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Application of Methylene Blue Adsorption Technique in the Determination of Specific Surface Area of Termite Feathers

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Abstract: Methylene Blue (MB) adsorption technique was employed in the measurement of the Specific Surface Area (SSA) of Termite Feathers (TF). The adsorption study was carried out at 25°C and 270 rpm after which the residual concentration of MB was determined spectrophotometrically at a wavelength of 660 nm. The adsorption data was found to conform to the Langmuir model within the concentration range studied and Langmuir constants were determined for TF. The specific surface area was then calculated from the Langmuir isotherm constant 'b'. Effect of pre-treatment temperature on SSA was also considered at 30, 40, 50 and 60^{O}C. The specific surface area was found to be 58.85 m^2/g for the raw TF with values of 60.34, 78.52, 99.64 and 118.26 m^2/g for the samples pre-treated at 30, 40, 50 and 60^{O}C respectively. Finally, the specific surface area value obtained by MB adsorption technique was then compared with those obtained by Orth phenanthroline (OP) and p-nitrophenol (PNP) adsorption.

Keywords: Methylene Blue, Adsorption, Langmuir Constants, Specific Surface Area.

1. Introduction

Specific surface area is defined as the accessible area of solid surface per unit mass of material. It is a surface characteristic of a material just like surface roughness, pore size, reflectivity etc. that is associated with its surface. Surface characteristics have wide application in adsorption, semiconductors, heterogeneous catalysts and also in biological research.

Various techniques have been applied in the determination of surface area such as: Brunauer-Emmett-Teller (BET) method, moisture adsorption nitrogen adsorption NMR etc [1-4]. Surface areas can be determined from heats of immersion or adsorption and this technique has been greatly simplied with the introduction of the flow microcalorimeter [5].

Adsorption techniques such as adsorption from solution were suggested [6-8]. Adsorption studies have been described with fatty acids, aromatic acids, esters, phenols, iodine, polymers, and dyestuffs using a range of analytical techniques [9]. Surface areas may also be calculated from size distribution data and this transformation is the subject of a British Standard [10].

The use of adsorption from solution in determining surface areas is of secondary importance, but it still has the attraction that the experimental procedure is much simpler than in any method requiring a vacuum apparatus, and if routine measurements on a large number of samples are involved, it is usually much quicker. Each method presents inconveniences and difficulties because of modifications in the surface area caused by the surrounding phase.

Methylene blue method was chosen in this work due to the strong adsorption of methylene blue onto solids and its recognized usefulness in characterizing adsorptive material and because adsorbate concentration can be determined Spectrophotometrically thereby simplifying the experiment [4, 11-14].

The methylene blue adsorption method for specific surface area determination has been applied widely for different natural solids such as graphite, charcoal, silica, activated carbon etc [15]. Its application to keratinous materials had not previously been reported.

The structure of Methylene blue or 3, 7-bis (dimethylamino)-phenothiazin-5-ium chloride, which is a popular cationic dye majorly used in the paper and textile industries is shown in Figure 1 below [16]. The

dye forms ionic bonds with the substrates owing to its cationic (basic) nature. It has a molecular weight of 373.9 g mol^{-1}.

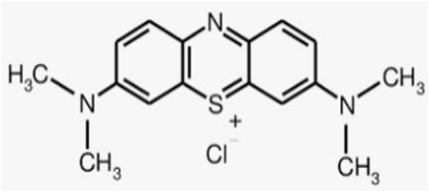

Figure 1: Structure of Methylene Blue

Keratin belongs to a group of fibrous structural proteins that protects epithelial cells from damage and makes up the outer layer of human skin [17]. It is the major structural component of wool, hair, feathers, horn and nail providing them with the required strength and toughness for masticatory organs, such as the tongue [18]. Keratinous materials sometimes constitute waste materials around us thereby making their use as adsorbent attractive either after pretreatment or in their raw form. Feathers are made up of about 91% keratin, 1.3% fat, and 7.9% water, making them a suitable sorbent for heavy metals removal [17].

From available literature, it was observed that no work has been reported on the specific surface area determination of feathers by methylene blue dye adsorption. This motivated our attempt to determine the specific surface area of TF using this technique and to determine the effect of pre-treatment temperature on the specific surface area of the TF

The Langmuir equation was used to calculate the specific surface area of the adsorbent. The nonlinear form and linear forms are presented in Table 1.

2. Materials and Methods

2.1 Materials

Termite Feathers (TF) were collected at night immediately after rainfall, washed several times with distilled water and then left to dry at room temperature. The feathers were cut into smaller sizes using a scissors. The smaller sized feathers were used in the biosorption experiments.

2.2 Chemicals

All the chemicals used in this work were of analytical grade. Preparation of adsorbate was carried out by preparing 1000 mg/L Methylene Blue stock. Methylene Blue was dried at 110°c for 2 hours before use. 1.127g Methylene blue was dissolved in 1000 ml distilled water. This gives the Methylene stock. 1000 mg/L of Orth phenanthroline and Para nitrophenol stock were also prepared accordingly.

