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ADSORPTION CAPACITY AND KINETICS STUDY OF AQUEOUS ETHANOL PURIFICATION USING NIGERIAN WOODS SAWDUST

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ABSTRACT

Bio-ethanol offers advantages of clean burning and reduced engine emission. However, its bioconversion technology is not cost- and energy-effective especially its purification pass the azeotropic point, hence the need for improving on the separation technology of its production. Adsorption by zeolites has been put forward as a means of concentrating the bio-ethanol above 95.5% w/w ethanol. This study investigates the capacity of some Nigerian woods sawdust as adsorbent for aqueous ethanol purification by liquid phase equilibrium adsorption process. To enhance adsorption capacity, the samples were modified using NaOH and H_2SO_4. Also, pseudo first- and second- order kinetics of the sorption process were studied. Out of the samples experimented; *Cordia millenii, Milicea excelsia* and *Masilania accuminata* demonstrated high capacity for water removal with percentage removal of 82, 80 and 75 percent, respectively. Upon acid modification, the capacity improved greatly. The adsorption process followed pseudo second order kinetics with particle-diffusion controlling the transport process. Modification with H_2SO_4 enhances the performance of the adsorbent.

Key Words: *Adsorption, ethanol, sawdust, diffusion, kinetics*

1. INTRODUCTION

Nations across the world demand more energy to fuel transport and industry sectors of their economy. Sourcing this energy demand with fossil fuel has lead to increasing negative climatic impact. Also, the world is facing huge shortages and increasing cost of petroleum fuels. Therefore, research is tending towards cleaner fuels from renewable sources globally, especially ethanol[1], commonly sourced from fermentation of glucose and fructose. Ethanol, a plant-derived fuel, is clean-burning and reduces engine emissions [2]. An improve octane index of gasoline by anhydrous ethanol addition has been reported [3,4].

Traditionally, ethanol purification is by fractional distillation. However, the approach has thermodynamic limitations because ethanol attains azeotropic point at 96% w/w. Though benzene forms a tertiary azeotrope to remove water, but small amounts of benzene remain in the ethanol. A popular alternative is the use of molecular sieve zeolite adsorbents whereby the small water molecule (kinetic diameter, d , 0.28 nm) is taken into the pores of the zeolite while ethanol (d 0.44nm) is not [5]. But due to high cost of these materials, cheap and effective alternatives are being sourced.

Several innovations have been attempted using adsorbents such as calcium chloride, lime, barium oxide and silica gel [6]. However, the extensive redrying process of these desiccants entails high energy consumption. Another novel technique for ethanol-water separation is the utilization of the preferential adsorption of water by carbohydrate materials such as cellulose and starch [7]. These desiccants are found to be energy saving since less energy is needed to dry carbohydrate materials.

South western Nigeria is endowed with abundant forest resources, among these are softwoods and hardwoods timbers[8], which have been utilized significantly in building and construction industries. In the process of these applications, a lot of sawdust wastes are produced which form refuse heap at the milling industries [9,10]. Disposal of these lignocellulose wastes, usually by burning, releases to the atmospheres, compounds which are not environmentally friendly. The increased level of environmental contamination as a consequence of industrial development is posing a very serious problem to the global environment [11,12]. These wastes materials had been established to have adsorptive characteristics for heavy metals [6,13]; with adsorptive capacity varying from species to species[14]. Assessment of these materials as adsorbent for bio-synthesis industry may pave the way for cheaper production of absolute alcohol. The objective of this study therefore is to assess the sawdust of different wood from southwestern Nigeria for preferential adsorption of water in aqueous-ethanol system and study the kinetics of the sorption process.

2. MATERIAL AND METHODS

2.1 Materials

Sawdust of various woods were sourced at Atagijere plank sawmill company in Ile-Ife, southwestern region of Nigeria. The sun-dried sawdust was screened first in a 1.44 mm and then 0.71 mm sieve (Endecotts Ltd., England) to filter out the large particles.

