

Effect of modification of cassava starch on the kinetics of the adsorption of water from ethanol-water systems

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ABSTRACT

The importance of ethanol as a fuel and for other industrial uses has resulted in the need to produce large quantities of it with higher purity, that is, with particular reference to dehydration. The use of normal and modified starch in the dehydration of ethanol was investigated. The modification of starch was found to significantly increase its mechanical property thus having a positive effect on its rate of adsorption as shown by the scanning electron microscopy (SEM) analysis. The kinetics of the adsorptive process was also studied. It was however observed that the kinetics of the adsorption of water from ethanol-water mixture by native starch (CS) best correlated to the pseudo first order, with a rate constant of 0.0180 s^{-1} , while that of the modified cassava starch best correlated to the first order with a rate constant of 0.9342 s^{-1} . The dehydrating property of native starch was also observed to be significant, and the acidic modification of it with the use of hydrochloric acid, conferred on it much higher dehydrational properties.

Keywords: Adsorption, cassava starch, modification, kinetics, ethanol-water mixture.

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INTRODUCTION

The main objectives of the present ecological policy includes reduction of energy consumption of the economy and development of branches related to renewable energy sources which include energy provided from biomass, wind, geo-thermal, water and solar energy. Renewable energy sources enable both improvement of environmental protection and are an important element of sustainable development. According to the experts programs of the world committee of energy council, it is predicted that in 2070, the contribution of renewable energy to the total world energy balance will be about 60%. This will result mainly from depletion of the territorial energy sources and general availability of unconventional energy. The resultant effect will be the improvement in environmental protection due to reduction of the emissions of carbon, sulphur and nitrogen oxides and waste minimization (Bauen, 2006).

Due to high-energy values, ethanol is the most promising future biofuel. At present, it is used in the fuel industry as an additive to petrol that heightens its octane number and combustibility. A small addition of ethanol to

petrol significantly increases the octane number of the mixture and at 10% wt content the present engine structure need not be modified (Wladyslaw et al., 2008). Addition of ethanol to fuel means that combustion is more efficient and emission of exhaust gases is reduced. In view of the development of recoverable fuel production and ecological aspect, according to the EU recommendations, ethanol will be produced and subsidized in the period of the nearest several years (Jonquieres et al., 2002)

The only barrier for a broad application of production capacities of ethanol as a composition of petrol is a high production cost. Despite this limitation, the market of ethanol used for fuel production increases on a global scale and in 2005 it reached a capacity of $3 \times 10^{10}\text{ dm}^3$ (Wladyslaw et al., 2008). The leading world producers of ethanol are the countries of America, Asia, Europe, Africa and Oceania. Besides the fuel industry, the other recipients of anhydrous or dehydrated ethanol include food industries (mainly alcohol distilleries), pharmaceuticals, paint and varnish industry, research

laboratories, etc.

Ethylene hydration or brewing provides an ethanol-water mixture, and for most industrial and fuel uses, the ethanol must be purified by dehydration. Fractional distillation can only concentrate ethanol to 95.6% by volume (89.5 mole %). The ethanol-water mixture produced forms a positive homo-azeotrope with a boiling point of 78.1°C and cannot further be purified by distillation.

However, improving adsorptive processes for the dehydration of ethanol-water mixture demands a constant search for new adsorbents. In the specific case of ethanol-water mixture separation, zeolites are successfully being used. The use of non-conventional adsorbents to substitute zeolites, mainly starchy adsorbents, by virtue of their known chemical affinity for water, has recently been proposed (Okewale et al., 2012). Two areas of current research in the bio-based fuel alcohol industry are the sorption of ethanol from the fermentation broth and the adsorption due to the formation of azeotrope of ethanol-water mixtures at 95.6wt% of ethanol. The adsorption of water from ethanol-water mixtures using starch or cellulose materials was first demonstrated by Ladisch and Dyck (1979). When distillation is used to dehydrate ethanol 50% of the total energy is consumed, this frequently results in a negative energy balance where the energy spent on the anhydride ethanol production exceeds the energy obtained from its combustion (David et al., 1978). Starch, cellulose, hemi cellulose and starch-based materials have affinity for water and can be regenerated at temperatures of 80°C and below. Conventional techniques used for separating water from ethanol includes: low pressure distillation, azeotropic distillation, with pentane, benzene, and di ethyl ether and extractive distillation with gasoline or ethylene glycol or third component (Black, 1980). The distillation scheme breaks the azeotrope which forms between ethanol and water at 95.6wt% ethanol (at atmosphere pressure). Some materials which have been used to research the liquid-phase adsorption of ethanol include divinyl benzene and cross-linked polystyrene resins (Gulati et al., 1996). Similarly, materials that have been researched for vapour-phase adsorption of water from ethanol-water mixture include corn grits (Ladisch and Dyck, 1979), molecular sieves, (Garg and Ausikaitis, 1983), and activated alumina (Rao and Sircar, 1993). The advantages of these starch-based adsorbents in uptake of water from ethanol-water mixture includes re-use of materials in fermentation, biodegradability, efficiency, relative availability, and cheapness, non-toxic nature and its derivation from renewable sources (Okewale et al., 2012).

