Adsorption isotherm of non-azeotropic solution onto porous adsorbents

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Abstract. Adsorption isotherm is essential component in the understanding of the adsorption process. Several methods of the measurements, analysis and interpretation of adsorption from solution have been reported in the literature. Most of the measurements of adsorption isotherm from solution were involved the measurement of excess isotherm conducted at low region of sorbates concentration. Direct interpretation of excess adsorption isotherm as adsorption isotherm is always been practice. Therefore, in this work a study on the measurement of the adsorption isotherm from solution of non-azeotropic organic solvent mixture onto porous adsorbents for whole range of liquid concentration was conducted. The study included the measurement of excess adsorption isotherm using conventional technique. Theoretical analysis and interpretation of adsorption isotherm from the excess isotherm were conducted using Pseudo Ideal Adsorption, Gibbs Dividing Plane Model and Langmuir-Fruendlich binary isotherm model. For organic solvents, acetone and propanol were chosen as the adsorbates due to the non-azeotropic properties in the mixture. Activated carbon and silicalite were chosen as adsorbents due to the different in their porosity such as macro porous and micro porous structure. The result of the study has revealed that the adsorption isotherm of non-azeotropic mixture onto activated carbon and silicalite can be interpreted as monolayer type of adsorption.

1. Introduction

Adsorption process is a well-established technology in the separation process due to its relative simplicity of design, insensitivity to toxic substances, ease of regeneration and low cost [1]. Adsorption process have been widely employed in the industrial applications such as removal of unwanted component from a solution [2], removing dye from colored textile wastewater [4], removing color and taste [5], [6] and also phenol removal from water and wastewater [7]. In order to utilize the technology of adsorption process, knowledge in adsorption isotherm and adsorption kinetic is essential. The information of adsorption isotherm is always required for the basis of analysis, design and prediction of adsorption processes[8]. For example, adsorption isotherm, plays an important role in predictive modeling for analysis and design of adsorption systems [3,9], and gives useful information, such as determination of surface area, volume of pores, size distribution of adsorbent [10], description of the adsorbates interacts with adsorbent and thus optimizing the adsorption of

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adsorbent [3,11] and determination information of relative adsorptivity of a gas or a vapor on a given adsorbent with respect to chosen standards [12].

Therefore precise measurement and accurate analysis of adsorption isotherm is vital key of success in the prediction of realistic industrial scale adsorption processes. Many measurement and models of adsorption isotherm are reported in the literatures [8,11], [13–15]. Most of measurements were conducted in lower liquid concentration [13, 16-17] and the adsorption isotherms were directly interpreted from measured excess isotherm [18]. The models of adsorption isotherm are also well documented in the standard text book [19]. The measurement of adsorption across whole range of mixture concentration will provide a lot of information on the behavior of the adsorption of the adsorbates onto the adsorbent itself [19–21]. There are few analysis of adsorption isotherms based on the combination of measured excess isotherm across whole range mixture concentration and the theoretical model and are available in the literature [15], [20–22].

Thus, in this work a study on the determination of adsorption isotherm from across whole range of liquid mixture concentration was conducted. Non-azeotropic binary mixture, acetone-propanol was chosen as adsorbates and activated carbon and silicalite were chosen as the adsorbents. The selection of solvent was based on the similarity of molecular size. Nevertheless, the selection of the adsorbent was based on pore structure. Activated carbons (ACs) are usually having macropore structure, whereas silicalite contain micropore structure. The molecular size of solvents and adsorbent pore size properties were selected due to the capability to form monolayer adsorption behavior. Three independent theoretical models which were Pseudo-Ideal monolayer theory, Gibbs Dividing Plane monolayer model and Langmuir-Freundlich isotherm model were chosen for the analysis and interpretation of adsorption isotherm along with the measured excess isotherm.

