ADSORPTION AND KINETIC MODELLING OF THE UPTAKE OF WATER FROM ETHANOL – WATER SYSTEMS USING STARCHY ADSORBENTS.

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ABSTRACT

In this work adsorption and kinetic modelling of the uptake of water from ethanol – water mixtures using starchy adsorbents was undertaken. These include modified cassava starch (MSAD), cassava starch (CSAD), cassava pellet (CPAD), and cassava shred (ABAD).

The kinetic data were obtained in a finite volume bath cell circulation at room temperature (28^{o}C). Five kinetic models including First order, Pseudo – first order, Pseudo – second order, Pore diffusion and Elovich equations were tested for uptake of water by these starchy adsorbents from ethanol – water systems. The results revealed that the adsorbents types and molecular diffusion of water molecules on the surface of the adsorbents play an important role in the uptake of water by these adsorbents. The performance of the adsorbents for the net uptake of water was found to be in the order; MSAD> CSAD> CPAD> >ABAD.

KEYWORDS: Cassava based Adsorbents, Ethanol, Adsorption, Kinetic

INTRODUCTION

Improving the adsorptive processes demands a constant search for new adsorbents. In the specific case of ethanol – water mixture adsorption, 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 been proposed. One area of current research in the bio – based fuel alcohol industry is the adsorption of water from process stream after distillation due to the formation of azeotropes 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 [1]. Distillation process operates on the principle of the difference in volatility of component mixtures, the use of distillation as compared with adsorption becomes impractical if the relative volatility is less than 1.2 [2]. When distillation is used to dehydrate ethanol, 50% of the total energy is consumed [3, 4].

Adsorption is the process of transferring certain components from the bulk of fluid to the surface of a solid (adsorbents) [5]. 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 [6], or third component in these distillation schemes breaks the azeotrope which forms between ethanol and water at 95.6wt% ethanol (at atmospheric pressure). Three potential methods of adsorbing water from high ethanol concentration feeds in the liquid phase are described as follows; the use of room temperature inert gas to pass through a vessel containing a liquid ethanol – water solution [7], the liquid phase ethanol feed could pass through saponified starch g – poly (acrylonitrile), which would selectively adsorb the water and will need to selectively adsorb the water and will need to be air – dried before being used again [8], and liquid phase ethanol feed stream could be passed over a bed of activated alumina, which does not have high regeneration temperature as that of molecular sieves [9].

The starch based adsorbents adsorb water by forming hydrogen bond between the hydroxyl groups on the surface of the adsorbent and the water molecules [10]. Adsorption isotherms indicate how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [11]. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [12]. The advantages of these starch – based adsorbents in uptake of water from ethanol – water mixtures include; re – used of materials in fermentation, biodegradability, efficiency, relatively available and cheap, non – toxic, and derived from renewable sources.

In this work a study was carried out on adsorption and kinetic modelling of water uptake from ethanol – water mixtures using starchy adsorbents through liquid phase adsorption.

The kinetic data were obtained at room temperature (28^{o}C). Thus, uptake of water from ethanol – water systems kinetic were investigated including the water removal capability of the starchy adsorbents was performed through five kinetic models. The starch based materials derived from cassava such as; adsorbent cassava starch, adsorbent cassava pellet, adsorbent cassava shred, and adsorbent modified starch were used for the water uptake from ethanol – water systems.

MATERIALS AND METHOD

Cassava starch, cassava pellet, and cassava shred were purchased from the market, sun – dried and thermally treated in an oven at 105^{o}C for 16hours and thereafter classified into particle sizes ranging from 2.00 – 6.00mm. For modified starch preparation the method of [13] was used and thereafter classified as well. Physico – chemical characterization of these starchy materials included starch content, mean particle diameter obtained by Tyler/Mesh method, mean mass, and bulk density of the adsorbents were obtained by water picnometry method. The results are listed in table 1.0.

The ethanol – water solutions are prepared at the required mass concentrations (concentration of 90wt% 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 experimental concentration range.

Table 1.0 Physico - Chemical Characterisation of Adsorbents.

