Comparative Studies on Some Starchy Adsorbents for the Uptake of Water from Ethanol – Water Mixtures.

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***Abstract*--** **In this work a comparative study on the uptake of water from ethanol – water mixture using starchy adsorbents was undertaken. These include modified starch (MSAD), Cassava shreds (ABAD), Cassava pellet (CPAD), and Cassava starch (CSAD). The thermodynamic results were obtained at 30^{o}C, 40^{o}C, 50^{o}C, and 55^{o}C. The effect of process parameters – temperature, particle size and type of adsorbent were investigated. Using a Graeco – Latin square plan of experiment, it was seen that temperature had the most significant effect on the uptake of water from ethanol – water mixtures studied. The kinetic data were presented by means of an uptake rate curve which showed the influence of the mean particle size on the adsorption (uptake of water).**

The results obtained showed that the adsorption rates were strongly dependent on the particle size of the adsorbents studied. An increase in mean particle sizes favoured a decrease in the uptake of water by the various starchy adsorbents studied. Statistical analysis of the results performed using ANOVA showed that temperature has a significant effect on the uptake of water from ethanol – water mixtures at 0.05 confidence interval of significance. Modified starch showed the best result in all the adsorbents studied.

***Index Term*--** **Ethanol, Starch - based adsorbents, Adsorption, Analysis of Variance**

I. INTRODUCTION

Improving adsorptive processes 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. Two areas of current research in the bio – based fuel alcohol industry are the sorption of ethanol from the fermentation broth and the adsorption of water from the process stream after distillation due to the formation of azeotropes of ethanol – water mixtures at 95.6 wt% of ethanol. The separation of ethanol – water mixtures using starch or cellulose materials was first demonstrated by [1]. One of the main problems related to the production of anhydride ethanol derived from fermentation is the high energy cost of separating ethanol from the fermenting must. When distillation is used to dehydrate ethanol, 50% of the total energy is consumed [2, 3]. This frequently results in a negative energy balance where the energy spent on the anhydride ethanol production exceeds the energy obtained from its combustion [4]. Starch, cellulose, hemicellulose and starch – based materials have affinity for water [1] and are able to be regenerated at temperatures of 80^{O}C and lower [4]. Conventional techniques used for separating water from ethanol includes low – pressure distillation, azeotropic distillation with pentane, benzene, and diethyl ether, and extractive distillation with gasoline or ethylene glycol [5], or third component in these distillation schemes breaks the azeotrope which forms between ethanol and water at 95.6 wt% ethanol (at atmospheric pressure). Some materials that have been used to research the liquid – phase adsorption of ethanol include divinyl benzene cross – linked polystyrene resins hydrophobic molecular sieves and silicalite [6]. Similarly, materials that have been researched for vapour – phase adsorption of water from ethanol – water mixture include; corn grits [7, 8] molecular sieves [9], and activated alumina [10]. The drying of organic liquids, ethanol and methanol using zeolites produced from Ukpor kaolinite clay obtained from Ukpor in Anambra state were investigated where it was revealed that micro- pores or crystalline (about 8A in diameter) as well as micro – pores (about 4A in diameter) were actively involved in water removal from the solvents [11]. The advantages of these starch – based adsorbents in uptake of water from ethanol – water mixtures includes re – used of materials in fermentation, biodegradable, efficiency, relatively available and cheap, non – toxic, and derived from renewable sources. In this work a study was carried out in order to study comparative adsorptive capacity of different starchy adsorbents through the liquid phase adsorption of water from ethanol – water mixtures with the intent of defining their adsorptive capacity at 30^{O}C, 40^{O}C, 50^{O}C, and 55^{O}C temperatures. The kinetic data were obtained at room temperature (28^{O}C). The starch based materials used in this study were adsorbent cassava starch, adsorbent cassava pellet, adsorbent cassava shred (Abacha), and adsorbent modified starch.

II. MATERIALS AND METHODS

Cassava starch, cassava pellet, and cassava shred (Abacha) were purchased from the market, sun – dried and thermally treated in an oven at 105^{o}C for 16hrs and thereafter classified into particle sizes ranging from 2.00 to 6.00mm. For modified starch preparation the method of [12] was used. Physical characterization of these materials included mean particle diameter obtained by Tyler/Mesh method, mean mass, and density of the adsorbents by water picnometry method.

