STUDY OF THE DRYING OF ETHANOL USING ZEOLITE MOLECULAR SIEVES

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ABSTRACT

Anhydrous alcohol was obtained by passing industrial alcohol (95% by vol.) over a fixed bed of molecular sieves zeolite 3A and the effluent concentration was measured with time. Breakthrough curves and adsorption isotherms were determined and analyzed according to the Langmuir and Freundlch's equations. The effect of flow rates (3 and 6) cm^3/min and bed depth (25 and 56)cm. were also studied.

INTRODUCTION

Ethanol or ethyl alcohol, CH_3CH_2OH, a colorless liquid with characteristic odor and taste; commonly called grain alcohol or simply alcohol. It is used in coatings as carrier liquid, if a fast drying process is required and no drying oven for the drying of water base products is available. In addition, ethanol is used if other constituents of the coatings may react with water and form hydrates like aluminum nitride. It is preferred to other solvents such as 2-Propanol (isopropyl alcohol) due to the more favorable exposure limits.

Ethanol is miscible with water in all proportions and is separated from water only with difficulty; ethanol that is completely free of water is called absolute ethanol. It forms a constant-boiling mixture, or azeotrope, with water containing 95% ethanol, with a boiling point below that of pure ethanol, so absolute ethanol cannot be obtained by simple distillation.

Formerly, anhydrous alcohol was made by using quick lime to absorb the remaining water. This process was expensive and had been suspended [2]. However, if benzene is added to 95% ethanol, a ternary azeotrope of benzene, ethanol, and water, with boiling point 64.9°C, can form; since the proportion of water to ethanol in this azeotrope is greater than that in 95% ethanol, the water can be removed from 95% ethanol by adding benzene and distilling off this azeotrope. Because small amounts of benzene may remain, absolute ethanol prepared by this process is poisonous [1,8]. Molecular sieves are an excellent alternative for drying ethanol to very low moisture levels[3,10]. Zeolites were considered as rigid, crystalline sponges capable of imbibing large amount of the right shapes, but unable to sorb molecules having wrong sizes or shapes, for this, they were termed molecular sieves [4]. The zeolite family adsorbents are selective and of high capacity because they separate molecules based upon size and configuration. So that, separation can be achieved according to molecular- size differences [5,6]. They have high affinity for water and other polar molecules (e.g. NH_3, H_2S, SO_2, and CO_2), therefore they can be used for general drying[7]. Zeolite 3A (potassium exchanged zeolite A) has window size of about 0.29 nm which is large enough for water molecules (0.26 nm) to pass into crystal cavities, while ethanol has a molecular diameter of 0.45 nm and hence, excluded from the crystal cavities [9]. The process of ethanol drying can be carried out in two ways:

1. Drying of vaporized ethanol –water mixture.
2. Drying of liquid streams of ethanol – water mixture.

Union Carbide company (which has long experience in this field since 1956) had operated an adsorptive heat recovery drying system (AHR) which enables much of the heat released on adsorption to be retained by the adsorbent bed thus enabling the stored heat to be utilized for the regeneration step of the cycle. In this process, two adsorbent beds are employed each acting alternately as an adsorber or regenerator. The feed is first superhea ted sufficiently to prevent liquid formation within the adsorber and the capillary condensation in the adsorbent pore structure. The time required to complete the adsorption step is typically 10 to 60 minutes, which is much shorter than the conventional thermal swing process. Regeneration is achieved within a closed loop utilizing a non condensable gas such as N_2 , CO_2 or natural gas.

The drying of liquid streams[9,11] is also accomplished using two packed beds. The velocity through the bed should not exceed 7.5 cm/s according to the recommendation of the adsorbent manufacturers W.R.Grace and the company. Cycle period for the adsorption stage is not less than 24 hours so that the energy required for heating and cooling the beds and associated vessels and piping is minimized. Hot carbon dioxide or natural gas ,may be used for regeneration[9].

EXPERIMENTAL WORK

Materials Used

Technical local solution of 95% of ethanol, and imported type of zeolite 3A (Fluka AG,Union Carbide 1/8 inch pellets) was used during this study.

