

Full Length Research Paper

# Modeling of adsorption isotherm of benzoic compounds onto GAC and introducing three new isotherm models using new concept of Adsorption Effective Surface (AES)

M. Davoudinejad\* and S. A. Ghorbanian

School of Chemical Engineering, University of Tehran, I.R. Iran.

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In this research, by using derivation of Langmuir isotherm model and sharing point of this model with Volmer, Kiselev and Fowler-Guggenheim models, a new simple approach to derivation of isotherm models named Adsorption Effective Surface (AES) was introduced. Using AES method, one can explain such behavior of theoretical models as in predicting maximum adsorption capacity ( $q_m$ ). In this method, adsorption and desorption follow first order kinetics and all non-idealities appears in term  $S_{eff}(\theta)$ . Three new isotherm models, two models with monolayer adsorption mechanism based on Langmuir equation and one model with monolayer-multilayer adsorption mechanism based on Langmuir and Elovich equations are derived using AES method. The adsorption equilibrium isotherms of five benzoic compounds from aqueous solutions onto two granular activated carbons (GAC) with average granulometries of 1.5 and 2.5 mm were studied. Benzene (B), Toluene (T), Phenol (P), Chlorobenzene (CB) and Nitrobenzene (NB) were chosen for adsorption test and effect of adding groups such as methyl, hydroxide, chlorine and nitroxide on benzene ring in its adsorption were discussed. Uptake of Benzoic compounds increase in the following order  $P < B < T < NB < CB$ , which correlates in general with increase in polarisability and decrease in solubility. Activated carbon adsorbent with lower particle size (1.5 mm) has more adsorption capacities about 10% in average. The proposed equations named AES, Logarithmic and Hybrid model were used to model the experimental data, and results were compared with corresponding equations. Regression results showed that in all cases, the new models had better fittings with experimental data than corresponding models.

**Key words:** Isotherm model, adsorption effective surface, benzoic compounds, activated carbon.

## INTRODUCTION

Benzoic compounds are toxic and carcinogenic pollutants, which with an increasing level, exist in the environment. These pollutants are released by several industries as chemical, petrochemical, oil refinery and coal conversion industries. The most important compounds of this group are benzene, toluene, phenol, chlorobenzene and nitrobenzene. These compounds are

represented as priority pollutants by the USA Environmental Agency. Benzoic compounds have several uses in the chemical industries that are used as raw materials and solvent in a great extent in the manufacturing processes. Even existence of a small amount of these pollutants in the environment is harmful for animals and plant organs. Because of their stability

\*Corresponding author. E-mail: [m.davoudinejad@gmail.com](mailto:m.davoudinejad@gmail.com)

**Table 1.** Characteristics of adsorbates and experimental maximum adsorption capacities.

Parameter	P	B	T	NB	CB
MW (g/mole)	94.11	78.11	92.13	123.11	112.56
C <sub>aq</sub> (g/L)	84	1.8	0.52	1.9	0.4
(Lide, 2009) α (×10 <sup>-24</sup> cm <sup>3</sup> )	11.1	10	11.8	14.7	14.1
1.5 mm q <sub>m</sub> (mg/g)	231	245	308	446	518
2.5 mm q <sub>m</sub> (mg/g)	208	226	277	409	482

and highly toxicity and remaining long time in the environment, they are great menace for human health (Dabrowski, 1999; Chiou, 2002; Newcombe, 2008).

Adsorption by the granulated activated carbon is a simple, effective and economical method that is used in a great extent for removing and adsorption of organic pollutants from industrial wastes. This method is introduced as one of the best methods in the environmental control technology by the USA Environmental Protection Agency (EPA). Several experiments are done on adsorption of benzene, toluene, phenol, chlorobenzene and nitrobenzene from liquid phase onto different activated carbons, and several isotherms are produced (Dobbs and Cohen, 1980; Valenzuela and Myers, 1989; Chatzopoulos et al., 1993; Hindarso et al., 2001; Maarof and Hameed, 2004; Hamdaoui and Naffrechoux, 2007; Haderlein and Schwarzenbach, 1993; Sennour et al., 2009).

Activated carbon, the most important commercial adsorbent, has high surface area and high porosity. The main advantage using activated carbon is its easy separation from liquid flow. This characteristic causes the simplicity and flexibility of the process and lower costs. Adsorption of organic soluble in the liquid phase is an important application of activated carbon and includes a great range of systems as potable water and waste treatment. Unique surface characteristic of activated carbon in comparison with other adsorbents is the existence of oxide groups and inorganic impurities that give non-polar or low polarity properties to surface which can adsorb non-polar and low polarity molecules very well (Yang, 2003). Adsorption of liquid solution because of the presence of solvent is complicated. There are adsorbate-adsorbent, solvent-adsorbent and solvent-adsorbate interactions. Generally, low solubility cause more adsorption. Adsorption capacity depends on several factors as surface area, polarisability of adsorbent, structure and distribution of adsorbent pores. Characteristics of adsorbate that influence the process of adsorption are solubility, polarity and adding groups on benzoic ring in aromatics. The size of molecules determines its ability to reaching adsorbent pores and solubility determines hydrophobic interactions. The adding groups of aromatic ring effects on dispersion interactions between adsorbate and adsorbent grafene layer (Bansal and Goyal, 2005).

In this research, adsorption of five benzoic compounds on two granular activated carbons (GAC) with different size is studied. Also their adsorption capacity on activated carbon and the effect of adding groups in benzoic ring as methyl, hydroxide, chlorine and nitroxide on benzene ring in its adsorption are investigated.

## MATERIALS AND METHODS

Adsorption equilibria information is the most important piece of information in understanding an adsorption process. No matter how many components are present in the system, the adsorption equilibria of pure components are the essential ingredient for the understanding of how many those components can be accommodated by a solid adsorbent. With this information, it can be used in the study of adsorption kinetics of a single component, adsorption equilibria of multicomponent systems, and then adsorption kinetics of multicomponent systems.

Five organic molecules were selected for the study of adsorption onto two granular activated carbons: benzene (B), phenol (Ph), toluene (T), chlorobenzene (CB) and nitrobenzene (NB). The adsorbates, purchased from Merck with purity greater than 99%, and distilled water were used to prepare the aqueous solutions for the adsorption tests. The principal characteristics of the studied adsorbates are regrouped in Table 1. The GACs used in this study were purchased from Merck and have average granulometries of 1.5 and 2.5 mm.

