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Effect of Ultrasound on Adsorption of Azeotropic and Non-Azeotropic Mixture onto Activated Carbon

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Abstract

Experimental study was performed to evaluate the effect of ultrasound on the adsorption isotherms of azeotropic and non-azeotropic mixture onto activated carbon. Acetone-ethanol solution was selected as an azeotropic mixture and methanol-ethanol solution as non-azeotropic mixture. Adsorption equilibrium experiments were separately conducted at constant temperature with and without ultrasound. For the experiments without ultrasound, known amount of activated carbon was added to the selected mixture and left for equilibrium to achieve. Once the equilibrium was achieved, the mixture of samples were filtered and diluted before they were injected in to GCMS for analysis. For the effect of ultrasound, the experiment was repeated with the application of ultrasound. The Ultrasound was applied at a frequency of 21 kHz with 25% amplitude at atmospheric pressure. Adsorption of azeotropic and non-azeotropic mixtures were analyzed by monolayer theory. The results were found that the adsorptive capacity of azeotropic and non-azeotropic mixtures on activated carbon decreased but increased the selectivity.

Keywords: Adsorption isotherm, Excess isotherm, Langmuir adsorption.

1.0 Introduction

Adsorption is well established technology in chemical engineering praactice due to its high separation efficiency and mild operating conditions. Many important processes such as purification, catalysis and bulk separation are currently enjoying application in chemical synthesis. However, the low mass transfer rate and the difficulty of azeotropic adsorption/ separation limit its development and application. Ultrasound has been proved to be a very useful tool in intensifying the mass transfer process and break the affinity between adsorbate and adsorbent by ultrasonic cativation, which made the use of ultrasonics for adsorption/ desorption popular [1]. Several researchers have studied the role of the ultrasound on adsorption and desorption processes [2-4]. Hamdaoui *et al* [5] investigated the effect of ultrasound on adsorption and desorption of *p*-chlorophenol on granular activated carbon. In Suslick *et. al* [10] investigated the effect of pulse ultrasound an adsorption of Genipoisde on resin 1300.

For adsorption, Breitbach *et al.* [8] have studied the ultrasonic effect in a fixed bed packing with polymeric resins by varying ultrasonics (frequency, power, etc.) and process parameters (flow rate, temperature, etc.). However, these above studies were mostly focused on capacity of

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adsorbent in adsorption/desorption process were studied in a restricted range of experimental conditions. However, the adsorption isotherm and the effect on azeotropic system in the presence of ultrasound have not been studied systematically yet. To have clear understanding of adsorption of azeotropic and non-azeotropic binary systems from hydrophobic adsorbent by using ultrasound, it is necessary to study the difference of azeotropic and non-azeotropic liquid system adsorption isotherm in the presence and in the absence of ultrasound. The aim of this research is to study the adsorption isotherm of azeotropic and non- azeotropic binary systems onto activated carbon in the absence and in the presence of ultrasound. Acetone-ethanol as azeotropic and methanol-ethanol as non-azeotropic system are chosen for the present study

2.0 Materials and Methods

Reagents: acetone 99.8%, HPLC grade (Labs-scan); Methanol 99.9% HPLC grade (Mallinckrodt Chemicals); Ethanol 99.9% HPLC grade (Mallinckrodt Chemicals);Activated carbon (for general purpose).
Instrumentation: GCMS (Model: Agilent MS 5973N, GC 6890N); Incubator thermoforma orbital shaker (Hepa filter); Ultrasonic Processor 21 kHz .

The measurement of excess isotherm was conducted using conventional method[5,7,11], where known amount of adsorbent W_s, was added into initially known concentrationof solute x_{1o}, and known mass of liquid mixtue W_o, in a volumetric flask. the mixture were then left for equilibrium, once equilibrium is achieved the liquid phase were drawn and analysed using Gas Chromatography to find out the equilibrium concentration of adsorbate, x_1.

For the experiments in the absence of ultrasound, 2.0 g of activated carbon was added into 20gmixture. The samples were placed in incubator (orbital shaker) at 100rpm and 30°C for equilibriation. The 0.2g of liquid phase were drawn and filtered using 0.45µ m Whatman syringe filter and diluted with 9.8g solvent before injected into GCMS for analysis. For the effect of ultrasound, the experiment was repeated with the subject of ultrasound as shown in figure 1. Ultrasound was applied at the rate of 21 kHz with 25% amplitude.

