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Kinetics Modeling of The Column Adsorption for The Dehydration of Ethanol-Water Mixtures using Biomass Adsorbents

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Abstract

This study has explored the use of biomass - based adsorbents other than the conventional materials as adsorbent for the dehydration of ethanol - water mixtures. The column study was carried out using enzyme modified corn starch and un- modified corn starch for the adsorptive dehydration of ethanol - water mixtures. The effect of bed heights and flow rates on the breakthrough curves revealed that adsorption efficiency decreased with increased flow rate and increased with bed height. The throughput volume of the anhydrous ethanol - water mixtures increased with increase bed height, due to availability of more sorption sites on the adsorbents. Thomas, Yoon and Nelson, and Adams - Bohart kinetic models were used to describe the packed column study. The column kinetics was best described by Yoon and Nelson and Adams - Bohart models. The presence of the hydroxyl O - H stretch group's spectroscopy confirmed the chemical affinity of these adsorbents for water in the ethanol - water mixture. The amorphous or crystallinity nature of the adsorbents was investigated using the X - RD analysis.

Keywords: Starch; X-RD; FTIR; Kinetics; Packed bed column; Adsorption; Ethanol - water mixtures

Introduction

A lot of research efforts continue to focus on the improvement of the dehydration of ethanol - water mixtures. Protection of the global environment and depletion of the conventional hydrocarbon fuel supplies have motivated researchers to develop alternative fuels including hydro, wind, biofuels, solar and geothermal energy [1,2]. Fuel grade ethanol, biodiesel and biogas are the most promising biofuels being explored in recent times [3]. Among these proposed substitutes, biofuels have drawn more attention. Ethanol is commonly used as a fuel itself or an additive that helps enhanced the octane number and combustibility of gasoline [4]. The use of biofuel is beneficial from the standpoint of the environment, energy security, and economic development [2]. One of the main advantages of using biofuels instead of fossil fuels is reduced carbon dioxide emissions, which are responsible for global warming. One of the energy efficient techniques widely used for ethanol dehydration is process of adsorption. Compared to distillation, which required about 2.8×10^6 J/L of ethanol to break the azeotrope using benzene [5] adsorption is energy efficient with estimates of 5.6×10^5 J/L to arrive at 99.6% ethanol from a 95% solution using starch [6] and 2.0×10^6 J/L to go from 85% to 99.5% using corn meal [7,8].

Low operation cost, high efficiency, and vast variety of sorbents contributed to the use of adsorption in the industrial separation processes. Energy saving potential separation processes like the various pressure swings and thermal swing adsorption process has been used as an alternative separation processes. Adsorption can be carried out either in static or dynamic conditions.

Adsorption by dynamic methods gives the possibility of studying the breakthrough curves, to find the adsorption capacity of the material, the length of the working zone (the one with the constant concentration profile), the breakthrough time (life time of the bed), as well as the velocity at which the external mass transfer resistance can be neglected. Fixed bed operations is influenced by equilibrium (isotherm capacity), kinetics (diffusion and convention coefficients), and hydraulic (liquid hold - up, geometric analysis, and mal - distribution factors [9,10], used complementary X-ray data to show that their 110-120^{0}C starch endotherms were caused by the melting of crystalline V - type amylose - lipid complexes. These structures are formed from collapsed amylose helices in which chemical adjuncts are trapped inside [11]. Waxy maize has an A structure and lipids similar to those in maize but amylose is absent [11].

The starch based adsorbents adsorb water by forming hydrogen bond between the hydroxyl groups on the surface of the adsorbents and the water molecules [12].

Wheat straw and wood chips derived from cellulosic based materials used xylans and cellulose as the major adsorbing mechanism instead of amylopectin used in starch materials. The predisposing characteristics of starch based and other polysaccharide adsorbents lie in their chemical composition, hydrophilic nature and their subsequent regeneration ability [12-15]. The corn starch that is made use of in this work is more cost effective and less energy consuming compared to the other conventional materials that has been employed in ethanol - water separation. The present work was carried out to evaluate the starch based materials potential ability to adsorptively dehydrate ethanol - water mixtures in a fixed bed adsorption column. The adsorption process data were analyzed to study the breakthrough profiles and kinetics. Fourier transform infrared was used to identify the functional group while the X-ray diffractogram was used to determine the amorphous or crystallinity nature of the adsorbents. Enzyme modified corn starch

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and un- modified corn starch were used for the adsorptive dehydration of ethanol - water mixtures. Three models (Thomas model, Yoon and Nelson model, and Adams - Bohart model) were used to analyze the column performance.

