Development and Characterization of Biobased Adsorbents from Banana Stem for Bioethanol Dehydration

Snehal R. Patil, Nilesh P. Patil* Vilas S. Patil
University Institute of Chemical Technology, North Maharashtra University, Jalgaon
Umavinagar, P. O. Box No. 80, Jalgaon-425 001 (Maharashtra), India

Abstract

In current scenario, biofuel especially bioethanol has potential to come up as an environmentally clean fuel while meeting the ever increasing energy requirements of different sectors. It was observed that besides its advantages; economically bioethanol without subsidies cannot compete with gasoline because of highly energy intensive nature of bioethanol production process. Most of the energy consumed in process is utilized for dehydration of ethanol since complete dehydration of bioethanol is necessary for blending with gasoline. Generally molecular sieves are used for dehydration of ethanol; however in past few years' development of biobased adsorbents is gaining a momentum due to in abundant availability of raw material and specific characteristic properties associated with them. In this paper a detail process of development of biobased adsorbent from banana stem is elaborated. Also the subsequent characterization of developed adsorbent is done by using advanced characterization techniques like GC, FTIR & FESEM etc. The obtained results are also discussed in detail. It was observed that when compared on economical ground, biobased adsorbent developed from banana stem is quite superior as compared to molecular sieves.

Keywords: Gas Chromatography, FTIR, FESEM, Biobased Adsorbents, Molecular Sieves, Bioethanol etc.

1. Introduction

Ethanol fuel has potential of providing renewable energy that solves the major problems such as fossil fuels depletion and global warming. Gasohol, a blend of ethanol and gasoline is a promising alternative to gasoline. The addition of ethanol to conventional fuel leads to decreased emissions of CO (carbon monoxide) and carcinogenic volatile organic compounds causing potential reductions in ozone precursors by 20 – 30 %. Furthermore, the ethanol, raises the octane number of gasoline, is an antiknock agent and also has high engine compression ratios that increase engine efficiency and performance [1]. In many countries the government provides strong support for Bioethanol programs which iccludes tax credits and regulations making use of biofuel obligatory.

The production of bioethanol from molasses involves three steps microbial fermentation, distillation and dehydration. To be competitive and for economical acceptance, cost of conversion of biomass to bioethanol must be lower than gasoline, so more attention should be given towards optimization of biomass conversion techniques [2]. For blending with gasoline ethanol to be used must be dehydrated since hydrated ethanol with more than 2% (v/v) water is not completely miscible with gasoline. There are many processes available for dehydration of ethanol beyond azeotropic point. The energy consumption in azeotropic distillation of ethanol-water azeotrope is about 88 kJ/m^3 of ethanol, which is much higher than the energy consumption in adsorption process using corn grits 32 kJ/m^3 of ethanol [3]. It reveals that adsorption by any means is less expensive as compared to that of azeotropic distillation.

Till date pressure swing adsorption (PSA) process employing molecular sieves is the lowest energy consumption process [4]. This process employs commercial 3-A° molecular sieves. The process consists of two sieve beds operating in a cycle of dehydration followed by adsorbent regeneration. Though the process has lowest energy consumption; higher cost of molecular sieves regeneration is a serious concern with this process [5]. In addition, disposal of exhausted molecular sieves is also a severe problem to the environment. It was observed that biobased adsorbents are generally less expensive to regenerate. Moreover, if regeneration is not practical and economical, the used adsorbents can be used as a feedstock for production of ethanol or biogas [6]. Deposition of biobased adsorbents in nature is environmental friendly and also cannot cause any harm to life on the earth since these are biodegradable. These facts motivate for the search and development of new and more efficient biobased adsorbents. It was observed that ability of natural materials like starch and cellulose as adsorbents in selective adsorption of water is a result of interaction of hydrogen bonding between free hydroxyl groups (-OH) units and the water molecules [7].

