

Research Article

Water Removal from an Ethanol-Water Mixture at Azeotropic Condition by Adsorption Technique

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The separation of ethanol-water mixture is employed in the present work to produce pure ethanol, the present investigation on the separation of water from the ethanol to achieve pure ethanol by adsorption process. The different parameters like quantity of adsorbent, flow rate of feed mixture, and different adsorbents which are zeolite 3A, zeolite 4A, and silica gel are selected to study purification of ethanol by adsorption. The effect of process parameter for purification is also recorded and studied to evaluate the performance of adsorption equipment and adsorbent. The experiments are conducted at 30°C. The feed mixture is 95.6% (v/v) concentration of ethanol and 4.4% (v/v) of water. The designed adsorption column is suitable for purification of ethanol. The highest ethanol concentration 99.9443% obtained at 20 ml/min flow rate of feed mixture using 50 g of zeolite.

1. Introduction

The anhydrous ethanol is produced by using various techniques. The methods and techniques include calcium oxide and ion exchange, and azeotropic distillation with benzene and pentane as solutes. The extractive distillation technique and molecular sieve as adsorbents used in recent years. The extractive distillation and azeotropic distillation techniques can be used for the production of anhydrous ethanol. But these methods have the problems of organic impurities which yield huge investment and high energy requirement with low production rate [1, 2]. The more volatile components will remove by drying first, then as per the boiling points, the remaining components will remove. The energy sustainable issue is linked to global challenges of poverty and climate change. The sustainable energy related issues are most common in developing countries [2–4].

Adsorption method is introduced and commercialized since 1980 but still the efficient adsorbent required producing high purity ethanol. The new dehydration technology employed to produce the pure products. The different adsorbents are available such as activated carbon, alumina, molecular sieve, silica gel, and cereal powder. Molecular sieve adsorption has the high capacity and selectivity among all of them. In addition to that, it has good mechanical and thermal stability. There is no swelling during adsorption process and no ravel due to wetness. The duration or life time of adsorbent is 5–7 years. Hence, this technology is applied to produce anhydrous ethanol [5, 6]. Distillation and extraction processes are the processes that can remove the water from ethanol-water mixture. But these processes have limitations to achieve 100% ethanol. Adsorption is the suitable one which can enhance the purity of the ethanol compared to distillation and

TABLE 1: Physical property of adsorbent.

Specification	Zeolite 4A	Zeolite 3A	Silica gel
Molecular formula	$\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \times \text{H}_2\text{O}$	$\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \times \text{H}_2\text{O}$	SiO_2
Particle size (mm)	1.6	1.4	3.2
Bulk density (g/cm^3)	0.721	0.65	0.75
Pore diameter (\AA)	4	2.99	13
Pore volume (Cm^3/g)	0.45	0.597	0.625
Porosity (%)	0.55	0.61	0.8
Moisture (wt %)	1.21	1.15	3.0
Adsorption capacity as $\text{g H}_2\text{O}/100 \text{g zeolite}$	23.0	24	27.0
Efficiency (%)	92	95	68
pH (5% slurry)	9.5	8.4	6.5

extraction process. The ethanol-water form azeotropic mixture; hence, distillation process is not useful to achieve 100% ethanol. Similarly, the extraction also requires suitable third component to separate water. Even the extraction process is also not possible to achieve 100% ethanol. In the present process, adsorption process gives maximum purity of ethanol [1, 2].

The azeotrope or constant boiling point mixture is a mixture of two or more liquids whose proportions cannot be altered or changed by simple distillation. This happens because when an azeotrope is boiled, the vapor has same portion of constituents as un-boiled mixture. The azeotropic composition of ethanol and water is 95.635 of ethanol and 4.375 of water by weight. Ethanol boils at 78.4°C and water boils at 100°C , but the azeotrope boils at 78.2°C which is lower than either of its constituents.

The zeolite types of molecular sieves are better adsorbents for the removal of minute amount of water from the organic solvents. Because of the small diameter 0.28 nm, the water molecule which has low diameter 0.27 can easily pass through the zeolite canals and ethanol which has 0.44 nm diameter is stopped by the zeolite adsorbents. Scale up level production of anhydrous ethanol from the azeotropic mixture of ethanol-water can be done by extractive distillation. This process is very difficult, and an alternate method has been employed such as liquid-liquid extraction, adsorption, and membrane separation process.

The concentration swing adsorption or the concentration thermal swing adsorption process is attractive for the separation of ethanol-water mixture using selected adsorbents with multiple column adsorption process. This process is one of the attractive because the pure ethanol can be obtained with low energy requirement and higher recovery of desired component.

The adsorption of ethanol-water mixtures passed on to a column which is packed with silicate pellets has been studied [7]. The authors have developed a model and estimated the performance of modified cycle for separation of 8% of ethanol-water mixture. They observed that 99.5% by weight of pure ethanol have been produced and 95% of ethanol recovery. The membrane separation process is less feasible for water removal due to its swelling nature of membranes.

