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Research Article

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Separation of benzene-cyclohexane mixtures by using adsorption technique

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ABSTRACT

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or, more rarely, a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Exchange adsorption, Physical adsorption and chemical adsorption have been recognized as adsorption types. This study involves the separation of an azeotropic mixture (benzene-cyclohexane) by adsorption technique using Eu-GAC(Granular Activated Carbon) *and Sand. The Eu-GAC was produced by thermal pyrolysis of Eucalyptus tree branches and leaves and the Sand was collected from El-Khums seaside. The influence of several parameters such as dose or mass of adsorbent, pH, mesh number and contact time were investigated. The optimum adsorption efficiency occurred at pH 3. The optimum contact time for both adsorbents was found to be 3 hours. The adsorption of azeotropic mixture (benzene-cyclohexane) improved by increasing adsorbent dose and mesh number (Mesh No 100). This study has concluded that it is possible to use activated carbon produced from locally available Eucalyptus trees (Eu-GAC) or Sand collected from seaside to separate the azeotropic mixture (benzene-cyclohexane) for obtaining a purified cyclohexane.*

Key words: Azeotropic mixture, adsorption activated carbon, Sand, Eucalyptus.

INTRODUCTION

The term “azeotropy” denotes a mixture of two or more components where the equilibrium vapor and liquid compositions are equal at a given pressure and temperature. More specifically, the vapor has same composition as the liquid and the mixture boils at a temperature other than that theboiling points of purified components.

Azeotropic mixture is a special mixture with a boiling point higher or lower than its components. Therefore, the common distillation methods widelyused have not led to separate the azeotropic mixture into purified components. Several methodssuch as decompression distillation and additive distillation have been applied to separate azeotropic, however, these processes have accompanied with wasting excessive energy.

Although chromatography has an important role in the mixtures separation including azeotropic mixtures, it is just used for the analysis due to the disability to separate large amount of the mixture. Some adsorbents, such as synthetic resins, dehydrating agents and more, are very expensive to achieveeconomically separation process of azeotropic mixtures [1, 2].

Benzene and cyclohexane classify as important materials since they constitute the raw materials of various petrochemical products. Because the boiling points of these compounds are very close, azeotropic and extractive distillation are frequently used for separating them by adding a third component.

During the last decade, a number of polymer membranes have been developed for the separation of a benzene/ cyclohexane mixture. However, in the separation the polymer membranes become swollen due to the accumulation of highly adsorptive compounds in the membrane resulting reducing the separation factors. Thus, inorganic membranes such as zeolite are expected to be effective membranes to separate benzene- cyclohexane mixture. Separation of benzene and cyclohexane is recognized to be the most important and difficult processes in the petrochemical industry. Cyclohexane is produced by catalytic hydrogenation of benzene. The unreacted benzene occurred in the reactor's effluent stream and must be removed forpurified cyclohexane retrieving. Separation of benzene - cyclohexane is difficult by a conventional distillation process because these components have close boiling mixtures at the entire range of their compositions. Presently, azeotropic distillation and extractive distillation are used for this separation. These two processes, however, suffer from complexity and high energy consumption. For all these reasons, the industry has always been eager to look for an alternative method to the conventional separation processes.

Recently, pervaporation (PV)separation has emerged as an economical and simple alternative method which was usedfor many organic/organic separation applications. the separation mechanism in pervaporation is not based on the relative volatility of components, but on the difference in adsorption and the diffusion properties of the feed substances as well as the permselectivity of the membrane[3, 4]. The investigation of the adsorption isotherm aimed to measure the adsorption capacity of the adsorbents (Eu-GAC and Sand) and to determine the equilibrium distribution of the solute concerned (e.g. benzene in the azeotropic mixture benzene-cyclohexane).In this study, the investigation of the efficiency of Eu-GAC and Sandto separate the azeotropic mixture benzene-cyclohexane was carried out.

