



# Adsorption of methylene blue onto the outside of manufactured twin propensity for - goethite propensity has been studied in glycerol solution

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## Abstract

Adsorption of methylene blue onto the surface of synthetic twin habit of -goethite habit has been investigated in glycerol solution at 25, 30 and 35°C. For the twin habit adsorbent, it appears the results are consistent with an adsorbed phase confined to monolayer model with edgewise orientation of methylene blue (MB) molecules on the surface. Composite isotherms were calculated from the apparent adsorption isotherms by well established method. The data was adequately described by the three - isotherm equations (Langmuir, Freundlich and Temkin models) and the data follow a dubinin isotherm. The combined adsorption isotherm and spectroscopic results have shown that the surface of this habit could be heterogeneous, if the presences of two acidic sites are presumed to be the adsorption sites which have been identified as of the Lewis and Br nsted acid type. Thermodynamic quantities for the adsorption of MB on the twin habit,  $H_a$ ,  $G_a$  and  $S_a$  are calculated, and an attempt is made to correlate the trend observed with thermodynamic laws as well as nature of interactions at the interface.

**Keywords:** Adsorption isotherms, methylene blue, twin - goethite.

## INTRODUCTION

Reuss's (Mellor, 1934) pioneering achievement when he discussed goethite ( -FeOOH) formation in nature provided much of the impetus behind the synthesis of - goethite that started early through the 19<sup>th</sup> century. This iron oxide is dispersed throughout the soil matrix in the form of finely divided particles, possibly as coating on the surface of other clay minerals. The development of synthetic - FeOOH subsequently broadened on an unsuspected scale and fertilized its use in adsorption, structural studies (Parfitt et al., 1976), the description of interfacial process (Breeuwsma and Lyklema, 1973) and surface complication model (Kelvin et al., 1985).

However, it has not been realized that this - goethite may form twin as well as acicular habit (Mackenzie and Meldau, 1959), until Atkinson et al. (1968), established that -goethite preparation could be nucleated into two crystalline habits referred to as acicular and twin. These habits may be expected to present different crystal faces and therefore differ as adsorbents. Thus, laboratory synthesis of twin habit might not be difficult to accomplish. Most attention is given to the synthesis, characterization and reactions quantifying acid-base properties of this oxide, acicular habit. This is because of its various activities such as retention of fertilizer and pesticide and in immobi-

lizing cation in lateritic soil (Russell et al., 1974). In addition to its occurrence in soils and sediments, and as surface coatings on other minerals, its adsorption characteristics are of considerable geochemical and pedological interest.

Earlier work reported on methylene blue (MB) adsorption from liquid solutions was from aqueous solutions (Faruqi et al., 1967; Bodenheimer and Heller, 1968; Kipling and Wilson, 1960; Hang and Brindley, 1970 and Margaret et al., 1958) unto mainly Clay, Kaolinite, Montmorillonite, and silica solid surfaces. None of these reports to our knowledge covers the adsorption of this solute, (methylene blue) onto twin habit of - goethite from organic solvent and even discussed the adsorption isotherms. It is well known that the hydroxyl group on this oxide surface act as primary site for the physisorption of water molecule where we have hydroxyl group classified as A, B, and C. In addition to surface oxide ion which have been identified as C<sup>+</sup> (Parfitt et al., 1976). The surface chemistry of this oxide in contact with an aqueous solution is determined largely by the dissociation of these hydroxyl groups arising from the interaction of water with the surface planes to achieve valency saturation (Parfitt, 1976). Previous studies of adsorption (Sigg and Stumm,

1981; Rudzinski and Partyka, 1981) from aqueous medium show the solvent as an active participant in the adsorption process. Also from the work of Rudzinski and Partyka (1981), adsorption equilibrium depends on the ratio of the surface ( $r$ ) area covered by solute and solvent molecules except where this ratio is unity. This would be an additional complication in aqueous solvent since the molecules are much smaller than the methylene blue molecules, assuming that the molecules planes are oriented parallel to the solid surfaces in each case. We expect ( $r$ ) to be near unity for glycerol. To overcome complication and surface interactions that arises from water/adsorbent interface, we propose to replace water with less polar and less ionizing solvent such as glycerol to limit these strong surface interactions and to facilitate the study of adsorption on the twin habits surfaces. It is also our hope that in spite of the known chemical heterogeneity of  $\alpha$ -goethite surface (Russell et al., 1974), a single component adsorption isotherm might be obtained from adsorption data (at different temperatures) from solution. And from relatively simple measurements, information about the adsorption patterns of this solute onto twin habits surfaces might be extracted. Thus, enabling the assessment of the nature of the adsorbed phase, the distribution of micropore volumes in the possible adsorption sites and to interpret thermodynamic adsorption quantities from the basis of reaction scheme.