2.3 Batch Adsorption

The experimental solution was prepared by diluting the stock solution with distilled water to the required concentrations. Batch sorption was carried out at 270 rpm in batch mode and the residual concentration determined at 660nm. A calibration curve was prepared at a pH of 7 – 8 using known concentration of MB.

MB uptake was determined using the equation below:

$$q\ (mg/g) = \frac{(C_i - C_f) \times V}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 1$$

where C_i and C_f are the initial and final concentrations (mmol/L) of MB, q is the metal adsorption capacity of adsorbent (mmol/g) at tested operating conditions, V is adsorbate solution volume (L) and W is the adsorbent amount (g), respectively.

Similar procedure described above were used for OP and PNP.

Table 1. Nonlinear and linear forms of the Langmuir isotherm

Non linear form	Linearized forms			Plot
	Types	Title	Equation	
$q_e = \frac{Q_{max} b C_e}{1 + b C_e}$	I	Hanes-Woolf linearization	$\frac{C_e}{q_e} = \left(\frac{1}{Q_{max}}\right) C_e + \frac{1}{Q_{max} b}$	$\frac{C_e}{q_e}$ vs C_e
	II	Lineweaver-Burk linearization	$\frac{1}{q_e} = \left(\frac{1}{Q_{max} b}\right) \frac{1}{C_e} + \frac{1}{Q_{max}}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$
	III	Eadie-Hoffsie linearization	$q_e = \left(\frac{-1}{b}\right) \frac{q_e}{C_e} + Q_{max}$	q_e vs $\frac{q_e}{C_e}$
	IV	Scratchard linearization	$\frac{q_e}{C_e} = -b q_e + Q_{max} b$	$\frac{q_e}{C_e}$ vs q_e

3. Results and Discussion

Table 2. Physicochemical Analysis of Sorbent

Parameters	Values
pH	8.40
Moisture (%)	6.97
Loss of mass (%)	86.60
Bulk density (g/cm^3)	0.0132

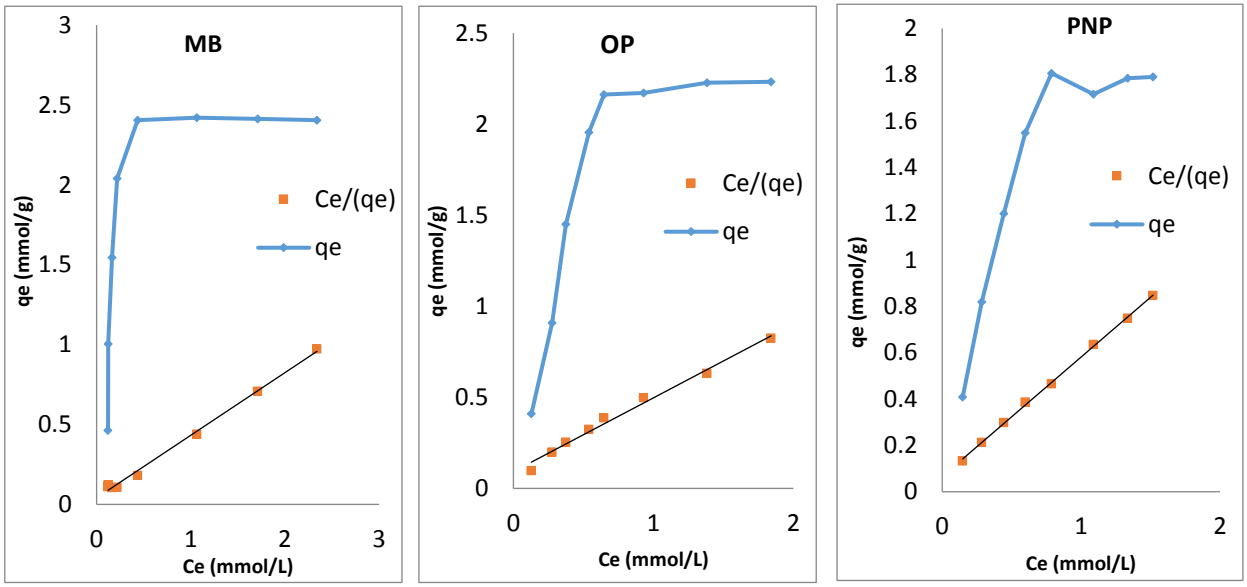

Figure 2. Adsorption isotherm and Langmuir line for (a) TF/MB (b) TF/OP (c) TF/PNP

Table 3. Langmuir constants

Dye	Qmax (mmol/g)	b	R_L	R^2
MB	0.0752	1.70	0.00649	0.9956
OP	0.0247	4.40	0.00252	0.9875
PNP	0.0194	7.86	0.00141	0.9992

Table 4. Specific surface area of TF

Dye	SSA (m^2/g)
MB	58.85
OP	8.92
PNP	6.13

Table 5. Effect of pre-treatment temperature on specific surface area by MB adsorption

Adsorbent	Drying temperature (^{O}C)	SSA (m^2/g)
TF60	60	118.26
TF50	50	99.64
TF40	40	78.52
TF30	30	60.34
TF	Raw	58.85