EXPERIMENTAL SECTION

The feasibility of separating an azeotropic mixture (benzene - cyclohexane) by adsorption technique was investigated. The experiments were done using a batch, fixed bed reactor. In addition, equilibrium studies were carried out. The parameters investigated in this work included the adsorbents dose, adsorbateconcentration, pH, and stirring speed.

Materials

In this study, we have used activated carbon obtained from Eucalyptus tree branches (Eu-GAC) and Silica adsorbent (Sand) from seaside of El-Khoms. The carbon was produced by thermal pyrolysis of Eucalyptus tree branches in the absence of oxygen. The activated carbon was used without any further treatment except drying in an oven at 100˚C before usage. The surface of the activated carbon and sand was examined using a Scanning Electron Microscope.

The carbon was ground and screened through different standard sieves into three kinds of particles size for the separation of azeotropic mixtures,

- 10 Mesh No collected between the sieves with 10 Mesh No and 25 Mesh No.
- 30 Mesh No collected between the sieves with 30 Mesh No and 60 Mesh No.
- 100 Mesh No collected between the sieves with 100 Mesh No and 140 Mesh No.

The second adsorbent "Sand" used in this study was taken from seaside.

- The sand was washed with ethanol and then dried at 100˚C.
- The sand sieved similarly and screened through different standard sieves into three kinds of particles size.
- 10 Mesh No, 30 Mesh No and 100 Mesh No were collected and used for adsorption studies.

Table 1 shows mesh sizes and particle sizes of Eucalyptus granular (Eucalyptus-GAC) and Sand.

Table 1:Properties of Eucalyptus Activated carbon and Sand

Mesh size	Particle size Range (mm)	Average Particle Diameter (mm)
10 Mesh No	2.38 – 1.19	1.7850
30 Mesh No	1.19 – 0.149	0.6695
100 Mesh No	0.149 – 0.047	0.0980

2.1 Azeotropic Mixtures:
The azeotropic mixtures were prepared from commercial fine reagents according to the components and the ratios. Three types of azeotropic mixtures of benzene and cyclohexane were prepared containing 4%, 6% and 8% benzene in cyclohexane.

2.2 Adsorbate
An azeotropic mixture of benzene-cyclohexane was selected for this study.

2.3. Analytical Techniques:
2.3.1 Preparation of calibration curve:
In order to know the concentration of a liquid sample, a calibration curve was prepared. Plotting A (absorbance) versus concentration of solution (as shown in (Figure 3)) was prepared. Solutions of different concentration were prepared. After mixing, the absorbance's were measured at λ_{max}=255 nm ($\lambda_{max}$for benzene).

2.3.2 Spectrophotometric measurements:
All readings were made on a UV-Visible spectrophotometer (model 8700 series Unicam UV/Vis)(Figure2). The absorbance's of the solutions were measured at the wavelength (255 nm) [5], as benzene absorbs at this wavelength while, cyclohexane has no absorbance above 200 nm. The absorbance readings obeyed Beer's law in this range.A_i = S * C_iWhere:A_i : absorbance (%), S : constant, slope of curve and C_i : concentration, mg / L

Figure (2) UV-Visible (Spectrophotometer)

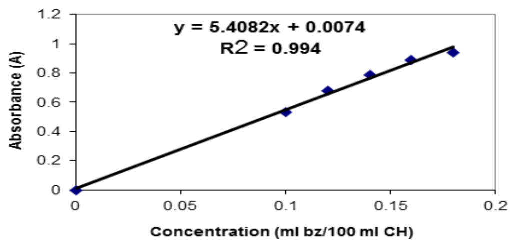


Figure (3) Calibration Curve for the Azeotropic Mixture, (Benzene- Cyclohexane)

