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ADSORPTION EQUILIBRIUM STUDIES OF LIGNOCELLULOSIC SAWDUST FOR SEPARATION OF AQUEOUS ETHANOL MIXTURE

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ABSTRACT

This study investigated the effects of initial water concentration on the adsorption capacity of lignocellulosic sawdust in Southwestern Nigeria. The performance of these adsorbents in aqueous ethanol purification was also evaluated with a view to finding cheap and readily available alternatives to the costly commercial zeolites. Liquid phase batch equilibrium experiments were conducted on hardwood (*Khaya senegalensis*) and softwood (*Annona senegalensis*) sawdust pretreated with 25% (w/w) calcium chloride ($CaCl_2$). Modified *Khaya senegalensis* (M25C) was observed to be more suitable for dehydration than 3A zeolite at 15% (w/w) initial water concentration due to equilibrium mechanism. The performance of the sawdust measured by the Freundlich ($1/N_f$) and Sips ($1/N_s$) isotherms was favourable in ranges 0.4531 - 0.8884 and 0.5622 – 0.9399, respectively. The system became more heterogeneous as the values approached zero and the performance improved upon chemical modification with $CaCl_2$. The surface areas as determined by the BET isotherm for modified *Khaya senegalensis* and *Annona senegalensis* were 736 and 286 m^2/g, respectively. These results indicated that *Khaya senegalensis* sawdust adsorbed water better than *Annona senegalensis* on chemical modification. It was concluded that Sips isotherm with the highest coefficient of determination (R^2 = 0.9726) was the most suitable isotherm for designing the adsorption process.

Keyword: *Ethanol, zeolite, sawdust, adsorption capacity, calcium chloride, isotherm*

1. INTRODUCTION

Production of fossil-based fuel can barely meet the increasing population demand for energy. Yet, there is fluctuation in its price while its use results to resource depletion, pollution and global warming. There is therefore a need to develop renewable energy source from ethanol which could provide adequate supplies of clean, safe and sustainable energy (Venkatasubramanian and Keim, 1985). For ethanol to be used as a gasohol instead of methyl tertiary butyl ether (MTBE) or fuel, its purity has to go beyond its azeotrope. Conventional distillation processes (low-pressure, azeotropic and extractive) and adsorption are employed to break the ethanol-water azeotrope. Adsorption has the advantage of low operating costs because it is a non-thermal separation process with low-heat requirements (Black, 1980).

Commercial zeolites are efficient in ethanol purification due to their uniform pore sizes and molecular shape. However, the high cost of regeneration posed a major disadvantage to its commercial utilization (Carmo and Gubulin, 1997). Biomass adsorbents such as starch and lignocellulosics have been found to demonstrate similar positive effects for the removal of water from ethanol system. They may be better alternatives to zeolites since they are cheap, renewable and readily available (Berthold *et al*., 1995).

Studies on the adsorption characteristics of manioc starch pellets (Carmo and Gubulin, 1997), white corn grits (Beery and Ladisch, 2001), hardwood sawdust and bleached wood pulp (Benson, 2003) have shown that these adsorbents demonstrated the ability to preferentially adsorb water past the azeotropic point. The hydroxyl (OH^-) groups in starch (amylose and amylopectin) and lignocellulosics (cellulose and xylan) attract the necessary hydrogen (H^+) needed for hydrogen bonding with water molecules (Han, 1998). Chemical pretreatment of lignocellulosics is necessary to eliminate the chemical and physical barriers, increase the micropores on the adsorption surface and enhance their adsorption capacity (Ramos, 2003).

Southwestern Nigeria is endowed with thick forest having varieties of hardwood and softwood species utilized in building, furniture and construction industries. Consequently, there are many timbering and sawmilling activities that produce sawdust as waste. Utilizing these indigenous woods sawdust as lignocellulosic adsorbents for separation of aqueous ethanol mixture will minimize drastically, the waste disposal problems besetting the industry, curb its consequent environmental pollution and as well, add to the local content of the nation's industrialization. The objectives of this study therefore, are to investigate the effects of initial water concentration on adsorption capacity and evaluate the performance of hardwood (*Khaya senegalensis*) and softwood (*Annona senegalensis*) sawdust in Southwestern Nigeria, for aqueous ethanol purification.

