Full Paper

EVALUATION OF SAWDUST AND SUGARCANE AS MOLECULAR SIEVE IN ADSORPTIVE CONCENTRATION OF AQUEOUS ETHANOL

E. A. Taiwo
*Department of Chemical Engineering,
Obafemi Awolowo University, Ile-Ife*
etaiwo@oauife.edu.ng

O. Adeodu
*Department of Chemical Engineering,
Obafemi Awolowo University, Ile-Ife*

ABSTRACT

Availability of ethanol in its absolute form is required for its use as automobile fuel additive. Purification of aqueous ethanol by conventional distillation is energy intensive with attendant difficulty of azeotrope formation. Effectiveness of dehydration of the aqueous ethanol mixtures past the azeotropic point by adsorption using hardwood sawdust and sugarcane fibre as adsorbents was therefore investigated in this study. Batch liquid-phase experiments were performed with both adsorbents at 10°C. Equilibrium data obtained from the experiments was fitted to Freundlich relation, Langmuir and BET correlation. Both the Langmuir and infinite form of the BET equilibrium theories were used to estimate the surface areas of the adsorbents. Sawdust preferentially adsorbed water from aqueous ethanol mixture while Sugarcane fibre relatively adsorbed ethanol from the mixtures. For the sawdust adsorbent, an improved ethanol concentration was obtained with increased concentration of ethanol in the feed as well as increased adsorbent to aqueous ethanol ratio. The experimental data fitted well into the Freundlich expression with an adsorption isotherm constant 'n' value of 1.3. However, BET and Langmuir gave a better fit with correlation coefficients of 0.9932 and 0.9978 respectively. Active surface area of adsorbent estimated using Langmuir and BET theories were 3.6339 x 10^6 and 3.3126 x 10^6 m^{2}kg^{-1}, respectively.

1. INTRODUCTION

World energy demand increased sharply over the last decade due to the recent heavy industrialization of populous countries like China and India. Nigeria energy sector depends heavily on petroleum fuel, especially, for transportation and electricity generation. To supplement the energy source, sustainable augmentation is required. This drives attention to renewable ones which will equally alleviate the attendant pollution problems. Ethanol, which is a popular alternative, presents several advantages over other fuels. As a renewable fuel, ethanol used in fuel-cell vehicles (Mattos and Noronha, 2005) or for stationary power plants generates far fewer greenhouse gases than conventional fuels such as gasoline or natural gas, since the CO_2 produced in the process is consumed in crop growths (Bentley and Derby, 2002, Duke 2003). The plan of NNPC to develop bioethanol in 10% blend with Premium Motor Spirit (PMS) as a first goal, would extend the life span of Nigeria's proven oil reserves of 36 billion barrels (CIA, 2006) appreciably.

Primarily, ethanol is produced on a commercial scale by the fermentation of sugar obtained from some local biomass: cassava in Nigeria, sugarcane in Brazil and corn in the United States. The fermentation product is quite dilute, containing about 10wt% ethanol. The high purity of ethanol requirement (greater than 99.5%) for automobile use is a dilemma (Adnadevic et. al., 2008). Distillation can only remove water from aqueous ethanol to a maximum ethanol concentration of 95%wt which is the azeotropic point of ethanol/water mixture. This is then followed by azeotropic distillation. Even, when distillation is used to obtain dehydrated ethanol, 50% of the total energy is consumed during this process (Carmo and Gubulin 1997). Thus, energy consumption problem in the process of dehydration of aqueous ethanol solutions obtained from fermentation broths is left to be solved. Also, the use of benzene as mass separation agent in azeotropic distillation makes the process not environmentally friendly. Selective adsorption onto zeolitic materials as an alternative to dehydration via distillation, is presently the most promising procedure for anhydrous ethanol production (Einicke et. al, 1995; Einicke, et. al., 2004; Bugaje and Muhammed, 2007). Adsorption of alcohols such as methanol (Badlani and Wachs, 2001) and ethanol (Benson, 2003) on the metal oxides surface occurs through an alkoxide species formed from the scission of the O–H bond.

The use of molecular sieves has grown quite rapidly mainly because sieves can be tailor-made to retain a specific adsorbate from a mixture. Regeneration characteristics were also impressive albeit at high temperatures. However, the relatively high manufacturing and regeneration costs of molecular sieves drove the need for investigation into cheaper adsorbents. The high density of hydroxyl groups present in both cellulosic and starchy biomass could enhance their water retaining capacity hence, the efficacy of local cellulosic biomass as adsorbent to dehydrate ethanol is investigated in this study towards enhancing the overall economy of bioethanol production.

