

## A new adsorption isotherm model of aqueous solutions on granular activated carbon

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**Abstract.** Equilibrium adsorption of aniline, benzaldehyde, and benzoic acid on granular activated carbon (GAC) has been investigated. Experiments were carried out on two sizes of activated carbon. The equilibrium data were analyzed using the ordinary least square approach. The results show that the adsorption process was more effectively described by Hill and Koble-Corrigan isotherm models based on the values of the least square parameter, Durbin-Watson Test, and mean relative percent error. Furthermore, the results show that benzoic acid has been adsorbed more in comparison with the other adsorbates and benzaldehyde has been adsorbed more than aniline. Moreover, a new isotherm model has been presented which is in good agreement with experimental data. The suggested model has a 7.41% smaller error than the Hill and Koble-Corrigan models.

**Keywords:** adsorption, isotherm, aniline, benzaldehyde, benzoic acid, modelling, GAC

### 1 Introduction

Over the past decades, the population and social civilization have grown. Due to changes in daily life and resource use, and continuing improvement of the industrial and technologies has been accompanied by a quick modernization and metropolitan development<sup>[11, 38]</sup>. The increasing of industrial activities intensified anthropogenic attacks on ecosystems, seriously threatening human health and the environment<sup>[12, 24]</sup>. Increasing concern for public health and environmental quality has led to the establishment of rigid limits on the acceptable environmental levels of specific pollutants<sup>[10, 41, 48]</sup>. Thus, the removal or destruction of aniline, benzaldehyde, and benzoic acid from process or waste streams becomes a major environmental problem. The presence of these compounds even at low concentrations can be an obstacle for the reuse of water. These compounds are present in the wastewaters from coking plants, fertilizer, pharmaceutical, plastics, organic chemical, steel, and petroleum industries, dye manufacturing, and paint-stripping operations. They are considered as pollutants because of their toxic and carcinogenic characteristics<sup>[33, 40]</sup>. Thus, the removal of these pollutants from wastewater stream is one of the major environmental challenges. Several methods are available for removal of this material such as photocatalytic degradation<sup>[4, 28]</sup>, combined photo-Fenton and biological oxidation<sup>[31]</sup>, advanced oxidation processes<sup>[42]</sup>, aerobic degradation<sup>[34]</sup>, nanofiltration membranes<sup>[2]</sup>, ozonation<sup>[29]</sup> and adsorption. In this respect, adsorption on activated carbon is an effective and useful technique in the treatment of organic components containing wastewater<sup>[33, 37]</sup>. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies<sup>[5, 46]</sup>. Despite its industrial importance, adsorption from liquid phase has been studied much less extensively than adsorption from the vapor phase<sup>[6, 47]</sup>. Adsorption equilibrium occurred when an adsorbate

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containing phase has been contacted with the adsorbent for adequate time and adsorbate concentration as the bulk solution is in a dynamic balance with the interface concentration<sup>[9, 12, 30, 33]</sup>. Physical modelling for any engineering application is usually based on proposing empirical relations with a large amount of experimental data and the relevant non-dimensional parameters using regression techniques<sup>[7]</sup>. The empirical correlation, which represents a significant role towards the modelling analysis, operational design and applied practice of the adsorption systems, is typically displayed by graphically expressing the solid-phase against its residual concentration<sup>[12, 25]</sup>. In the present study, the adsorption capacity and equilibrium coefficients for adsorption of aniline, benzaldehyde, and benzoic acid by two sizes of activated carbon have been obtained. In order to correlate our experimental data, several equations (Langmuir, Freundlich, Jovanovic, Redlich-Peterson, Hill, and Koble-Corrigan) that have been proposed in the literature were investigated. Finally, a new and modified model was proposed for correlating of adsorption isotherm data.

## 2 Experimental

### 2.1 Materials

The adsorbents used in the experiments were GAC with two different sizes (1.5 and 2.5mm). Furthermore, Aniline (A), Benzaldehyde (B), and Benzoic Acid (BA) were used as adsorbates. All of used substances were purchased from Merck Company, Lindenplatz, Germany. The properties of solutes and GAC are presented in Tab. 1 and Tab. 2.