Therefore a biobased adsorbent from banana stem which is actually a cellulosic material is developed. In this paper a detail process of development of biobased adsorbent from banana stem is elaborated. Also subsequent characterization of developed adsorbent to determine properties like surface area, selectivity is done by using advanced characterization techniques like GC, FTIR, FESEM etc. Isotherm explaining nature of the adsorbent and breakthrough study is also studied. The obtained results are also discussed in detail. It was observed that when compared on economical ground, biobased adsorbent developed from banana stem is quite superior as compared to molecular sieves.

2. Materials and Experimental Methodology

In this work, new biobased adsorbents from banana stem is developed and subsequently used for dehydration of azeotropic water–ethanol mixture.

Molecular sieve, type 3A used were purchased from Merck Specialties Private Limited, Worli (Mumbai).

1. The molecular sieves were dried in an oven at temperatures of 190–210°C for 24 hours. This is to make sure that all humidity within molecular sieves is evaporated. The dried molecular sieves were kept in bottles, contained silica gel to make sure that no humidity would be adsorbed on the molecular sieves.

2. Vermiculite is brought from market and directly used as adsorbent after drying it in oven for 10 hours at 80°C.

3. The spherical pearls of Tapioca sago were dried for 10 hours at 80°C before use.

2.1 Banana Stem based Adsorbents Preparation

1. The raw banana stem fibers were washed with distilled water and then dried in an oven at temperatures of 70–80°C for 24 hours.

2. Dried banana fibers were crushed and again dried.

3. Banana stem fiber based adsorbents were prepared by pre-treatment.

4. This pre-treatment include three stages mainly:
   a) dewaxing
   b) alkali treatment
   c) bleaching

5. Raw banana stem fibers were treated in soxhlet extractor for removal of wax and oil in dewaxing process.

6. The alkali treatment was done on dewaxed fibers for removal of unwanted alkali soluble material.

7. Bleaching is done with sodium chlorite solution in a bioreactor developed specifically for carrying out biochemical reactions [8].

8. After each of the above stages of pre-treatment, adsorbent is dried in oven at 105°C for 20-30 min.

9. Raw banana fibers, dewaxed fibers, alkali treated fibers and bleached fibers were used as adsorbents.

2.2 Study of Liquid Phase Adsorption (Soaking at Rest)

Firstly adsorbent is prepared and whether it is suitable for ethanol-water system or not was examined. Ethanol-water azeotrope was analyzed for its initial alcohol concentration and then samples were examined for its volume and weight determination. Figure.1 shows various forms of banana based adsorbents.

Figure.1: Various forms of banana based adsorbents

In this investigation method, various adsorbents of 5 g weight were soaked in 50 ml water-ethanol azeotrope in container and allowed to settle it for time periods of 3 hrs to check the feasibility towards the process of separation. Then sample was filtered and granule and solution parts were separated. Weight of granules and solution was measured and the alcohol concentration of solution was measured. To determine the water uptake in adsorbents weight difference of wet and dry adsorbent, weight difference of solution before and after soaking; also initial and final alcohol concentration was measured.

We had performed further experiments as per following table.1. We had taken three parameters for variation to find the optimized batch. Here variation in initial concentration between 10 to 15 wt percent is taken. Contact time varied between 3 to 5 hours and dose rate of adsorbent varied from 20 to 40 grams. The orthogonal array method is adapted for trial and error, and by permutation and combination the table.2 is drawn. Various batches are taken as per table 2 and optimized batch is decided.

Table.1: Parameter Variation

	Parameters	Level 1	Level 2	Level 3
A	Initial conc. Of water (wt %)	5	8	10
B	Contact Time (hrs)	3	4	5
C	Dose Rate (gms)	3	4	5

Table.2: Calculation of experimental runs

Batches	A (wt %)	B (hrs)	C (gms)
1	5	3	3
2	5	4	4
3	5	5	5
4	8	3	3
5	8	4	4
6	8	5	5
7	12	3	3
8	12	4	4
9	12	5	5

2.3. Study of Vapour Phase Adsorption (Fixed Bed Adsorption Column)

The glass adsorption column with an inside diameter of 1.54 cm and a length of 35 cm was packed with 5-20 g of adsorbent. For neglecting wall effects height to diameter ratio should be more than 20:1.For better efficiency bed internal diameter should be 10 times the particle size and length of column should be 100 times more than the particle size [9]. The column wall temperature was maintained constant at about 90°C by circulating hot water through the jacket. The jacket was insulated with heating tape. The temperature of the mixture in the boiling flask was measured constantly using thermocouple. Ethanol-water mixtures of 250 ml in each run with various water contents used as starting solutions and heated from a 500-ml flask surrounded by an electric heating mantle.