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		

EXPERIMENTAL PROCEDURE

To obtain the kinetic data a locally designed finite volume circulating device similar to that developed by Azevedo [14] was used within a finite volume of liquid (~250ml) circulates continuously in 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 predetermined calibration graph.

RESULTS AND DISCUSSION

Kinetic Modelling

In order to analyze the adsorption kinetic; First order, Pseudo – fist order, Pseudo – second order, Pore diffusion and Elovich equation were investigated for the uptake of water from ethanol – water systems.

First order

$$-dC / dt = KC^n \qquad (1.0)$$

For first order n = 1. Integration of equation (1) above and apply boundary condition as t =0, to t =t, and C = 0 to $C_t = C_t$, $\ln (C_t /C_o) = K_1 t$. Where $K_1(\text{min}^{-1})$ is the rate constant, C_t and C_o are the concentration of adsorbate at time t and the initial concentration of the adsorbate, and n is the order of reaction. A plot of $\ln (C_t / C_o)$ against t gives k_1 as slope. It was seen from Fig.1-2 that the water uptake from ethanol – water systems follows first order kinetic as depicted by the correlation co –efficient (R^2) value of all the starchy adsorbents.

The similar value of rate constant (K_1) gotten for the adsorbents shows that rate of adsorption of water in all the adsorbents was constant.

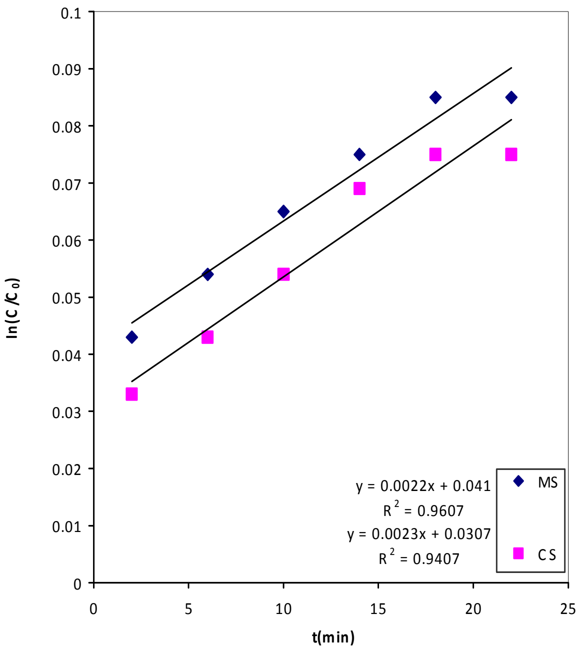

Fig. 1.0 First order plot for uptake of water from ethanol-water mixture using MSAD and CSAD

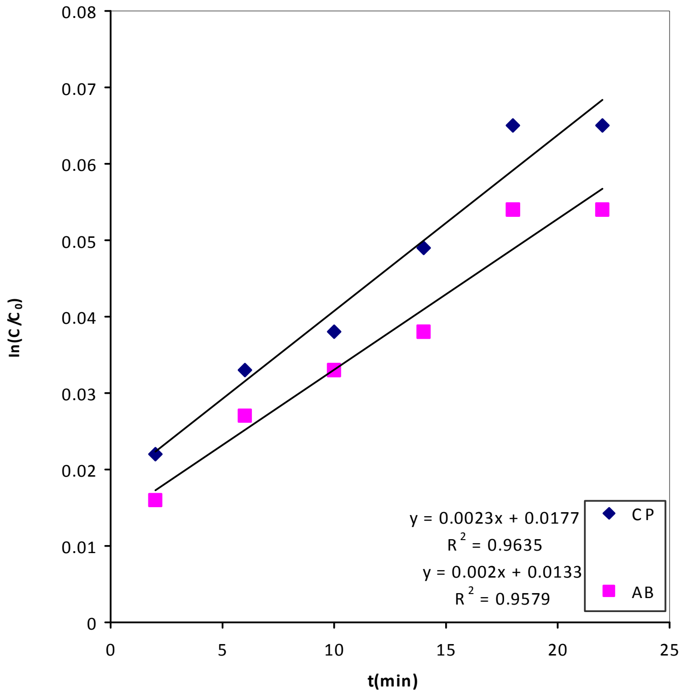

Fig. 2.0 First order plot for uptake of water from ethanol-water mixture using CPAD and ABAD

Pseudo – first order

The pseudo – first order equation is generally expressed as follows;

$dq_t / q_t = K_1 (q_e – q_t)$ (2)

q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g). K_1 is the rate constant of pseudo – first order adsorption (min^{-1}).