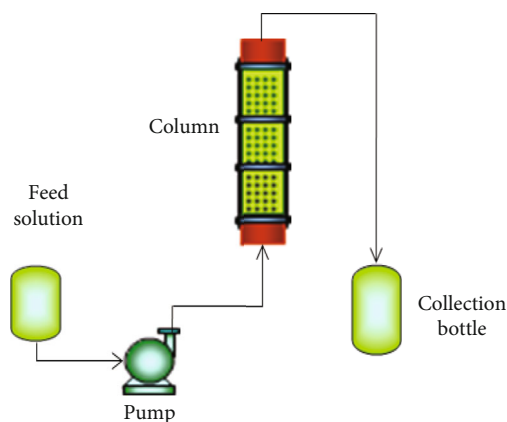


FIGURE 1: The adsorption apparatus.

TABLE 2: Adsorption column specification.

Specification	Size
Height (mm)	300
Inside diameter (mm)	25
Outside diameter of column (mm)	55
Outside diameter of jacket (mm)	70
Volume of adsorption column (mm^3)	147187.5
Volume of column (ml)	147.188

The authors studied the separation of ethanol from water and ethanol mixture by using temperature swing type adsorption in presence of granular activated carbon (BPL 4×10) as adsorbent [8]. Adsorption and desorption process using BPL activated carbon was performed and compared with model predictions. The regeneration process has been modeled for this system. Isotherms on activated carbon in liquid and vapor phases for ethanol-water mixture have been studied experimentally. The kinetic parameters have been derived from the experimental data.

The authors described the controlled kinetics and removal of water from ethanol vapors by desiccants [9]. They explained that the starch based adsorbents can remove the liquid phase water from 1 to 20% by wt without dissolving of adsorbents. The adsorption rate per gram

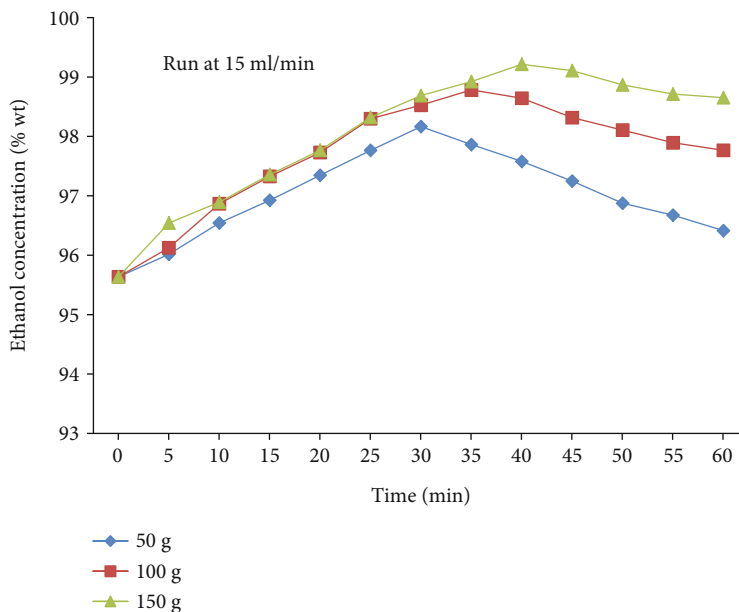


FIGURE 2: Concentration profile using zeolite 3A at 15 ml/min.

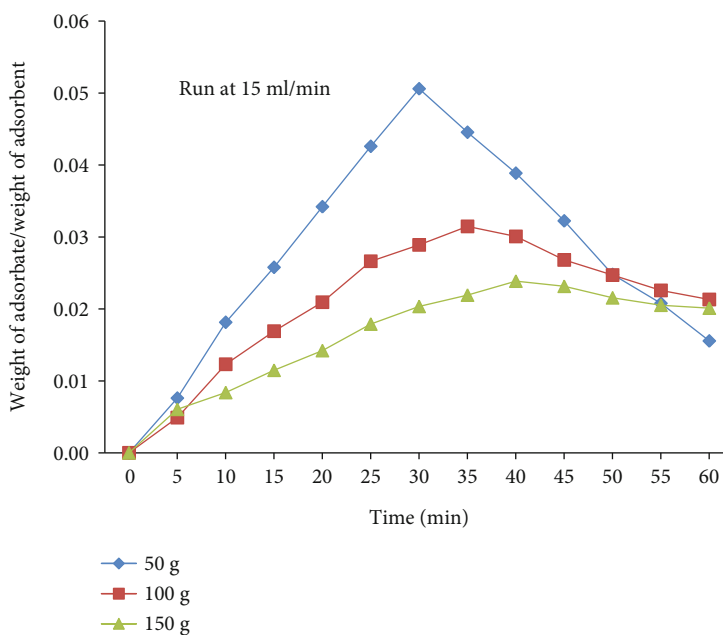


FIGURE 3: Adsorption isotherm of zeolite 3A at 15 ml/min.

of adsorbents increases with increasing the water content. In the comparisons of this adsorbent to silica gel and molecular sieves, the inorganic desiccants have greater capacity per gram when the mixture contains water less than 10 wt%.

