EQUILIBRIUM SORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING PSH, PNS AND HB ACTIVATED CARBON.

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Abstract

Pilliostigma thonningii (PSH) known as camel's foot, monkey bread. Hildegardia barteri (HB) – Christmas tree. Perqutinia nigrescens (PNS) were used to remove methylene blue (MB) from aqueous solution which is one of the most commonly used substance for dyeing cotton, wood and silk. This dye when inhaled it is associated with injury of the eye, burning sensations, nausea, worming, profuse sweating, and mental confusion. The effects of various operating parameters such as contact time (30 to 300 min), adsorbent dosage (0.1-2 g), pH (2-8), temperature (30 -70o C) and initial concentration (10-400 mg/g) was studied. The result shows that PSH, PNS and HB were able to remove up to 99% MB at various initial dye concentration. The equilibrium data were also fitted to Temkin, Langmuir and Freundlich isotherm models. It was discovered that the data fitted well to Freundlich, R2 was 0.9092(PSH), 0.9482 (PNS) and 0.9484(HB) and Temkin R2 for PSH, PNS and HB was 0.8699, 0.8302 and 0.827 respectively. The adsorption data obtained for the three adsorbents fitted into pseudo second order kinetic model with R2 as 0.9999, 1 and 1 for PSH, PNS and HB respectively.

Keyword: Adsorption, Pilliostigma thonningii, methylene blue, Adsorbent, Hildegardia barteri, Perqutinia nigrescens

Introduction:

These days, industrial activities signify an important pollutant source, mainly regarding the addition of heavy metals and dyes in the soil. This contributes a remarkable increase on the concentrations of those ions in waters which represent an important source of contamination of the aquatic bodies, especially when these kind of heavy metals and dyes enter food chain (Rocha *et al* 2009)

A basic and cationic dye, methylene blue, is the most commonly used substances for dying cotton, wood and silk. If inhale, it can cause difficulty in breathing while if on direct contact it may cause permanent injury of the eyes of human, burning sensations, nausea, profuse sweating, methemoglobinemia and mental confusion (Edris *et al*, 2012). All over the world , improper treatment and disposal of dye contaminated wastewater from ink, dying, printing, textile and related industries have cause serious environmental concerns (Edris *et al*, 2012). Physical, physico-chemical, biological and /or chemical processes have been applied for the removal of dye in wastewater. These include enzymatic treatment (Gholami-Borujeni *et al*, 2011), photocatalytic process (Liu and Chiou, 2006) and ozone treatment (Kusvuran *et al*, 2011), were used for the removal of dye from textile effluents. Some of these methods are however, limited due to their high operational costs and large volume of sludge. Conventional treatment involving a process of coagulation/ flocculation may be combined with biological treatment or used alone, as a way of removing suspended solids and organic material, as well as promoting the extensive discarding of dyes from textile industrial effluents (Anjaneyulu et al, 2005).

The best procedure for the removal of synthetic dyes from industrial effluents is the adsorption process, because the dye species are transferred from the water effluents to a solid phase diminishing the effluent volume to a minimum (Edris *et al*, 2012). Subsequently, the adsorbent can be regenerated or kept in a dry place without direct contact with the environment. Also, adsorption has proven to be a reliable treatment methodology due to its ease of operation, insensitivity to toxic substances, simplicity of design and its low capital investment cost, but its application is limited by the high price of some adsorbents and the large amounts of wastewater normally involved. Few of the adsorptive materials that have been tested for the treatment of wastewater included quaternary chitosan (Liu et al, 2009), Activated carbon (Abdus- Salam and Buhai, 2014), Iron oxide (Abdus –Salam and Adekola, 2005), Agricultural by-product (Wang *et al*, 2008), biopolymer such as chitosan beads (Chiou and Li, 2002).

The use of low cost starting materials (industrial or agricultural residues) for the preparation of activated carbon has emerged as a potential alternative in other to reduce preparation cost (Bhatnagar and Sillanpaa, 2010). The conversation of agricultural waste to low cost adsorbents also added value to these residues solves the problem of biomass disposal and besides, this reduces cost. Agricultural waste-based carbon has the advantage of exhibiting low ash content, high surface area, reasonable hardness and/or adequate porous structure (Bhatnagar and Sillanpaa, 2010). The choice of activated carbon precursor largely depends on its availability, purity and cost but the manufacturing process and intended applications of the products are also important considerations. The evaluation of biomass therefore, is getting increased attention over the world as it is widely available, cheap, environmental friendly and renewable (Adebayo et al, 2014)

This current study focuses on assessing the removal efficiency of MB from aqueous solution using HB, PNS and PSH activated carbon. The adsorption was measured as a function of initial concentration, contact time, pH, temperature and adsorbent dosage by batch method. The adsorption data were fitted to three isotherms and three kinetic models to determine the adsorption capacity as well as the rate of adsorption of MB onto the surface of PSH,

HB and PNS activated carbon. The isotherms were Temkin, Langmuir and Freundlich while the kinetics was pseudo first order, pseudo second order and intra- particle diffusion.

