It was observed that the amount of MB (mg/g) adsorption by the loofah increased with increase in the MB concentration. The amount of the MB uptake also increased with contact time and at some point in time reached an almost constant value where the amount of dye being removed from aqueous solution onto the loofah is in a state of dynamic equilibrium with the amount of dye desorbed from the loofah. For each of the concentrations of dye used in the present study, the greater amount of dye was removed within the first 5 min of study. This shows that the sorption of MB onto loofah is an extremely rapid reaction process. The rapid reaction rate could be ascribed to a large number of vacant sites available at the initial stage; as a result an increased concentration gradient exists between the MB molecules in solution and on the adsorption surface.

4.3.2. Pseudo-First-Order Kinetics. The parameters derived from the pseudo-first-order kinetic model and the correlation coefficient (r^2) of the sorption of MB on loofah at different initial concentrations is presented in Table 3. The values of the correlation coefficients (r^2) of the pseudo-first-order plots were poor (0.410–0.781). The experimentally determined equilibrium dye sorption capacity $q_{e(\text{exp})}$ was compared with the predicted values, from the pseudo-first-order plot $q_{e(\text{mod})}$ and large disparities in values were observed. The poor correlation coefficient values and the large disparity between the $q_{e(\text{exp})}$ and $q_{e(\text{mod})}$ values are pointers to the inability of the pseudo-first-order model to adequately describe this sorption process.

4.3.3. Pseudo-Second-Order Kinetics. The applicability of the pseudo-second-order kinetic model to the data obtained from the sorption of MB onto loofah is presented in Figure 4 and 5. The pseudo-second-order parameters and the correlation coefficient values are presented in Table 3. From the results presented in Table 3, it can be inferred that increase in MB concentration caused an increase in the equilibrium sorption capacity, q_e , initial sorption rate, h , but reduced the overall sorption rate, k_2 . The values of the r^2 were extremely high ($r^2 = 1.000$). The q_e value was predicted by applying the calculated kinetic constants in their corresponding kinetic expressions for MB. The predicted q_e values from the pseudo-second-order kinetic model for the sorption of MB onto loofah at different initial concentration are shown in Figure 4. The results presented in Figure 4 showed that for the entire sorption period, and all the initial concentrations used, the pseudo-second-order expression adequately predicts the sorption kinetics.

The extremely high values of r^2 and the calculated values of the predicted equilibrium sorption capacity, q_e , which are very much in agreement with experimental data for all initial MB concentrations, confirm that the sorption process follows a pseudo-second-order mechanism. According to Ho and McKay,¹⁴ if the dye uptake is chemically rate controlled, the pseudo-

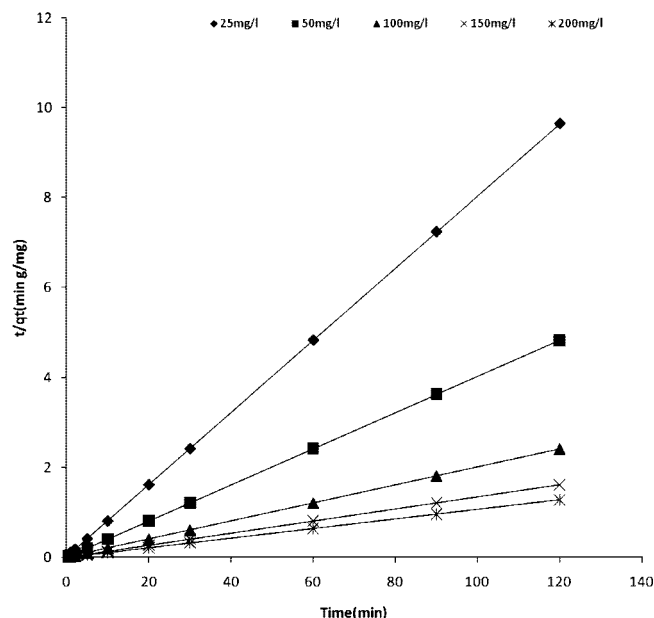


Figure 5. Pseudo-second-order plot of the sorption of MB on loofah at different initial MB concentration.

second-order constants will be independent of particle diameter and flow rate and will depend on concentration of the ions in solution.

