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DESIGN OF ADSORPTIVE DISTILLATION FOR SEPARATION OF ETHANOL-WATER AZEOTROPIC MIXTURE USING BIO-BASED ADSORBENTS

FARIBA TADAYON[a,*], FERESHTEH MOTIEE[a], ATENA ERFANI[a] and BABAK RONAGH BAGHBANI[a]

ABSTRACT. Ethanol is an important and commonly used solvent. Anhydrous ethanol is widely used in painting, medicine, cosmetics, perfume and chemical industries. Use of recyclable and cheaper alternatives such as bio-based adsorbents that are composed of cellulose and starch which exhibit strong affinity to water, is already developed as a part of purification and filtration process. A new design of setup for adsorptive distillation was used in this paper to separate water from ethanol due to its low energy consumption. Six raw materials namely sweet potatoes, sticky rice, corn, corn cobs, crystal sugar and date pits were evaluated for their efficiency of ethanol dehydration. Among the biobased adsorbents examined, sweet potato and sticky rice adsorbents due to higher starch consisted of amylopectin gave the best separation of ethanol-water azeotrope. By means of the selective water adsorption that was carried out in a fixed-bed adsorber packed with sticky rice and sweet potato, 99.9% anhydrous ethanol with high efficiency is obtained.

Keywords*: biobased adsorbents, adsorption, adsorptive distillation, azeotrope, ethanol dehydration*

INTRODUCTION

Ethanol is considered as one of the most important organic chemicals in the world. Anhydrous ethanol is widely used in industries, such as pharmaceuticals, organic syntheses, painting, cosmetics, perfumes and it can also be used as an additive to the diesel fuels that helps enhancing the octane number and combustibility of gasoline [1, 30]. Ethanol is produced through the anaerobic fermentation of sugars, which can be obtained from

[a] *Department of Chemistry, North Tehran Branch, Islamic Azad University, Shariati str., Postal Code: 1913674711, Tehran, Iran*
** Corresponding author: Fariba.tadayon@hotmail.com*

a variety of biomass. Production of anhydrous ethanol poses a technological problem, because of the notorious azeotrope formation at 78.15 °C and 1.013 bar, with 4.4% of water that cannot be removed by a normal distillation [2-5].

Various techniques have been developed to break the azeotrope of ethanol and water mixture, such as azeotropic distillation, extractive distillation, pervaporation and adsorptive distillation. In azeotropic and extractive distillation, dehydration is performed in the presence of entrainers such as benzene and ethylene glycol. However benzene, as being a highly carcinogenic substance, is a major health concern.

Furthermore, these distillation methods have a high energy requirement [6-10]. A membrane process known as pervaporation is a separation technology which involves the transition of ethanol through a membrane and it is a cheaper alternative to distillation methods. The disadvantage of pervaporation is low water capacity [11]. However, the energy efficiency can be improved by integrating a common distillation process with a pertinent adsorption system [31]. Among separation methods of azeotrpic mixtures, adsorptive option offers a simple alternative process and due to its energy saving is mainly attractive [12-14]. Low operation costs, high efficiency, as well as a wide variety of selective sorbents make the adsorption method an appealing choice for separation purposes.

The adsorbents used for adsorptive distillation is various, ranging from organic starch [15-18] to inorganic zeolites [19-22]. Dehydration of ethanol using a fixed-bed adsorbents with type A molecular sieves is a well known process [23]. However, molecular sieves are expensive and can only be discarded after being saturated with water, which makes the process uneconomical. Hence, an increasing interest has been focused on the cheaper and recyclable adsorbents. It has been proved that bio-based adsorbents, in particular those composed of cellulose and starch, can adsorb and remove water from alcohol vapors [24-26, 14, 32]. Because of polar attraction between water molecules and the hydroxyl groups on the starch chains, water can adsorb on the adsorbent stronger than ethanol [27, 15, 33].