Materials and Methods

Materials:

Methylene blue (MB) is a cationic dye with maximum absorption of light (λmax) of 670 nm and molecular weight of 319.86 g/mol. The methylene blue (MB) (C16H18CIN3S) used in this work was of analytical grade (Sigma-Aldrich). For the treatment experiments the dye solutions with concentrations in the range of 10 to 400 mg/L were prepared by serial dilution of the stock solution (1000 mg/L) with deionized water. All other chemicals used in this study were of analytical grade from Sigma – Aldrich

Adsorbent Preparation

The fruit of PSH, PNS and HB were obtained from nearby farms in Offa local gov't area of kwara state, Nigeria.This natural adsorbents were firstly washed with deionized water to removed impurities, soluble and colored components, dried at 105oC for 24 hrs burned off in pyrolizer at 400oC for 1hr, crushed in a domestic grinder and sieved to obtain particle size in the range 0 - 0.5 mm (Edris *et al*, 2012). The chemical activation of the biomass was carried out with 75% H3PO4 by soaking at room temperature for 24 hrs. The powdered adsorbent was stored in an airtight container until use.

Determination of Adsorption Capacity

A 25 ml of varying concentration of MB (dye) 10, 30, 50, 100, 150, 200, 300 and 400 mg/L were contacted with 0.2 g of the adsorbent. The reator contents were agitated on a thermostated mechanical shaker (SHZ 82 and SHA- B) for a period of 3 hrs. The un-adsorbed dye was determined with Jenway 7305 UV- visible spectrophotometer. The quantity adsorbed was calculated from Eqn 1(Abdus-Salam and Buhari, 2014)

$$qe = Co - Cf \quad V \qquad (1)$$
$$M$$

Where qe is the quantity of dye adsorbed (mg/L), Co and Cf are the initial and final concentration of the dye (mg/L), V is the volume of the standard solution used (ml) and M is the mass of the adsorbent (g) used.

Adsorption percentage, which is the dye removed from aqueous solutions by the adsorbent (% Rem), was calculated from Equ 2

$$\% Rem = Co - Cf \quad 100 \qquad (2)$$

Where %Rem = Percentage removal of dye, C_o and C_f = Initial and final concentration of dye (mg/l)

Effect of initial Concentration

A 25ml of different dye concentration of 10 to 400 mg/L were prepared by serial dilution of stock solution and contacted separately with 0.2 g of PSH, PNS and HB biomass at 30oC for 3 hrs. Then the solution was filtrate and the un-adsorbed dye in the filtrated was then analyzed using Jenway 7305 UV- visible Spectrophotometer. The quantity and percentage sorbed were calculated from Eqn 1 and 2.

Effect of Contact time

A 0.2 g of PSH, PNS and HB was weighed separately into 100 ml conical flasks. A 25 ml of the optimum concentrations obtained from the effect of concentration was added separately to each of the flasks. The flasks were labeled for time difference of 10, 15, 30, 45, 60, 90, 120, 180, 240, and 300 minutes. The arrangement was carried out in duplicates and the flasks were tightly covered and agitated for the appropriate time using a thermostatic mechanical shaker. The un-adsorbed dye was determined with Jenway 7305 UV- visible Spectrophotometer. The quantity and percentage adsorbed was calculated from Eqns 1 and 2.

Effect of Adsorbent Dosage on Adsorption

The effect of adsorbent dosage on the adsorption of methylene blue (MB) by PSH, PNS and HB activated carbon was performed according to a literature work (Asiagwu et al, 2012). A variable mass 0.2, 0.5, 1.0, 1.5 and 2g of the adsorbent were weighed into different conical flasks. A 25 ml of the dye solution were measured into two (2) sets of the five conical flasks. The experiment was performed in duplicates. The flask were tightly covered and labeled for dosage differences. They were agitated on a thermostatic mechanical shaker for 1hr 30mins The un-adsorbed MB was determined using Jenway 7305 UV – visible Spectrophotometer and the quantity and percentage adsorbed was calculated using Eqns 1 and 2

Effect of Temperature on Adsorption

The effect of temperature on adsorption was performed according to Mishra et al, (2009). A 0.2 g of the adsorbent was weighed into conical flasks in duplicates; 25 mls of the dye solution were measured into the flasks. The flasks were labeled for temperature differences of 30,40,50,60 and 70oC. The flasks were tightly covered and heated at the appropriate temperatures using water bath thermostatic shaker SHZ 82 and SHA - B. The un-adsorbed dye was determined with Jewway 7305 UV-visible spectrophotometer. The quantity and percentage adsorbed was calculated using Eqns 1 and 2.