The corresponding linear plots of the values of q_e and h against C_0 were regressed to obtain expression for these values in terms of the initial MB concentration with high correlation coefficients of 0.999 and 0.922, respectively. The empirical parameters have the following values:

$$A_q = 0.504; \quad B_q = 0.058; \quad r^2 = 0.999$$

$$A_h = 5.765; \quad B_h = 48.24; \quad r^2 = 0.922$$

Consequently, it was further considered that q_e and h can be expressed as a function of C_0 for MB as follows:

$$q_e = \frac{C_0}{A_q C_0 + B_q} \quad (20)$$

$$h = \frac{C_0}{A_h C_0 + B_h} \quad (21)$$

Substituting the values of q_e and h into eqs 20 and 21 and then into eq 6, the rate law for a pseudo second order and the relationship of q_e , C_0 , and t can be represented as follows:

$$q_t = \frac{C_0 t}{5.765 C_0 + 48.24 + (1 \times 0.504 C_0 + 0.058) t} \quad (22)$$

Equation 22 represents the generalized prediction models for MB sorbent at any time and the initial MB concentration within the given range. The equation can be used to derive the amount of dye sorbed at any given concentration and reaction time.

4.4. Diffusion Processes. Removal of a solute from solution using an adsorbent involves solute transfer, which is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. In order to investigate the possibility of dye being transported within the pores of the loofah, the experimental data were fitted into an intraparticle diffusion plot and the intraparticle diffusion

Table 4. Intraparticle Diffusion Parameters for the Sorption of MB by Loofah at Different Initial Concentrations (mg/L)

init concn (mg/L)	K_{id1}	intercept	r^2	K_{id2}	intercept	r^2
25	2.835	7.581	0.949	0.533	10.88	0.748
50	5.787	14.81	0.979	0.950	21.85	0.765
100	9.194	33.01	0.944	1.874	43.47	0.793
150	19.72	43.37	0.956	1.901	68.33	0.781
200	22.18	58.12	1.000	1.860	87.24	0.823

parameters are presented in Table 4. The plot of amount sorbed q_t (mg/g) versus $t^{0.5}$ ($\text{min}^{0.5}$) in (Figure 6) shows that the sorption process followed two distinct phases. These types of multilinearity, in the shape of the intraparticle diffusion plot, for MB adsorption have been reported.^{13,16,22} The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds via surface sorption and an intraparticle diffusion stage. The initial curved portion of the plot indicates boundary layer effect; the second portion is due to intraparticle diffusion. The slope of the second portion of the plot is defined as the intraparticle diffusion parameter k_{id} ($\text{mg/g min}^{0.5}$). On the other hand, the intercept of the plot reflects the boundary layer effect. The larger the value of the intercept, the greater the contribution of the boundary effect.²³ Panday et al.²⁴ opined that the deviation of the straight lines from the origin (Figure 6) may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption. The calculated intraparticle diffusion coefficient k_{id} values obtained from the plots are 1.860, 1.901, 1.874, 0.950, and 0.533 $\text{mg}/(\text{g min}^{0.5})$, which indicates a reduction in the k_{id} value as the initial MB reduced from 200 to 25 mg/L. The linear correlation (r^2) of the plot was found to be low (0.823–0.748). The multiple nature of the intraparticle plot, the deviation of the straight line from the origin, and the low linear correlation of the intraparticle portion of the multilinear steps show that the intraparticle diffusion plot is not the sole rate-controlling step in the sorption of MB onto loofah.

Sequel to the inability of the intraparticle diffusion model to satisfactorily describe the sorption of MB by loofah, the liquid film diffusion model was also used in the analysis of the data obtained. In order to test the possibility of MB molecule diffusion from the bulk liquid phase to the surface of the loofah playing a significant role in the determination of the rate of