Several theories have been advanced in an attempt to describe the relationship between the fraction of adsorption sites, covered on the surface, and the total concentration of the species in the liquid phase. The simplest of these is the Langmuir model and is based on the assumption that the energy of adsorption is the same for all active sites on the adsorbent surface. In the majority of adsorption in aqueous media, this is not the case. Temkin and Freundlich have referred deviation from the Langmuir model as being due to surface heterogeneity (Glasstone, 1956). Necessity has thus, arose as to test whether or not the observed adsorption data obtained in twin habit of

$\alpha$ -goethite/glycerol interface system fit the Langmuir, Freundlich and Temkin model since these models have previously been adopted as the local isotherm in a variety of adsorbent/water interface.

As our contribution to this area of studies, we reported the adsorption on the twin habit of  $\alpha$ -goethite in non-aqueous medium and fit the adsorption isotherms determined to adsorption models. XRD might be expected to give some indication of the different respective crystalline phase(s) present in the twin habit. For this reason, we proposed to use the powder patterns to qualitatively identify the habit from its diffraction patterns so as to ascertain its crystallographic purity. Furthermore, attempt will be made to explore surface acidities in terms of Lewis/Bronsted acid sites by pyridine adsorption via infrared spectroscopy especially in the  $1400 - 1700 \text{ cm}^{-1}$  region. Such a simultaneous analysis should provide information about surface homogeneity/heterogeneity.

## MATERIALS AND METHODS

The twin habits of  $\alpha$ -goethite were synthesized following the method of Atkinson et al., (1968), for twinned morphological type of  $\alpha$ -goethite, sample 1a. All reagents used were of analytical grade and were stored in plastic bottles. All experiments were carried out in plastic vessel (Teflon) to avoid silicate contamination that is possible at high pH. The solution, suspension and washing of precipitate were carried out using freshly prepared doubly distilled water. Sodium hydroxide solutions were prepared by diluting a concentrated carbonate-free NaOH solution.

### Quantitative determination

Sample in HCl solution reduced to  $\text{Fe}^{2+}$  with  $\text{SnCl}_2$  titrated against a standard  $0.0167 \text{ mol/l Cr}_2\text{O}_7^{2-}$  solution in the presence of 1% diphenylamine as indicator.

### Infrared investigation

Sample were milled (about 10mg) with 200 mg of KBr in a polished agate mortar and pressed between  $\text{CaF}_2$  discs. For the case of pyridine absorption, sample previously evacuated under pressure is allowed to absorb pyridine for a period of 2 h. The pellets obtained were studied in a Genesis II Fourier Transform Infrared Spectrophotometer calibrated with polythene film.

### X - ray diffraction studies

X - ray diffraction analysis was carried out on powder mounts by back filling rectangular aluminum frame, using a PW Phillip X - ray diffract meter with a graphite monochromator and a Copper target tube ( $\text{CuK} = 1.5425 \text{ \AA}$ ) operated at 40 kv and 55 mA. The scattering region of  $2\theta$  was scanned.

### Adsorption studies

Adsorption was effected in the special apparatus (cell) whose diagram is shown in Figure 1 (Uzoamaka, 1994). The basic design of the cell contains an adsorption cell proper, F consisting of a sintered glass filter number 1 with stopper S. The cell is design to give a minimal dead volume. Adsorbent twin (sample) was placed in the adsorption cell F and the stopper S replaced. The cell was out gassed by evacuating it under heat by means of hot air blower round it from outside. The tap to the vacuum pump was shut (with the vacuum pump on) and the glycerol solution of adsorbate introduced from the quick fit separatory funnel into B3. When certain volume of adsorbate in glycerol had been introduced, tap 1 was shut. The adsorbate went in drops. The valve D was opened by means of a strong magnet from outside and the adsorbate solution went into the adsorption cell F.

At the end of the filling process, valve D was shut and the apparatus mounted in a bed of water bath maintained at constant temperature. For gentle agitation, the bed under goes a rocking motion for 3 h equilibrium time and the solution concentrations (after the content of the cell transfer and centrifuged continuously until a solution free of adsorbent particles was obtained). Estimated spectrophotometrically at the wave length corresponding to maximum absorbance,  $\lambda_{\text{max}}$  using a spectrophotometer (Thermo Spectronic UV-He $\lambda$ ios). The above procedure was repeated using solution of different initial concentrations of adsorbate in glycerol.