Effect of pH on Adsorption

A 25ml of the optimal concentrations of the adsorbate (MB) were adjusted to pH of 2, 3, 4, 5, 6, 7, 8 and 9 by adding either 0.1M NaOH or 0.1M HCl. These solutions were contacted with the optimal doses of the adsorbents (PSH, PNS and HB) and shaken on the mechanical shaker for the optimal contact time at 30oC. The un-adsorbed dye was determined by Jenway 7305 UV – visible spectrophotometer at a predetermined wave length of maximum adsorption 670 nm (λmax). The quantity adsorbed by the adsorbents qe, and the percentage removal was calculated from Eqns 1 and 2.

Isotherms of Adsorption

Three isothermal equations were used to find out the relationship between the equilibrium concentration of the adsorbate in the liquid phase and in the solid phase. More importantly, to determine which of the isotherms best describes the adsorption process. Experimental data were substituted into the equations and appropriate graphs, constants and other variables were generated for each of the following equations.

Freundlich:- The freundlich isotherm does not consider all sites on the adsorbent surface to be equal, that is, adsorption surface with sites that have different energies of adsorption and are not equally available. The freundlich isotherm unlike the Langmuir does not indicate an

adsorption limit when coverage is sufficient to fill a monolayer (Freundlich, 1907). It assumes that, once the surface is covered, additional adsorbed species can still be accommodated. In other words, multilayer adsorption is predicted by this equation

$qe = KfCe1/n$ (3)

The linearized form of freundlich equation is given by

$\text{Log } qe = \log Kf + 1/n \log Ce$ (4)

Where Kf and n are the freundlich constants relating to overall adsorption capacity (mg/g) and adsorption intensity or surface heterogeneity respectively. Ce and qe are the equilibrium concentration of MB in liquid phase and in solid phase respectively. The gradient of the plot of log qe versus Ce is 1/n while the intercept is log Kf

Temkin

The Temkin isotherm assumes that the heat of adsorption of all molecules in layer decreases linearly with coverage due to adsorbent – adsorbate interactions and that the adsorption is characterized by a uniform distribution of the bonding energies up to some maximum binding energy, linearly it is represented thus

$qe = BlnAT + Bln Ce$.(5)

Where B = RT/b = Temkin constant related to heat of sorption (J/mol), AT is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol/K), T is the absolute temperature (K) and b is the Temkin isotherm constant (Gerente et al., 2007) and Ce is the equilibrium concentration.

Langmuir

The Langmuir isotherm describes adsorbate –adsorbent system in which the extent of adsorbate coverage is limited to one monolayer of adsorbent, that is the definite sites on the surface can only hold one adsorbate molecules. It assumes that the energy associated with adsorption is the same for all individual sites and the adsorbates are assumed to be incapable of interacting with neighboring adsorbate molecules (Faust and Aly, 1983). The linearized form of Langmuir is given thus

$Ce/qe = 1/bqm + (1/qm) Ce$

Where Ce is the equilibrium concentration of the solute in the bulk solution (mg/l), qe is the amount solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), qm is the Langmuir constant relating to maximum adsorption capacity (mg/g) and b is the energy of adsorption (L/mg). From the plot of Ce/qe versus Ce, the slope and intercept were obtained as 1/qm and 1/bqm respectively.

Result and Discussion

Batch Adsorption Experiment

Effect of Initial Concentration of MB

The results of initial concentrations on the rate of adsorption of MB were plotted in Fig. 1. It was found that the amount adsorbed increased proportionally when the initial concentration increased Fig 1. The initial increase in MB concentration provides a significant driving force to resolve the resistance of mass transfer between the solid adsorbent and the aqueous phase of the adsorbate can be due to this adsorption pattern. There was a fixed number of active adsorption sites on the surface of the adsorbent with constant adsorbent dose and as the initial MB concentration increases, the available active sites decreases. Accessibility to the fewer active sites remaining becomes more difficult but increase in the MB concentration provide the require driving force to break the resistance to the availability of the remaining sites. This makes the removal of MB dependent on the initial concentration (Zohre *et al*., 2010).