**Table 1.** Solutes properties

	A	B	BA
Molecular weight (kg/kmole)	93.12	106.12	122.12
Density (kg/m <sup>3</sup> )	1024	1048	1086
Solubility in water (kg/m <sup>3</sup> )	3.6	3.3	2.9
Maximum adsorption capacity of adsorbent (1.5 mm), $q_m$ (mg/g)	161.57	233.44	250.00
Maximum adsorption capacity of adsorbent (2.5 mm), $q_m$ (mg/g)	112.54	165.87	187.38

**Table 2.** Granular activated carbon properties

	1.5mm	2.5mm
Charcoal activated granular, extra pure	1.5mm	2.5mm
Identity	Conforms	Conforms
Substances soluble in nitric acid	0.7%	7%
Chloride (Cl)	500ppm	200ppm
Cyano compound (CN)	Passes test	Passes test
As (Arsenic)	5ppm	
Pb (Lead)	20ppm	20ppm
Fe (Iron)	500ppm	
Zn (zinc)	100ppm	100ppm
Polycyclic aromates	Passes test	Passes test
Tar products	Passes test	Passes test
n-Hexane adsorption	33%	30%
Residue on ignition (600 °C)	5%	8%
Loss on drying	5%	10%

### 2.2 Method

The study of adsorption was carried out at a constant temperature ( $20 \pm 1$  °C) under continuous stirring. Two series of experiments have been done. The first and second series of experiments have been performed

with adsorbent size 1.5 and 2.5 mm, respectively. For both series, various weights of activated carbon (0.01 to 0.05 g) were agitated in 100 mL of a solution containing an adsorbate with a concentration of 300 mg/L. Furthermore, each adsorbate was treated with nine different weights of activated carbon for both series of experiments. Therefore, 27 experiments were performed for each series of experiments, 54 experiments totally. The contact time to reach equilibrium was set for two days. In addition, the equilibrium concentration of the solutions was obtained by a Unico UV/visible spectrophotometer. The adsorbed amount was determined from the following formula:

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

where  $q_e$  is the amount of adsorbed solute per weight of adsorbent at equilibrium,  $V$  is the solution volume,  $m$  is the mass of activated carbon,  $C_0$  and  $C_e$  are the initial and equilibrium concentration of adsorbate respectively.

### 3 Results and discussion

#### 3.1 Adsorption isotherms

The adsorbed amount is expressed in mg of adsorbate weight per gramme of adsorbent. The adsorption isotherms were measured at 293.15 K. To correlate our experimental adsorption data. The Langmuir, Freundlich, Jovanovic, Redlich-Peterson, Hill, and Koble-Corrigan equations were used.

##### 3.1.1 Langmuir isotherm model

Langmuir adsorption isotherm was originally developed to describe gas-solid phase adsorption on activated carbon<sup>[12, 15]</sup>. This model is based upon two assumptions that the forces of interaction between adsorbed molecules are negligible and once a molecule occupies a site no further sorption takes place. In its derivation, Langmuir isotherm refers to homogeneous adsorption, with no transmigration of the adsorbate in the plane to the surface<sup>[1, 12, 25, 33, 36]</sup>. The model has the following hypotheses:

- (1) Monolayer adsorption (the adsorbed layer is one molecule thick);
- (2) Adsorption takes place at specific homogeneous sites within the adsorbent;
- (3) Once a dye occupies a site, no further adsorption can take place at that site;
- (4) Adsorptional energy is constant and does not depend on the degree of occupation of an adsorbent's active center;
- (5) The strength of the intermolecular attractive forces is believed to fall off rapidly with distance;
- (6) The adsorbent has a finite capacity for the dye (at equilibrium, a saturation point is reached where no further adsorption can occur);
- (7) All sites are identical and energetically equivalent;
- (8) The adsorbent is structurally homogeneous;
- (9) There is no interaction between molecules adsorbed on neighboring sites.

