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J. Appl. Sci. Environ. Manage. *December*, 2010

Vol. 14 (4) 141 - 145

Estimation of Specific Surface Area using Langmuir Isotherm Method

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ABSTRACT: A comparison of four widely used linear equations of the Langmuir types of isotherm (The Langmuir Type 1, 2, 3 and 4) were examined in an experiment using dye sorption onto derived acid and salt treated Fish Activated Carbon (H_3PO_4-FAC and $ZnCl_2$-FAC respectively). Isotherm parameters obtained from the four Langmuir linear equations differed. Though Langmuir type 1 is the most popular form, but the type 2 had the highest coefficient of determination (R^2 = 0.931-0.984) compared with the other Langmuir linear equations (with R^2 values ranges of 0.696-0.982, 0.613-0.926 and 0.613-0.926 for Langmuir type 1,3 and 4 isotherm models respectively). 3,7 bis(dimethylamino) phenothiazin-5-ium ion was used to measure the Extent of monolayer coverage (q_m) and specific surface areas (S_{MB}) following the application of type 1 isotherm. From this study, Value obtained for the Acid treated carbon (H_3PO_4-FAC with S_{MB} ; 18.170) is higher than that of the Salt treated carbon, ($ZnCl_2$-FAC, S_{MB} ; 13.579) which compared more to that of commercial carbon, CAC (S_{MB} ; 13.884) units in multiple of $10^{-3}km^2kg^{-1}$. The reliability of the Langmuir type 1 and 2 methods seems very good in specific surface area estimation. @JASEM

Equilibrium relationships between sorbents and sorbates are described by sorption isotherms which give the capacity of a sorbent for a sorbate (Yuh,2006). Isotherms can be obtained by examining batch reactions at fixed temperatures. Linear regression is frequently used to determine the best-fitting isotherm. In this present study, the linear least-squares method via the correlation coefficient (R^2) was used (Yuh,2006).Specific surface area is defined as the accessible area of solid surface per unit mass of material. Because the surrounding phase can modify the surface area, each method that was studied for measuring surface had shortcomings (Chongrak *et al.*,1998)

The interference by the surrounding phase was especially problematical for the Nitrogen adsorption/desorption isotherm method in which case the entire surface was modified by vacuum dried treatment before Nitrogen adsorption (Chongrak *et al.*, 1998). This method measures only the external and not the internal surface area. The method of adsorption of methylene blue in liquid phase for specific surface area determination has been adopted widely for various natural solids: activated carbon, charcoal, graphite, and silica, for example. The method of methylene blue adsorption for measuring the specific surface area of fish carbon, as established here, can provide a common reference method for adsorbent characterization in quality control, much like other mechanical properties. The objective was to estimate the specific surface area of derived Fish carbon, to compare, in the future, with the surface area determined by other methods. The Langmuir equation was used to calculate the specific surface area of the adsorbent. The general form of Langmuir isotherm is (Chongrak *et al.,*1998).

$$Y = KC_e/(1+KC_e) \quad (1)$$

where *Y* is the fraction of fish carbon surface covered by adsorbed methylene blue molecules, *K* is a constant, and C_e is the equilibrium methylene blue solution concentration. In this study, $Y = N/Nm$, where *N* (taken as q_e) represents the number of moles of methylene blue adsorbed per gram of derived sorbent at equilibrium concentration, C_e, and *N*m is the number of moles of methylene blue per gram of sorbent required to form a monolayer (Taken as q_m), with units in mg/g. After making the substitution and rearranging Eq. 1, it became

$$q_e/q_m = KC_e/(1+KC_e) \quad (2)$$

On rearrangement, equation 2 becomes

$$C_e/q_e = (1/q_m)C_e + 1/Kq_m \quad (3)$$

For all adsorption isotherms of methylene blue onto fish carbon, the plot of C_e/q_e vs. C_e gives a straight line with slope equal to $1/q_m$, and intercept equal to $1/Kq_m$. Therefore, the Langmuir isotherm is an adequate description of the adsorption of the methylene blue onto adsorbent. The specific surface area was calculated by the following equation (Chongrak *et al.*,1998; Itodo *et al.,*2010a,b)

$$S_{MB} = (q_m \times a_{MB} \times N_A \times 10^{-20})/ M \quad (4)$$

S_{MB} is the specific surface area in $10^{-3}km^2\ kg^{-1}$; q_e is the number of molecules of methylene blue adsorbed at the monolayer of fibers in mgg^{-1} . a_{MB} is the occupied surface area of one molecule of methylene blue =197.2 Å² (Graham, 1955; Ardizzone *et al.,*2003) ; N_A is Avogadro's number, 6.02 x 1023 mol^{-1} ; and M is the molecular weight of methylene

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blue, 373.9 g mol^{-1}. Equation 3 is typical of the Langmuir type 1 isotherm. Other forms are summarized in Table 1.

