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Brown Sea Bean (Mucuna Sloanei) Shell, an Effective Adsorbent for Cationic Dye Removal

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Abstract

Brown sea bean (mucuna sloanei) shell has been used as an alternative adsorbent for removing cationic dye from aqueous medium. The effects of pH, initial dye concentration, temperature, and contact time were investigated using the batch technique. The result indicated that the adsorption was strongly dependent on the four factors. The FTIR analysis of the functional groups present on both the precursor and the activated carbon revealed that many peaks present on the precursor disappeared on the activated carbon while those remaining were weak. This is as a result of breakage of many bonds on the KOH impregnated precursor leading to the liberation of volatile species. The kinetic data were fitted to first order model, second order model and Boyd model. Dye uptake process followed the Boyd kinetic model more appropriately. The isotherm data were fitted to Langmuir and Freundlich isotherm models, the Freundlich isotherm best fitted the process. Thermodynamic parameters such as: Gibb's free energy change (ΔG), standard enthalpy change (ΔH), standard entropy change (ΔS) calculated, indicated spontaneous and endothermic nature of the process.

Keywords: Activated carbon, Brown sea bean (mucuna sloanei), Cationic dye, Methylene blue, Thermodynamic study

Introduction

Dyes used in textile industries have complex aromatic molecular structures which make them inert and biodegradably difficult when discharged into the environment [1]. When discharged into water bodies, they are harmful to aquatic lives. Even at very low concentration, it can be highly toxic to aquatic systems. They can hinder light penetration and may in consequence disturb biological processes in water bodies [1]. Methylene blue (MB) is a cationic dye that is most commonly used for colouring among all other dyes of its category and is generally used for dying cotton and silk [3]. This dye has been studied because of its known strong adsorption onto solids, and it often serves as a model compound for removing organic contaminants and coloured bodies from aqueous solutions [4,5,6]. Due to the harmful impacts of such dye, it is environmentally important to remove them from waste streams before discharge the public water sources.

In the last few decades, adsorption has been proved to be a well-established and cheap pollutant removal process among other types of existing effluent treatment techniques due to its easy applicability, and good efficiency.

From different available adsorbents, activated carbons are one of the most popular for both liquid and gas purification due to their unique properties, including porous structure, high specific surface areas and large sorption capacities [7]. In spite of its extensive use in waste water treatment, commercial activated carbon remains an expensive material [8]. This has lead many researchers to find out cheaper sources to prepare activated carbon.

Previously, coal, lignite and wood which are carbonaceous sources are commonly used precursors for production of activated carbon, but recently, agricultural by-products have been successfully used to produce activated carbon due to their high carbon and low ash content [8].

Mucuna belongs to the enormous legume family fabaceae. There are many species of Mucuna throughout tropical regions of the world, including M.Urens, M. Pruriens and M. Sloanei. Most species of Mucuna are climbing woody wines called lianas that twine through the rain forest trees like "botanical boa constrictors" [9]. It is found in the tropical and sub-tropical regions of the world. The seeds are brown in colour, commonly polished and are known as "sea beans because they are commonly carried by rivers into ocean.

The edible inner part of Mucuna solanei is used in preparing various soups as soup thickeners. In addition to their thickening property, it has gelatin properties and imparts a gummy texture when used in soup [10]. The frequent use of this legume as a thicker in soups results in pollution of the environment with the inedible shells.

In this study, the inedible part of the sea bean (mucuna sloanei) shell was used as a precursor in the production of activated carbon for MB removal .

Materials and methods

Preparation of sea bean (mucuna sloanei) shell.

The seeds were sorted to remove dirts and stalks. The cleaned seeds were cut open to remove the shell from the inner edible part. The shell was washed and dried. The dried sample was stored for further use.

Adsorbate

Methylene Blue (MB) (C1. 52015) with empirical formular $C_{16}H_{18}N_3SC1$ and formular weight of 319.9g/mol was supplied by De Cliff Integrated Ltd Ogbete Enugu, Enugu State Nigeria (97% purity). It has maximum absorbance at wavelength 661nm.

Preparation of Activated Carbon

The preparation of the adsorbent was in accordance of the method used by [11] with slight modification.

Preparation of Methylene Blue Solution

Double distilled water supplied by Pymotech Research Center Abakpa Enugu State of Nigeria was used for the preparation of the solutions. A 1000mg/l stock solution was prepared and from there, necessary dilutions were made to obtain the desired concentration.

Characterization of Activated Carbon

The surface functional groups and structure were studied by fourier transform infrared spectroscopy [Buck 530 IR]. The FTIR spectra of the raw material and activated carbon were scanned at a wavelength of 600–4000nm to obtain its spectra lines.

Effect of pH on MB Adsorption

To study effect of pH on adsorption of MB on hamburger seed shell activated carbon, the experiments were carried out at 30mg/l, 50mg/l and 80mg/l initial concentration with 0.02g of the adsorbent per 50ml of the adsorbate at room temperature for 4 hours equilibrium time. The initial pH values were adjusted to 2,4,6,8,10 with 0.1M Hcl or 0.1m NaOH using pH meter (Jenway Model 3510, England). At the end of the process, the suspension was centrifuged and the residual dye was analysed using Shimadzu UV-Vis 1601 spectrophotometer. All the measurements were made at 661nm, a wavelength corresponding to the maximum adsorbance.