Adsorption experiments have been conducted to ethanol-water azeotropic for absolute ethanol production [10]. The adsorption column has been designed and tested for the azeotropic mixture formation. The process parameters that are varied in their investigation were adsorbent

type, its amount, and flow rate of feed. The best results obtained from their investigation as 60 g of Zeolite 3A give better separation at a flow rate of 5 ml/min.

Developing a suitable solution for production of anhydrous ethanol is in need of world fuel consumer. Ethanol being used by pharmaceutical industries and to blend with petroleum product required to have the purest ethanol that is anhydrous ethanol but after the one time use of pure ethanol it becomes hydrated. While dehydrating it by means of distillation, it forms an azeotropic mixture at 95.635 wt%

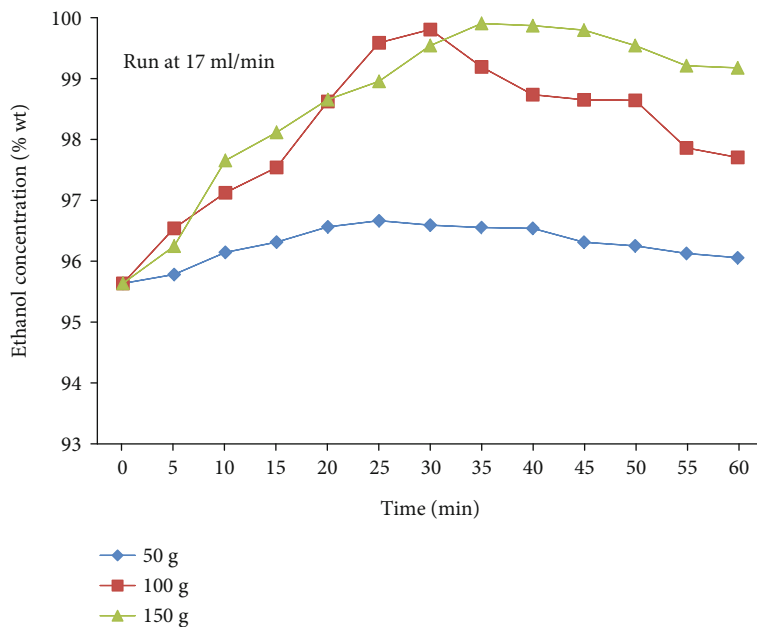


FIGURE 4: Concentration profile using zeolite 3A at 17 ml/min.

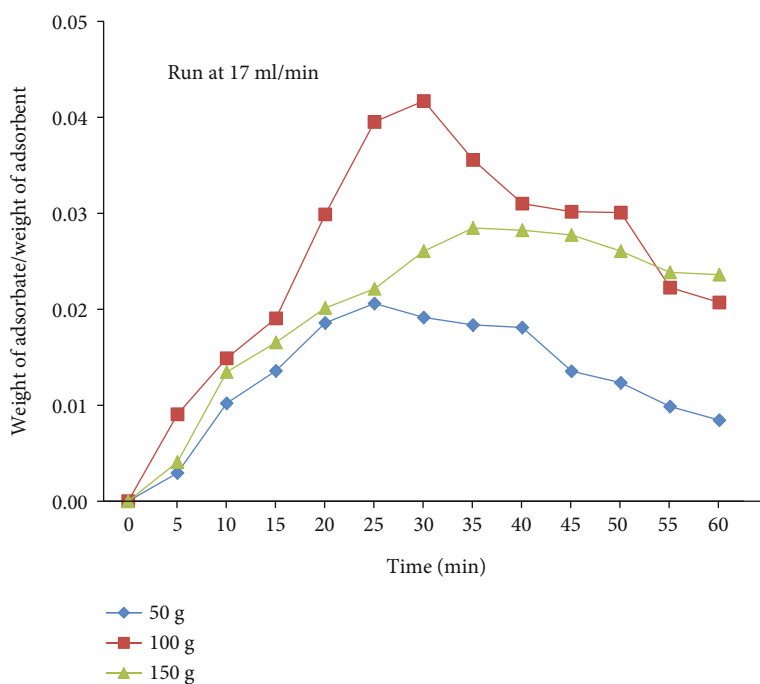


FIGURE 5: Adsorption isotherm of zeolite 3A at 17 ml/min.

ethanol and 4.365 wt% water. 25% ethanol blended with gasoline. The ethanol 25% and 75% gasoline are the composition of blended fuel.

