Kinetics and Isotherm Studies of the Adsorptive Dehydration of Ethanol-Water System with Biomass Based Materials

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Abstract:- This study has explored the possibility of using biomass based adsorbents other than the conventional materials as adsorbent for dehydration of ethanol-water mixtures. These biomass based adsorbents are; Cassava starch (CAS), Corn starch (COS), Acid modified cassava starch (MCAS), and Enzyme modified corn starch (EMCOS). The adsorption kinetics found to best correlate the experimental data was intra-particle diffusion in comparison with the other models. The presence of the hydroxyl O-H stretch group's hydrogen bond in the starch as shown by the FTIR spectroscopy confirmed the chemical affinity of these adsorbents for water in the ethanol-water system adsorption. The intra-particle diffusion model suggested that the boundary layer has less significant effect on the diffusion mechanism but the particle diffusion was the rate limiting step of the adsorption of water on the starch-based adsorbents studied. EMCOS gave the best result as compared to the other adsorbents.

Keywords: **Starch, FTIR, adsorption, kinetics, ethanol-water mixtures.**

I. INTRODUCTION

The world in the 21st century presents many critical challenges. One of the most essential challenges is the environment. The recent depletion of fossil fuels along with the problem of global warming has made bio-ethanol receive an increasing attention as an alternative chemical source in addition to its potential for providing renewable energy [1]. Advances in technology have allowed development of alternative renewable energy sources, which is more dependable than the fossil fuels [1]. Ethanol is commonly used as a fuel itself or an additive that helps enhancing the octane number and combustibility of gasoline [2]. Anhydrous ethanol is one of the bio-fuels produced today; others include biodiesel, and biogas. One of the energy-efficient techniques widely used for ethanol dehydration is adsorption process. The separation of ethanol-water mixtures using starch or cellulose materials was first demonstrated by [3]. It has been shown that ethanol dehydration by adsorption requires far less energy than the conventional azeotropic distillation. Adsorption with biomass adsorbent is also less-energy consuming than adsorption with other adsorbents [4]. Biomass materials that have been investigated and found to be viable adsorbents include cassava starch, corn grits, potato starch, ligno-cellulosic, amylose, and corn starch [5]. Adsorbed component of the fluid is known as the adsorbate. To separate ethanol using adsorption from a feed mixtures containing ethanol-water, the mixture is contacted with the adsorbent and the water is more selectively adsorbed and retained by the adsorbent while ethanol is relatively un-adsorbed and is removed from the interstitial void spaces between the particles of the adsorbent and the surface of the adsorbent. Adsorption isotherm is basically important to describe how solutes interact with adsorbents whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and is critical in optimizing the use of adsorbents [6]. Starch based adsorbents adsorb water by forming hydrogen bond between the hydroxyl groups on the surface of the adsorbent and the water molecules [7]. Advantages of these starch based adsorbents in dehydration of ethanol-water mixtures include; non-toxicity, availability, biodegradable and renew ability [8]. The present work was carried out to evaluate the starch based materials potential ability to dehydrate ethanol-water systems. The adsorption system data were analyzed to study adsorption kinetics, and isotherms. The functional group of the starchy materials used was analyzed using the Fourier transform infrared spectroscopy. The experimental data were obtained at a temperature of (30°C). The starch materials like unmodified cassava starch adsorbent, chemically modified cassava starch adsorbent, unmodified corn starch adsorbent, and enzyme modified corn starch adsorbents were used for the adsorption of water from ethanol-water systems.

A. Materials and Methods

Unmodified cassava starch was purchased from the market, sun-dried and thermally treated in an oven at 105°C for 16hours and thereafter classified into different particle sizes. For the chemically modified cassava starch preparation the method of [9] was used. Analytical grade of ethanol, de-ionized water, α- amylase, sodium azide, sodium phosphate, sodium chloride, and sodium hydroxide were purchased from accredited chemical dealers in Onitsha, Anambra State, Nigeria, using a scale with an accuracy of 0.01g. The method of [18] was used for the enzyme modification of the corn starch. Ethanol-water solutions are prepared at the required mass concentrations of 90wt% ethanol. The fluid phase concentration was measured with the aid of an Abbe refract meter with automatic calibration in the experimental range of concentration.