Figure.3: Fixed bed adsorber column

The atmospheric pressure was assumed constant at 760 mmHg. The temperature of the jacket was controlled and kept constant during the runs. The vapour passed through the column, and the exit stream condensed using cold water. The condensate was removed after every four minutes analyzed for finding ethanol concentration. The adsorbent was removed from the bed and regenerated for further use at the end of experiment. The average flow of the condensate was maintained of about 2.5 ml/min for each run. The ethanol/water mixtures were blended using 200- proof ethanol and distilled water to make about 250 ml of solution as per required concentration at start of run [10]. The time for completion of run depends upon the adsorbent and the feed composition.

2.4. Isotherm Study

For the isotherm study batches are carried out at different concentration for Ethanol and water. Three batches are carried out for each adsorbent for the isotherm study. Volume of each batch is 250 ml. Concentration of the ethanol for the batches taken 90, 92, 95 wt%. Contact time is 2 hr. Amount of adsorbent is varied as per adsorbent used. Effluent of the all the batches are sent for the analysis. The uptake of water can be calculated by,

$$q_e = \frac{C_f - C_l}{C_f} \times \frac{V}{M} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(1)$$

Where q_e (mg/g)   - is the amount of water adsorbed onto the dry adsorbent.

C_f and C_l (wt %)   - are the final and initial mass fraction of ethanol in solution.

V (ml)   - is the volume of aqueous phase.

M (g)   - is mass of dry adsorbent used [40].

The sorption equilibrium is expressed by the distribution coefficient, Kd, as

$$K_{d = \frac{q_e}{C_e}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{ (2)}$$

The percentage sorption is calculated by,

$$\% \text{ Sorption } = \frac{C_0 - C_e}{C_0} \times 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3)$$

Where K_d (L/g)   - is the distribution coefficient.

C_0 and C_e - are the initial and final concentration of water in the solution.

3. Results and Discussions

In investigation method of soaking the adsorbents in azeotrope at rest for different time periods from 3 hrs to 5 hrs, resulted in the alcohol concentration increase in the range of 8 to 14 % from the initial concentration. Water uptake was found to be higher for the 4 hour soaking at rest, but in first hour itself it gave satisfactory output. Water uptake was fast within the first 60 minutes of adsorption. The adsorbents

feasible for dehydration of ethanol- water mixture were decided. It was observed that, colour of the ethanol-water azeotrope was changed, it may be due to the higher concentration of water and the longer retention time the adsorbent was slightly dissolved in azeotrope. Since the vapour phase water adsorption from ethanol-water mixture is more energy efficient after deciding the adsorbents to be used for dehydration than liquid phase adsorption. The further work is performed on vapour phase adsorption in fixed bed adsorber column.

3.1. Gas Chromatography (GC) Analysis

GC 7890 B by Agilent Technologies was used for analyzing the concentration of ethanol. The 0.1 µL sample was injected through back inlet to the 0.53 mm id capillary column. Oven inlet temperature was set to $120℃$ for 0 min and $50℃/min$ to $250℃$ for 10 minutes. Splitless flow was selected for injection temperature of $150℃$. Septum purge flow of 3 ml/min and make up flow (N_2) of 25 ml/min was selected. Air flow and H_2 flow were set to 100 ml/min and 30 ml/min respectively. The results were obtained in the form of chromatographs using flame ionization detector (FID), given peak for ethanol for retention time (RT) of about 2.4 min. The area of peak used for calculating concentration of ethanol. The calibration data obtained by injecting dilute samples of ethanol of various concentrations. Area of 100% obtained describe that no impurity is present in sample. The concentration of ethanol in sample calculated by GC decides whether adsorbent is suitable for making fuel grade ethanol.