2. Experimental methods
a. Materials
Two types of adsorbents, AC and silicalite were used in this work. AC was purchased from Fluka, whereas silicalite from Zeolyst International. Both solvents used (acetone and propanol) were High-performance liquid chromatography (HPLC) grade and purchased form Fisher Scientific.

b. Excess adsorption isotherm
A conventional technique of excess adsorption isotherm measurement was employed in this study [21]. The quantities of adsorbent and liquid solvent mixture were set to a weight ratio of 1:10. To achieve equilibrium, the mixture of adsorbent and liquid sorbates were kept in a 250 mL sealed conical flask and placed in orbital shaker at 30°C and 100 rpm for 4 h. The system of the experimental work was designed as shown Table 1.

Table 1. Adsorption system of experimental work

System	Component	Adsorbent	Preference Adsorbate
1	Acetone-propanol	commercial powdered AC	Acetone
2	Acetone-propanol	Silicalite (alumina free ZSM-5, MFI framework)	Acetone

The liquid phase concentration of the adsorption system was determined using Gas chromatography mass spectrometer (GCMS). The method was involved, the withdrawal of liquid sample using 0.45μm Whatman syringe filter. Samples were then injected into GCMS using auto sampling device. The compositions of initial mixture of component 1, x_{10}, equilibrated mixture, x_1, weight of liquid mixture, W_0 and the weight of adsorbent, W_s were then used for the determination of the numerical value of excess adsorption isotherm of component 1, Γ_1 as in (1), [20, 23-25].

$$\Gamma_1 = \frac{W_0(x_{10}-x_1)}{W_s} \tag{1}$$

c. Analysis procedure of mixture composition

The mixture liquid phase concentration was determined using Agilent GCMS Model 7890. Capillary column, 24079 Supelcowax types of column was used with helium as carried gas at 35 kPa and 1.6 mL/min. The injection volume was 1 µL and the initial temperature was kept at 40°C for 2 min before it was ramped at 25°C/min to 65°C with holding time for 1 minute. Finally, the GCMS oven as ramped at 25°C/min to 100°C and held for another 1 minute and injector temperature was set at 150°C with split ratio value of 100:1.

2.4 Adsorption isotherm analysis and interpretation

For the purpose of analysis and interpretation of adsorption isotherm, Gibbs dividing plane isotherm model [15,26], Pseudo-ideal monolayer adsorption theory [20,23-24] and Langmuir-Freundlich isotherm model [22] were used. Following section will discuss and explain briefly of the theory and model used here.

2.4.1 Gibbs dividing plane model

Based on excess isotherm of adsorption in whole range of sorbates concentration , the volume of sorbates adsorbed can be identified using Gibbs dividing plane monolayer adsorption model [15]. The volume of adsorbed layer $a_{tot}(C_e)$ was calculated by the addition of experimentally measured excess adsorption numerical value and the product of the equilibrium adsorbates concentration on the specific volume of adsorbed layer as shown in equation 3. Whereas, the specific adsorbed volume of sorbates, V_a was calculated using the information of the negative of gradient of excess isotherm as shown in equation 2.

Specific volume of adsorbed layer:

$$\frac{d\Gamma(C_e)}{d(C_e)} = -V_a \tag{2}$$

Volume adsorbed layer:

$$a_{tot}(C_e) = \Gamma(C_e) + C_e.V_a \tag{3}$$

In getting the value of excess isotherm gradient, the excess isotherm itself was plotted in mole/m^2 unit and the equilibrium concentration (C_e) in mole fraction.

2.4.2 Pseudo-ideal monolayer adsorption theory

Pseudo-ideal monolayer adsorption was derived from the combination of the materials balance of adsorption system and idealized equilibrium adsorption equation [20]. Below are the important equations that derived from the theory and used in the analysis in this work;
conformity of Pseudo-ideal equation:

$$\frac{x_1 x_2}{\Gamma_1} = \frac{1}{N_s}\left[x_1 + \frac{1}{K-1}\right] \tag{4}$$

Concentration of adsorbed phase:

$$x_1^s = \frac{Kx_1}{1+(K-1)x_1} \tag{5}$$

Number of moles of adsorbed phase:

$$n_1^s = N_s \frac{Kx_1}{1+(K-1)x_1} \tag{6}$$

Here, K is the equilibrium constant, N_s is the total mole of adsorbed phase (adsorption saturation value), equilibrium concentration, $x_2 = (1 - x_{1)}$, x_1^s is the concentration of component 1 in adsorbed phase and n_1^s is the mole of component 1 adsorbed.