Aimed at practical application this research investigates on a laboratory scale, the comparative study of adsorption capacity, and kinetics of dehydrating ethanol-water binary system using modified and native starches from cassava as an adsorbent.

METHODOLOGY

Production of unmodified cassava starch (CS)

The cassava starch was obtained in a lump form and broken down into small particles and allowed to dry under the sun for two days. It was thereafter dried in the oven at 105°C for 8 h before classification (sieving) into different sizes.

Production of modified starch (MCS)

The cassava starch was obtained from the market as a moist lump. The lump was broken into small particles and allowed to dry in the sun for two days. 1 kg of the dried cassava starch was dispersed in 1000 cm³ of distilled water to form slurry and constantly stirred for 30 min. 0.5 M of HCl was added to the starch slurry (at room temperature). At the end of the reaction, 1.0 M of NaOH was added to neutralize the starch slurry, and to adjust the pH to 6.8.

Particle size classification

The procedure is in accordance with the Tyler/mesh method (Perry, 1997). Sieves of 0.15, 1.20, 2.05, 3.15 and 4.75 mm diameters were obtained and used. The mean particle diameters obtained were as follows 3.95, 2.60, 1.625 and 0.150. The mean mass of each particle diameter was obtained (Table 1).

Determination of mean masses of particles

The particles were classified using different sieve sizes, and the masses of three different particles on each sieve sizes were measured using the digital weighing balance after which the mean masses were calculated by summing up the averages.

Determination of particle mean density

The density of each adsorbent was determined by water picnometry method (Okewale et al., 2012). 15 g of the sample was weighed into a 250 ml measuring cylinder filled with water to 150 ml mark. The volume of water displaced is equal to the volume of the 15 g of the adsorbent.

Hence the density of adsorbent = 15 g/volume (ml).

Determination of pH of adsorbent

2.5 g of the sample was measured and poured into a 250 ml measuring cylinder filled to 25 ml mark. After a reasonable agitation, the sample was allowed to settle and the pH was determined using the Metler-Toledo pH meter.

A delta pH meter was used to measure the pH level of the samples (adsorbents). The probe of the pH meter was gently removed from the buffer solution and gently inserted into the sample. While stirring constantly until a stable pH was obtained in the measurement. The physico-chemical properties are shown in Table 2.

Determination of starch content of adsorbent

A calibration curve with a suitable carbohydrate standard for the unknown samples was prepared. Carbohydrate and deionized water quantities were varied as shown in Table 3. 0.5 ml of 5% phenol solution was added to the six test tubes with thorough

Table 1. Physical characterization of adsorbents.

Adsorbents	Mean diameter (mm)	Tyler/mesh (mm)	Mean mass (mg)	Bulk density (g/mol)
Modified starch (MS)	3.950	4.75 – 3.15	70.00	1.5000
	2.600	3.15 – 2.05	33.00	1.6667
	1.625	2.05 - 1.20	21.00	1.8750
	0.675	1.20 – 0.15	15.00	1.8750
Native starch (CS)	3.950	4.75 – 3.15	57.00	1.5000
	2.600	3.15 – 2.05	30.00	1.3636
	1.625	2.05 - 1.20	25.00	1.3636
	0.675	1.20 – 0.15	18.00	1.3636

Table 2. Physico-chemical properties of adsorbents.

Starch sample	Ph (hydrogen ion concentration)	Starch content	Moisture content	Colour
Native starch	7.6	85	35	White
Modified starch	6.2	85	35	White

Table 3a. Kinetic data for modified starch of different particle sizes at various intervals.

Particles sizes (mm)	Modified starch (MS)					
	0 min	20 min	40 min	60 min	80 min	100 min
	$^{28}n_D$	$^{28}n_D$	$^{28}n_D$	$^{28}n_D$	$^{28}n_D$	$^{28}n_D$
0.6750	1.3600	1.3605	1.3610	1.3620	1.3635	1.3635
1.6250	1.3600	1.3605	1.3605	1.3610	1.3625	1.3625
2.6000	1.3600	1.3605	1.3605	1.3610	1.3620	1.3620
3.9500	1.3600	1.3605	1.3605	1.3605	1.3615	1.3615

Table 3b. Kinetic data for unmodified starch of different particle sizes at various intervals.

Particles sizes (mm)	Unmodified cassava starch (CS)					
	0 min	20 min	40 min	60 min	80 min	100 min
	$^{28}n_D$	$^{28}n_D$	$^{28}n_D$	$^{28}n_D$	$^{28}n_D$	$^{28}n_D$
0.6750	1.3600	1.3605	1.3610	1.3610	1.3625	1.3625
1.6250	1.3600	1.3605	1.3610	1.3610	1.3620	1.3620
2.6000	1.3600	1.3605	1.3605	1.3605	1.3615	1.3615
3.9500	1.3600	1.3605	1.3605	1.3605	1.3610	1.3610

Table 4. Summary.