2. MATERIALS AND METHODS

2.1. Materials

The woods sawdust were sourced at Atagijere sawmill company in Ile-Ife. They were sun-dried to cure, oven-dried and screened on a series of 2.0, 1.4 and 0.71 mm test sieves (Endecotts Ltd., England).

2.2. Sample Pretreatment

The samples were washed several times in distilled water to leach the extractives until the liquor was clear. Chemical pretreatment was done in 25% (w/w) calcium chloride ($CaCl_2$) for *Khaya senegalensis* (M25C) and *Annona senegalensis* (E25C) sawdust samples. The sawdust-$CaCl_2$ solution was mixed in ratio 1:10 (w/v) in a pyrex flask. The unmodified samples of *Khaya senegalensis* (M0) and *Annona senegalensis* (E0) were used as blanks for all the experiments while commercial 3A zeolite was the control adsorbent.

The flask was placed in a water bath (Lemfield, England) regulated at 70 °C for about 1 h before oven-drying at 80 °C to constant weight. The slurry was washed exhaustively with distilled water to leach out all traces of the chemical. The samples were again oven-dried and stored for use.

2.3. Physical Characterisation of Sample

2.3.1. Bulk Density Determination

Two grams of sample was weighed and transferred into 10 ml of distilled water in a measuring cylinder. The volume of liquid displaced was noted (Aneke and Okafor, 2004). The bulk density was calculated from the equation below:

$$\text{Bulk density} = \frac{\text{Mass of sample (g)}}{\text{Volume of water displaced (ml)}} \quad (1)$$

2.3.2. Moisture Content Determination

Standard method of ASTM D2016-25 was used to determine the moisture content. Two grams of sample was dried in an oven at 105 °C until a constant weight of the sample was obtained (Debdoudi *et al*., 2005). The moisture content was calculated as given by the equation:

$$\%\ \text{Water} = \frac{W_i - W_f}{W_i} \quad (2)$$

2.3.3. Pore Volume and Porosity Determination

Two grams of sample was weighed and transferred into a 10 ml measuring cylinder to obtain the total volume of the particle. This was poured into a beaker containing 20 ml of distilled water and the volume of water displaced was noted. The mixture was then boiled for 5 min to displace air in the sample. It was filtered, superficially dried and weighed (Aneke and Okafor, 2004). The pore volume was calculated using equation (3):

$$\text{Pore volume} = \frac{W_f - W_i}{\rho_{H_2O}} \quad (3)$$

The porosity of each sample was calculated as below:

$$\text{Porosity} = \frac{\text{Pore volume of the particle}}{\text{Total volume of the particle}} \quad (4)$$

2.4. Liquid-Phase Adsorption Studies

Liquid-phase (equilibrium) batch adsorption experiments were carried out in glass vials equipped with air tight caps at 30 °C. A known weight of each sawdust sample was added separately to a known volume of initial water-ethanol concentration varied at 3, 5, 10 and 15% (w/w). The mixture was stirred homogenously on a hot plate with magnetic stirrer (Model AM-3250B, Surgifriend Medicals, England) until equilibrium was attained.

Samples were filtered, centrifuged and ethanol concentration in the supernatant determined using digital refractometer (Model RX-5000α, Atago Co. Ltd., Japan) and density calibration until a constant concentration was obtained for three consecutive samplings.