As the amount of MB per unit volume of solution increases, the ratio of the amount of MB at the surface of the available adsorption sites also increases and more MB in solution can be adsorbed which result in the increase of the equilibrium adsorption capacity (Zohre *et al*., 2010).

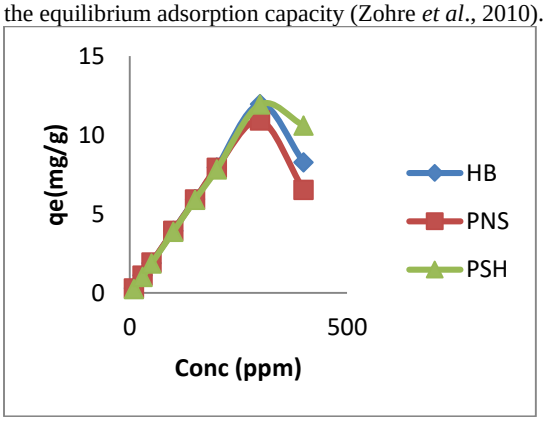

Fig 1: Effect of conc. of MB on HB, PNS & PSH AC

Effect of Contact Time

The plot of effect of agitation time on the adsorption of MB on HB, PSH and PNS AC are depicted in Fig 2. A biphasic kinetic was observed with an initial fast phase (0 – 90 min), where adsorption was rapid and contributed essentially to the equilibrium uptake of MB by HB 5.82 mg/g (97.87 %), PNS 5.83mg/g (97.18 %) and PSH 5.74 mg/g (95.68 %). The second phase is a practically constant phase that occurs after the optimum adsorption from 120 min to 300 min. The first phase is an instantaneous phase which is caused by external adsorption onto HB, PNS and PSH. The process of agitation of the adsorbate-adsorbent phase has the tendency of exposing active surfaces which otherwise, may be inaccessible. Similar observation was earlier reported by Abdus-Salam and Buhari, (2014). The optimum time for adsorption of this dye onto HB, PSH and PNS was 90min.

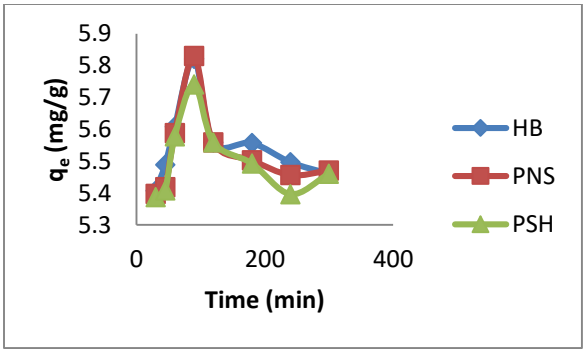

Fig 2: Effect of time on MB on HB,PNS, and PSH AC

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of MB from aqueous solution is plotted in Fig.3. As the adsorbent dose increases, the quantity of MB adsorbed by PSH, HB and PNS decreases. The decrease in the quantity of MB adsorbed may be due to inaccessibility of active sites brought about by the overlapping of the adsorbent particles.

The number of active locations per unit mass has therefore decreased, resulting in comparatively less adsorption (Hashem, 2012).

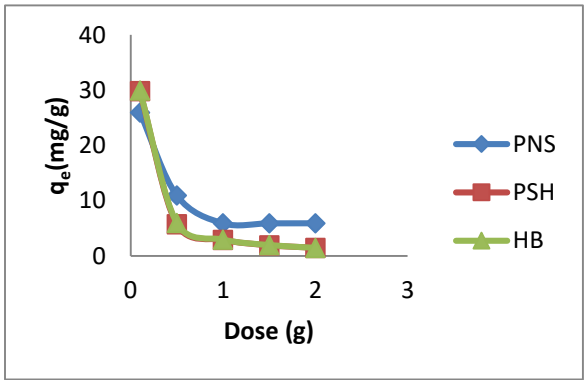

Fig 3: Effect of adsorbent dosage on adsorption capacity of MB onto PNS, PSH & HB Activated Carbon

Effect Of pH On Adsorption Property Of PSH, PNS and HB

The results of effect of pH on adsorption of MB is plotted in Fig 4. At lower pH between 2- 4, adsorption of MB dye from aqueous solution by the three adsorbent was relatively faster. This may be due to the hydrolysis of the adsorbents in water, which create positively charged site, leading to the competition of H+ ions with the cationic molecules of the dye causing a decrease in the amount of dye absorbed (Gary et al.,2004). The adsorption then increased more slowly from pH 5 to 8 which was almost constant. The maximum adsorption was achieved at pH 8. Methylene blue (cationic dye) bearing a positive charge and thus, a basic dye showed maximum quantity adsorbed at higher pH of 8 (Fig 4). This is as a result of electrostatic interaction between the OH- group at higher pH on the surface of the adsorbent and the positive charge of the dye leading to better efficiency at higher pH, unlike what was observed at lower pH where the presence of H+ competes (electrostatic repulsion) with the dye for active sites of the adsorbent (Rattanaphani et al.,2007).

