Dyes uptake onto Processed and Raw Mango seed Back

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ABSTRACT

This remediation study attempts the use of mango seed shells as filters for removing dyestuff from solution. This was tested in both batch and pour through or column mode. The uptake of Methylene blue dye by these two adsorbents were carried out by varying the initial dye concentration as well as contact time. Adsorption experimental data fits the Frendlich model as well as predicting the surface coverage for the activated samples, which demonstrated an adsorption capacity (K_f) of 0.580 and intensity value ($^1/_n$) as 0.621. A test of the inactivated raw biomass are not to the same estent. It was concluded that dye uptake onto heterogeneous surface with over 80% removal efficiency was actualized. There is a great proximity between the values of generated data to those reviewed elsewhere. This is an indication that our substrate seed shells could compare well in usage as both filters and adsorbents.

Keywords: Mango, Dyestuff, Raw, Processed, Adsorbents, Inactivated, Seed back.

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INTRODUCTION

Great number of low cost adsorbents have been tried for dye removal. These include cola nut and Groundnut shells [1,2], palm kennel and sheanut shell [3], bird droppings [4], bird waste[5] etc. Thermally cracked or active carbons are high porosity, high surface area material manufactured by carbonization and activation of carbonaceous materials which find extensive use in the adsorption of pollutants from gaseous and liquid streams [6]. Activated carbon is a carbonaceous material which is amorphous in nature and in which a high degree of porosity is developed by the process of manufacturing and treatment [7]. Its high degree of porosity and surface area makes it the most versatile absorbent to be used for effective removal of organic

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solid that has extraordinarily large internal surface and pore volumes. These unique pore structures play an important role in many different liquid and gas phase applications [7].

Major properties of activated carbon are dependent on the raw material source [8]. Charcoal with high specific surface area and pore volumes can be prepared from a variety of carbonaceous material such as coal, coconut shell, wood, agricultural wastes and industrial wastes. In industrial practices, coal and coconut shell are the two main sources for the production of activated carbon [9]. Other materials like lignite, petroleum, coke, saw dust, peat, fruit pits and nut shell may be to manufacture activated carbon but the properties of the finished material are governed not only by the raw material used but also the method of activation used. The source of this raw material was based on the need for developing low cost absorbent for pollution control as well as reducing the effect of environmental degradation poised by agricultural waste.

Biosorption is the adhesion of a substance onto the surface of adsorbent solids. [10]. It is also the formation of layer of gas, liquid or solid to the surface of a solid or less frequently a liquid [10]. Adsorption occurs at solid-solid, gas-solid, liquid-liquid and liquid-gas interfaces [10]. It is often confused with absorption, where the substance being collected or removed actually penetrate into the solid. The reason why activated carbon is such an effective adsorbent material is due to its large number of pores. These provide a large surface area, relative to the size of the actual carbon particle and s visible exterior surface.

An isotherm is a functional expression for the variation of adsorption relative to the concentration of adsorbate in the bulk solution at constant temperature [11]. It describes the relation of between the adsorbate retained by the activated carbon and the adsorbate equilibrium concentration [11]. It was defined as a graphical representation showing the relationship between the amounts adsorbed by a unit weight of adsorbent for example activated carbon and the amount of adsorbate remaining in a test medium of equilibrium. It maps the distribution of adsorb able solute between the liquid and solid phases at various equilibrium concentration [12].

Sorption isotherm is based on data that are specific for each system and the isotherm must be determined for every application. An adsorption isotherm besides providing a panorama of the course taken by the system under study in a concise form, it indicates how efficiently a carbon will allow an estimate of the economic feasibility of the carbons commercial application for the specific solute [12]. The major factors in determining the shape of an isotherm are:

1. The number of compound in the solution.
2. The relative adsorb abilities of the compound.
3. The initial concentration of the solution.
4. The degree of competition among solutes for adsorption sites.
5. The characteristics of the specific carbon.

Adsorption isotherm can be generated based on numerous theoretical explanations and the two main well known isotherms are: Langmuir isotherm and Freundlich isotherm [13].

