Adsorption Isotherms and Kinetics Models of Starchy Adsorbents on Uptake of Water from Ethanol – Water Systems

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Abstract

The adsorption equilibrium and kinetics of ethanol-water systems on starch-based adsorbents prepared from cassava were undertaken. These include modified cassava starch (MS), cassava starch (CS), cassava pellet (CP), and Cassava shred (AB). The adsorption equilibrium data were best represented by the Langmuir adsorption isotherm. The adsorption kinetics was found to follow second order kinetics model. Adsorption mechanism process was determined from the intra-particle diffusion model where it was seen that the boundary layer has less significant effect on the diffusion mechanism of water uptake on the starch-based adsorbents studied. The Boyd kinetic model showed that the adsorption of water from ethanol – water mixtures was mainly due to external mass transport. The monolayer adsorption capacities are found to be 4.44, 5.75, 6.41, and 7.09g/g for AB, CP, CS, and MS respectively.

Keywords: Isotherms, Adsorption, Ethanol-Water Systems, Kinetics, Starch-Based Adsorbents.

Introduction

A lot of research efforts continue to focus on the improvement of adsorptive processes of dehydrating ethanol – water mixtures. The use of non – conventional adsorbents to substitute zeolites, mainly starch and agricultural waste ligno-cellulosic adsorbents by virtue of their known chemical affinity for water has recently been proposed. Adsorption of water from ethanol – water mixtures using starch or cellulose materials was first demonstrated by (Ladisch and Dyck, 1979). The separation of ethanol – water mixtures using distillation process is becoming worrying because of the high energy consumed and azeotrope formation. Adsorption techniques of dehydrating anhydrous ethanol has been of growing importance due to its energy saving. The starch based adsorbents adsorb water by forming hydrogen bond between the hydroxyl groups on the surface of the adsorbents and the water molecules (Beery and Ladisch, 2001). Biomass materials that have been investigated and found to be viable adsorbents include cassava starch, corn grits, potato starch, amylase, ligno-cellulosic and corn starch. These materials used xylans and cellulose as the major adsorbing mechanism instead of amylopectin in the case of starch (Mya, 2011). Adsorption is the process of transferring certain components from the bulk of fluid to the surface of a solid (adsorbents) (Coulson and Richardson, 1980). The analysis of adsorption equilibrium data by fitting them into different adsorption isotherm models is an important step to find the suitable model that can be used for the purpose of design (El-Guendi, 1991). Adsorption isotherms or known as equilibrium data, are fundamental requirements for the design of adsorption systems (Zawani, et al, 2009).

Adsorption 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 (Tan and Hameed, 2010). 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 renewable (Okewale, et al, 2011). The present study was carried out to evaluate the potentiality of starch based adsorbents to dehydrate ethanol – water mixtures. The adsorption process data were analyzed to study adsorption isotherms, and kinetics of starch – based adsorbents on adsorption of water from ethanol – water systems. The experimental data were obtained at 30°C.

The starch – based materials derived from cassava such as; adsorbent cassava starch (CS), adsorbent cassava pellet (CP), adsorbent cassava shred (AB), and adsorbent modified starch (MS) were used for the adsorption of water from ethanol – water mixtures.

Materials and Methods

Cassava starch, cassava pellet, and cassava shred were purchased from the market, sun –dried and thermally treated in an oven at 105°C for 16hours and thereafter classified into a particle size of 2.5mm. For modified starch preparation method of (Ogungbenle, 2007) was used.

The ethanol –water solutions are prepared at the required mass concentrations (concentration of 90wt% ethanol). Analytical grade of ethanol was procured 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.