For starch content determination the method of [13] was used. The results are listed in Table 1.0. The ethanol – water solutions are prepared at the required mass concentrations (Concentration range of 10 to 50 wt% ethanol was used for the thermodynamic test and 90 wt% ethanol for the kinetic test). Analytical grade of ethanol was purchased from accredited chemical dealers in Onitsha market, Anambra state, and de – ionized water, using a scale with an accuracy of 0.01g. The fluid phase concentration was measured with the aid of an Abbe refractometer with automatic calibration in this experimental concentration range.

Table I

Physico - Chemical Characterisation of Adsorbents. EXPERIMENTAL PROCEDURE

Adsorbents	**Mean Diameter (mm)**	**Tyler/Mesh**	**Mean Mass (mg)**	**Bulk Density (g/mol)**	**Starch Content (%)**
Cassava Starch	2.50	2.00 – 3.00	0.882	1.88	86
	3.50	3.00 – 4.00	13.00		
	4.50	4.00 – 5.00	35.00		
	5.50	5.00 – 6.00	58.00		
Cassava Pellet	2.50	2.00 – 3.00	5.80	0.6	84.43
	3.50	3.00 – 4.00	5.00		
	4.50	4.00 – 5.00	26.00		
	5.50	5.00 – 6.00	76.00		
Cassava Shred	2.50	2.00 – 3.00	5.00	1.50	79.90
	3.50	3.00 – 4.00	8.57		
	4.50	4.00 – 5.00	14.00		
	5.50	5.00 – 6.00	20.00		
Modified Starch	2.50	2.00 – 3.00	0.100	1.48	85.24
	3.50	3.00 – 4.00	0.300		
	4.50	4.00 – 5.00	0.630		
	5.50	5.00 – 6.00	1.190		

The equilibrium data were obtained by the static method, which consists of a specific amount M_S of thermally treated (105^{o}C for 16hr) adsorbents (~5g) in contact with a specific mass M_f of aqueous ethanol solution (~20g) of a well defined initial concentration W^{o}. Several initial concentrations were used in order to obtain wide range of data at 30^{o}C, 40^{o}C, 50^{o}C, and 55^{o}C temperatures. The flasks were corked and left to stand in the thermostated water bath with an accuracy of ±0.1^{o}C in the laboratory for 2hrs and gently shaken, after which the concentration of fluid phase was measured and the end concentration of the liquid was determined, W^{e}_{b}. To obtain the amount of water adsorbed in the solid phase, a mass balance was used between the phases, where ethanol was considered the non – adsorbable component. This hypothesis agrees with the work of [14], where it was demonstrated that the chemical affinity of starch to water is much greater than that of ethanol. The mass balance is described by equation 1.0, where at equilibrium when $t \rightarrow \infty$, $W_b \rightarrow W_b^{e}$.

$$q_s = \frac{M_f}{M_s} \frac{\{W_b - W^o\}}{W_b} \quad 1.0$$

M_f – Mass of liquid, (g), M_s – Mass of adsorbent, (g), q_s – Amount of water adsorbed in the solid phase after a specific time interval, (mg/g), W_b – Final concentration of adsorbed phase, and W^o – Initial water – ethanol concentration.

To obtain the kinetic data a locally designed finite volume circulating device similar to that developed by [15] was used a closed loop through a packed bed of adsorbents particles (~5g). 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 the predetermined calibration graph.

III. RESULTS AND DISCUSSION

(a) Results from GRAECO – LATIN Design of Experiment

The effect of process variables like particle sizes: X1; 2.5, X2; 3.5, X3; 4.5, and X4; 5.5mm, Temperature ranges: α; 30, β; 40, γ; 50, and δ; 55^{o}C, Time: 30, 60, 90, and 120min, and Types of adsorbents; A, cassava starch, B; cassava pellet, C; cassava shred (Abacha), and D; modified starch, on the uptake of water from the binary mixture studied.