Thereafter, it was washed severally with distilled water until no coloration was observed in the washing water. The adsorbent was then oven dried at 90°C and kept for use. Part of the dried sawdust adsorbent was taken and divided into two portions (1 and 2). Each portion was soaked in 2M NaOH and 2M H_2SO_4 for 8 hours at ambient condition and stirred occasionally. The product was filtered, washed severally with distilled water and dried in oven at 90 °C for 24 hours. The wood samples and their names are reported in Table 1.

Table 1: Names of wood samples experimented

Samples	Vernacular names	Scientific names
S1	Òmò	*Cordia millenii*
S2	Ìrókò	*Milicea excelsia*
S3	Ayùnré	*Albizia zygia*
S4	Iré	*Funtumia africana*
S5	Koóko-igbò	*Cynodon dactylon*
S6	Milaina	*Masilania accuminata*

2.2. Adsorption Studies

About 2.0 g of adsorbent sample was added to 0.04 L aqueous ethanol solution of 95% w/w in an adsorption vessel placed in a thermostatically controlled water bath (Lemfield, England) at a room temperature of 30°C. During the adsorption process, the adsorption system was homogenized by stirring at 400 rpm. Samples were taken from this adsorption system at regular time intervals, centrifuged and the concentration of ethanol in the supernatant solution was determined using a digital refractometer (RX-5000 model, supplied by Atago, Japan).

2.2.1. Adsorption Capacity

The specific adsorption capacity of adsorbent, ($gH_2O.g$ adsorbent^{-1}) calculated from the equation:

$$q = \frac{(c_O - c)v}{m} \tag{1}$$

where, C_o is the amount of water in the ethanol solution before adsorption (gL^{-1}), C is the amount of water in ethanol solution after a certain adsorption time (gL^{-1}), V is the volume of solution (L) and m is the mass of adsorbent (g).

2.2.2. Percentage removal of water

The percentage of water removed (%RE) from the solution by the adsorbent was calculated using the equation

$$\%RE = \frac{100(C_O - C)}{C_O} \tag{2}$$

2.2.3. Degree of adsorption

The adsorption degree of water (α) was calculated from equation:

$$\alpha = \frac{q}{q_e} = \frac{C_o - C}{C_o - C_e} \tag{3}$$

where, q_e is the maximum specific adsorption capacity of adsorbent.

2.3. Kinetic Models

Adsorption kinetics models are important characteristics defining the efficiency and degree of adsorption. In this study, the models were analysed using Origin 6.1 and Excel 2007 with consideration of non-linear least square regression method.

2.3.1. Pseudo first-order model

Lagergren rate equation [15] given by equation (9) is usually adopted in the pseudo first order kinetics of sorption process.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

Where, q_e and q_t are the adsorbent sorption capacities at equilibrium and at time t (mg/g), respectively and k_1 is the equilibrium rate constant of pseudo-first-order adsorption.

By integrating the equation between limits, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, a linearised form of the equation is obtained as,

$$\log(q_e - q_t) = \log q_e - k_1 t \tag{5}$$

The slope and intercept of the plot of log (q- q_e) versus t would give the first-order rate constant k_1 (h^{-1}) and equilibrium adsorption capacity, q_e ($g.g^{-1}$), respectively.

2.3.2. Pseudo second-order model

The pseudo second-order kinetic model[16] can be expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t, (mgg^{-1}) respectively and k_2 is the rate constant of the pseudo-second order sorption ($g.mg^{-1}$ min^{-1}). Integrating the equation between the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the linearised model equation will be,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

The slope and intercept of the plot of (t/qt) versus t in equation (7) would give equilibrium adsorption capacity, q_e and the second-order rate constant k_2 respectively.

2.3.3. Intra-particle diffusion model

Shrihari et al [17] described sorption kinetics based on intra-particle diffusivity by the equation

$$q_t = K'_{id} t^{1/2} + x_i \tag{8}$$

Where K'_{id} is the rate of sorption controlled by intra-particle diffusivity, ($g.(gh)^{-0.5}$) and is a measure of diffusion coefficient and x_i represents the boundary layer thickness. If the sorption follows the intra-particle diffusivity equation, then a plot of q_t versus $t^{1/2}$ should give a linear relationship from where K'_{id} and x_i can be determined from the slope and intercept of the plot respectively.