In the present investigation, the effectiveness of adsorbents for the removal of water from the water-ethanol mixture is fixed as the first objective to achieve pure ethanol. Three types of adsorbents have been tested for the removal of water to achieve pure ethanol. The best adsorbent have been suggested for the removal of water from the water-methanol mixture. By using different adsorbents, an efficient

ethanol-water separation process have been designed for an efficient adsorbent.

2. Experimental

2.1. Physical Property of Adsorbents. The chemicals such as ethanol 95% by wt purity, zeolites 3A and 4A, and silica gel were purchased from SD fine chemicals, India. The physical properties of zeolite 3A, zeolite 4A, and silica gel are given in Table 1.

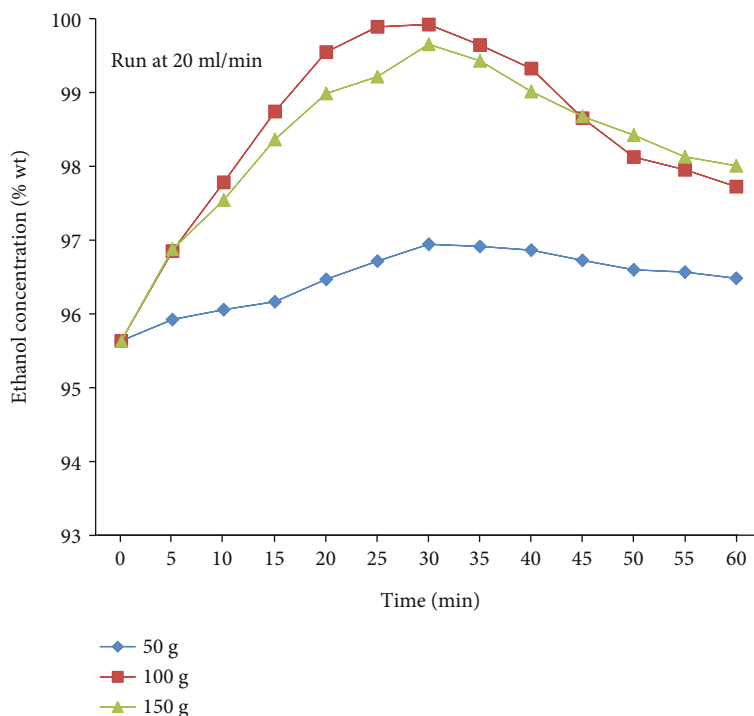


FIGURE 6: Concentration profile of zeolite 3A at 20 ml/min.

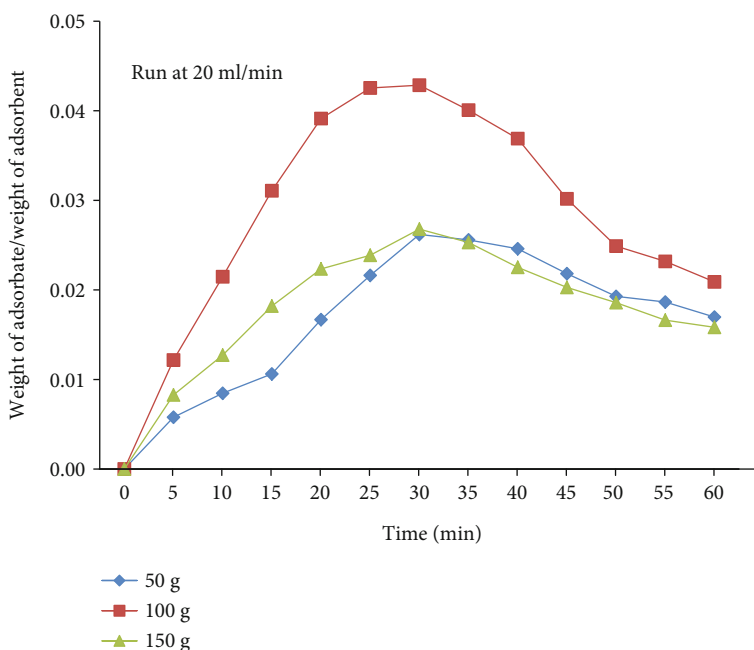


FIGURE 7: Adsorption isotherm of zeolite 3A at 20 ml/min.

2.2. Column Specification

2.2.1. *Experimental Set-up and Procedure.* Ethanol is used as raw material having 95.6% (v/v) concentration and 4.4% (v/v) of water. For adsorption, different adsorbents like silica gel, zeolite 3A, and zeolite 4A with different weights are used. The adsorption apparatus is shown in Figure 1 as similar to the pro-

cess of Carino et al. [10]. The column specifications are given in Table 2. Adsorbent is charged initially in the packed column of inside diameter of 50 mm. The procedure is as following.