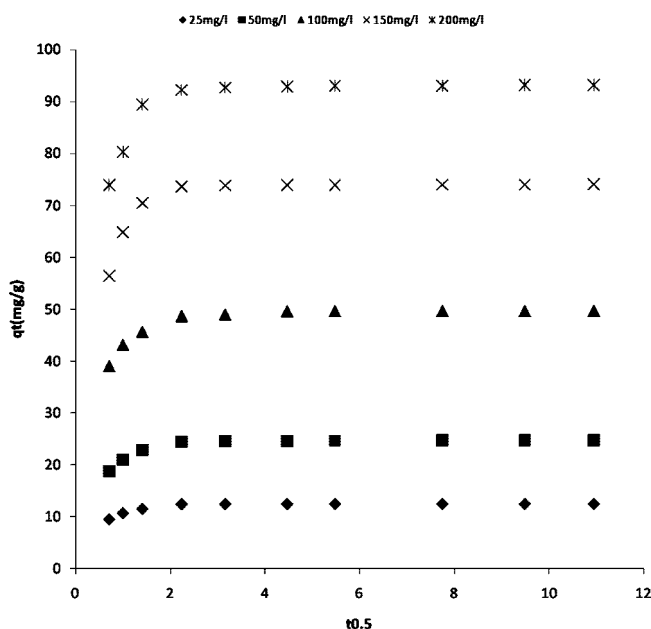


Figure 6. Intraparticle Diffusion plot of the sorption of MB on loofah at different initial MB concentration.

Table 5. Liquid Film Diffusion Parameters for the Sorption of MB by Loofah at Different Initial Concentrations (mg/L)

init concn (mg/g)	overall			first 5 min		
	K_{fd2}	intercepts	R^2	K_{fd1}	intercepts	R^2
25	0.048	3.856	0.414	0.905	0.939	0.994
50	0.037	2.961	0.576	0.605	0.605	0.994
100	0.055	3.307	0.572	0.503	0.503	0.988
150	0.045	3.680	0.477	0.793	0.793	0.988
200	0.067	3.245	0.560	0.662	0.662	0.953

adsorption, $-\ln(1 - F)$ was plotted against t , in accordance with the liquid film diffusion model. A linear plot of $-\ln(1 - F)$ versus t , with zero intercept, would suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the loofah.

This was tested for the entire period of study and for the first 5 min of the sorption process. The values of the liquid film diffusion parameters are presented in Table 5. The values of the intercepts of the plots were closer to the origin at the inception of the sorption process than that of the overall sorption process. This is a pointer to the significance of liquid film diffusion in rate determination at the inception of the sorption of MB by loofah. The linearities of the plots were also higher for the first 5 min than when the overall sorption process was considered.

4.5. Desorption Studies. 4.5.1. Batch Desorption Studies. In order to explore the possibilities of loofah regeneration for reuse and the recovery of the sorbed dye, batch desorption studies were carried out. Mall et al.²⁵ reported that desorption studies could be used to elucidate the mechanism of an adsorption process. If the dye adsorbed on the adsorbent could be desorbed by water, it can be said that the attachment of the dye onto the adsorbent is by weak bonds. If strong acid or strong base can desorb the dye, the attachment of the dye to the sorbent is regarded as ion exchange. If organic acid can desorb the dye, the adsorption of the dye onto the adsorbent is taken to be chemisorption.²⁵

Different eluting solvents (deionized water, HCl, NaOH, and CH₃COOH) that cut across these classifications were used in the desorption of the MB from the loofah. The results obtained are presented in Figure 7. A very low desorption of the dye was observed when NaOH and deionized water were used while an appreciable amount of dye was desorbed when HCl and CH₃COOH were used separately, though HCl gave the optimum dye desorption (Figure 7). The appreciable amount of dye desorbed with the use of both HCl and CH₃COOH could be ascribed to the role of both ion exchange and chemisorption in the uptake of MB by loofah. An overview of the total amount of dye desorbed from the loofah showed that 82.23% of the dye adsorbed was desorbed by all the eluting solvent used. The undesorbed portion of the dye in the sorbate could be ascribed to the complex formation between the MB and the active sites on the loofah, and hence the inability of the eluting solvents to completely desorb the dye.

4.5.2. Fixed Bed Desorption. In a typical batch desorption system, the desorbed pollutants remain in the batch system, making a complete desorption difficult. Moreover, applicability of the data to most treatment system, where contact time is not sufficient for the attainment of equilibrium is limited. Fixed bed desorption allows more efficient use of the biosorbent as a consequence of the enhanced use of the pollutant concentration difference between solution and sorbent.