Kinetic model	Correlation co-efficient (R^2)		Rate constants (K)	
	Native starch (CS)	Modified starch (MS)	Native starch (CS)	Modified starch (MS)
Pseudo-first order	0.9911	0.9325	$K_1 = 0.0180$	$K_1 = 0.0182$
First order	0.8966	0.9342	$K_2 = 0.0031$	$K_2 = 0.9342$
Pore diffusion model	0.8882	0.8320	$K_d = 0.0314$	$K_d = 0.0433$
Elovich equation	0.9179	0.8957	$\beta = 4.2882$ $\alpha = 0.0376$	$\beta = 6.4144$ $\alpha = 0.0020$

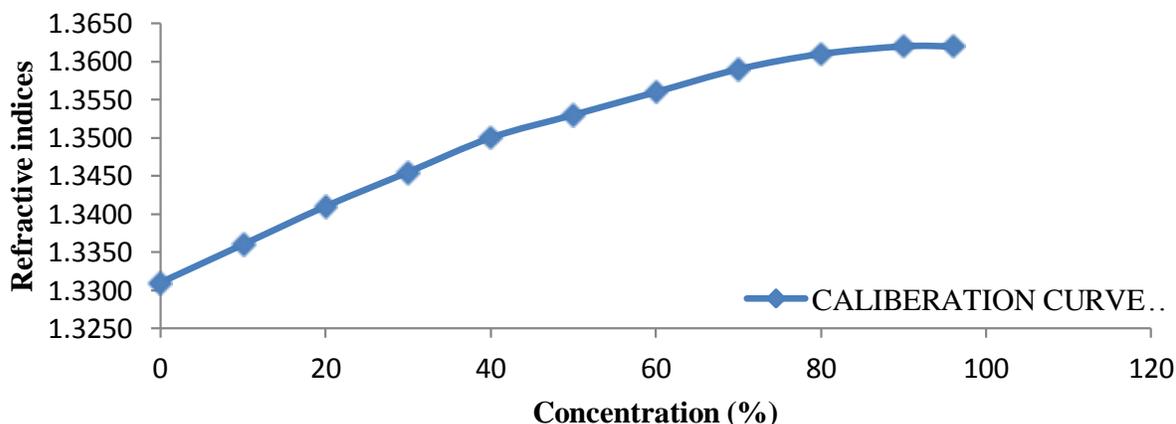


Figure 1. Calibration curve of ethanol-water solution.

mixing. 2.5 ml of concentrated sulphuric acid was added to each tube and mixed thoroughly. The set-up was allowed to stand for 20 min and read in a spectrophotometer at 470 nm. Unknown samples are treated equally as standard in duplicates and concentrations extrapolated from the calibration curve (Figure 1).

Determination of moisture content of the adsorbents

15 g of modified and native cassava starch adsorbents were weighed into an evaporating dish respectively and placed in an oven set at 105°C (ASTMD 2867-91 (1991)). The starches were weighed periodically at an interval of 15 min until constant weights were attained.

The moisture content was obtained using the formula:

$$M_c = \frac{W_0 - W_1}{W_0} \quad (1)$$

Where M_c is the moisture content and W_0 , W_1 are initial and final weights of the adsorbents.

Scan electron microscopy analysis (SEM)

The surface morphology of the solid adsorbents was inspected using a scanning electron microscope (SEM) PHENOMWORLD operating at 25 kV. Micro-particles for SEM studies were mounted on metal stubs with double – side adhesive, and coated with gold in vacuum using an IB-3ion coater. The analysis also includes the surface area, pore size and diameter of the various adsorbents.

Fourier transform infrared spectroscopy (FT-IR) analysis

Infrared spectra of the samples were recorded on an FT-IR (BULKER TENSOR 27) equipped with an mct detector, for the purpose of determining the molecular changes. Wave numbers were from 400 to 4000 cm^{-1} , representing the average of 64 scans. All optical measurements were performed at room temperature.

Preparation of ethanol-water solutions

The concentration of analytical ethanol as obtained was 96.0wt% ethanol. For the kinetics test, a concentration of 90% was prepared. Concentrations of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100% were also needed to obtain data for the calibration graph.

The dilution formula used in preparing these concentrations is:

$$C_1 V_1 = C_2 V_2 \quad (2)$$

Where: C_1 = concentration of undiluted ethanol = 96.0wt%

V_1 = volume of undiluted ethanol required=?

C_2 = required concentration = 10%

V_2 = required volume = 250ml

Hence, $V_1 = 10 \times 250 / 96.0 = 26.042$ ml

Kinetic test

To obtain the kinetic data a locally designed finite volume circulating device similar to that developed by Azevedo and Cinetico (1992), was used within a finite mass of liquid (~50.0 g) circulates continuously in a closed loop through a packed bed of adsorbents particles (~10 g). This device permits flow conditions at which the external resistances to mass transfer becomes negligible. The equipment possesses a rubber suction pump that continuously removes liquid at the bottom of the cell and sends this liquid to the top in a closed loop with the aid of a suction pump which was operated manually. The liquid concentration was measured at regular time intervals. The sample concentration was measured by means of refractometry and the end concentration obtained from predetermined calibration graph (Figure 2).