B. Preparation of enzyme modified corn starch

The modification process was carried out using an enzyme, B. subtilis α-amylase. The α-amylase solution was prepared by adding the enzyme in a 1/50 dilution to

phosphate buffer at a pH of 6.9. The buffer was prepared by combining water that had been treated by reverse osmosis and deionization with 2.4g/l of sodium phosphate (monobasic NaH_2PO_4) and 0.391g/l of sodium chloride. The pH was then adjusted to 6.9 with aqueous sodium hydroxide. Sodium azide was also added as an antimicrobial agent. Ten milliliters of the diluted enzyme solution were added to 1 gram of corn starch at room temperature. The enzyme-starch solution was soaked for 8 days, filtered and dried in an oven for 24 hours at 40°C.

C. Starch content determination

Calibration curve with a suitable carbohydrate standard for the unknown sample were prepared. Six test tubes were labeled 1 to 6. The carbohydrate standard was dispensed. Distilled water was added to make it up to 0.5ml. 0.5ml of 5% phenol solution was added and thorough mixed. 2.5ml of concentrated sulphuric acid was dispersed to each tube and mix thoroughly this is allowed to stand for 20mins and reading taking in a spectrophotometer at 470nm wave length. Unknown samples were treated equally as standard in duplicates and concentrations extrapolated from the predetermined calibration curve.

Table 1.0 Physico-chemical Characterization of the Adsorbents

Physico-chemical parameters	Unmodified corn starch	Enzyme modified corn starch	Unmodified cassava starch	Modified cassava starch
pH	5.6	5.4	7.6	6.2
Moisture content (%)	29.1	30.4	29.15	31.00
Colour	Yellowish white	White	White	White
Starch content (%)	86.00	86.00	85.00	85.00
Bulk density	1.39	1.429	1.36	1.48

II. EXPERIMENTAL PROCEDURE METHOD

For the kinetics test, aqueous samples were taken from the 90wt% concentration of ethanol-water mixtures that circulating continuously in a closed loop through a packed bed of adsorbents particle at regular time intervals using filtered syringe and thereafter, the end concentration of the sample was determined using refractometry method and the end concentration obtained from the pre-determined calibration graph.

The amount of water adsorbed was obtained using the formula;

$$q_e = \frac{M_l}{M_A}\left(\frac{C_{f}-C_l}{C_f}\right)$$

...................…... (1.0)

Where q_e=the amount of water adsorbed per unit mass of adsorbent (g H_2O/g adsorbent).

C_f and C_L= final mass fraction of ethanol in solution and initial mass fraction of ethanol in solution (wt %), M_L=

mass of liquid phase, (g), and M_A=mass of the adsorbent used (g). [5]. The kinetics data were then fitted using the first order, second order, pseudo-second order, Intra-particle diffusion, Boyd, and Elovich equation models.

III. RESULTS AND DISCUSSION
A. Effect of Particle Size

The kinetic results were presented by uptake rate curves, where the amount adsorbed was related to the adsorption time for the starch adsorbents studied. It may be noted as shown in fig. 1 -- 4 that the rate of water uptake decreased as particle size of these starchy adsorbents is increased. This is as a result of the existence of a larger total area in agglomerates of smaller particles, where the area of contact between the particles decreased in relation to the same mass of larger particles, such that diffusion path is smaller for the smaller size particle, diminishing the time it takes for the molecules to pass through the intricate net work of meso and macro-pores on their way to the intra-crystalline cavities. This result in a greater period of time spent to hydrate all the hydroxyl amide groups. This corroborates the work of [10,11].
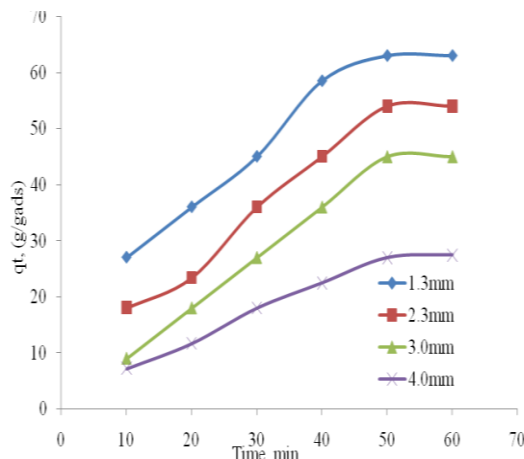