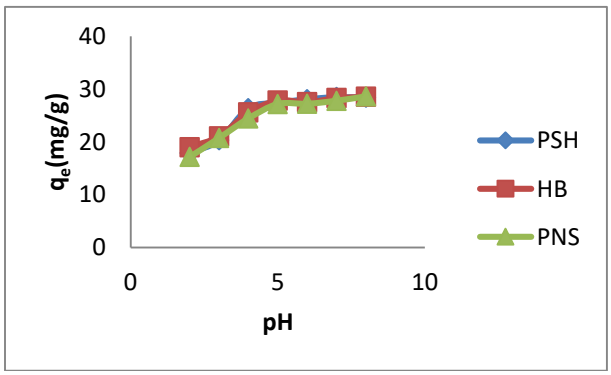

Fig 4: Effect of pH on the adsorption capacity of MB onto PSH, HB & PNS Activated carbon

Effect of Temperature on Adsorption Property of PSH, PNS & HB

Fig 5 show the influence of temperature change on the quantity of MB adsorbed from aqueous solution using the three adsorbents. It was observed from the results that the quantity of MB adsorbed, qe increased from 27.303 mg/g to 28.312 mg/g, from 27.403 mg/g to 28.122 mg/g and from 27.503 mg/g to 28.169 mg/g for HB, PNS and PSH respectively, when the temperature increased from 30 oC to 50 oC. The optimum adsorption temperature was achieved at 50 oC for the three adsorbents (PSH, PNS and HB), beyond this temperature there was slight decrease in the quantity of MB adsorbed for all the adsorbents.

The increase in quantity adsorbed may result from the swelling effect within the internal structure of the carbon of the adsorbent, enabling large dye molecule to penetrate further at higher temperature (Gupta et al., 2000). The little change experience after the optimum temperature is as a result of saturation of the active sites and adsorbate – adsorbent bond start breaking down.

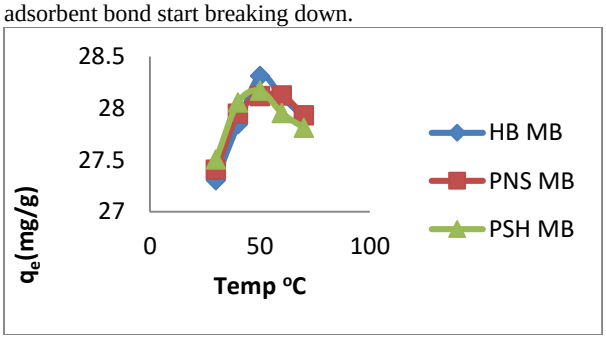

Fig 5: Effect of temperature on adsorption capacity of methylene blue (MB) onto HB, PNS & PSH activated carbon.

Isotherm Studies

Isotherm Study of Methylene Blue (MB) Adsorption onto PSH, PNS and HB

The equilibrium adsorption isotherm of methylene blue (MB) was modeled using Freundlich, Temkin and Langmuir isotherm, The Figs: 6a – 6c show the isotherms. The value of Kf which measures the adsorption capacity of the adsorbent and n which determine the adsorbent surface heterogeneity and also indicates the degree of non-linearity between solution concentration and adsorption were obtained from the slope and intercept of the plot of log qe against log Ce from eqn 4. The Kf and n values from fig 6a: are given in Table 1 as 1.4676 mg/g and 1.4288 for PSH, 1.7894 mg/g and 1.8169 for PNS and 2.6140 mg/g and 2.1173 for HB respectively. The values of n are greater than one (n > 1) which indicates good adsorption process for the three adsorbent (Goldberg, 2005). The Kf values show that HB has higher ability to adsorbed MB dye compared with PSH and PNS. The linearity of the plot with R2 values that are very close to unity is an indication that the adsorption process followed Fruendlich model (Abdus-Salam and Buhari, 2014).