3.1 Physicochemical Analysis of Sorbent

Table 2, showed the physicochemical properties of the adsorbent. The pH of the raw adsorbent was found to be 8.40 indicating a slightly basic value. Moisture is the presence of a liquid, especially water, often in trace amounts [19]. The moisture content was found to be 6.97%. It has been observed that high moisture content generally decreases the adsorption capacity for organic dyes [20, 21]. Bulk density is the amount of a powdered sample by weight that is present in a defined volume. The sample used in this work has a bulk density of 0.0132 g/cm^3

3.2 Adsorption Isotherms

From the correlation coefficient (R^2) as shown in Table 3, it is evident that Langmuir model fits the adsorption data giving credence to the formation of monolayer surface of MB on the adsorbent surface [22].

Obtained adsorption data were analyzed according to Langmuir type 1 (Hanes-Woolf linearization) [23].

linearization) [23].

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max}b} \quad \text{.....2}$$

Where:

Ce = equilibrium concentration of adsorbate in solution (mg/L)

qe = uptake at equilibrium (mg/L)

b = Langmuir adsorption constant indicating bonding energy (L/mg)

Qmax = qm = monolayer capacity (mg/g)

The assumptions of the Langmuir model are: (i) the sorbent surface has a fixed number of energetically uniform sites (ii) the adsorbed species do not interact (iii) only a monolayer surface is formed after saturation (iv) adsorbed species do not transmigrate [23].

For adsorption of MB onto TF, the typical Langmuir type 1 adsorption isotherm as shown in Table 1 was employed. This Langmuir type 1 isotherm model is generally associated with monolayer coverage. From the plots, it is evident that the slopes of the plots do not lie too close to the y-axis. This is an indication that the MB-TF (sorbate-sorbent) affinity is moderate and likely due to Van der Waals force [24].

From the Langmuir isotherm plots shown in Figure 2, uptake of MB increases as the concentration increases up to the point of saturation. Provided there are sorption sites, MB uptake will increase as concentration of MB increases. Beyond the saturation point, further increase in concentration will cause no further increase in MB uptake. This is as a result of limited number of sorption sites.

An important feature of Langmuir isotherm equation is a dimensionless constant known as separation factor or equilibrium parameter, R_L. Its value indicates the adsorption nature to be either unfavourable if R_L>1, linear if R_L =1, favourable if 0< R_L<1 and irreversible if R_L=0. As can be seen in Table 3, R_L values were all less than 1 indicating that the equilibrium sorption was favorable [25]

3.3 Calculation of SSA

Methylene blue is often used in the determination of SSA due to it very fast adsorption on solid sorbents. This technique is also simple with high reliability with most solids. The specific surface area (SSA) was calculated using the equation below

$$SSA = q_m \times \omega \times N_A \quad \text{..... 3}$$

Where:

q_m = monolayer capacity in mol/g

ω = area occupied by adsorbate molecule in the filled monolayer on the adsorbent surface in m^2.

N_A = Avogadro's number in mol^{-1} (6.02 x 10^{23} mol^{-1})

From literatures, area occupied by MB molecule (ω) ranges between 60Å^2 (vertical monomer) and/or 120 Å^2 (flat dimer) [26-28] to 100 Å^2 [29], 130 Å^2 [30], 178 Å^2 [31] and up to 200 Å^2 [32].

Occupied area for MB, OP and PNP were taken as 130 Å^2, 60 Å^2 and 52.5 Å^2 respectively. Various factors that affect the adsorption of dyes unto sorbent surfaces account for the discrepancies in these values [10].

3.4 Comparing the SSA of MB, OP and PNP

The values of the SSA obtained for MB, OP and PNP are presented in Table 4. From the results obtained, it is obvious that the value obtained for MB is significantly higher than those obtained for OP and PNP. The specific surface area for OP and PNP are closer compared to the value obtained for MB.

3.5 Effect of pre-treatment temperature on SSA

From Table 5 it is evident that temperature of treatment can affect the SSA and hence uptake of MB. The sample treated at 60^{O}C has the highest SSA that is almost twice the value obtained for sample treated at

30^{O}C. the raw sample was found to have the lowest SSA. This may be due to a higher area in the sample treated at 60^{O}C. Also, samples treated at higher temperature contain less adsorbed water at the surface when compared with those treated at lower temperature and raw sample.

Finally, the amount of accessible area of solid surface (sorbent) per unit mass of material (sorbate, MB) is in the following order: TF60 > TF50 > TF40 > TF30 > TF.

4. Conclusion

From the results obtained, it is clear that the MB technique allows for the determination of specific surface area of TF. It can be concluded that this method is simple and requires simple laboratory apparatus and less time. The adsorption isotherms were found to follow the Langmuir equation. Finally, highest MB adsorption corresponding to highest specific surface area of 18.26 m^2/g was achieved by TF sample pre-treated at 60^{O}C.

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Conflict of interest

The Authors have no conflicts of interest to declare that they are relevant to the content of this article.

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