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Equilibrium and Kinetic Studies of Methylene Blue (MB) Dye Biosorption on Macadamia Seed Husks

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Abstract
Biosorption of Methylene Blue (MB) from aqueous solution using macadamia seed husks (MSH) biomass obtained from dumpsite of the Jungle industry in Thika. The isotherm data fitted Freundlich mathematical models with maximum dye adsorption of 3.7171mg g^{-1}. Evaluation of the outcome of batch experiments indicated that the sorption process was greatly depended on the time of contact, initial concentration of the dye solution, temperature of the aqueous solution, adsorbent dosage and MSH particle size. The kinetics of the adsorption studies perfectly followed the pseudo second order kinetic model. The experimental data best fitted in the Freundlich adsorption isotherm equation with a high correlation coefficient of (R^2 = 0.9552) and hence it was used to explain the sorption equilibrium. The FTIR results revealed hydroxyl (-OH), methyl (-CH_3), and carbonyl (C=O) functional groups on MSH which a vital role in biosorption of MB dye. These results prove that MSH is an eco-friendly, locally available, effective and economical adsorbent for the removal of MB cationic dye from industrial wastewaters and aqueous solutions.

Keywords *Macadamia Seed Husks, Methylene Blue dye, Biosorption, Kinetics, equilibrium*

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I. Introduction

Wastewaters released from textile dying, cosmetics, leather, printing, paper-making, construction, food processing and wood industries bear solvent and dye remnants. The demand for dyes and colorants by industries has greatly increased due to increased industrialization and urbanization in the world. Discharge of effluents contaminated by organic dyes into the environment without treatment have caused severe health risks and environmental pollution challenge because dyes are toxic, carcinogenic, and mutagenic [1], [2], [3]. In addition, coloured effluents are a great hazard to the aquatic environs even in very small amounts because they obstract photosynthetic action by hindering light transmission and penetration into water bodies while reducing oxygen concentration hence interfering with the aquatic ecosystem [4]. The aromatic groups and complex structure of synthetic dyes like MB, makes it resistant to biodegradation, stable to light and oxidation. Therefore it's very difficult to efficiently treat dye bearing effluents through conventional treatment techniques such as ozonation, flocculation, membrane filtration, oxidation, precipitation, photo degradation, ion exchange and enzymatic decomposition [5], [6]. Drawbacks including long operation time, high cost, high production of sludge and ineffectiveness in the treatment of enormous range of aqueous solutions has largely limited their application [7], [8]. However, over time, the adsorption process has gained preference over the other methods due to its effectiveness, ease of operation, possibility of regeneration of the adsorbent used and affordability. In the recent past, great attention has been directed to investigating the efficiency of bio renewable adsorbents obtained from agricultural waste products with little economic value. A large number of such sorbent waste materials such as spirogyra [9], dried *Neurospora crrassa* [10], Agro-industrial and municipal waste [11], eco-friendly activated carbon prepared from *Sargassm wightii* seaweeds [12], Coffee Husks Powder [13] brewery waste biomass [14] and potato peels (*Solanum tuberosum*) [15] have been successfully studied.

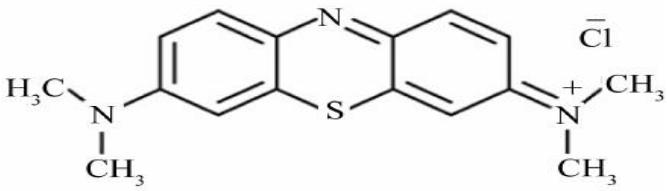

Fig. 1. Molecular structure of Methylene blue (MB) dye

Macadamia nut production has been on the rise for the past decade due to its ability to fetch higher prices in the market. The rise is expected to be higher in the next coming years because both small scale and large-scale famers are turning to macadamia farming [16], [17]. The edible macadamia kernel is highly nutritious as compared to other nuts. The nuts are mainly used for food or cold pressed for production of macadamia oil while the husks are mainly disposed in dumpsites polluting the environment. The rise in production has adversely affected the environment because the MSH are very hard and take a very long time to decompose hence filling landfills (which are very expensive to manage), providing breeding places for pathogens like mosquitoes, snails and snakes as well as causing soil leaching. At present, there is very limited information in the previously recorded literature where MSH has been utilized for the sorption process of MB dye. Therefore, efforts to provide an alternative use for the MSH are very necessary in solving the environmental pollution challenge. In this study, the efficiency of MSH in the biosorption of MB dye from aqueous solution was investigated. The effect of time of contact, MSH particle size, initial MB dye concentration, pH, adsorbent dosage, and different temperatures of aqueous solution was studied. The Freundlich and Langmuir adsorption isotherms were employed in studying equilibrium sorption process while pseudo second order kinetic model was used to analyse the adsorption kinetics. This research provides the opportunity to utilize MSH as an effective, economical and locally available adsorbent in the removal of MB dye from aqueous solutions.