2. THEORY

Adsorption occurs primarily on the walls of the pores or specific sites in the particle. The differences in the size, shape and polarity of species in the fluid mixture results into preferential adherent of some molecules (adsorbing species) on these sites. Adsorption isotherm, which is the relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at equilibrium, can be used to assess the feasibility of adsorption operation for specific separation at a known temperature. In other words, the rate of adsorption is proportional to the adsorbate fluid concentration and the fraction of unoccupied space on the solid. The equation for liquid adsorption (Richardson et. al., 2002) is given as

$$\frac{C}{V} = \frac{C}{V_m} + \frac{1}{BV_m}$$

(1)

where,

C = solute concentration in liquid,

V = volume of solute adsorbed,

V_m = volume of solute in a monolayer spread over the adsorbent surface,

B = constant.

Equation (1) is Langmuir correlation. A system is described adequately by the Langmuir theory if a plot of (C/V) versus C gives a straight line. While Langmuir assumes a single layer of molecules, the theory developed by Brunauer *et. al.*, (1938) extended the Langmuir theory to a multilayer adsorption, built on different parts of the solid surface, with no interaction between each adsorption layer. The amount of surface associated with a particular thickness (monolayer, bilayer, etc.) is however constant. Richardson *et. al.*, (2002) detailed the mathematical derivation of the relation which can be adapted to liquid adsorption as

$$\frac{V}{V^1} = B_2 C \frac{1-(n+1)C^n + nC^{n+1}}{(1-C)[1-(B_2-1)C - B_2 C^{n+1}]} \qquad (2)$$

where,

V = volume of solute adsorbed per unit adsorbent mass

V^1 = volume adsorbed contained in a monolayer spread over the surface

n = maximum number of adsorbate layers formed

B_2 = constant

C = initial concentration of the liquid phase

When n = 1, Equation (2) reduces to the Langmuir correlation, that is, Equation (1), but when n = ∞, Equation (2) is expressed linearly as

$$\frac{C}{V(1-C)} = \frac{1}{V^1 B_2} + \frac{B_2 - 1}{V^1 B_2} C \qquad (3)$$

Equation (3) is an infinite form of the BET equation for dilute solute concentrations. A plot of the left hand term against C gives a straight line from which V^1 and hence active surface area can be calculated.

The empirical equilibrium relationship for liquid adsorption proposed by Freundlich (1926) is expressed as

$$C_s = \alpha (C^*)^n \qquad (4)$$

where,

C_s = mass of solute adsorbed per unit adsorbent mass

C^* = equilibrium concentration of solute in solution

α and n are constants.

The expression has been shown to be quite accurate for dilute solutions. A logarithmic plot of C_s versus C^* gives a straight line from which α and n can be determined.

3. METHODOLOGY

The hardwood sawdust, and sugarcane fibre adsorbents studied were obtained locally in Ile-Ife. Sawdust was collected from the local sawmill industry while sugarcane fibre were obtained from the willd.

3.1. Adsorbent Pretreatment

Both the hardwood sawdust and sugarcane fibre were sundried, ground, sifted and clarified in a pretreatment process. These adsorbents were sifted first in a 40-mesh (0.0130 mm opening) screen to remove fine particles of material that might swell during operation. A 10-mesh (1.651 mm opening) screen was then used to filter out large particles. The adsorbents were then clarified in a pretreatment process

to remove any impurities that may reside on the surfaces of the adsorbent particles. In pretreating the samples, 25 g of material were placed into a 500 ml Erlenmeyer flask, and enough distilled water added, to fill the flask to 500 ml. The mixture was stirred, the impurities were allowed to leach into the water medium and then drained. The washing was repeated several times until clear water was obtained. Then the adsorbent was oven dried at 90°C, chosen to keep the xylan and glucomannan polymers from changing to furfural polymers.

3.2. Determination of True Density

The adsorbent (20.0 g) was weighed and completely immersed in water using an overflow can. The true density was determined using the displaced volume of water by the equation:

$$\rho_{true} = \frac{m_{ads}}{v_{disp}} \qquad (5)$$

where ρ_{true} is the true density, m_{ads} mass of the adsorbent and v_{disp} is the volume of water displaced.