Effect of Dosage

The effect of adsorbent dosage on equilibrium uptake of MB was studied at initial MB concentration of 30mg/l, 50mg/l 80mg/l and 110mg/l at adsorbent dosage of 0.02g, 0.05g, 0.08g, 0.11g, 0.14g, 0.17g and 2g per 50mls of the solutions. The experiments were performed by shaking the different adsorbent concentration with the above different adsorbent dosage for 3 hours. After centrifugation the residual MB was analyzed.

Effect of Initial Concentration

The effect of different initial concentration of MB was analyzed using initial concentration of 30mg/l, 50mg/l, 80mg/l, 110mg/l, 140mg/l and 180mg/l at adsorbent dosage of 0.02g and pH of 4 and 10. The solutions were equilibrated for 4 hours after which they were centrifuged. The residual dye was analyzed.

Adsorption Isotherm

Batch isotherm studies were carried out in 250ml conical flask at different temperature of 303K, 313K, 323Km 343K on an Isothermal sheker for 6 hours to ensure equilibrium. 0.02g of the adsorbent was mixed with 50ml of 30mg/l, 50mg/l, 80mg/l and 110mg/l of the solution at different pH of 4, 8 and 10. The pH was adjusted using 0.1M Hcl or 0.1M NaOH before addition of the adsorbent. At the end of equilibrium time of 6 hours, the reaction mixture was centrifuged and the residual MB concentration analysed. The amount of MB adsorbent at equilibrium qe(mg/g) was calculated from the following equation (3).

$$qe = \left(\frac{Co - Ce}{W}\right)V \qquad (1)$$

Results and discussion

Infrared Spectroscopy Analysis

The well known activity, reactively and adsorption efficiency of activated carbon and other carbonaceous sorbents are mainly based and dependent on the various loaded functional groups on the surface of these sorbents [17]. FTIR spectroscopy is an important technique used to identify characteristics surfaces functional groups on the adsorbent, which in some cases are responsible for the binding of the adsorbent molecules.

The functional groups on the adsorbent surface were identified by analyzing the spectra using available literature [12], [13], [14], [15], [16].

Fig. 1 shows the FTIR spectra of the activated carbon and it's precursor in the range of 600-4000cm-^{1}. Several distinct and sharp absorption bands were observed as well as relatively low intensity peaks for all sample spectra.

The raw hamburger-shell shows indication of various surface functional groups. The wide peaks between 3185.033 – 3803.987 cm^{-1} indicates 0-H stretching vibration of hydroxyl functional groups including hydrogen bonding or adsorbed water. The peak at 2972.8 can be ascribed to C-H stretching which described the presence of –CH and ≡CH groups present in the lignin structure of the hamburger shell. The trichotomous peaks at 2743.85325, 2628.28106 and 2531.97435 cm^{-1} are attributed to C-OH stretching vibrations in carboxylic acid derivatives. The peaks in the ranges of 2266.137 – 2425.026cm^{-1} can be linked to the C≡C stretching vibration in alkyne groups. The peak at 1794.616cm-1 depicts –C = O stretching from carboxylic acid group. The band located at 1678.55cm^{-1} corresponds to the formation of oxygen functional groups based on highly conjugated C = O stretching in carboxylic or carboxylate group as well as carbonyl group. The skeletal C=C vibration in aromatic rings cause band at 1438.687cm^{-1}. The appearance of a band at 1364.13cm^{-1} can be attributed to C – O stretching vibration in carboxylate groups. The band at 1140.975cm^{-1} and band at about 1008.632cm^{-1} can be assigned to C-O stretching vibration in alcohols, phenols, or ether or ester groups. The bands at 867.49412cm^{-1} and relatively intense band at 773.2506cm^{-1} are C-H out of plane bending of benzene derivatives. Finally, the band caused by O-H out of plane bending vibrations band is located at 672.5205cm^{-1}.

The FTIR spectra of activated carbon are equally shown in fig. 1. Fewer functional groups were detected, indicating that the surface functional groups of hamburger shell experienced chemical changes during carbonization. Many peaks present in the raw hamburger shell spectrum absolutely disappeared in the activated carbon spectrum while those remaining were weak to a great extent. This is consistent with the breaking of many bonds in the KOH impregnated raw hamburger shell leading to the libration and elimination of volatile species and partial aromatization during carbonization [13], [17].