2.4.3 Langmuir-Freundlich isotherm model

For the curve fitting purposes, isotherm model of the Langmuir-Freundlich of binary adsorption [22] as shown in equation 7 was used.   The value of adsorbed concentration, x_1^s was calculated using equation 8, this equation was derived from the material balance of adsorption system as explained elsewhere [20]. In order to use equation 8, the value of excess isotherm, Γ_1 was obtained experimentally and the values of total adsorption, N_s were obtained from the intercept of the plot of equation 4. The values of parameters $\overline{K}_{12}$ and m, were estimated using Solver of Microsoft Excel. The solver is devised to minimize a nonlinear sum of squares (SSQ) function subject to the constraints given.

$$x_1^s = \frac{(\overline{K}_{12}x_{12}^l)^m}{1+(\overline{K}_{12}x_{12}^l)^m} \tag{7}$$

$$x_1^s = \frac{\Gamma_1}{N^s} + x_1 \tag{8}$$

3. Results and discussions

The excess adsorption isotherms for both binary mixtures of non azeotropic solution onto activated carbon and silicalite were determined experimentally as shown in figure 1. The excess isotherm for both systems (acetone-propanol/AC and acetone-propanol/silicalite) obtained confirmed to mono-layer type of U shape. The U-shape excess isotherm indicates a preference for one component from the mixture/solution over the entire concentration range. It can be seen clearly that the excess adsorption of silicalite is higher than activated carbon in comparison with the same binary mixture which is acetone-propanol. It shows that silicalite were able to be more selective toward smaller sorbates molecule compare to AC. This behavior is also can be related to the porous structure of the adsorbents used. The U shape of excess adsorption of organic solvent on porous adsorbent are also reported in previous work of Farhadpour and Bono [20,21] and Swiatkowski et. al [22].
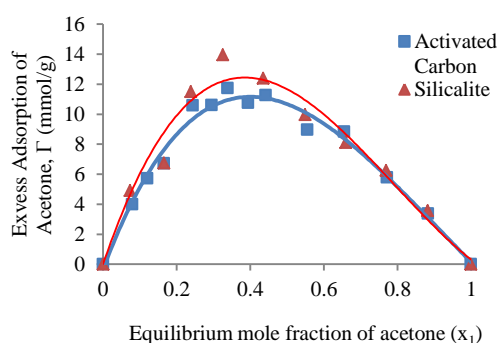

Figure 1. Excess adsorption isotherm for binary organics solvent non-azeotropic mixture onto AC and silicalite at 30°C

Surface specific adsorption isotherm using Gibbs dividing plane model shown in figure 2. It can be seen that the total adsorption of acetone onto ACs were slightly higher than onto silicalite which is in line with the pore volume of AC is higher than silicalite used. The adsorption of acetone for both

adsorbents was found to be predominantly monolayer fashion. This is essentially consistent with the same behavior observed previously for the adsorption organic effluent components on the surface of reversed-phase phenyl modified adsorbents [15].
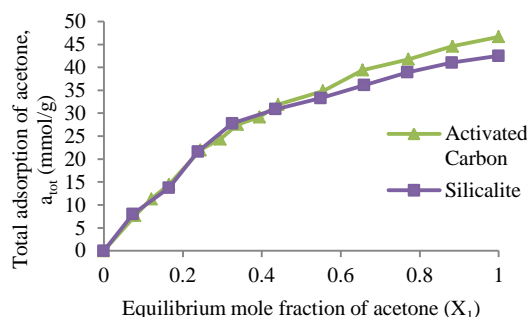

Figure 2. Analysis of total of acetone adsorbed from binary mixture onto AC and silicalite using Gibbs dividing plane model

The analysis of both adsorption systems using equation 4 has shown conformity to Pseudo-ideal monolayer adsorption theory. The slopes and intercepts of the plots in equation 4 were used for the determination of the equilibrium constant, K and saturation adsorption capacity, N_s as presented in Table 2.