Table II
Design of Experiment (Graeco-Latin Square)

Process Durations	**30mins**	**60mins**	**90mins**	**120mins**	**Total**
X1	Bγ(86)	Aβ(87)	Dδ(80)	Cα(78)	331
X2	Aδ(78)	Bα(83)	Cγ(82)	Dβ(90)	333
X3	Dα(87)	Cδ(80)	Bβ(92)	Aγ(83)	342
X4	Cβ(87)	Dγ(86)	Aα(83)	Bδ(84)	340
Total	338	336	337	335	1,346

Table III
Analysis of Variance (ANOVA)

Variation	**Degree of Freedom**	**Mean Square(S^2)**	**F (S^2/S^2_{res})**	**F (Table) .95, 3,3**
Rows	3	7.083	2.299	9.28
Columns	3	0.4167	0.135	9.28
Adsorbents	3	19.583	6.357	9.28
Temperature	3	51.75	16.802	9.28
Error	3	3.08		
Total	15			

It was shown from the ANOVA results that the effect of process duration, and types of adsorbents was very insignificant going by the very small value of its Fisher's test (F-test) at 0.05 confidence interval. On the other hand, the effect of temperature was shown to be very significant at 0.05 confidence interval on the uptake of water from the binary mixtures studied.

(b) Effect of Process Variables

(i) **Temperature**

The effect of temperature was shown by relating the initial and end concentrations of the adsorbed phase of ethanol – water mixtures with various starch – based adsorbents used at 303K, 313K, 323K, and 328K which can be seen in fig. 1 – 4.

