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Interpretation of Adsorption Isotherm of Non Azeotropic Mixture 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 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.

Key words: Pseudo-ideal adsorption, gibbs dividing plane model, langmuir-freundlich binary isotherm, excess isotherm

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 (Soto *et al*., 2011). Adsorption process have been widely employed in the industrial applications such as removal of unwanted component from a solution (Rahchamani *et al*., 2011; Ahmed and Theydan, 2012), removing dye from colored textile wastewater (Mahmoodi *et al*., 2011), removing color and taste (Juang *et al*., 2006; Hanzlik *et al*., 2004) and also phenol removal from water and wastewater (Rengaraj *et al*., 2002). 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 (Allen *et al*., 2003). For example, adsorption isotherm plays an important role in predictive modeling for analysis and design of adsorption systems (Ahmed and Theydan, 2012; Hameed *et al*., 2007) and gives useful information, such as determination of surface area, volume of pores, size distribution of adsorbent (Qi and Schideman, 2008), description of the adsorbates interacts with adsorbent and thus optimizing the adsorption of adsorbent (Ahmed and Theydan, 2012; Abdullah *et al*., 2009) and determination information of relative adsorptivity of a gas or a vapor on a given adsorbent with respect to chosen standards (Bansal and Goyal, 2005). 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 (Allen *et al*., 2003; Abdullah *et al*., 2009; Ahmed *et al*., 2012; Al-Degs *et al*., 2007; Chan *et al*., 2005). Most of measurements were conducted in lower liquid concentration (Ahmed *et al*., 2012; Abdelwahab, 2008; Chan *et al*., 2008) and the adsorption isotherms were directly interpreted from measured excess isotherm (Hamdaoui *et al*., 2003). The models of adsorption isotherm are also well documented in the standard text book (Puah *et al*., 2005).

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 (Puah *et al*., 2005; Farhadpour and

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Bono, 1988; Bono *et al*., 2008). 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 (Chan *et al*., 2005; Farhadpour and Bono, 1988; Bono *et al*., 2008; Swiatkowski *et al*., 2004). Thus, in this study, 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 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 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.

MATERIALS AND METHODS

Materials: Two types of adsorbents, activated carbon and silicalite were used in this study. Activated carbon was purchased from FLUKA, whereas silicalite from Zeolyst International. Both solvents used (acetone and propanol) were HPLC grade and purchased form Fisher Scientific.

Excess adsorption isotherm: A conventional technique of excess adsorption isotherm measurement was employed in this study (Bono *et al*., 2008). 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.

The liquid phase concentration of the adsorption system was determined using GCMS. The method was involved, the withdrawal of liquid sample using 0.45 μm Whatman syringe filter. Samples were then injected into Gas Chromatography Mass Spectrometer (GCMS) using auto sampling device. The compositions of initial mixture, 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 as shown in Eq. 1 (Farhadpour and Bono, 1996a, b, 1988):

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

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^{-1}. 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^{-1} to 65°C with holding time for 1 min. Finally, the GCMS oven as ramped at 25°C min^{-1} to 100°C and held for another 1 min and injector temperature was set at 150°C with split ratio value of 100:1.

Adsorption isotherm analysis and interpretation: For the purpose of analysis and interpretation of adsorption isotherm, Gibbs Dividing Plane isotherm Model (Chan *et al*., 2005; Kazakevich *et al*., 2001), pseudo-ideal monolayer adsorption theory (Farhadpour and Bono, 1996a, b, 1988) and Langmuir-Freundlich isotherm model (Swiatkowski *et al*., 2004) were used.

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 (Chan *et al*., 2005). 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 Eq. 2. 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 Eq. 3.

Volume adsorbed layer:

$$a_{tot}\,(C_e) = \Gamma(C_e) + C_e.V_a \quad (2)$$

Table 1: Adsorption System of experimental work

System	Component	Adsorbent	Preference adsorbate
1	Acetone-propanol	Commercial powdered activated carbon	Acetone
2	Acetone-propanol	Silicalite (alumina free ZSM-5, MFI framework)	Acetone

Specific volume of adsorbed layer:

$$V_a = -\frac{d\Gamma(C_e)}{d(C_e)} \quad (3)$$

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.

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 (Farhadpour and Bono, 1988). Below are the important equations that derived from the theory and used in the analysis in this study.

Conformity of Pseudo-ideal equation:

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

Concentration of adsorbed phase:

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

Number of moles of adsorbed phase:

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

where, K is equilibrium constant, N_S is total mole adsorbed or adsorption saturation value, x_1^s is component 1 adsorbed phase concentration and n_1^s is amount of component 1 adsorbed.