2.1 Analysis of volatile binary mixture using gas chromatography

GCMS were used for the purpose of liquid phase concentration measurement.
The features of GC/MS are detailed as below:

i.	Type of column	HP-5ms
ii.	Type of carrier gas	He, 35kPa
iii.	Volume of injection	0.05µL
iv.	Type of inlet mode	Split
v.	Split ratio	200:1
vi.	Flow rate of the mobile phase	1.6mL/min
vii.	Gas chromatography run time	2.50 minutes
viii.	Oven temperature	

	Temperature
Initial	40°C
Final	65°C
Rate	25°C/min

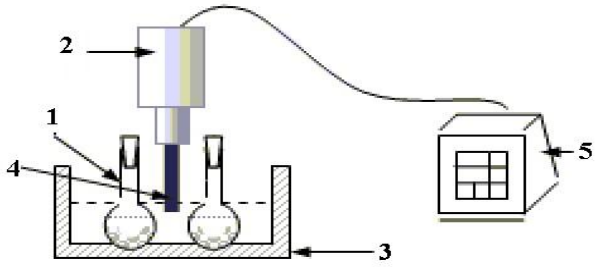

Figure1 Experimental Set-up of for Measurement of Excess Isotherm with Ultrasonic: (1) Volumetric Flask with Rubber Bung. (2) Ultrasonic Converter (3) Isolated Water Bath (4) Ultrasonic Probe (5) Ultrasonic Generator.

2.2 Determination of excess isotherm and characterization of adsorption

The excess isotherms of the systems in the absence and in the presence of ultrasound were calculated by using Eq. (1) as given below,

$$\Gamma_1^w = \frac{W_o\left(x_{1o} - x_1\right)}{W_s} \qquad (1)$$

The graphs of Γ_1^w, excess isotherm to x_1, mole fraction equilibrium were plotted for both binary systems.

2.3 Analysis of binary system using Langmuir monolayer theory

Using simple material balance and equilibrium equation of Langmuir monolayer theory, equation (1) can be manipulated to derive equations (2) [4, 5, 6, 11, and 12]

$$\frac{x_1 x_2}{\Gamma_1^w} = \frac{1}{N_s}\left(x_1 + \frac{1}{K-1}\right) \qquad (2)$$

2.4 Determination of individual adsorption

General Langmuir monolayer of binary adsorption for the concentration of adsorbed phase of component 1 can be presented as equation (3);

$$x_1^s = \frac{Kx_1}{1+(K-1)x_1} \qquad (3)$$

and component 2 can be calculated as (1- x_1^s)
The amount of component 1 adsorbed can be obtained by rewrite equation (3) into equation (4):

$$n_1^s = N_s \frac{Kx_1}{1+(K-1)x_1} \qquad (4)$$

and component 2 can be written as;

$$n_1^s = N_s(1-x_1^s) \qquad (5)$$

The individual adsorption isotherm of binary systems can be calculated using equation (4), whereas the selectivity can be presented using equation (3).

3.0 Results and Discussion

Fig. 2 shows the isotherms of acetone-ethanol on activated carbon with and without the presence of ultrasound. In the case of adsorption without ultrasound, the azeotropic point for acetone-ethanol system is in between 0.65 to 0.70 mole fraction. Whereas with ultrasound, the azeotropic point is slightly shifted by 0.03 of mole fraction to the left. This phenomena shows that ultrasound does bring some effect to the azeotropic adsorption. It can be seen that the isotherms of acetone-ethanol system obtained in the presence of ultrasound is lower than that obtained in the absence of ultrasound.

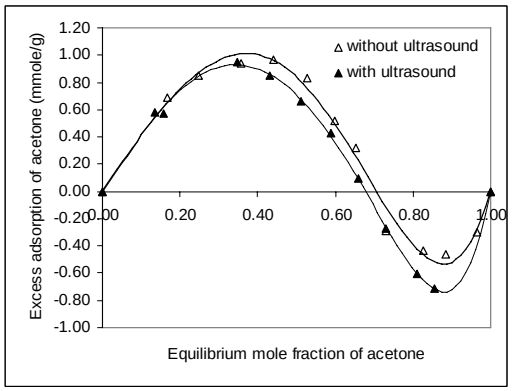

Figure 2 Comparison between isotherms of acetone-ethanol onto activated carbon at 30°C with and without ultrasound.

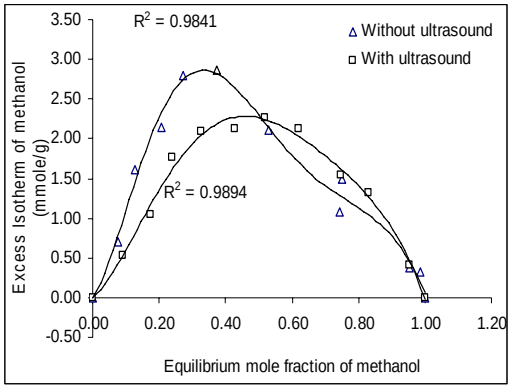

Figure 3 Comparison of Excess isotherms of methanol-ethanol onto activated carbon at 30°C with and without ultrasound

Figure 3 shows that isotherm of methanol-ethanol onto activated carbon with and without ultrasound. No negative adsorption is obtained in this system. However, the excess adsorption with ultrasound was clearly lower compared to in the absence of ultrasound. Figures 4 and 5 represent the adsorption characteristics of binary systems onto activated carbon according to Langmuir Monolayer theory equation (2). The figures show that both of the binary systems obeying the Langmuir theory. The values of N_s and K obtained from figure 4 and figure 5 are shown in table 1. This table indicates N_s were decreased due to ultrasound for both azeotropic and non-azeotropic systems. This phenomena was also observed by Li[3].