Freundlich isotherm equation is a special case for heterogeneous surface and it is usually used to measure adsorption from solution in environmental engineering and specifically drinking water

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treatment application, the Freundlich isotherm is used and is therefore the most popular model for a single solute system. The general equation for Freundlich equation is given as:

$$q_e = K_f C^{i/n} \qquad\qquad 1$$

K_f = is a constant measuring adsorption capacity
C stands for equilibrium concentration of the adsorbate in solution
qe = equilibrium surface coverage (amount of adsorbate adsorbed per unit weight of carbon).

The Freundlich isotherm model is an empirical equation based on the distribution of solute between the solid phase and aqueous phase at equilibrium often useful as a mean for data description. The equation is adequate to describe non-linear adsorption in a narrow range of adsorbate concentration and its mathematical simplicity enables it to be used easily. It also described adsorption processes on surface sites that are energetically heterogeneous. However, theoretically, the amount of adsorbed solute may become infinite as bulk solute concentration increases and this is a disadvantage [14].

Fitting equation (1) into straight line gives the logarithm form as:

$$logqe = logkf + 1/nlogc \qquad\qquad 2$$

a plot of this equation gives a straight line curve when logqe is plotted against logc with slope as 1/n and intercept as logkf. The kf value increases with the total adsorption capacity of the adsorbent to bind the adsorbate. It is roughly an indicator of adsorption capacity and the 1/n is the adsorption intensity. The numerical value of n is a useful index of adsorption efficiency and is related to the energy of adsorption. The Freundlich model only agrees with the Langmuir equation and experimental data over moderate range of concentration. Unlike the Langmuir equation, Freundlich equation does not reduce to linear adsorption expression at a very high concentration nor does it agrees with the Langmuir equation at a very light concentration since n must reach some limit when the surface is fully covered.

The Freundlich equation commonly used for the comparism of carbon for water treatment is given by equation 3:

$$\log K_f + 1/n \log C \qquad\qquad 3$$

The amount of Dye at equilibrium, q_e was calculated from the mass balance equation given in equation 4 [15]

$$q_e = (C_O - C_e) V/W \qquad\qquad 4$$

where C_o and C_e are the initial and final Dye concentrations (mg/L) respectively. V is the volume of dye solution and M is the mass of the acid catalyzed Poultry waste sorbent (g). while t is the equilibrium contact time, when $q_e = qt$, equation 1 will be expressed as equation 5 below[16]

$$q_t = (C_o - C_t)v/w \qquad\qquad 5$$

where $q_e = q_t$ and C_t is the concentration at time t. The calculations and graphical representation were performed in the Microsoft Excel package. The percent dye removal (RE %) was calculated for each equilibration by the expression presented as equation 6

$$R E(\%) = (C_0 - C_e)/Co \times 100 \qquad\qquad 6$$

Where R (%) is the percent of dye adsorbed or removed. The % removal and adsorption capacities were used to optimize the activation condition [16]. The test were done at a constant temperature of 25 ± 2^0C.

The present study is focus at studying the adsorption properties and evaluating activated carbon from mango seed shells. The objectives are as follows:

I. To generate activated carbon from Mango seed, a locally available agricultural by products, and thereby adding value to the waste and reducing solid wastes from the environment
II. To investigate the adsorptive properties of the prepared activated carbon
III. To design isotherms for the prepared activated carbon adsorption studies
IV. To study the applications of generated activated carbon in areas like dye adsorption, using spectrophotometer
V. To compare the generated data with that of inactivated biomass labeled as Mango Seed Biomass (MSB).

MATERIALS AND METHODS

Semi dried mango seeds were randomly obtained from waste baskets, waste depots and sites within Aliero market, in Kebbi state. The collected samples were deseeded. The semi hard barks were properly washed, using sponge and plenty water to remove all surface impurities and were then sundried. The samples were dried over night in an over at a temperature of 100^oc after which they were pounded using a local mortar and pistil followed by sieving. The obtained powdered sample were stored in an air tight container. The method adopted for the sampling was described elsewhere [13].