Fig. 1.0 Effect of particle size on adsorption capacity of MCAS for adsorption of water from ethanol-water system
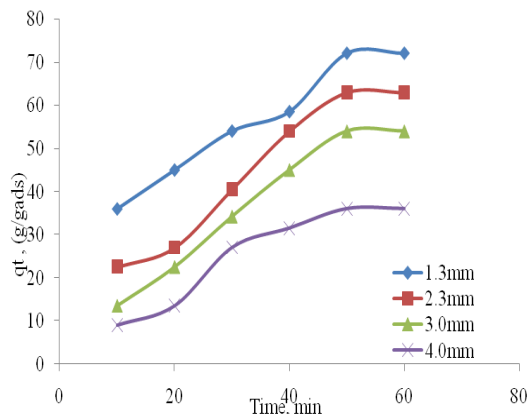

Fig. 2.0 Effect of particle size on adsorption capacity of EMCOS for adsorption of water from ethanol-water system
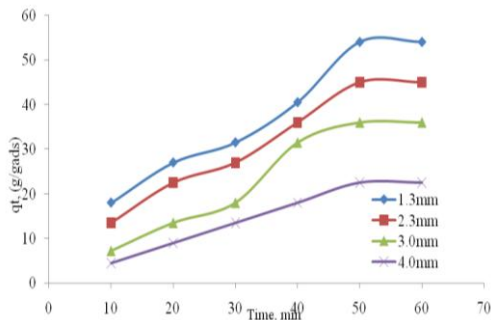
Fig. 3.0 Effect of particle size on adsorption capacity of MCAS on adsorption of water from ethanol-water system
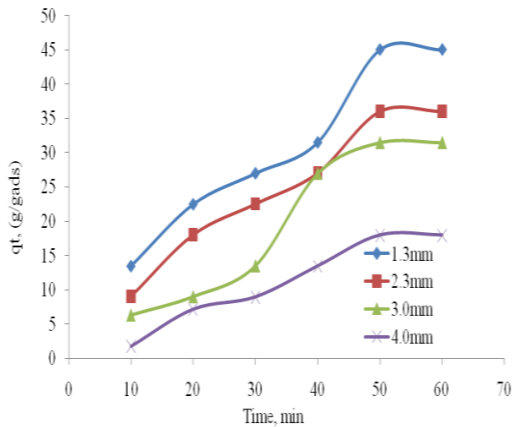

Fig. 4.0 effect of particle size on adsorption capacity of CAS on adsorption of water from ethanol-water system

B. Kinetics of the Adsorption Process

The constant rate of adsorption was determined from first order, second order, pseudo-second order, intra-particle diffusion, and Boyd and Elovich equations models.

C. First Order Equation

The sorption kinetics may be described by a simple first order equation [12]. The change in bulk concentration of the system using the following simple first order rate equation;

$$C_t = C_0 e^{k_1 t} \quad \text{.. (1)}$$

Equation 5 can be re-arranged to obtain a linear form:

$$\log C_t = \frac{K_1}{2.303}(t) + \log C_0 \quad \text{.. (2)}$$

Where C_t and C_0 are the concentration of the solute at time t and initially (mg/L), respectively and k_1 is the first order rates constant, (1/min.). If first-order kinetics is applicable to the system, then the plot of $\log C_t$ versus t of equation (2) will give a linear relationship with $K_1/2.303$ and $\log C_0$ as slope and intercept respectively. The experimental data conform to the first order equation.
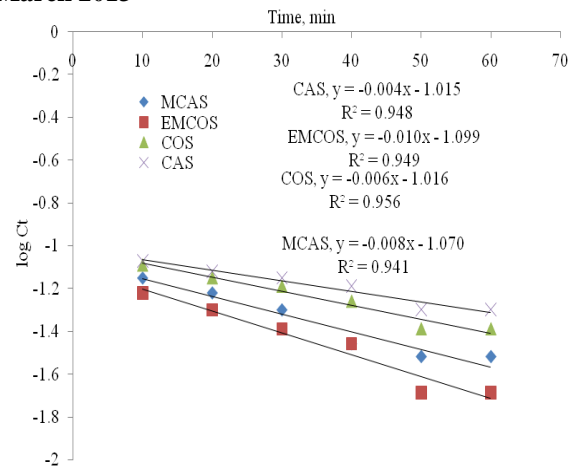