The intra-particle diffusion model as described by Demirbas *et. al.* [18] as equation (9):

$$R = K_{id}t^a \qquad (9)$$

Where R is the percentage water adsorbed, t is the contact time, **a** is the adsorption mechanism, K_{id} is the intra-particle diffusion rate constant (h^{-1}). A linear form of Eqn 6 [19] is:

$$\log R = \log K_{id} + a\log t \qquad (10)$$

The constants "a" and "K_{id}" can be determined from the slope and intercept of the plot of log R versus log t.

2.3.4. Mass Transfer Equation

The mass transfer equation for kinetic modeling of adsorption [20] is generally expressed as

$$C_o - C = De^{K_o t} \qquad (11)$$

where t is time (h), D is a fitting parameter, K_o is the mass transfer adsorption coefficient, K_o is related to the adsorption constant K as $K_o = Km$, and m is the mass of the adsorbent (g). A linearised form of equation (11) is:

$$\ln(C_o - C) = \ln D + K_o t \qquad (12)$$

Plot of ln (C_o – C) versus time 't' should give a linear relationship. The constants K_o and D can be obtained from the slope and intercept of the plot respectively.

3. RESULTS AND DISCUSSION

The capacity of the sawdust adsorbents of the woods experimented are reported in figures 1-3. While figure 1 shows the percentage water removal, figure 2 reported the adsorption capacity of the wood adsorbents. The fractional adsorption capacity variation with time is presented in figure 3. Figures 4 to 9 presented the adsorption kinetics representing the order and mechanism of the adsorption process.

The percentage removal of water (%RE) from the aqueous ethanol mixture by the various adsorbent (figure 1) ranged from 68 to 82 percent with sample S1 (*Cordia millenii*) and S6 (*Masilania accuminata*) having the highest and lowest result, respectively. This was attained within 5 hours of adsorption. The performance of the adsorbent in terms of moisture removal is in the order S6‹S5‹S3‹S4‹S2‹S1. With the NaOH modified adsorbents, the percentage moisture adsorbed was in the range of 72 and 90 percent. This reflects an improvement in performance of the adsorbent with the trend following the order B4‹B6‹B3‹B5‹B2‹B1. H_2SO_4 modified adsorbent records a performance trend order of A5‹A3‹A4‹A6‹A2‹A1, with the range of 78 and 92 percent %RE. The acid acts as a better agent than the base in modifying the adsorbent for the purpose of moisture removal from the aqueous ethanol solution.

A critical observation of figure 1 shows that samples S1 and S2 have high capacity for moisture adsorption both as raw unmodified samples and on modification both with base and acid modification. Also with modification, the least performed adsorbent i.e. S6 capacity for moisture removal was improved relatively from 68% to 82% resulting into better performance over others except samples S1 and S2.