Treatment of the inactivated biomass involved collection of samples, which were then washed with plenty of water to remove the surface impurities. The samples were then allowed to dry under sun and later subjected to oven drying at 100^oC over night. This was followed by grinding, using mortar and pestle, followed by sieving with less than 2mm mesh size sieve. The less than 2mm samples were kept in airtight container

The one scheme process was used and in this process, 3g of the raw sample was mixed with the activating agent (prepared chemicals) the mixture was left standing for 24 hrs after which it was placed in the   furnace at a temperature of 800^oc for five minutes. The sample was removed, poured out into an ice bath, the excess water was drained and the sample was allowed to stand at room temperature. The procedure was repeated for different residual time (5 min, 10 min) using the activating agent [17,18]

The activated carbon generated from the above process was washed using 0.1M HCL to remove surface ash followed by hot water. The washed sample was rinsed using distilled water to

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remove residual acid. The sample was oven dried at temperature of 110°c over night. Washing of the sample was completed when a pH of 6 to 8 was ascertained [19,20]

Batch adsorption technique:

In this process adopted for the commercial and generated activated carbon, a quantitative amount of adsorbent was mixed continuously with a batch of adsorbate in beakers and the equilibrium concentrated of the adsorbate was estimated after a predetermined time. The amount adsorbed was taken as the different between the final and initial concentrations of the adsorbates .

For the Pour through (column method), which was adopted for the inactivated biomass. The dried pulverized shell samples were loaded in a column (no specification provided). For each initial dye concentration, 20g of sample biomass was introduced through the top of the column and $100cm^{3}$ dyestuff solution (200ppm standard solution) was then introduced from the open top of the column. The solution passed through the column and the volume of the eluents was taken at 5 minutes, 10 minutes, 15 minutes and 20 minutes in different beakers and the absorbance values were measured at predetermine wavelength using spectrophotometer. The same procedure was employed for 400ppm, 600ppm, 800ppm and 1000ppm using fresh adsorbent for each analysis.

RESULTS AND DISCUSSION

Physicochemical parameters were studied. The optimum temperature for activation was experimentally determined elsewhere to range between 600- 800°c [21-25].

Table 1:Physicochemical Parameters of Adsorbents

Adsorbent	Ash(%)	App. Density(g/cm^3)	Bulk Density(g/cm^3)	Porosity
Raw mango back	29.12	0.30	0.14	0.13
Activated back	17.66	0.50	0.53	0.46

Table 2: Adsorption isotherm experimental constants of Methylene blue adsorption onto 1M H2SO4 treated mango shell activated carbon

Co(mg/L)	Ce(mg/L)	qe(mg/g)	log Ce	log qe	%RE	1/qe	1/ce
10	2.020997	0.7979	0.305566	-0.09805	79.79003	1.253289	0.494805
15	2.896087	1.210391	0.461812	0.082926	80.69275	0.826179	0.345293
20	5.054244	1.494576	0.703656	0.174518	74.72878	0.669086	0.197854
25	7.393244	1.760676	0.868835	0.245679	70.42702	0.567964	0.135259
50	17.64706	3.235294	1.246672	0.509914	64.70588	0.309091	0.056667

Table 3. Adsorption Isotherm Experimental data for for dye adsorption onto inactivated Mango seed shell biomass

Co	Ce	Log Ce	1/Ce	qe	1/qe	Log qe
200	132.1623	2.121108	0.471452	0.339188	2.948214	-0.46956
400	179.1009	2.253098	0.443833	1.104496	0.905391	0.043164
600	299.4562	2.476333	0.403823	1.502719	0.66546	0.176878
800	488.9429	2.689258	0.37185	1.555286	0.642969	0.19181
1000	678.0906	2.831288	0.353196	1.609547	0.621293	0.206704

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Table 4: Freundlich and Langmuir isotherms parameters of Methylene Blue uptake by Mango shell Activated Carbon

Isotherms	Eqn (y =)	R^2	Parameters	Values.
Freundlich Comm.	0.584x+0.112	0.939	1/n	0.564
			k_f	1.274
Freundlich MAC.	0.601x-0.248	0.975	1/n	0.611
			k_f	0.584

MAC – 1M H_2SO_4 treated Mango shell activated carbon. Comm.- Commercial activated carbon K_F (units in mgg^{-1} ($1mg^{-n(n)}$)