3.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The aim of using FTIR analysis is to determine the identification of functional groups and its characteristics peaks based on the studies reported. The analysis of functional group was done by using Fourier Transform Infrared (FTIR – 8400, Shimadzu). In FTIR small amount of adsorbent is mixed with KBr. FTIR of alkali treated banana fibers is taken using KBr pelletization technique and spectrum was recorded. FTIR spectrum of developed adsorbent is as shown in figure.4 below. The type of bond with reference to the wave numbers obtained are mentioned in literature, so presence of bonds, stretching, bending or deformation happened are confirmed.
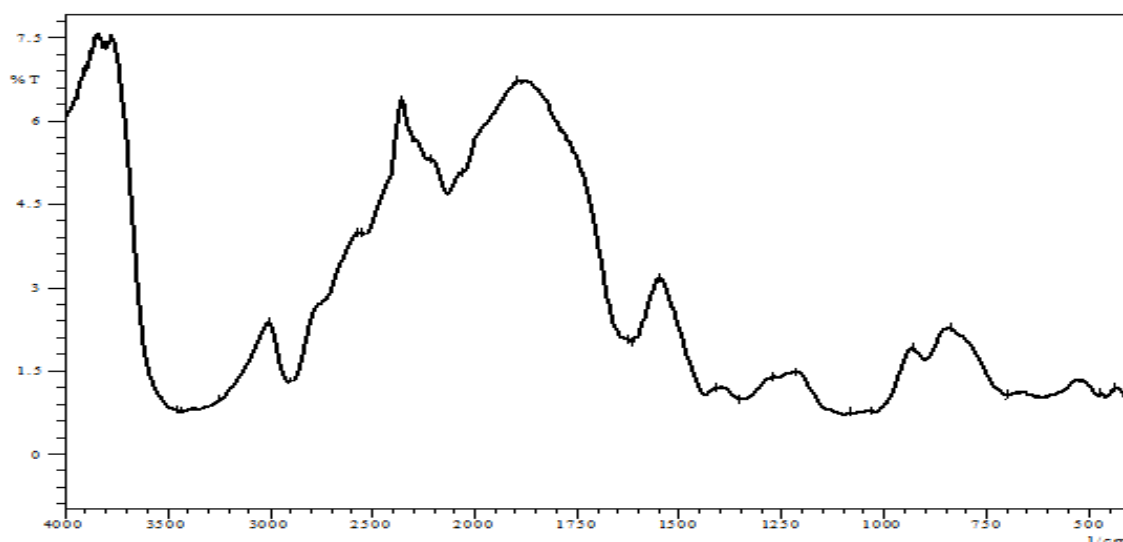
Figure.4: FTIR spectra of alkali treated banana fibers

Table.3: FTIR spectra wave numbers for alkali treated banana fibers

Wave numbers	Type of bond
3437 cm-1	O-H Stretching
2889 cm-1	C-H Stretching
1618 cm-1	O-H Bending
1101 cm-1	C-O Stretching