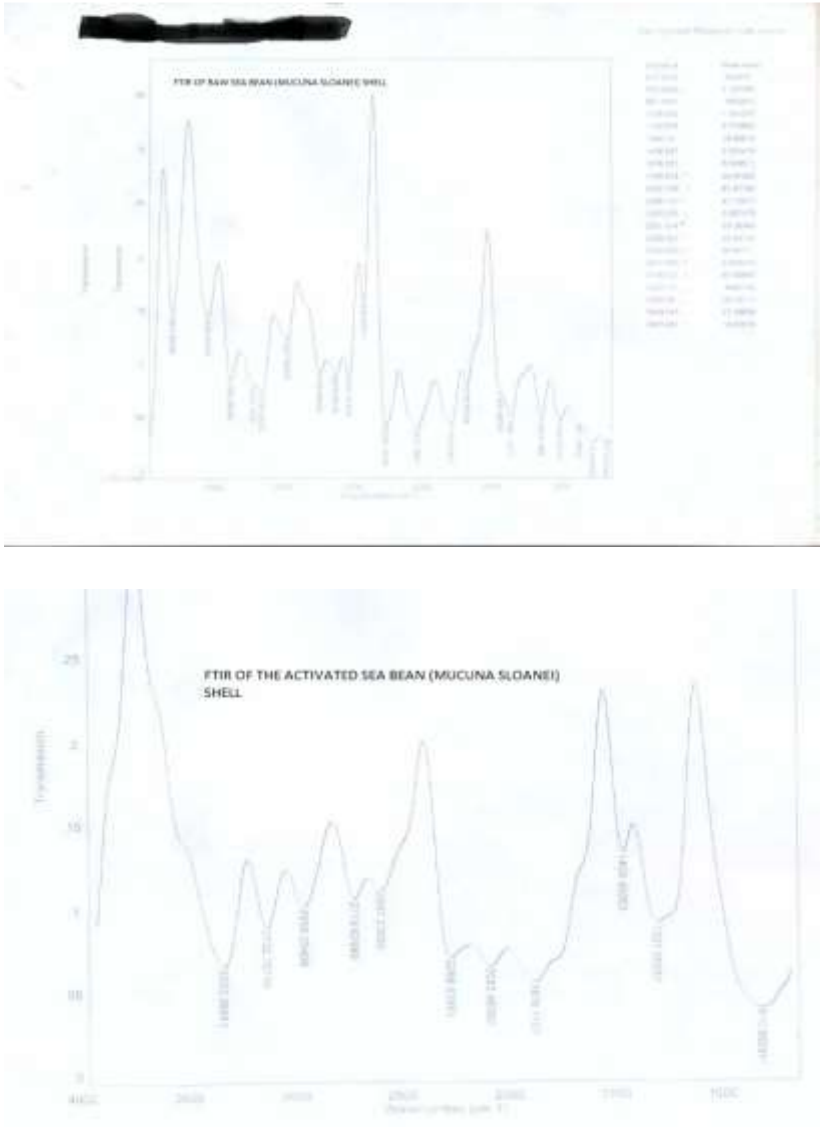
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Figure 1. FTIR analysis

Effect of pH

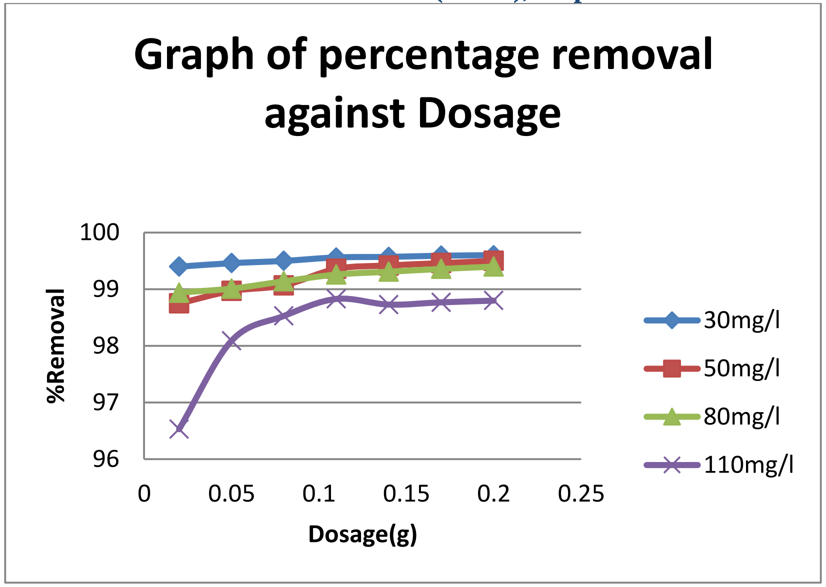
Activated carbons are species with amphoteric character; thus depends on the pH of the solution. Their surface might be positively charged or negatively charged [18]. The pH of dye solution plays an important role in the whole sorption process and particularly on the adsorption capacity because it affects the solubility of adsorbates, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. The pH [2 – 10] studies result in fig. 2 revealed that electrostatic and ion exchange activities between the MB and adsorbent surface increased at high pH. The percentage removal was 97.69% at pH 10.

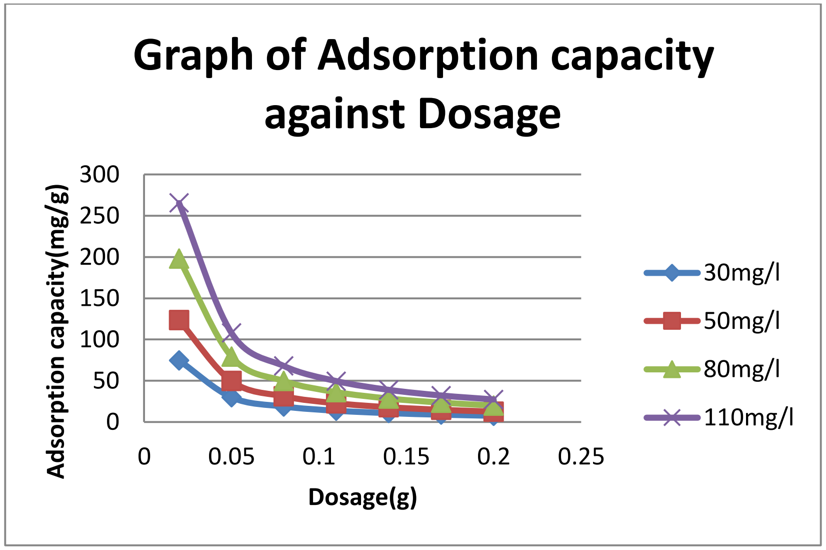
It is known that ionic dyes upon dissolution release coloured ions in solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge which in turn influenced by the solution pH [19]. At basic pHs, the negatively charged species start dominating and the surface tend to acquire negative charge while the adsorbate species are still positive charge. As the adsorbent surface is negatively charged, the increasing electrostatic attraction between negatively charged adsorbent particles and positively charged adsorbate species would lead to increased adsorption of dye.