The drop in concentration of solute (MB) in glycerol per unit mass of adsorbent has been plotted against the concentration of the solute. The specific surface area of the  $\alpha$ -goethite habit was estima-

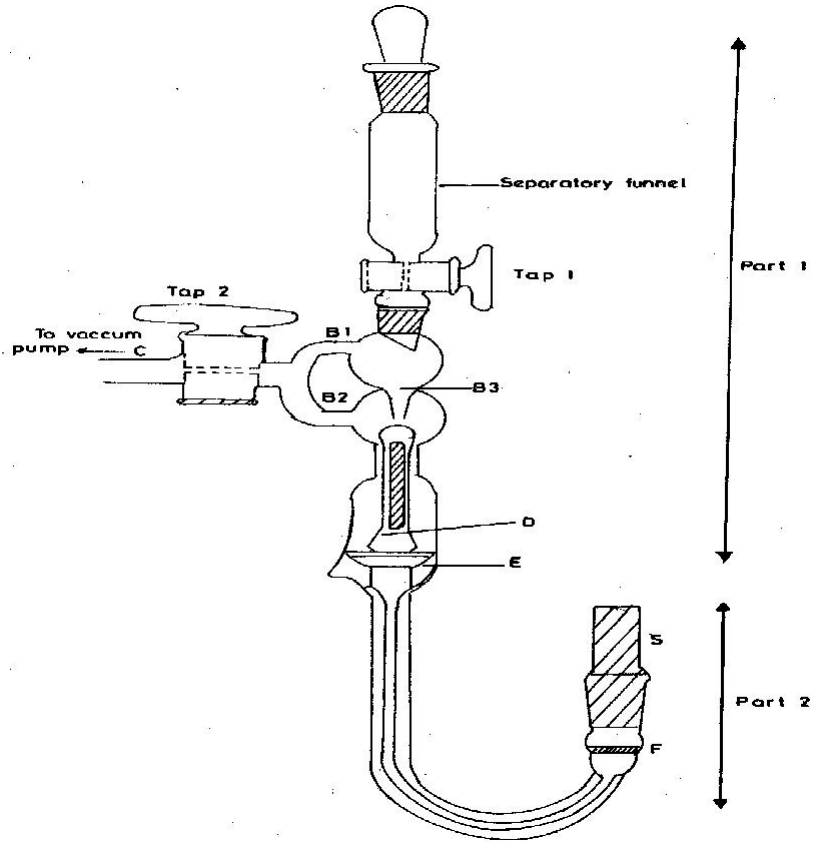


Figure 1. Adsorption apparatus.

ted from  $x_m$  and the cross-sectional area per molecule  $A_m$  using the relation (Gregg and Sing, 1967).

$$s = X_m \cdot N \cdot A_m \cdot 10^{-20} / M \quad (1)$$

$x_m$  = monolayer coverage in mol/g from the isotherm quantitatively.  
 $A_m$  = cross-sectional area per molecule in on the surface of goethite.

It has been assumed that the flat portion or plateau on the isotherm do indicate the completion of monolayer coverage at least for this adsorbate. The point when the extrapolated linear plot cut the adsorption at equilibrium concentration equals zero was taken as  $X_m$ . In order to use the above formula (equation 1), it is necessary to know the value of the cross-sectional area,  $A_m$  of adsorbate molecule. Brunauer et al. (1938) proposed that  $A_m$  can be calculated from the density of the adsorbate in the liquid form as

$$A_m = (M / dN)^{2/3} \cdot 10^{16} \quad (2)$$

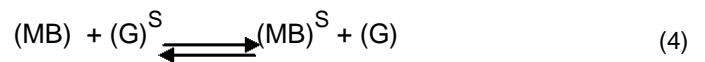
$A_m$  = Cross Sectional Area occupied by methylene blue,  $M$  = Molecular weight of the adsorbate;  $N$  = Avogadro's constant and  $F$  = Packing factor; the value of which depend on the number of nearest neighbor.

For a common arrangement, the value of  $F$  equals 1.091, hence we have

$$A_m = 1.09 (M / dN)^{2/3} \cdot 10^{16} \quad (3)$$

In order to ascertain the existence of micro porosity, method of Dubinin (Gregg and Sing, 1967) was used in which log of fractional coverage,  $W$  ( $x/m$ ) was plotted against log of  $(C_0/C)^2$ . The total micropore volumes estimated from the intercept of the linear portion of the plot.

On the basis of Everett's (1964) thermodynamic theory of adsorption from solution and employing the simple chemical equilibrium to equation 4 we proposed phase exchange reaction between solvent and solute from solution in the presence of excess solvent to estimate equilibrium constant.