3.3 Field Emission Scanning Electron Microscope (FESEM) Analysis

In order to visualize the structure of adsorbents, SEM analysis is done. The morphological changes in the surface of adsorbent were analyzed by means of scanning electron microscopy (SEM). Morphology of adsorbent was characterized by Field Emission Scanning Electron Microscope (FE – SEM, Model: Hitachi S – 4800). Beam acceleration technology was used. Operating between 100 volts to 2 Kv. Sample was coated with a gold coating. A SEM study of adsorbents before and after adsorption, noticeably images the morphological changes in the surface texture of adsorbents. The SEM image shows smooth, pores and irregular shaped particles. The SEM micrograph clearly revealed the surface texture and morphology of the sorbent at different magnifications. The SEM analysis revealed important information on surface morphology where there is a formation of thin layer on the surface.
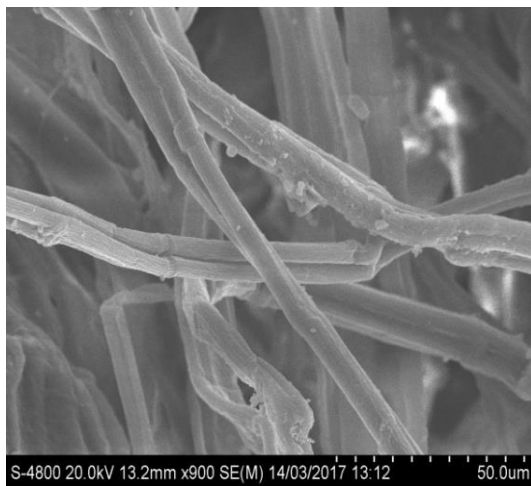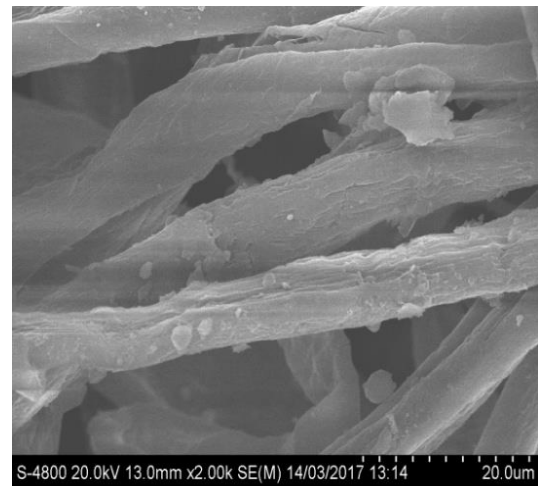
Figure.5 (A)

Figure.5 (B)

Figure.5: (A) and (B) are SEM images of Fresh Alkali Treated Banana Fiber Adsorbent
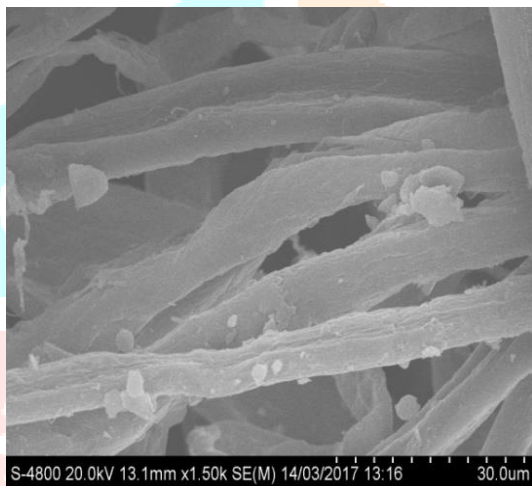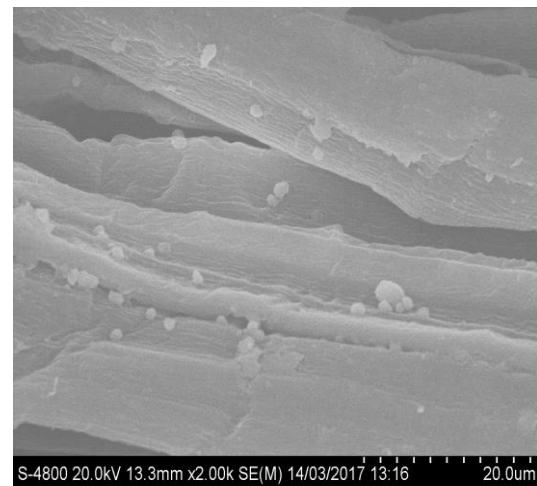

Figure.6 (A)

Figure.6 (B)

Figure.6: (A) and (B) are SEM images of water saturated Alkali Treated Banana Fiber Adsorbent after used for ethanol dehydration.