In figure 2, the adsorption capacity increases with contact time. The raw samples S1 and S2 have the adsorption capacity of about 0.84 and 0.82 g/g adsorbent, respectively, within saturation time of about 5 hours. Upon modification, the adsorption capacity improved to 0.8805 and 0.8630 for base modified and 0.9410 and 0.9494 g/g adsorbent for acid modified sample S1 and S2 respectively. These findings revealed sample S1 and S2 as a better adsorbent for aqueous ethanol purification among the wood samples studied. It could be noticed that the slope of the plots decreases with increased contact time. This reflected a decreased water removal rate with time, until equilibrium adsorption level was attained. This gave credence to full availability of active sites for adsorption at the initial stage of the process, thereafter, the sites were covered with the adsorbed water molecules, thereby reducing further uptake of moisture at saturation.
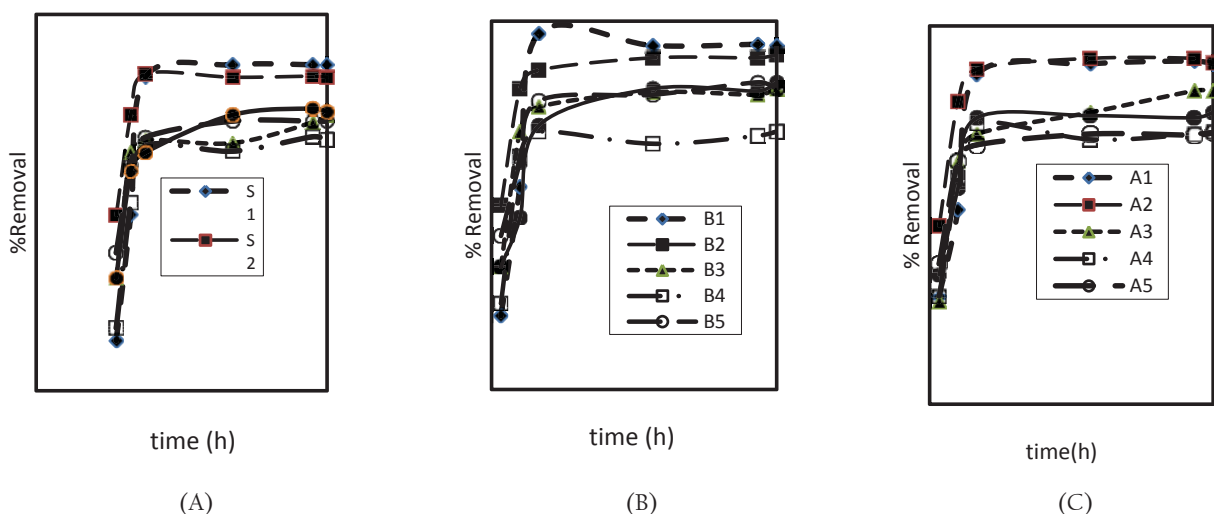

(A)   (B)   (C)

Figure 1: Percentage removal of moisture by various wood sawdust adsorbent from 95% w/w ethanol solution.
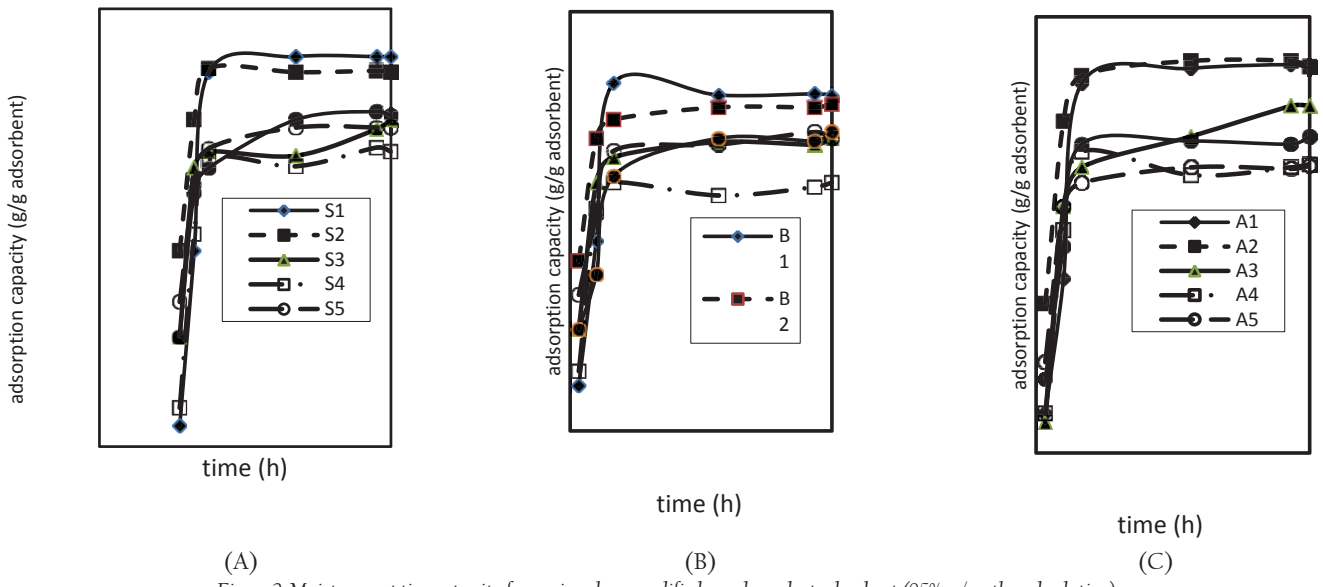*[A-Unmodified sawdust; B-Base modified; C- Acid modified]*