(Where  $(MB)^S$  is the methylene blue on the surface,  $(G)^l$  is the glycerol in bulk phase,  $(MB)^l$  is the methylene blue in the bulk phase, and  $(G)^S$  is the glycerol on the surface) is given by

$$K = K_{eqm} = X_1^S / X_1 \quad (5)$$

Where  $X_1^S$  and  $X_1^l$  are the equilibrium concentrations of component 1 (methylene blue) in the surface and in the bulk liquid phase respectively. The overall free energy change as observed by Groszek (1960) on adsorption involves the change in the free energy for concentration change taking place at the interface as well as for those taking place in the bulk phase. However, if we consider a solid adsorbent being brought into contact with a binary liquid solution, the change in free energy which occurs when adsorption equilibrium has been established for any one of the

component, can be represented as

$$G = -RT \ln X_1^S / X_1 \quad (6)$$

Where R is a universal gas constant, T is the absolute temperature in Kelvin. The temperature dependence of  $K_{eqm}$  could be used to determine the enthalpy of adsorption H. To determine this quantity, we make use of Van't Hoff equation, (Glasstone, 1956).

(7)

By means of Gibbs-Helmholtz equation the entropy change of adsorption of methylene blue substance when the MB is transferred from the bulk solution to the surface phase and adsorption equilibrium established can be calculated, so that,

$$d(\ln K) / dT = H / RT^2 \quad (8)$$

Plot of  $\ln K$  with  $T^{-1}$  was found to be linear and H was computed from its slope. The thermodynamic definition of entropy is based on the expression,

$$S = (H - G) / T$$

The definition in equation (9) can be used to formulate an expression for the change in entropy of the surroundings,  $S_{surr}$ . Therefore, we can adapt the definition of entropy change in equation (7) to write

$$ds = \frac{dq_{rev}}{T} \quad (9)$$

Furthermore, the temperature of the surroundings is constant whatever the changes. For the surroundings it is assumed that the heat can be transformed reversibly and isothermally, so that

$$ds = \frac{dq_{surr, rev}}{T_{surr}} = \frac{dq_{surr}}{T_{surr}} \quad (11)$$

Where  $q_{surr}$  represent the heat absorbed in the reversible change. Since the pressure is constant, the reversible heat is equal to the change in enthalpy, H so that,

$$S_{surr} = \frac{q_{surr}}{T_{surr}} \quad (12)$$

That is, regardless of how the change is brought about in the system, the change in entropy of the surroundings can be estimated by dividing the heat transferred by the temperature at which the transferred take place. So that, total entropy is

$$S_{total} = S_{surr} + S_{syst} \quad (13)$$

With the above assertions, 2<sup>nd</sup> law of thermodynamic (Atkins, 1998) can be verified whether adsorption onto twin habits of goethite is impossible, reversible or spontaneous and irreversible process.

## RESULTS AND DISCUSSION

### Composition and X - ray identification

Percentage purity determined as iron content was 89%

$$S_{total} = S_{surr} + S_{syst}$$

(77.2 ± 0.02% Fe). This high percentage Fe content of twin habits is so high compare with the theoretical value

of 62.90% for Fe in -FeOOH. Result from X - ray fluorescence (XRF) also indicated high percentage Fe content as (86% ± 0.785% Fe) for the habits. Particle size was between 0.18 and 0.2 Å assuming the crystallite of twin have four exposed faces/ planes corresponding to A, B, C and C' Parfitt et al., (1976).

Characteristics peaks for neat twin habit were observed for angle, 2θ, at 21.405, 33.635, 34.820, 36.735, 40.080, 41.305, 45.135, 47.450, 50.790, 53.225, 55.120, 61.415, and 64.125 with corresponding d - value for 1 + 2/2(Å) at 4.15 (4.20), 2.67 (2.68), 2.58 (2.58), 2.45 (2.40), 2.25 (2.26), 2.18 (2.19), 2.01 (2.08), 1.92 (1.91), 1.80 (1.83), 1.72(1.72), 1.56 (1.56), 1.51 (1.52) and 1.45 (1.46), res-

pectively. All the values within brackets are similar values obtained in literature (Heller and Peters, 1970). Thus, angle 2θ 23.5 with corresponding d -value of 3.70 Å is characteristic of - goethite (- goethite polymorph). The X -ray results containing - goethite support earlier high percentage Fe content of twin sample from classical analysis as due to the presence of -goethite presumably. This prominent peak for - goethite agrees well with the work of Murad (1979) and Mackay (1960) where 3.728 and 3.70 Å diffraction lines were used to identify - goethite respectively.

### IR analysis / absorption by Vaporous Pyridine

The important infrared absorption frequencies (spectrum not shown) are given in Table 1. According to Landa and Gast (1973), the absorption feature at 795 and 870 cm<sup>-1</sup> band are the lattices O-H bending vibrations, in addition

to 599 cm<sup>-1</sup> for Fe-O stretch characteristic of - goethite. In the twin spectrum, these bands are apparently centered at 784,899 and 601 cm<sup>-1</sup> (Table 1). These lattice vibrations at the lower frequencies are higher than frequencies than normally observed for - goethite. These lattice vibration couple with sorbed water vibrations gives rise to the higher frequencies because sorbed water

peaks have been observed in this work. The shoulder which occurs between 2800 and 3200 cm<sup>-1</sup> is certainly the O - H stretching mode. The absorption band at 3705 cm<sup>-1</sup> for neat twin sample is assigned to relatively free surface OH groups similar to what was reported by Russell et al. (1975), 3660 cm<sup>-1</sup> for dried - goethite. No bulk OH stretch could be observed from the IR spectrum.