Integration and applying boundary condition t = 0, to t = t, and $q_e = 0$ to $q_t = q_t$.

The integrated form becomes;

$\log (q_e – q_t) = \log (q_e) – (t) K_1/ 2.303$ (3)

A plot of $\log (q_e – q_t)$ against t gives $–k_1/2.303$ as the slope and $\log (q_e)$ as the intercept.

From the results obtained and plotted in fig.3.0 – 5.0. It may be noted from the correlation co –efficient (R^2) value that uptake of water from ethanol – water mixtures follow the pseudo – first order kinetic.

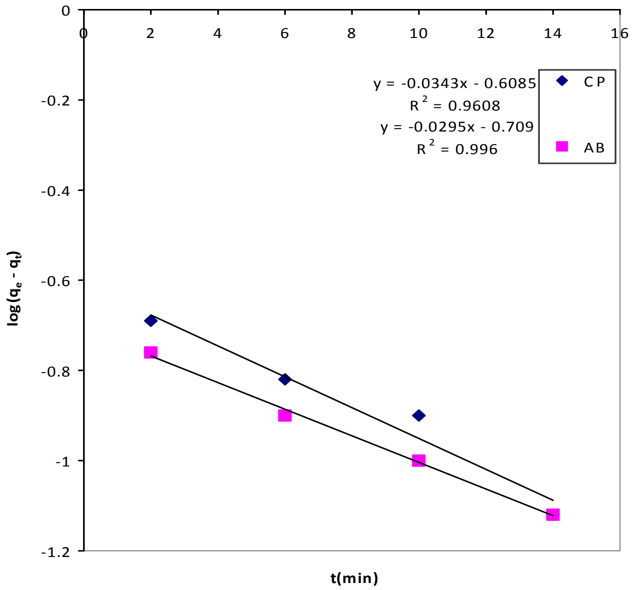

Fig. 3.0 Pseudo-first order plot for uptake of water from ethanol-water mixture using CPAD and ABAD

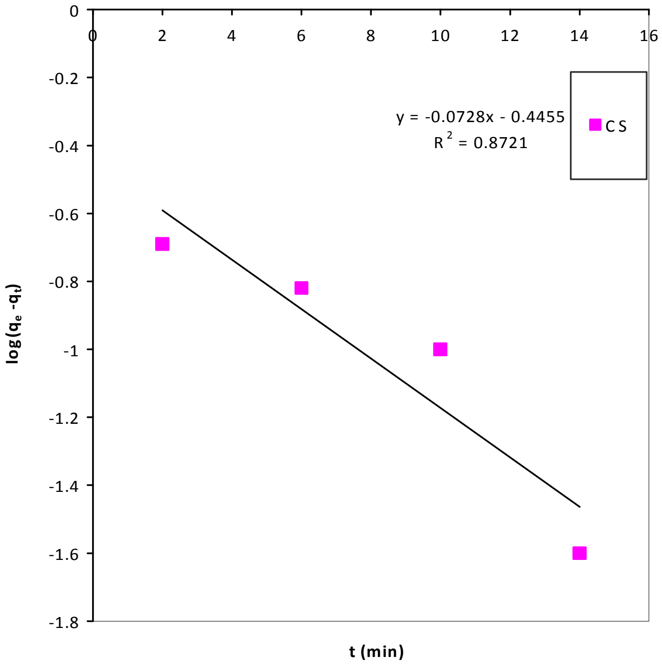

Fig. 4.0 Pseudo-first order plot for uptake of water from ethanol-water mixture using CSAD.