Materials and Method

Un- modified corn starch was procured from Eke - Awka market, Awka, Anambra Sate, Nigeria. It was sun dried and thermally treated in an oven at 110°C for 16hours and thereafter classified into the desired particle size. 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 0.01 g. The starch adsorbents were packed in an air tight plastic container which was kept in a desiccator prior to use. The method of Beery et al. [16] was used for the enzyme modification of the corn starch. Ethanol - water mixture is prepared at the required mass concentrations of 90 wt% ethanol. The fluid phase concentration was measured with the aid of an Abbe refractometer with automatic calibration in the experimental range of concentration.

Characterization of the corn starch

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 0.5 ml. 0.5 ml of 5% phenol solution was added and thoroughly mixed. 2.5 ml of concentrated sulphuric acid was dispersed to each tube and mix thoroughly this is allowed to stand for 20 minutes and reading taking in a spectrophotometer at 470 nm wave length. Unknown samples were treated equally as standard in duplicate and concentrations extrapolated from the predetermined calibration curve.

Determination of pH: The pH was determined using standard test ASTMD 3828 - 80 ASTM, [17].

Moisture content determination: The moisture content of the starchy adsorbents was determined using standard test ASTMD 2867 - 91 ASTM, [18].

Determination of bulk density: 5 gm each of the adsorbents was poured through a short - stemmed glass funnel into a 100 ml graduated measuring cylinder filled with water to the 50 ml mark.

The rise in volume, the volume of water displaced was obtained. The volume of water displaced is equal to the volume of the 5 g of the adsorbent.

Fourier Transform Infrared (FTIR)

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

X - Ray Diffractogram (X - RD) Analysis

The amorphous and crystallinity nature of the adsorbents was examined using a diffractometer system (EMPYREAN) using radiation Cuα (α1 = 1.540598A° and α1= 1.544426A°) and a secondary graphite monochromator (No), angle 2θ swept and the scan range (-0.002 - 74.99997°).

Experimental procedure

The column studies were carried out using a glass column of 30 cm length and internal diameter 3 cm. The particle size of 600 μm was used for the adsorbents. The prepared adsorbent was packed in the column with glass wool layer at the bottom of the bed. Bed heights of 40 mm, 80 mm, and 120 mm were used. Peristaltic pump was used to supply the concentration of the ethanol - water mixture (adsorbate) used into the adsorption column at constant flow rate of 6 ml/min, 10 ml/min, and 14 ml/min while the initial adsorbate concentration used was 90 wt%. The effluent samples were collected at various time intervals and the resulting concentration determined using refractometry method and the earlier obtained calibration curve. The studies were terminated when the exhaustion of column is reached.

Results and Discussion

Characteristics of the prepared adsorbents

The physico - chemical properties of the starchy adsorbents are shown in Table 1.

Breakthrough Curves

Effect of bed heights on breakthrough curves: The effect of bed heights 40 mm, 80 mm, and 120 mm on the uptake of water figure 1 at an inlet flow rate of 6 ml/min, and inlet ethanol - water mixture of 90 wt% concentration is shown in figures 2.0 and 3.0. The results indicate that there was a decreased in the sorption equilibrium capacity of the starch material as the bed height is increased due to less availability of number of sorption sites. In the batch mode the probability of contact between adsorbate and adsorbent is high compared to the fixed bed mode of operation, which usually results in small sorption equilibrium capacity experienced in column study. Saturation of bed occurs in less time for smaller bed heights compared to the higher bed heights. At higher bed height the availability of the effective surface area of adsorbent is more which offers more active sites to adsorption and it also broadens the mass transfer zone length [19].

Effect of flow rates on breakthrough curves: The effect of flow rate for the sorption of water on to the starch at flow rates of 6 ml/min,

Properties	Modified corn starch (EMCOS)	Native corn starch (NCOS)
pH	6.0	5.6
Moisture content (%)	3.04	2.91
Colour	White	Yellowish white
Starch content (%)	86.5	87.5
Bulk density (g/ml)	1.57	1.37
Micro pore volume ($\mu m^2/g$)	0.2	0.1
Diameter (μm)	7.99	6.68
Oxygen (%)	86.6	87.3
Carbon (%)	13.4	12.7

Table 1.0 Physico-chemical properties of Corn starch.

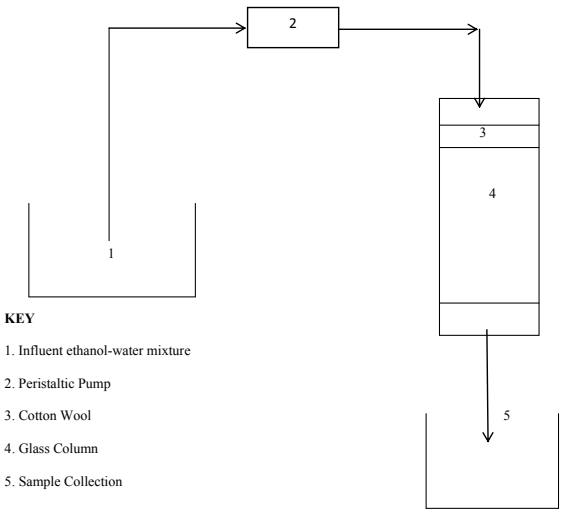

Figure 1: Block Diagram of the Experimental Set – up for Column Adsorption Study.