The mass balance is described by Equation 3

$$Q_s = \frac{M_f}{M_s} \left(\frac{W_f - W_b^0}{W_b^0} \right) \quad (3)$$

Where

Q_s = amount of water adsorbed in the solid phase gml/gads.

M_f = mass of aqueous ethanol solution (g)

M_s = mass of adsorbent (g)

W_b^0 = initial concentration of ethanol in the solution.

W_b = end concentration.

RESULTS AND DISCUSSION

FT-IR analysis

The molecular level changes during the modification process were studied by FTIR, as shown in Figure 3a to b. The spectra 'a' and 'b' represent the native cassava

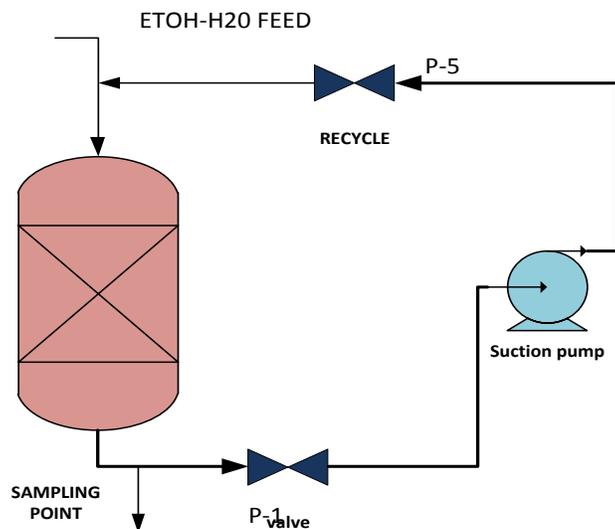


Figure 2. Process flow diagram for the dehydration of ethanol-water mixture.

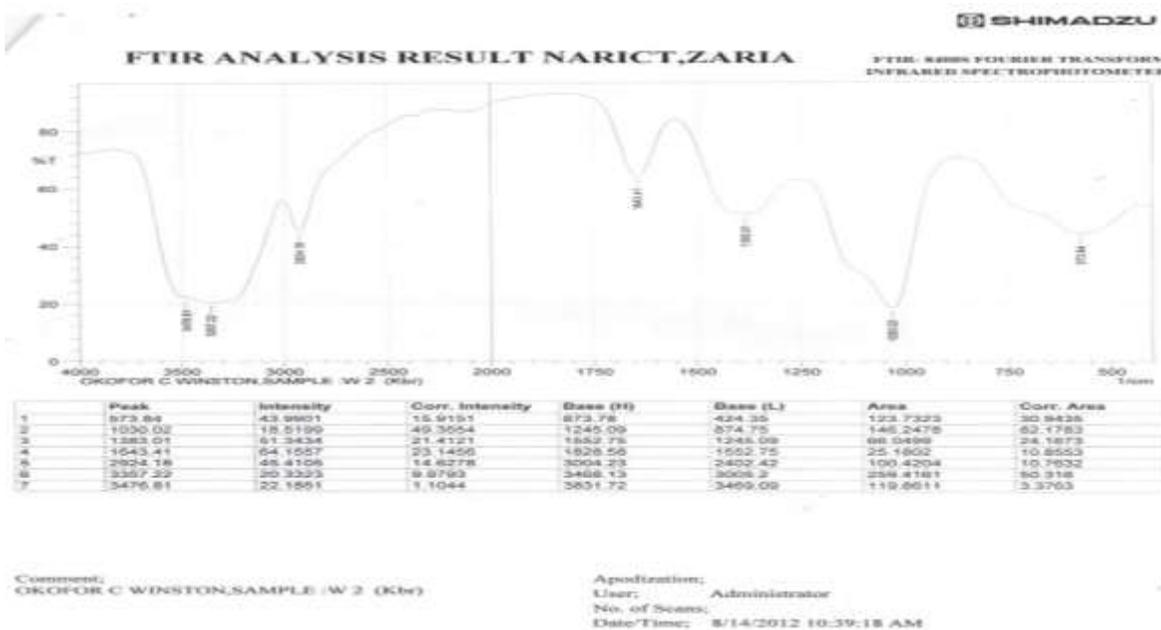


Figure 3a. FT-IR spectra of unmodified cassava starch (CS).

starch and the acidic modification of starch respectively. Both spectra in the region below 800 cm^{-1} exhibited complex vibrational modes due to the skeletal mode vibrations of the pyranose ring in the glucose unit this was similar to the results obtained by Kizil and Seetharaman (2002). Peaks at around 1080 to 1158 cm^{-1} were characteristic of a C-O-H bond also in line with results obtained by Fanta et al. (1980). The peaks between 990 and 1030 cm^{-1} , which represent the anhydrous glucose ring O-C stretch, were different after

acidic modification. This phenomenon may be related to the stability and intensity of hydrogen bonds. Pawlak and Mucha (2003) showed that the stability and strength of hydrogen bonds were indicative of correlative peak shifts and the peak style changes. A characteristic peak occurred at 1644 cm^{-1} in native starch, which is presumably a feature of tightly bound water (Fanta et al., 1980). Irudayaraj and Yang (2002) showed that the absorbances at around 3389 and 2930 cm^{-1} can be assigned to O-H and C-H bond stretching, respectively.