2.4.1. Adsorption Capacity Determination

The adsorption capacity of the adsorbents was calculated using equation (5):

$$q = \frac{M_L}{M_A}\left(\frac{C_{f,EtOH} - C_{i,EtOH}}{C_{f,EtOH}}\right) \quad (5)$$

2.4.2. Optical Microscopy

The micro-structural differences in the sawdust samples as compared to the 3A zeolite were studied by optical microscopy. Thin sections of the adsorbents were prepared on glass slides. Optical micrographs were taken using Celestron microscope (Model MK II-4060 BN, United States) at a magnification of x2600.

2.4.3. Adsorption Isotherms

Origin 7.0 and Excel 2007 packages were employed for the non-linear regression analysis of the adsorption isotherms such as Langmuir, Freundlich, Sips and Brunauer-Emmett-Teller (BET). Experimental data are fitted into adsorption isotherms in order to find the suitable isotherm that can be used for design purpose. Statistical evaluation of these isotherms was carried out using chi-square (χ^2) and coefficient of determination (R^2).

The linearized form of Langmuir isotherm is expressed as follows (Oke *et al*., 2008):

$$\frac{1}{q_e} = \frac{1}{q_L} + \frac{1}{k_L q_L}\frac{1}{C_e} \quad (6)$$

A plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ will yield a straight line from which k_L and q_L can be determined from the slope and intercept, respectively.

Langmuir isotherm expressed in terms of the separation parameter (R_L), is (Saswati and Ghosh, 2005):

$$R_L = \frac{1}{1 + q_L C_0} \quad (7)$$

If the value of $R_L > 1$ (favourable), $R_L = 1$ (linear adsorption), $R_L = 0$ (irreversible) and $0 < R_L < 1$ (reversible).

Freundlich isotherm is expressed as (Freundlich, 1926):

$$\log q_e = \log k_f + \frac{1}{n_f}\log C_e \quad (8)$$

A plot of log q_e versus log C_e will give a linear relationship from which the Freundlich constants $1/n_f$ and k_f can be obtained

from the slope and intercept of the plot, respectively. $1/n_f$ is a measure of the performance of adsorbent. When the value of $1/n_f < 1$ (normal Freundlich adsorption), $1/n_f > 1$ (cooperative adsorption) and $0 < 1/n_f < 1$ (favourable adsorption).

Sips isotherm is expressed by Sohn and Kim (2005) as:

$$\ln\frac{q_e}{q_S - q_e} = \frac{1}{n_S}\ln(C_e) + \ln(k_S) \quad (9)$$

The constants q_s, q_e and k_s are evaluated by a pseudo-linear plot of equation (9) using a trial and error optimization method.

The BET isotherm when adapted to liquid adsorption is expressed as (Oubagaranadin *et al*., 2007):

$$\frac{C_e}{q_e(C_o - C_e)} = \frac{1}{q_m k_B} + \frac{(k_B - 1)}{q_m k_B}\frac{C_e}{C_o} \quad (10)$$

A plot of $\frac{C_e}{q_e(C_o - C_e)}$ versus $\frac{C_e}{C_o}$ yields a satisfactory straight line, the q_m and k_B can be calculated from the slope and intercept of the plot, respectively.

Specific surface area (SSA) of the adsorbent is calculated from equation (Richardson *et al*., 2002):

$$SSA = \frac{q_m \times N_A \times a}{M} \quad (11)$$

3. RESULTS AND DISCUSSION

3.1. Effects of Chemical Modification on Physical Properties of Adsorbent

The physical properties of the selected sawdust samples studied are presented in Table 1. Modified *Khaya senegalensis* (M25C) sample had the highest bulk density, pore volume and porosity, while unmodifed *Annona senegalensis* (E0) sample had the lowest. On the other hand, the percentage moisture content was in the range 1.54 - 1.78% with E0 having the highest. High bulk density, porosity and pore volume as well as low moisture content are indicators of high adsorption capacity.