Fig. 5.0 Fisrt order plot for the aadsorption of water from ethanol-water system

D. Second Order Equation

The typical second-order rate equation in solution systems is as follows;

$$dC_t/dt = -k_2 C_t^2 \quad \text{...} \quad \text{.................... (3)}$$

Integrating equation above with the boundary conditions of $C_t=0$ at t=0 and $C_t=C_t$ at t=t to yield; $1/C_t = K_2 t + 1/C_0$ .... (4)

Where C_0 and C_t (mg/L) is the concentration of solute at equilibrium and at time t (min), respectively, and k_2 (L/ (mg. min)) is the rate constant of second order. If the second-order kinetics is applicable to the system, then the plot of $1/C_t$ versus t of equation (4) will give a linear relationship with K_2 and $1/C_0$ as slope and intercept respectively [13]. The data fitted well to the second order equation from the obtained value of correlation co-efficient.
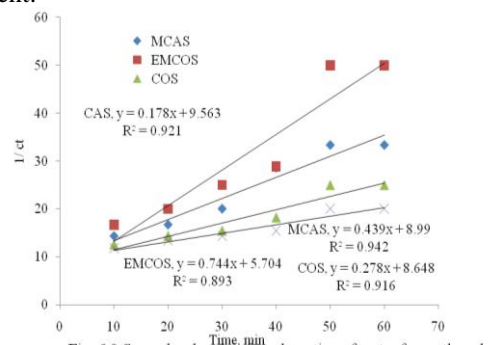

Fig. 6.0 Second order plot for adsorption of water from ethanol-water system

E. Pseudo-second order

The Pseudo-second order equation given by [14];

$$t/q_t = 1/K_2 q_e^2 + (t) 1/q_e \quad \text{.. (5)}$$

K_2 (ml / min) is the rate constant for pseudo – second order kinetic and t = time.

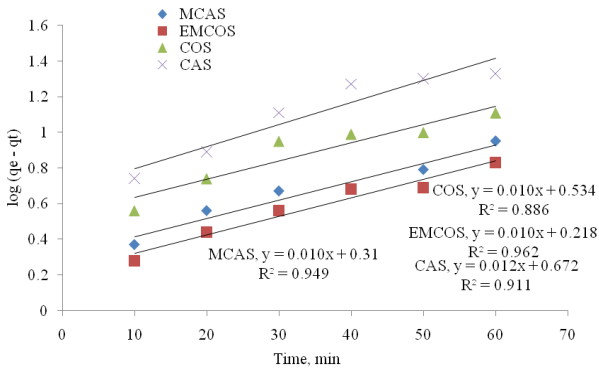A plot of t/q_t against t gives $1/q_e$ as the slope and $1/k_2 q_e^2$ as the intercept.

Fig. 7.0 Pseudo-Second order plot for adsorption of water from ethanol-water system

F. Elovich equation

$$dq_t/dt = \alpha e^{-\beta q_t} \quad \text{......(6)}$$

where α and β, known as the Elovich coefficients. q represents the amount of gas adsorbed at time t, α and β, known as the Elovich coefficients. Where α is the initial adsorption rate (mg/g.min) and β is the adsorption constant (g/mg) during any experiment [15].

To simplify the Elovich equation, Chien and Clayton assumed $\alpha\beta \gg t$ and by applying the boundary conditions at qt = 0 at t = 0 and $q_t = q_t$ at t = t the equation becomes:

$$q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln (t) \quad \text{......(7)}$$

If the Elovich's kinetics equation is applicable to the system, then the plot of q_t versus ln t of equation (7) will give a linear relationship with $1/\beta$ and $1/\beta \ln(\alpha\beta)$ as slope and intercept respectively.
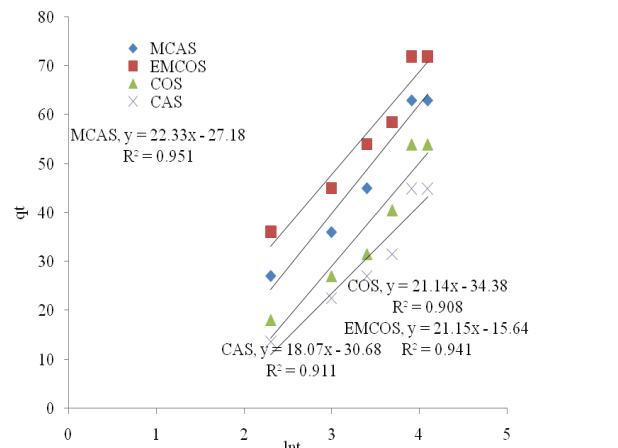