II. Materials and Methods

2.1 Preparation of the Dye Solution

Methylene blue (MB) dye of analytical grade ($C_{16}H_{18}N_3CIS$; Molecular weight 319.85; λ_{max}=664 nm, Molecular Structure Fig.1) was obtained from Sigma Aldrich, Nairobi, Kenya and used without further purification. A stock solution of the dye (1000 mg/L) was prepared by dissolving the required amount of the dye powder in 250 mL of water and then topped up to one litre in a volumetric flask. To obtain lower concentrations of the dye solution suitable for the sorption studies, the stock solution was diluted using double distilled water. All reagents used were of analytical chemical grade. Drops of 0.1 M HCl and 0.1 M NaOH were used to adjust the pH as required. The concentrations of the MB dye solution were spectrophotometrically determined by measuring the absorbance at maximum wavelength of 664 nm against a blank reagent using (HALO RB-10) UV-VIS spectrophotometer.

2.2 Preparation of MSH

Dry macadamia seed husks (MSH) were collected from the Thika Jungle industry, Thika, Kenya, which processes macadamia nuts and washed with tap water thoroughly to remove impurities, colour, other soluble substances and adhering dust particles. The husks were dried, ground into smaller particles, extensively washed with double distilled water (until no colour was released) and afterwards sun dried them for around 2 days. The dried MSH powder were then separated into 6 different particle sizes 150 µm - 300 µm, 300 µm - 600 µm, 600 µm - 1180 µm, 1180 µm - 2360 µm, 2360 µm -4750 µm, 4750 µm using standard sieves and stored in well labelled airtight containers for use during the adsorption studies.

2.3 FTIR Characterization

The functional groups on MSH surface were identified by Fourier Transform Infrared Spectrophotometry (FTIR) using the potassium bromide disc technique. 5 g each (used and unused MSH) were ground into a uniform fine powder and mixed with potassium bromide (KBr) powder, at an approximate ratio of 1/200, triturated then made into a 1 mm pellets for FTIR analysis at frequency range of 4000 – 400cm^{-1}. Graphical results were then interpreted to ascertain the key compounds present in the matrix of the materials.

2.4 Batch Adsorption Experiments

Batch adsorption experiments were conducted in 100 mL conical flask containing 50 mL of MB solution and 0.4g of MSH at room temperature. The flasks were shaken on a KJ-201BD oscillator rotating at 240 rpm running at diverse time intervals. The concentrations of the dye solution prior and after adsorption were spectrophotometrically determined at λ_{max}=664 nm 664 nm. Aliquots 3 mL from the supernatant solution were put in 10 mm wide cuvettes and the absorbance measured against the blank reagent using a UV-VIS spectrophotometer (HALO RB-10) after every 10 minutes of shaking and returned in the aqueous solution immediately. All experiments were conducted in duplicates and only the average value was reported. The effect of the of initial dye concentration was studied by varying the initial MB concentration from 2.612 to 10.554 mg/L. 0.4g of MSH were added to 50 mL volume of the dye solution at normal temperature and pH. The difference in concentration of the residual dye solution was monitored through measuring of absorbance after every 10 minutes of shaking. The effect of contact time was investigated using 0.4 g of MSH and 50 mL of the dye solution of initial concentration 10.544 mg/L at room temperature and normal pH. The effect of particle size was studied by employing 50 mL volume of dye solution of 10.23 mg/L MB dye concentration, and 0.4 g of MSH of particle

sizes 300 - 600, 600 - 1180, 1180 - 2360, 2360 - 4750, and 4750 µm. The effect of adsorbent loadings was investigated using 10.554 initial MB concentration with dose loadings of 0.2 g, 0.4 g, 0.6 g, 0.8 g, 1.0 g, 1.2 g, 1.6 g. The effect of pH on the adsorption capacity of MB onto MSH was studied using 50 mL of dye solution of (10.554 mg/L) initial dye concentration and 0.4g of the adsorbent. The pH value of the samples was adjusted to a range of 2-12 using 0.1 M NaOH and 0.1 M HCl. The effect of temperature was studied at 25 °C, 30 °C, 40 °C, 50 °C, 60 °C, and 70 °C, using 0.4g of MSH on a constant temperature water bath (for each temperature) for around 100 minutes. The amount of the dye adsorbed at equilibrium onto MSH Q_e (mg/g) was calculated using equ.1 [18], [19] while the percentage dye removed was calculated using the equ.2 [20].

$$Q_e = \left(\frac{c_o - c_e}{w}\right) V \quad (1)$$

$$\% \text{ Removal} = \left(\frac{C_o - C_e}{C_o}\right) \text{x } 100 \quad (2)$$

Where; C_o and C_e are the initial and equilibrium MB dye concentrations in mg/L respectively, V the volume of the aqueous solutions in L and W weight of the adsorbent in grams. Adsorption isotherms and kinetics of dye removal was investigated using variable MB dye concentration at 25 °C, 0.4g of MSH powder mixed with 50 mL MB dye solution in 250 mL conical flasks quivering at 150 rpm. Aliquots of 3 mL were drawn at 10-minute time intervals and the remaining MB dye concentration determined.