Table 1: Physical Properties of Adsorbents

Properties	M0	M25C	E0	E25	3A zeolite
Bulk density (g/ml)	0.216	0.313	0.124	0.186	0.658
Moisture content (%)	1.66	1.54	1.78	1.72	0.65
Pore volume (ml)	0.425	0.582	0.224	0.348	2.438
Porosity	0.139	0.182	0.070	0.109	0.871
Specific Surface Area (m^2/g)	120	736	83 286		1824

3.2. Effects of Initial Water Concentration on Adsorption Capacity

The adsorption capacity of the *Khaya senegalensis* and *Annona senegalensis* sawdust samples compared with 3A zeolite are reported in Figs. 1 and 2. M25C showed the highest adsorption capacity of 0.817 g g^{-1}, followed by 3A zeolite (0.802 g g^{-1}) and M0 with 0.595 g g^{-1} at equilibrium for 15% (w/w) initial water-ethanol concentration.

There was a general increase in adsorption capacity as initial water concentration increased and upon modification. This may be due to the attraction of more H^+ from the water molecules for bonding with the OH^- stemming from the xylans of lignocellulosics. It could also be due to increased pore spaces available for adsorption on the adsorbent. This led to higher driving force for greater adsorption at higher water loadings. However, the adsorption capacity of zeolite was slightly lower to M25C at 15% (w/w) initial water concentration. This could be as a result of equilibrium mechanism based on the adsorbents having different abilities to accumulate different species as observed in literature (Duong, 1998). M25C may therefore be more suitable for dehydration than zeolite at high initial water concentration of 15% (w/w).

Similar trend was observed for the softwood samples though their adsorption capacities were lower. These results indicate that adsorption capacity of the sawdust samples was better determined with increase in initial water-ethanol concentration. The observed trend is in agreement with literature (Berthold *et al*., 1995; Carmo and Gubulin, 1997).

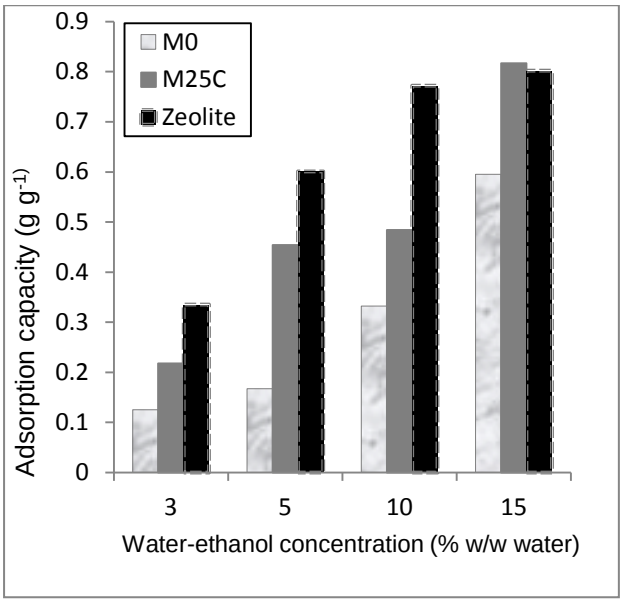

Fig. 1: Equilibrium adsorption of water onto Khaya senegalensis sawdust and 3A zeolite

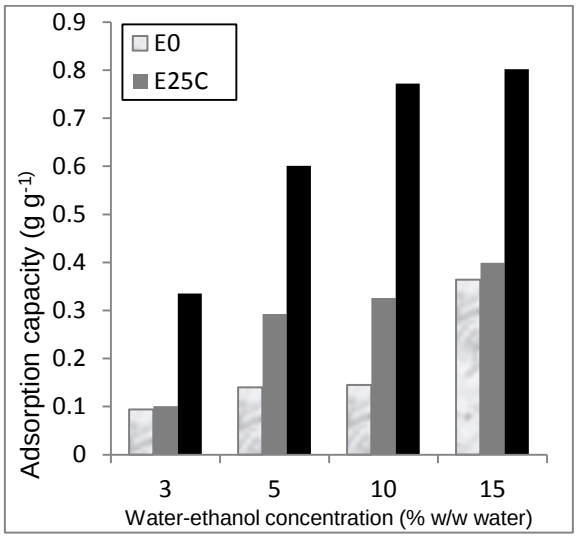

Fig. 2: Liquid-phase equilibrium adsorption of water onto Annona senegalensis sawdust and 3A zeolite