Table 5: Freundlich Adsorption Constants for dye adsorption onto inactivated Mango seed shell biomass

Sorbent	Isotherms	R^2	Equation Y=	Langmuir $q_m(mgg^{-1})$	$K_a(Lmg^{-1})$	Freundlich 1/n	k_f
MSB	Freundlich	0.646	0.826x + 2.449	NA	NA	0.726	0.378

k_f unit is ($mg1^{-1}/n$ (dm^3)$^{1/n}$ g^{-1}), NA-Not Applicable, MSB- Mango shell Biomass (inactivated)

Effect of Initial Dye Concentration: Figure 1 and 2 are charts explaining the % dye removal (%RE) by the adsorbents. For figure 2, the selected adsorbent mass to adsorbate volume ratio (20:100 $^w/_v$) or 2:10 $^w/_v$ is most suitable for the 400ppm initial dye concentration it gave approximately 50 and over 55% dye removal by adsorbent respectively. Least % RE value for the 1000ppm dye concentration could be linked to possible adsorption after equilibration is reached.

Applicability of sorption isotherm (Surface coverage study): The data in Table 2 and 3 were constants generated from figures of type 3-5 which are characterized with good positive correlation coefficient. The Figure 3 which is typical of Table 2 shows that the modeling of data generated using Freundlich isotherm gave a better linearity and applicability ($R^2>0.975$) for sorbent prepared by activation. It thus implies that adsorption of methylene blue dye onto the derived activated carbon was onto a heterogeneous surface [24]. This correlation coefficient is however poor for the inactivated mango shells (figure 5), indicating an R^2 value of 0.646

Equilibrium concentration (Ce): Table 2 and 3 also gave experimental data generated for adsorption onto activated and inactivated Mango seed shells respectively. Increase in equilibrium phase dye concentration with time were made evident in both Tables. The least % dye removal (64.706) for the highest initial dye concentration (50mg/L) is an indication of desorption in Table 2. The phenomenon is typical for cases after equilibration is attained [25]. From Table 3, the unadsorbed concentration (C) is high for 1000ppm and least for 200ppm initial dye concentrations. This is an indication that adsorption of Methylene blue dye onto biomass is a function of initial concentration.

Evaluation of adsorption intensities and capacities: The degree of heterogeneity of adsorption surface was also measured from the 1/n values. According to previous findings [21-24], Freundlich equation slope (1/n), ranging between 0 and 1 is a measure of surface heterogeneity. Surface become more heterogeneous as 1/n values get closer to zero [24]. Based on this, Sorbents, with least 1/n value, 0.564 presented a more heterogeneous surface as made evidence by the commercial carbon (Table 4). This finding could be linked to the particle size and the nature of activating agent [24]. It should also be noteworthy that 1/n ranging between 0 and 1 is a