Experimental Setup

A bench scale arrangement Fig (1) was used. It consisted of a glass column (0.016 m) internal diameter and Zeolite 3A was placed in. On the top of the column there is a separating funnel and a conical flask was placed on the end of the column for collecting the effluent solution.

Procedure

(i) Effect of flow rate and bed height. these The solution was allowed to pass over the fixed bed of adsorbent by using the separating funnel on the top of the column. The flow rate was carefully adjusted so that to obtain constant flow rates during the cycle. A sample of the effluent solution was withdrawn at different intervals and tested for the concentration of water. The test was based on evaluating the density of the solution, using (Paar precision density meter, DMA 02D). This procedure was employed for two flow rates 3 and 6cm^3/min. Another two experiments were made for bed heights of 25-and56 cm.

(ii) Adsorption equilibrium curve. Different amounts of zeolite (5,10,15,and 25g) were placed individually in a conical flask containing a constant volume (100 cm^3) of the 95% ethanol solution. The flask was set in the oscillator until equilibrium was reached. (constant concentration of solution).After measuring the concentration, the amount adsorbed was estimated by material balance:

$$q_{eq} = V\left(C_o C_{eq}\right)/M \qquad (1)$$

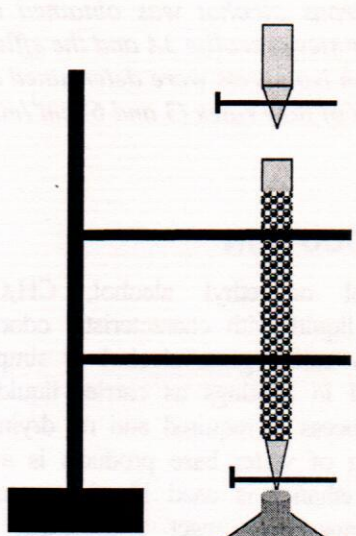

Fig. (1) Schematic diagram for the laboratory arrangement

EXPERIMENTAL WORK

Langmuir and Freundlich Isotherms

The adsorption isotherm for water onto zeolite shown in Fig(2), was found similar to the type (I) classification which is favorable to adsorption among other types and the microporous materials that possess a saturation limit. Zeolites are well known to have such type of isotherms [12,13] and this behavior is attributed to the high affinity for water and other polar materials. The adsorption isotherm (in the present work) had been analyzed according to Langmuir and Freundlich isotherms which are represented by equations (2) and (3). Figure (3) represents the applicability of the Langmuir equation, and Fig (4) represents that the equilibrium data for adsorption are also well correlated to Freundlich equation, but the Langmuir isotherm gives a better fit . The constants for these equations and predicted values in literatures are are listed in Table(1).

$$q_{eq} = QbC_{eq} / (1 + bC_{eq}) \qquad (2)$$

$$q_{eq} = KC_{eq}^{1/n} \qquad (3)$$

Table (1) Langmuir and Freundlich constants for water on zeolite 3A

	Langmuir		Freundlich	
Constants	Q (g/g)	B (cm^3)	K (g/g)	1/n (cm^3/g)
	0.195	91.9	0.3667	0.2708
Predicted values		b>0		n<1
Equations	$q_{eq}=17.921\ C_{eq}/(1+91.9C_{eq})$		$q_{eq}= 0.3667\ C_{eq}^{0.2708}$	
Correlation coefficient	99.46%		98.13%	