III. Results and Discussion

3.1 FTIR Characterization of the Adsorbent

FTIR study was done to establish the core functional group present on the surface of MSH liable for dye binding. Fig. 2 shows the FTIR spectrum of MSH before and after adsorption. FTIR spectrum exhibited broad absorption peak at 3329.14 cm^{-1} due to the O-H stretching vibration of hydroxyl groups from a phenol or alcohol. The peaks observed at 2924.09 is owed to stretching vibration of aliphatic (SP^3) -CH groups while a strong infrared absorption peak at 1708.93 cm^{-1} is characteristic of Carbonyl compounds. The strong peak at 1022.27 cm^{-1} is due to C-O stretching in phenols, ethers and esters [21], [22]. After adsorption, the absorption peak shifted as follows 3329.14 to 3305.99 indicating O-H group participation in dye uptake. Similarly, absorption shift from 2094.69 to 2086.98 cm^{-1}; 2260.57 to 2268.29 cm^{-1} and 1022.27 to 1029,99 cm^{-1} indicates new bond formation between MB dye and C≡C, C–H and C-O functional groups in MSH respectively [23]. It was evident hydroxyl (-OH), methyl ($-CH_3$), and carbonyl (C=O) functional groups on MSH play a vital role in biosorption of MB dye. These results are characteristic of the chemical groups present in lignin, hemicelluloses, and cellulose, which are the key constituents of MSH [24].

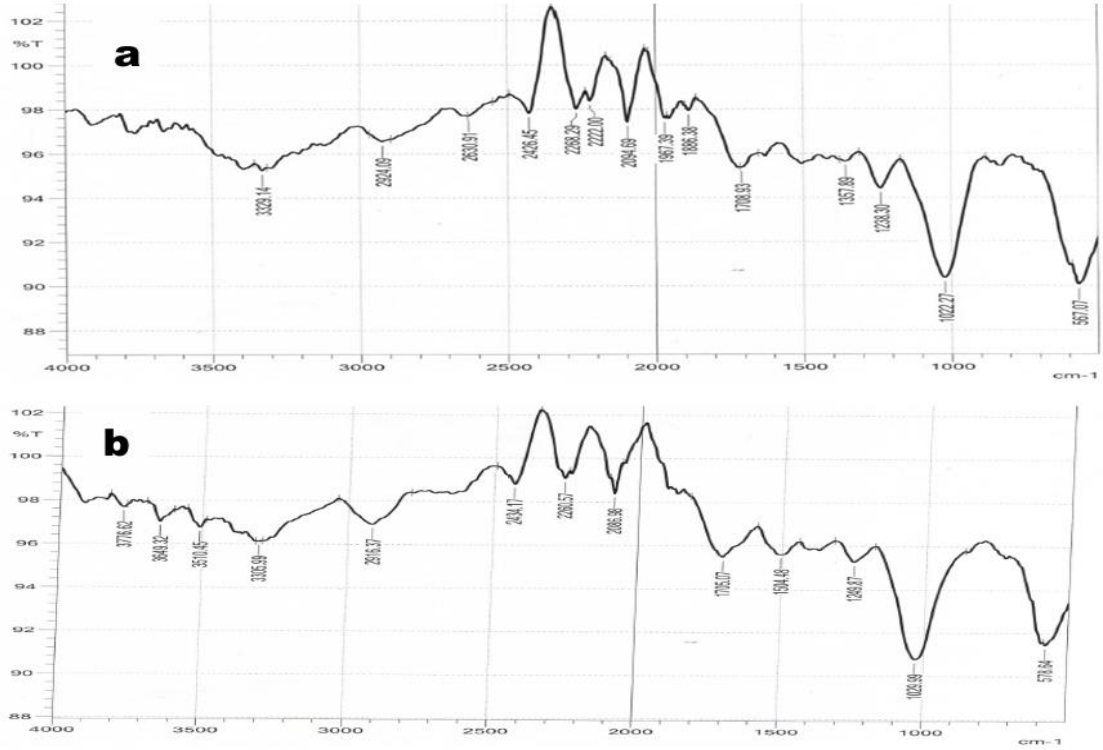

Fig. 2. FTIR spectrum of Macadamia Seed Husks (MSH): (a) before adsorption (b) after adsorption of MB dye

3.2 . Effect of contact time on MB dye biosorption

The effect of contact time is a very vital aspect in adsorption because it establishes the equilibrium time of adsorbate uptake by the adsorbent [25]. Fig.3. Presents a plot of the amount of MB adsorbed, q_e (mg/g) on MSH versus time in minutes. The results indicates that adsorption process reached equilibrium within the first 40 minutes, after which further sorption against time was negligible. It can be easily observed that the increase in contact time was accompanied by an increase in the quantity of dye removed. The high adsorption rate within the early stages of contact time can be ascribed to presence of large numbers of vacant adsorption sites during the initial times of the sorption process. The adsorption capacity of MB onto MSH reduced with elapsing time because most of the available adsorption sites on the MSH surface were occupied during the initial phase of the process. The remaining sites became difficult to be occupied due to repulsive forces between the solute MB molecules on the solid MSH adsorbent and the bulk phases thus the ability of the adsorbent reduced over time. A similar trend has been previously reported in the literature for synthetic dye removal [26].