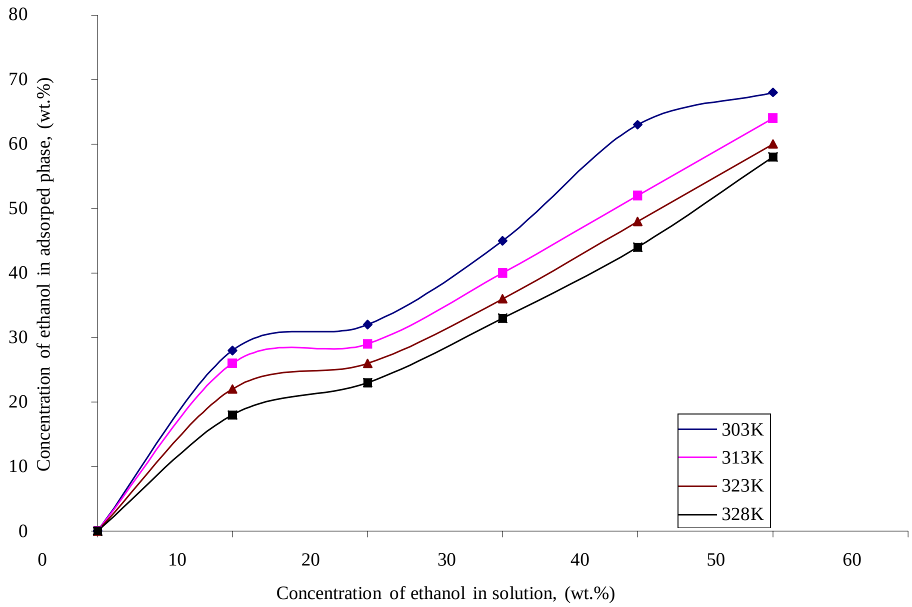


Fig. 1.0. Effect of temperature on adsorption using CPAD

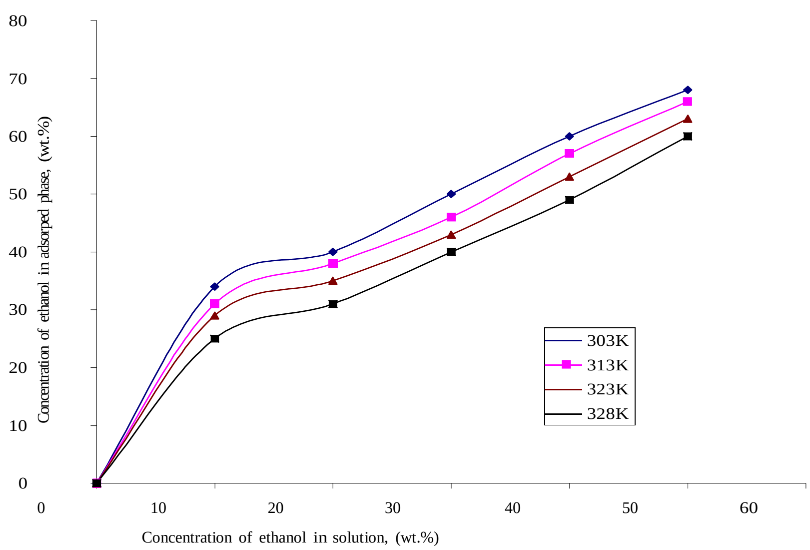


Fig. 2.0 Effect of temperature on adsorption using CSAD

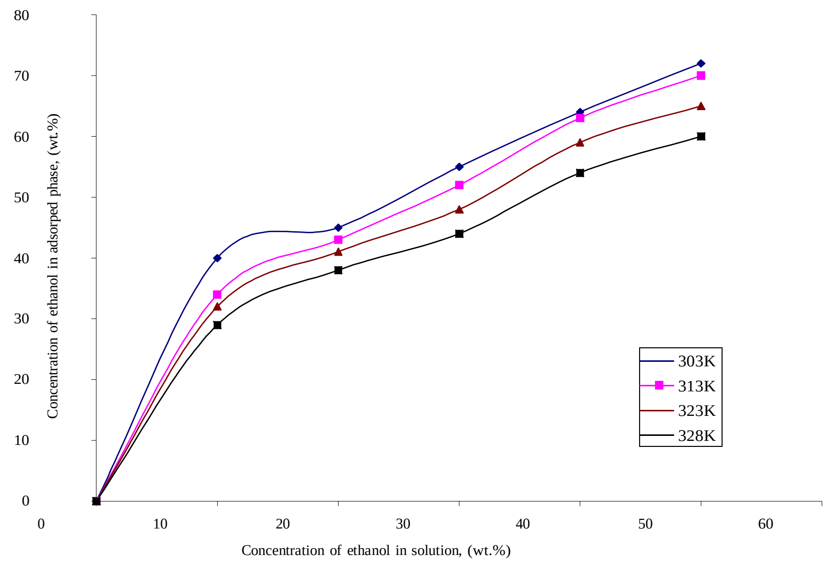


Fig. 3.0 Effect of temperature on adsorption using MSAD

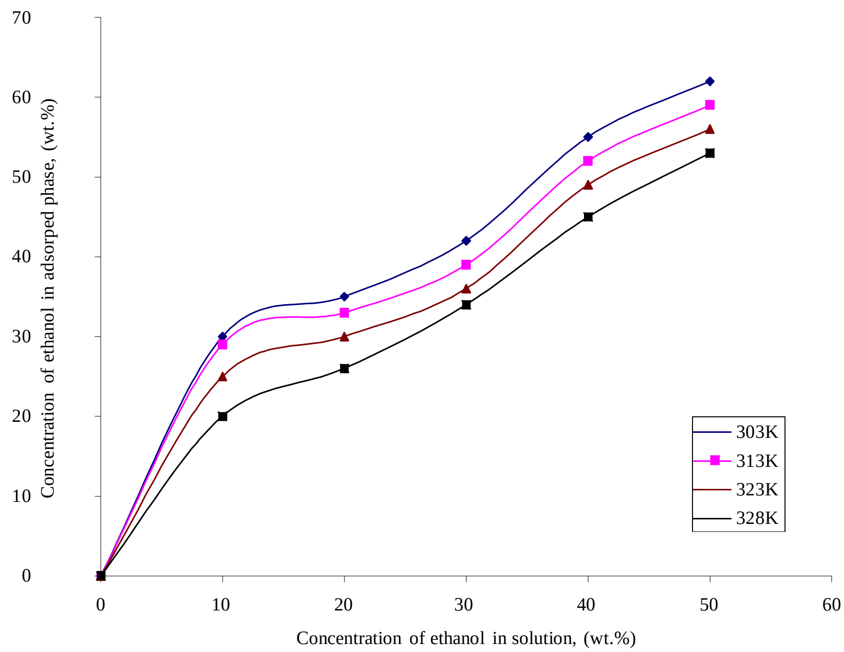


Fig. 4.0 Effect of temperature on adsorption using ABAD

It was confirmed from the plots that as the temperature is increased the adsorbing capacity decreased for all the starchy adsorbents studied this can be explained by the increased in the vibrational energy of the molecules, which at higher temperatures allows a smaller net number of molecules to be adsorbed at equilibrium, due to the exothermic nature of the adsorption process, an increased in temperature shifts the equilibrium to the region unfavourable to adsorption.

(ii) **Particle size**

Kinetic results were presented by means of uptake rate curves, where the amount adsorbed was related to the adsorption time for the starchy adsorbents studied. The effect of the mean particle sizes to uptake of water from ethanol – water mixtures was also studied. From the results obtained and plotted in fig.5.0 – 8.0, it may be noted that the rate of uptake decreased as mean particle sizes of the adsorbents increased. This can be explained 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 particles, diminishing the time it takes for the molecules to pass through the intricate network 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.