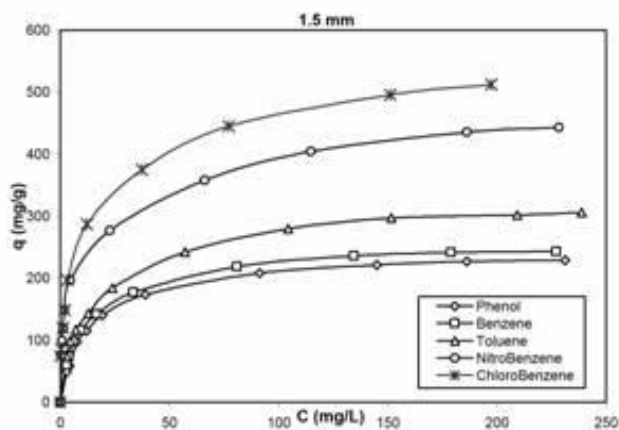
Adsorption experiments were carried out by adding a known mass of activated carbon (0.02 to 0.6 g) to a series of 100 mL glass-stoppered flasks filled with 100 mL of solution with initial concentration 300 mg/L. The glass-stoppered flasks were then placed in a thermostatic shaker water bath with temperature 20°C. The initial and equilibrium concentrations of adsorbate solutions were determined by means of a Unico UV/visible spectrophotometer at a wavelength of 254, 206, 270, 210 and 268 nm for benzene, toluene, phenol, chlorobenzene and nitrobenzene, respectively. The amount adsorbed on the activated carbon was determined from the initial liquid-phase concentration and equilibrium concentration:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

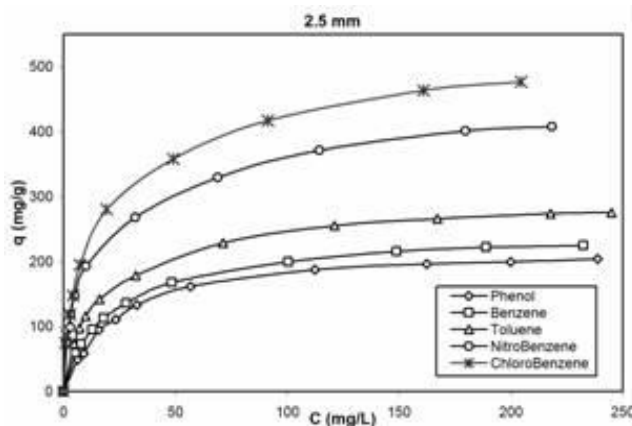
Here  $C_0$  and  $C_e$  are the initial and equilibrium concentrations respectively,  $V$  is the volume of solution, and  $m$  is the mass of activated carbon.

The experimental adsorption isotherms of benzoic compounds from aqueous solutions onto GACs are presented in Figures 1 and 2. The obtained results show that the order of adsorption on GACs is: Ph < B < T < NB < CB. The shape of the isotherms is the first experimental tool to diagnose the nature of a specific adsorption phenomenon. The isotherms have been classified according to the classification of Giles et al. (1960). Giles have classified adsorption isotherms into four main groups: L, S, H, and C. According to the above classification, the isotherms of benzoic compounds displayed an L curve pattern. The L shape of the adsorption isotherms means that there is no strong competition between solvent and the adsorbate to occupy the adsorbent surface sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface (molecules adsorbed flat on the surface). Table 1 shows that the values of experimental maximum adsorption capacity ( $q_{m, \text{experimental}}$ ) for the five benzoic compounds onto GAC 1.5 mm are about 10% more than GAC 2.5 mm.

Some parameters affecting adsorption of benzoic compounds



**Figure 1.** Adsorption isotherms of benzoic compounds onto GAC with average granulometry of 1.5 mm.



**Figure 2.** Adsorption isotherms of benzoic compounds onto GAC with average granulometry of 2.5 mm.

onto activated carbon are shown in Table 1. In adsorption of molecule with low polarity onto activated carbon, polarisability and solubility of adsorbate are effective. Molecule with low solubility and high polarisability has a better adsorption. In Table 1, two ranges of polarisabilities are seen. Benzene, toluene and phenol have polarisability in range of 10 to 12 and chlorobenzene and nitrobenzene have polarisability of 14 to 15. In these two groups, molecules with lower solubility and higher polarisability have more adsorption.

### Modeling

According to Langmuir theory (Langmuir, 1916) if surface coverage is  $\theta$ , the remaining adsorption surface in front of molecules is  $(1 - \theta)$ . In fact  $(1 - \theta)$  is a criterion for bare surface of adsorbent. In monolayer adsorption, only one layer of molecules can occupy the adsorbent surface sites. According to this theory, adsorbate molecules have been adsorbed on specific areas without any moving and interaction (including repulsive and attractive forces and spatial prohibition). Adsorbent surface has been assumed to be a flat surface with high accessibility. But in practical, the adsorbent

surface is porous and very non-homogeneous and comprises many pores with different accessibility. Langmuir equation is achieved by equating adsorption and desorption rates in equilibrium condition:

$$k_a C_e (1 - \theta) = k_d \theta \quad \Rightarrow \quad b C_e = \frac{\theta}{1 - \theta} \quad (2)$$

Where  $k_a$  and  $k_b$  are adsorption and desorption coefficient, respectively. The parameter  $b$  is called the affinity constant or Langmuir constant. The isotherm Equation (2) written in the form of fractional loading is not useful for the data correlation as isotherm data are usually collated in the form of amount adsorbed versus pressure or concentration:

$$q_e = q_m \frac{b C_e}{1 + b C_e} \quad (3)$$

Where  $q_e$  is the amount adsorbed per unit mass and  $q_m$  is the maximum saturation capacity.

Adsorption in practical solids is a very complex process owing to the fact that the solid structure is generally complex and is not so well defined. The complexity of the system is usually associated with the heterogeneity between the solid and the adsorbate concerned. In other words, heterogeneity is not a solid characteristic alone but rather it is a characteristics of the specific solid and adsorbate pair. In practical condition, many factors are affecting the adsorption process. Spatial prohibition, intense molecular forces between solvent and soluble molecules in liquids, surface tension in liquids, un-accessibility of very small and microscopic pores of solids, heterogeneity of surface energy and chemical impurities in solid construction are highly affecting the physical adsorption process (Suzuki, 1990; Duong, 1998; Toth, 2002; Imae, 2007).

All the mentioned factors will increase by increasing the adsorption amount and loading the adsorbent surface. It is obvious that the regions of adsorbent surface with high energy levels and more accessibility to molecules will be loaded earlier. In practical operation, maximum saturation capacity of adsorbent cannot be used because of mass transfer effects in solid-fluid contact process. Langmuir assumptions are very ideal, because according to the remaining surface of Langmuir adsorption,  $(1 - \theta)$ , adsorbent surface from the beginning to the end of the adsorption process and reaching equilibrium condition, will be loaded with an constant slope, but it is obvious that with loading adsorbent surface, driving force will reduced.