3.3. Equilibrium Data Determination

The equilibrium data were obtained by the static method, which consists of placing inside 125ml flask a specific amount of the adsorbent in contact with specific mass of aqueous ethanol solution of known initial concentration. Several known initial concentrations were used in order to obtain wide range of isotherms at different temperatures. The flasks were maintained at constant temperature in a thermostatically controlled bath (NE2-D model supplied by Jenkon, UK) with an accuracy of ±0.1°C. Fluid phase concentrations were measured and the amount of water adsorbed by the adsorbent were determined by taking a mass balance between the phases, where ethanol was considered as the non-adsorbable component. This is given by the equation (Carmo and Gubulin, 1997)

$$q_x = \left[\frac{w_i - w_e}{w_i} \right] \left(\frac{M_{sol}}{M_{ads}} \right) \qquad (6)$$

where,

q_x is the concentration of adsorbed phase after a specific time,

w_i is initial mass fraction of ethanol in solution

w_e is mass fraction of ethanol in solution at equilibrium

M_{sol} is mass of solution and M_{ads} is mass of adsorbent.

This equation assumes that the adsorbed material is primarily water, not ethanol. This hypothesis is in conjunction with the work of Rebar *et. al.* (1984), in which, the chemical affinity of starch to water was shown to be much greater than that of starch to ethanol. The same is also true for cellulosic materials with their high content of xylans (Benson, 2003).

3.4. Determination of the adsorption capacity

About 5 g of adsorbent sample was added to 50 g aqueous ethanol solution of known concentration in an adsorption vessel placed in the thermostatically controlled water bath (NE2-D model supplied by Jenkon, UK) at a pre-determined temperature. During the adsorption process, the adsorption system was homogenized by stirring at 400 rpm using electric motor-driven stirrer. Samples were taken from this adsorption system at regular time intervals. After centrifugation, the concentration of ethanol remaining in the supernatant was determined by measuring its refractive index using a Reichart-Jung Auto Abbe refractometer. The specific adsorption capacity of adsorbent (x) at a given temperature after certain adsorption period was calculated from the equation:

$$x = \frac{C_O - C}{m}(m_s) \qquad (7)$$

where,

C_o is the initial concentration of the ethanol solution before adsorption (wt%),

C is the concentration of the ethanol solution after a certain adsorption time (wt%),

m_s is the mass of the solution (g),

m is the mass of adsorbent (g).

The adsorption degree of ethanol (α) was calculated from equation:

$$\alpha = \frac{x}{x_{max}} \qquad (8)$$

where,

x_{max} is the maximum specific adsorption capacity of adsorbent for ethanol at a given temperature.

3.5. Determination of active surface area

The active surface area was determined from the plot of Langmuir and BET correlation, using Equations (1) and (3).

4. RESULTS AND DISCUSSION

Fig. 1 shows the particle size distribution of the adsorbents studied. High percentage of both the sugarcane fibre and the sawdust has particle size in the range of 10 and 40 mesh sizes representing 0.013 and 1.651mm diameter. This particle range was used for the adsorption because particles of lower sizes can easily sift away. Thus, if used in column for adsorptive separation, it may result into clogging. This may lead to excessive column flooding which is undesirable for adequate column performance (Black, 1980). Higher particle size adsorbent on the other hand, may inhibit adsorption by reducing the surface area available for mass transfer, and hence, the amount of available adsorption sites.
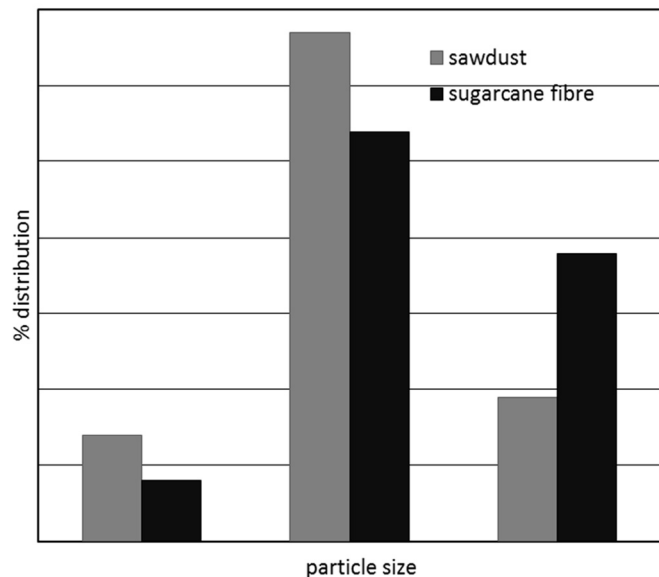

Figure 1: Particle size distribution for the adsorbents

The measured true density of sawdust and sugarcane adsorbents was 0.218 and 0.132 gcm⁻³ respectively. Thus, sawdust adsorbent having higher true density is expected to be more suitable adsorbent. It would provide a greater intimate contact since a more compact arrangement of the particles would be achieved inside the adsorption column. Greater surface area per unit volume would therefore be provided for adsorption to take place. The physical properties of the solvents (ethanol and water) used are reported in Table 1.