Table 1: Langmuir Isotherm showing the type 1,2,3 and 4 linear forms

Isotherm	General Form	Linear Form	Plot
Langmuir Type 1	$q_e = (q_m K_a C_e)/1+K_a C_e$	$C_e/q_e=(1/q_m)C_e + 1/Kq_m$	C_e/q_e Vs C_e
Langmuir Type 2		$1/qe=(1/K_a q_m)1/C_e +1/q_m$	$1/q_e$ Vs $1/C_e$
Langmuir Type 3		$q_e = q_m - (1/K_a)\ (q_e/C_e)$	q_e Vs (q_e/C_e)
Langmuir Type 4		$q_e/C_e= K_a q_m - K_a\ (q_e)$	q_e/C_e Vs q_e

(Itodo *et al*.,2009 a, b, c, d, e; ;Yuh,2006)

In this present study, Methylene blue was chosen because of its known strong adsorption onto solids and its recognized usefulness in characterizing adsorptive material (Ardizzone *et al.,*2003) . It has a molecular weight of 373.9 x 10^{-3} kg mol^{-1} .The structure of this dye is shown in Fig. 1.

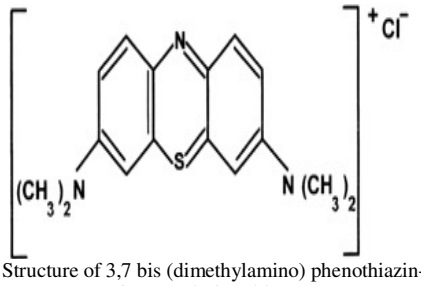

Fig. 1: Structure of 3,7 bis (dimethylamino) phenothiazin-5-ium ion (Methylene blue)

MATERIALS AND METHODS

Fish (*Oreochromis niloticus*, popularly called Nile tilapia) of slight spoilage evidence was procured from Sokoto central market. The Fish samples were washed with plenty of water to removes surface impurities, Boiled several time to reduce oil contents, rinsed and sundried. Fish samples were dried in an oven at 100^{O}C overnight (Omonhenle *et al,* 2006) and pulverized, followed by sieving with a < 2mm mesh size sieve. The less than 2mm samples were stored in airtight containers. A one step Activation process,earlier described elsewhere (Gimba *et al*., et al.,2001; Itodo et al.,2009a,b,c,d,e) was adopted with slight modification. Approximately 3g of each pretreated fish sample, of < 2mm mesh size) were mixed separately with 3cm^3 of each 1M activating agent (H_3PO_4, $ZnCl_2$) .The sample mixtures were subjected to the furnace at 800^{O}C for 5 minutes. The samples were removed, poured into ice water bath, excess water was drained and allowed to stand at room temperature. The procedure was repeated for different residual time (5min, 10min) for the different activating agents . As a modification. the activated carbon generated above were washed, using 10% HCl to removed surface ash, followed by warm water. Rinsing was done with distilled water to removed residual acid . The sample was then dried in an oven at 110^{O}C overnight and ball milled into sizes that passes through both <0.5 and< 2mm sieve .Washing of activated samples was complete when a pH of 6-8 was ascertained (Itodo *et al*.,2008).

Methylene blue stock (1000mgl-1) and standard solution: Methylene blue; MB (purchased from S.D Chem, Boiser) and obtained as sealed from the chemical store of UDUSOK. The MB was dried at 110°c for 2 hours before use. All of the Methylene blue solution was prepared with distilled water. The basic dye (Methylene blue) was used without further purification. (i) A stock solution of 1000mgl^{-1} was prepared by dissolving 1.127g Methylene blue in 1000ml distilled water (Omomnhenle *et al.*, 2006). This gives the Methylene stock. The experimental solution was prepared by diluting the stock solution with distilled water in the range of 10,15,20,25 and 30mgl^{-1}. The concentration of MB was determined at 630nm by the UV – visible spectrophotometer (Chongrak *et al.,*1998). A calibration curve of optical densities against methylene blue concentrations was obtained by using standard methylene blue solutions of known concentrations at pH values between 7 and 8. This was done to verify the wavelength for a 30mg/L concentration. An adsorption study was carried out in a batch mode at a predetermined 1h interaction time in series of 50ml conical flasks after agitation.

RESULTS AND DISCUSSION

The optimum temperature for activation was earlier experimentally determined to be 800^{o}c above which high level of residual ash sets in. Result in Tables 2 showed that activation burn off is high with a resultant low % yield at a longer activation dwell time (10 minutes). The entire results fall within the range for published data (Odebunmi and Okeola, 2001).