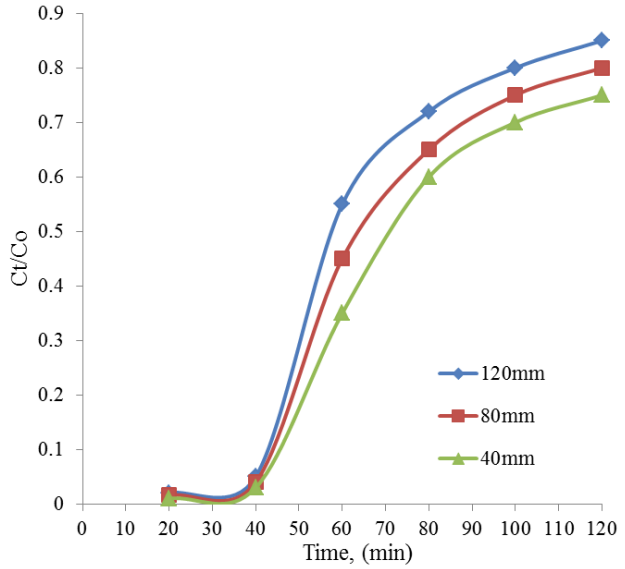

Figure 2: Effect of bed height on breakthrough curve for adsorption of water on EMCOS

10ml/min, and 14 ml/min, at an inlet concentration of 90 wt%, and bed height of 90 mm as shown in figures 4.0 and 5.0. It is seen from the figure that sorption of water is rapid in the initial stages and there was decreased in rate and thereby reaching saturation finally. As the flow rate increase, the breakthrough is reached quickly because at higher flow rate, the time of contact between the ethanol - water mixtures and the waste biomass is reduced.

This corroborates the results obtained in the works of Nwabanne, Sivakumar and Palanissamy [20,21]. It can also be seen from figures 4.0 and 5.0 that breakthrough occurred at a comparatively faster rate at higher adsorbate flow rate and less time was taken to reach the saturation breakthrough. This can be explained from the mass transfer vicinity, the rate of mass transfer gets increased at higher flow rate leading to faster saturation. Increasing the flow rate, the mass transfer rate increases due to the decreased in the boundary layer thickness. At low flow rate, it takes a longer time for the adsorbate (ethanol-water mixtures) to diffuse towards the starch adsorbents because of the thickness of the film and resistance surrounding the starch adsorbents. The effect of flow rate is helpful for the large - scale treatment systems in order to utilize the bed for its maximum capacity with minimal flow rate [21].

Kinetic study

Three models (Yoon and Nelson model, Thomas model and Adams - Bohart model) were employed to analyze the column performance.

Yoon and nelson model: The linearized form of the model is given as equation (1) Kavak and Öztürk,[22]

$$\ln\left(C_e / C_o - C_e\right) = K_{YN}t - \tau K_{YN} \quad \text{..... (1)}$$

Where C_o and C_e are the inlet sorbate (solute) and effluent concentrations respectively. K_{YN} is the Yoon and Nelson kinetic rate constant, τ is the time required for 50% of the adsorbate to breakthrough (minute), t, the breakthrough (sampling) time (min). Based on the Yoon and Nelson model, the amount of water being adsorbed in a fixed bed is half of the total water entering the adsorption bed within 2τ period Aksu and Ttezer, [23].

For a given bed;

$$q_{OYN} = \frac{q(total)}{m} = \frac{1/\ 2C_0\left[\left(\frac{r}{1000}\right)\times 2\tau\right]}{m} = \frac{C_0 \times r \times \tau}{1000m} \quad \text{..... (2)}$$

Where r is the flow rate, q_{OYN} is the adsorption capacity and m is the mass of the adsorbent.

A plot of $\ln C_e/C_0$ - C_e against t gives a straight line with slope of K_{YN} and intercept of $-\tau K_{YN}$ (Figures 5- 8). The results indicated that the kinetic constant rate increased with flow rate. The adsorption capacity increased with increase in flow rate while it decreased with increase in bed height because it has been established that K_{YN} and τ are inversely proportional. The high values of co-efficient of regression obtained indicate that Yoon and Nelson model fitted well to the experimental data. The time required for 50% breakthrough, τ decreased with increase in flow rate, and bed height respectively. The ethanol -water mixtures has more time to move through the column, which results in reduced adsorption rate experienced at higher bed height.