Table 2. Equilibrium constant K and saturation adsorption capacity, N_s of adsorption acetone-propanol mixture

System	Parameters	
	K	Ns (mmol/g)
AC	2.00	62.50
Silicalite	3.00	45.45

The total adsorption sorbates onto AC shows higher compared to the adsorption onto silicalite as expected due to the porosity volume of AC is higher than silicalite. The adsorption plot based on Pseudo-ideal monolayer adsorption theory is presented in figure 3, it also show that the adsorption of acetone in AC is higher than silicalite. Both of adsorption isotherms are also showing the monolayer behavior across sorbates concentration range.
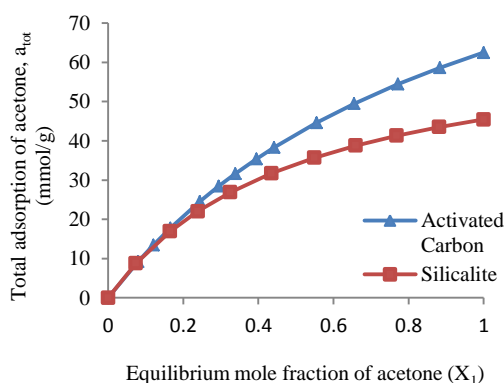

Figure 3. Analysis of total of acetone adsorbed from binary mixture onto AC and silicalite using Pseudo-ideal monolayer adsorption theory

In the curve fit exercise of adsorption isotherm of non-azeotropic adsorption using Langmuir-Fruendlich isotherm model as in equation 7, the adsorbed phase concentration were calculated using equation 8 with the value of excess isotherm obtained experimentally. The values of parameters of Langmuir-Fruendlich binary isotherm model, $\bar{K}_{12}$ and m were obtained by fitting equation 7 using Solver of Microsoft Excel and presented in Table 3.

Table 3. Equilibrium constant, $\bar{K}_{12}$ and saturation value, m of adsroption

System	Parameters	
	$\bar{K}_{12}$	m
AC	1.22	1.05
Silicalite	1.72	0.96

The plots of Langmuir-Freundlich binary isotherm shown in figure 4. Both adsorption isotherms of acetone onto AC and silicalite are fitted well with Langmuir-Freundlich isotherm model and also showed that their well explainable as mono-layer adsorption type.
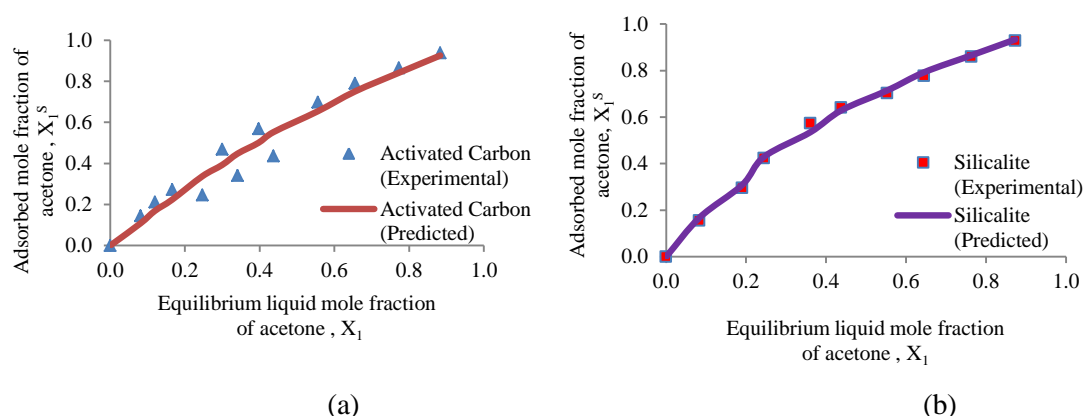

(a)   (b)

Figure 4. Experimentally measured and predicted of acetone adsorbed onto (a) AC and (b) silicalite based on Langmuir-Freundlich isotherm model.