- (1) Preparation of ethanol-water mixture of 2 liter by taking 1912 ml of ethanol and 44 ml of water which are mixed to form the uniform solution

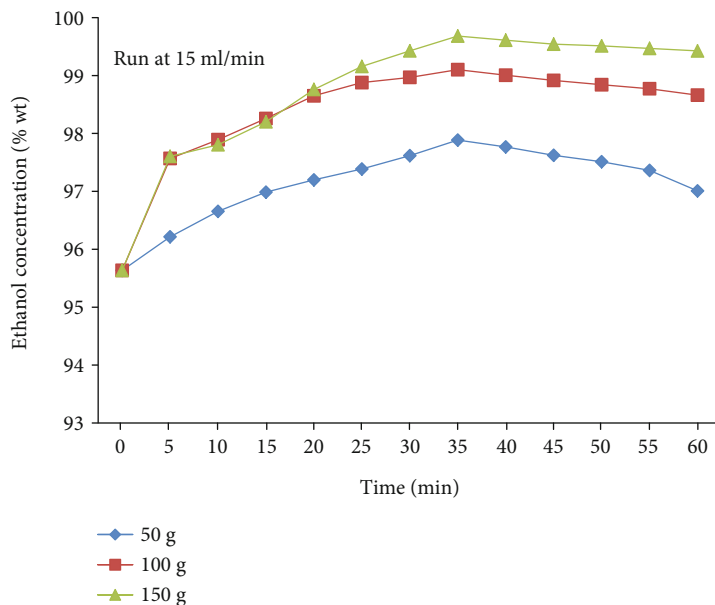


FIGURE 8: Concentration profile using zeolite 4A at 15 ml/min.

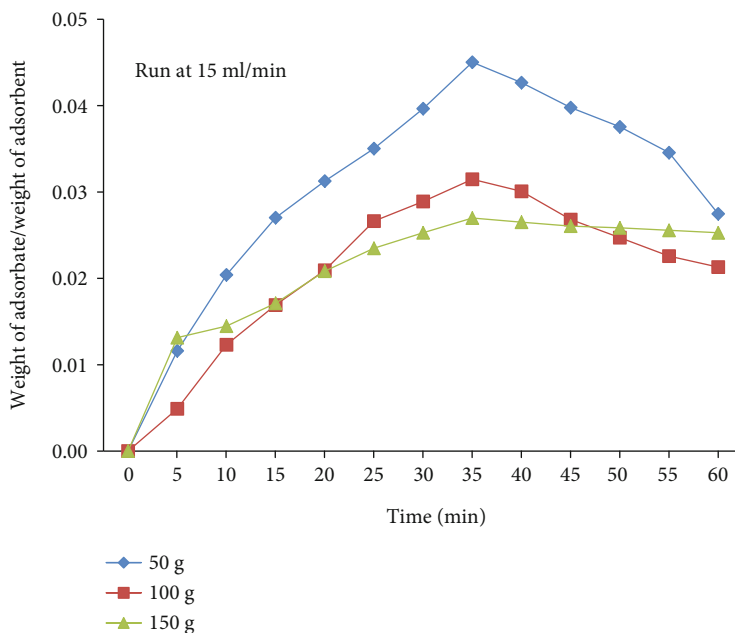


FIGURE 9: Adsorption isotherm of zeolite 4A at 15 ml/min.

- (2) Before adding adsorbent, adsorbent was washed with pure ethanol to remove unwanted impurity and dried for 8 hrs at 150°C
- (3) The desired quantity of adsorbent has fed into the column by removing the upper part of the column
- (4) The peristaltic pump was used to feed the solution to the column by flexible rubber tube
- (5) The flow rate was maintained to the column by adjusting the knob of peristaltic pump to the desired value
- (6) The column allowed filling with mixture. When first drop of mixture comes out from that moment time was noted
- (7) The samples have been collected for every 5 min of interval
- (8) The densities of sample were analyzed by gravity bottle and recorded the value
- (9) After completion of experiment, the valve of peristaltic pump has closed and the valve of nitrogen through the same line was opened to dry the column