Thomas model: Thomas model is as given in equation (3) Kavak and Öztürk, [22]

$$\ln\frac{C_0}{C_t} - 1 = \frac{K_{TH}q_0X}{Q} - \frac{K_{TH}}{Q}V \quad \text{..... .....(3)}$$

Where C_o and C_e are the inlet solute and effluent concentrations respectively, q_o is the maximum adsorption capacity (g/g), x is the total mass of the adsorbent (g), K_{TH} is the Thomas rate constant (ml/min/g), V is the throughput volume (ml), and Q is the volumetric flow rate (ml/min).

The kinetic co -efficient K_{TH} and adsorption capacity of the column q_o can be determined from a plot of

$\ln\frac{C_0}{C_t} - 1$ Versus V (Figures 9 -12). K_{TH} is dependent on the flow rate. The adsorption capacity, q_o, increased with increase in bed height. The results indicate that the EMCOS adsorbent is capable of holding a maximum of 10.39 g/g of water at 14 ml/min flow rate as shown in Table 2. The values of K_{TH} and R^2 obtained are similar to that of Jayanta

et al. [19]. High values of correlation co-efficient determined indicates that the kinetic data also conformed to Thomas model.

Adams - Bohart Model: For the Adams - Bohart model, the mass transfer rates obey the following equations

$$\frac{\partial q}{\partial t} = -K_{AB}C_b \quad \text{...} \quad (4)$$

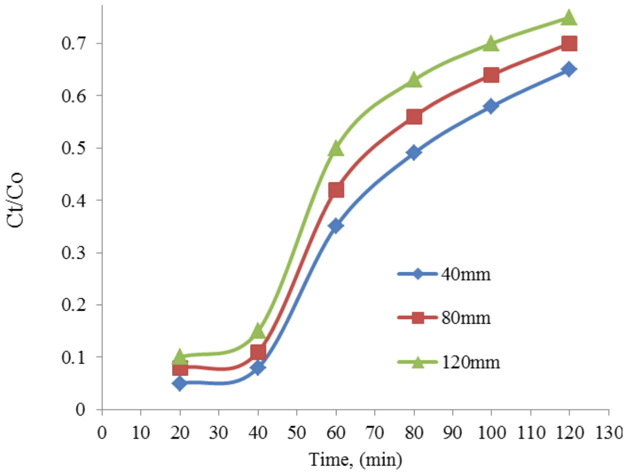

Figure 3: Effect of bed height on breakthrough curve for adsorption of water on NCOS.

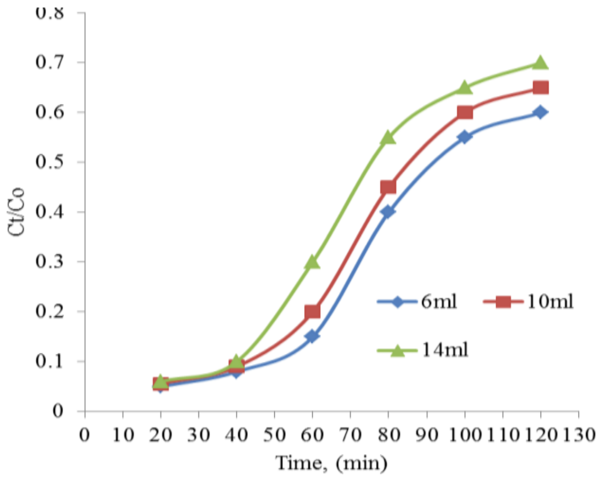

Figure 4: Effect of Flow rate on breakthrough curve for adsorption of water on EMCOS.

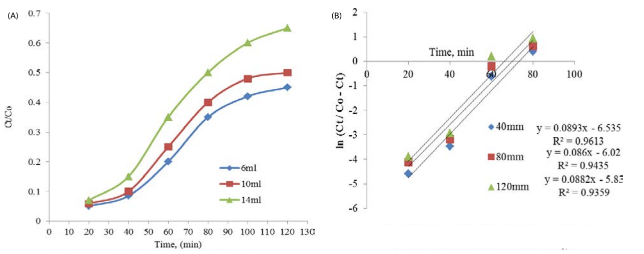

Figure 5: (a) Effect of Flow rate on breakthrough curve for adsorption of water on NCOS (b) Yoon and Nelson plot for the adsorption of water on EMCOS: Effect of Bed height

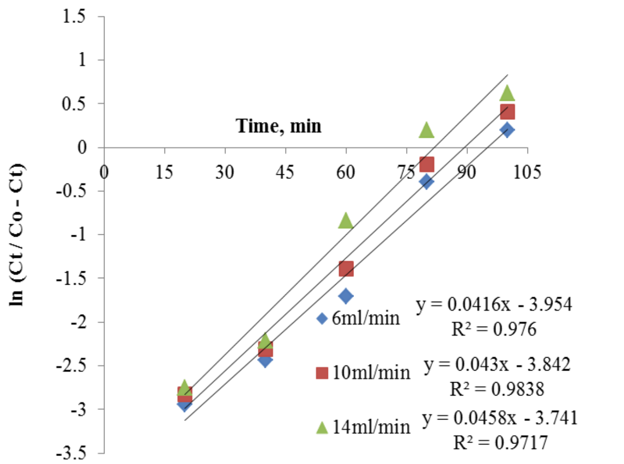

Figure 6: Yoon and Nelson plot for the adsorption of water on EMCOS: Effect of Flow rate.