Fig. 8.0 Elovich equation for adsorption of water from ethanol-water system

G. Intra-Particle Diffusion Model

Weber-Morris found out that in many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t [16].

$$q_t = K_{id} t^{1/2} \quad \text{.... (8)}$$

The logarithmic form of the above equation is

$$\log q_t = \log K_{id} + 0.5 \log t \quad \text{...... (9)}$$

where k_{id} is the intra-particle diffusion rate constant. According to Equation (9), a plot of log q_t versus 0.5logt

should yield a straight line with a positive intercept for intra particle diffusion controlled adsorption process. The data fitted well to the intra-particle pore diffusion model from the value of R^2 obtained.
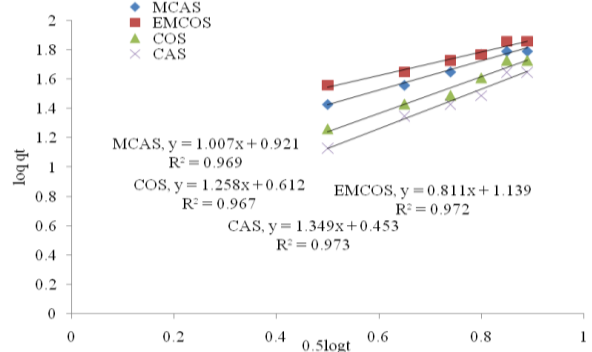

Fig. 9.0 Intra-Particle diffusion model for adsorption of water from ethanol-water system

H. The Boyd kinetics model

To suggest the slow step involved in the adsorption process the kinetics data were also subjected to Boyd kinetics model analysis.

$$B_t = -0.4977 - \ln(1 - F) \quad \text{......... (10)}$$

Where F represents the fraction of solute adsorbed at any time, t (min), as calculated from

$F = q_t/q_o$. The three sequential steps in the adsorption are;

1. Film diffusion, where adsorbate ions travel towards the external surface of the adsorbent.

2. Particle diffusion where adsorbate ions travel within the pores of the adsorbent excluding a small amount of adsorption that occurs on the exterior surface of the adsorbent

3. Adsorption of the adsorbate ions on the interior surface of the adsorbent [6]. The plot of B_t against time (min). Figs. 10 and 11 showed that the points were scattered and did not pass through the origin. It can be suggested that the dehydration of water from ethanol water system on the biomass based adsorbents was mainly governed by the external mass transport where intra-particle diffusion was the rate limiting step [17].
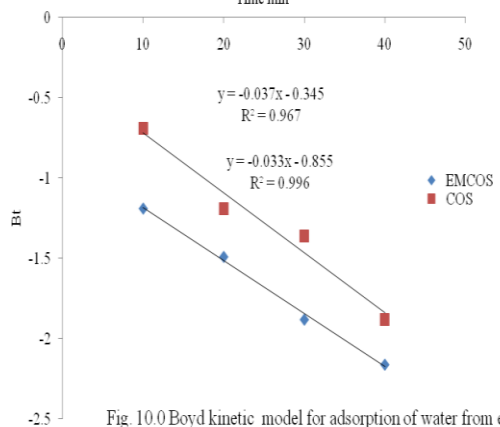

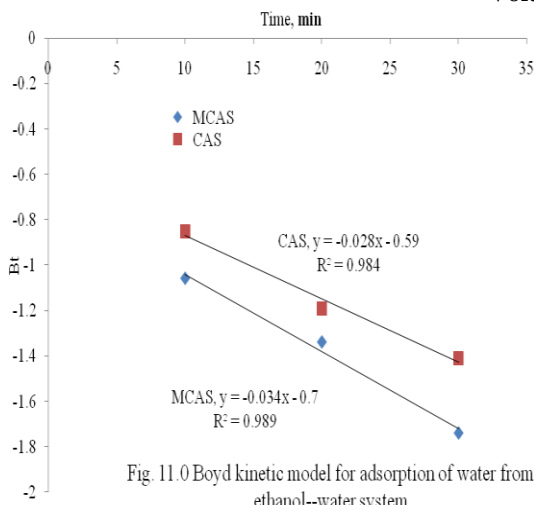Fig. 10.0 Boyd kinetic model for adsorption of water from ethano water system