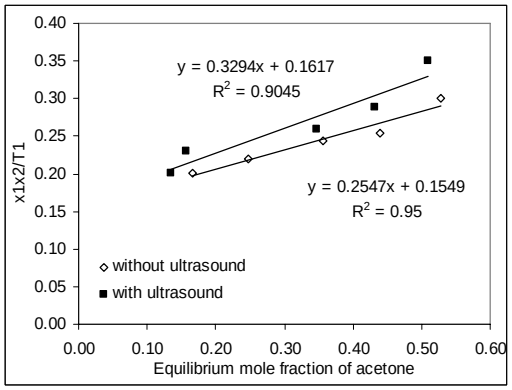

Figure 4 Apparent conformityadsorption of system acetone – ethanol on activated carbon with and without ultrasound to Langmuir monolayer Theory.

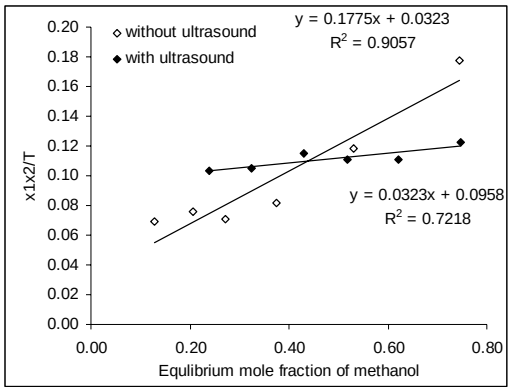

Figure 5 Apparent conformity adsorption of methanol – ethanol system onto activated carbon with and without ultrasound to Langmuir Theory

Table 1 Saturation value of adsorption, N_s and Adsorption Equilibrium constant, K According to Langmuir monolayer theory.

system	{Acetone-ethanol}		{methanol-ethanol}	
	Before Ultrasound	After ultrasound	Before Ultrasound	After Ultrasound
N_s	3.9262	3.0358	3.9231	0.3372
K	1.6443	3.0337	2.1456	8.2556

The individual adsorptions of both components in solution were calculated by Eq. (4) and are shown in figure 6, 7, 8 and 9. Whereas the selectivity was calculated using equation (5) and plotted in figure 10 and 11.

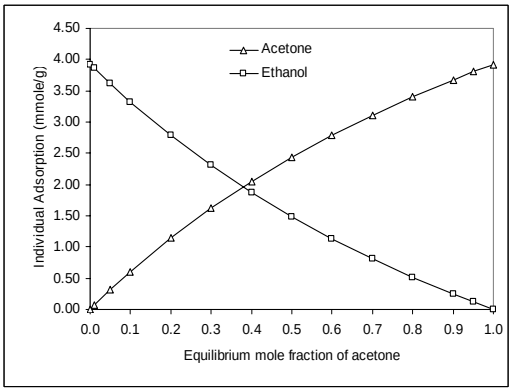

Figure 6 Individual adsorption isotherms for {acetone- ethanol}/ activated carbon system at 30°C without ultasound.

Figure. 6 and 7 represent the adsorption azeotropic mixture. They show that adsorption is favorable to acetone component with ultrasound. This can be clearly explained by figure 10 which shows that the adsorption of acetone is increased compared to in the absence of ultrasound.

The individual adsorption of methanol-ethanol system in the presence and in the absence of ultrasound were shown in fig 8 and 9. Based on the above figures, ultrasound increases the adsorptivity of methanol compared to ethanol. This can be shown clearly in figure 11 which favorable adsorption of methanol with ultrasound.