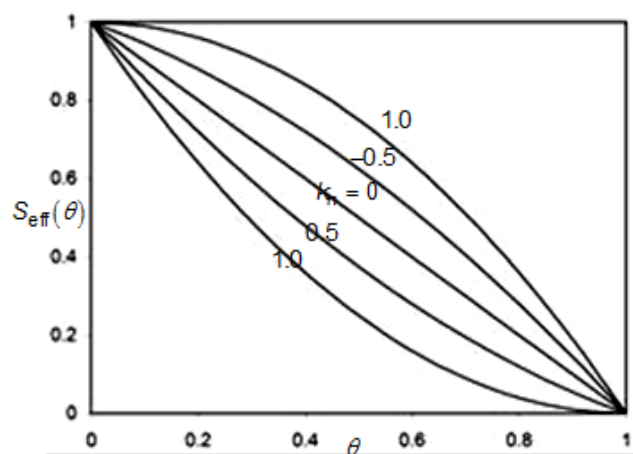
If other theoretic models like Volmer (Duong, 1998), Fowler-Guggenheim (Fowler and Guggenheim, 1939) and Kiselev (Kiselev, 1958) as Langmuir, we see that each of them, regardless how they have been derivated, predict an apparent residual surface for adsorbent, hence we call it Adsorption Effective Surface (AES). These models and their residual surface have been shown in Table 2. With this approach, these models can be written as:

$$K C S_{\text{eff}}(\theta) = \theta \quad (4)$$

Where  $S_{\text{eff}}(\theta)$  is adsorption effective surface which for Langmuir model is  $(1 - \theta)$ . In Figure 3, Volmer effective surface has been compared with Langmuir model bare surface of adsorption. The ability to move the adsorbate molecules on adsorption surface in Volmer theory causes a more covered adsorbent surface and lower AES than Langmuir one. Sensible characteristic of predicted effective surface in Volmer model is its high deviation from the ideal state in Langmuir model, especially with increasing the amount of adsorption. When  $\theta > 0.8$  this surface reaches zero

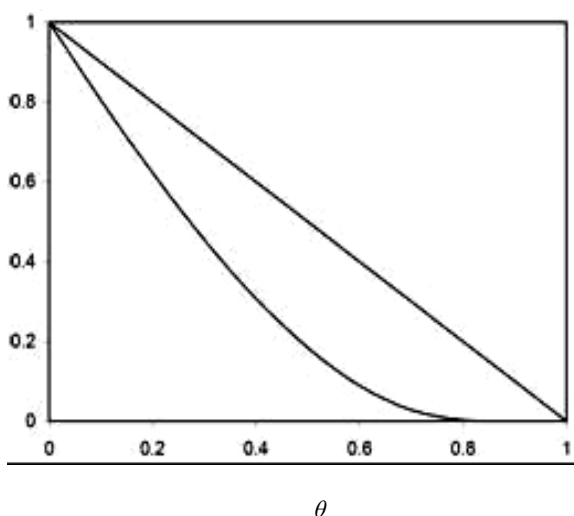
**Table 2.** Adsorption Effective Surface for Langmuir, Volmer, F-G and Kiselev models.

Isotherm	Langmuir derivation form	$S_{\text{eff}}(\theta)$
Langmuir	$K_L C(1-\theta) = \theta$	$(1-\theta)$
Volmer	$K_V C(1-\theta) \exp\left(\frac{\theta}{\theta-1}\right) = \theta$	$(1-\theta) \exp\left(\frac{\theta}{\theta-1}\right)$
F-G	$K_{FG} C(1-\theta) \exp(-\alpha\theta) = \theta$	$(1-\theta) \exp(-\alpha\theta)$
Kiselev	$k_i C(1-\theta)(1+k_n\theta) = \theta$	$(1-\theta)(1+k_n\theta)$



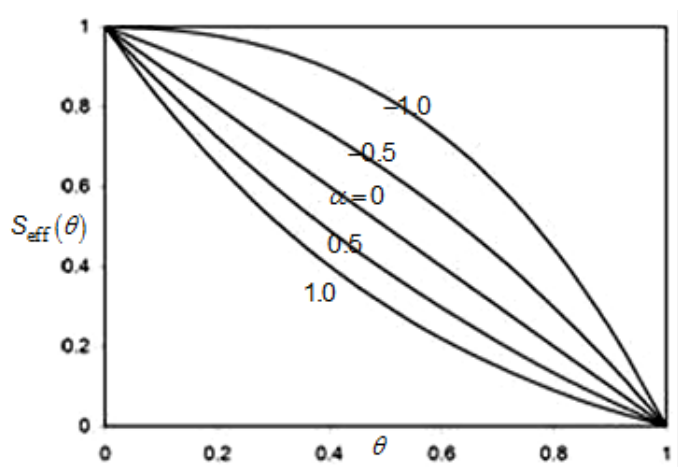
**Figure 5.** Comparing AES of Kiselev with Langmuir.

very higher than the other models and experimental values. So the experimental saturation capacity is always lower than real value. This means that there are always regions in adsorbent surface that would never be used. In F-G model, parameter  $\alpha$  shows the group  $2u/R_g T$ , that implies attractive and repulsive forces between adsorbed molecules. In Figure 4,  $S_{\text{eff}}(\theta)$  is plotted versus  $\theta$ , with different values of  $\alpha$ . This model presents different patterns of effective surface in different conditions. When  $\alpha$  is positive, the interaction between adsorbed molecules is repulsive and for negative amount of  $\alpha$ , interaction between adsorbed molecules is attractive. For  $\alpha = 0$ , there is no interaction between adsorbed molecules (Langmuir theory).



**Figure 3.** Comparing AES of Volmer with Langmuir.

According to Figure 4, When there is an attractive force between adsorbed molecules,  $\alpha < 0$ , the effective surface is more than Langmuir surface and when the forces are repulsive  $\alpha > 0$ , these surfaces are lower than Langmuir surface. It is obvious that repulsive forces between adsorbed molecules decrease the amount of adsorption that it appears in decreasing in adsorption effective surface and vice versa. The larger amount of  $|\alpha|$  causes higher deviation from the straight line (Langmuir surface). In start of adsorption process, when there is a little amount of adsorbed molecule on a wide surface of adsorbent, it is expected that interaction between adsorbed molecules is negligible and Langmuir model is to be valid. On the other hand, it is expected that in low surface coverage, AES of F-G model be coincided on Langmuir surface of adsorbent. But it is not as seen in Figure 4, which is an incompetence of F-G model.



**Figure 4.** Comparing AES of F-G with Langmuir.

For Kiselev model,  $S_{\text{eff}}(\theta)$  has been plotted against  $\theta$  in Figure 5. In this model for  $k_n > 0$ , adsorbed molecules form complex on adsorbent surface that improve adsorption. This improvement can be seen in increment of effective surface compare to Langmuir surface. For  $k_n \leq 0$ , there will be no complex. For  $k_n = 0$ , the equation is same with Langmuir equation (the straight line) and for  $k_n < 0$  the effective surface is less than real surface.

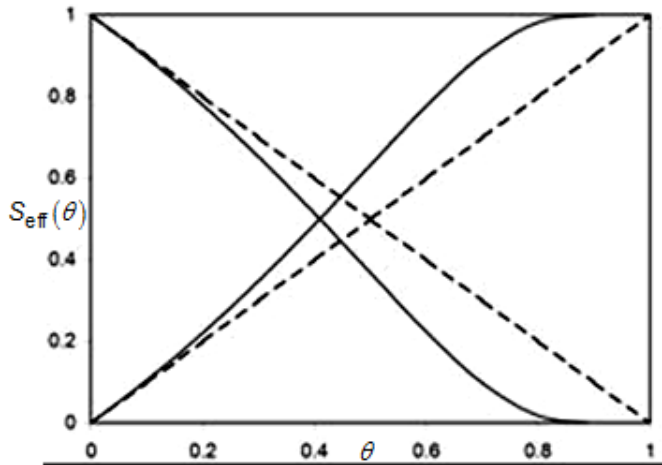
approximately.