3.4 Adsorption Isotherms

An adsorption isotherm describes the equilibrium adsorption of a material at a solid surface at constant temperature. It represents the amount of material bound at surface as a function of the material present in a gas phase or in the solution. The adsorption data have been studied with Temkin isotherm. Temkin isotherm assumes that adsorption energy decreases linearly with surface coverage due to adsorbent-adsorbate interactions and can be described as:

$$q_e \ = \ \frac{RT}{b_T}\ln K_T + \ \frac{RT}{b_T}\ln C_e \text{.. (12)}$$
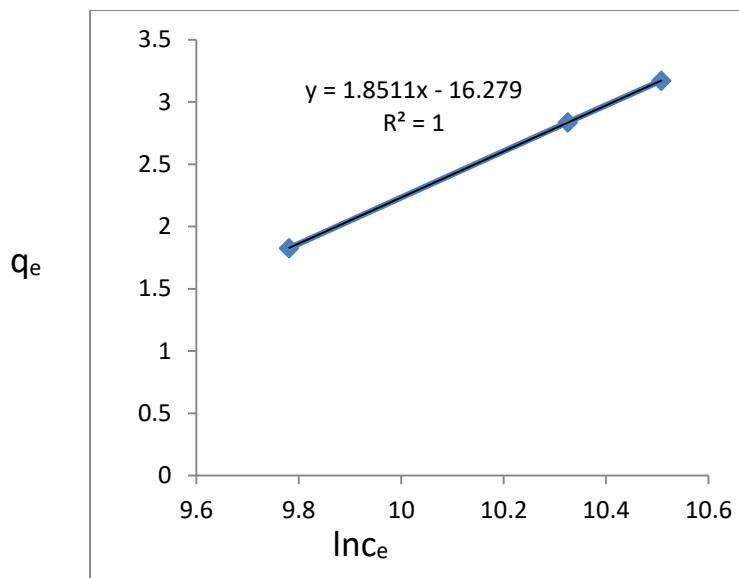
Figure.7: Temkin Isotherm for water adsorption with alkali treated banana fiber adsorbent

The linear plot of q_e versus lnC_e helps to determine the constant K_T and b_T. The values of K_T and b_T for alkali treated banana fiber adsorbent are 0.1544 ml/mol and 1.5858KJ/mol respectively. High value of b_T indicates that, there is strong interaction between adsorbate and adsorbent surface. Therefore, the process follow Temkin isotherm.

3.5 Breakthrough Curves

Alkali treated banana fiber adsorbent was used to study the breakthrough behavior, a sudden increase in water concentration in the effluent, of water adsorption using three different water concentrations of ethanol–water mixtures. The breakthrough curve of water sorption is plotted for the different pore sizes of developed adsorbent at the different water concentrations. The results are as shown in figure.8 for water contents of 5, 8, and 10 wt %, respectively. Separation of ethanol from water is only achieved by the selective sorption of the adsorbent used. It is also worth mentioning that the breakthrough behavior likely resulted in less than complete water removal given that the column was relatively short.

The breakthrough time is arbitrarily designated to be the time required to reach 2 wt % of water content in the effluent stream. This value was chosen because it is observed that water concentration in the first droplet of condensate was greater than 1 wt % for some adsorbents. The data of wt % of ethanol versus time is plotted. It is important to emphasize that the data are plotted as water content in effluent stream divided by initial water content (C/C0) versus time, therefore, the breakthrough time varies depending on the initial water content.
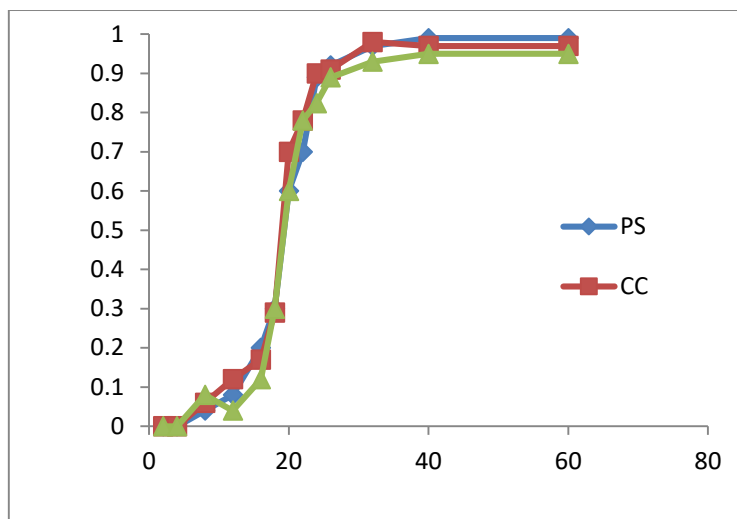
Figure.8: Breakthrough curve for water adsorption with alkali treated banana fiber adsorbent