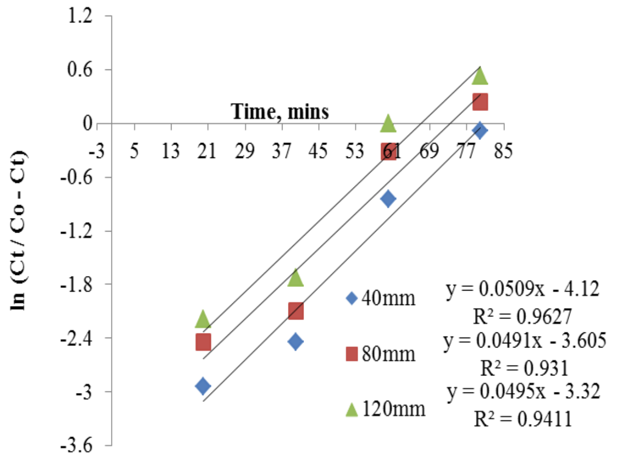

Figure 7: Yoon and Nelson plot for the adsorption of water on NCOS: Effect of Bed height.

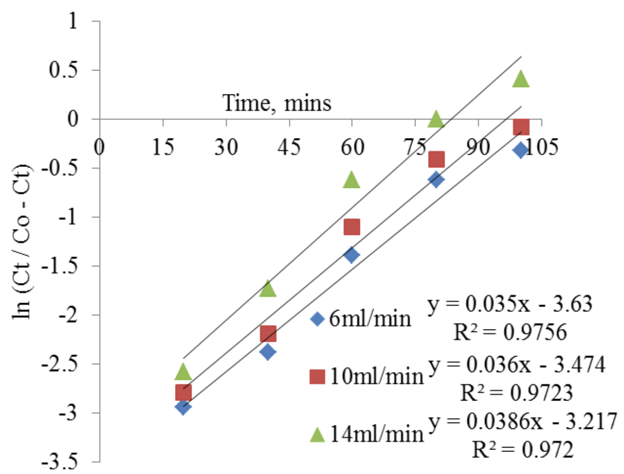

Figure 8: Yoon and Nelson plot for the adsorption of water on NCOS: Effect of Flow rate.

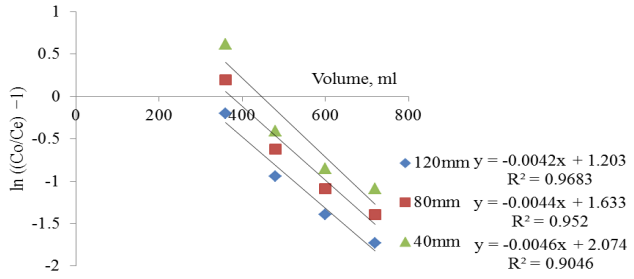

Figure 9: Thomas Kinetic plot for the adsorption of water on EMCOS: Effect of Bed height.

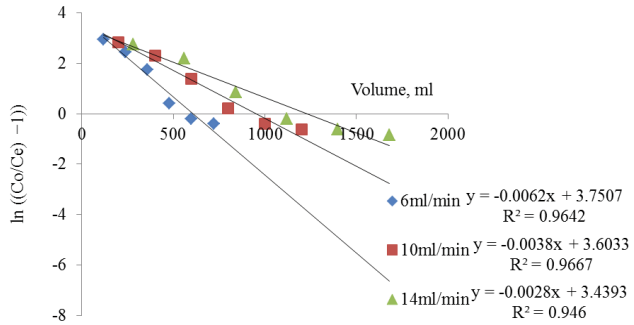

Figure 10: Thomas Kinetic plot for the adsorption of water on EMCOS: Effect of Flow rate.

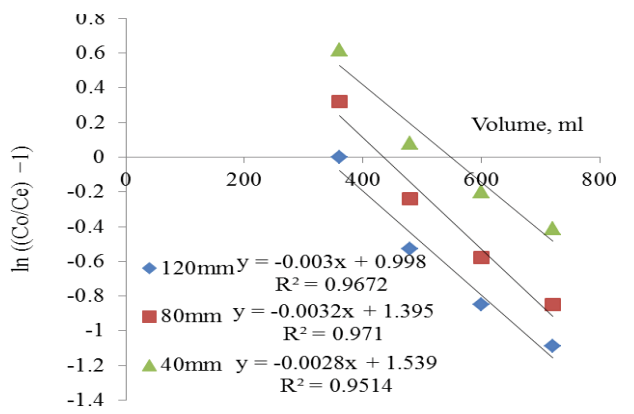

Figure 11: Thomas Kinetic plot for the adsorption of water on NCOS: Effect of Bed height.