In Volmer's point of view, reaching the saturation capacity is very difficult; hence the predicted saturated capacity in Volmer model is

**Introducing a new isotherm model based on the concept of Adsorption Effective Surface**

To introduce new equation, two postulations are considered:

- (1) In low adsorption values,  $\theta < 0.1$ , the adsorption effective



**Figure 6.** Comparing adsorption and desorption effective surfaces of logarithmic with Langmuir.

surface becomes compatible with the Langmuir surface. When the adsorbed amount on the adsorbent surface is much less than the saturated capacity of adsorption, in practice the interaction between adsorbed molecules is negligible and the Langmuir theory is valid.

2) By increasing in the adsorbed amount, this surface deviates from the ideal (Langmuir) value and finally it reaches zero asymptotically. Gradually by increasing in the amount of adsorbed molecules and occupying adsorption sites, the molecular interactions increase and spatial prohibitions cause decreasing effective molecular striking on the surface and the adsorption decreases in such a way that this phenomenon can be shown as a decrease in effective surface.

One of the equations that can be expressed based on these two postulations is Equation 4. This equation in low amount of adsorption is compatible with Langmuir model but in high adsorption values it deviates from ideal state.

$$S_{\text{eff}}(\theta) = \exp\left(\frac{\theta}{\theta-1}\right) \quad (5)$$

Variation of AES in this equation is compared with Langmuir surface in Figure 5. Substituting Equation 5 in Equation 4, the new isotherm model hereafter Adsorption Effective Surface model (AES model) is formulated:

$$K_{\text{AES}}C = \theta \exp\left(\frac{\theta}{1-\theta}\right) \quad (6)$$

The mechanism the model is based on is the mechanism of localized monolayer adsorption of Langmuir model that all non-idealities have been applied generally.

### Langmuir-Like Logarithmic model

Theoretical isotherm equations written in the form of fractional loading is not useful for the data correlation as isotherm data are usually collated in the form of amount adsorbed versus pressure or concentration. For isotherm AES by using properties of the Langmuir model can develop a new model in the form of amount adsorbed versus concentration. In Langmuir model, the summation

of the remaining adsorption surface  $(1-\theta)$  and covered surface  $\theta$  is equal to one in the across adsorption process. But for other theoretical models, the summation of adsorbed and covered surface always is less than one. According to these models, some regions of the adsorption surface are out of reach. For AES model by adding non-reachable surface to covered surface of adsorbent and considering this summation as desorption surface, it can be obtained from 1 minus effective surface (apparent remaining adsorption surface). By doing this, a new model in from of Equation 7 is obtained.

$$bC \exp\left(\frac{\theta}{\theta-1}\right) = 1 - \exp\left(\frac{\theta}{\theta-1}\right) \Rightarrow bC = \exp\left(\frac{\theta}{1-\theta}\right) - 1$$

$$\Rightarrow 1 + bC = \exp\left(\frac{\theta}{1-\theta}\right) \Rightarrow \ln(1 + bC) = \frac{\theta}{1-\theta}$$

$$\theta = \frac{\ln(1 + bC)}{1 + \ln(1 + bC)} \quad (7)$$

This model is like Langmuir model but it has a logarithmic shape. In Figure 6, effective adsorption and desorption surfaces are represented. This model is called the logarithmic model. In this model, desorption surface of Langmuir and non-applicable adsorbent surface for molecules are accompanied together. Consequently, it is increased compared to desorption surface Langmuir.

### Introducing a multilayer adsorption model with usage of Adsorption Effective Surface concept

In multilayer adsorption, it is supposed that molecules are adsorbed in several layers on the adsorption surface. One of the equations that predicted multilayer adsorption with unlimited layers is Elovich equation (Elovich and Larinov, 1962). This model is based on a kinetic principle that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption.

$$K_E C_e = \theta \exp(\theta) \quad (8)$$

Rearranging Elovich equation in from of Equation (4), effective surface is given as:

$$K_E C \exp(-\theta) = \theta \quad (9)$$

In this model, it is assumed that adsorption sites increase with adsorption process and the area of adsorbed molecules is added to the adsorbing surface. Adsorption effective surface of this model is related exponentially with surface coverage:

$$S_{\text{eff}}(\theta) = \exp(-\theta) \quad (10)$$

In Figure 7, effective surface of Elovich model is compared to remaining surface of Langmuir. As can be seen, Elovich effective surface has a slow decreasing manner with increasing amount of adsorption.

In the small amount of adsorption,  $\theta < 0.1$ , the effective surface of Elovich model is compatible with adsorption surface of Langmuir model which can be concluded that in the small amount of adsorption, the adsorption is monolayer approximately.

Proceeding adsorption process gradually, the adsorption of

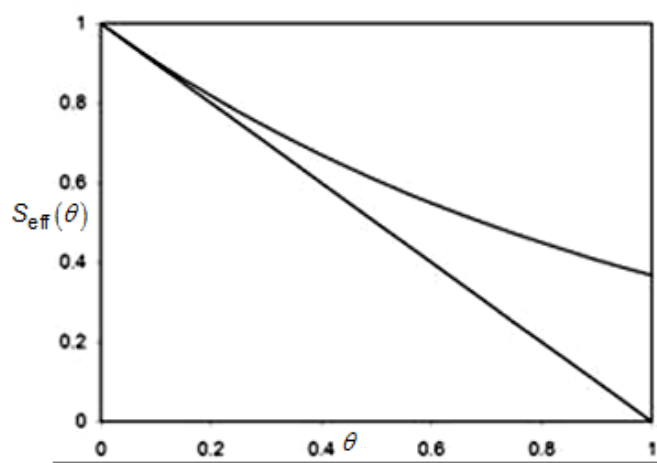


Figure 7. Comparing AES of Elovich with Langmuir.

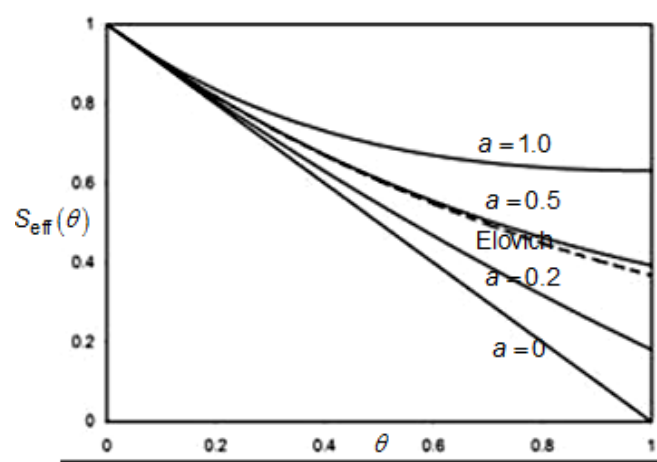


Figure 8. Comparing AES of Hybrid with Elovich and Langmuir.

molecules takes place in next layers and consequently the effective surface is greater than Langmuir surface. This model predicts the saturated capacity of adsorption less than experimental value. This can be explained using AES concept. As seen in Figure 7, Elovich effective surface does not reach zero when adsorbent is saturated. And at  $\theta = 1$ , surface with ability of adsorption exists; yet in fact, this model does not predict any final point for the operation of adsorption. According to Elovich model, there is no difference between the adsorption of molecules on bare adsorbent surface and adsorbed molecules. With this mechanism, molecules can be adsorbed in several layers and it seems that the adsorption would never end.