In addition, The advantages of these starch-based adsorbents in Uptake of water from ethanol-water mixture includes re-use of materials in fermentation, biodegradability, efficiency, relative availability, and cheapness, non-toxic nature and its derivation from renewable sources [34]. Their regeneration also requires less energy [35]. The objective of this work is the development and use of new bio-based desiccants that are able to separate the azeotropic water–ethanol mixture for producing the fuel grade ethanol (>99.9% w/w).

RESULTS AND DISCUSSION

Characterization and structure of bio-based materials

Starch is the principal polysaccharide produced in plants as a way of storing energy. It exists in two forms: amylose and amylopectin. Both are made from α-glucose. Amylose is an unbranched polymer of α-glucose. The molecules coil into a helical structure. It forms a colloidal suspension in hot water. Amylopectin is a branched polymer of α-glucose. It is completely insoluble in water [28]. A major mechanism for the selective adsorption of water is known to be the interaction of water molecules with the hydroxyl groups of the adsorbent. Both kinds of starch chains, amlylose and amylopectin, interact with water molecules in this way. Based on the mechanism of adsorption of water, different functional groups present in bio-adsorbents were evaluated.

It was found, sweet potato has the high proportion of starch (amylose and amylopectin), sticky rice displays amylopectin and corn represents amylose. Corn cobs have hydroxyl and carboxyl, crystal sugar is a single carbohydrate and content of date pits are hydroxyl, fructose, sucrose and D-glucose.

Design of adsorption system

As shown in Figure 1, a fixed-bed adsorber apparatus was designed. This system consisted of a glass tube (column) with an internal diameter of 25 mm and a height of 20 cm. The different natural adsorbents were packed in this tube. The column was sited on a flask within the water bath. A water pump was sited into another water bath that circulates hot water around the glass tube to avoid condensation. A vacuum tee was placed on the graded u tube and the tube was placed on the column and finally in order to suck the vapors, the whole system was connected to a vacuum pump. As soon as vapor was generated from the flask, ethanol-water vapor enters a column which is packed with adsorbent via vacuum pump. Then water molecules start diffusing through the pores of the adsorbent and were adsorbed by adsorbents. The stream coming from the adsorbed was condensed after coming in contact with the cold pipe wall.

The final purified product was taken from the bed once every two minutes and a volume of about 5 ml was collected. The samples were analyzed by gas chromatography. A column packed with GDX-203 was used in a gas chromatography to analyze the composition. Analysis at 120 °C was monitored by a thermal conductivity detector. At the end of the experiment, the adsorbent was removed from the bed and dried for further use. The adsorbents were efficient after 3 cycles of the process.