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measure of adsorption Intensity. Hence, $1/n < 1$ and > 1 are indication of normal and cooperative adsorption respectively. It thus implies that the adsorption of dye onto mango shell biosorbent is a normal type of adsorption which could be linked to the possible suitability of biomass [24] K_f, is the Freundlich constant which denote or depicts the adsorption capacity, unit in mgg^{-1} $(1mg^{-1})^n$ of adsorbent[21]. It is defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto the sorbent for a unit equilibrium concentration. Biomass, activated with 1M acid presented a higher value (1.274) compared to that of the commercial carbon. The higher the value of K_f (intercept),the higher the absorption capacity [24] . K_F (units in mgg^{-1} $(1mg^{-n(n)})$ is defined as the distribution coefficient and represents the quantity of dye, adsorbed onto the activated carbon for a unit equilibrium concentration. This high adsorption capacity by derived sorbent could be accepted based on Freundlich interpretation for a non uniform surface coverage.
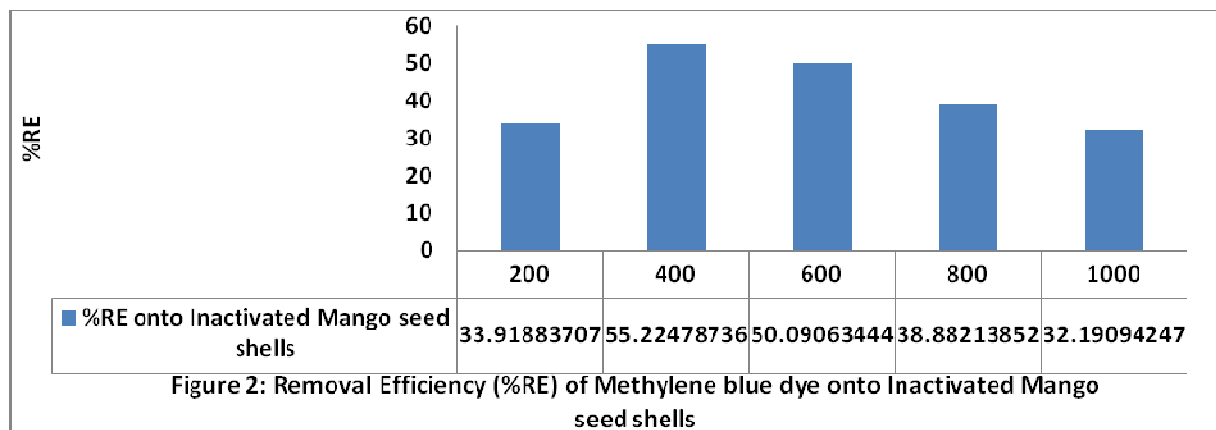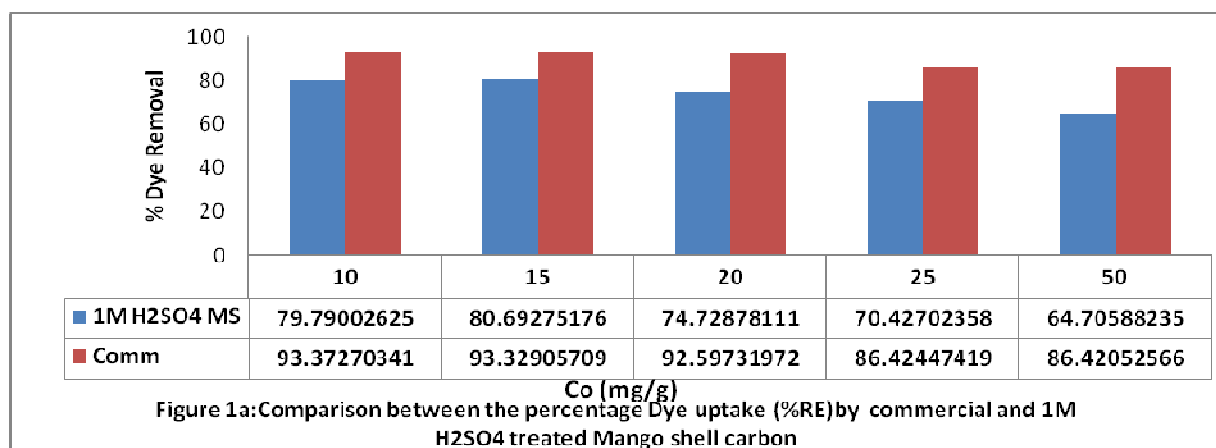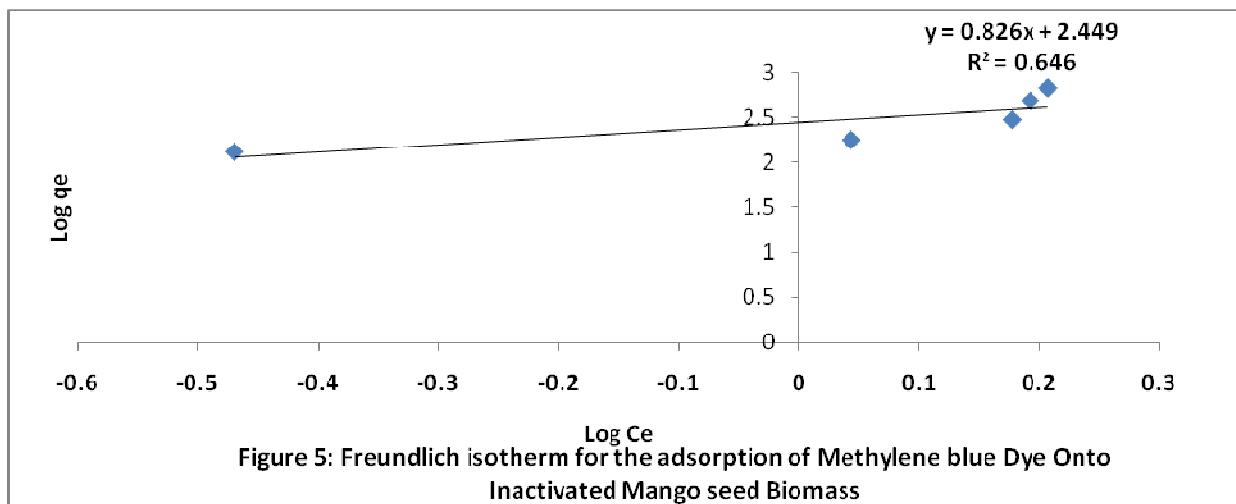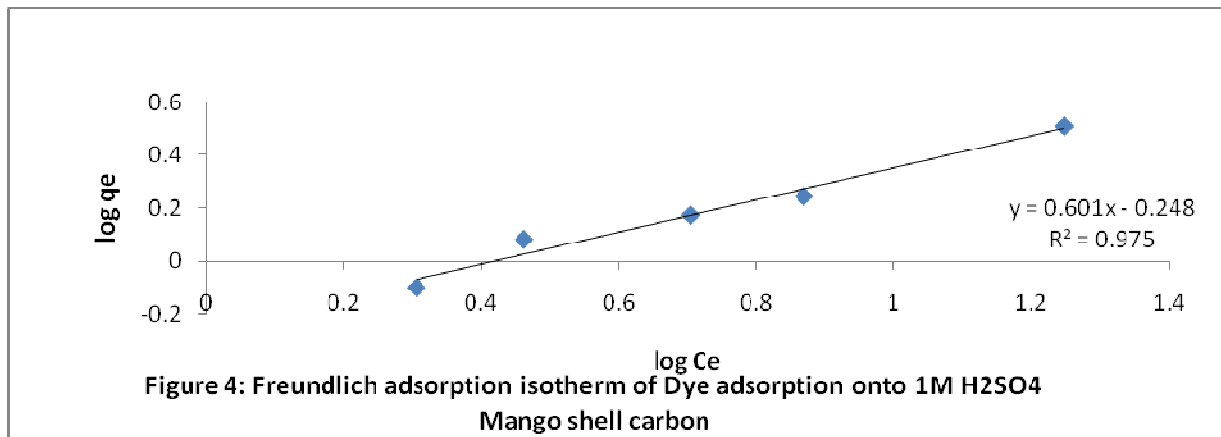