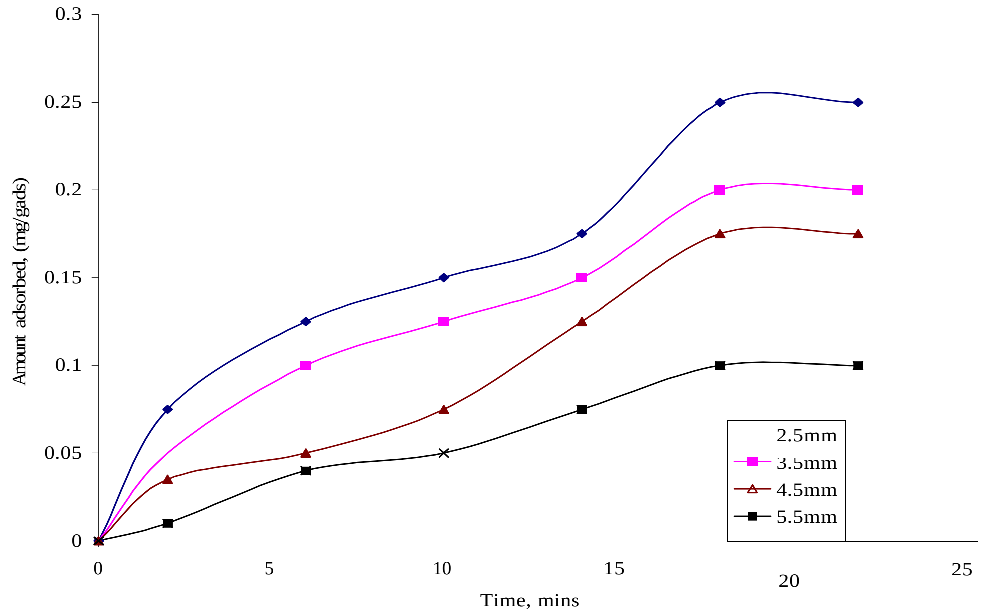


Fig. 5.0 Effect of particle size on adsorptive capacity of ABAD for ethanol - water mixtures

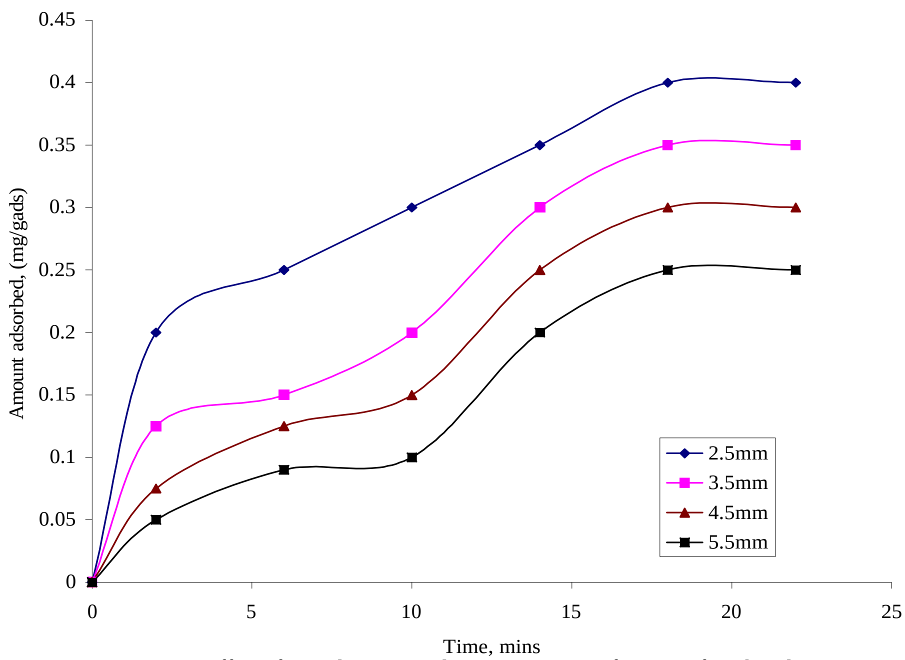


Fig. 6.0 Effect of particle size on adsorptive capacity of MSAD for ethanol - water mixtures