Experimental Procedure

Adsorption equilibrium was carried out to obtain the equilibrium isotherms using static method. 250ml Erlenmeyer flasks were used where 150g of ethanol – water solutions with initial concentrations of (10 – 50%) ethanol were placed in these flasks. 5g of each of the prepared adsorbents with particle size of 2.5mm was added to each flask and kept in a thermostated water bath with an accuracy of ±0.1 at 30°C for 2hours in the laboratory to reach equilibrium. For the kinetics test aqueous samples were taken from the 90wt% concentration of ethanol-water mixtures that circulates 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;

$$q_e = \frac{M_l}{M_A}\left(\frac{C_{f-}\ C_l}{C_f}\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.0)$$

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). (Mya, 2011). The equilibrium data were then fitted with three different adsorption isotherms models, namely; Freundlich, Temkin, and Langmuir models. The kinetics data were fitted using the second order, pseudo-second order, Intra-particle diffusion, and Boyd models.

Results and Discussion

Adsorption isotherms

Adsorption isotherm study was carried out on three adsorption isotherm models, namely, the Temkin, Freundlich, and Langmuir models. The applicability of these isotherms equation to describe the adsorption process was adjudged by the correlation co-efficients, R^2 values.

For the Freundlich isotherm, the plot of $logq_e$ against $logC_e$ gives a straight line with slope of 1/n and intercept of $logK_f$. The plot of q_e against lnC_e for the Temkin isotherm gives a straight line with slope of B and intercept of (BlnA). For Langmuir isotherm, the plot of C_e/q_e against C_e gives a straight line with slope of 1/Qo and intercepts $1/Q_oK_L$ (Tan and Hameed, 2010). Table 1.0 showed the three isotherm models used, together with all the constants and R^2 values obtained from each plot. The Langmuir gave the best fit with R^2, (co-efficient of correlation) value equal or higher than 0.949 as compared to the other models.

With the experimental data conforming into Langmuir isotherm revealed the homogeneity nature of starch- based adsorbents surface i.e. each ethanol – water mixtures molecules/starch – based adsorption had equal adsorption energy of activation. The results also indicated the formation of monolayer coverage of ethanol – water molecules at the surface of the starch – based adsorbents. Similar observations were reported by the adsorption of MB on activated carbons prepared from olive – seed waste residue (Stavropoulos and Zabaniotu, 2005). The modified starch adsorbent had the highest adsorption capacity compared to other starch – based adsorbents. Temkin isotherm constant B gives an idea of the heat of adsorption which is positive for all the starch – based adsorbents for water uptake from ethanol – water mixtures.

Adsorption Kinetics

The constant rate of adsorption was determined from second order, and pseudo-second order equations. The Pseudo-second order equation given by (Ho and Mckay, 2000);

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

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.

Second Order Equation

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

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

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

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 (Zawani, et al, 2009). The constants and R^2 values obtained were summarized in table 2.0. It was found that for second order equation, the R^2 values were relatively high as compared to the pseudo-second order equation. It was observed that there was an agreement between the experimental results of the equilibrium adsorption value as depicted in the correlation co-efficient (R^2) values. The data also conform to the pseudo-second order equation as well. The R^2 values obtained for the pseudo-second order model suggested the applicability of the pseudo-second order kinetic model to describe the adsorption process of water uptake on the starch-based adsorbents. This indicates that the overall rate of the adsorption process was controlled by chemisorption which involved valency forces through sharing or exchange of electrons between the sorbent and the sorbate (Ho and McKay, 1999).

Adsorption Mechanism

The adsorption mechanism was investigated using the intra-particle diffusion model and Boyd kinetics model.

Intra – particle diffusion model

Intra-particle diffusion model empirically noted that most common functional relationship to adsorption process where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time, t, according to this theory;

$$q_t = K_{id} t^{1/2} \text{...} (5)$$

The logarithmic form of the above equation is;

$$\log q_t = \log K_{id} + 0.5 \log t \text{...} (6)$$

where k_{id} is the intra-particle diffusion rate constant obtain from the intercept. According to Equation (6), a plot of $\log q_t$ versus $0.5 \log t$ should yield a straight line with a positive intercept for intra particle diffusion controlled adsorption process. The intercept gives an idea of the thickness of the boundary layer i.e. the larger the intercept, the greater the boundary layer effect (Tan and Hameed, 2010).