Figure 2: Moisture sorption capacity for various base modified wood sawdust adsorbent (95% w/w ethanol solution)

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The time dependency of fraction of moisture adsorbed was reported in Figure 3 for the various raw and modified adsorbent samples. As the interaction time increases, equilibrium concentration decreases, implying an increase in the adsorbed sorbate concentration with time. This attained a constant value for most of the adsorbent before or at the 5th minute contact time. The extent at which contact time influences adsorption is only significant within the first 4 hours.

Appropriate kinetic parameter is highly important in process equipment facilities design. This underscores the significance of the kinetic data modeling for industrial application of sorption. The pseudo first order model plot

(eqn 5) is reported in figure 4. From the figure, the model fairly represents the experimental data, with weak coefficient of determination (R^2) in the range of 0.959- 0.989 (table 2) with low rate constants. The predicted saturation sorption capacity was far different from the experimental values. The validity of the model was determined by the sum of error squares (SSE, %) given by:

$$SSE(\%) = \sqrt{\frac{\sum \left(q_{e,expt} - q_{e,cal} \right)^2}{N}} \qquad (13)$$

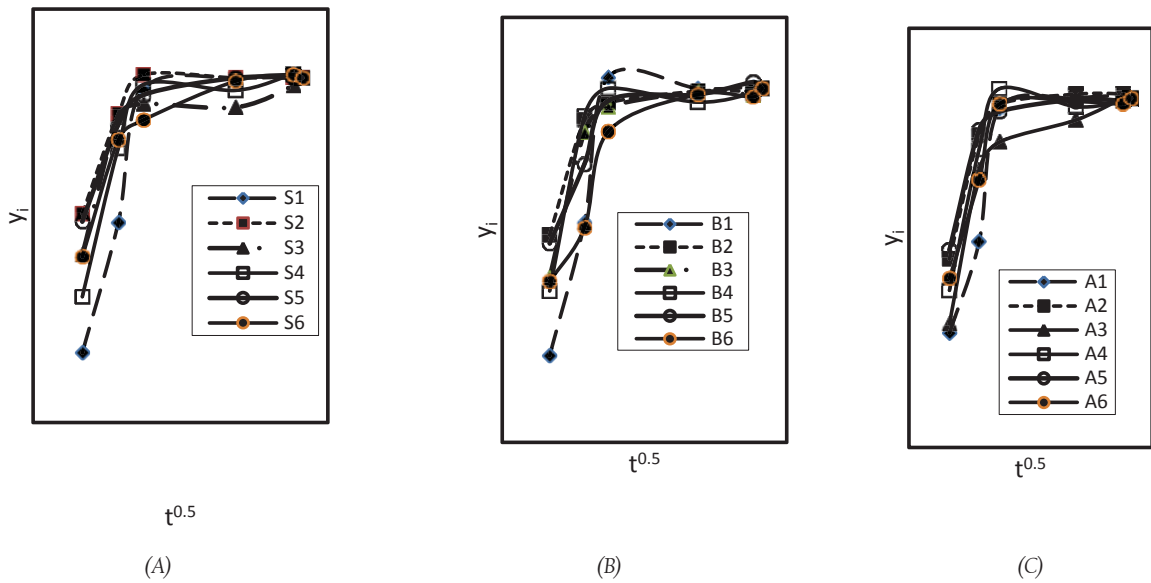Where N is the number of data points.