Table 1. Physical Properties of Ethanol and Water

Property	Ethanol	Water
Molecular Formula	CH_3CH_2OH	H_2O
Molecular Weight	46.07	18.016
Specific Gravity	0.789	1.00
Melting Point(°C)	-112 0	0
Boiling Point(°C)	78.4	100
Solubility	∞ (in water)	

The preliminary adsorption experiments showed that sawdust adsorbed water from the aqueous ethanol solution, while sugarcane showed no significant adsorption for aqueous ethanol system. Adsorption capacity of 0.00022 g H_2O/g adsorbent was observed as the highest capacity for sugar cane fibre. Thus, sugarcane fiber was not experimented further. The equilibrium adsorption isotherms for the ethanol-water/ sawdust system at the temperatures of 30, 40, 50 and 60 °C are reported in Fig. 2. It is noticeable from this figure that its adsorption capacity decreased with increasing temperature. This might be due to increased kinetic and vibrational energy of the molecules with temperature, rendering only small net fraction of the molecules available for adsorption at equilibrium. At increased temperature, equilibrium shifts towards region unfavorable for adsorption due to exothermic character of adsorption process. The horizontal plateau zone in Fig. 2 represents the adsorbing capacity of the adsorbent at the varying temperatures.
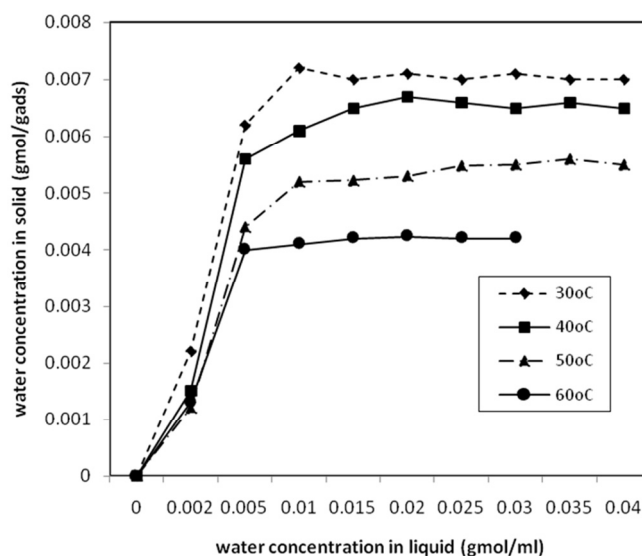

Figure 2: Equilibrium adsorption isotherms for the ethanol-water system on sawdust adsorbent

The adsorption capacity increases with increased initial water concentration in the mixture. This increased adsorption capacity with moisture content supports the theory of increasing capacity with increased water content until saturation point whereby no further site is available for adsorption. In this context, the uptake of water by sawdust adsorbent as the water concentration in the ethanol/ water mixture increases from 1 to 10 wt% reflected progressive water molecules uptake by hydroxyl group adsorption sites as the number of water molecules per unit volume increases. This increase in the concentration gradient leads to a significantly higher driving force. The cellulosic adsorbent has lignin, xylans and glucans. These polysaccharides, and the lignin, contain abundance of hydroxyl groups for the attachment of the water molecules. Thus the ligno-cellulosic substance offers the structural basis for adhesion to the cellulosic mass.