The residual absorption band 1630 cm<sup>-1</sup> is assigned to HOH for sorbed water (Nakamoto, 1978) and Russell et al., (1974). The absorption of vaporous pyridine was used for the study of surface acidity, and infrared spectrometry has been adapted. The important infrared vaporous absorption frequencies of neat twin habit as recorded by IR are summarized in Table 1. The assignments of the frequencies were made in accordance with Parry (1963) and Delafosse et al. (1974). A band at 1541 and 1652 cm<sup>-1</sup>, due to pyridinium ions which could be attributed to

**Table 1.** Selected IR absorption bands and their assignment for twin habit.

Analysis type	Peak position /cm <sup>-1</sup>	Assignments
IR absorption for neat sample	784 <sub>w</sub> , 942 <sub>w</sub>	Fe-O <sub>str</sub> frequencies
	899 <sub>s</sub>	O-H <sub>str</sub> frequencies
	1042 <sub>w</sub> , 1146 <sub>w</sub> , 1117 <sub>w</sub>	Fe-O <sub>w</sub> asymmetric stretch
	1456 <sub>m</sub>	O-H <sub>bend</sub>
	1630 <sub>m</sub>	δ(HOH), H <sub>2</sub> O of Crystallization.
	2349 <sub>w</sub> 2925 <sub>sh</sub>	Intramolecular H-OH frequencies
	3362 <sub>B</sub>	(HOH), H <sub>2</sub> O of Crystallization stretching frequencies
Vaporous pyridine Absorption	3705 <sub>m</sub>	Surface OH <sub>str</sub>
	601 <sub>w</sub>	Fe-O <sub>str</sub> for - goethite
	1541 and 1652	Bronsted acid sites
	1457 and 1508	Lewis acid sites

Bronsted acid or Bronsted acidity, while a band at 1457 and 1508 cm<sup>-1</sup>, due to coordinatively bonded pyridine, is characteristic of Lewis acidity. Thus, it is reasonable to say that twin sample contain elector accepting sites (Lewis acidic site) and (proton donor) sites. Band 1491cm<sup>-1</sup> in the spectrum (no shown) is an indication of both type of Lewis and Bronsted acid sites. This assignment are in accord with those of Ward, (1968) (1490 cm<sup>-1</sup>) on study of Absorption coefficient of pyridine adsorbed on Lewis and Bronsted acid sites. A number of other bands are observed in the spectrum which chemisorbed pyridine, but are not useful for diagnostic purposes.

### Shape of the isotherms

The apparent isotherms for the adsorption of MB onto Twin -goethite surface which is a measure of the net effect on the concentration of the solution rise steeply at low equilibrium concentrations as shown in Figure 2. The resemblance of the isotherms to the S- type (Giles et al., 1960), based on the initial section of the curve being convex to the concentration axis showing definite plateau of constant adsorption led to the assumption by analogy that the plateau represent complete coverage of the surface by a monolayer of solute (MB). This isotherm, thus apparently indicates a tendency for large adsorbed molecules to associate rather to remain as isolated units. It is evident that adsorption capacity increases with increasing equilibrium MB concentrations. Figure 2 shows that, the adsorption capacity increases rapidly from 5 to 29.7 X 10<sup>-5</sup> mol/dm<sup>3</sup>/g for the equilibrium concentration of 0.1 to 1.65 X 10<sup>-5</sup> mol/l at 25°C. Further, a

gradual increase in adsorption capacity was observed with increase in equilibrium concentration and it reaches up to maximum of 31.9 X 10<sup>-5</sup> mol/dm<sup>3</sup>/g for the equilibrium concentration of 4.25 mol/l at higher temperature of 30 and 35°C. There is apparent change of adsorption capacity rapidly from 5.0 to 31.2 mol/dm<sup>3</sup>/g and 5 to 31.4 x 10<sup>-5</sup> mol/dm<sup>3</sup>/g respectively.

At 25, 30 and 35°C, kink in the isotherms between 0.5 and 1.5 x 10<sup>-5</sup> mol/l equilibrium concentration was observed and merges at high concentrations. This long flat plateau is significant in that for long plateau; high-energy barrier has to be overcome before additional adsorption can occur on new sites after the surface has been saturated. The increase in adsorption with temperature (Figure 2) suggested that the active site surface centres available for adsorption have increase with temperature.