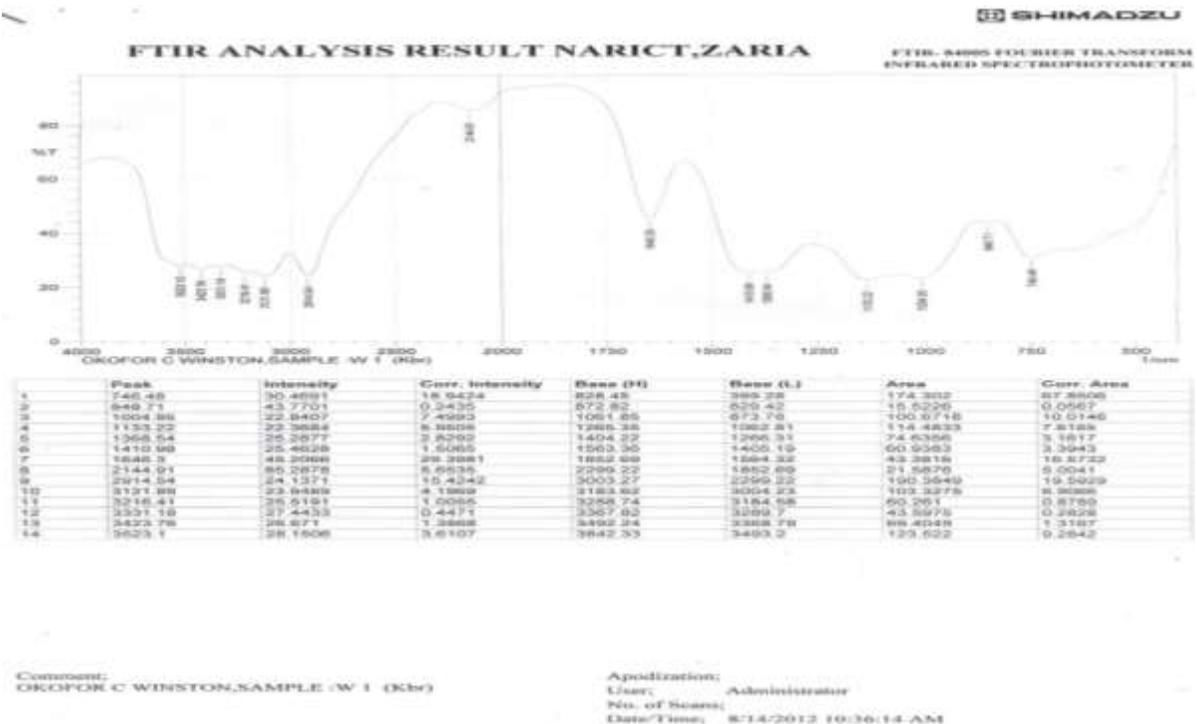


Figure 3b. FT-IR spectra of modified cassava starch (MS).

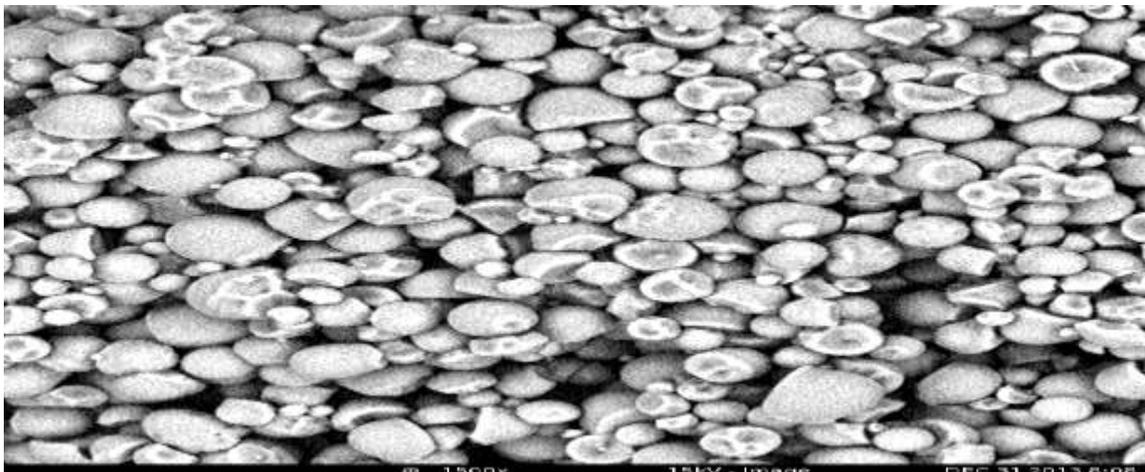


Figure 4a. Scanning electron microscopy of modified cassava starch (MS).