Langmuir-freundlich isotherm model: For the curve fitting purposes, isotherm model of the Langmuir-Freundlich of binary adsorption (Swiatkowski *et al*., 2004) as shown in Eq. 7 was used. The value of adsorbed concentration, x_1^s was calculated using Eq. 8, this equation was derived from the material balance of adsorption system as explained elsewhere (Farhadpour and Bono, 1988). In order to use Eq. 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 Eq. 4. The values of parameters $\bar{K}_{12}$ 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 (Tan *et al*., 2009):

$$x_1^s = \frac{\left(\bar{K}_{12} x_{12}^1\right)^m}{1+\left(\bar{K}_{12} x_{12}^1\right)^m} \quad (7)$$

$$x_s^1 = \frac{\Gamma_1}{N^s} + x_1 \quad (8)$$

RESULTS AND DISCUSSION

The excess adsorption isotherms for both binary mixtures of non azeotropic solution onto activated carbon and silicalite were determined experimentally as shown in Fig. 1. The excess isotherm for both systems (acetone-propanol/activated carbon and acetone-propanol/silicalite) obtained confirmed to mono-layer type of U shape as classified by Schay and Nagy (Oscik, 1982). The U-shape excess isotherm indicates a preference for one component from the mixture/solution over the entire concentration range (Song *et al*., 2013). 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 activated carbon. This behavior is also can be related to the porous structure of the adsorbents used. This trend is similar as reported by Farhadpour and Bono (1988), Bono *et al*. (2008) and Swiatkowski *et al*. (2004).

Surface specific adsorption isotherm using Gibbs dividing plane model was shown in Fig. 2a. It can be seen that the total adsorption of acetone onto activated carbons were slightly higher than onto silicalite which is

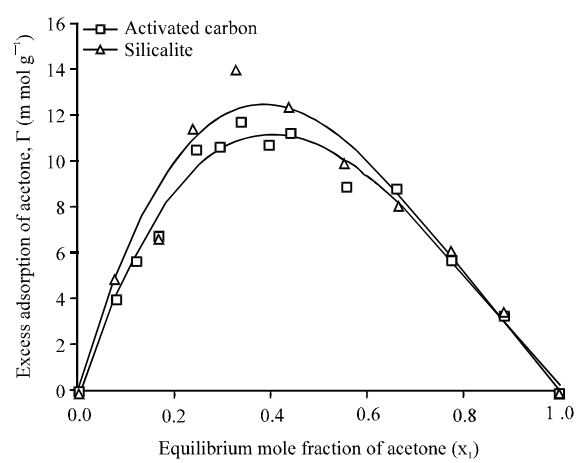

Fig. 1: Excess adsorption isotherm for binary organics solvent non-azeotropic mixture onto activated carbon and silicalite at 30°C

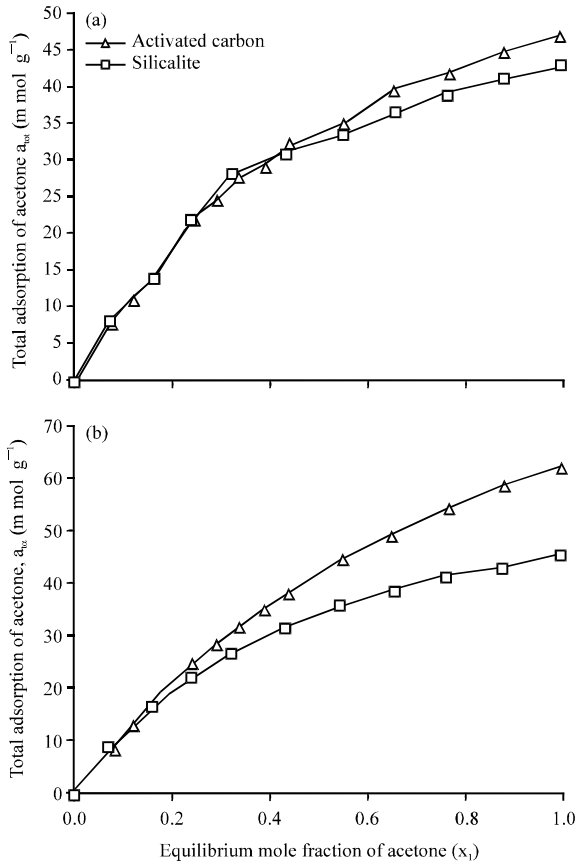

Fig. 2(a-b): Analysis of adsorbed amount of acetone in binary mixture onto activated carbon and silicalite using (a) Gibbs dividing plane model and (b) Pseudo-ideal monolayer adsorption theory