Investigation of the variation of concentration by adsorption using sawdust shows a progressive increase in concentration over time (Fig. 3). At about 120 – 200 mins, the concentration gradient (slope of curves) dropped indicating saturation zone. Above this point, no further adsorption takes place hence the maximum capacity of the adsorbent. This zone increases with decreasing concentration of

water content in the feed mixture. Fig. 3 also shows a dependence of final concentration on the initial feed concentration. At a feed concentration of 94 % ethanol by mass, an almost absolute ethanol was obtained. This significantly reflects purification pass the azeotropic point. Thus, by successive adsorption runs, absolute ethanol could be obtained using sawdust as adsorbent. As water moves from ethanol-water solution and adheres to the adsorbent particles, the thermodynamics of ethanol-water system is altered which in turn, modify the azeotropic situation resulting to breakage of the azeotropic tie between water and ethanol molecules.
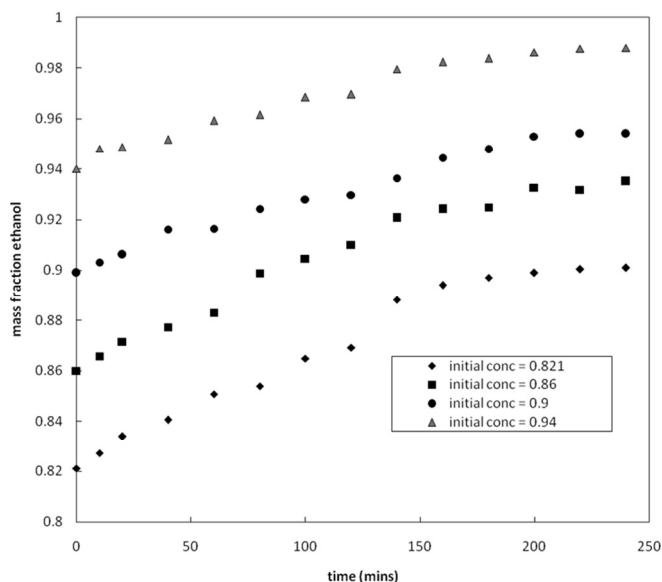

Figure 3: Adsorption characteristics of sawdust at varying ethanol concentration

The adsorption equilibrium data for sawdust adsorbent was fitted to the empirical Freundlich relation (Equation 4) in the MATLAB environment. The graph of logarithmic plot of Cs versus *C** is shown in Fig. 4. The values of n and α were calculated from the slope and intercept and were found to be 1.3 and 26.3755, respectively. Since n is a measure of performance of adsorbent, the value obtained, coupled with the correlation coefficient value, $R2$ of 0.8930 suggests that dehydration of ethanol using sawdust as adsorbent is favorable, but there is need to improve upon the adsorbent to produce higher capacity for industrial application.
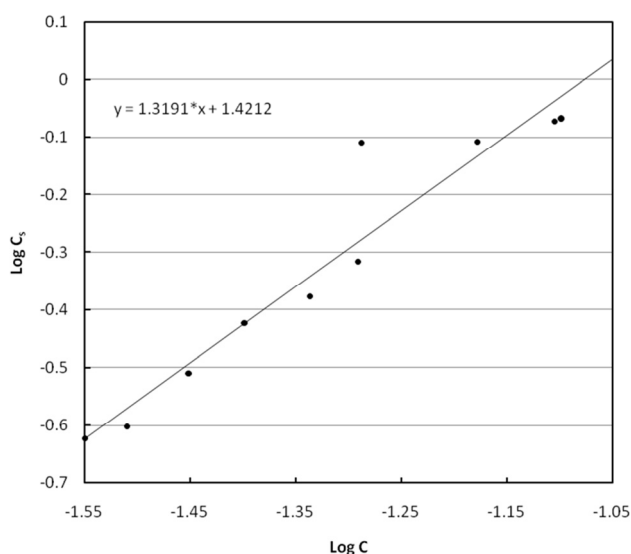

Figure 4: Freundlich correlation for sawdust adsorbent

By fitting the equilibrium data to a linear form of Langmuir and BET correlations represented by Equations (1) and (3), respectively,

good correlation having correlation coefficients 'R^2' values of 0.9978 and 0.9932 for Langmuir and BET correlations respectively were obtained (Fig. 5). These values reflect a nearly homogeneous sorbent surface with a monolayer spread of adsorbed solute. An estimated volume of adsorbed solute contained in a monolayer spread over the homogeneous adsorbent surface was in the range 1.6505 and 1.8083 cm^3/g. Similarly, the active surface area in the range of 3.6339 x 10^6 and 3.3126 x 10^6 m^2kg^{-1} were obtained from the slope and intercept of plot.
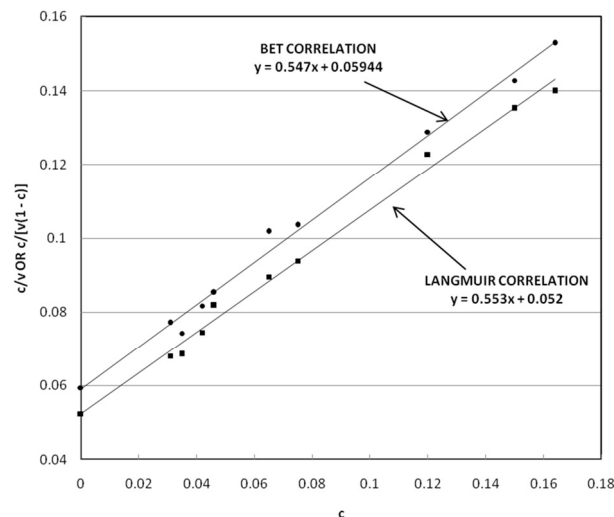