3.3. Evaluation of Adsorbent Performance

The plots of Langmuir and Freundlich isotherms for M25C and E25C, respectively are shown in Figs. 3 and 4. The Langmuir parameter (q_L) for *Khaya senegalensis* samples, increased from 0.8085 for the M0 to 0.8138 for M25C as presented in Table 2. There was a similar increase for *Annona senegalensis* samples from 0.3551 to 0.4230 for E0 and E25C, respectively. The Langmuir parameters (q_L and k_L) generally increased upon chemical modification. High k_L indicated high affinity for the binding of sawdust. The separation parameter (R_L) was in the range 0.8543 to 0.9987 ($0 < R_L < 1$) implying that the adsorption process was feasible for all the adsorbents.

The performance of the sawdust samples measured by the Freundlich's surface heterogeneity term ($1/n_f$) was in the range 0.4531 - 0.8884 ($0 < 1/n_f < 1$) as presented in Table 2. This implied that all the adsorbents performed favourably. As the values approached zero, the surface became more heterogeneous, indicating the formation of strong bond between the adsorbate and the adsorbent. The Freundlich constant, k_f, increased from 0.0470 to 0.2283 upon modification with $CaCl_2$.

Fig. 5 and 6 are the plots of Sips and BET sotherms for M25C and E25C, respectively. Sip's surface heterogeneity ($1/n_s$) constant in the range 0.5622 to 0.9399 ($0 < 1/n_s < 1$) implying that all the adsorbents performed favourably. Acharya *et al.* (2008) also observed the same trend in parameters with zinc chloride pretreated tamarind wood.

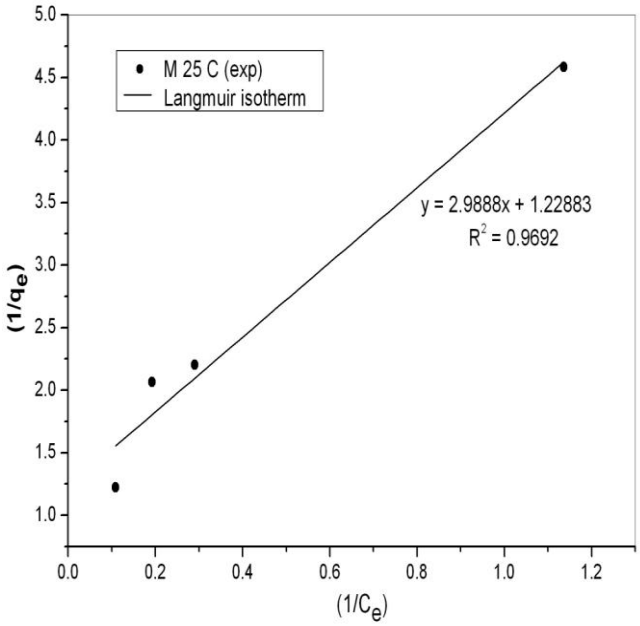

Fig. 3: Langmuir adsorption isotherm of water onto M25C

The maximum adsorption capacity on a mono-layer surface (q_m) as determined by the BET isotherm for the sawdust samples were in the range 0.0061 - 0.1931. The specific surface area of M0 and M25C were 120 and 736 m^2/g, respectively. These were higher than 83 and 286 m^2/g obtained for E0 and E25C, respectively. They increased upon chemical modification indicating that the pretreatment chemical (25% w/w $CaCl_2$) opened up more pores (active sites) on the sawdust for adsorption of water. The surface area of the modified adsorbents conformed to the range 300 – 1200 m^2/g specified for practical purpose (Schweitzer, 1996).