It can be introduced as an equation for effective adsorption surface in multilayer adsorption that varies from the effective surface of Elovich model to remaining surface of Langmuir model. These variations perform according to different values of parameter  $a$  in the following equation:

$$S_{\text{eff}}(\theta) = 1 - \theta \exp(-a\theta) \tag{11}$$

This equation is drawn in Figure 8 for different value of

parameter  $a$ . The above effective surface equation for  $a = 0$  is same to ideal surface of Langmuir.

Corresponding isotherm model from Equation 11 is derived according to AES approach with assumption that desorption surface is equal to one minus the adsorption effective surface (Equation 12):

$$\begin{aligned} KC[1 - \theta \exp(-a\theta)] &= 1 - [1 - \theta \exp(-a\theta)] \\ &= \theta \exp(-a\theta) \Rightarrow \theta \exp(-a\theta) = \frac{KC}{1 + KC} \\ \theta &= \frac{KC}{1 + KC} \exp(a\theta) \end{aligned} \tag{12}$$

The obtained isotherm model can be considered as a hybrid between Langmuir and Elovich models. This model is simplified to Langmuir isotherm at  $a = 0$ . In this model like Elovich model, final point of adsorption process is unknown and as it is mentioned before, in this kind of models that adsorption effective surface do not reach zero at the point of adsorption saturation, the maximum

**Table 3.** Fitting equations of Langmuir, AES and Volmer models.

Isotherm	Fitting Equation
Langmuir	$C_e = \frac{1}{K_L q_m} \frac{q_e}{1 - q_e / q_m}$
AES Model	$C_e = \frac{1}{K_{AES} q_m} q_e \exp\left(\frac{q_e / q_m}{1 - q_e / q_m}\right)$
Volmer	$C_e = \frac{1}{K_V q_m} \frac{q_e}{1 - q_e / q_m} \exp\left(\frac{q_e / q_m}{1 - q_e / q_m}\right)$

capacity of adsorption becomes less than experimental values. This model can move between two mechanism of multilayer and monolayer of adsorption. This model is named Hybrid model hereafter.

### Statistical analysis

In studying single component isotherm, determination of the best regression model is an important tool in mathematical description of adsorption system according to related conclusive assumption. Two parameters often used by researchers for calculating the error in regression include the mean absolute percentage error (MAPE) and correlation coefficient ( $R^2$ ).  $R^2$  measures the success of the regression in predicting the values of the dependent variable within the sample. This statistic will equal one if the regression fits perfectly. But there are some useful statistical tests that seem useful and necessary in a perfect regression. One of these useful tests is Student t-test. T-test investigates the significance of the model parameters (Montgomery, 1997; Vining, 1998; Ncibi, 2008). Regression of models with experimental data was done by ordinary least square (OLS) method using software Eviews 3.1. Mean absolute percentage error (MAPE) is calculated by Equation (13) and indicated the fit between the experimental and predicted values of adsorption capacity used for plotting isotherm curves:

$$MAPE = \frac{1}{N} \sum_{i=1}^N \frac{|(q)_{Exp} - (q)_{Mod}|}{(q)_{Exp}} \times 100 \quad (13)$$

$N$  is the number of experimental data. T-test is performed separately for each parameters of model. The t-statistic, which is computed as the ratio of an estimated coefficient to its standard error, is used to test the hypothesis that a coefficient is equal to zero. To interpret the t-statistic, one should examine the probability of observing the t-statistic given that the coefficient is equal to zero. This probability is also known as the *p-value* or the *marginal significance level*. Given a *p-value*, one can tell at a glance that a coefficient is zero or not. For example, if test is perform at the 95% significance level, a *p-value* lower than 0.05 is taken as evidence to reject the null hypothesis of a zero coefficient.

## RESULTS AND DISCUSSION

### Comparison of AES model with Langmuir and Volmer models

The fitting of two-parametric theoretical models of Langmuir and Volmer to the equilibrium adsorption data

of benzoic compounds were compared with AES model. The fitting equations used are shown in Table 3. Results are shown in Tables 4 and 5 for adsorbent 1.5 and 2.5 mm, respectively. For arising equal condition for three models, Langmuir model is written as  $C_e$  versus  $q_e$  too. The prediction of adsorption isotherms of benzoic compounds onto GAC 1.5 and 2.5 mm by these models is shown in Figures 9 and 10, respectively.

The behavior of AES model is same with Langmuir model. With increment of adsorption amount, its efficiency for describing isotherms decreases. Values of  $R^2$  for AES model vary from 0.9894 to 0.9990 and MAPE in comparison with Langmuir model are improved. In low adsorption values (phenol, benzene, toluene), MAPEs are very small (1.67 to 4.778). For isotherms of nitrobenzene and chlorobenzene, MAPE become higher but they are very low compared to Langmuir model.

AES model is very suitable for describing isotherms with low to average adsorption amount. Regarding Tables 4 and 5, it is observed that values  $R^2$  for Langmuir vary from 0.9888 to 0.9989.

For Langmuir model in low amount of adsorption (phenol, benzene, toluene), the MAPEs are relatively low (1.82 to 11.37) but with increase of the adsorption value, nitrobenzene and chlorobenzene increases greatly. In general, Langmuir model is convenient for describing isotherms of materials with low to average adsorption. The Volmer Model represents better results in high adsorption values compared to both Langmuir and AES.

Values  $R^2$  for this model vary from 0.9816 to 0.9990 and the MAPEs vary from 4.24 to 19.13. Between two-parametric models, values of maximum adsorption capacities predicted by this model are maximum.

### Comparison of Logarithmic model with Langmuir and Freundlich models

Regression results of logarithmic, Langmuir and Freundlich models on adsorption equilibrium data of benzoic compounds are compared. Here the usual form of Langmuir equation ( $q_e$  versus  $C_e$ ) is used. Regression equations of these models are shown in Table 6. Results of regression for two adsorbent are shown in Tables 7 and 8.