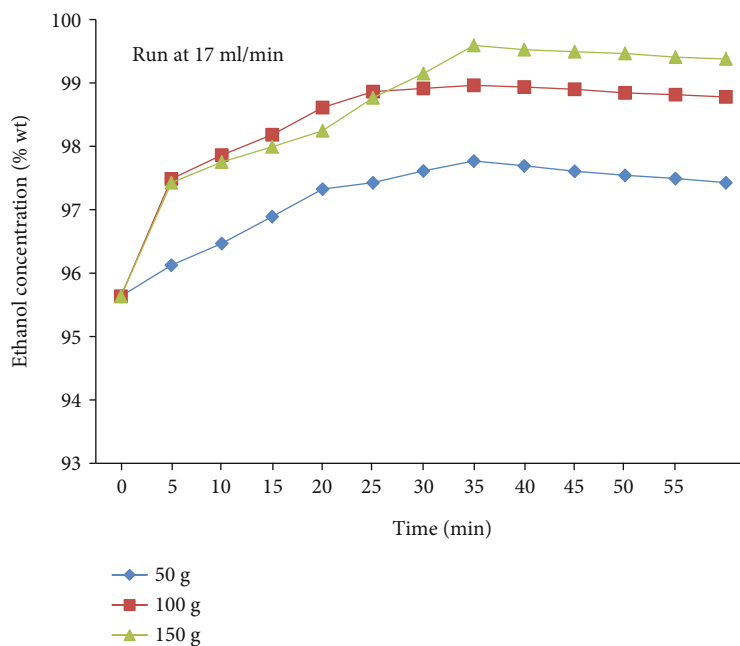


FIGURE 10: Concentration profile using zeolite 4A at 17 ml/min.

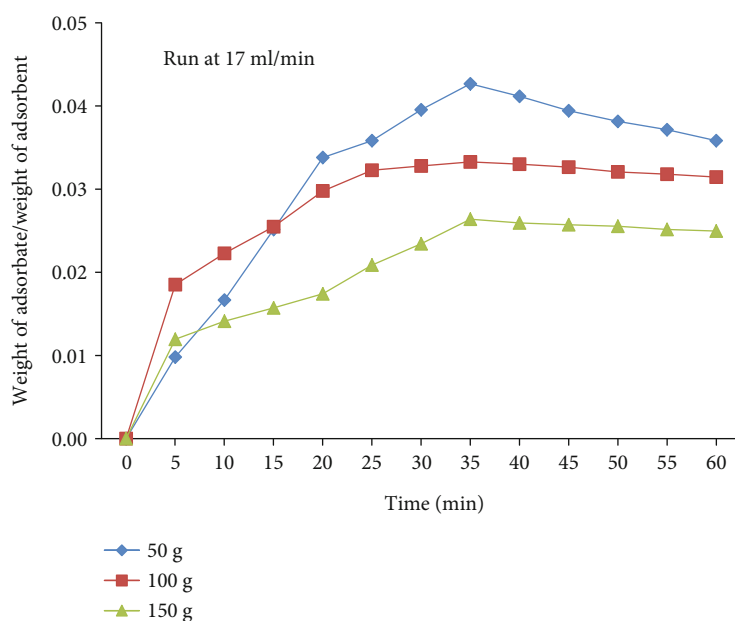


FIGURE 11: Adsorption isotherm of zeolite 4A at 17 ml/min.

(10) After drying of column, the adsorbent has been removed and dried the adsorbent for 8 hrs at 150°C

3. Result and Discussion

The experiments have been carried out under different flow rates and adsorbents by keeping other parameters as constants.

(1) The adsorbent surface is uniform to maintain equal sites. The adsorption surface is uniform because the

water molecules can be adsorbed uniformly on the surface as per their transportation to the surface. The remaining molecules will attach to the gap between the molecule and adsorbent. At steady state, the adsorption capacity will stop. If the surface is not the same, then the molecules will escape and exist with ethanol-water mixture

(2) There is no interaction between the adsorbed molecules. The interaction of the molecules is formed, and the molecules cannot adsorb on the surface of the adsorbent which leads less purification of ethanol. If

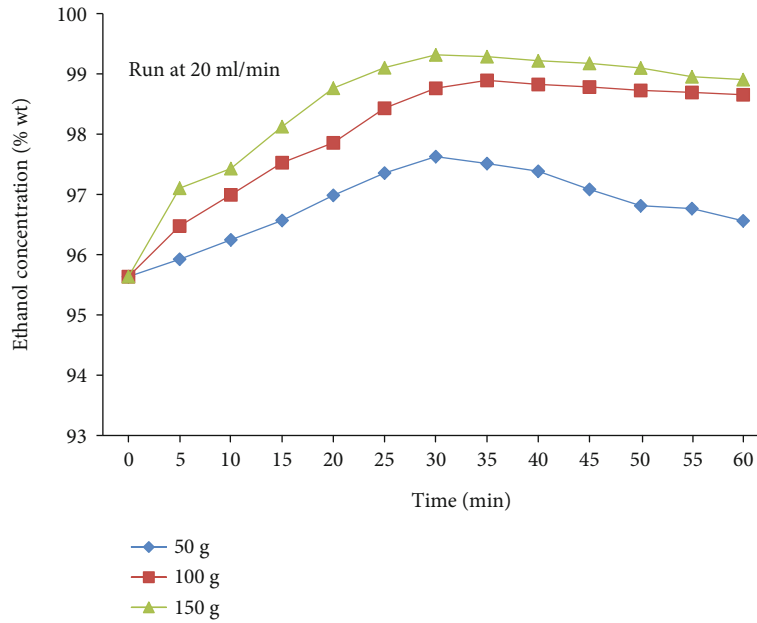


FIGURE 12: Concentration profile using zeolite 4A at 20 ml/min.