The statistical evaluation of the adsorption isotherms using chi square (χ^2) showed the least χ^2 in Freundlich (0.0025), followed by Sips (0.0139), Langmuir (0.0961), and BET (1.6532). Table 2 showed that these values decreased upon modification for all the adsorbents. The coefficient of determination (R^2) range was highest for Sips isotherm (0.8751 – 0.9726), followed by Freundlich (0.8454 – 0.9701, Langmuir (0.8393 – 0.9692) and BET (0.0611 – 0.8459). Low χ^2 and high R^2 are indications of suitable isotherm as observed in literatures (Hameed *et al*., 2006; Adie *et al*., 2010). The results showed that Sips isotherm was the most suitable followed by Freundlich isotherm for describing the adsorption of water onto sawdust adsorbents. The Freundlich fitness confirmed that the sawdust samples had more heterogeneous adsorption sites such as OH^- that could enhance strong H^+ bonding with water molecules (Rebar *et al*., 1984).

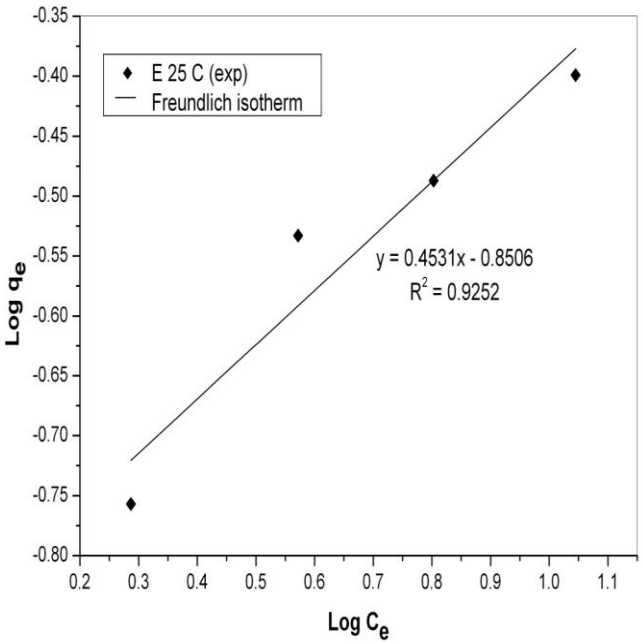

Fig. 4: Freundlich adsorption isotherm of water onto E25C

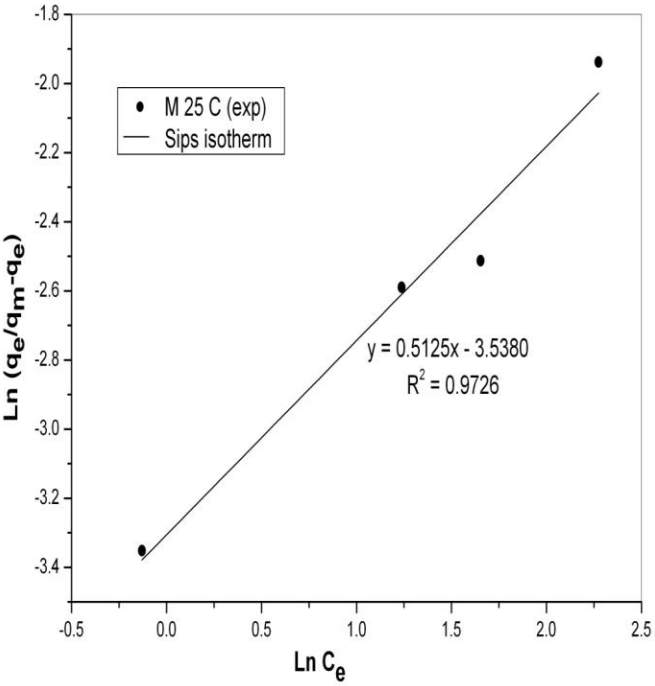

Fig. 5: Sips adsorption isotherm of water onto M25C

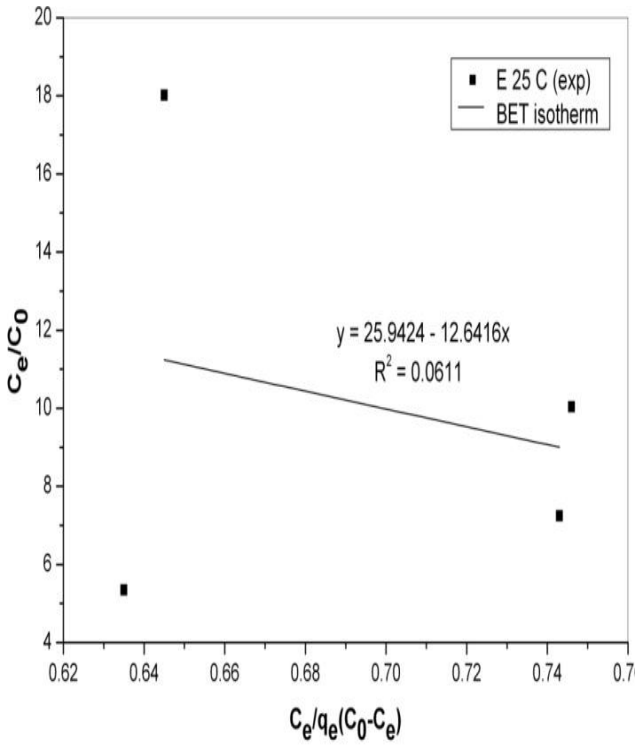

Fig. 6: BET adsorption isotherm of water onto E25C

3.4. Surface Texture of Adsorbent