Regarding Tables 7 and 8, values  $R^2$  for Langmuir model vary from 0.9082 to 0.9988 and MAPEs vary from 1.82 to 19.20. As it can be predicted in a range of low to average adsorption amount, this model has better performance, logarithmic model compared to Langmuir model gave better results either regarding values  $R^2$  (0.9716 to 0.9991) or MAPEs (1.72 to 10.64). Also in the range of low to average adsorption amount (phenol, benzene, toluene), this model has the best performance. Values  $R^2$  for Freundlich model vary from 0.9564 to 0.9874 and MAPEs vary from 7.41 to 12.70. By increasing in the amount of adsorption, the compatibility of Freundlich model with experimental data becomes

**Table 4.** Parameters of the Langmuir, AES and Volmer isotherms for the adsorption of benzoic compounds on GAC 1.5 mm.

Parameter	Ph		B		T		NB		CB	
	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.
<b>Langmuir</b>										
$K_L$	0.0661	0.00	0.0788	0.00	0.0561	0.00	0.0462	0.00	0.0512	0.00
$q_m$	244.80	0.00	257.67	0.00	329.06	0.00	485.20	0.00	562.43	0.00
$R^2$	0.9960		0.9888		0.9960		0.9949		0.9952	
MAPE	4.52		7.28		11.37		34.71		29.00	
<b>AES model</b>										
$K_{AES}$	0.0614	0.00	0.0729	0.00	0.0500	0.00	0.0381	0.00	0.0428	0.00
$q_m$	308.45	0.00	324.15	0.00	416.84	0.00	621.12	0.00	718.91	0.00
$R^2$	0.9971		0.9894		0.9976		0.9956		0.9971	
MAPE	1.74		3.11		4.56		19.86		25.32	
<b>Volmer</b>										
$K_V$	0.1125	0.00	0.1353	0.00	0.0876	0.00	0.0604	0.00	0.0678	0.00
$q_m$	327.12	0.00	343.05	0.00	444.44	0.00	671.59	0.00	777.00	0.00
$R^2$	0.9921		0.9816		0.9912		0.9971		0.9990	
MAPE	10.42		9.19		4.63		16.01		19.15	

**Table 5.** Parameters of the Langmuir, AES and Volmer isotherms for the adsorption of benzoic compounds on GAC 2.5 mm.

Parameter	Ph		B		T		NB		CB	
	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.
<b>Langmuir</b>										
$K_L$	0.0463	0.00	0.0446	0.00	0.0481	0.00	0.0413	0.00	0.0429	0.00
$q_m$	222.42	0.00	247.28	0.00	299.13	0.00	453.93	0.00	531.07	0.00
$R^2$	0.9989		0.9975		0.9982		0.9961		0.9966	
MAPE	1.82		3.66		6.26		23.90		23.03	
<b>AES model</b>										
$K_{AES}$	0.0395	0.00	0.0352	0.00	0.0413	0.00	0.0323	0.00	0.0335	0.00
$q_m$	283.61	0.00	318.47	0.00	380.95	0.00	585.82	0.00	685.40	0.00
$R^2$	0.9990		0.9979		0.9988		0.9964		0.9972	
MAPE	1.67		3.24		4.78		17.86		20.32	
<b>Volmer</b>										
$K_V$	0.0657	0.00	0.0539	0.00	0.0698	0.00	0.0481	0.00	0.0495	0.00
$q_m$	304.79	0.00	346.38	0.00	408.33	0.00	640.20	0.00	750.19	0.00
$R^2$	0.9957		0.9939		0.9959		0.9975		0.9986	
MAPE	12.90		4.24		11.43		14.90		14.69	

better because of its unlimited power functionality.

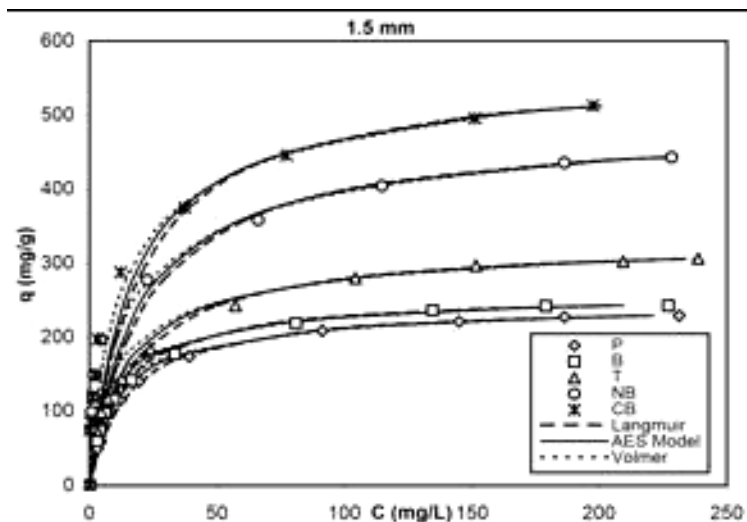
The magnitude of the exponent  $n_F$  gives an indication on the favorability of adsorption. It is generally stated that values of  $n_F$  in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics (Treybal, 1981). Values of  $n_F$  in Tables 7 and 8 shows that activated carbon is good adsorbent for

benzoic compounds ( $3.1942 \leq n_F \leq 4.0584$ ). For comparing results of these models, superposition curves are drawn, for two adsorbent, in Figures 11 and 12.

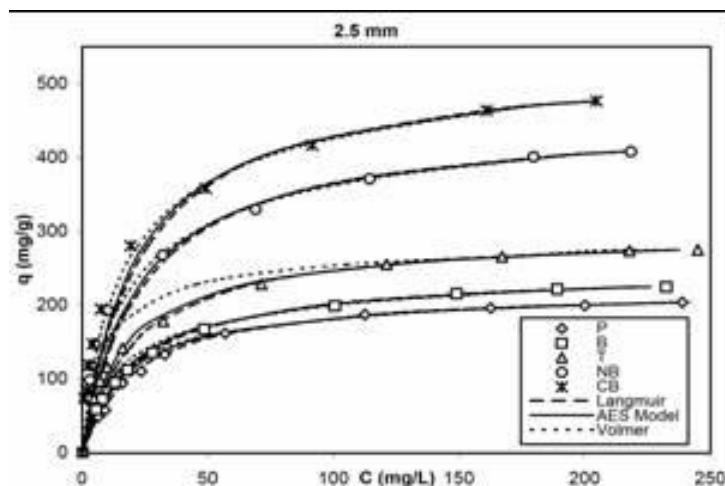
#### Comparison of hybrid model with Elovich model

The fitting of Hybrid isotherm models are compared with





**Figure 9.** Comparing between superposition of Langmuir, AES and Volmer models on adsorption isotherms of Benzoic compounds onto GAC 1.5 mm.



**Figure 10.** Comparing between superposition of Langmuir, AES and Volmer models on adsorption isotherms of Benzoic compounds onto GAC 2.5 mm.

**Table 6.** Fitting equations of Langmuir, AES and Volmer models.

Isotherm	Fitting equation
Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$
Logarithmic Model	$q = \frac{q_m \ln(1 + b C_e)}{1 + \ln(1 + b C_e)}$
Freundlich	$q_e = K_F C_e^{1/n_F}$

Freundlich model. Table 9 shows the regression equation

of these models. The regression results are shown in Tables 10 and 11 for adsorbents 1.5 and 2.5 mm, respectively.

In high values of adsorption, the Elovich model has better compatibility with experimental data. For adsorption of nitrobenzene and chlorobenzene, MAPEs are low but for three other materials results are poor. In this case, in addition having high MAPEs, parameters of Elovich model, regarding the statistical test, are also non-significant that it shows the infirmity of this model. But the major problem of this model is in prediction of the maximum saturation capacity of adsorption. As shown in Tables 9 and 10, it is obvious that the predicted

**Table 7.** Parameters of the Langmuir, Logarithmic and Freundlich isotherms for the adsorption of benzoic compounds onto GAC 1.5 mm.