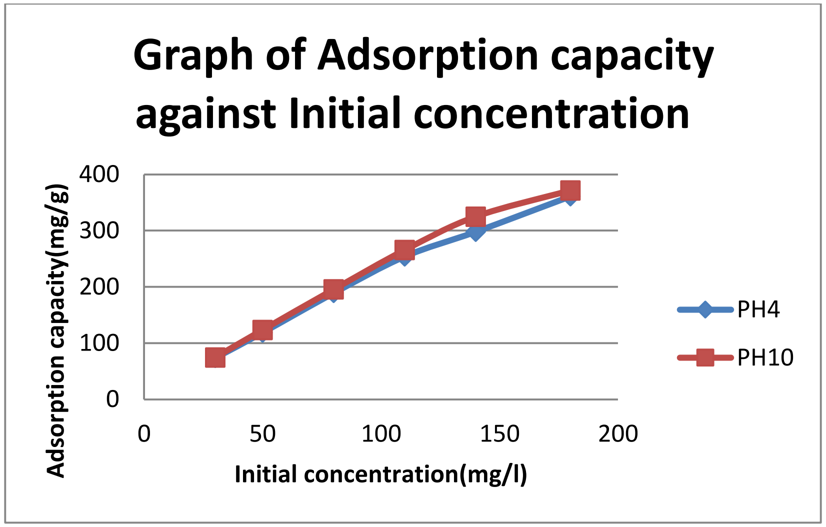
Effect of adsorbent dosage

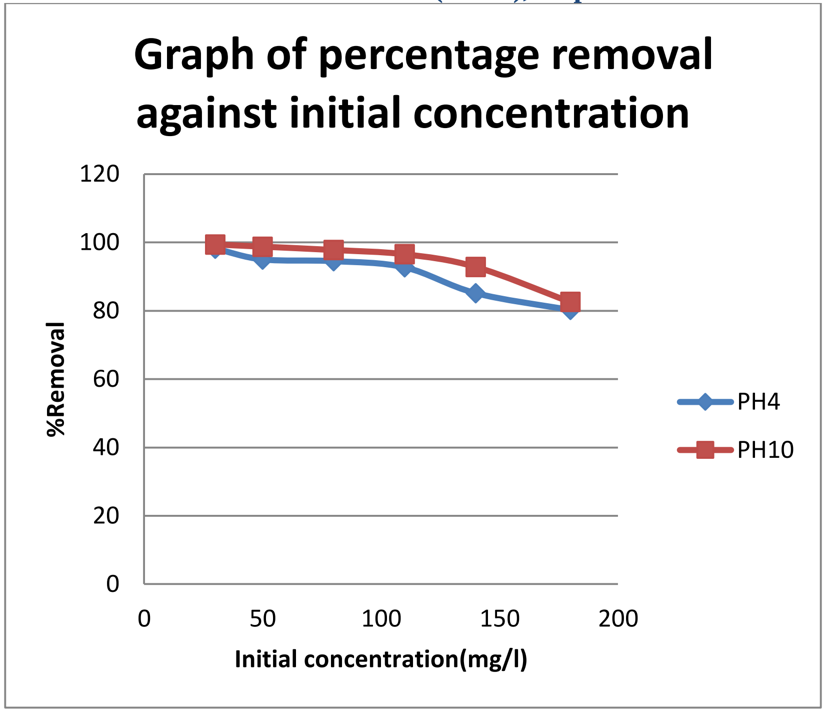
The adsorbent dosage in solution plays an important role in the dye uptake as well as in the percentage of colour removal [20]. Fig. 2 shows the effect of adsorbent dosage in the percentage removal of and the adsorptive capacity of MB at different initial concentration of the MB solution. From the graphs, it shows that the removal efficiency increased as the adsorbent dosage was increased at all the concentrations studied with higher effect at lower concentration. This adsorptive enhancement is ascribed to an increase in adsorption surface area of microspores and availability of removal adsorption site [20, 21]. The rate of removal decreased with increase in initial concentration because at higher concentration, the binding active site may be saturated.

On the other hand, the adsorbed amount of dye per unit mass of the adsorbent decreased with the increase in the adsorbent dosage. This can be attributed to the splitting effect of flux (concentration gradient) between adsorbates with increasing adsorbent concentration causing a decrease in amount of dye adsorbed onto unit weight of adsorbent [22,23]. Equally, the high adsorbent dosage may influence the physical characteristics of the solid – liquid suspensions, such as by increasing the viscosity and inhibiting the diffusion of dye molecules to the surface of the adsorbent [24]. Since the concentrations of MB were fixed, the adsorption capacity decreased as the adsorbent dosage increased.