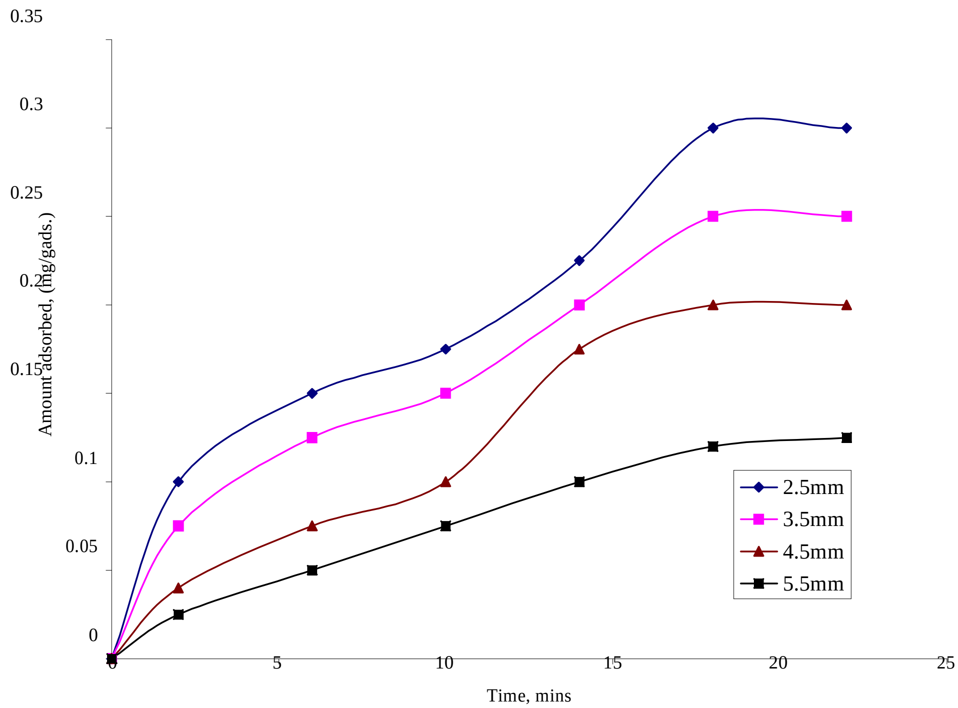


Fig. 7.0 Effect of Particle size on adsorptive capacity of CPAD for ethanol - water mixtures

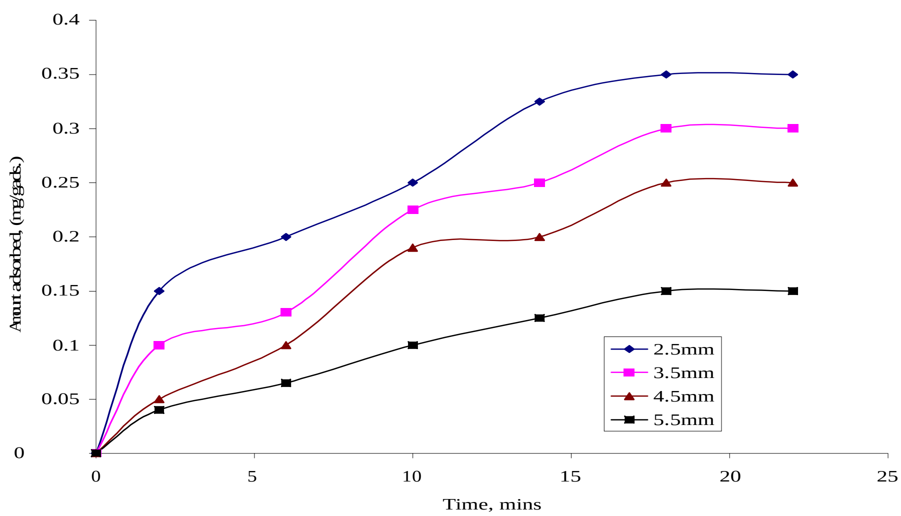


Fig. 8.0 Effect of particle size on adsorptive capacity of CSAD for ethanol - water mixtures

(iii) **Type of adsorbents**

The nature of different starchy adsorbents was investigated at different particle size to know the adsorbent capacity of these starchy adsorbents as shown in fig. 9 – 12. The high adsorptive capacity of modified starch can be attributed to the modification process which create pores and increased the surface area per gram of the modified starch without radically reducing the size of the particles thereby making the molecular diffusion of water molecules inside the modified starch to be increased. The adsorptive capacity is MSAD > CSAD > CPAD > ABAD.