The optical micrographs of M25C, E25C and 3A zeolite are shown in Plates 1-3. More pores were observed in the hardwood sample, M25C, as compared to E25C which had more of microfibrous surface structure. This revealed that most of the fibres of *Khaya senegalensis* were moderately short as compared to those of the moderately long *Annona senegalensis*. It confirmed the occurrence of higher lignification in the softwood than hardwood; hence, making the hardwoods sawdust to be more susceptible to pretreatment that enhanced their adsorption capacity.

The commercial 3A zeolite had large and orderly knitted porous matrix which provided a good network for selective adsorption of water. Therefore the presence of more pores and openings enhance adsorption capacity.

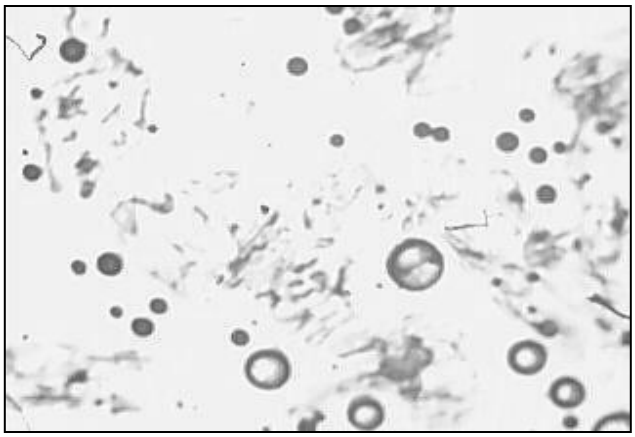

Plate 1: Optical micrograph of M25C

4. CONCLUSION

The results obtained in this study demonstrated that sawdust which is readily available in Southwestern Nigeria is good adsorbent for aqueous ethanol purification. It was found that initial water concentration can influence the adsorption capacity of adsorbents. This work also showed that hardwood (*Khaya senegalensis*) sawdust adsorbs water better than softwood (*Annona senegalensis*) and the capacity can be improved upon by chemical modification using 25% (w/w) $CaCl_2$.