It can be seen from the small value of the intra-particle diffusion constant that the boundary layer has less significant effect about the diffusion mechanism of water uptake on the starch-based adsorbents. The deviation of figs.5.0 and 6.0 from the origin might be due to the difference in the mass transfer rate in the initial and final stages of adsorption (Mohanty, et al, 2005).

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.

$B_t = -0.4977 - \ln(1 - F)$ ……………………………………………………………. (7)

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 (Tan and Hameed, 2010). The plot of

B_t against time (min) as shown in Figs.7 and 8 revealed that the deviation of the water uptake from ethanol – water system on the starch – based adsorbents from the origin as depicted by the plots showed that the adsorption mechanism was governed by external mass transport where particle diffusion is the rate limiting step. It can also be adjudged from the R^2 values of the two kinetics models that intra-particle diffusion model best correlated the adsorption mechanism of ethanol – water mixtures on these adsorbents studied.

Conclusion

Adsorption isotherms and kinetics of starch-based adsorbents on uptake of water from ethanol-water systems was investigated.

The adsorption equilibrium data were fitted to Freundlich, Langmuir, and Temkin isotherms and the equilibrium data fitted well to Langmuir isotherm model, with the maximum monolayer adsorption capacity of 4.44, 5.75, 6.41, and 7.09 g/g for AB, CP, CS, and MS respectively at 30°C. The kinetic model was found to follow second order model compared to pseudo-second order model as evident in their (R^2) values. 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 that the intra-particle diffusion model played an important role as the limiting step in water uptake from ethanol-water systems studied. Modified starch had the highest monolayer adsorption capacity as compared to other adsorbents studied.

Table 1.0 Summary Results of Isotherms Model

Adsorption parameters	MS	CS	CP	AB
Langmuir $C_e/q_e = 1/Q_oK_L + (C_e)1/Q_o$ R^2	0.949	0.966	0.926	0.994
Q_o	7.09	6.41	5.75	4.44
K_L	4.55	4.88	7.25	5.00
Freundlich $\log q_e = \log K_F + (1/n)\log C_e$ R^2	0.866	0.946	0.960	0.953
n	0.92	1.05	1.45	1.93
K_F	0.826	0.772	0.719	0.225
Temkin $q_e = B\ln A + B\ln C_e$ R^2	0.872	0.993	0.945	0.951
A	1.43	1.38	1.59	1.07
B	13.80	11.75	7.52	10.93