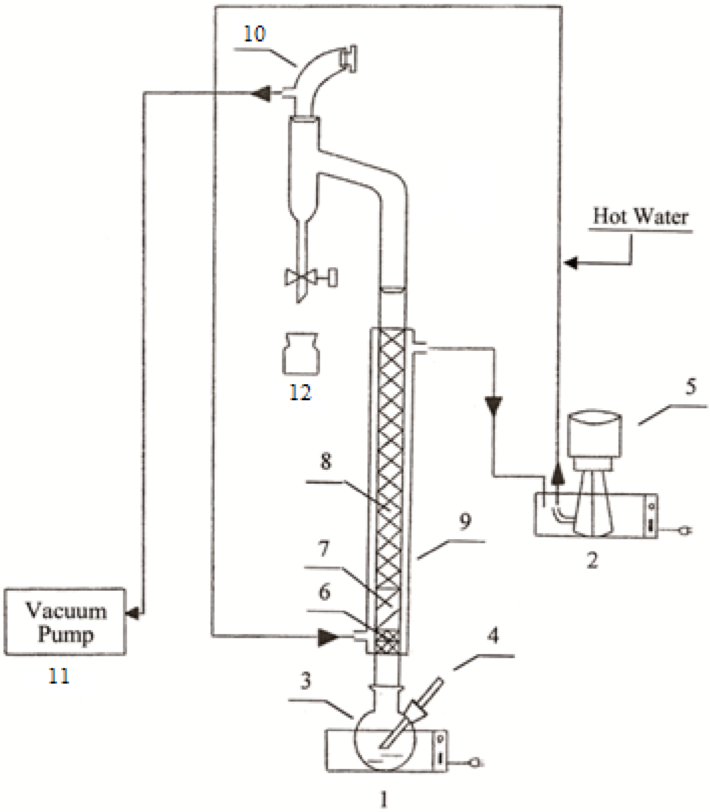

Figure 1. Schematic diagram of fixed-bed adsorption system: (1,2) electric hot plate waterbath; (3) boiling flask; (4) thermocouple; (5) water pump; (6) stainless steel wire guaze; (7) quartz sand; (8) adsorbent; (9) glass tube; (10) vacuum tee; (11) vacuum pump; (12) sample

Initial conditions

The column was filled and packed with 10 g of the different bio-based adsorbents. In this regard, all adsorbents were tested in adsorption experiments under the same condition to select the best materials. The bottom temperature of the tower was 78 °C, fixed-bed temperature 82 °C and feed concentration 96 wt%.

By GC method, the breakthrough curves of six raw materials are illustrated in Figure 2. It can be seen that among the different bio-based adsorbents examined, maximum ethanol concentration was obtained by sweet potato and sticky rice. Thus, sweet potato and sticky rice were chosen as basic materials to achieve the best results.

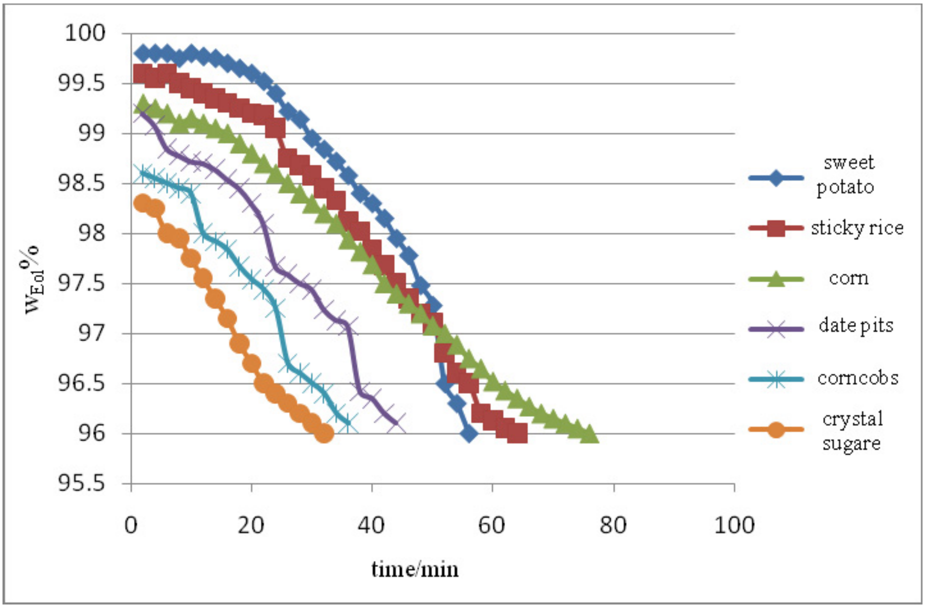

Figure 2. Breakthrough curves of variable natural materials for ethanol/water

The UV-Vis spectrophotometric determination of water content in alcohol was developed based on the color change in the reaction of cobalt (II) chloride ($CoCl_2$) with water [29]. The calibration curve for standard ethanol solutions of $CoCl_2$ *versus* water content is shown in Figure 3.