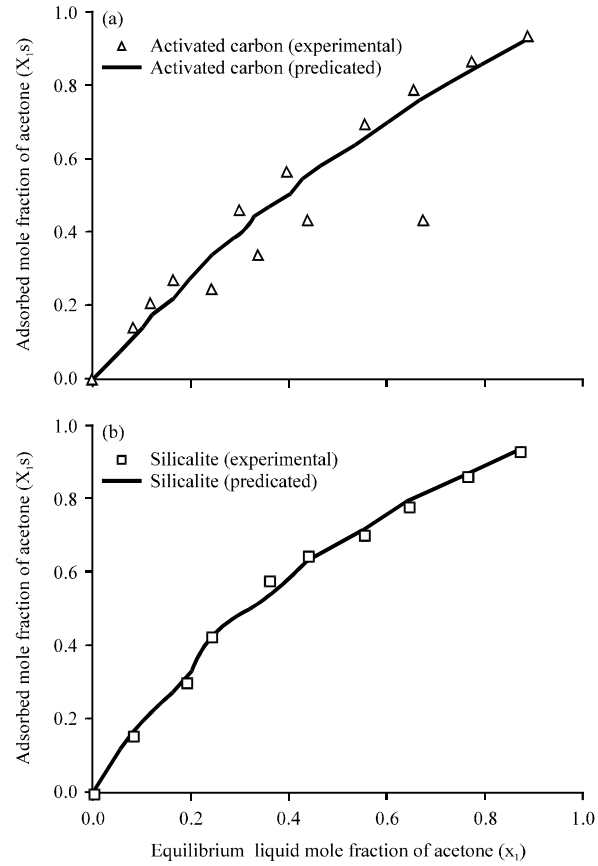

Fig. 3(a-b): Experimentally measured and predicted of acetone adsorbed onto (a) Activated carbon and (b) Silicalite based on Langmuir-Freundlich isotherm model

Table 2: Equilibrium constant (K) saturation value of adsorption, N_S of adsorption acetone-propanol mixture

System	Activated carbon	Silicalite
K	2.00	3.00
Ns (mmol/g)	62.50	45.45

in line with the pore volume of activated carbon 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 (Chan *et al*., 2005).

The analysis of both adsorption systems using Eq. 4 has shown conformity to Pseudo-ideal monolayer adsorption theory. The slopes and intercepts of the plots of Eq. 4 were used for the determination of the equilibrium constant, K and saturation adsorption capacity, N_s as presented in Table 2. The total adsorption sorbates onto activated carbon shows higher compared to the adsorption onto silicalite as expected due to the porosity volume of activated carbon is higher than silicalite. The adsorption plot based on pseudo-ideal monolayer adsorption theory is presented in Fig. 2b, it also show that the adsorption of acetone in activated carbon is higher than silicalite. Both of adsorption isotherms are also showing the monolayer behavior across sorbates concentration range.

In the curve fit exercise of adsorption isotherm of non-azeotropic adsorption using Langmuir-Fruendlich isotherm model Eq. 7, the adsorbed phase concentration were calculated using Eq. 8 with the value of excess isotherm obtained experimentally. The values of total adsorption were obtained from the Pseudo-ideal monolayer adsorption isotherm analysis of Eq. 4 and the numerical value are shown in Table 2. The values of parameters of Langmuir-Fruendlich binary isotherm model, K_{12} and m were obtained by fitting of Eq. 7 using Solver of Microsoft Excel. The values are shwon in Table 3.

The plots of Langmuir-Freundlich binary isotherm are shown in Fig. 3. Both adsorption isotherms of acetone

Table 3: Langmuir-Freundlich parameter for acetone-propanol mixture obtained from excel programme

System	Parameters	
	K_{12}	m
Activated carbon	1.22	1.05
Silicalite	1.72	0.96

onto activated carbon and silicalite are fitted well with Langmuir-Freundlich isotherm model and also showed that their well explainable as mono-layer adsorption type.

CONCLUSION

The excess adsorption isotherm of acetone from non azeotropic mixture of acetone and propanol onto activated carbon and silicalite was confirmed to U-shaped of preference adsorption isotherm. Silicalite shows more on the preference adsorption of acetone over activated carbon 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 activated carbon is higher than silicalite. Both adsorption of acetone from non-azeotropic mixture are explainable as mono-layer type across entire range of concentration.

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