Table 2.0 Summary Results of Kinetics Model

Kinetic parameters	MS	CS	CP	AB
Second Order, R^2	0.825	0.954	0.951	0.991
K_2, (ml/min)	1.504	0.99	0.347	0.211
Pseudo – Second order, R^2	0.955	0.892	0.910	0.972
K_2 (ml/min)	0.00579	0.00288	0.0034	0.01
Intra-particle diffusion, R^2	0.968	0.974	0.986	0.982
K_{id}	0.504	0.284	0.284	0.215
Boyd model, R^2	0.877	0.870	0.995	0.960
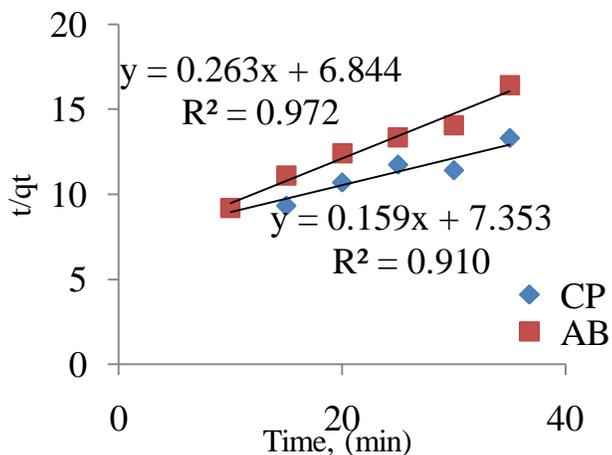
Fig. 1.0 Pseudo-second order plot for uptake of water from ethanol-watermixture using CP andAB
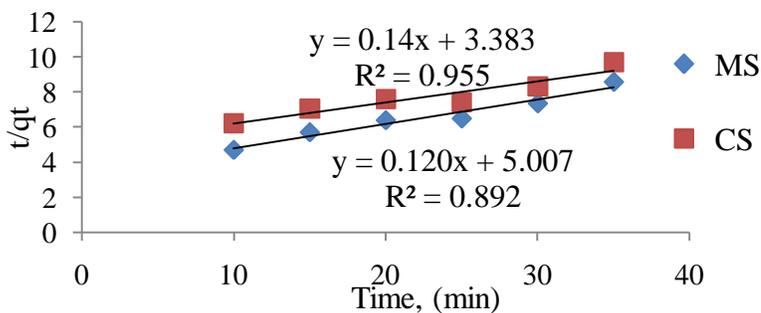
Fig. 2.0 Pseudo-second order plot for uptake of water from ethanol-water mixture using MS and CS
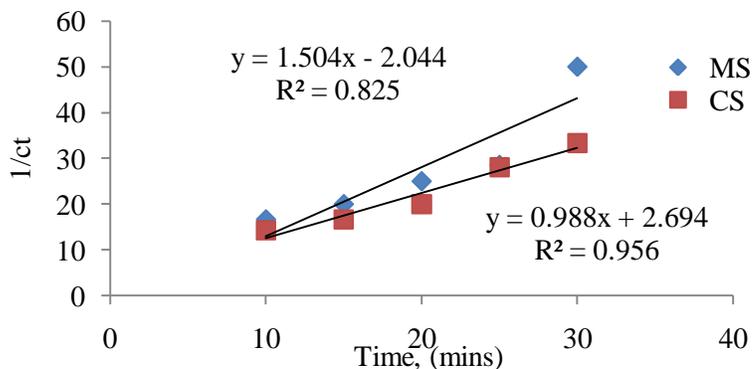
Fig. 3.0 Second order plot for uptake of water from ethanol-water mixture using MS and CS