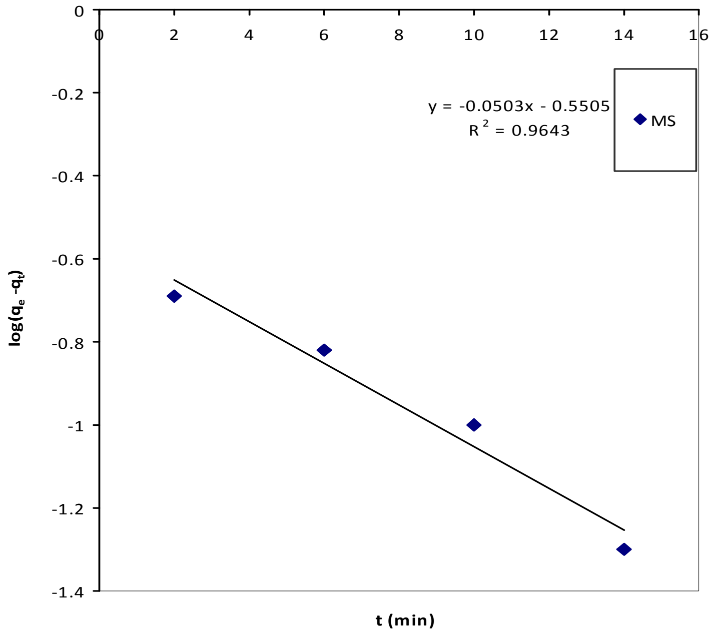

Fig. 5.0 Pseudo-first order plot for uptake of water from ethanol-water mixture using MSAD.

Pseudo – second order

The pseudo – second order kinetic model as expressed by [15] is given below;

$t / q_t = 1/ K_2q_e^2 + (t) 1/ q_e$ (4)

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 $1/ k_2q_e^2$ as the intercept. As shown in fig. 6.0 – 7.0, it was noted from the correlation co – efficient (R^2) value that the data also conform to pseudo – second order kinetic.

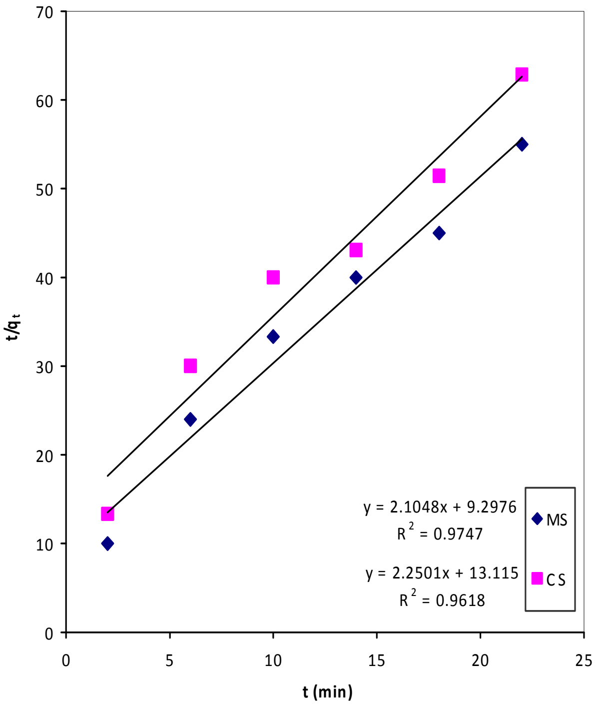

Fig. 6.0 Pseudo-second order plot for uptake of water from ethanol-water mixture using MSAD and CSAD.