2.3.3 Equilibrium Adsorption studies:
Batch equilibrium adsorption isotherm studies were conducted using an azeotropic mixture prepared by mixing 0.1-0.18 ml (874 - 1572 mg/L) of benzene with cyclohexane to obtain 100ml solutions containing 4 %, 6 % and 8 % benzene solutions. The experiments were performed at the following conditions:

- The experiments were carried out using Eucalyptus GAC and Sand as adsorbents.
- The equilibrium isotherm measurements were carried out for different solution/solid ratios.
- The batch experiments were carried out at constant temperature of 25 ± 2˚C.
- The equilibrium shaking time (contact time) was varied from one to 15 hours at an stirring speed of 200 rpm.
- The experiments were conducted in 125 ml Erlenmeyer flasks on a magnetic stirring apparatus as showed in (Figure 4).
- The ratio of solution/adsorbent was varied from 1 to 3 gm.
- During these experiments; samples were collected at the intervals time.
- To prevent the removal of adsorbent from the solution during sampling, a syringe was used as filter.
- Samples were analysed by UV/VIS spectrophotometer by measuring absorbance of the samples at λ_{max} (255 nm) for benzene - cyclohexane.

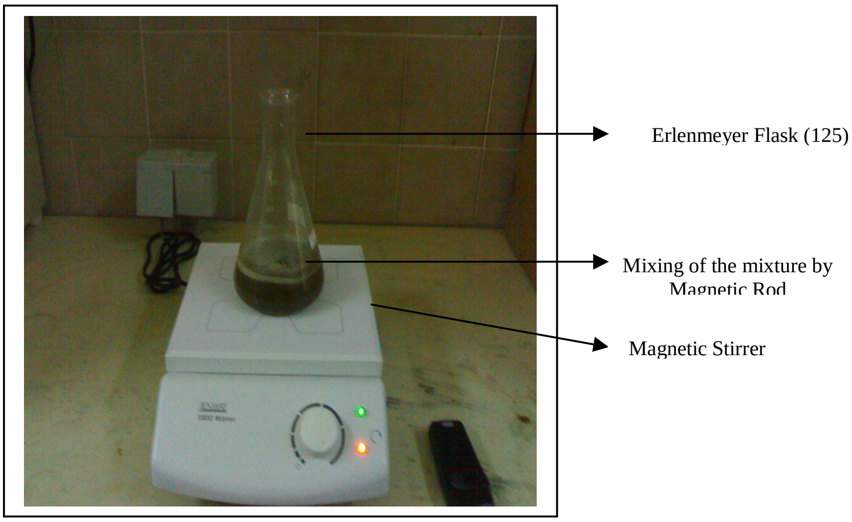


Figure (4)Continuously Stirred Batch Adsorption vessel for Kinetic Studies

RESULTS AND DISCUSSION

The investigation of the adsorption isotherm aimed to measure the adsorption capacity of the adsorbents (Eu-GAC and Sand) and to determine the equilibrium distribution of the solute concerned (e.g. benzene in the azeotropic mixture benzene-cyclohexane).

- In previous work, the biopolymer derivative chitosan has been found to be able to separate some liquid mixtures [6].
- It has also been found that the biopolymer, chitin can be used as an efficient separation agent for azeotropic mixtures.
- The separation can be carried out in mild conditions, under 1 atm and at room temperature to obtain the purified components.
- Considered as a cheap material, chitin shows an excellent ability for separation of azeotropic mixture.

3.1Eucalyptus Granular Activated Carbon(Eu-GAC) and Sand Surface Scan

- The Eu-GAC and Sand were subjected to microscopic Surface Scan (Figure 5 and 6).
- Eu-GAC possess a high porosity therefore a high adsorption is expected. While Sand possess a low porosity therefore a low adsorption is expected.