Parameter	Ph		B		T		NB		CB	
	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.
<b>Langmuir</b>										
<i>b</i>	0.0779	0.00	0.0914	0.00	0.0746	0.00	0.2531	0.00	0.1932	0.00
<i>q<sub>m</sub></i>	239.84	0.00	251.51	0.00	316.07	0.00	410.09	0.00	483.27	0.00
<i>R</i> <sup>2</sup>	0.9976		0.9937		0.9873		0.9551		0.9582	
<i>MAPE</i>	2.67		4.28		7.07		13.37		19.25	
<b>Logarithmic</b>										
<i>b</i>	0.0666	0.00	0.0638	0.00	0.0648	0.00	0.2329	0.00	0.1806	0.00
<i>q<sub>m</sub></i>	313.46	0.00	327.10	0.00	412.11	0.00	517.06	0.00	614.78	0.00
<i>R</i> <sup>2</sup>	0.9990		0.9974		0.9924		0.9725		0.9716	
<i>MAPE</i>	1.95		2.58		5.38		10.10		15.64	
<b>Freundlich</b>										
<i>K<sub>F</sub></i>	55.085	0.00	62.138	0.00	71.460	0.00	121.776	0.00	135.193	0.00
<i>n<sub>F</sub></i>	3.6172	0.00	3.7567	0.00	3.6023	0.00	4.0584	0.00	3.8168	0.00
<i>R</i> <sup>2</sup>	0.9595		0.9691		0.9792		0.9874		0.9867	
<i>MAPE</i>	12.70		9.74		7.54		9.65		10.29	

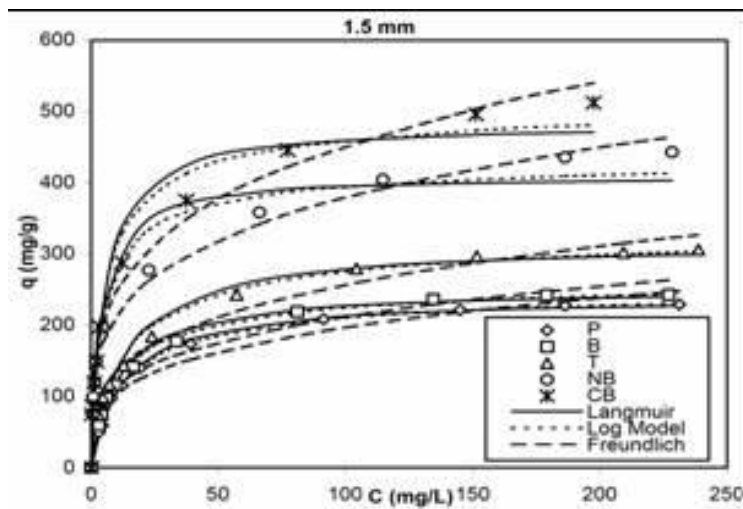
**Table 8.** Parameters of the Langmuir, Logarithmic and Freundlich isotherms for the adsorption of benzoic compounds onto GAC 2.5 mm.

Parameter	Ph		B		T		NB		CB	
	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.
<b>Langmuir</b>										
<i>b</i>	0.0431	0.00	0.0494	0.00	0.0635	0.00	0.0984	0.00	0.0967	0.00
<i>q<sub>m</sub></i>	224.88	0.00	242.87	0.00	288.24	0.00	403.81	0.00	474.03	0.00
<i>R</i> <sup>2</sup>	0.9988		0.9978		0.9942		0.9814		0.9820	
<i>MAPE</i>	1.81		2.69		3.93		8.42		11.58	
<b>Logarithmic</b>										
<i>b</i>	0.0351	0.00	0.0408	0.00	0.0540	0.00	0.0845	0.00	0.0836	0.00
<i>q<sub>m</sub></i>	300.10	0.00	322.51	0.00	278.05	0.00	525.59	0.00	617.54	0.00
<i>R</i> <sup>2</sup>	0.9989		0.9991		0.9975		0.9895		0.9890	
<i>MAPE</i>	1.72		1.64		2.52		6.14		9.11	
<b>Freundlich</b>										
<i>K<sub>F</sub></i>	39.560	0.00	45.443	0.00	62.944	0.00	89.320	0.00	100.684	0.00
<i>n<sub>F</sub></i>	3.1942	0.00	3.2640	0.00	3.5788	0.00	3.4157	0.00	3.2933	0.00
<i>R</i> <sup>2</sup>	0.9564		0.9752		0.9785		0.9830		0.9812	
<i>MAPE</i>	11.8		8.24		7.41		9.70		11.51	

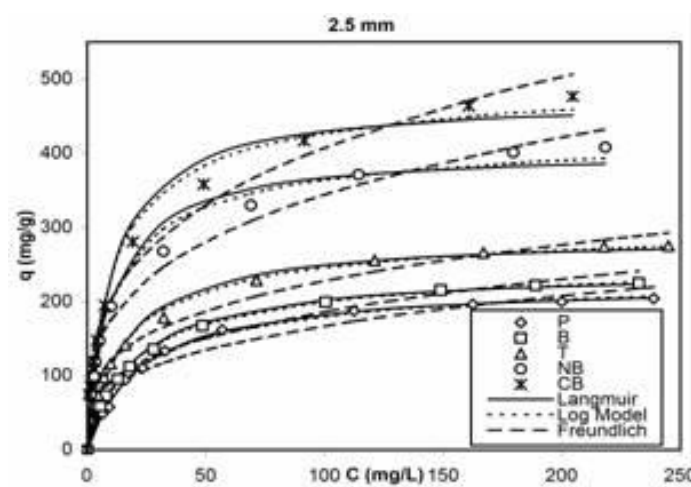
adsorption capacity by this model is much less than their experimental values.

For Hybrid model, the regression either regarding *R*<sup>2</sup> or *MAPE* is much better than Elovich model in all range of

adsorption. For this model the *R*<sup>2</sup> varies from 0.9965 to 0.9999 and *MAPE* vary from 0.41 to 4.02, but still the maximum capacity of adsorption is less than experimental values. So it can be concluded that for



**Figure 11.** Comparing between superposition of Langmuir, Logarithmic and Freundlich models on adsorption isotherms of Benzoic compounds onto GAC 1.5 mm.



**Figure 12.** Comparing between superposition of Langmuir, Logarithmic and Freundlich models on adsorption isotherms of Benzoic compounds onto GAC 2.5 mm.

**Table 9.** Fitting equations of Elovich and Hybrid models.

Model	Fitting Equation
Elovich	$q_e = q_m K_E C_e \exp\left(-\frac{q_e}{q_m}\right)$
Hybrid Model	$q_e = \frac{q_m K_N C_e}{1 + K_N C_e} \exp\left(-a \frac{q_e}{q_m}\right)$

models that the predicted effective surface by them in  $\theta=1$  is not equal to zero, their maximum saturation capacity of adsorption is less than experimental values.

For this model just over adsorption of phenol on adsorbent 2.5 mm, the parameter  $a$  becomes non-significant that by removing it from the equation, Langmuir isotherm is produced. This shows that in very low amounts of adsorption, the Langmuir model is acceptable and adsorption is closer to monolayer adsorption mechanism. Superposition curves of these models for adsorbent 1.5 and 2.5 mm are shown respectively in Figures 13 and 14.