The intensity and shape of the 2930 cm^{-1} peak in modified starch was substantially different from that of native starch. All the above observations support the claim that acidic modification changes the structure and bonding of the starch substrates.

Scanning electron microscope (SEM) analysis

Figure 4a shows the scanning electron microscope analysis of the modified cassava starch which shows

particle compartment with a reduction in the porosity of the adsorbent and an increase in the surface area available for the adsorption process due to mechanical disintegration of the adsorbent. It confirmed that modification using hydrochloric acid plays a positive role in the uptake of water from ethanol-water mixture as seen from the uptake rate curve.

Similarly, Figure 4b shows the SEM analysis of the native starch which indicated no visible effect of modification as the particles were not compacted, thus the rate of adsorption was not influenced as seen from

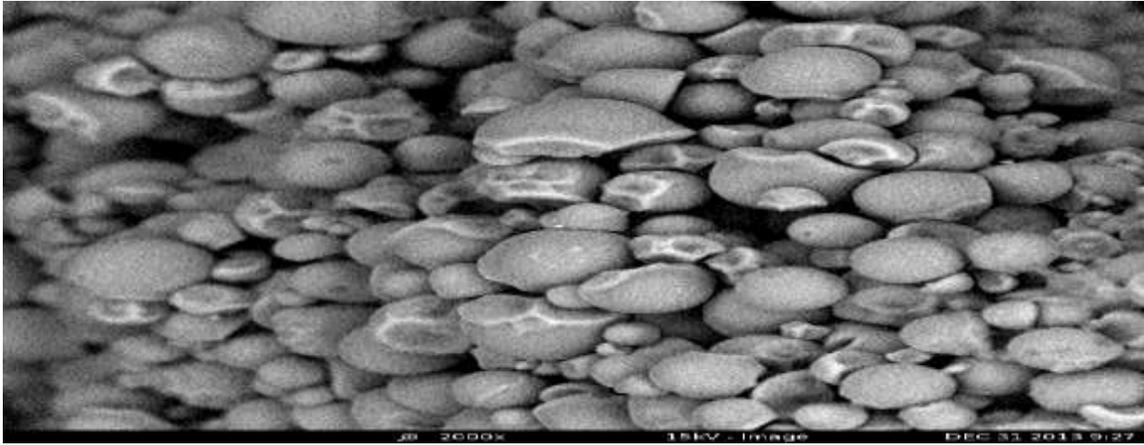


Figure 4b. Scanning electron microscopy of native cassava starch (CS).

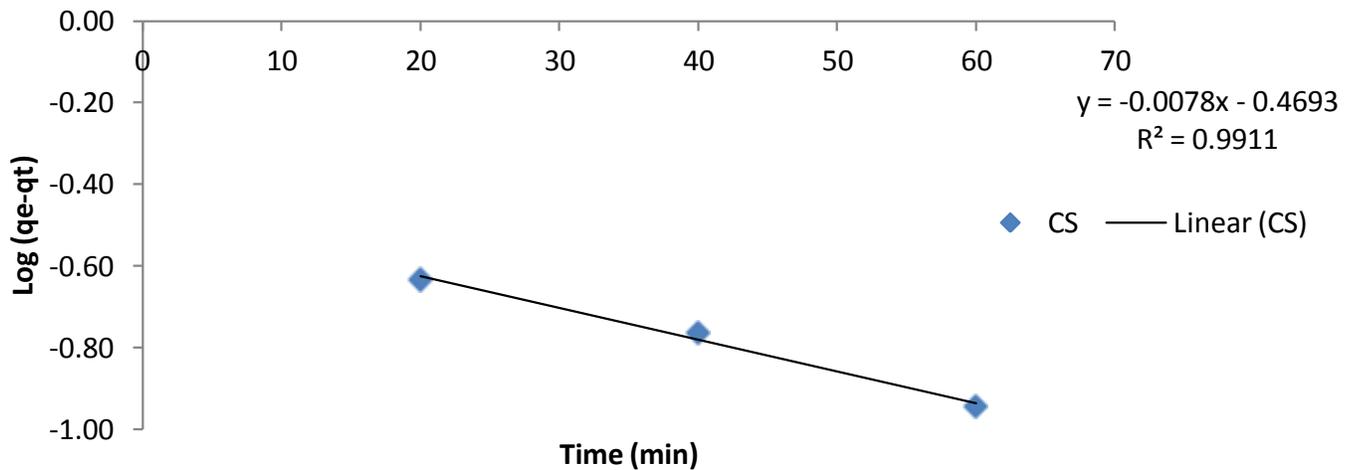


Figure 5a. Pseudo-first order plot for uptake of water from ethanol-water mixture using CS.

the uptake rate curve.

Kinetic modelling

In order to analyze the adsorption kinetics, first order, pseudo first order and Elovich equations were investigated for the uptake of water from ethanol-water systems.