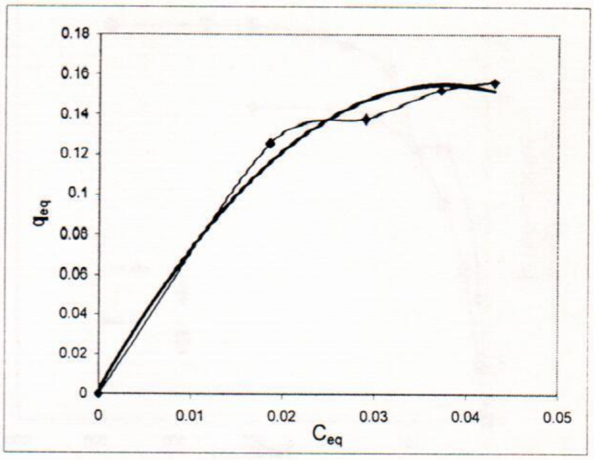

Fig. (2) Adsorption isotherm of water on zeolite 3A

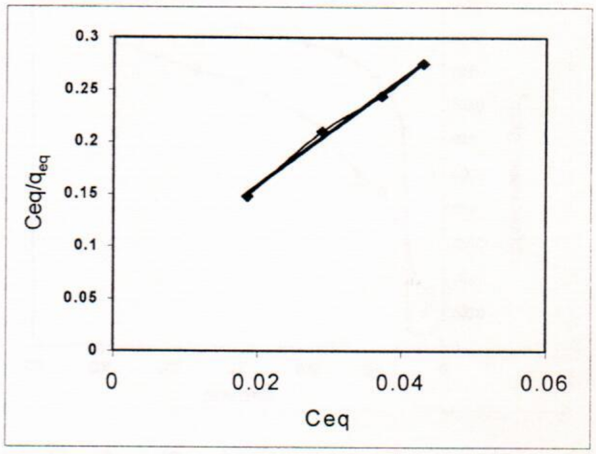

Fig. (3) Determination of Langmiur Constants

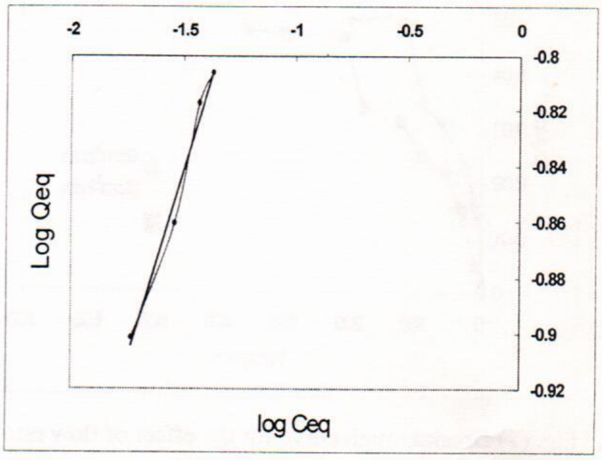

Fig. (4) Determination of Frendlich constants

The Effect of Bed Height

Breakthrough curves indicates that the amount of water adsorbed is increased as the solution of 95 % alcohol passes through the adsorbent and this increase is large in the beginning of the cycle, but as the time increases, the amount adsorbed decreases gradually reaching a constant value, being a characteristic amount for a specific bed height and flow rate of the solution passing through. Fig (5 and 6), shows that the amount of water adsorbed increases with increasing bed height, also the exit concentration decreased as a result of the higher uptake of water .This is due the higher surface area available for adsorption when increasing bed height.

The Effect of Flow Rate

By examining Fig (7 and 8), it is clearly obvious that the rate of adsorption is inversely proportional to the solution flow rate, (i.e.) the amount adsorbed is decreased with increasing flow rate, and the exit concentration will be higher. This can be explained by that there is not enough time for the molecules to diffuse into the pores when the flow rate is high.

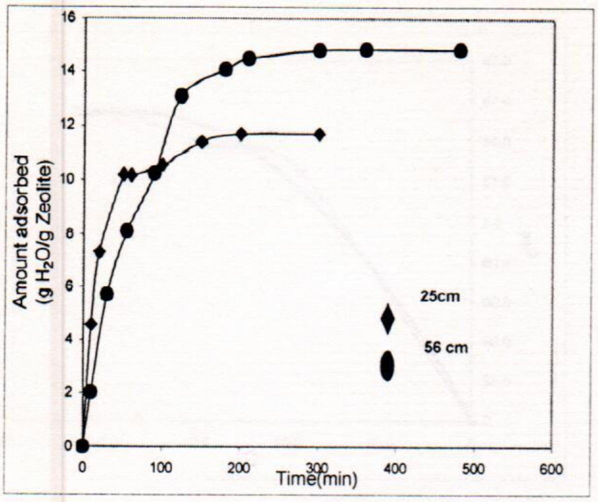

Fig. (5) Breakthrough curves for H2O on zeolite 3A for the bed height effect on the amount adsorbed