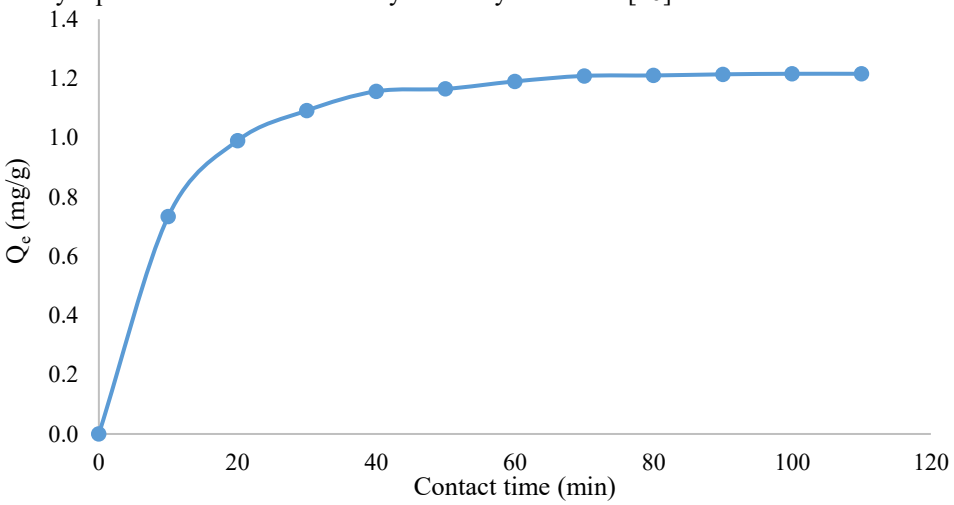

Fig.3. Effect of time of contact on MB dye biosorption. Conditions: (MB: 10.554 mg/L, MSH 0.4g/50ml, particle size; 300 - 600 µm, pH 10; at 25 ˚C).

3.3 . The effect of particle size on MB dye biosorption

Size of the particles greatly affects the available surface area for the biosorption process and a crucial parameter to consider when treating wastewaters. An increase in surface area increases the extent of adsorption [27]. Fig.4. Presents the results of the effect of different particle sizes on the adsorption process of MB dye onto MSH. From the plot, it is clear that the sorption of MB dye onto MSH gradually decreased with increase in MSH particle sizes. This outcome can be credited to the fact that smaller particles have large total external surface area when compared to large particles for equal quantity of adsorbent. This indicated that smaller particles with greater surface area were more suitable for the sorption process. Similar tendency was reported earlier in the literature for dye removal from effluents [24], [28].

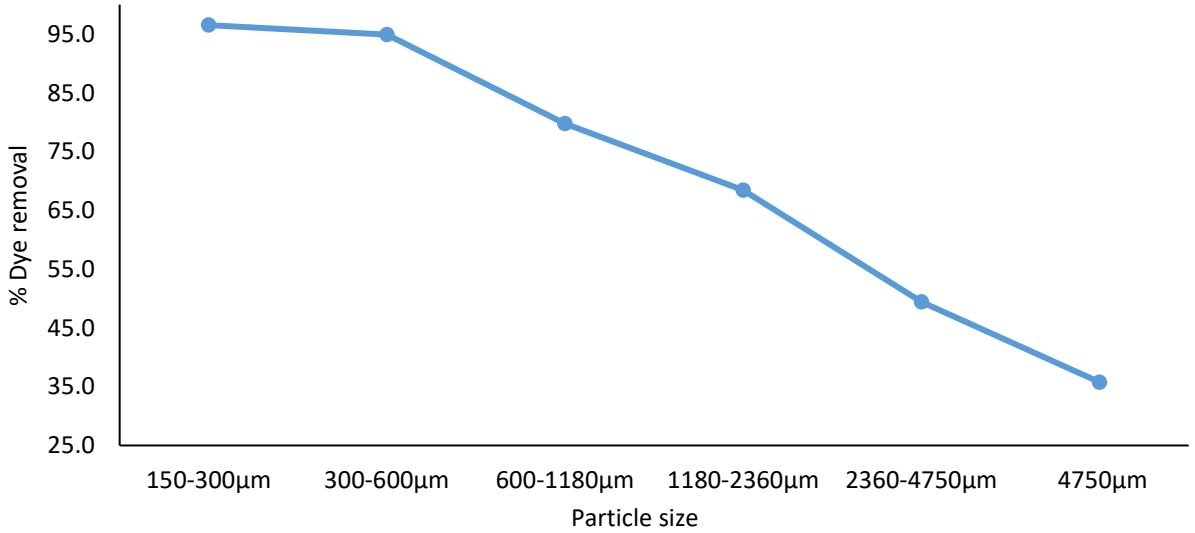

Fig.4. Effect of MSH particle size on MB dye sorption. Conditions: (MB: 10.554 mg/L, MSH 0.4 g/50 m, pH 10; at 25 ˚C).

3.4 . Effect of temperature on MB dye biosorption

Temperature affects adsorption by increasing the rate at which the dye molecules diffuses within the sorbent pores due to decrease in viscosity of the free solution [29]. The effect of temperature on adsorption of MB onto MSH was investigated and the results presented in fig. 5. The percentage MB dye removal increased with increase in temperature when studied at 25, 30, 40, 50, up to 60 ^{0}C. This indicated that the adsorption process was endothermic. Beyond 60^0 C there was a gradual decrease in the percentage removal of the dye. This specifies that 60 ^{0}C was the optimum temperature for the removal of MB dye onto MSH where 98.68% of the dye was adsorbed. The increase in the dye removal initially as the temperatures increased can be related to an increase in the mobility/ reduced viscosity of the MB dye molecules and thus more dye molecules could interact with the active sites on MSH adsorbent. This can further be attributed to an increase in the strength of the intermolecular forces between the active adsorption sites of the adsorbent and the MB dye molecules than those between the solvent and the MB dye molecules. The decrease of adsorption capacity beyond 60^{0}C can be explained by a decrease in the adsorptive forces between the dye molecules and the active adsorption sites on the MSH surface. The results obtained were similar to those reported for the sorption process of Reactive Black 5 dye onto chitin prepared from Shrimp shells [30], adsorption of methylene blue dye onto poly (cyclotriphosphazene-co-4,4'-sulfonyldiphenol)nanotubes [31] and adsorption of methylene blue dye onto activated carbon prepared from rice husks [32].