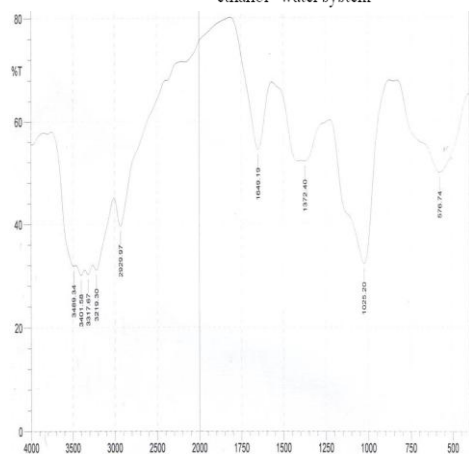Fig. 11.0 Boyd kinetic model for adsorption of water from ethanol--water system

Fig. 12 FTIR spectroscopy of the cassava starch (CAS)

I. Determination of the functional group in the starch based materials

The structural organization of the adsorbents was investigated to identify the functional groups presents. The adsorbents were examined using SHIMADZU FTIR-8400S spectrophotometer with the range 500 – 4000cm^{-1}. KBr was used as background material in the analysis.
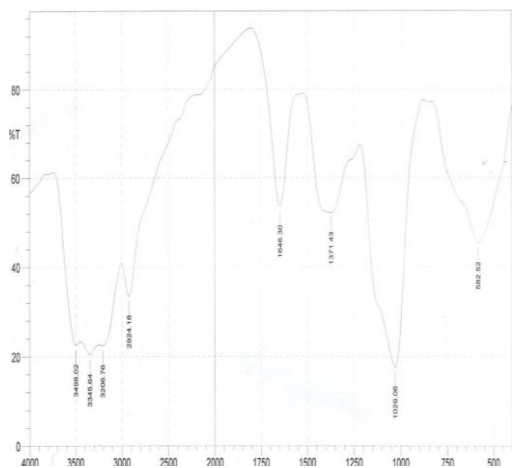

Fig.13 FTIR Spectroscopy of the Modified Cassava Starch (MCAS)
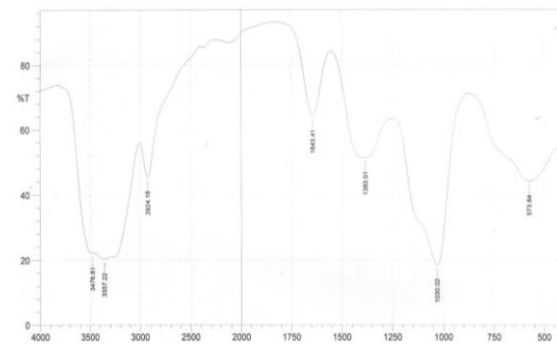

Fig. 14 FTIR Spectroscopy of the Corn Starch (COS)

Figs. 12 and 13 give the FTIR spectrum of both the unmodified cassava starch (CAS) and acid modified cassava starch (MCAS). From fig. 12 the broad band (3121.89cm^{-1}, 3216.41cm^{-1}, 3331.18cm^{-1}, 3423.76cm^{-1} and 3523.1cm^{-1}) exhibit the hydroxyl group, H bonded O-H stretch while the broad band(1368.54cm^{-1}, and 1410.98cm^{-1}) exhibit the C-O-C stretch of the α -1, 4, glycosidic linkages present in the cassava starch that resulted from the amylose structures of the starch [18]. It indicated that water is adsorbed in the amorphous part of the starch. Broad band 746.48cm^{-1} that is <800cm^{-1} exhibited complex vibrational mode due to skeletal mode of vibrations of the glucose pyranose ring(Tu etal, 1979). The highest peak was observed at broad band (2144.91cm^{-1}) which suggests that CH stretching of the cassava starch is very strong. Fig. 13 broad bands (2924.18cm-1, 3357.22cm^{-1}, and 3476.81cm^{-1}) indicate hydroxyl group, H bonded OH stretch and this corroborate the work of [19] where it was shown that broad bands (3000 – 3600cm^{-1}) exhibit OH stretch while 573.84cm^{-1} exhibit complex vibrational modes due to skeletal mode vibrations of the glucose pyranose [20]. The highest peak value of 1643.41cm^{-1} of N-H stretching of amine (acrylamide) which was as result of the acid modification process suggest the reduction in the water adsorption capacity of the modified cassava starch.
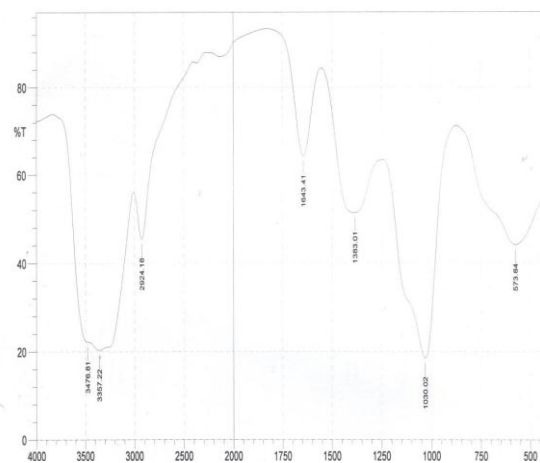