### Specific surface areas

The area occupied per molecule of methylene blue, A<sub>m</sub> onto twin - goethite surface was estimated on the assumption that the monolayer of adsorbed methylene blue is not exceeded at the equilibrium concentrations we have considered.

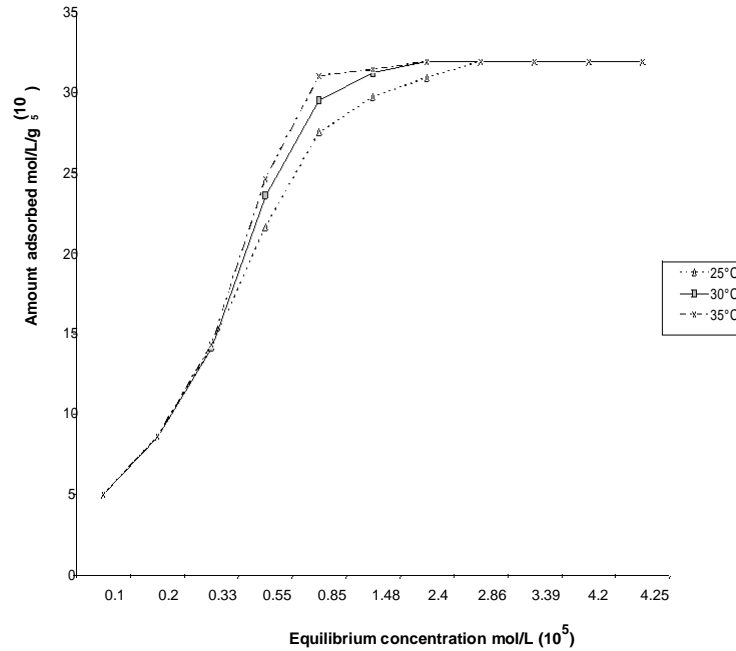
Table 2 below gives the estimated specific surface area (S) and the monolayer coverage (X<sub>m</sub>) for methylene blue at three different temperatures in addition to the calculated A<sub>m</sub> of MB. The specific surface area taking the area occupied per adsorbed molecule as 73<sup>2</sup> as shown in Table 2. This low value is reasonable enough to be accounted for by an adsorbate molecules oriented vertically (adsorbed edgewise) on the twin - goethite surface. This value correspond very closely to those calculated for edgewise (78<sup>2</sup>) for graphitized carbon (Giles et al., 1954).

The specific surface areas estimated from the maximum amount bound to the surface (monolayer coverage) by taking the area occupied per adsorbed molecule to be 73<sup>2</sup> to be within the range of 130 - 139<sup>2</sup>/g for twin habit. Specific surface areas linearly vary with temperature with several orders of magnitude at 35°C higher than 25°C. From Table 2, the specific surface areas when compared with the different temperature studied shows temperature dependence. The results demonstrate that the area of twin -goethite accessible to MB molecules is sensitive to temperature. It is therefore suggestive that the surface properties of twin habit have been modified with increasing temperatures.

In addition, the twin habit pore volume was enhanced as temperature increases. This increase in pore volume as temperature of the experiment increases for twin is also in consonance with apparent adsorption of MB (Figure 1).

### Adsorption Isotherms

In order to model the adsorption behaviour and calculate



**Figure 2.** Apparent Isotherms for the adsorption of MB in glycerol at various temperatures.

**Table 2.** Estimated surface properties and thermodynamic quantities ( $A_m = 73 \text{ \AA}$ ).

T (K)	$X_m$ (mol/g) $10^5$	S ( $m^2/g$ )	H (kJ/mol)	G (kJ/mo)	$AS_{sists}$ (J/mol/k)	$S_{total}$ (J/mol/k)	Pore vol. $cm^3(10^4)$
298	31.9	131	-20.79	-7.76	-43.72	26.05	2.56
303	31.5	136	-20.79	-8.53	-40.46	28.15	2.94
308	31.6	138	-20.79	-9.25	-37.46	30.05	3.22

adsorption capacity, the adsorption isotherm data was analyzed with Langmuir, Freundlich and Temkin isotherms. The three linearized isotherms equations were given in equation (14) to (16).