Graph of Adsorption capacity against Initial concentration
Adsorption capacity(mg/g)
400
300
200
100
0
0
50
100
150
200
Initial concentration(mg/l)
PH4
PH10


Graph of percentage removal against initial concentration
%Removal
120
100
80
60
40
20
0
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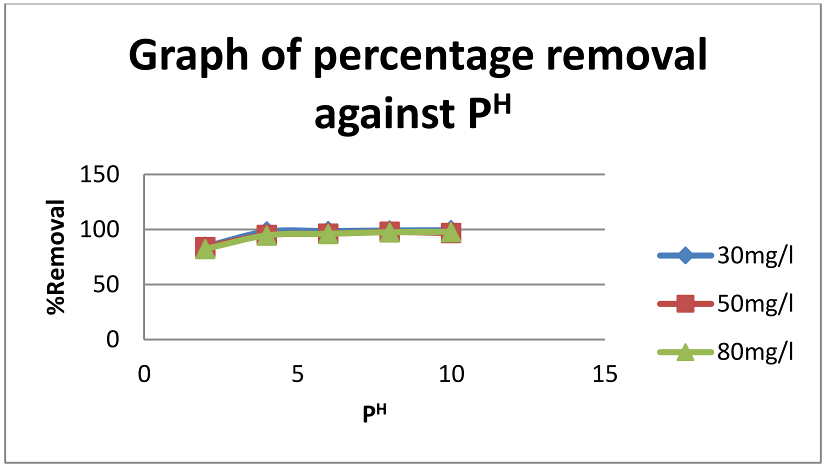
50
100
150
200
Initial concentration(mg/l)
PH4
PH10


Graph of percentage removal against P^H
%Removal
150
100
50
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0
5
10
15
P^H
30mg/l
50mg/l
80mg/l

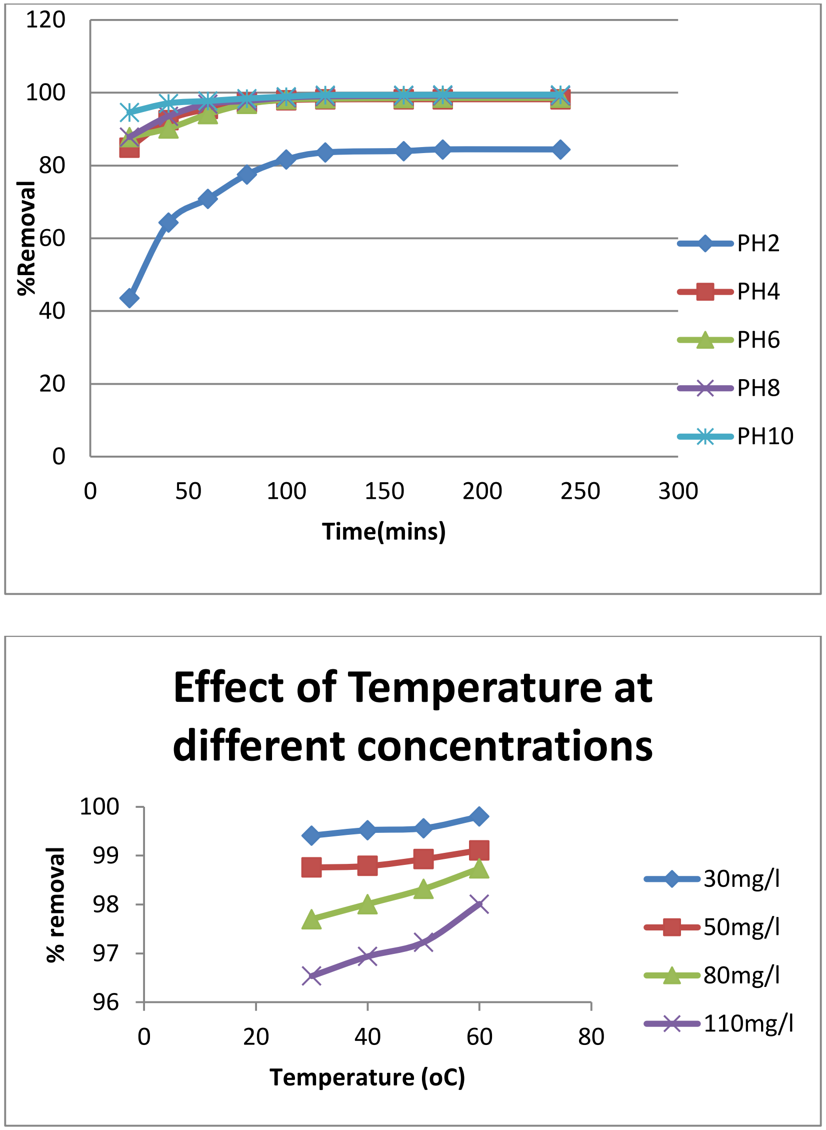


Figure 2. Effect plots

Effect of initial dye concentration

The study of effect of initial dye concentration on the adsorbent adsorption capacity is a useful aspect of adsorption process. The initial concentration played an important role in the adsorption capacity of MB on the adsorbent. From the figure 2, the result shows that the removal efficiency decreased from 99.4% to 82.58% as the initial concentrations were increased from 30mg/l to 80mg/l. This phenomenon is because at higher initial concentrations, outrageous MB molecules were in solution as compared with the available active vacant sites of the adsorbent. At lower initial MB concentration, the possibility of absolute uptake of limited MB molecule was higher leading to higher removal efficiency.

But in terms of adsorptive capacity, the reverse was the case because increase in initial concentration increased the driving force to overcome the mass transfer resistance for MB transfer between the solution and the surface of the activated carbon [25]. The MB molecule countered the boundary layer effect and then diffused from the boundary layer film onto adsorbent surface and finally diffused into the porous structure of the adsorbent [26].