Figure 5: Langmuir and BET correlations for sawdust adsorbent

5. CONCLUSION

Sawdust preferentially adsorbs water from aqueous ethanol mixture and would be a good adsorbent for the purification of aqueous ethanol pass the azeotropic point with little or no energy consumption. This is of significance to ethanol/ biofuel production and national economy.

Adsorption capacity of the sawdust adsorbent is as high as 0.007gmol H_2O/g of adsorbent and decreases with increasing temperature. The active surface area fell between 3.6339 x 10^6 and 3.3126 x 10^6 m^2kg^{-1} with monolayer spread volume of 1.6505 and 1.8083 cm^3/g for the adsorbed solute.

REFERENCES

Adnadevic B.; Mojovic Z. and Abu-Rabi A. " The kinetics of ethanol adsorption from the aqueous phase onto zeolite NaZSM-5" Adsorption. 14:123-131. 2008

Badlani, M. and I. Wachs I. "Adsorption of methanol and methoxy on α-CrO(0001) surface Catal. Lett. 75, 137-139. 2001.

Benson T. J. "Dehydration of an ethanol-water mixture using lignocellulosic based Adsorbents", Unpublished M.Sc thesis, Dave Swalm School of Engineering, Mississippi State University. 2003.

Bentley, J. and Derby, R. "Ethanol and Fuel Cells: Converging Paths of Opportunity" Report for the Renewable Fuels Association, 2002.

Black C. "Distillation Modeling of Ethanol Recovery and Dehydration Processes for Ethanol and gasohol". Chemical Engineering Progress. 1980

Brunauer, S., Emmett, P.H. and Teller, E. "Adsorption of gases in multimolecular layers", Journal of American Chemistry. 60, 309 -314 , 1938

Bugaje I. M. and Muhammed I. A. "Biofuels as Petroluem extenders: Prospects and challenges in Nigeria". Petroleum Training Journal,4(1), 11-21, 2007

Carmo M. J. and Gubulin J. C. "Ethanol-Water Adsorption on commercial 3A zeolites: Kinetic and Thermodynamic data". Brazilian Journal of Chemical Engineering. 14(3), 1-12. 1997

CIA (2006) World Fact Book, available at http://www.cia.gov/cia/publications/factbook/nigeria. (Accessed in 3rd March 2008).

Duke J. S. "Burning Buried sunshine: Human consumption of ancient solar energy". Climatic Change, 61. 31-44. 2003.

Einicke W. D.; Gläser B.; Lippert R. and Heuchel M. "Liquid-phase adsorption of ethanol–water mixtures on NaZSM-5 zeolite with inorganic and organic binders". J. Chem. Soc. Faraday Trans. **91**(5), 971–974. 1995

Einicke W. D., Gläser B. and Schöllner R. "In-situ recovery of ethanol from fermentation broth by hydrophobic adsorbents". Acta Biotechnol. **12**(4), 353–358. 2004

Freundlich H. "Colloid and Capillary Chemistry". Methuen, London. 1926

Mattos, L.V. and Noronha F.B. "Hydrogen production for fuel cell applications by ethanol partial oxidation on Pt/CeO2 catalysts: the effect of the reaction conditions and reaction mechanism". Journal of Catalysis. 233, 453–463. 2005

Rebar V., Fischbach E. R., Apostolopoulos D., and Kikini J. L. "Thermodynamics of Water and Ethanol Adsorption on Four Starches as Model Biomass Separation Systems," Biotechnology and Bioengineering, Vol. XXVI, 513 – 517. 1984.

Richardson J. F., Harker J. H. and Backhurst J. R. "Particle Technology and Separation Processes' 5th ed. Elsevier, New Delhi, pp.979-986. 2002.