Langmuir equation:

$$\frac{1}{X_m} = \frac{1}{K_L C_e} + \frac{1}{K_L X_m} \quad (14)$$

Freundlich equation:

$$\log X_m = \log k_f + \frac{1}{n} \log C_e \quad (15)$$

Temkin equation:

$$\ln X_m = B \ln A + b \ln C_e \quad (16)$$

Where  $B = RT/b$  and is the fractional coverage by the adsorbed molecule by a definite mass of adsorbate (mol/g) and  $C_e$  is the equilibrium concentration (mol/l) of MB in solution. The  $K_L^1$  and  $K_L^2$  are the Langmuir isotherm

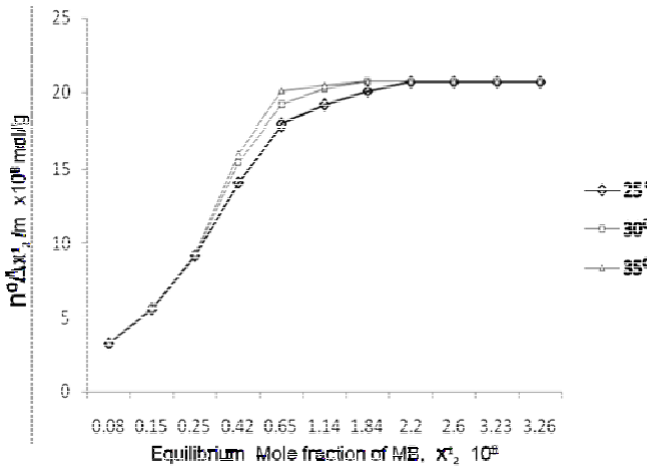
constants, reference to the adsorption energy and adsorption capacity respectively.  $k_f$  and  $n$  are the Freundlich constants related to the adsorption capacity and process intensity respectively, while  $A$  and  $B$  are the Temkin isotherm constants obtained from the (least square) intercept and slope of the experimental data. Estimated parameters for the different models and related correlation coefficients were shown in Table 3. As the correlation coefficient ( $r^2$ ) measures the strength of the linear relationship, it was used to determine how well the model represents the data.

Our experimental data are found to fit well in the three models Equation (9), (10) and (11) in terms of  $r^2$  values. Very surprising fit for Langmuir model in view of the uncertainties and assumption inherent in the Langmuir model that assumes surface homogeneity and molecular adsorption for a given site is independent of the occupation of neighbouring sites.

The observed fit of the experimental data to Langmuir model (Table 2) suggests that MB is selectively adsorbed at same site of similar enthalpy of adsorption onto goethite surface at low concentration of MB with deviation at high concentrations. In other word, the MB cannot discri-

**Table 3.** Langmuir, Freundlich and Temkin isotherm constants.

Temp. T (K)	Langmuir			Freundlich			Temkin		
	$k_L^2$ (mol/g)	$k_L^1$ l/mol( $10^3$ )	$r^2$	$k_f$	$n^{-1}$	$r^2$	A l/g( $10^{-6}$ )	B ( $10^3$ )	$r^2$
298	0.018	0.025	0.9	0.05	0.48	0.96	1.9	7.81	0.98
303	0.018	0.023	0.9	0.04	0.48	0.93	2.4	7.53	0.93
308	0.018	0.021	0.9	0.04	0.45	0.90	2.6	7.46	0.93



**Figure 3.** Composite Isotherms for the system MB/glycerol adsorbed on twin habit at various temperatures.

minate between different adsorption sites on goethite surface as MB concentration increases. The fact that Langmuir isotherm fits the experimental data may be due to homogeneous distribution of active sites on the goethite surfaces. Langmuir coefficient  $k_L^1$  (adsorption energy) decreases with temperature, showing that the energy of adsorption does not seem to change as temperature of the experiment changes.

Fitting of the experimental data into Freundlich and Temkin model exhibit both behaviours at low MB concentration. Deviation is significant from both isotherms at high MB concentrations. Presumably the surface coverage does not relate logarithmically with equilibrium concentration. Thus, at low concentration of MB, it could tentatively discriminate different adsorption energies. The slope  $n^{-1}$  ranging between 0 and 1 is a measure of adsorption intensity and surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghsersht, 1998).

### Surface excess

The composite adsorption isotherms (plots of  $n^0 x_2^1 / m$  against  $x_2^0$ ) are shown in Figure 3. These isotherms give the surface excess of the MB in the adsorbed layer as  $n^0 x_2^1 / m$ . The surface excess given by these isotherms is related to the actual concentration of the component (MB)

at the surface by the equation,

$$n^0 x_2^1 / m = n_1^s x_2^s - n_2^s x_1^s \quad (17)$$

$x_2^1$  is the change in the mole fraction of component 2 (MB) in the bulk liquid which occurs when 0.1g of adsorbent are brought into contact with  $n^0$ , the total amount of original solution.  $x_1^1$  and  $x_2^1$  are the mole fraction of component 1 (glycerol) and 2 (MB) respectively in the bulk liquid at equilibrium; and  $n_1^s$  and  $n_2^s$  are the amount of component 1 and 2 respectively adsorbed per gram of adsorbent.