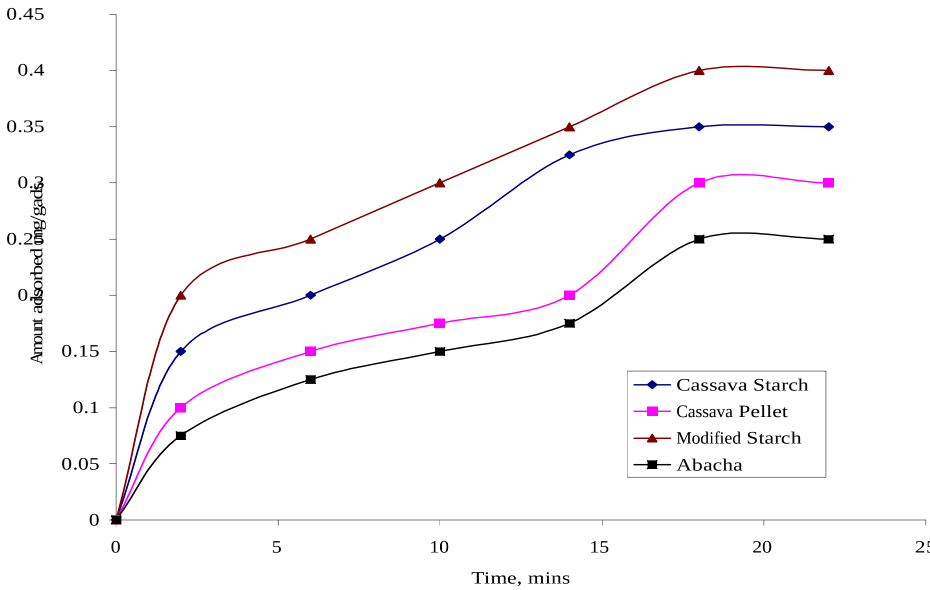


Fig. 9.0 Uptake curves of various adsorbents for ethanol-water mixtures (Dp = 2.5mm)

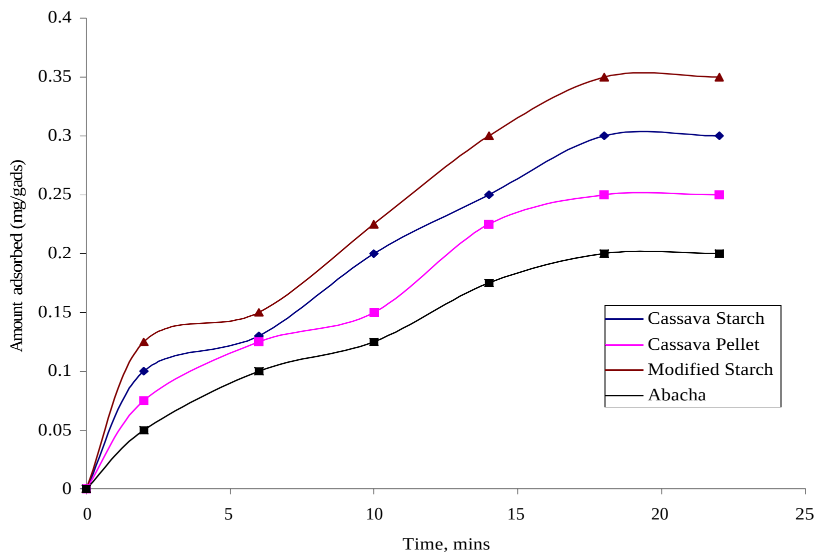


Fig. 10.0 Uptake curves of various adsorbents for ethanol -water mixtures (Dp = 3.5mm)