Table 2: Percentage Burn off, % Yield and Bulk density of Acid and Salt Treated Fish Carbon

Sample	Activation burn off (%)	Yield (%)	Bulk density ($glcm^3$)
H_3PO_4-FAC /5min	29.24	70.76	1.520
H_3PO_4-FAC /10min	37.33	62.67	1.570
$ZnCl_2$-FAC /5min	18.42	81.58	1.710
$ZnCl_2$-FAC /10min	20.00	80.00	1.862

H_3PO_4-FAC /5min- acid(H_3PO_4) treated Fish Activated Carbon at 5mins activation, $ZnCl_2$-FAC /10min- Salt ($ZnCl_2$) treated Fish Activated Carbon at 10mins activation

No considerable impact of activation time on yield is observed for the adsorbent prepared by $ZnCl_2$ modification. On the contrary, activating agents plays a major role as made evidence on Table 2. $ZnCl_2$ treated adsorbent presented higher yield compared to their corresponding Acid treated adsorbent.

Table 3: Langmuir Adsorption Isotherm Experimental Data for Commercial Activated Carbon (CAC).

C_o	C_e	q_e	C_e/q_e	$1/q_e$	$1/C_e$	q_e/C_e
10	0.469	0.956	0.490586	1.046025	2.132196	2.03838
15	0.767	1.423	0.539002	0.702741	1.303781	1.85528
20	1.119	1.888	0.592691	0.529661	0.893655	1.687221
25	1.949	2.305	0.845553	0.433839	0.513084	1.182658
30	6.25	4.373	1.429225	0.228676	0.16	0.69968

Table 4 : Langmuir Adsorption Isotherm Experimental Data for Acid Treated Fish Carbon (H_3PO_4-FAC).

C_o	C_e	q_e	C_e/q_e	$1/q_e$	$1/C_e$	q_e/C_e
10	0.933	0.906	1.029801	1.103753	1.071811	0.971061
15	1.121	1.187	0.944398	0.84246	0.892061	1.058876
20	1.909	1.809	1.055279	0.552792	0.523834	0.947617
25	2.856	2.214	1.289973	0.451671	0.35014	0.77521
30	5.723	4.427	1.292749	0.225887	0.174734	0.773545

Linear regression is frequently used to determine the best-fitting isotherm, However, the Langmuir isotherm can be linearized as four different types (Table 1), and simple linear regression will result in different parameter estimates The more popular linear forms used are Langmuir-1 and Langmuir- 2, and the best fit is obtained using Langmuir-2 because of the minimal deviations from the fitted equation resulting in the best error distribution or perfect correlation (R^2=1.00). Figures 3 to 6 show the four linear Langmuir equations with the experimental data for the sorption of dye onto Fish carbon at various initial concentrations (Co). Values of the Langmuir constants, the saturated monolayer sorption capacity, q_m, and the sorption equilibrium constant, Ka, are presented in Table 5 for the sorption of dye onto Fish carbon at room temperature. These values of the coefficient of determinations, R^2, obtained from Langmuir-1, indicate that there is strong positive evidence that the sorption of dye onto the adsorbent follows the Langmuir isotherm (Yuh,2006).

The linear analysis using different linear forms of the Langmuir equation will significantly affect calculations of the Langmuir parameters. Table 5 shows typical results of the Langmuir constants. It seems that the Langmuir isotherm obtained from Langmuir-2 provided a better fit to the experimental data.

Specific Surface Area (S_{MB}) Determination: The typical Langmuir type 1 adsorption isotherm of Methylene blue on Fish carbon represented by equation 3 was made (figure not shown) for commercial activated carbon and figure 3 for the acid treated activated carbon. The type 1 isotherm is generally associated with monolayer adsorption . However, their initial slopes do not lie very close to the *y*-axis. This either shows that the affinity of methylene blue for the adsorbent is moderate or, on the other hand, that this affinity may be ascribed to a Van der Waals force (Yuh,2006). The Langmuir isotherm shows that the amount of methylene blue adsorbed increases as the concentration increases up to a saturation point. Beyond this point, increasing the methylene blue concentration will not cause further increase. This behavior is typical of sorbents with a limited number of accessible sites. As long as there are available sites, adsorption will increase with increasing methylene blue concentration, but as soon as all of the sites are occupied, a further increase in the quantity of methylene blue will result to a negative adsorption (desorption) at the monolayer. The acid treated activated carbon (H_3PO_4-FAC) proves to have a higher surface area (S_{MB} = $18.170 \times 10^{-3} km^2 kg^{-1}$) than the salt treated fish carbon (S_{MB} = $13.579 \times 10^{-3} km^2 kg^{-1}$) which compares more to that of the commercially available activated carbon

(S_{MB} = 13.884 $\times 10^{-3} km^2 kg^{-1}$). The trends therefore imply that the level of accessible area of solid surface (Fish carbon) per unit mass of material (Methylene blue dye) follows the order of; H_3PO_4-FAC > CAC > $ZnCl_2$-FAC.