The isotherms (Figure 3) at the temperature of measurement are S- Class isotherms according to the classification of Giles (1960) based on the initial section of the curve being convex to the concentration axis. These also indicate vertical orientation of the adsorbed molecules (where appropriate) on the surface. The composite isotherms seen to have a defined knee, the process is sensitive to temperature at some stages in the adsorption process and at higher concentration, the composite isotherms tend to constant value.

The evidence from the composite adsorption point to the occurrence of adsorbed phase within the concentration range considered does confined to a monolayer of MB oriented to the surface on the assumptions that only solute was adsorbed, the interaction between the surface of the habit and solvent (glycerol) is the same as that of pure solvent, and that the surface of the adsorbent is completely covered by adsorbate (MB) at all concentrations.

### Thermodynamic parameters

Thermodynamic quantities estimated of interest are G, S and H, refer to as Gibbs energy change, enthalpy and entropy change of adsorption of MB are shown in Table 2. The heats of adsorption calculated from the isotherm by the Van't Hoff equation are shown in Table 2. Surprisingly they are all constant in each case over the measurable range of the temperature. The negative value of H shows the adsorption onto the adsorbent is highly exothermic. Since the observed values of H is within the expected range of physisorption (20.9 kJ/mol), so the result indicated physisorption.

From Table 2, we see that the thermo dynamic treatment of the adsorption process indicates that G values

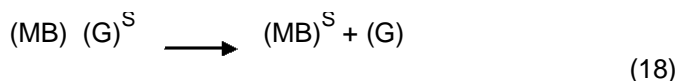
were negative for the MB concentrations. The G values decrease with increasing temperatures. This indicates that the adsorption process of MB by twin habit of -goethite can be enhanced by increasing temperature. The negative value of G indicates the spontaneous nature of adsorption of MB on the twin habit of -goethite. The G values obtained in this work for the MB are < -10 KJ/mol, which indicate that physical adsorption was the predominant mechanism in the adsorption process. The adsorptive forces were strong enough to overcome the potential barrier between the MB species in the solid - liquid interface.

The amount adsorbed at equilibrium must increase with increasing temperature (Figure 2), because G decreases with increasing temperature (Table 2) of the solution. This explains the more negative values of G with increasing temperature and perhaps the increasing equilibrium constants implying a strengthening of the adsorbate-adsorbent interaction at higher temperatures.

The  $S_{\text{syst}}$  values are negative throughout, but decrease with increasing temperature. Not only does this decrease reflect the affinity of twin habits for methylene blue but the decrease in entropy of adsorption is also in accord with more ordered arrangement of methylene blue on the surface of twin habits than in the bulk phase as the adsorption progresses.

When both system and surroundings are considered, a different result arises (Table 1, column 7). The calculated  $S_{\text{total}}$  for twin habits is positive taken into cognizance the change in entropy of the surroundings,  $S_{\text{surr}}$ . In line with 2<sup>nd</sup> law of thermodynamic, (the entropy of an isolated system in the course of a spontaneous change:  $S > 0$ ). We therefore infer from  $S_{\text{total}}$  being positive that not only did the phase transition exothermic and spontaneous; the adsorption of MB onto twin habits is irreversible. That is, the total entropy of an isolated system including its surroundings increases as required by inequality of  $S > 0$  for irreversible process.

We therefore formulate the mechanism for the reaction scheme with irreversibility sign as:



As table 2 illustrate, total micropore volume depend on the temperature of measurement. The pore volumes were enhanced as temperature increases. This increment is in consonance with increase in surface area of the twin habit as temperature is increase. At 30°C, more pore volume on a twin habit thus increase adsorbent pore filling.

## Conclusion

Classical analysis complemented with the X - ray analysis have found the twin habit synthesis to contain -goethite as crystalline trace. The surface of twin habit not

only does it exhibit Lewis acidity, which in this case could be ferric ion but also shows Bronsted acidity toward pyridine vapour. Furthermore, the surface of this habit could be heterogeneous if the locations of the sites are presumed to be the adsorption sites. These properties appear to be related to the presence of the two acid sites or OH groups.

The adsorption pattern conforms to monolayer of solute (MB). The equilibrium data have been analyzed and correlated with three adsorption models. The amount of adsorbed MB increases with increasing temperature, due to the increasing in the total pore volume and surface area of the twin habits. All the parameter calculated appears to have definite significance. The enthalpy is constant and highly exothermic. The calculated  $S_{\text{total}}$  for twin habit is positive taken into cognizance the change in entropy of the surroundings,  $S_{\text{surr}}$ .

In summary, the mechanism of adsorption on the basis of a reaction scheme at the twin -goethite habits/glycerol interface is irreversible and the mode of binding is physisorption. As a working hypothesis we may say that the adsorbed molecules are oriented perpendicularly to the surface. Further work on acicular habit would be discussed in a later publication.

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