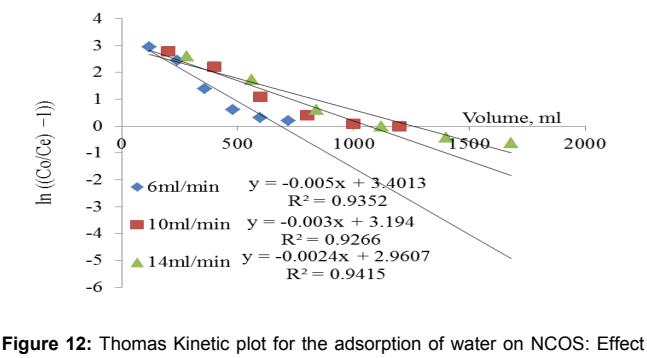

Figure 12: Thomas Kinetic plot for the adsorption of water on NCOS: Effect of Flow rate.

$$\frac{\partial C_b}{\partial Z} = \left(\frac{K_{AB}}{U_0}\right) q\, C_b \quad \text{..... (5)}$$

Two assumptions are made for the solution of these differential equation systems: $t \to \infty$ and $q \to N_o$ Quintelas et al., [24]. Solving the differential equations (4) and (5).

The following equation is obtained

$$\ln\left(Ce/C_o\right) = K_{AB}C_o t - K_{AB}N_o\left(Z/U_o\right) \text{.....} \quad (6)$$

The values of K_{AB}, and N_o can be evaluated from a plot of $\ln(Ce/C_o)$ against t (time) at a given bed height (z) and flow rate (U_o). Where K_{AB} is the Adams - Bohart rate constant, and N_o is the adsorption capacity (g/g). It can be seen from Figures 13 -16 that the N_o decreased as the bed height increases and increased as the flow rate increase. This can be explained because at high flow rate the number of adsorbate molecules passing through the adsorbent is more which increases the rate. The K_{AB} rate constant obtained is similar to the rate constant obtained when Thomas and Yoon and Nelson models were used to analyze the column performance. The R^2 obtained showed the data best fitted to Adams - Bohart model.

Determination of the Functional Group in the Starch

Figures 17 and 18 give the FTIR spectroscopy of both the Enzyme modified corn starch (EMCOS) and unmodified corn starch (NCOS). Figure 17 Bands of (2924.18 cm^{-1}, 3206.76 cm^{-1}, 3345.64 cm^{-1}, and 3498.02 cm^{-1}) indicated the presence of hydroxyl group, H bonded OH stretch Okewale et al, [14]. The highest peak value of 1646.3 cm^{-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 EMCOS. Figure 18 broad bands (2929.97 cm^{-1}, 3219.3 cm^{-1}, 3317.67 cm^{-1}, 3401.58 cm^{-1}, and 3489.34 cm^{-1}) exhibited the OH stretch group. 1372.4 cm^{-1} showed OH bend. COH bending was shown in 1025.2 cm^{-1} band. The highest peak of 1649.19 cm^{-1} suggests that water is adsorbed at the amorphous parts of the corn starch.

X - Rays Diffractogram analysis (X-RD)

Figure 19 which is the X - RD patterns for the adsorbents. The strong X - ray diffractogram patterns of the corn starch noticed are; 14.664°, 17.212°, and 22.776° this corroborate the works of Quintero and Cardona, Bertuzzi et al., [25,26] which indicated a typical A type diffraction pattern. The amorphous zone present in the diffractograms is mainly due to amylopectin as reported in the works of Ahmad et al. [26].

Amylopectin α - 1, 6 branched structures has an overlapping hydroxyl groups which are proposed to correspond to more hydroxyl groups per unit area of the starch surface [27,28], reported that corn has an A - type structure, 27% amylose and polar lipids that can complex with the amylose fraction to form V crystals this also corroborate the result of X - RD reported in this work where it was shown that amylopectin is the main constituent of corn starch and it is type A structure. Thus, it was revealed that the greater adsorption capacity noticed in starch based adsorbents was as a result of the amorphous nature of the adsorbents which resulted from the amylopectin structure as revealed in the X - RD analysis carried out on the adsorbents. It was shown from Table 3 that the adsorbents fall into small category which means that the adsorbents can also be said to be mesopores in nature which makes these adsorbents to be able to dehydrate ethanol - water mixtures similar result of this classification was obtained by Lindeboom et al. [29].