The heat of adsorption adsorbent – adsorbate interaction was evaluated using Temkin isotherm model. From the plot of qe against lnCe, the values of B and AT were calculated from the slope and intercept of Fig. 6b and are listed in Table 1. The maximum binding energy AT is 3.0036, 1.1128 and 1.0191 L/mg for PSH, PNS and HB respectively. The values of B are 4.9012, 4.8347 and 4.9447 Jmol-1 for PSH, PNS and HB respectively, showing the heat of adsorption of methylene blue on the three adsorbents. The correlation co-efficient of (R2) 0.8699,

0.8302 and 0.827 for PSH, PNS and HB respectively, shows that the adsorption of methylene blue onto PSH, PNS and HB fitted the adsorption data well with Temkin isotherm (Abdus-Salam and Buhari, 2014).

For Langmuir isotherm, the values of the adsorption capacity (qm) and the adsorption constant relating to the rate constant (KL) was obtained from the slope and intercept as 55.2486 mg/g and 0.006 L/mg for PSH, 20.1613 mg/g and 0.0850 L/mg for PNS, and 19.2678 mg/g and 0.1453 L/mg for HB respectively. The correlation co-efficient (R2) are 0.9974, 0.9937 and0.9718 for PSH, PNS and HB respectively. The results show that the experimental data fitted well into the isotherms in the order: Langmuir > Fruendlich > Temkin. The value for the dimensionless separation factor RL for PSH, PNS and HB are 0.9434, 0.5405 and 0.4077 respectively, it was found to be between 0.4 and 0.9 which shows that the adsorption of methylene blue onto the three adsorbent is favourable (Safa and Bhatti, 2011). Table 2 shows the comparison of maximum adsorption capacity of different adsorbents for the adsorption of MB. The three adsorbents used in this work have higher adsorption capacity than all other adsorbents reported by other researchers.