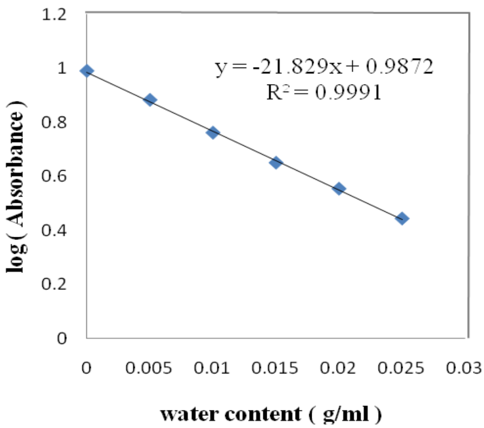

Figure 3. The standard plot of the log(A_{656}) versus water content in ethanol solution containing $CoCl_2$ (9.52×10^{-3} mol/L)

As shown in Fig.3, the calibration curve was prepared by dissolving standard solutions of $CoCl_2$ (9.52 × 10 $^{-3}$ mol/L) in ethanol solvent with different amounts of added water. The absorbance at λ_{max}= 656 nm decreased with water content and good linear relationships were obtained between the logarithm of the absorbance at λ= 656 nm of $CoCl_2$ and the water concentration in ethanol with 0.999 as good coefficient of correlation. The results are presented in Table 1.

Examining different amounts of sweet potato and sticky rice adsorbents

Experiments in this section include the following steps:

Increasing the amount of adsorbent: Column was packed with increasing the amount 10 g to 20 g of natural adsorbents.

Using discrete columns: The column was filled with 20 g of sweet potato and the sample was passed through the adsorbent. The sample was once again passed through the column which this time was filled with sticky rice. The final sample was collected after this stage.

Mixing the adsorbents: In this part, column was packed with adsorbents via two kinds of mixing status: i) Blending 6 g of sticky rice and 14 g of sweet potato. ii) Blending 8 g of sticky rice and 12 g of sweet potato. The results are indicated in Figure 4 and Figure 5, respectively.

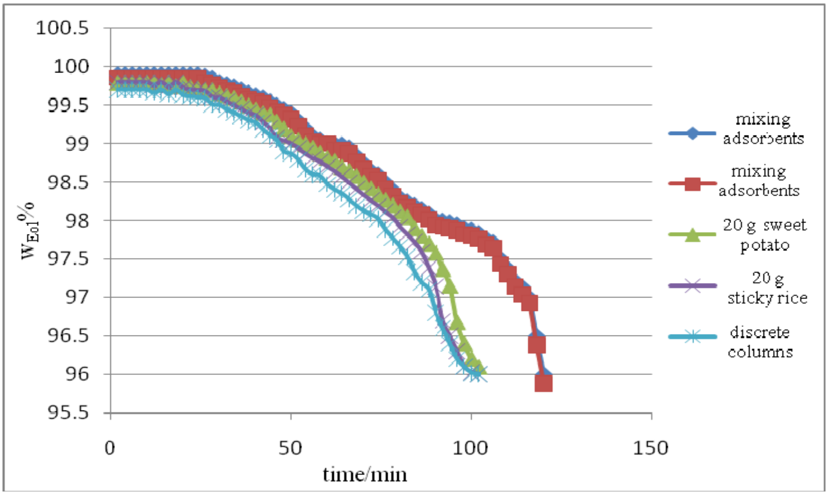

Figure 4. Breakthrough curves of the selective materials for ethanol/water

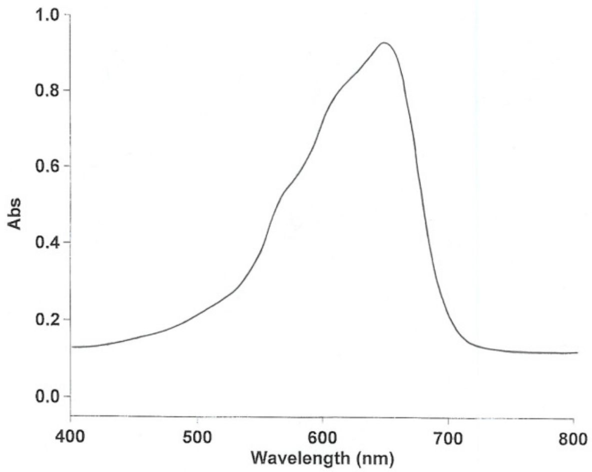

Figure 5. Vis absorption spectrum of $CoCl_2$ in ethanol solution in the presence of 0.1% water.