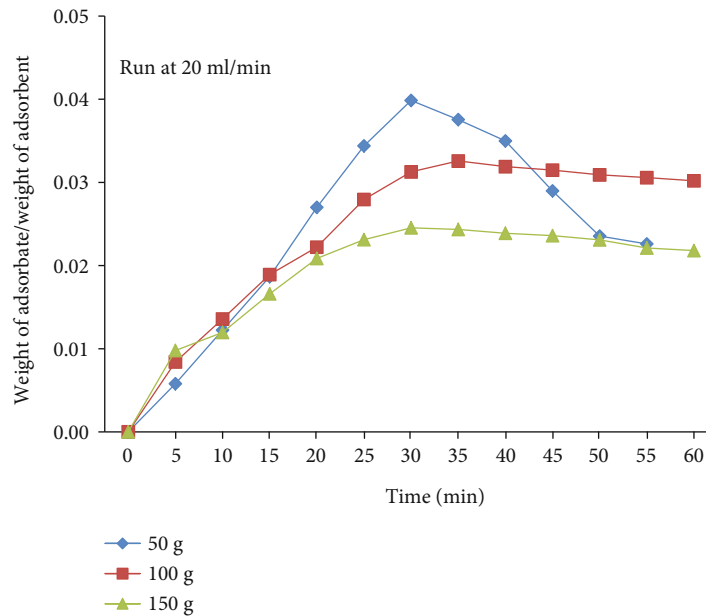


FIGURE 13: Adsorption isotherm of zeolite 4A at 20 ml/min.

the process system is having no interaction, the molecules separate effectively

- (3) The mechanism of adsorption is the same for all the adsorbents
- (4) Monolayer is formed at the maximum adsorption. The molecules of adsorbates deposit on the adsorbents. The remaining adsorbates deposited on the free space of adsorbent

3.1. *Zeolite 3A as an Adsorbent.* The experiment was conducted by using zeolite 3A at 15 ml/min of flow rate of feed

solution and the column is filled with different amounts of adsorbent. The observation is shown in Figures 2 and 3. The optimum result obtained at this flow rate with 150 g of adsorbent after 40 min of run is 99.2147% of ethanol concentration. Ethanol concentration increases as the time proceeds as shown in Figure 2, which show that the adsorbent can absorb water. When it reaches its maximum concentrations, there are only slight decreases in its concentrations. It is because continuous flow of mixture to adsorbents has reached a saturated level of water adsorption. That is there is no availability of active sites to absorb the water molecule on the adsorbent.

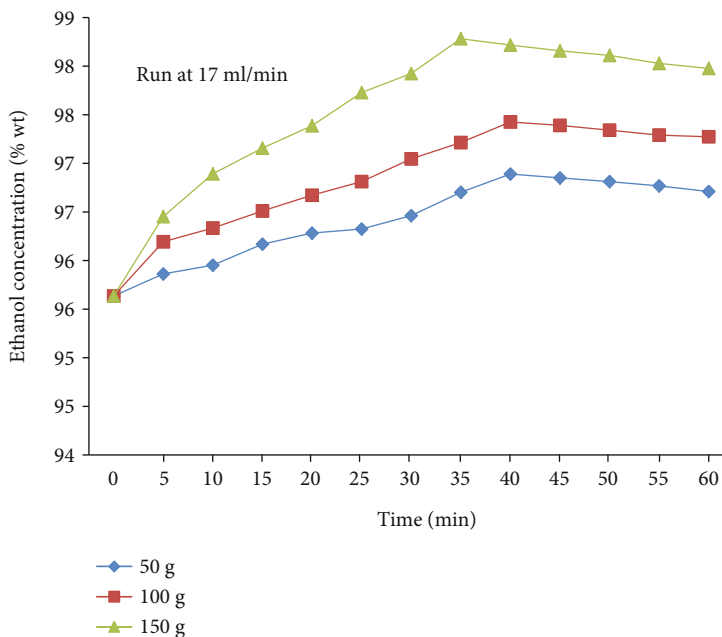


FIGURE 14: Concentration profile using silica gel at 17 ml/min.