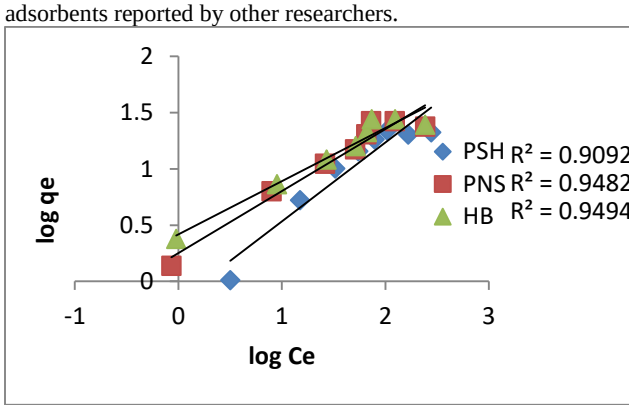

Fig 6a: Freundlich Plot for MB on PSH, PNS & HB

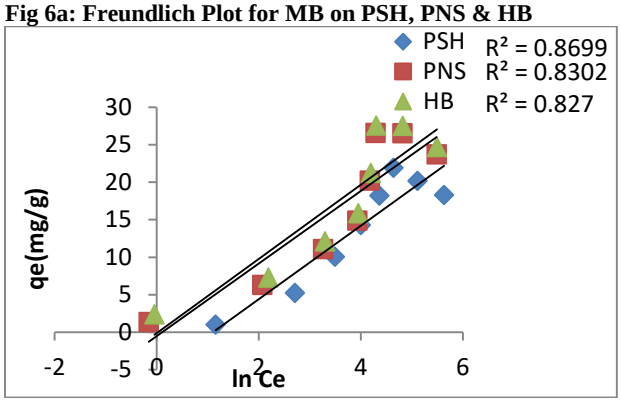

Fig 6b: Temkin Plot for MB on PSH, PNS & HB

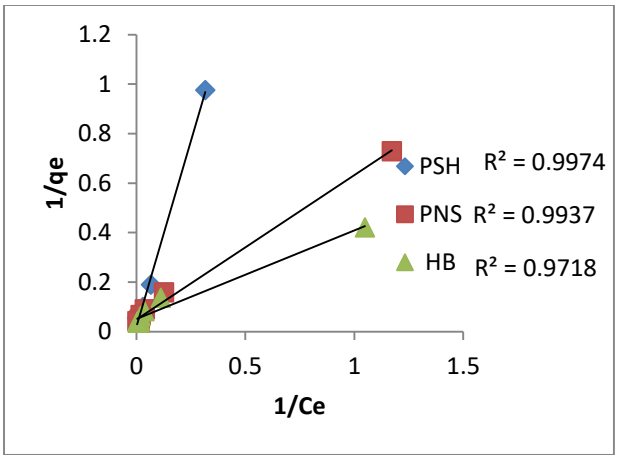

Fig 6C: Langmuir Plot for MB on PSH, PNS & HB

Table 1: Isotherm parameter for MB Adsorption on PSH, PNS and HB

Isotherm model	Parameter	PSH	PNS	HB
Freundlich Isotherm	Kf	1.4676	1.7894	2.6140
	n	1.4288	1.8169	2.1173
	R2	0.9092	0.9482	0.9494
Temkin Isotherm	AT (L/mg)	3.0036	1.1128	1.0191
	B (Jmol-1)	4.9012	4.8347	4.9447
	R2	0.8699	0.8302	0.827
Langmuir Isotherm	KL (L/mg)	0.0060	0.0850	0.1453
	qm (mg/g)	55.2486	20.1613	19.2678
	RL	0.9434	0.5405	0.4077
	R2	0.9974	0.9937	0.9718

Table 2: Comparison of maximum adsorption capacity of different adsorbents for the adsorption of MB.

Adsorbents	Adsorbent capacity qm(mg/g)	Reference
Poplar Sawdust	4.34	Pekkuz and Guzel, 2008
Brazil nut shells	7.81	Dutta et al., 2011
Posidonia oceanic (L) fibres	5.56	Neibi et al.,2007
Oyster shell	0.084	Wen-Tien et al, 2009
Short-neck clam shell	0.893	Wen-Tien et al, 2009
Hildegardia barteri (HB) AC	19.27	This work
Piliostigma thonningii (PSH) AC	55.25	This work
Perqutinia nigrecens (PNS) AC	20.16	This work

Kinetic analysis of methylene blue (MB) adsorption onto PSH, PNS and HB.

The data obtained from the contact time effect in the batch adsorption experiment were subjected to three distinct kinetic models including pseudo first order, pseudo second order and intra-particle diffusion in order to evaluate the adsorption rate and predict details about the adsorbent-adsorbate interaction of methylene blue (MB) on PSH, PNS and HB. The parameters of pseudo first order (k1 and qe cal) are presented in Table 3. The correlation co-efficient R2 (3.0 x 10-5 for PSH, 0.0265 for PNS and 0.4861 for HB) shows that the adsorption of MB does not fit into pseudo - first order model. The value of the calculated adsorption capacity (qe cal) (0.3046 for PSH, 0.0157 for PNS and 0.0078 for HB) shows that there is a considerable difference between the calculated qe cal and the experimental qe exp values for MB adsorption . This confirms that MB adsorption on the three adsorbents (PSH, PNS, and HB) does not obey the kinetic model of pseudo first order.

The pseudo second order rate constant (k2) and the adsorbed quantity of qe cal were obtained from the plot slope and intercept of t / qt vs. t (Figure 7) and are shown in Table 3. It was observed from the Table that the calculated qe cal values (5.4407 for PSH, 5.7937 for PNS and 5.814 for HB) were in close agreement with the experimental (qe exp) value for the three adsorbents unlike the pseudo - first order. Hence, the adsorption of MB onto the three adsorbents follows a pseudo second order kinetic model; this is further confirmed with a linear plot of very high correlation co-efficient values, R2 of 0.9999 for PSH, 1 for both PNS and HB. The fitting of the pseudo second order to the adsorption of MB on to PSH, PNS and HB indicates that the concentration of MB and the adsorbents are involve in rate determining step (Li *et al*., 2008).

The intra-particle rate constant Kid (-0.0077 for PSH, -0.0024 for PNS and -0.0038 for HB) are presented in table 3. The result indicates that the plot was not linear over the whole time range and it does not pass through the origin, which shows that intra-particle diffusion is not the only rate determining step in the adsorption of MB but other kinetic model may control the rate of adsorption (Panida and Xianshe, 2016). The low values of Kid also indicate that intra-particle diffusion mechanism is not the predominant mechanism in the adsorption of MB onto the three adsorbents (Idris *et al.*, 2012).

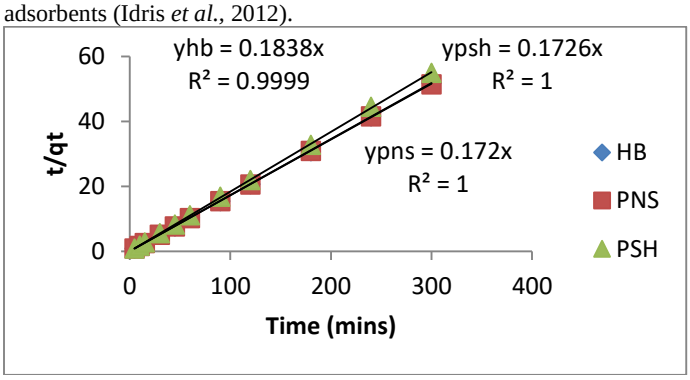

Fig 7: Pseudo second order plot of MB adsorption on HB, PNS and PSH.