As seen in figure 5, water content in the organic solvent caused the evident presence of peak around 656nm. This $CoCl_2$ solution absorbed red light, while the organic solvent solutions of $CoCl_2$ were blue green.

According to the results, compared to other parts, mixing the adsorbents part due to higher starch and protein content of amylopectin gave the best separation of ethanol-water system and 99.9% anhydrous ethanol was obtained with high efficiency.

Among the reported methods, the UV-VIS spectrophotometric method is a simple, rapid, reproducible and environmentally friendly method. This method had been applied in determination of the water content in some organic solvents with good reproducibility, high sensitivity on 1% as the relative standard deviation and 0.001 g/ml as detection limit. This method has great application in the determination of water content in raw materials, basic chemicals, cosmetics, drugs, foodstuffs, biological samples, petrochemical products, paints, solvents, gaseous samples, etc. In addition, other method for determining water content, such as gas chromatography, is an expensive apparatus, which could determine the water content simply and rapidly.

It can be concluded from data of Table 1 that among the different bio-based adsorbents examined, sweet potato and sticky rice adsorbents gave the desirable separation of ethanol-water system. However, In order to achieve the best results, experiments were tested on two adsorbents.

Table 1. Water content in different biobased adsorbents

Adsorbents	c_{water} (g/ml)	Water content (UV-Vis)
Sweet potato	0.0043	0.43 %
Sticky rice	0.0021	0.21 %
Corn	0.008	0.80 %
Corncobs	0.0140	1.39 %
Crystal sugar	0.0170	1.73 %
Date pits	0.0102	1.02 %

The size of sieved starch-based materials are indicated in below Table 2.

Table 2. Particle size of adsorbents

Adsorbents	Mesh. No	Mean Diameter (mm)
Corn	40 - 80	0.420 – 0.177
Corncobs	70 - 120	0.210 – 0.125
Crystal sugar	40 - 120	0.420 – 0.125
Date pits	70 - 120	0.210 – 0.125
Sticky rice	40 – 120	0.420 – 0.125
Sweet potato	80 – 120	0.177 – 0.125

CONCLUSIONS

A new, simple alternative and, inexpensive process as adsorptive distillation was developed for ethanol drying. The results of water sorption on six starch-based materials showed that sweet potato and sticky rice were found to be more affinitive for water than other biobased adsorbents. The optimum condition was achieved by mixing adsorbents which yielded 99.9% anhydrous ethanol with high efficiency. Furthermore, the proposed technique is more efficiency than other methods and plays a crucial role for separation of ethanol-water system.

EXPERIMENTAL SECTION

Materials and methods

All raw materials used as natural bio-based adsorbents namely sweet potatoes, sticky rice, corn, corn cobs, crystal sugar and date pits were of food quality and purchased in the market. Chemicals such as ethanol 99.9% (absolute), ethanol 96% were purchased from Scharlau Chemie (Spain) and 2-propanol, cobalt(II) chloride ($CoCl_2$) were provided from Merck (Germany). Gas chromatography (Shimadzu GC-17A) and UV-Vis spectrophotometer (Varian, cary 100 Bio, USA) techniques were used in this work.

Preparation of adsorbents

Sweet potatoes, sticky rice, corn, crystal sugar were dried in a vacuum oven at 90 oC for 12 h. Date pits were washed with distilled water and then dried in an oven at 80 oC for 24 h. Corncobs were cut into small pieces and washed with distilled water and then dried in a packed bed using nitrogen at 90 oC for 6 h. This was to ensure that no biological debasement happened to the polysaccharides of corn cobs [16]. All the materials were then milled and sieved into different particle size with shaker. The biobased adsorbents were kept in bottles, which contained with silica gel.

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SI Units and Symbols

Symbol	Unit	Deffinition
cm	centimeter	distance
^oC	degree Celsius	temprature
g	gram	mass
h	hours	time
mm	millimeter	distance

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