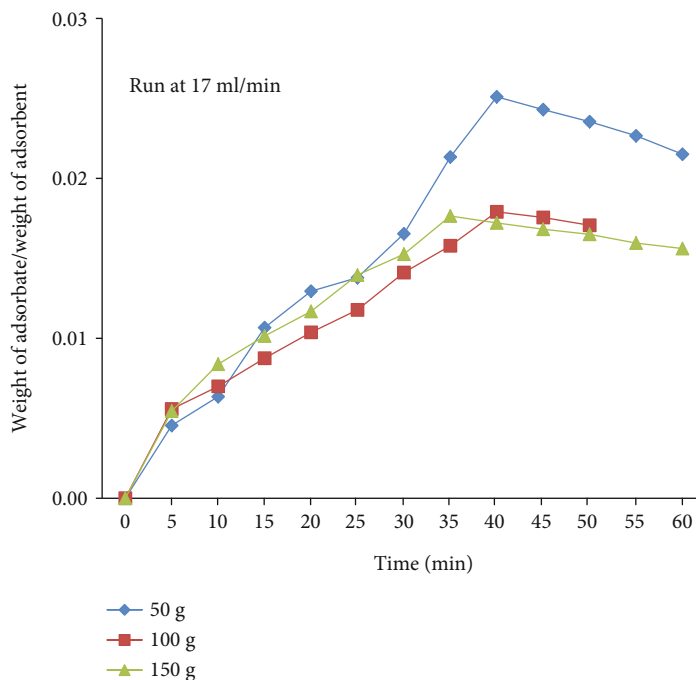


FIGURE 15: Adsorption isotherm of silica gel at 17 ml/min.

The experiment was conducted by using zeolite 3A at 17 ml/min of flow rate of feed solution and the column is filled with different amounts of adsorbent. The observation is shown in Figures 4 and 5. The optimum result obtained at this flow rate with 150 g of adsorbent after 35 min of run is 99.9045% of ethanol concentration. Ethanol concentration increases as the time proceeds as shown in Figure 4, which show that the adsorbent can absorb water. When it reaches its maximum concentrations, there are only slight decreases

in its concentrations. 100 grams of adsorbate gives maximum ethanol purity after that even increase in adsorbent weight gives almost same purity of ethanol. 100 grams is the optimal amount of adsorbent in the present study.

The experiment was conducted by using zeolite 3A at 20 ml/min of flow rate of feed solution and the column is filled with different amounts of adsorbent. The observation is shown in Figures 6 and 7. The optimum results obtained at this flow rate with 100 g of adsorbent after 30 min of run is 99.9212% of

ethanol concentration. This is the optimum result among all the experiments carried out using zeolite 3A.

3.2. Zeolite 4A as an Adsorbent. The experiment was conducted by using zeolite 4A at 15 ml/min of flow rate of feed solution and the column is filled with different amounts of adsorbent. The observation is shown in Figures 8 and 9. The optimum result obtained at this flow rate with 150 g of adsorbent after 35 min of run is 99.6821% of ethanol concentration which is highest among the experiment carried out by using zeolite 4A.

The experiment was conducted by using zeolite 4A at 17 ml/min of flow rate of feed solution and the column is filled with different amounts of adsorbent. The observation is shown in Figures 10 and 11. The optimum result obtained at this flow rate with 150 g of adsorbent after 35 min of run is 99.5921% of ethanol concentration.

The experiment was conducted by using zeolite 4A at 20 ml/min of flow rate of feed solution and the column is filled with different amounts of adsorbent. The observation is shown in Figures 12 and 13. The optimum result obtained at this flow rate with 150 g of adsorbent after 30 min of run is 99.3156% of ethanol concentration. At 20 ml/min, zeolite 4A gives highest concentration of ethanol as shown in Figure 12. It is because of more surface area available and also high capacity of water on to the zeolite 4A.

3.3. Silica Gel as an Adsorbent. The experiment was conducted by using silica gel at 17 ml/min of flow rate of feed solution and the column is filled with different amounts of adsorbent. The observation is shown in Figures 14 and 15. The optimum result obtained at this flow rate with 150 g of adsorbent after 35 min of run is 98.2824% of ethanol concentration.

4. Conclusion

The experiments have been performed in a packed column for three different adsorbents under various conditions. All these experiments were conducted with different adsorbents and with different flow rates. From the experiment, the best adsorbent was zeolite 3A. Zeolite 3A was capable to remove maximum quantity of water from ethanol and give the highest concentrated ethanol compared to zeolite 4A and silica gel. Zeolite 4A can also perform better for the water removal but compared with zeolite 3A, its performance is low. It has resulted as 99.6821% as ethanol concentration at 15 ml/min flow rate using 150 g of zeolite 4A. It was also observed that we were getting purity within the run of experiment and while completing the experiment, the purity is getting reduced up to certain extent because after word the adsorbent was getting saturated. The highest concentration obtained 99.9443% at 20 ml/min flow rate using 50 g of zeolite 3A as adsorbent. The adsorbents were regenerated and used for water removal from the ethanol-water mixture effectively.

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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