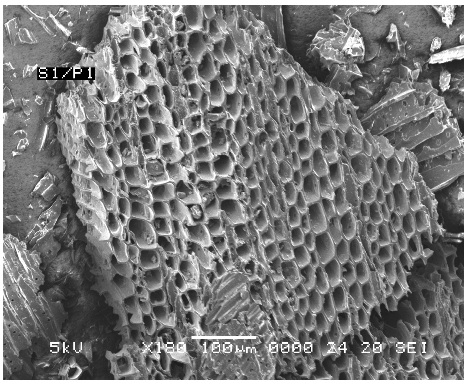


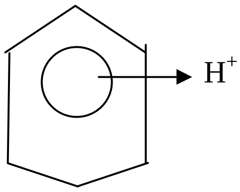
Figure (5)Surface Scan by Electron Microscope for Eu-GAC

Figure (6) Surface Scan by Electron Microscope for Sand

3.2 Effect of pH

The pH values, which were used to examine the effect of pH on the adsorption efficiency process, were from 1 to 8. The optimal adsorption efficiency defined in **equation (1)** occurred at pH 3. This result meet with Belessi, Romanos [7] findings by which they confirmed that maximum monolayer adsorption capacity obtained from the Langmuir model was approximately 87 mg/g at pH 3.0. The adsorption efficiency decreased when the high pH values were applied [8].

$E(\%) = 100 *[(C_i – C_e) / C_i]$ ---------------------------**(1)**



(π-complex)

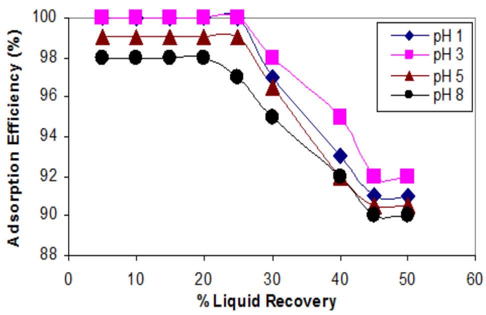


Figure (7) The adsorption efficiency of Azeotropic Mixture, (Benzene-Cyclohexane) (4%; 96% wt) (100ml), by Sand (1g ; Mesh No 100) at different pH values between pH 1-pH 8,T=25 °C,1 atm

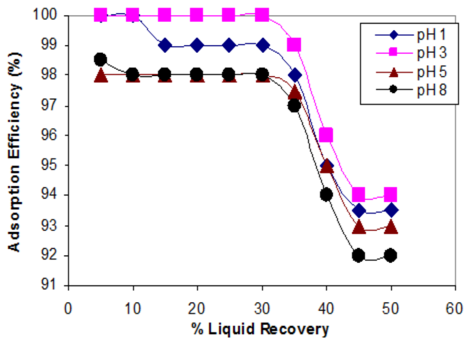


Figure (8) The adsorption efficiency of Azeotropic Mixture, (Benzene-Cyclohexane) (4%; 96% wt) (100ml), by EU-GAc (1g ; Mesh No 100) at different pH values between pH 1-pH 8,T=25 °C,1 atm

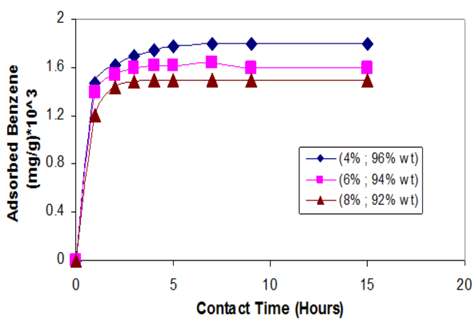


Figure (9) Effect of Contact Time on the Adsorption of Azeotropic Mixture, (Benzene-Cyclohexane) of different initial concentrations, by EU-GAC (1g ; Mesh No 100) pH=3; Stirring Speed 200rpm; T= 25 °C,1atm