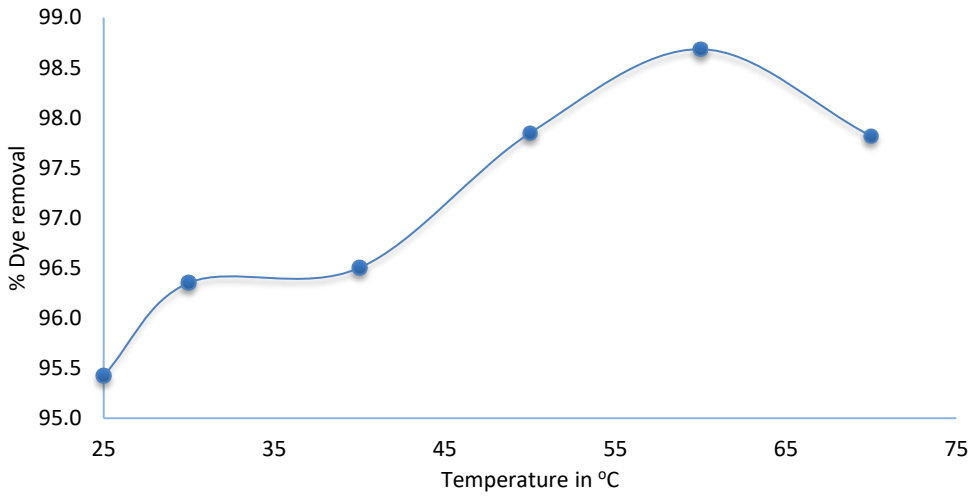

Fig.5. Effect of temperature on MB dye removal. Conditions: (MB: 10.554 mg/L, MSH 0.4g/50 mL, particle size; 300- 600 µm, pH 10; 25 – 70 ˚C).

3.5 . Effect of adsorbent dosage on MB dye removal

The study of this parameter is essential for it aids selection of the apposite dose to employ during sorption experiments. The effect of adsorbent dosage on the adsorption of MB dye onto MSH experiment was examined and the results presented in Fig.6. The outcome indicate that the percentage of dye adsorbed increased as the adsorbent dosage increased from 0.2 g to 1.4 g. 0.4 g was selected as the most suitable dose for optimal dye removal. This observation can be attributed to greater surface area and high ratio of available active adsorption sites on the MSH surface to the MB dye molecules at higher adsorbent doses when compared to lower doses. These results were consistent with related studies previously reported [33], [34].

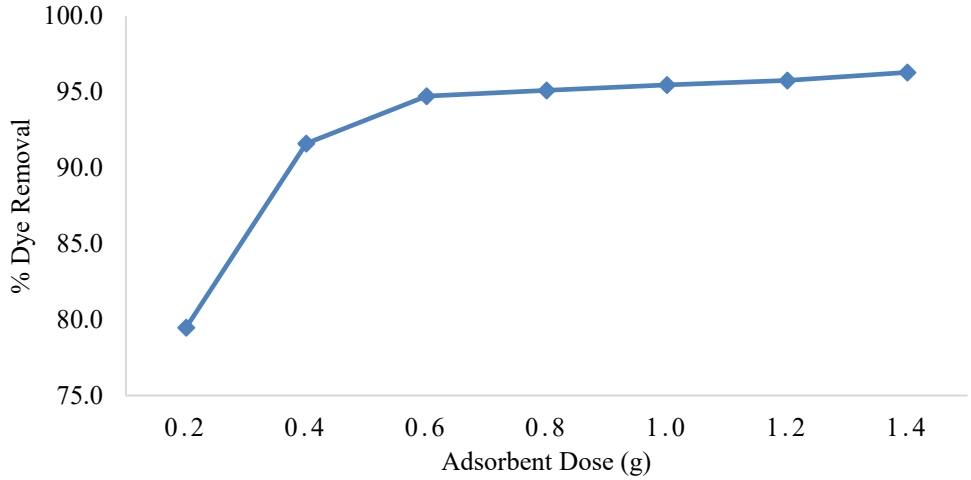

Fig. 6. Effect of MSH adsorbent dose on MB dye sorption. Conditions: (MB: 10.554 mg/L, MSH 50 mL, 300 - 600 µm, pH 10; at 25 ˚C).

3.6 . Effect of initial dye concentration on MB dye removal

The effect of different initial dye concentrations on the sorption process of MB onto MSH, is shown in Fig.7. The graph evidently shows that the amount of MB adsorbed increased with increase of the initial MB dye concentration. For example, the amount of MB dye adsorbed at equilibrium increased from 0.323 to 1.288 mg/g when MB dye concentration increased from 2.612 to 10.554 mg/L. This can be accredited to an increasing concentration gradient acting as an increasing driving force to overcome all mass transfer resistances of the MB dye molecules between the free solution and MSH solid phase leading to an increasing equilibrium adsorption process until saturation is attained.