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}, \quad (2)$$

where  $q_e$  is the amount of solute adsorbed per unit weight of the adsorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $C_e$  the equilibrium concentration of the solute in the bulk solution ( $\text{mg L}^{-1}$ ),  $Q_0$  the maximum adsorption capacity ( $\text{mg g}^{-1}$ ), and  $b$  is the constant related to the free energy of adsorption ( $\text{L mg}^{-1}$ ). Eq. (2) can be linearized to four different linear forms as shown in Tab. 3.

The constants of all models were obtained by ordinary least squares using the "Application software"<sup>[35]</sup>. The calculation results from the Langmuir model were shown in Tab. 4.

In Application software, several examinations were performed for the analyzing and fitting of data. The models are developed based on the statistical function such as the least square parameter ( $R^2$ ) and Durbin-Watson Test (D.W.T).  $R^2$  is the most important parameter to obtain the model's ability in fitting of various

**Table 3.** Isotherm models and their linear forms

Isotherm	Nonlinear form	Linear form	Plot	Reference
Langmuir	$q_e = \frac{Q_0 b C_e}{1 + b C_e}$	$\frac{C_e}{q_e} = \frac{1}{b Q_0} + \frac{C_e}{Q_0}$	$\frac{C_e}{q_e} \text{ vs } C_e$	[27]
		$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{b Q_0 C_e}$	$\frac{1}{q_e} \text{ vs } \frac{1}{C_e}$	
		$q_e = Q_0 - \frac{q_e}{b C_e}$	$q_e \text{ vs } \frac{q_e}{b C_e}$	
		$\frac{q_e}{C_e} = b Q_0 - b q_e$	$\frac{q_e}{C_e} \text{ vs } q_e$	
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e \text{ vs } \log C_e$	[13]
Redlich-Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	$\ln(K_R \frac{C_e}{q_e} - 1) = g \ln(C_e) + \ln(a_R)$	$\ln(K_R \frac{C_e}{q_e} - 1) \text{ vs } \ln(C_e)$	[45]
Hill	$q_e = \frac{q_H C_e^{n_H}}{K_D + C_e^{n_H}}$	$\log \frac{q_e}{q_H - q_e} = n_H \log(C_e) - \log(K_D)$	$\log \frac{q_e}{q_H - q_e} \text{ vs } \log(C_e)$	[22]
Koble-Corrigan	$q_e = \frac{A C_e^D}{1 + B C_e^D}$	$\frac{1}{q_e} = \frac{1}{A C_e^D} + \frac{B}{A}$		[23]

**Table 4.** Calculation results of the Langmuir model constants

Model	Parameters	1.5mm			2.5mm		
		A	B	BA	A	B	BA
Langmuir	$Q_0$	177.81	249.32	255.78	114.30	183.55	186.96
	b	0.06	0.05	0.09	0.08	0.10	0.18
	MRPE	3.51	2.93	4.73	4.00	1.56	3.07
	$R^2$	0.99	0.99	0.99	0.99	0.99	0.99
	D.W.T	1.34	1.67	1.68	1.43	2.38	1.21
	Average MRPE				3.30		

conditions provided as the basis of experimental data. In general, the value of this parameter is between 0.0 and 1.0, and the quality of fit increases with the nearness of  $R^2$  to 1.0. The D.W.T parameter comprises the difference in value between each measured data point and the value produced by the model, with this difference being known as the residual value. In fact, this parameter determines the relation between residual data. The amount of D.W.T must be at least 1.0 for a good model. Moreover, the mean relative percent error (MRPE) was used to compare the predicted results with the experimental data. MRPE was calculated from the following formula.

$$MRPE = \frac{1}{N} \sum_{i=1}^N \frac{(q_e)_{exp} - (q)_{mod}}{(q_e)_{exp}}, \tag{3}$$

where  $N$  is the number of experiments,  $(q_e)_{exp}$  is the measured  $q_e$  from experiments and  $(q_e)_{mod}$  is the calculated  $q_e$ .