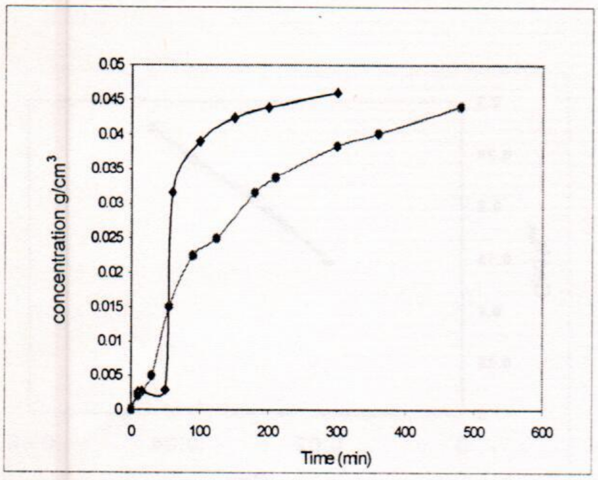

Fig. (6) Breakthrough curve for the effect of bed height on the exit concentration

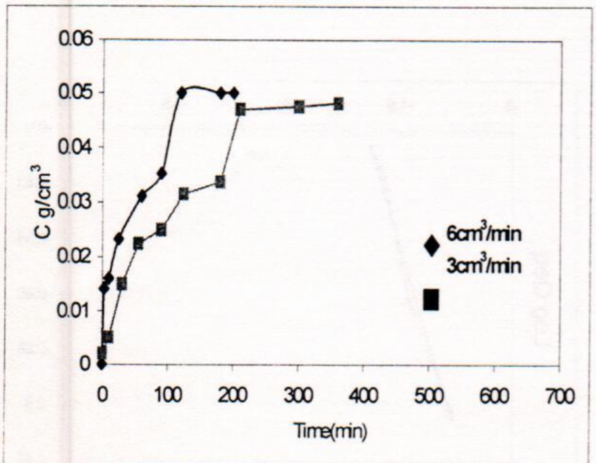

Fig. (7) Breakthrough curve for the effect of flow rate on the exit concentration

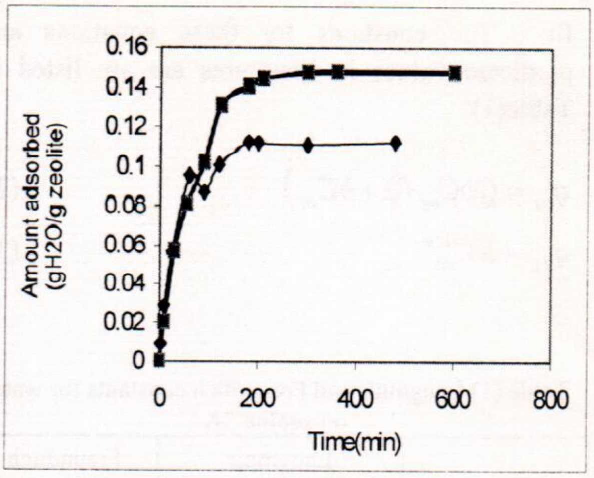

Fig. (8) Effect of the flow rate on the amount adsorbed

CONCLUSIONS

1. The adsorption isotherm for water on zeolite 3A is of type (I) which is favorable among other types of isotherms and was well represented by Langmuir and Freundlich`s equations.

2. Increasing bed height and decreasing flow rate increases the capacity of the adsorbent and hence, decreases the exit concentration of solution.

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NOMENCLATURE

b	Langmuir equilibrium constant (cm^3/g).
C	Concentration of adsorbent in the liquid phase (g/cm^3)
C_{eq}	Concentration of adsorbent in the liquid phase at equilibrium(g/cm^3).
K	Freundlich equilibrium constant (g/g).
M	mass of zeolite used to evaluate the equilibrium curve (g)
1/n	Freundlich equilibrium parameter (cm^3/g).
Q	The amount of solute adsorbed per unit mass of adsorbent(g/g).
q	Concentration of adsorbate in solid phase(g/g).
q_{eq}	Concentration of adsorbate in solid phase at equilibrium(g/g).

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