Co (mg/g)	10	15	20	25	50
1M H2SO4 MS	79.79002625	80.69275176	74.72878111	70.42702358	64.70588235
Comm	93.37270341	93.32905709	92.59731972	86.42447419	86.42052566

Figure 1a:Comparison between the percentage Dye uptake (%RE)by commercial and 1M H2SO4 treated Mango shell carbon

	200	400	600	800	1000
%RE onto Inactivated Mango seed shells	33.91883707	55.22478736	50.0906344	38.8821385	32.19094247

Figure 2: Removal Efficiency (%RE) of Methylene blue dye onto Inactivated Mango seed shells
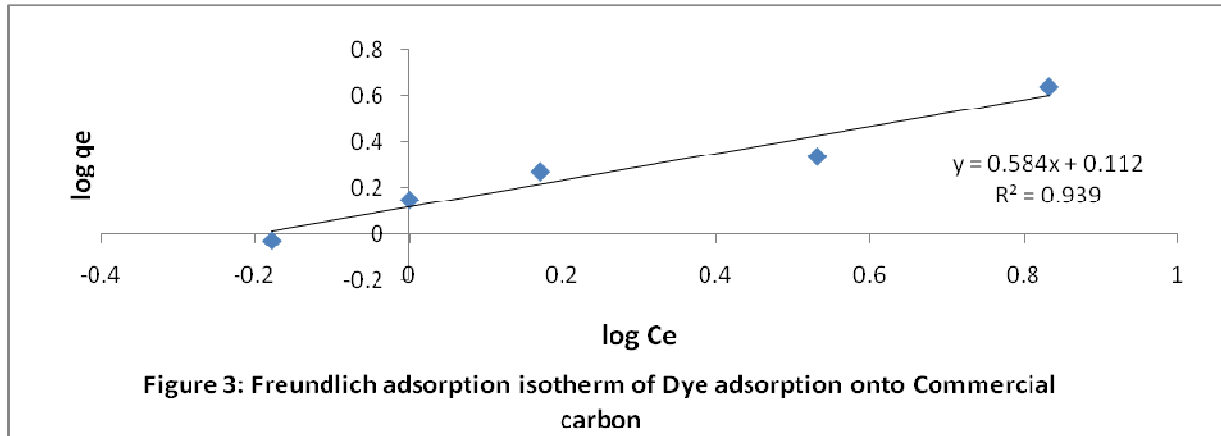
Table 5 represents the Freundlich adsporption isotherm constants for the generated data. Results obtained from adsorption isotherm revealed that the Frendlich isotherm presented fairly high adsorption capacity value ($k_f = 0.378$). Since the Frendlich isotherm gave least coefficient of determination ($R^2 = 0.646$ for inactivated biomass), it thus implies that the adsorption capacity and intensify estimation based on the Frendlich isotherm is not worth considering for the raw biomass as does for the corresponding activated carbon. Hence, the dye uptake by activated

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mango seed shells gave a better adsorption capacity while dye adsorption onto inactivated shells present a higher adsorption intensify ($^{1}/_{n}$ = 0.726) as predicted using the Frendlich isotherm model.

Figure 3: Freundlich adsorption isotherm of Dye adsorption onto Commercial carbon

Figure 4: Freundlich adsorption isotherm of Dye adsorption onto 1M H2SO4 Mango shell carbon

Figure 5: Freundlich isotherm for the adsorption of Methylene blue Dye Onto Inactivated Mango seed Biomass
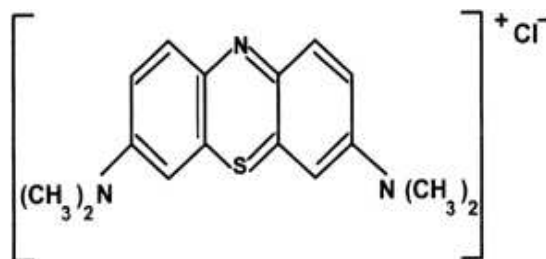
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Figure 6: Structure of 3,7 bis (dimethylamino) phenothiazin-5-iumion (Methylene blue)
Molecular formula:$C_{16}H_{18}ClN_3S$; Molecular mass : 373.9 g mol^{-1}
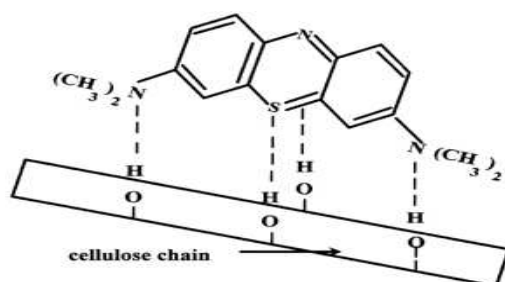

Figure7: Schematic model of methylene blue and Cellulose chain interaction

CONCLUSION

The results presented in this works shows that *Magnifera indica* shells are potentially low cost substrates for generation of activated biosorbent, giving up to 60% dye removal. Adsorption isotherm experimental agrees with those of researches reviewed earlier. To this regards, adsorption falls within favorable limits as confirmed from the Freundlich constants ($1/n <1$) and Applicability of the Frendlich models for the activated shells is not the same with that of the inactivated biomass as well as that of the commercial carbon due to different extent of surface coverage. The entire results fall within the range for published data. A considerable impact of activation was observed.

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