According to Tab. 4, the amounts of MRPE for the Langmuir model are agreeable (varies from 1.56 to 4.73) and  $R^2$  approximately is 0.99 for all of adsorbates. Furthermore, the D. W. T. is more than 1 for all the adsorbates.

### 3.1.2 Freundlich isotherm model

The Freundlich isotherm is the earliest known relationship describing non-ideal and reversible adsorption, not restricted to the formation of the monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [12, 14, 25, 33, 36].

Its linearized and non-linearized equations are listed in Tab. 3. Recently, Freundlich isotherm has been criticized for its limitation of lacking a fundamental thermodynamic basis, not approaching the Henry's law at vanishing concentrations<sup>[20]</sup>. The Freundlich expression is an exponential equation and therefore Tab. 5 shows the calculated result from the Freundlich model.

$$q_e = K_F C_e^{1/n}, \tag{4}$$

where  $K_F$  is a constant indicative of the relative adsorption capacity of the adsorbent ( $\text{mg}^{1-(1/n)}\text{L}^{1/n}\text{g}^{-1}$ ) and  $n$  is a constant indicative of the intensity of adsorption.

At present, Freundlich isotherm is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves (Fig. 1 and Fig. 2). The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies Chemisorptions process where  $1/n$  above one is an indicative of cooperative adsorption<sup>[1, 8, 16]</sup>.

To determine the maximum adsorption capacity, it is necessary to operate with constant initial concentration  $C_0$  and variable weights of adsorbent; thus  $\ln q_m$  is the extrapolated value of  $\ln q$  for  $C = C_0$ . According to Halsey<sup>[17]</sup>:

$$K_F = q_m / C_0^{1/n}, \tag{5}$$

where  $C_0$  is the initial concentration of the solute in the bulk solution ( $\text{mg L}^{-1}$ ) and  $q_m$  is the Freundlich maximum adsorption capacity ( $\text{mg g}^{-1}$ ).

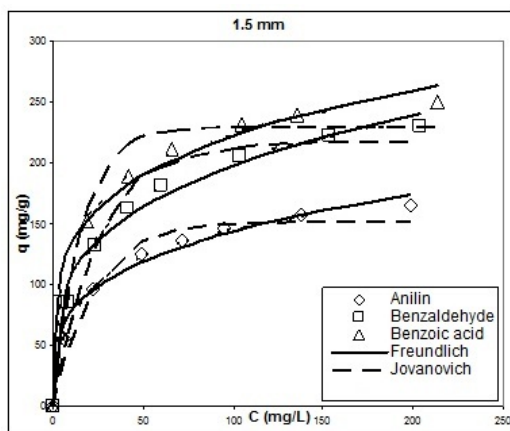


Fig. 1. Prediction of isotherm curves for A, B, and BA for activated carbon size of 1.5 mm

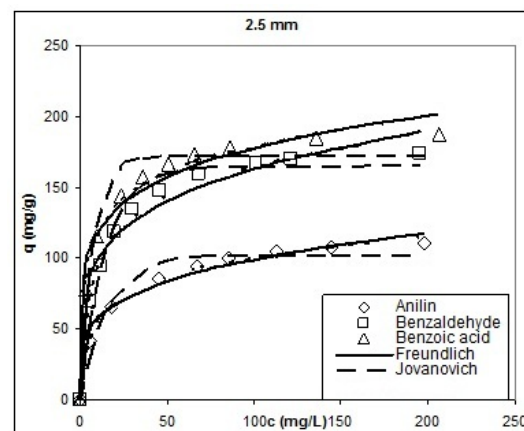


Fig. 2. Prediction of isotherm curves for A, B, and BA for activated carbon size of 2.5 mm