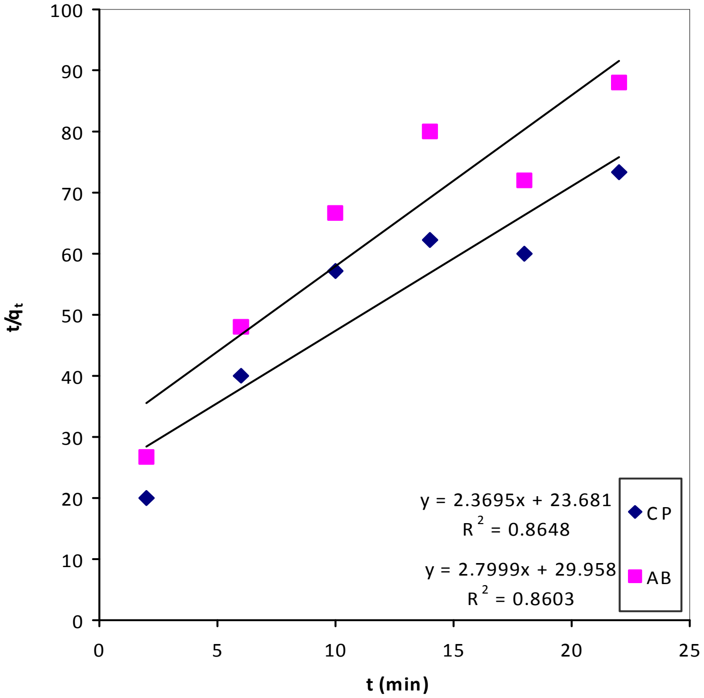

Fig. 7.0 Pseudo-second order plot for uptake of water from ethanol-water mixture using CPAD and ABAD.

Pore diffusion model

$$q_t = K_d t^{1/2} \qquad (5)$$

Where K_d (mg / gmin$^{-1/2}$) is the diffusion rate constant, and 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. It was revealed from fig. 8.0 – 9.0 that pore diffusion provided the highest correlation co –efficient (R^2) value in all the various adsorbents studied. This indicated that the molecular diffusion of water molecules on the surface of adsorbents played an important role in water removal capability of the adsorbents. The data fitted well to the pore diffusion model.

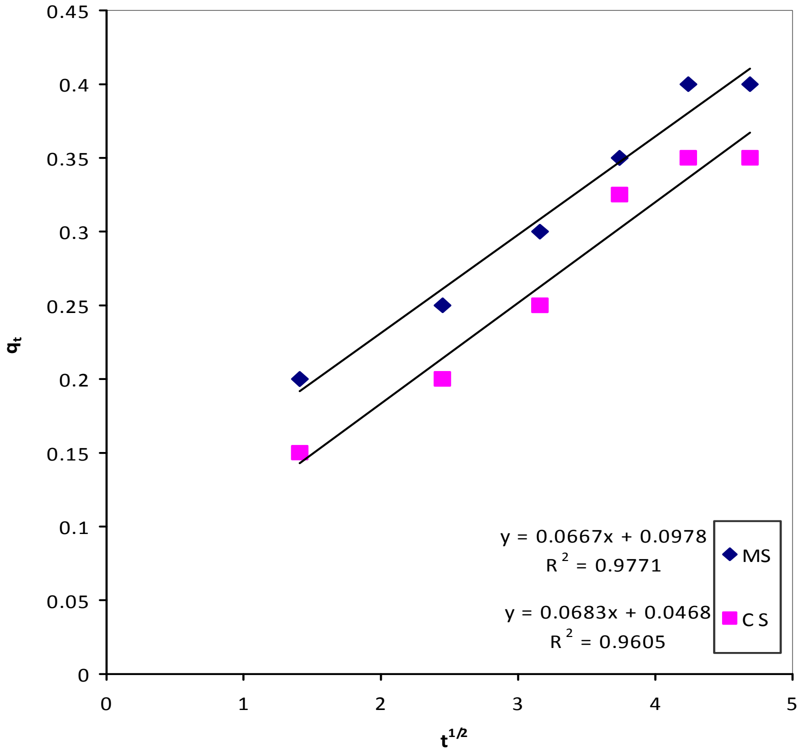

Fig. 8.0 Pore diffusion plot for uptake of water from ethanol-water mixture using MSAD and CSAD