Figure 3: Time-dependency of fraction of moisture adsorbed for various adsorbent

Table 2: Evaluated kinetic parameters of the adsorbents

| Samples	$q_{e,expt}$ (g/g)	Pseudo first-order				Pseudo second-order			
		k_1 (h^{-1})	q_e (g/g)	R^2	SSE (%)	k_2 g(g.h)$^{-1}$	q_e (g/g)	R^2	SSE (%)
S1	0.845	0.063	1.774	0.962	0.929	0.597	1.057	0.982	0.212
A1	0.945	0.049	1.758	0.975	0.813	1.005	1.032	0.993	0.087
S2	0.873	0.034	1.186	0.961	0.313	2.271	0.915	0.999	0.042
A2	0.943	0.037	1.449	0.983	0.506	1.647	1.038	0.999	0.096
S6	0.778	0.034	1.216	0.959	0.438	2.896	0.777	0.998	0.001
A6	0.863	0.040	1.384	0.989	0.521	1.411	0.973	0.996	0.110
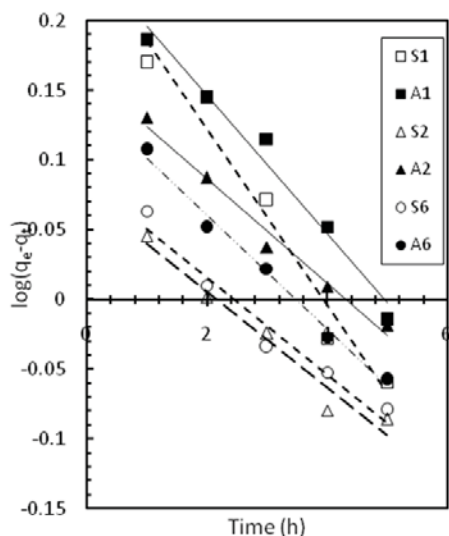
Figure 4: Pseudo-first order kinetics of sorption on various wood adsorbent

The observed % SSE values was high for the pseudo first order kinetics. The second order model showed a better fit of experimental data (fig 5). The coefficient of determination (R^2) showed a strong relationship between the experimental and correlated data. The R^2 values were in the range 0.982 – 0.999. Also, the equilibrium sorption capacity q_e values calculated from the relation were close to the experimental q_e values, with very low % SSE values. This gave credence to the findings of Itodo et.al [21] re-affirming pseudo second order kinetics as more appropriate in defining adsorption using sawdust adsorbent.
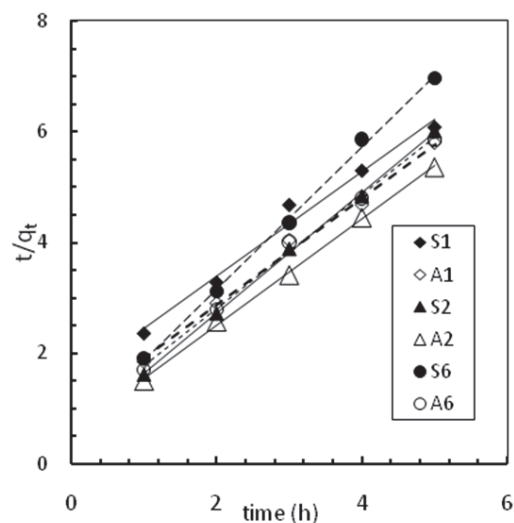

Figure 5: Pseudo second order kinetics for moisture sorption by various wood adsorbent

The adsorptive mass transfer rate could be controlled by several factors such as (i) diffusion of the solute from the solution to the film surrounding the particle, (ii) diffusion from the film to the particle surface (external diffusion), (iii) diffusion from the surface to the internal sites (surface diffusion or pore diffusion) and (iv) uptake which can involve several mechanisms such as physico-chemical sorption or complexation [22]. The solute movement by diffusion results from concentration gradient from one fluid body to the other and by intra-particle diffusion for transport of solute from the solution to the solid phase.