4. Conclusion

The excess adsorption isotherm of acetone from non azeotropic mixture of acetone and propanol onto AC and silicalite was confirmed to U-shaped of preference adsorption isotherm. Silicalite shows more on the preference adsorption of acetone over AC due to the micropore structure. The total adsorption of sorbates for adsorption carbon found to be higher than silicalite which is in line with the pore volume of AC is higher than silicalite. Both adsorption of acetone from non-azeotropic mixture are explainable as mono-layer type across entire range of concentration. Comparison of the adsorption analysis of non-azeotropic organic solvent mixture using three independent adsorption model show very small variation.

5. References

[1]   Soto M L, Moure A, Domínguez H and Parajó J C 2011 *J. Food Eng.* **105** pp 1–27
[2]   Rahchamani J, Mousavi H Z and Behzad M 2011 *Desalination* **267** pp 256–260
[3]   Ahmed M J and Theydan S K 2012 *Ecotox. Environ. Safe.* **84** pp 39–45
[4]   Mahmoodi N M., Salehi R and Arami M 2011 *Desalination* **272** pp 187–195
[5]   Juang R S, Lin S H and Cheng C H 2006 *Ultrason. Sonochem.* **13** pp 251–260
[6]   Hanzlík J, Jehlicka J, Sebek O O, Weishauptová Z and Machovic V V 2004 *Water Res.* **38** pp 2178–2184

[7]   Rengaraj S., Moon S H, Sivabalan R, Arabindoo B and Murugesan V 2002 *Waste Manage*. **22**, pp 543–548

[8]   Allen S J, Gan Q, Matthews R and Johnson P A 2003 *Bioresource Technol.* **88** pp 143–152

[9]   Hameed B H, Ahmad A A and Aziz N 2007 *Chem. Eng. J.* **133** pp 195–203

[10]   Qi S. and Schideman L C 2008. *Water Res.* **42** pp 3353–3360

[11]   Abdullah M A, Chiang L and Nadeem M 2009 *Chem. Eng. J.* **146** pp 370–376

[12]   Bansal R C and Goyal M 2005 *Activated Carbon Adsorption*. CRC Press Taylor and Frances Group, pp 1-167

 [13] Ahmed M J, Halim A, Mohammed A K, Amir A and Kadhum H 2012 *Fluid Phase Equilibr.* **313** pp 165–170

[14]   Al-Degs Y, Khraisheh M A M., Allen S J, Ahmad M N and Walker G M 2007 *Chem. Eng. J.* **128** pp 163–167

[15]   Chan F, Yeung L S, LoBrutto R and Kazakevich Y V 2005 *J. Chromatogr. A* **1082** pp 158–165

[16]   Abdelwahab O 2008 *Desalination* **222** pp 357–367

[17]   Chan L S, Cheung W H and McKay G 2008 *Desalination* **218** pp 304–312

[18]   Hamdaoui O, Naffrechoux E, Tifouti L and Pétrier C 2003 *Ultrason. Sonochem.* **10**, pp 109–14

[19]   Wei P C, May C Y, Ngan M A and Hock C C 2005 *University of Malaya* **1** pp 264–269

[20]   Farhadpour F A and Bono A 1988 *J. Colloid Interf. Sci.* **124** pp 209-227

[21]   Bono A, Sarbatly R, Krishnaiah D, San P M and Yan F Y 2008 *Catal. Today* **131** pp 472–476

[22]   Świątkowski A, Deryło-Marczewska A, Goworek J and Błażewicz S 2004 *Appl. Surf. Sci.* **236**, pp 313–320

[23]   Farhadpour F A and Bono A 1996 *Chem. Eng. Process.: Process Intensification* **35** pp 157–168

[24]   Farhadpour F A and Bono A 1996 *Chem. Eng. Process.: Process Intensification* **35**, pp 141–155

[25]   Anisuzzaman S M, Joseph C G, Daud W M A W, Krishnaiah D and Ho S Y 2015 *Int. J. Ind. Chem.* **6** pp 9-21

[26]   Kazakevich Y V, LoBrutto R , Chan F and Patel T 2001 *J. Chromatogr. A* **913**, no. 1–2, pp 75–87

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