Pseudo-first order

The pseudo-first order equation is generally expressed as follows:

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad (4)$$

Where;

q_e and q_t are the adsorption capacity at equilibrium and time t respectively (g/g ads) K_1 is the rate constant of pseudo first order adsorption (min)

Integrating and applying the boundary condition at $t = 0$ to $t = t$ and at $q_e = 0$ to $q_e = q_t$ the integrated form becomes:

$$\log(q_e - q_t) = \log q_e - t \frac{K_1}{2.303} \quad (5)$$

A plot of $\log(q_e - q_t)$ against t gives $-K_1/2.303$ as slope and $\log q_e$ as intercept respectively. The results obtained are plotted in Figure 5a and b. It may be observed that from the correlation coefficients (R^2) the uptake of water from ethanol water mixture follows the pseudo first order kinetics.

First order

The first order equation is given as:

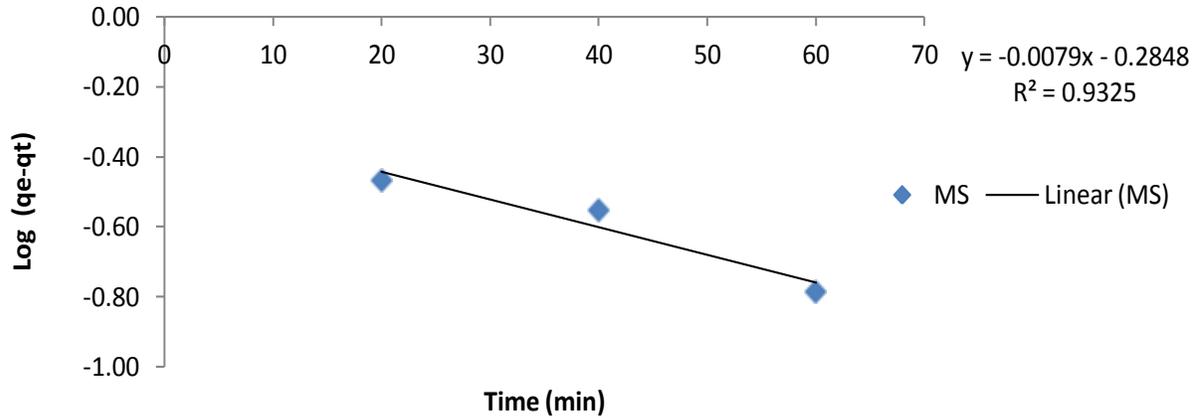


Figure 5b. Pseudo-first order plot for uptake of water from ethanol-water mixture using MS.

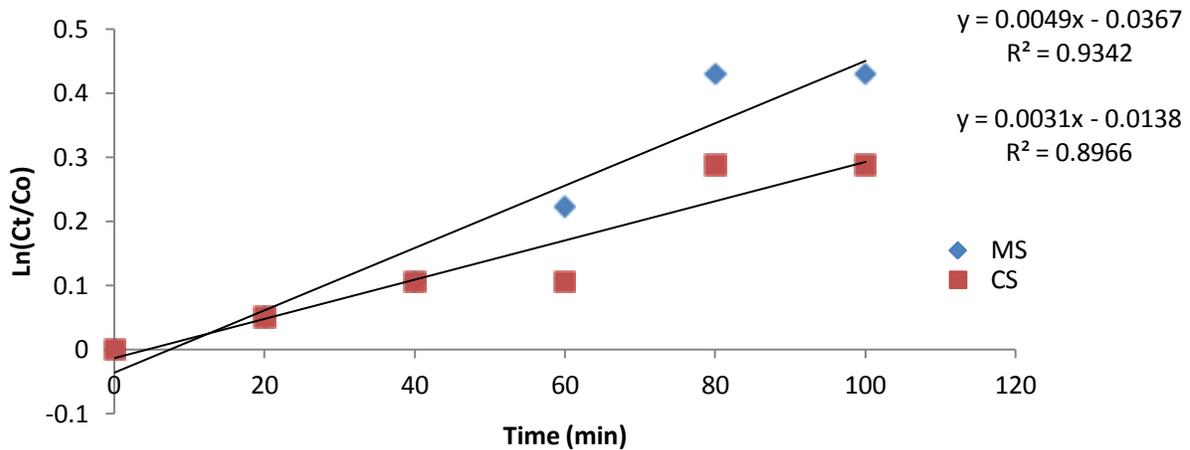


Figure 6. First order plot for uptake of water from ethanol-water mixture using MS and CS.

$$-\frac{dc}{dt} = KC^n \quad (6)$$

Applying the boundary conditions at $t = 0$ to $t = t$, and $C = 0$ to $C = C_t$, Equation 7 is obtained.

$$\ln\left(\frac{C_t}{C_0}\right) = K_1 t \quad (7)$$

Where K (min^{-1}) is the rate constant, and C_t and C_0 are the concentrations at time t and initial concentration of the adsorbent respectively, while n is the order of the reaction. A plot of $\ln(C_t/C_0)$ against t gives K_1 as slope. It can also be seen from Figure 6 that the water uptake from ethanol-water systems follows the first order kinetics as depicted by the correlation coefficient (R^2) value for the starchy adsorbent studied.