Kinetic model	Flow rate			Bed Height		
	6 ml/min	10 ml/min	14 ml/min	40 mm	80 mm	120 mm
	Yoon and Nelson Kinetics					
K_{YN} (min^{-1})	0.0416	0.043	0.0458	0.089	0.086	0.088
τ (min)	95.05	89.34	81.68	73.43	70.0	66.25
q_0 (g/g)	4.81	7.53	9.64	3.71	3.54	3.35
R^2	0.976	0.9838	0.9717	0.9613	0.9435	0.9359
	Thomas kinetic					
K_{Th} (ml/min/g)	0.372	0.38	0.372	0.276	0.264	0.252
q_0 (g/g)	5.10	7.99	10.39	3.80	3.13	2.42
R^2	0.9642	0.9667	0.946	0.9046	0.952	0.9683
	Adams – Bohart kinetic					
K_{AB} (min^{-1})	0.343	0.354	0.388	0.738	0.678	0.657
N_o (g/g)	2.23	2.49	2.53	3.76	1.85	1.21
R^2	0.9726	0.986	0.9802	0.9464	0.9274	0.92

Table 2: Summary of the Column Kinetics Model for EMCOS.

Kinetic model	Flow rate			Bed Height		
	6 ml/min	10 ml/min	14 ml/min	40 mm	80 mm	120 mm
	Yoon and Nelson Kinetics					
K_{YN} (min^{-1})	0.035	0.036	0.0386	0.0509	0.049	0.088
τ (min)	103.71	96.5	83.34	80.94	73.42	66.25
q_0 (g/g)	5.24	8.13	9.83	4.09	3.71	3.39
R^2	0.9756	0.9723	0.972	0.9627	0.931	0.9411
	Thomas kinetic					
K_{Th} (ml/min/g)	0.3	0.3	0.336	0.168	0.192	0.18
q_0 (g/g)	5.73	8.97	10.39	4.63	3.67	2.80
R^2	0.9352	0.9266	0.9415	0.9514	0.971	0.9672
	Adams – Bohart kinetic					
K_{AB} (min^{-1})	0.334	0.38	0.338	0.414	0.36	0.336
N_o (g/g)	2.24	2.32	2.58	4.28	2.11	1.36
R^2	0.9907	0.9916	0.9755	0.9336	0.9234	0.9327

Table 3: Summary of the Column Kinetics Model for NCOS.

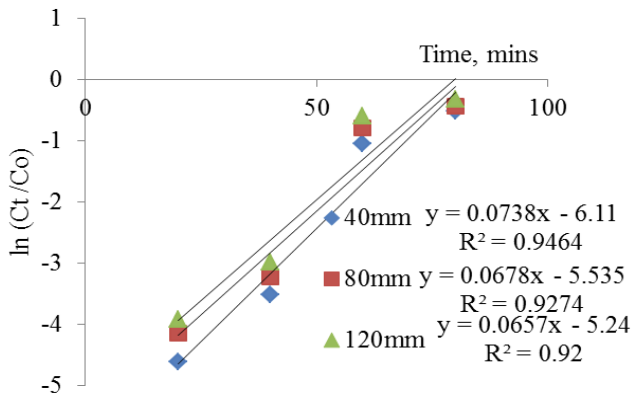

Figure 13: Adams- Bohart plot for the adsorption of water on EMCOS: Effect of Bed height.

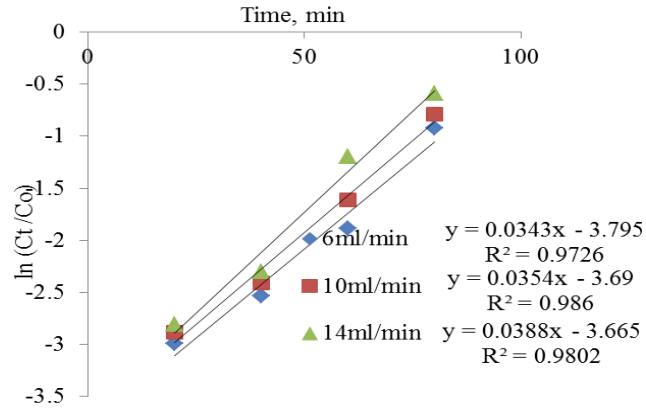

Figure 14: Adams- Bohart plot for the adsorption of water on EMCOS: Effect of Flow rate.

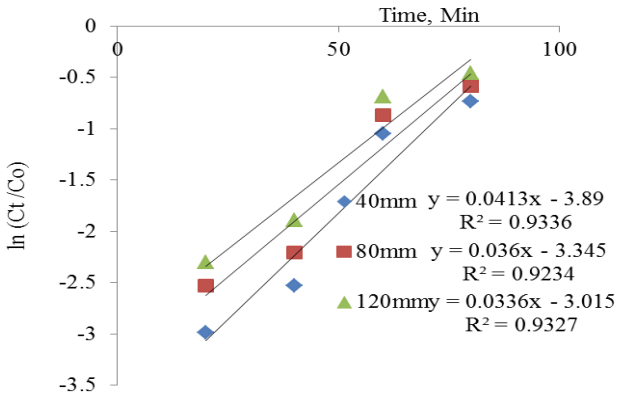

Figure 15: Adams- Bohart plot for the adsorption of water on NCOS: Effect of Bed height.