Taking into consideration the diffusion mechanisms and their related equations, the coupling between liquid and solid phases and the initial and boundary conditions, it therefore means that the rate of equilibrium attainment may be either film-diffusion controlled or particle-diffusion controlled. Though these two different mechanisms cannot be sharply divided [23]. From equation 8, the non zero adsorption mechanism constant 'x_i' in the intra-particle diffusion plot (fig 6) clearly showed existence of additional mechanism controlling the adsorption rather than intraparticle diffusion alone.
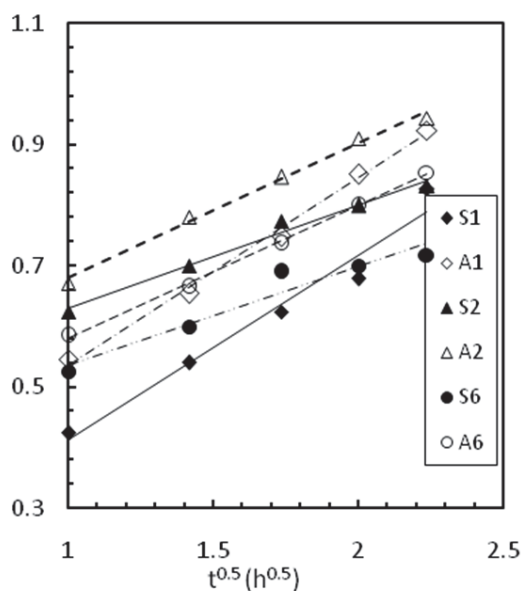

Figure 6: Plot of intraparticle diffusion kinetics

Sorption mechanism assumes intra-particle diffusion only if the straight line plots of q_t versus $t^{1/2}$ passes through the origin [24]. This is not the case in figure 6. This additional mechanism could probably be boundary layer influence, that is, external film resistance, resulting from viscous drag existing between the adsorbent surface and the solute in solution diffusing across its surface. From the plot, the boundary layer thickness ranged from 0.107 to 0.459 as reported in table 3.

The transport of the sorbate through the particle-sample interphase onto the pores of the particles, alongside adsorption on

the available active surfaces of the adsorbent may contribute significantly to adsorption. Plot of equation 10 shown in figure 7 gave credence to this. The constants k_{id} and 'a' are reported in table 3.
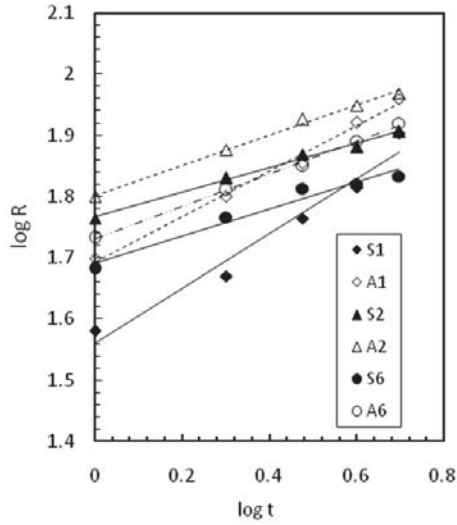

Figure 7: Plot of intraparticle diffusion model in terms of % moisture removal

Higher values of k_{id} obtained illustrated an enhanced adsorption rate while the larger values of 'a' showed a better adsorption consequential on improved bonding. Since higher value of k_{id} portrays an enhanced adsorption rate while larger 'a' relates to improved bonding between sorbent and adsorbent particles, the observed values in this study as reported in figures 6 and 7 and table 3 therefore show that attainment of sorption saturation is by either film-diffusion or particle diffusion or both. Using fractional attainment of equilibrium, relationship for particle diffusion controlled sorption processes is given by the equation

$$\ln(1 - y_i) = -k_p t \qquad (14)$$

Where k_p is the rate coefficient of particle diffusion controlled process and it correspond to the particle size of the sorbent. When plot of $\ln(1-y_i)$ versus time results in a linear relationship, then the sorption is particle-diffusion driven. From figure 8, linear plot with R^2 of 0.980 to 0.997 was obtained for the adsorbents and the k_p values are in the range $5.333 \times 10^{-4} – 1.120 \times 10^{-3}$ h^{-1}.