**Conclusion**

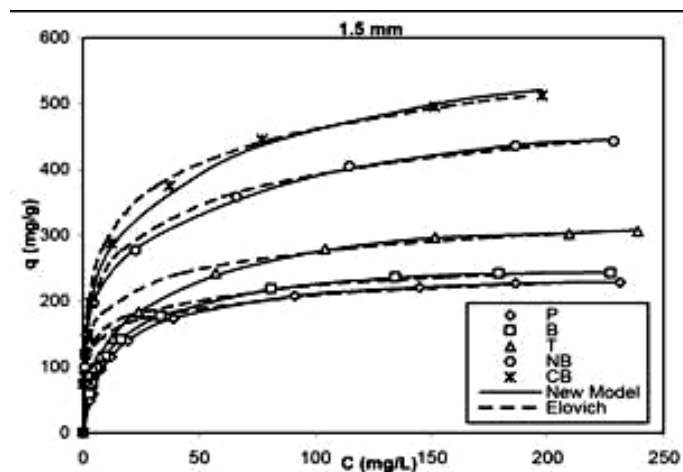
The adsorption equilibrium isotherms of five benzoic

**Table 10.** Parameters of the Elovich and Hybrid isotherms for the adsorption of benzoic compounds onto GAC 1.5 mm.

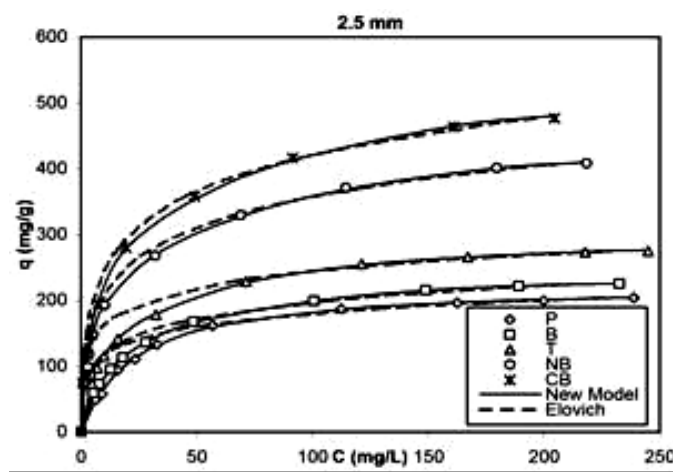
Parameter	Ph		B		T		NB		CB	
	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.
<b>Elovich</b>										
$K_E$	3.270	0.38	72.401	0.53	29.437	0.35	7.324	0.03	7.814	0.00
$q_m$	75.44	0.00	32.20	0.00	44.58	0.00	78.47	0.00	91.54	0.00
$R^2$	0.9821		0.9702		0.9805		0.9955		0.9980	
MAPE	31.97		28.79		24.73		5.67		4.84	
<b>Hybrid model</b>										
$K_N$	0.1978	0.00	0.3166	0.00	0.3811	0.00	1.3799	0.00	1.9214	0.00
$a$	0.3596	0.00	0.3723	0.00	0.3738	0.00	0.3664	0.00	0.3605	0.00
$q_m$	113.72	0.00	101.16	0.00	108.20	0.00	138.16	0.00	141.09	0.00
$R^2$	0.9995		0.9998		0.9996		0.9995		0.9985	
MAPE	1.13		0.80		0.97		1.89		4.02	

**Table 11.** Parameters of the Elovich and Hybrid isotherms for the adsorption of benzoic compounds onto GAC 2.5 mm.

Parameter	Ph		B		T		NB		CB	
	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.	Value	Prob.
<b>Elovich</b>										
$K_E$	10.0198	0.21	3.7121	0.14	15.529	0.21	3.0375	0.01	2.902	0.00
$q_m$	34.30	0.00	44.54	0.00	43.48	0.00	83.88	0.00	99.64	0.00
$R^2$	0.9835		0.9842		0.9868		0.9951		0.9970	
MAPE	26.92		18.30		20.28		8.34		10.95	
<b>Hybrid model</b>										
$K_N$	0.0635	0.15	0.1464	0.00	0.2323	0.00	0.4277	0.00	0.5017	0.00
$a$	0.2569	0.52	0.3713	0.00	0.3742	0.00	0.3729	0.00	0.3723	0.00
$q_m$	156.35	0.00	104.96	0.00	112.91	0.00	145.40	0.00	160.05	0.00
$R^2$	0.9990		0.9999		0.9999		0.9996		0.9987	
MAPE	1.60		0.54		0.41		1.59		3.40	



**Figure 13.** Comparing between superposition of Elovich and Hybrid models on adsorption isotherms of Benzoic compounds onto GAC 1.5 mm.



**Figure 14.** Comparing between superposition of Elovich and Hybrid models on adsorption isotherms of Benzoic compounds onto GAC 2.5 mm.

compounds from aqueous solutions onto two granular activated carbons (GAC) with average granulometries of 1.5 and 2.5 mm were studied. Benzene (B), toluene (T), phenol (P), chlorobenzene (CB) and nitrobenzene (NB) were chosen for adsorption test and effect of adding groups such as methyl, hydroxide, chlorine and nitrooxide on benzene ring in its adsorption were discussed. Uptake of Benzoic compounds increase in order of  $P < B < T < NB < CB$ , which correlates in general with increase in polarisability and decrease in solubility of adsorbate molecules. Activated carbon adsorbent with lower particle size (1.5 mm) has more adsorption capacities about 10% in average.

Three new isotherm models were developed. First the new concept of Adsorption Effective Surface (AES) was introduced. Then some theoretical models were investigated in this way and their properties were discussed and compared to other same models. Using AES method one, can explain such behavior of theoretical models as in predicting maximum adsorption capacity ( $q_m$ ). In this method, adsorption and desorption follow first order kinetics and all non idealities appears in term  $S_{\text{eff}}(\theta)$ . By using AES method, three new isotherm model, named as AES, Logarithmic and Hybrid model were developed. For investigating performance of these models, regression results of them on adsorption isotherm of benzoic compounds onto two activated carbons adsorbents, were compared to same models such as Langmuir (two forms), Volmer, Freundlich and Elovich models and following results were achieved:

1) AES model has a better compatibility with experimental data in all cases compare to Langmuir model and in a range of low and mean adsorption (phenol, benzene and toluene) compare to Volmer model. By increasing amount of adsorption, the performance of two models AES and Langmuir in describing experimental data becomes poor but Volmer model do not have an orderly behavior.

2) Logarithmic model compared to Langmuir model in all cases and compare to Freundlich model with two exceptions (adsorption of nitrobenzene and chlorobenzene on adsorbent 1.5 mm) has a better fitting with experimental data. By increasing the amount of adsorption, the performance of two models Langmuir and logarithmic decrease but results of Freundlich model do not change.

3) New Hybrid model compared to Elovich model has better results in all range of adsorption. This model has the ability of moving between multilayer and monolayer adsorption mechanisms. The problem of wrong prediction of maximum saturation capacity of L-shaped isotherm curves in hybrid model still exists like Freundlich model.

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