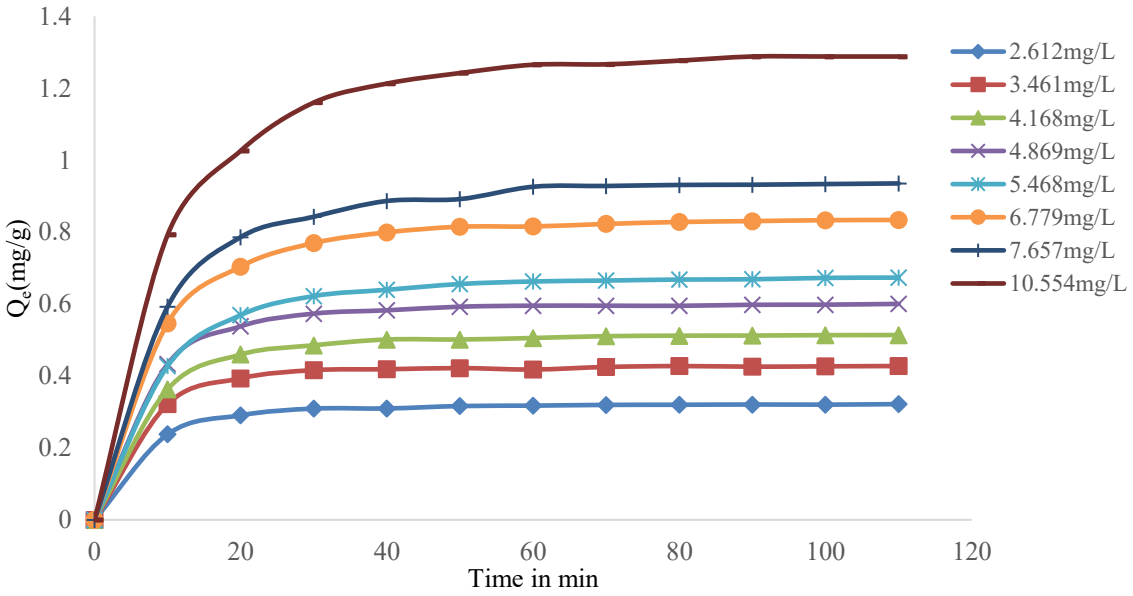

Fig. 7. Effect of initial dye concentration on MB dye sorption. Conditions: (MB: 2.612 - 10.554 mg/L MSH 0.4g/50ml; 300-600 µm, pH 10; at 25 ˚C).

3.7 Effect of pH MB dye sorption

The pH of the aqueous solution is an indispensable parameter which controls the sorption process by affecting the surface charge of the sorbent and the extent of ionization of the dye in solution [30]. Fig.8. illustrates a plot of the effect of pH on the adsorption of MB dye onto MSH on both acidic and alkaline conditions. The results point out that adsorption took place in both acidic and basic conditions. However, the percentage dye removal was higher in basic conditions when compared to acidic conditions. Maximum adsorption was attained at pH 10 with a percentage dye removal of 95 %. This outcome can be credited to change in MSH surface charge, dissociation of functional groups on the sorption sites of the sorbent material and aqueous chemistry of MB molecules. Similar results were obtained for the adsorption of recalcitrant dyes from solution [26], [32].

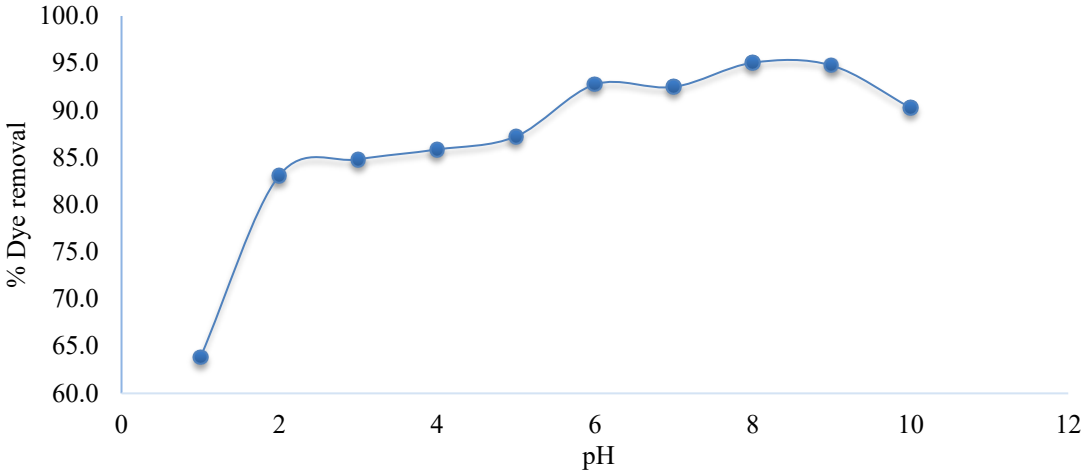

Fig.8. Effect of pH on MB dye removal. Conditions: (MB: 10.554 mg/L, MSH 0.4g/50ml; 300-600 µm; at 25 ˚C).