Fig. 15 FTIR Spectroscopy of the Enzyme Modified Corn Starch (EMCOS)

Figs. 14 and 15 showed the FTIR spectroscopy of both the unmodified corn starch (COS) and Enzyme modified corn starch (EMCOS). Fig. 14 broad bands (2929.97cm^{-1}, 3219.3cm^{-1}, 3317.67cm^{-1}, 3401.58cm^{-1}, and 3489.34cm^{-1}) exhibited the OH stretch group. 1372.4cm^{-1} showed OH bend. COH bending was shown in 1025.2cm-1 band. The highest peak of 1649.19cm^{-1} suggests that water is adsorbed at the amorphous parts of the corn starch.

Fig. 15 bands of (2924.18cm^{-1}, 3206.76cm^{-1}, 3345.64cm^{-1}, and 3498.02cm^{-1}) indicated the presence of hydroxyl group, H bonded OH stretch [19]. The highest peak value of 1646.3cm^{-1} in the enzyme modified corn starch suggest the amorphous crystalline nature of the starch which is responsible for the highest water adsorption experienced in the EMCOS.

Table 2.0 Summary Results of Kinetics Model

Kinetic parameters	EMCOS	MCAS	COS	CAS
First order, R^2	0.949	0.941	0.956	0.948
K_1, (min^{-1})	0.023	0.018	0.014	0.009
Second Order, R^2	0.893	0.942	0.916	0.021
K_2, (ml/min)	0.744	0.439	0.278	0.178
Elovich, R^2	0.941	0.951	0.908	0.911
α	0.24	0.39	0.52	0.24
β(g/g)	0.047	0.045	0.047	0.047
Pseudo – Second order, R^2	0.962	0.949	0.886	0.911
K_2 (ml/min)	100	100	100	83.3
Intra-particle diffusion, R^2	0.972	0.969	0.967	0.973
K_{id}	13.8	8.34	4.09	2.84
Boyd model, R^2	0.967	0.984	0.989	0.996

IV. CONCLUSION

In this work, starches adsorbents that were used as adsorbents for the dehydration of water from ethanol-water system are unmodified cassava starch (CAS), modified cassava starch (MCAS), unmodified corn starch (COS), and Enzyme modified corn starch (EMCOS). The kinetic models related to the water removal capacity of these adsorbents and molecular diffusion of water molecules on the adsorbents surface. The kinetic models were found to follow intra-particle diffusion, Boyd, first order, Elovich, and second order model as evident in their (R^2) values. Intra-particle diffusion model best correlated the experimental data. The intra-particle diffusion models showed that the boundary layer has less significant effect on the diffusion mechanism of the sorbate on the sorbent while the Boyd kinetics model revealed that the adsorption mechanism was mainly due to external mass transport. It is noted that the intra-particle diffusion model played an important role as the limiting step in the water uptake from ethanol-water systems studied. FTIR result of these starches also confirmed the chemical affinity of starch to water. The hydroxyl groups of the starch interact with water molecules by hydrogen bonding. EMCOS showed the best value for all the kinetic model parameters considered as compared to the other adsorbents. However, EMCOS has shown to be a good adsorbent for the dehydration of water from ethanol-water system.

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