Desorption procedure in a fixed bed is described using the concept of an elution curve, which is also known as a desorption step. The elution curve normally has an unsymmetrical fre-

quency distribution, with a rapid increase of the released sorbate concentration followed by a flat diminution.²⁶ This produces the appearance of a peak that provides two important parameters: C_p , the maximum concentration peak, which measures the eluted sorbate at this point, and t_p , the time passed until the effluent concentration peak reached its maximum value (it gives an idea of the elution rate). The elution curve can be described by the elution efficiency (E). This parameter was obtained by dividing the sorbate mass desorbed (m_d) by the sorbate mass bound to the sorbent in the previous adsorption step (m_{ad}):

$$E (\%) = \frac{m_d}{m_{ad}} \times 100 \quad (23)$$

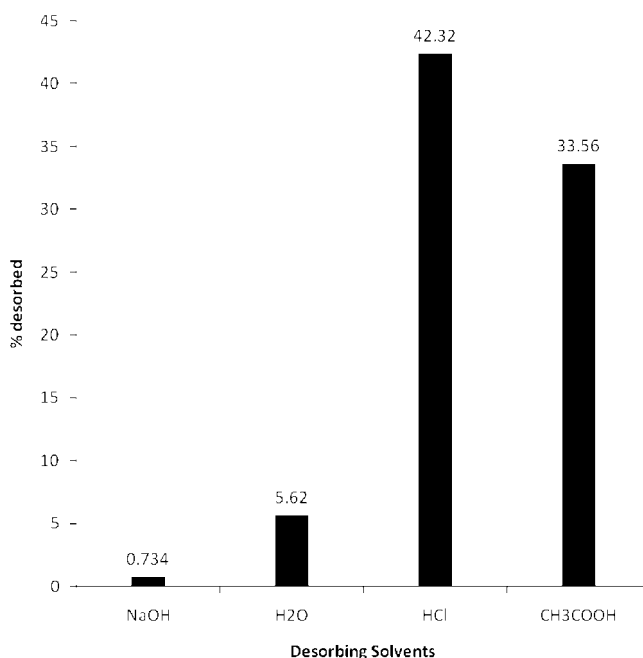
where m_d is calculated from the numerical integration of the regeneration curves from $t = 0$ to t_e with the following equation:

$$m_d = 0.06F \int_{t=0}^{t_e} C_d dt \quad (24)$$

where t_e is the time passed until residual sorbate concentrations (lower than 0.02 mg L⁻¹) were found in the effluent.

In the present studies, desorption was carried out in a fixed bed of previously MB loaded loofah using 0.1 M of HCl, the best eluting solvent, from the batch desorption studies. The elution curve obtained from the desorption of MB from loofah is presented in Figure 8. A rapid desorption of the sorbed MB was obtained at the inception of the studies and this was followed by a flat diminution. The C_p was 515 mg L⁻¹ and the t_p was 2 min. The elution efficiency, E , was 91. An elution efficiency of 91% could be considered to be high for any desorption process.

4.6. IR Spectroscopy Studies and Adsorption Mechanism. The nature of the possible loofah and MB interactions was studied by comparing the features of the spectra obtained from IR spectroscopy studies of MB-loaded and -unloaded loofah (Figure 9, a and b). The unloaded loofah sample showed a broad frequency at 3437 cm⁻¹ and was ascribed to N-H_{str}, present as NH₂ in either aromatic amine, primary amine, or amide. The band observed at 2924 cm⁻¹ was assigned to O-H_{str}

**Figure 7.** Batch desorption of MB from loofah using different eluting solvents.

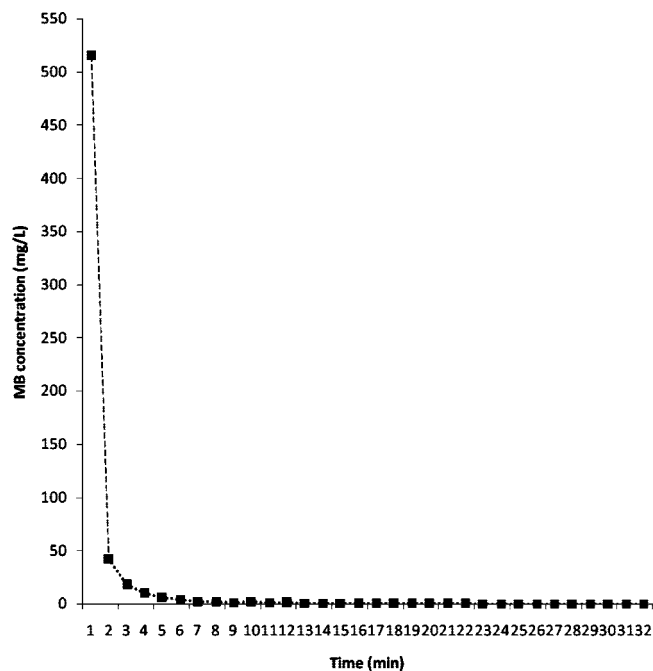


Figure 8. Elution curve for MB desorption in a fixed bed.