3.8 Adsorption Isotherms

Adsorption isotherms are ultimate in describing the adsorbent surface-adsorbate particles interaction at equilibrium. Langmuir and Freundlich isotherm models were utilized to expound the sorption mechanism of MB on MSH at equilibrium. The Langmuir model have been effectively applied for explaining single layer sorption on particular sites of equal energy distributed on a homogenous sorbent surface [35], [36]. The integral linear form of the Langmuir model [37] is given by;

$$\frac{C_e}{Q_e} = \frac{1}{Q_{Max}b} + \frac{1}{Q_{Max}}C_e \qquad (4)$$

Where; Q_e is the MB quantity on the MSH surface at equilibrium (mg/g), Q_{max} is the maximum MB capacity that can be adsorbed per unit weight of sorbent (mg/g), C_e the MB concentration in the aqueous media at equilibrium (mg/L) and b (L/mg) the Langmuir constant related to the affinity of the binding sites. Q_{max} and b were obtained from the slope gradient and intercept of the plot of $\frac{1}{Q_e}$ as a function of $\frac{1}{C_e}$.

The separation factor (equilibrium parameter) R_L articulated by equ.5 can be used to evaluate the essential characteristics of the Langmuir isotherm[38].

$$R_L = \frac{1}{1+b\,(C_o)} \qquad (5)$$

Where C_o (mg/g) is the initial MB concentration and b (L/mg) the Langmuir constant related to the affinity of the binding sites. The R_L value is an indicator of the shape of the isotherm as either unfavourable (R_L > 1), linear (R_L = 1), favourable (0< R_L<1) or irreversible (R_L = 0). Fig.9 presents a linear isotherm of the Langmuir model. The results indicate a regression coefficient value of R^2 = 0.9464, maximum single layer MB capacity adsorbed, Q_{max} = 2.3834 mg/g and b = 4.7301 L/mg. The dimensionless parameter (separation factor) ranged between zero and one (0< R_L <1) (R_L = 0.0196) depicting the sorption of MB dye onto MSH as favourable. Single layer sorption model was therefore applicable in explaining the MB adsorbate - MSH adsorbent interaction at equilibrium. The equilibrium data was similarly assessed using the Freundlich model perfect for multilayer sorption on homogenous adsorbent surface [18] and is given by equ.6.

$$ln\ Q_e = ln\ K_f + \frac{1}{n} ln C_e \qquad (6)$$

Where; Q_e is the amount of MB dye adsorbed at equilibrium (mg/g), C_e the concentration of dye solution at equilibrium (mg/L), K_f and n are the Freundlich constants, signifying the adsorption capacity of the adsorbent and adsorption intensity respectively. A value of n, (n > 1) is an indicator of favourable multilayer adsorption conditions. The values of n and K_f were calculated from the gradient and intercept of the plot of ln Q_e vs ln C_e (Fig.10). Freundlich adsorption capacity constant, K_f = 3.7171 (mg/g) (L/mg), sorption intensity, n = 1.5446 and regression coefficient value, R^2 = 0.9552 giving a favourable fit to the multilayer adsorption model. Therefore, the equilibrium data obeyed both the Langmuir and Freundlich sorption isotherms models. However, considering the higher regression coefficient of the Freundlich model, it could be argued that multiple layer adsorption dominated, making the Freundlich model the most apposite for describing the adsorption of MB on MSH. Related conclusions have been recorded [32], [39].

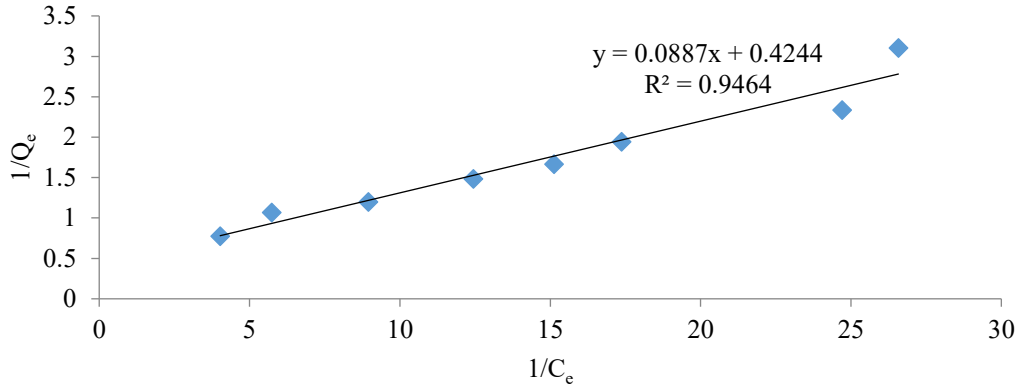

Fig.10. Langmuir adsorption isotherm for MB dye sorption on MSH

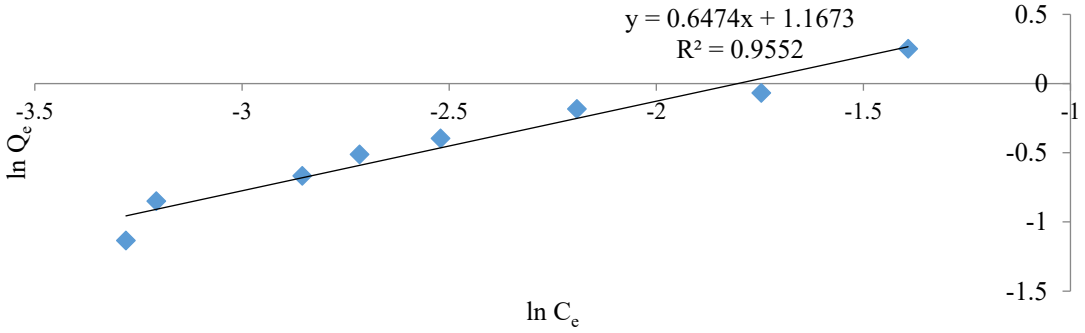

Fig.11. Freundlich adsorption isotherm for MB dye sorption on MSH

3.9 . Adsorption Kinetics

The kinetics of process was studied by modelling the experimental data with the pseudo second order kinetic model equation 7.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