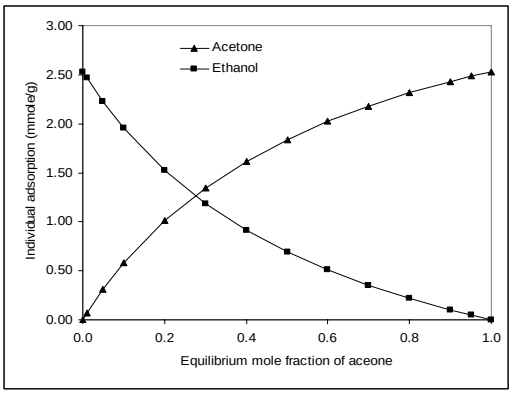

Figure 7 Individual adsorption isotherms for {acetone- ethanol}/ activated carbon system at 30°C in the presence of ultrasound

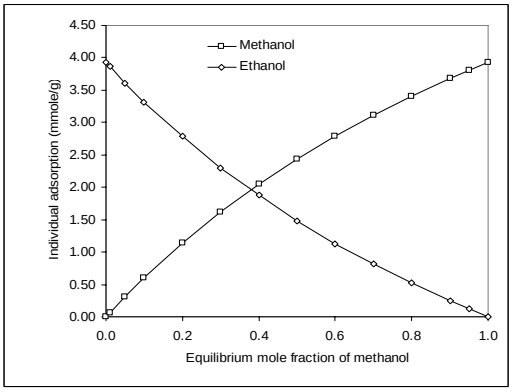

Figure 8 Individual adsorption isotherms for {methanol- ethanol} system onto activated carbon at 30°C without ultrasound

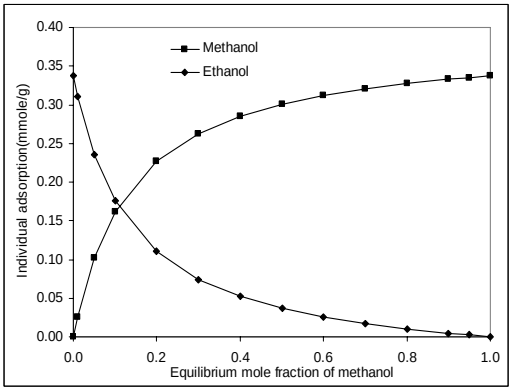

Figure 9 Individual adsorption isotherms for {methanol- ethanol} system onto activated carbon at 30°C in the presence of Ultrasound

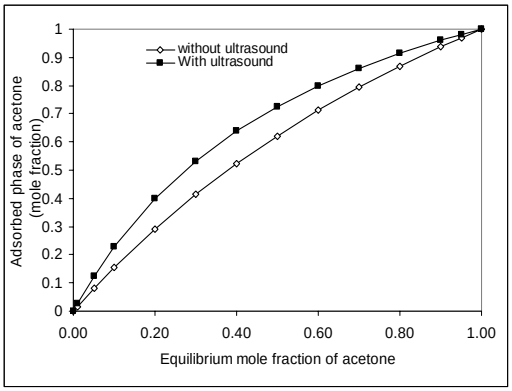

Figure 10 Adsorption Isotherms of acetone-ethanol on activated carbon at 30°C.

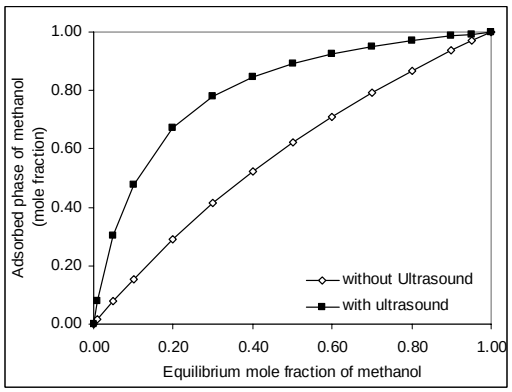

Figure 11 Adsorption Isotherms of methanol-ethanol on activated carbon at 30°C.

4.0 Conclusion

The adsorptions of both azeotropic and non-azeotropic systems are lower in the absence of ultrasound compared to in the presence of ultrasound. The effect of ultrasound shifted the azeotropic point of the adsorbed phase. Ultrasound also influences the adsorptivity and selectivity of adsorbents. On the other hand, the presence of ultrasound, can enhance the adsorption and purity of adsorbed phase. Therefore, further work is required to study the influence of ultrasound on the adsorption characteristics of wide range of azeotropic and nonazeotropic systems onto various adsorbents .

Nomenclature:

x_1 Equilibrium liquid concentration of component 1 (mole mole^{-1})
x_1^s Adsorbed phase concentration of component 1 (mole mole^{-1})
x_2 Equilibrium liquid concentration of component 2 (mole mole^{-1})

x_2^s Adsorbed phase concentration of component 2 (mole mole^{-1})
n_1^s Amount adsorbed of component 1 (mmole/g)
n_2^s Amount adsorbed of component 2 (mmole/g)
N^s Adsorption capacities (mmole/g)
K' Adsorption Equilibrium constant
x_{1o} Initial concentration of component 1 (mole mole^{-1})
Γ_i^w Excess isotherm (mmole/g)
W_s Mass of adsorbent (g)

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