Effect of contact time

The adsorption of MB onto the adsorbent was studied as a function of contact time in order to decide the sufficient equilibrium time. Equilibrium time is one of the most important parameters in the design of economical wastewater treatment system (24,27]. The effect of contact time is shown in fig. 2. The removal of MB by adsorption on the adsorbent was found to be rapid at the initial period and then to become slow and stagnate with the increase in contact time. This is as a result of large number of vacant sites on the surface of the adsorbent available during the initial stage of adsorption, and afterward, it becomes difficult to occupy the remaining vacant sites dye to the repulsive force between the adsorbed molecules on the solid and bulk phases.

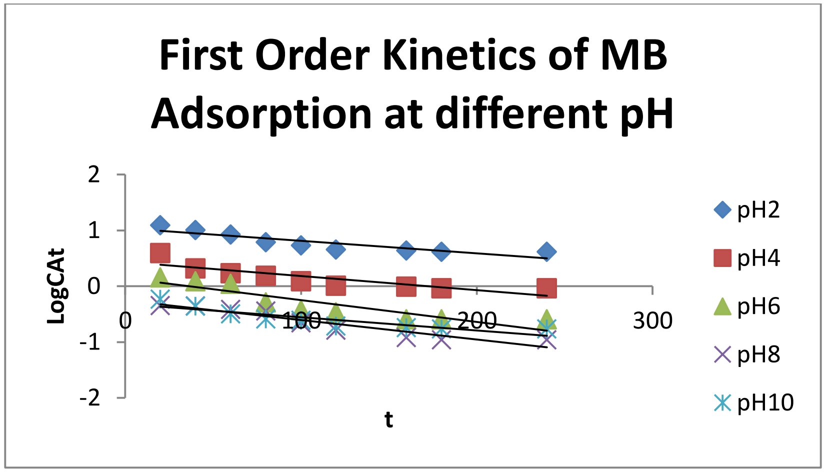
Effect of temperature

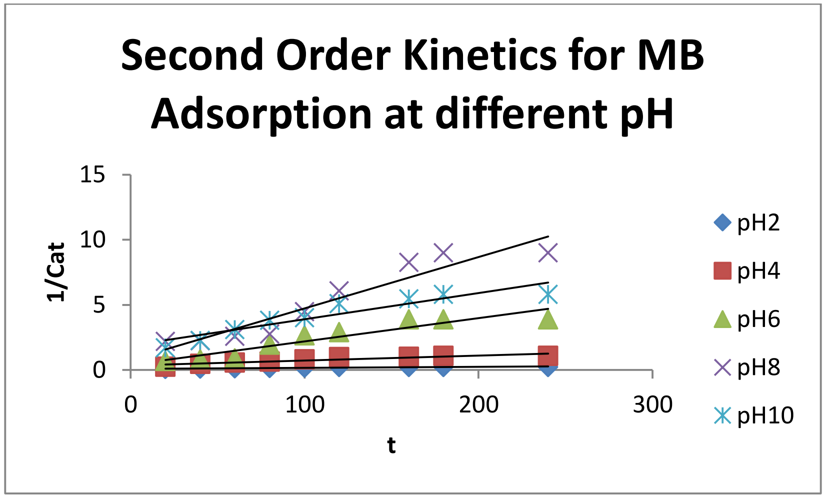
The temperature influence is an important controlling factor in the real applications of the proposed adsorptive dye removal process since most of the textile dye effluents are produced at relatively high temperature [26]. From the result, it can be seen that there was increase in the adsorption capacity of MB from the bulk solution as temperature was increased. Increase in temperature increased the entropy of the system resulting to more successful collision of solute and adsorbent which yielded more chances of adsorption [28]. There was an increase of mobility in the MB solution and decrease of resistance on the diffusion particles at higher temperature consequently boosting the adsorption capacity. In addition, the higher mobility of molecules facilitates the formation of a surface mono layer at higher temperature [29, 30].

2.7.0 Adsorption Kinetic Model

The adsorption kinetic produces valuable information about the reaction pathways and mechanism of the reactions. The kinetic of methylene blue adsorption was analysed using first order model, second order model, and Boyd model.

The low correlation coefficient (R^2) obtained at different pH values for first order model showed poor agreement of the first order model with the experimental data.





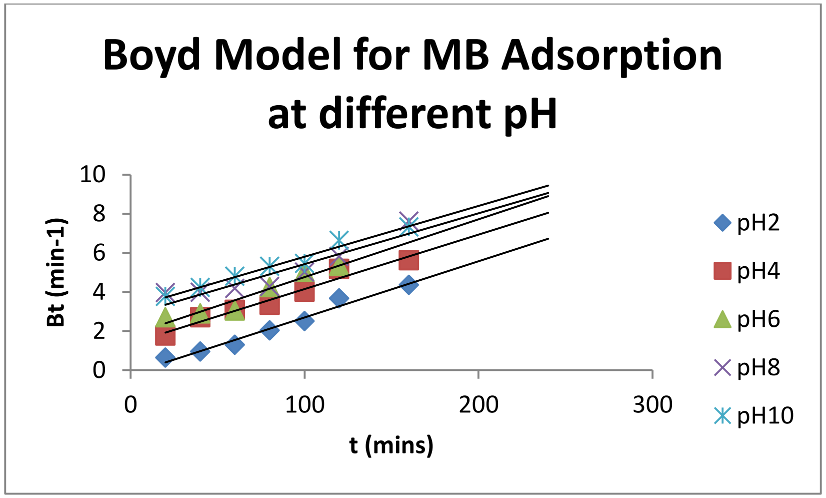


Figure 3. Kinetics graphs

The values of K_2 obtained for the second order model are presented in table (1) at different pH with their equivalent correlation coefficients (R^2). The values of the correlation coefficient were relatively small compared to that of the Boyd model meaning that the model did not fit the experimental values well.