The plot of $\frac{t}{q_t}$ versus t of the pseudo second order kinetic model for the sorption of MB onto MSH at different initial dye concentrations ranging from 2.612 to 10.554 mg/L is shown in Fig 10. The values of the rate constants K_2, the quantity of dye adsorbed at equilibrium q_e, and the R^2 for the tested concentrations were calculated and summarized in Table 1. The resulting values of the Pseudo-second order correlation coefficients (R^2) of the examined data were very high i.e. ($R^2 > 0.99$). The theoretical (q_e.cal) values were also very close to the experimental (q_e exp) values for all the initial dye concentrations tested concluding the sorption process of MB onto MSH followed the pseudo-second order kinetic model perfectly. These indicated that the overall rate of MB sorption depended on time and concentration and that chemisorption including valency forces through exchange or sharing of electron between adsorbate and adsorbent dominated. Similar results have been reported previously in the literature [25], [33], [40], [41].

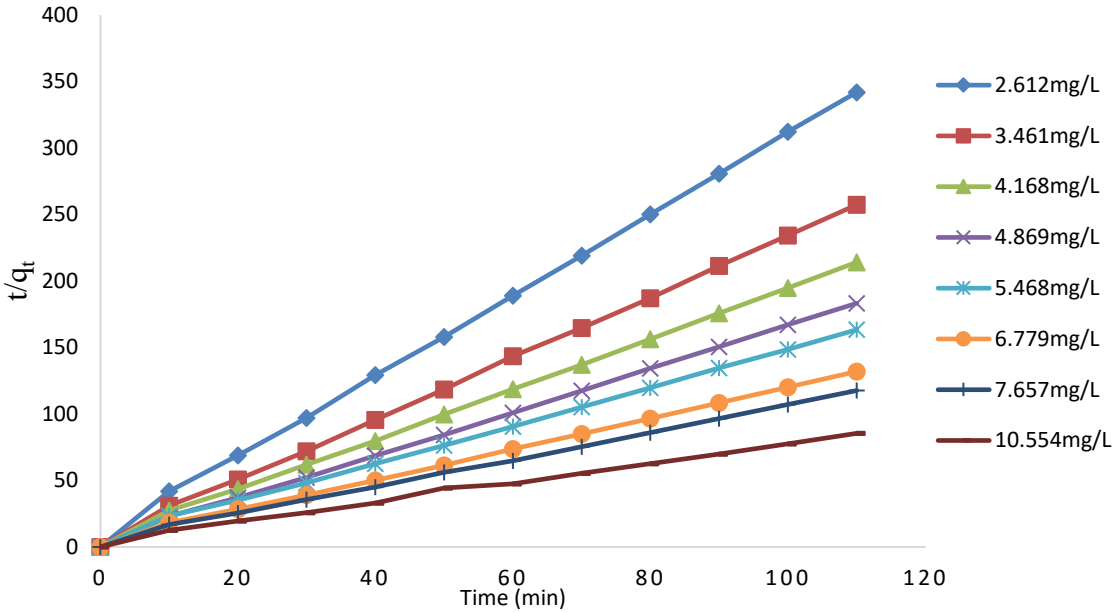

Fig.10. Pseudo-second order kinetics plot for the sorption process of MB dye by MSH

Table 1. The pseudo second order kinetic model

Concentration of MB (mg/L)	$Q_{e\ cal}$(mg/g)	$Q_{e\ exp}$ (mg/g)	K_2(g/mg/min)	R^2
2.612	0.327	0.322	1.587	0.9995
3.461	0.434	0.428	1.398	0.9995
4.168	0.525	0.514	0.842	0.9993
4.869	0.611	0.6	0.812	0.9993
5.468	0.694	0.673	0.438	0.9985
6.779	0.858	0.834	0.372	0.9987
7.657	0.968	0.935	0.287	0.9983
10.554	1.342	1.288	0.160	0.9962

IV. Conclusion

This study demonstrates that MSH is an effective adsorbent in the removal of MB dye from aqueous solutions. Experimental data clearly showed that the sorption process greatly depended on the variable parameters like contact time, particle size, initial dye concentration, MSH dosage and temperature. The percentage of MB dye adsorbed onto MSH was found to increase with increase in contact time, temperature and adsorbent dosage. The percentage of dye removal also increased with increase in initial dye concentration and decreased with the increase of particle size. FTIR results showed the present of lignin, hemicelluloses and cellulose groups in MSH and responsible for dye uptake. The results indicated that the experimental data fitted better in the Freundlich adsorption isotherm with a higher correlation coefficient (R^2 = 0.9552) than the Langmuir adsorption isotherm model (R^2 = 0.9464). The kinetics studies indicated that sorption process perfectly followed the pseudo- second order kinetic model. These results conclude that MSH can be used effectively as an economical and locally available adsorbent for the removal of MB basic dye from wastewaters and aqueous solutions.

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