Plate 2: Optical micrograph of E25C

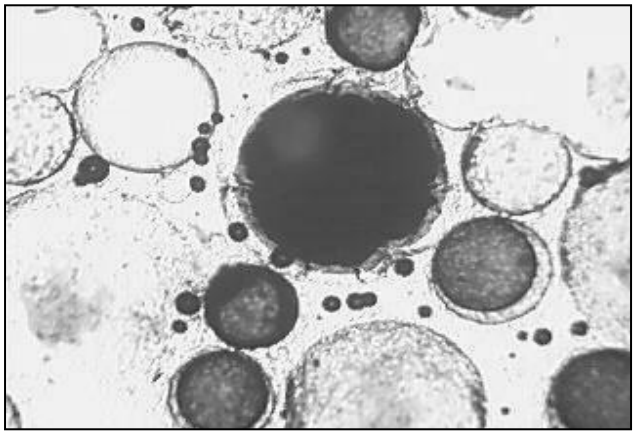

Plate 3: Optical micrograph of 3A zeolite

Sips isotherm is the most suitable isotherm for designing the adsorption process.

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Table 2: Estimated Parameters and Statistical Evaluation of Adsorption Isotherms

Parameters	M0	M25C	E0	E25C	3A Zeolite
Langmuir isotherm					
q_L	0.8085	0.8138	0.3551	0.4230	1.2379
k_L	0.0925	0.4111	0.1519	0.1828	0.4430
R_L	0.9863	0.9419	0.9777	0.9987	0.9377
χ^2	1.5167	0.0961	2.5369	1.5844	0.0390
R^2	0.8770	0.9692	0.8393	0.9127	0.9609
Freundlich isotherm					
$1/n_f$	0.8884	0.5355	0.4531	0.7251	0.2395
k_f	0.0625	0.2283	0.0470	0.1411	0.5380
χ^2	0.0103	0.0025	0.0142	0.0026	0.0005
R^2	0.9264	0.9701	0.8454	0.9252	0.9891
Sips isotherm					
$1/n_s$	0.9399	0.5622	0.8012	0.2687	0.2671
ks	0.0044	0.0367	0.0028	0.0505	0.0812
χ^2	0.0446	0.0139	0.0716	0.3296	0.0029
R^2	0.9449	0.9726	0.8751	0.9483	0.9900
BET isotherm					
q_m					
k_B	-0.9129	62.1563	-0.3132	0.5133	31.6689
χ^2	90.9940	1.6532	1097.2568	43.8676	0.0083
R^2	0.3324	0.4285	0.8459	0.0611	0.9514
*SSA, (m^2/g)	120	736	83	286	1824

**Specific Surface Area*

NOTATIONS

Symbol	Notation
M_L	mass of ethanol-water mixture (g)
M_A	mass of dry adsorbent (g)
W_i	initial weight (g)
W_f	final weight (g)
ρ_{H_2O}	density of water (g/ml)
$C_{i,EtOH}$	initial concentration of ethanol (% w/w)
$C_{f,EtOH}$	final concentration of ethanol (% w/w)
C_0	highest water concentration (% w/w)
C_e	concentration of ethanol at equilibrium (% w/w)
q	adsorption capacity ($g\ g^{-1}$)
q_e	adsorption capacity at equilibrium ($g\ g^{-1}$)
q_m	maximum adsorption capacity on a monolayer surface ($g\ g^{-1}$)
q_L	Langmuir parameter
q_s	Sips parameter
R_L	Langmuir separation parameter
k_L	Langmuir parameter
k_f	Freundlich constant indicating adsorption capacity
k_s	Sips parameter
k_B	BET constant
$1/n_f$	Freundlich constant indicating adsorption intensity
$1/n_s$	surface heterogeneity constant
N_A	Avogadro's number (molecules/kmol)
a	effective cross-section area occupied by one water molecule (m^2)
M	molecular mass of water (g/kmol)
χ^2	Chi square
R^2	coefficient of determination

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