Generally, mass transfer resistance outside the particle and intraparticle diffusion resistance influence the rate of adsorption of solute from the liquid solution by porous media. Mesko et al. [25] showed pore diffusion as the rate controlling mechanism of adsorption process, giving credence to intraparticle diffusion resistance. Based on this, the intercept of the linear plot of equation 12 reported in fig 9 gave pore diffusion coefficient of 4.874×10^{-4} to 8.331×10^{-4} m^2h^{-1} and k_o of 1.12×10^{-3} to 2.733×10^{-3} m h^{-1}. The values of these constants increase with the chemical modification of the adsorbent.
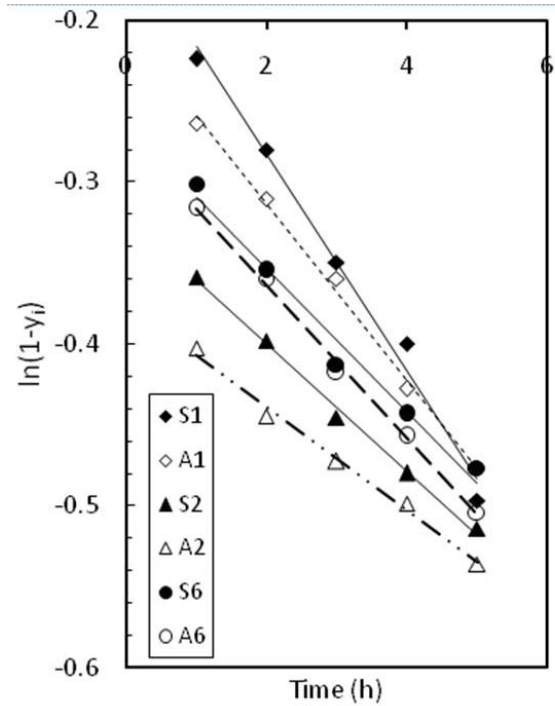

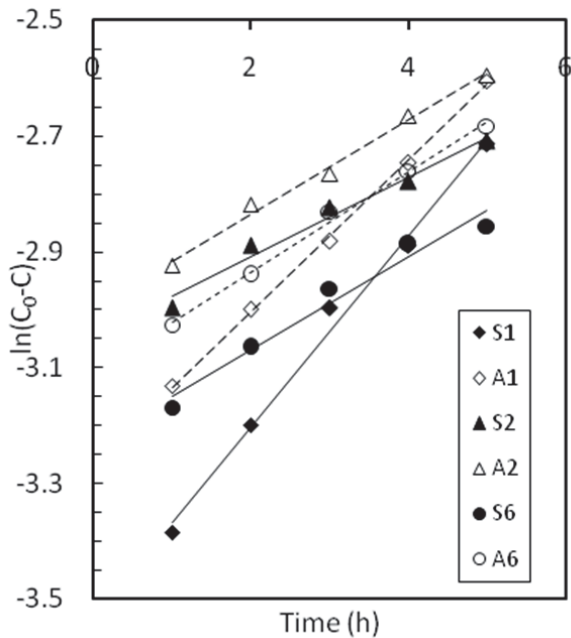*Figure 8: Particle diffusion controlled sorption plot*

Figure 9: Plot of adsorptive mass transfer correlation

Table 3: Adsorptive mass transfer models parameters

Samples	Equation 8			Equation 10			Equation 12		
	k_{id}	x_i	R^2	a	k_{id}	R^2	D	k_o	R^2
S1	0.305	0.107	0.964	0.446	4.759	0.964	0.029	0.164	0.991
A1	0.309	0.225	0.995	0.369	5.430	0.996	0.038	0.130	0.998
S2	0.171	0.459	0.983	0.200	5.847	0.991	0.048	0.068	0.977
A2	0.222	0.457	0.992	0.244	6.056	0.995	0.050	0.081	0.991
S6	0.162	0.374	0.936	0.220	5.419	0.960	0.040	0.080	0.966
A6	0.219	0.361	0.998	0.264	5.641	0.997	0.045	0.086	0.994

4. CONCLUSION

The study has revealed that *Cordia millenii* and *Milicea excelsia* sawdust are good adsorbent materials for concentrating aqueous ethanol and their capability for the purpose can be enhanced by chemical treatment. Estimation based on fractional attainment of equilibrium attest to the fact that the sorption process is principally particle diffusion controlled. The sorption process could best be designed based on pseudo second-order kinetics.

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