Pore diffusion model

The pore diffusion model equation is given as follows:

$$q_t = K_d t^{\frac{1}{2}} \quad (8)$$

Where;

K_d ($\text{mg/gmin}^{-1/2}$) is the diffusion rate constant, q_t is the amount of adsorbate adsorbed at time (t).

A plot of q_t against $t^{1/2}$ gives slope of K_d . Figure 7 shows that pore diffusion provided the highest correlation coefficient (R^2) value in all the various adsorbents studied. The implication is that the molecular diffusion of water molecules on the surface of adsorbents played an important role in the water removal capability of the adsorbent. The data equally fitted the pore diffusion model.

Elovich equation

The elovich equation is given as follows:

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t) \quad (9)$$

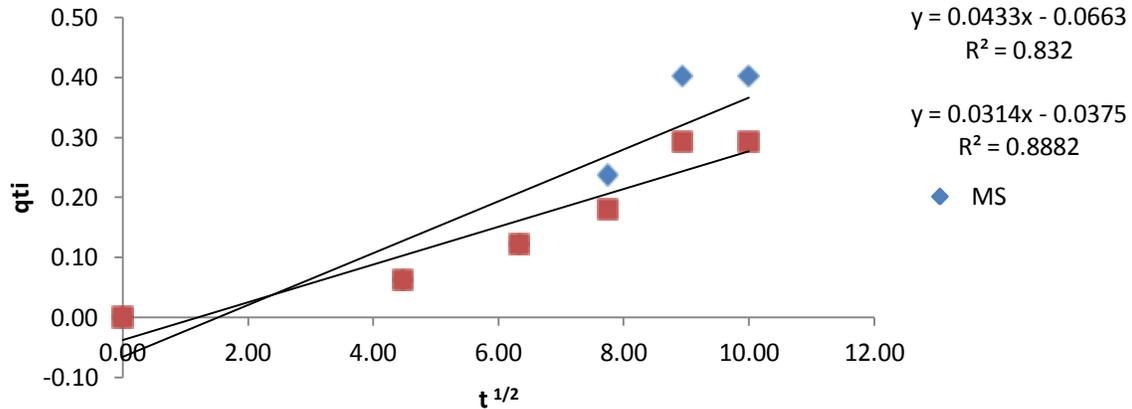


Figure 7. Pore diffusion model plot for uptake of water from ethanol-water mixture using CS and MS.

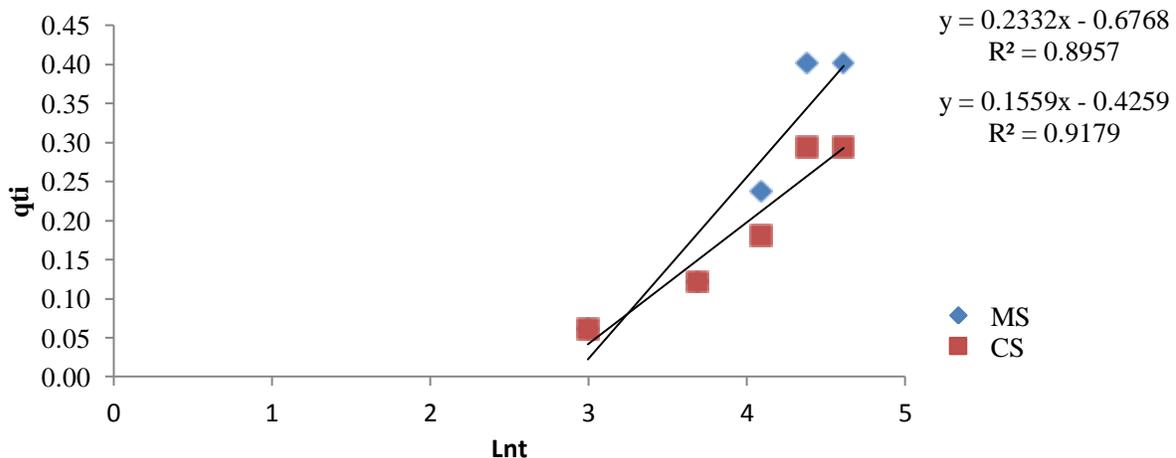


Figure 8. Elovich equation model plot for uptake of water from ethanol-water mixture using MS and CS.

q_t is the amount of adsorbate adsorbed per unit time (t). α and β are Elovich constant. From this equation we can obtain a plot of q_t against $\ln t$ gives $(1/\beta)$ as slope and $(1/\beta) \ln(\alpha\beta)$ as intercept. The results obtained from the data are shown in Figure 8. It was obvious from the correlation coefficient (R^2) value that the data conformed to Elovich equation as well.

CONCLUSION

It is observed that modification of starch significantly increased its mechanical property with a tantamount positive effect on its rate of adsorption. The kinetics of the adsorptive process was confirmed to follow the first order rate and also pseudo-first order. The kinetic models related to the water removal capacity of these adsorbents. The molecular diffusion of water molecules on the adsorbents surface through pore diffusion model was confirmed and found to be significant.

Although the native starch showed a significant

dehydrational effect on the ethanol-water mixture, the modified starch by virtue of the acidic modification yielded a better result.

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