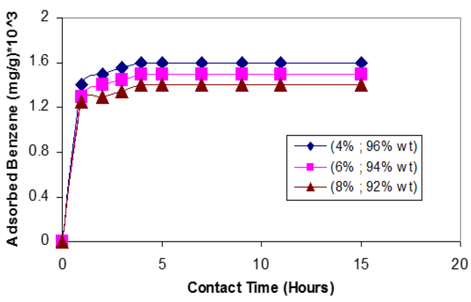


Figure (10) Effect of Contact Time on the Adsorption of Azeotropic Mixture, (Benzene-Cyclohexane) of different initial concentrations, by Sand (1g ; Mesh No 100),pH=3; Stirring Speed 200rpm; T= 25 °C,1atm

3.3 Effect of Contact Time

Results in Figure 9 and 10 show that the adsorbed benzene-cyclohexane increasedby an improving the contact time. Other parameters such as dose of adsorbent and pH of solution were kept at optimum situation as well as the temperature was kept at 25˚C. The adsorption efficiency ameliorated when contact time increased from 1 hours to 3hours. Optimum contact time for adsorbed benzene-cyclohexane in both adsorbent agents (EU-GAC and Sand) was found to be 3hours. This result agreed with what was found by Zayadi and Othman [9]. The optimum ferum, zinc, and plumbum removal of 64.2%, 91%, and 86% was achieved at 3 hours [9].

3.4 Effect of Adsorbent Dose

The adsorption of benzene-cyclohexane on Eu-GAC and Sand adsorbents was examined by using various amount of adsorbents doses ranging from 1g to 3g/100 ml. Figures (11, 12 , 13 and 14) present the adsorption efficiency of benzene-cyclohexane on two adsorbents. From these figures, we can conclude that the adsorption efficiency of the adsorbents generally improved by increasing adsorbents dose. The percentage removal of azeotropic mixture from the solution increased from 80-95% to 87-97% as the adsorbent dosage increased from 1 to 3 g for Eu-GAC adsorbent. Whereas the percentage removal of azeotropic mixture from the solution increased from 70-90% to 75-93% as the adsorbent dosage increased from 1 to 3 for sand. This result is expected because of the increased adsorbent surface area and availability of more adsorption sites caused by increasing adsorbent dosage [10, 11].

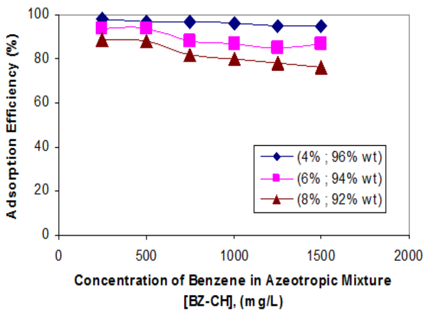


Figure (11) Adsorption percent of the Azeotropic Mixture, (Benzene-Cyclohexane) onto EU-GAC (1g ; Mesh No 100)with different compositions; T= 25 °C,1atm

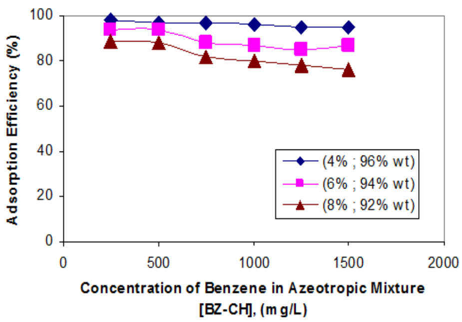


Figure (12) Adsorption percent of the Azeotropic Mixture,(Benzene-Cyclohexane) onto EU-GAC (3g ; Mesh No 100) with different compositions; T= 25 °C,1atm

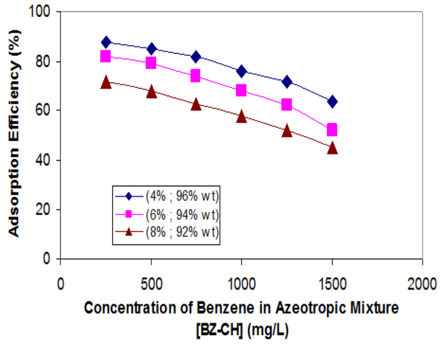


Figure (13) Adsorption percent of the Azeotropic Mixture, (Benzene-Cyclohexane) onto Sand (1g ; Mesh No 100) with different compositions; T= 25 °C,1tm