For the Boyd model, a linear plot of Bt against t, passing through the origin implies that pore-diffusion controls the rate of mass transfer. It seems the pore diffusion becomes more important at lower pH, as the intercept approaches 0 with decrease in pH as indicated on table (1). The correlation coefficient is between 0.873-0.976, meaning that it fitted the data reasonably well.

Adsorption isotherm Models

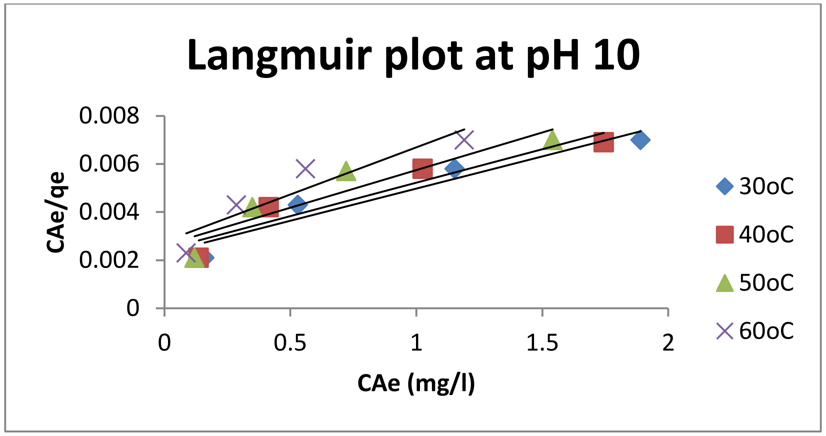
In this study, the experimental results were fitted to Langmuir and freundlich Isotherm models.

For Langmuir model, the K_L is a measure of heat of adsorption utilized to calculate dimensionless separation parameter R_L.

To determine if the adsorption process is favourable or unfavourable, for the Langmuir type adsorption process, the isotherm shape can be classified by a term "R_L" a dimensionless constant separation factor which is defined as below [31].

$$R_L = \frac{1}{(1+K_LCAo)} \qquad (2)$$

From table 2, K_L values were greater at higher temperature, which showed endothermic nature of MB adsorption. The R_L values for all the temperature and pH studied were between 0 and 1 indicating that the adsorption was favorable.



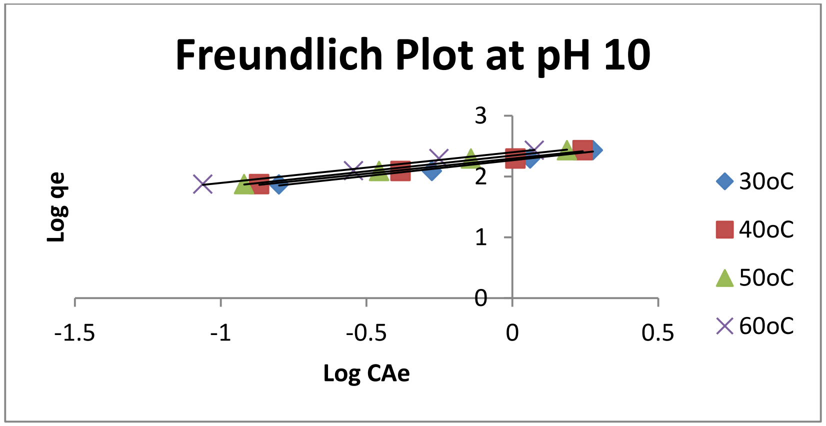


Figure 4. Isotherm graphs

The correlation coefficients were very close to unity showing that Langmuir isotherm model fitted the data well.

In Freundlich isotherm model, n is the constant related to the adsorption capacity. The value of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [32]. From the results obtained, the K_f and n values changed as the temperature was raised. The values of n suggested that MB adsorption was favorable. The value of correlation coefficients close to unity implied that the freundlich isotherm fitted the data reasonably well when compared to Langmuir isotherm. This was in accordance with the work done by Hui Deng et al on adsorption of methylene blue in adsorbent materials produced from cotton stalk [33].

Table 1. Kinetics parameters

KINETIC EQUATION	Ph		KINETIC PARAMETERS	R^2
First Order Kinetics (Natajan and Khalaf First)	2		$K_1 = -0.0046\ (min^{-1})$	0.796
	4		$K_1 = -0.0046\ (min^{-1})$	0.739
	6		$K_1 = -0.0069\ (min^{-1})$	0.797
	8		$K_1 = -0.0069(min^{-1})$	0.887
	10		$K_1 = -0.0046\ (min^{-1})$	0.796
Second order Model	2		$K_2 = 0$	0.852
	4		$K_2 = 0.003$	0.852
	6		$K_2 = 0.017$	0.871
	8		$K_2 = 0.039$	0.904
	10		$K_2 = 0.020$	0.876
KINETIC EQUATION	**pH**	**INTERCEPT**	**R^2**	
Boyd Model	2	-0.165	0.972	
	4	1.372	0.961	
	6	1.813	0.929	
	8	2.837	0.873	
	10	3.208	0.976	