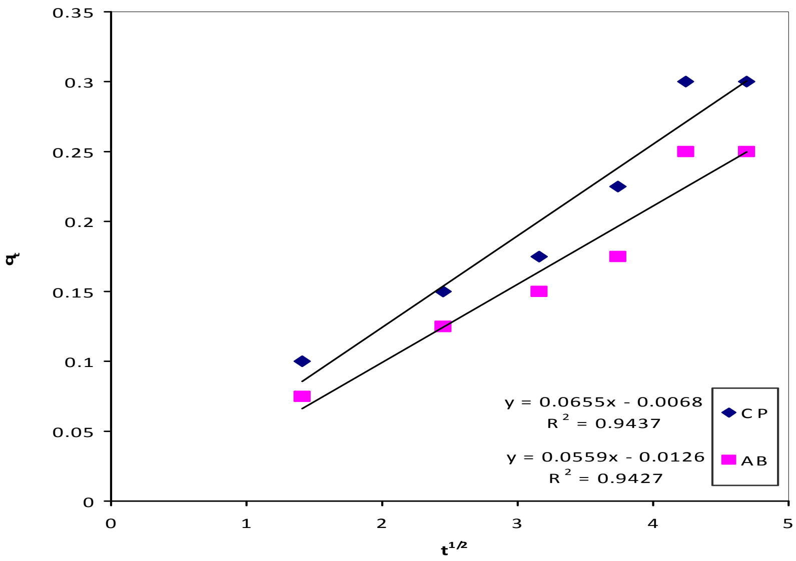

Fig. 9.0 Pore diffusion plot for uptake of water from ethanol-water mixture using CPAD and ABAD.

Elovich equation

$$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t \qquad (6)$$

q_t is the amount of adsorbate adsorbed per unit time (t). α and β are Elovich constant. A plot of qt against lnt gives (1/ β) as slope and (1/ β) ln (αβ) as intercept. The results obtained from the data and plotted in fig. 10.0 – 11, it was obvious from the correlation co –efficient (R^2) value that the data conform to Elovich equation as well.

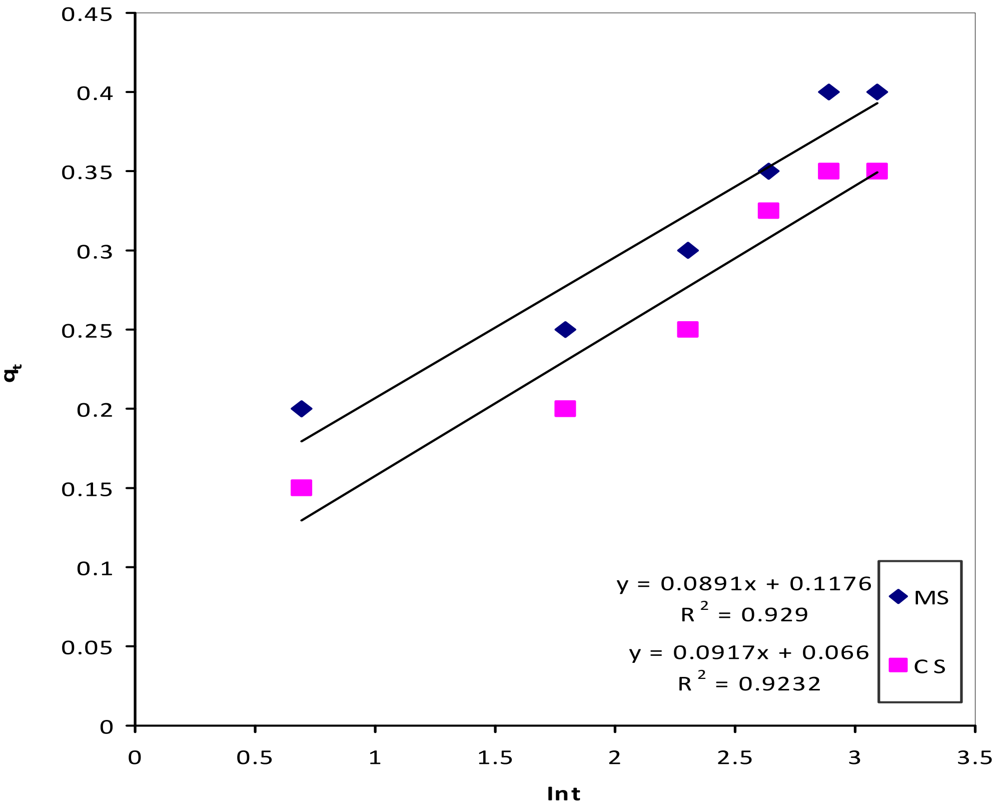

Fig. 10.0 Elovich plot for uptake of water from ethanol-water mixture using MSAD and CSAD.