4. Conclusion and Future Work

In recent years use of molecular sieves for dehydration of bioethanol is common. However higher cost of regeneration incurred through requirement of high temperatures needed for evaporation of collected water within sieve pores is a biggest drawback associated with molecular sieves. It was observed that lignocellulosic materials have strong affinity towards water. Their hygroscopic nature allows for the uptake of water molecules from ethanol-water mixture and hence can be effectively used as adsorbents in dehydration of bioethanol. It is observed that developed alkali treated banana fiber adsorbent selectively adsorbed and removed water from ethanol-water vapour, after saturation, it can be used as feedstock for further process to produce bioethanol and more importantly it is less expensive as compared to that of molecular sieves. Moreover biodegradable nature of developed adsorbent makes its disposal safe and environmental friendly.

This study elucidates that banana stem fibers could be a raw material for preparation of adsorbent with target use of water adsorption instead of putting pressure on corn as it has primary food value. Water adsorption with banana stem-based adsorbent used in study could be an economical technique to produce anhydrous ethanol biofuel. It was observed that developed adsorbent is feasible for vapour phase dehydration of ethanol. It may be possible to obtain anhydrous alcohol from lower grade feeds containing 88−95 wt % in this process. In conclusion, cellulose-based adsorbent like alkali treated banana fiber could be an economical alternative for dehydration of ethanol to produce anhydrous ethanol.

References

1. Simo, M., Brown, C. J., & Hlavacek, V. (2008). Simulation of pressure swing adsorption in fuel ethanol production process. *Computers & Chemical Engineering*, *32*(7), 1635-1649.

2. Patil, N. P., Patil, V. S., & Bhole, S. L. (2016). Production of bio-ethanol from cane molasses: energy optimization through internal and external heat integration in distillation column. *Journal of Advanced Chemical Sciences*, 215-218.

3. Ladisch, M. R., & Dyck, K. (1979). Dehydration of ethanol- New approach gives positive energy balance. *Science*, *205*(4409), 898-900.

4. Jeong, J. S., Jeon, H., Ko, K. M., Chung, B., & Choi, G. W. (2012). Production of anhydrous ethanol using various PSA (Pressure Swing Adsorption) processes in pilot plant. *Renewable energy*, *42*, 41-45.

5. Banat, F. A., Al-Rub, F. A. A., & Simandl, J. (2000). Analysis of vapor–liquid equilibrium of ethanol–water system via headspace gas chromatography: effect of molecular sieves. *Separation and purification technology*, *18*(2), 111-118.

6. Patil, N. P., & Patil, V. S. (2016). Operational and economic assessment of distillation column from the performance of tray. *Int. J. Eng. Trend. Technol*, *4*, 500-505.

7. Benson, T. J., & George, C. E. (2005). Cellulose based adsorbent materials for the dehydration of ethanol using thermal swing adsorption. *Adsorption*, *11*, 697-701.

8. Bhole, S. L., Patil, N. P., Patil, V. S., & Gharpure, M. G. (2016). Improvement in stage efficiency and reduction in energy consumption of distillation through artificial irrigation. *Journal of Advanced Chemical Sciences*, 219-222.

9. Chhajed, M. S., Patil, N. P., & Patil, V. S. (2017). Development of Reactor for Carrying Out Biochemical Reaction. *International Journal of Advanced Electronics and Communication Systems*, *6*(5).

10. Huang, H. J., Ramaswamy, S., Tschirner, U. W., & Ramarao, B. V. (2008). A review of separation technologies in current and future biorefineries. *Separation and Purification Technology*, *62*(1), 1-21.