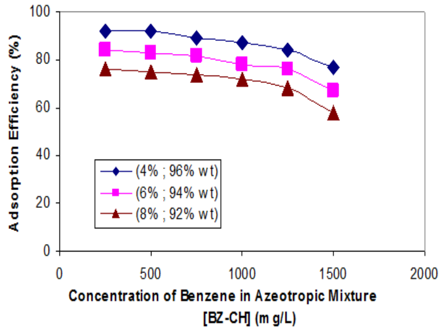


Figure (14) Adsorption percent of the Azeotropic Mixture, (Benzene-Cyclohexane) onto Sand (3g ; Mesh No 100) with different compositions; T= 25 °C,1atm

3.5Effect of Different Particle Sizes:

The effect of different particle sizes (100 Mesh No , 30 Mesh No and 10 Mesh No) of Eu-GAC and Sand adsorbents on the efficiency of adsorption was examined meanwhile all other parameters have been kept constant. As showed from Figure 15 and 16, the adsorption of Azeotropic Mixture (benzene-cyclohexane) improved by increasing mesh number (100 Mesh No). The surface area of an adsorbent depends on its structure.Therefore, the small size of particles have large surface area resulting more availability for adsorbent sites.

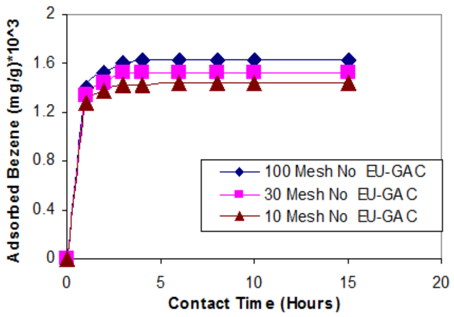


Figure (15) Effect of Contact Time on the Adsorption of Azeotropic Mixture, (Benzene-Cyclohexane), (4% ; 96% wt) by three different particle sizes of EU-GAC (1g); T= 25 °C,1atm

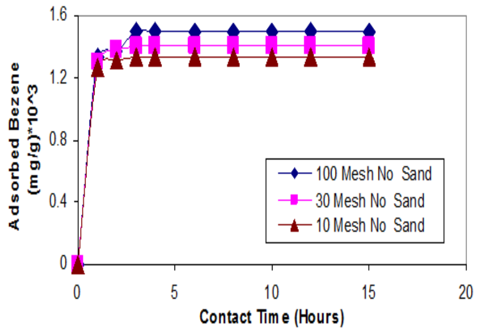


Figure (16) Effect of Contact Time on the Adsorption of Azeotropic Mixtur (Benzene-Cyclohexane), (4% ; 96% wt) by three different particle sizes of Sand (1g); T= 25 °C,1atm

CONCLUSION

The present investigation of the adsorption isotherms and adsorption efficiency of two adsorbents Eu-GAC and Sand to separate the azeotropic mixture (benzene-cyclohexane) was conducted in batch and fixed bed column flow techniques. The azeotropic mixture (benzene- cyclohexane) can be separated to obtain a purified cyclohexane. The results of this study leads to conclude that:

1- The adsorption efficiency of (benzene- cyclohexane) using two adsorbents depends on the pH of the solution. The best adsorption efficiency occurred at pH 3 value.
2- The adsorption efficiency improved with increase in contact time, the optimum contact time was 3 hours.
3- It was found that the adsorption efficiency process ameliorated by improving the adsorbent dose.
4- The behaviour of Eu-GACas adsorbent appeared to be better than the sand regarding the separation efficiency.

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