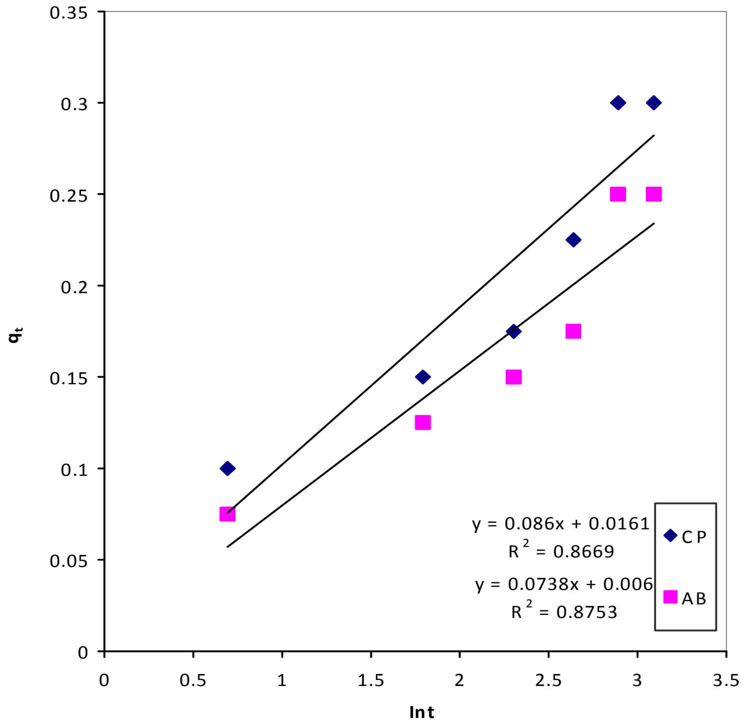

Fig. 11.0 Elovich plot of uptake for water from ethanol-water mixture using CSAD and ABAD

Table 2.0 Summary Results of Kinetic Model

Kinetic parameters	**Modified Starch**	**Cassava Starch**	**Cassava Pellet**	**Cassava Shred (Abacha)**
Pore diffusion, R^2	0.9771	0.9605	0.9437	0.9427
k_d (mg/gmin$^{-1/2}$)	0.0667	0.0683	0.0655	0.0559
First-order, R^2 K_1 (min^{-1})	0.9607 0.0022	0.9407 0.0023	0.9635 0.0023	0.9579 0.002
Pseudo-first order, R^2 K_1 (min^{-1})	0.9643 0.116	0.8721 0.168	0.9608 0.0789	0.996 0.0679
Pseudo–second order, R^2	0.9747	0.9618	0.8603	0.8648
$K_{2,}$ (ml/min)	0.476	0.387	0.262	0.237
Elovich, R^2	0.929	0.9232	0.8669	0.8753
α	0.33	0.188	0.104	0.0801
β(mg/g)	11.223	10.905	11.628	13.55

CONCLUSION

Adsorption and kinetic modelling of the uptake of water from ethanol – water systems was investigated, the affinity of starchy materials to water in the presence of ethanol – water systems was confirmed. The kinetic studies indicated that pore diffusion, first order and pseudo – first order best correlated to the data. The kinetic models related to the water removal capacity of these adsorbents and molecular diffusion of water molecules on the adsorbents surface through pore diffusion model played an important role in water uptake from ethanol - water mixtures studied. Modified starch showed the best value for all the kinetic modelling parameters considered as compared to other adsorbents.

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