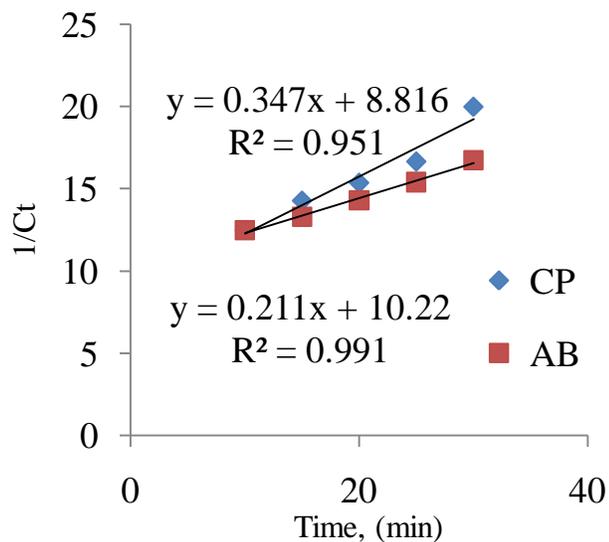
Fig. 4.0 Second order plot for uptake of water from ethanol-water mixture using CP and AB
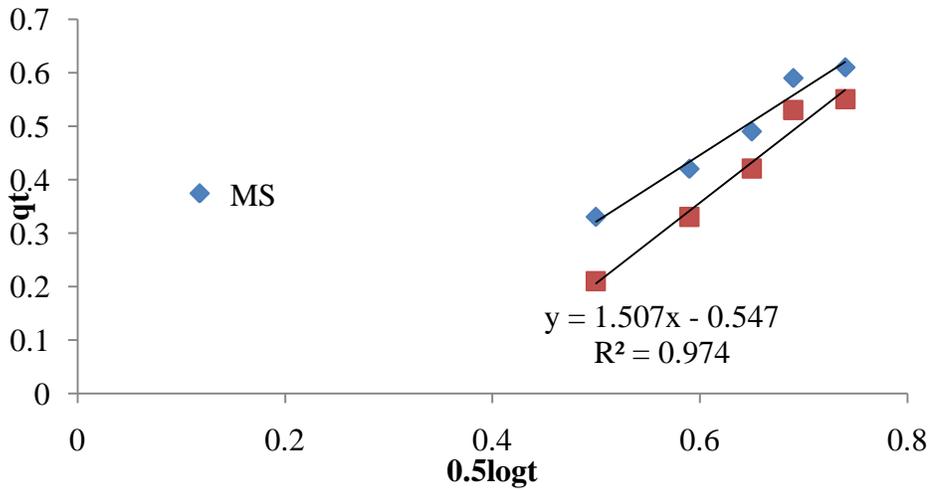
Fig. 5.0 Intraparticle diffusion model for uptake of water from ethanol-water mixtures using MS and CS
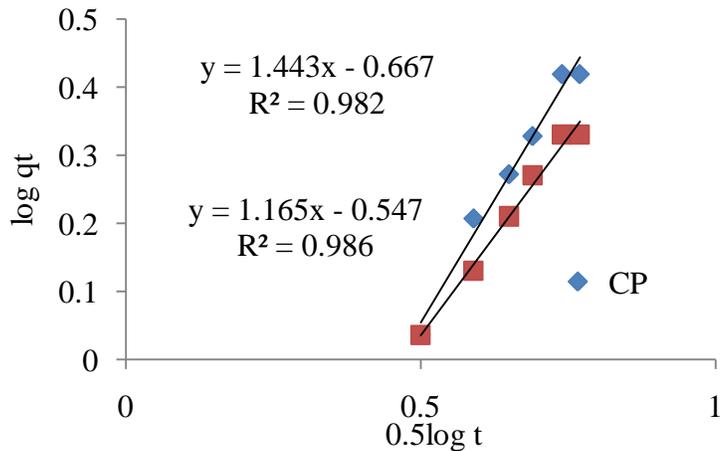
Fig. 6.0 Intraparticle diffusion model for uptake of water from ethanol water mixtures using CP and AB
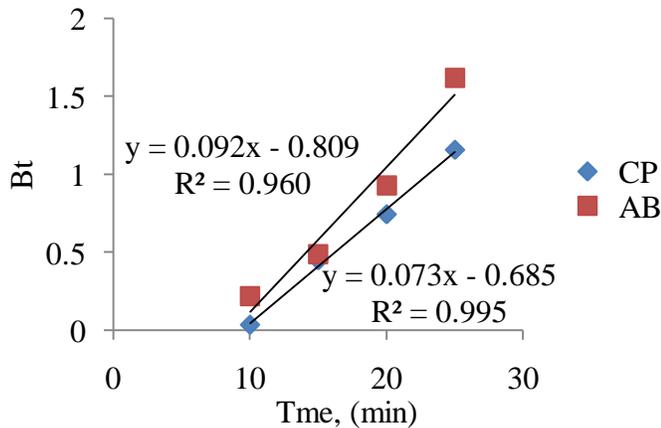
Fig. 7.0 Boyd diffusion plot for uptake of water from ethanol-watermixture using CP and AB
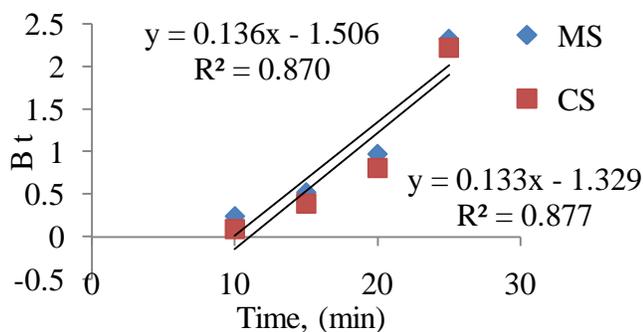
Fig. 8.0 Boyd plot for uptake of water from ethanol-water mixture using MS and CS

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