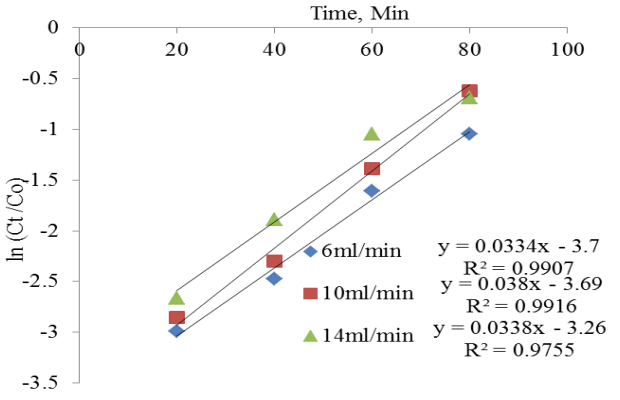

Figure 16: Adams- Bohart plot for the adsorption of water on NCOS: Effect of Flow rate.

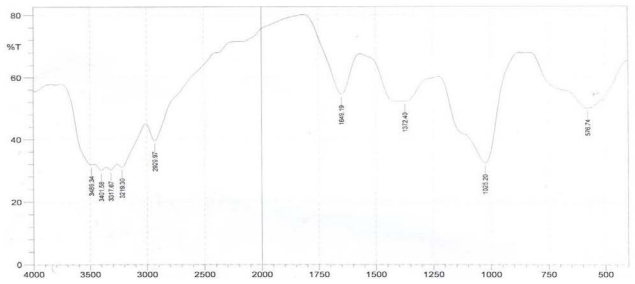

Figure 17: FTIR spectroscopy of the enzyme modified corn starch (EMCOS)

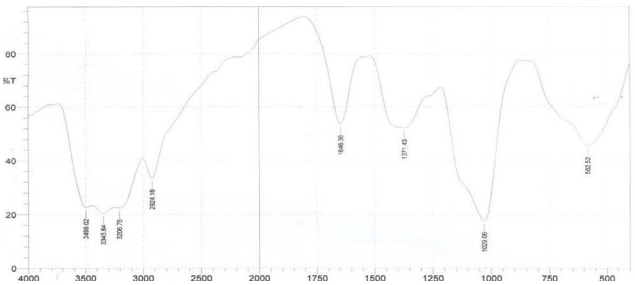

Figure 18: FTIR spectroscopy of the native corn starch (NCOS).

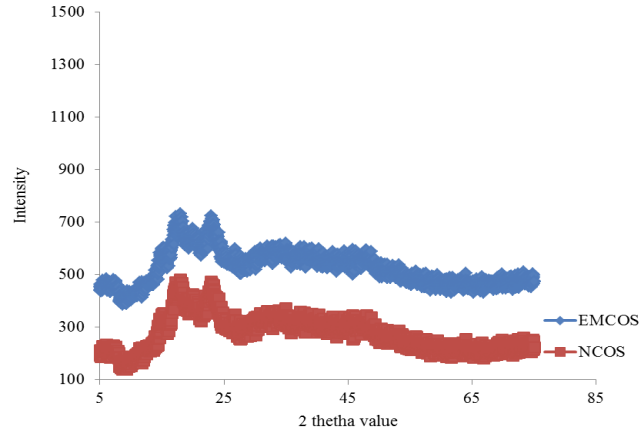

Figure 19: X-RD analysis of the adsorbents.

Conclusion

The flow rate effect on the uptake of water on the corn starch adsorbents at flow rates of 6, 10, and 14 ml/min, an inlet concentration of 90 wt% and bed height of 90 mm has been studied. The effects of flow rate, and bed height on the breakthrough curves obtained showed that the adsorptive dehydration efficiency decreased with increasing flow rate, and increased with increase in bed height. The dehydration efficiency is strongly dependent on bed height and flow rate. The adsorbents were able to hold 10.39 g/g maximum of water. The column kinetics was best described by Yoon and Nelson. The capacity of the adsorption decreased with increase in bed height and flow rate. The FTIR result of these adsorbents also confirmed the chemical affinity of starch to water. The highest peak value of 1646.3 cm^{-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 EMCOS. The A - type and amorphous nature of the adsorbents which resulted from the amylopectin structure was revealed in the X - RD analysis carried out on the adsorbents. The dehydration of water was made possible by the presence of amylopectin in the biomass studied.

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