Table 5: Langmuir Type 1, 2, 3 and 4 Isotherm Experimental Constants for Commercial, Acid and Salt Treated Fish Carbon.

Adsorbent	Langmuir Isotherm	Equation (y =)	R^2	q_m(mg/g)	K_a(Lmg^{-1})	S_{MB} ($10^{-3} km^2 kg^{-1}$)
CAC	Type 1	0.161x+0.438	0.982	6.211	0.368	13.884
	Type 2	0.402x+0.185	0.993	5.405	0.462	
	Type 3	-0.397x+2.363	0.926	-0.397	2.519	
	Type 4	-2.329x+5.666	0.926	2.433	2.329	
H_3PO_4-FAC	Type 1	0.068x+0.951	0.696	14.706	0.072	18.170
	Type 2	0.911x+0.086	0.984	11.627	0.094	
	Type 3	-0.071x+1.055	0.613	-0.071	14.085	
	Type 4	-8.634x+9.925	0.613	1.150	8.634	
$ZnCl_2$-FAC	Type 1	0.191x+0.456	0.781	5.236	0.419	13.579
	Type 2	0.914x+0.075	0.931	13.333	0.082	
	Type 3	-0.197x+1.400	0.919	-9.197	5.076	
	Type 4	-4.668x+6.708	0.919	1.434	4.668	

CAC- Commercial Activated carbon, H_3PO_4-FAC- Acid treated Fish Activated Carbon, $ZnCl_2$-FAC – Salt Treated Fish Activated Carbon

Monolayer Coverage: The theoretical concept behind the Langmuir are (1) The adsorption is an equilibrium process (2) The adsorption cannot proceed beyond monolayer coverage (3) All sites are equivalent and the surface is uniform i.e the surface is perfectly flat on a microscopic scale. Hence, the ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites (Hammaini *et al*., 2007; Itodo *et al.,*2010 a,b,c). A confirmation of the fitness of experiment data into Langmuir isotherm model indicates the homogenous nature of the adsorbent surface. The result will also demonstrate the formation of monolayer coverage of dye molecule at the outer layer of the adsorbent (Hammed *et al.,* 2006). q_{max} is the maximum sorption uptake. The Langmuir values (q_m) from isotherms were related to the maximum adsorption capacity (mgg^{-1}) or the saturated monolayer capacity (Yuh,2006) while K_a is the adsorption energy (Lmg^{-1}) (Itodo *et al.,*2010 a,b,c). In this research, q_m is defined as the amount of adsorbate per unit gram of adsorbent required to to form a monolayer coverage (Chongrak *et al*., 1998). Results on Table 5 which was based on the best fit isotherm (Langmuir type 2) indicates that the level of monolayer coverage follows the other of q_m for $ZnCl_2$-FAC (13.333) > H_3PO_4-FAC (11.627) > CAC (5.405) mg/g. It thus implies that the maximum adsorption capacity of adsorption onto a uniform surface follows the said trends or order. It also implies that $ZnCl_2$-FAC (q_m;13.333) exhibit more monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with less transmigration of adsorbate in the plane surface (Hameed *et al*., 2006). It also implies that the adsorbent is more homogenous in surface structure, thus, demonstrate also the formation of monolayer coverage of dye molecule at the outer layer of the adsorbent (Hammed *et al.,* 2006). It does not necessarily mean that the adsorbent is better.

Conclusion: It is not appropriate to use the coefficient of determination of the linear regression method for comparing the best-fitting isotherms. Langmuir type 1 is the most-popular linear form but did not present the best fit as a model for dye uptake by derived Fish carbon. Highlights in this analysis showed that the Type 2 isotherm (which had the highest coefficient of determination) could be used in estimating extend of monolayer coverage, The type 1 isotherm is suitable for estimating Specific surface area (S_{MB}), The type 3 isotherm is difficult to interpret and characterized with negative q_m values while the type 4 isotherm shared common characteristics with type 1 and 2. Generally, the adsorption of methylene blue allows the determination of the specific surface area of natural Fish carbon. This work has shown that the method is simple and requires less elaborate apparatus and time than other methods.

Acknowledgements: Authors are grateful to Itodo Praise Udoji for his resources utilized in this analysis and to the Technologists of Agric Soil Science Laboratory of Usmanu Danfodiyo University, Sokoto for donating the furnace and routine apparatus used in this research.

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