Table 2. Isotherm constants for MB adsorption on activated carbon

TEMPERATURE	LANGMUIR CONSTANT				FREUNDLICH CONSTANT			
TEMP(K)	**q_o(mg/g)**	**K_L(L/mg)**	**R_L**	**R^2**	**$^1/n$**	**n**	**K_F**	**R^2**
303	pH_4 0	0	1.0	0.997	0.859	1.164	78.7	0.999
	pH_{10} 500	1.0	0.032	0.923	0.517	1.934	185.35	0.989
313	pH_4 1000	0.25	0.118	0.701	0.765	1.307	164.8	0.987
	pH_{10} 500	2.0	0.016	0.950	0.501	1.938	198.6	0.994
323	pH_4 500	1.0	0.032	0.933	0.652	1.534	193.2	0.997
	pH_{10} 500	2.0	0.016	0.980	0.516	1.980	221.8	0.990
333	pH_4 500	1.0	0.032	0.991	0.608	1.645	213.8	0.985
	pH_{10} 500	2.0	0.016	0.967	0.505	1.996	251.2	0.997

Table 3. Thermodynamic Parameter for MB Adsorption at pH$_4$

Concentrations (mg/ls)	**DG(KJ/mol) P°**				**ΔH(KJ/mol)**	**$\Delta S(Jmol^{-1}K^{-1})$**
	30°C	**40°C**	**50°C**	**60°C**		
30mg/l	-11.556	-13.410	-15.264	-17.118	44.621	0.1854
50mg/l	-11.221	-12.844	-14.468	-16.092	37.978	0.1624
80mg/l	-11.009	-12.538	-14.067	-15.596	35.318	0.1529
110mg/l	-11.104	-12.283	-13.461	-14.640	24.618	0.1170

<u>AT pH$_{10}$</u>

Concentrations (mg/ls)	**ΔG(KJ/mol) P°**				**ΔH(KJ/mol)**	**$\Delta S(Jmol^{-1}K^{-1})$**
	30°C	**40°C**	**50°C**	**60°C**		
30mg/l	-15.424	-16.464	-17.504	-18.544	16.088	0.104
50mg/l	-13.642	-14.652	-15.662	-16.672	16.961	0.101
80mg/l	-12.827	-13.947	-15.067	-16.187	21.109	0.112
110mg/l	-12.395	-13.225	-14.055	-14.885	12.754	0.083

Adsorption thermodynamics

The thermodynamic parameters, such as the changes in the standard free energy (ΔG^o), theenthalpy (ΔH^o) and energy (ΔS^o) associated with the adsorption process were determined using the following relation:

$$\Delta G^o = \Delta H - T\Delta S \qquad (3)$$

$$\ln Kc = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (4)$$

The values of ΔS^o and ΔH^o were obtained from intercept and slope respectively of plot of ln Kc against $^{1}/_{T}$.

As seen in table 3, positive values of ΔH for all dye concentrations and pH and negative values of ΔG^o for all the temperatures indicated the feasibility of the process and the spontaneous nature of the adsorption. The value of ΔG^o became more negative with increasing temperature. This showed that increase in temperature was favorable for the removal process. The positive entropy change ΔS corresponds to an increase in the degree of freedom of the adsorbed species as temperature was increased.

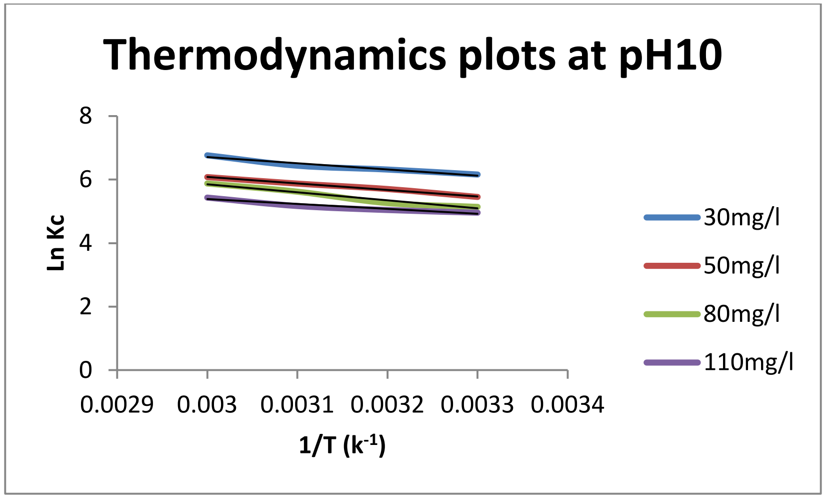


Figure 5. Thermodynamic plot

Conclusion

The present study confirmed that activated sea bean (mucuna sloanei) shell is an effective adsorbent for the removal of methylene blue dye from aqueous solution. In batch studies, the adsorption was dependent on initial dye concentration, adsorbent dosage, temperature and time of reaction. Langmuir and Freundlich equations were used to describe the adsorption of MB dye onto the activated carbon. The isotherm data indicates that both isotherm models fitted the process with Freundlich model more suitable. First order, second order and boyd model were used to for the kinetic study. The Boyd model fitted the kinetic data more appropriately. The thermodynamics properties such as ΔGº,ΔHº and ΔSº studied, confirmed the adsorption process as spontaneous and endothermic in nature. On the basis of the data, it can be concluded that sea bean (mucuna sloanei) shell activated carbon can be used as a cheap and efficient adsorbent for the removal of MB dye from aqueous solutions.

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