Table 3: Kinetic data for methylene blue (MB) adsorption on PSH, PNS and HB

Kinetic model	Parameter	PSH	PNS	HB
Pseudo First Order	k1(min-1)	-2.0 x 10-5	0.0026	0.0073
	qe cal(mg/g)	0.3046	0.0157	0.0078
	qe exp(mg/g)	5.7410	5.8454	5.8441
	R2	3.0 x 10-5	0.0265	0.4861
Pseudo Second Order	k2(gmg-1min-1)	0.00	0.00	0.00
	qe cal(mg/g)	5.4407	5.7937	5.814
	qe exp(mg/g)	5.7410	5.8454	5.8441
	R2	0.9999	1	1
Intra-particle Diffusion	Kid(mg/gmin-0.5)	-0.0077	-0.0024	-0.0038
	C	5.5242	5.848	5.853
	R2	0.1174	0.3705	0.6621

Thermodynamic model for methylene blue (MB)

Thermodynamic parameters such as Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) change of adsorption are presented in Table 4. The negative values of the free Gibb's energy ΔG indicates the degree of spontaneity of the adsorption of MB onto the surface of the three adsorbents (PSH, HB and PNS) and that the system does not gain energy from an external source. It can also be observed that the negative value of the free energy, ΔG increases from -2.21 to -2.57 kJmol-1, - 2.94 to -3.33 kJ/mol and -3.20 to -3.64 kJ/mol for PSH, HB and PNS respectively, reflecting a more energetic favourable

adsorption at higher temperature. Generally, the ΔG value between 0 and -20 kJ/ mol is consistent with the electrostatic relationship between adsorption sites and the adsorbing ion (physical adsorption), and the value of ΔG in the range of -80 to -400 kJ/mol may denotes that the adsorption concern command sharing or transferring from the adsorbent surface to the adsorbing ion forming a co-ordinate bond between them (chemical adsorption)(Amrhar et al.,2015). Therefore, the adsorption of MB onto the three adsorbents may be a physical adsorption with a weak force of attraction between MB molecules and the three adsorbents.

The negative value of the enthalpy change (ΔH) for PSH (-0.065kJ/mol) shows that the adsorption was exothermic in nature, while the positive value of the enthalpy change (ΔH) for HB 0.017 kJ/mol and 0.128 kJ/mol for PNS indicates that the adsorption of MB onto the two adsorbents are endothermic in nature. The positive values of the entropy change (ΔS) (7.30 J/mol/K for PSH, 9.77 J/mol/K for HB and 11 J/mol/K for PNS), suggest that there is increase in irregularity and randomness at the adsorbent-adsorbate solution interface during the adsorption of methylene blue (MB) onto the surface of PSH, HB and PNS (Amrhar et al.,2015). This favours adsorption of MB.

Table 4: Thermodynamic parameters calculated for the adsorption of methylene blue (MB) onto PSH, HB and PNS.

Adsorbent	T (K)	ΔG (kJ/mol)	ΔS(J/mol/K)	ΔH(kJ/mol)
PSH	303	-2.21	7.30	-0.065
	313	-2.35		
	323	-2.42		
	333	-2.49		
	343	-2.57		
HB	303	-2.94	9.77	0.017
	313	-3.04		
	323	-3.14		
	333	-3.24		
	343	-3.33		
PNS	303	-3.20	11	0.128
	313	-3.31		
	323	-3.42		
	333	-3.53		
	343	-3.64		

Conclusion:

From the present study, it can be seen that the PSH, PNS and HB fruit shells can be used effectively for the removal of methylene blue dye from aqueous solutions. The adsorption capacity qe decrease with increase in adsorbent dosage from 0.2 – 2 g. The Langmuir adsorption isotherm was found to fit best than the other isotherm models by its high correlation coefficients R2 > 0.94. All the process for the three activated carbon (HB, PNS and PSH) best fitted by pseudo – second order model suggesting that chemisorptions process could be the rate determining step in the adsorption process. The removal of the dye from aqueous solution was induced by adsorption on surface sites of the solid for low methylene blue dye concentration while both adsorption and internal exchange took place for high concentrations.

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