of carboxylic compounds. The strong peaks obtained at 1735 and 1646 cm^{-1} were assigned to $\text{C}=\text{O}_{\text{str}}$ of aldehydes and $\text{N}-\text{H}$ bond of amine, respectively. A number of bands obtained between 1059 and 1506 cm^{-1} were ascribed to the $\text{C}-\text{H}_{\text{def}}$ bond of alkane and alkyl groups. The absorption bands between 1621 and 1463 cm^{-1} are characteristics of the elongation of the aromatic $-\text{C}=\text{C}-$ bonds. The deformation vibration of the $\text{C}-\text{C}$ bonds in the phenolic groups absorbs in the region of 1500–1400 cm^{-1} . Peak around 1250 cm^{-1} is associated with the $\text{C}-\text{O}_{\text{str}}$ of the benzene ring. Peaks at 1100–1010 cm^{-1} are due to $\text{C}-\text{O}_{\text{str}}$ and $\text{C}-\text{H}_{\text{def}}$.

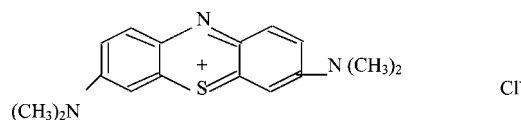
When the features of the peaks obtained from the IR spectra of the MB-unloaded spectra were compared with the spectra obtained from the MB-loaded sample, it was observed that there was a little shift in the absorption band from 3437 to 3422 cm^{-1} and an increase in the intensity of this absorption band. An increase in the intensity of the $\text{O}-\text{H}_{\text{str}}$ peak (2924 cm^{-1}) of the carboxylic functional group, $\text{C}=\text{O}_{\text{str}}$ of aldehyde (1735 cm^{-1}) and $\text{N}-\text{H}$ band of amine (1646 cm^{-1}) were noted. These showed that interactions occurred between the functional groups that absorbed at these frequencies and the MB dye molecules in the aqueous solution.

The surfaces of sorbents of biological origin have been reported to be made up of polar functional groups like aldehyde, ketone, acids, and phenolic groups. The results obtained from the determination of the surface functional groups, using Boehm titration procedure, revealed the predominance of these functional groups. The IR analysis also confirmed the presence of these functional groups and established interactions between the MB molecules and these functional groups.

The mechanisms by which dye molecules are adsorbed onto different biosorbents have been a matter of considerable debate. Different studies have supposed different mechanisms. These include ion exchange, surface adsorption, chemisorptions, microprecipitation complexation, and adsorption complexation. The results obtained from the fitting of the results, from the kinetic studies, to different kinetic models showed a higher fitting to the pseudo-second-order kinetic model. This is an indication of chemisorption as the paramount mechanism of

sorption of MB onto loofah. The results obtained from the desorption studies, using different solvents, showed that both chemisorption and ion exchange were the two underlying mechanisms that guided the sorption process.

Premised on the results obtained from the kinetic studies, desorption studies and the IR analysis, we surmised that the biosorption mechanism, underlying the sorption of MB onto loofah, might be partly ion exchange, chemisorption, and complexation between the positively charged MB molecules whose chemical structure is presented below:



and the polar functional groups identified on the loofah surface and could be represented by the schematic chemical equation presented under section 4.1.

5. Conclusion

The effects of pH on the MB uptake and initial MB concentration on the rate of sorption were examined in the present studies. The prospects of loofah regeneration in four different solvents were also examined. The amount of MB sorbed per gram of the loofah increased with increase in pH. The Freundlich isotherm models favored the prediction of the theoretical sorption capacity more than the Langmuir isotherm models. The sorption process was characterized by an initial rapid MB uptake which slows down with time as the sorption process proceeds. The pseudo-second-order kinetic model was found to best fit the experimental data within the time range of sorption. Studies on the mechanisms of the diffusion process showed that the diffusion of MB onto the loofah particle was not a straitlaced process but a combination of both intraparticle and liquid film diffusion processes. The results of the batch desorption studies showed that both chemisorption and ion exchange played prominent role in the sorption process. The elution curve obtained from the continuous desorption studies showed that the elution rate was very fast and a high elution efficiency could be obtained with 0.1 M HCl as an eluting solvent. The IR analysis confirmed the presence of polar functional groups and established interactions between the MB molecules and these functional groups.

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