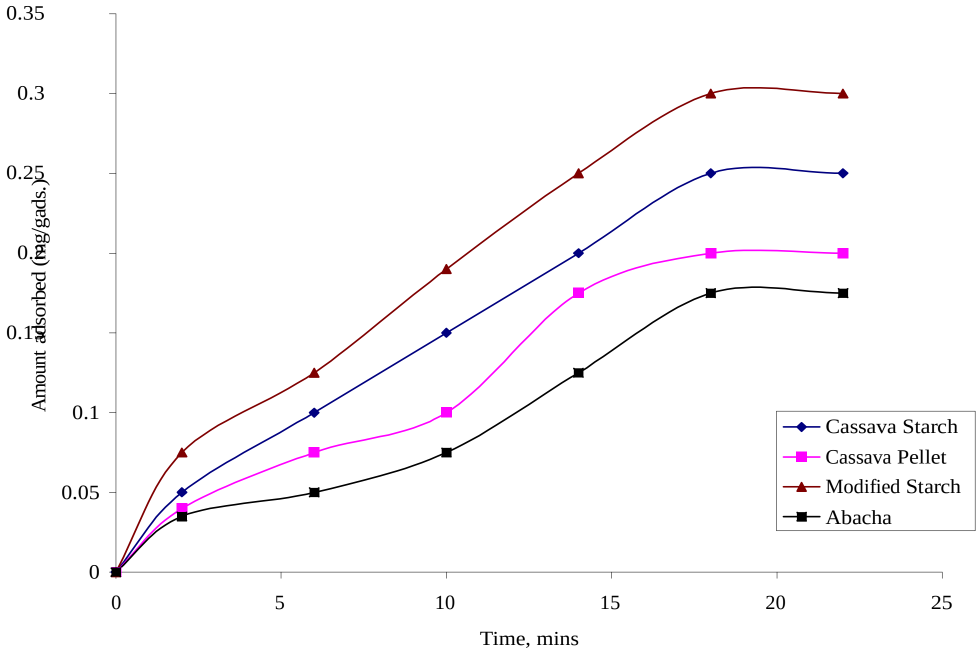


Fig. 11.0 Uptake curves of various adsobents for ethanol - water mixtures (Dp = 4.5mm)

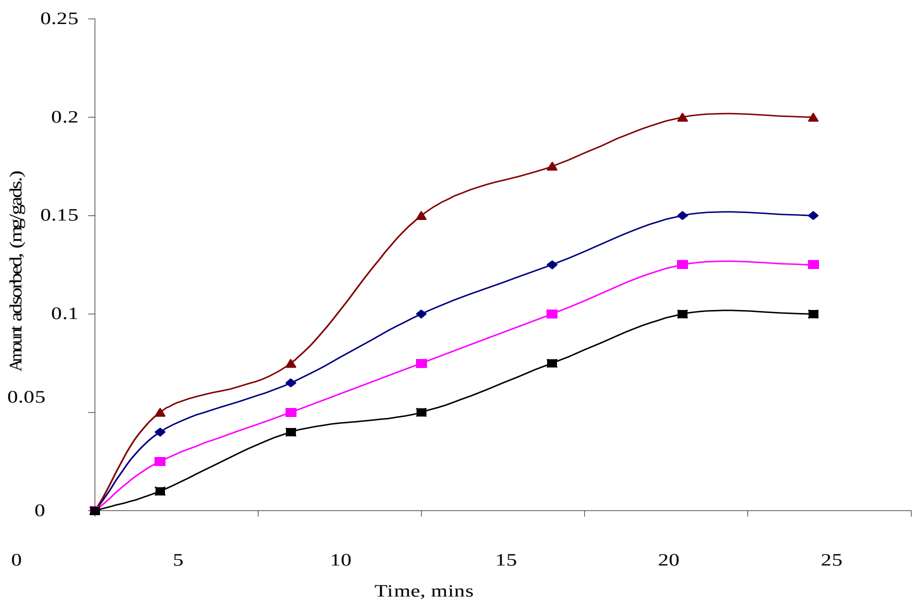
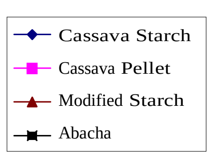


Fig. 12.0 Uptake curves of various adsorbents for ethanol - water mixtures (Dp = 5.5mm)



This indicates that the diffusion resistance inside the particle is predominantly located at the macro – pore level, without discarding the hypothesis that there might be a combined resistance effect of the micro and macro – pores [6]. The high adsorptive capacity of modified starch can be attributed to the modification process which create pores and increased the surface area per gram of the modified starch without radically reducing the size of the particles thereby making the molecular diffusion of water molecules inside the modified starch to be increased.

IV. CONCLUSIONS

It was confirmed that starchy materials has affinity for water in the presence of ethanol – water
mixtures as shown in fig. 1 – 4. The modified starch has the highest adsorptive capacity while cassava shred has the least. The kinetic test were shown to be depended on the parameters studied, the mean particle size, where it was established that as the mean particle size increased the uptake of water from ethanol – water mixtures decreased.

The optimum uptake of water was obtained with particle size of 2.5mm. The statistical results also established the significant effect of temperature on the uptake of water from ethanol – water mixture using starchy adsorbents.

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