Table 5. Calculation results of the Freundlich model constants

Model	Parameters	1.5mm			2.5mm		
		A	B	BA	A	B	BA
Freundlich	$K_F$	44.02	61.87	84.00	33.07	59.22	78.83
	$n$	3.97	4.04	4.84	4.18	4.54	5.66
	MRPE	5.44	5.16	4.70	4.26	6.80	5.69
	$R^2$	0.98	0.98	0.98	0.99	0.97	0.97
	D.W.T	1.18	0.94	0.91	1.07	0.90	1.06
Average MRPE			5.34				

According to Tab. 5, the amount of MRPE for the Freundlich model are higher in comparison with that of the Langmuir model (varies from 4.25 to 6.8) and  $R^2$  approximately changes from 0.97 to 0.99 for all of

adsorbates. However, D. W. T. is lower than 1 for some experiments. In addition, the exponent in Freundlich model is the adsorption capacity in which  $n > 1$ , represents a powerful adsorption which is more than 1 for all of our experiments.

### 3.1.3 Jovanovic isotherm model

In addition the same assumptions contained within the Langmuir model, the Jovanovic model considers the possibility of some mechanical contacts between the adsorbing and desorbing molecules<sup>[39, 44]</sup>. Tab. 6 presented the constant's estimation for the Jovanovic model.

$$q_e = q_m (1 - \exp(-K_J C_e)), \quad (6)$$

where  $q_m$  and  $K_J$  are constants.

**Table 6.** Calculation results of the Jovanovic model constants

Model	Parameters	1.5mm			2.5mm		
		A	B	BA	A	B	BA
Jovanovic	$q_m$	159.68	224.31	236.32	102.55	164.93	171.94
	$K_J$	0.04	0.04	0.06	0.05	0.07	0.13
	MRPE	8.40	7.03	8.76	8.25	5.56	7.42
	$R^2$	0.96	0.97	0.94	0.95	0.98	0.95
	D.W.T	1.07	1.20	1.39	1.18	1.07	1.01
	Average MRPE				7.57		

The calculation results show that the accordance of the Jovanovic model with experimental data is not very good (see Fig. 1 and Fig. 2). In addition, the amount of  $R^2$  varies from 0.94 to 0.98 but, D. W. T. are more than 1 for all of the adsorbates.

### 3.1.4 Redlich-Peterson isotherm model

The three empirical parameters Redlich–Peterson isotherm consists of both Langmuir and Freundlich isotherms<sup>[45]</sup>. To provide a wide concentration range, the model has a linear dependence on concentration in the numerator and an exponential function in the denominator and the mechanism of adsorption is a hybrid and dose no follow ideal monolayer adsorption (Tab. 3). It can be applied either in homogeneous or heterogeneous systems due to its adaptability<sup>[12, 19, 21, 32]</sup>. Tab. 7 shows the calculation result from the Redlich-Paterson model.

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}, \quad (7)$$

where  $K_R$  is the Redlich–Peterson isotherm constant ( $L g^{-1}$ ),  $a_R$  is also having a constant unit of  $(L mg^{-1})\beta$ , and  $\beta$  is an exponent that lies between 0 and 1.  $C_e$  is the equilibrium liquid-phase concentration of the adsorbate ( $mg L^{-1}$ ) and  $q_e$  is the equilibrium adsorbate loading onto the adsorbent ( $mg g^{-1}$ ).

At high liquid-phase concentrations of the adsorbate, Eq. (7) reduces to the Freundlich equation, i.e.:

$$q_e = (A/B)C^{1-\beta}, \quad (8)$$

where  $A/B$  and  $(1 - \beta)$  present, respectively, the parameters  $K_F$  and  $1/n$  of the Freundlich model. For  $\beta = 1$ , Eq. (7) reduces to the Langmuir equation, with  $b = B$  is the Langmuir adsorption constant ( $L mg^{-1}$ ) related to the energy of adsorption and  $A = bQ_{0L}$ , where  $Q_{0L}$  signifies the Langmuir maximum adsorption capacity of the adsorbent ( $mg g^{-1}$ ). For  $\beta = 0$ , Eq. (7) reduces to the Henry's equation, with  $A/(1 + B)$  is the Henry's constant.

The calculation results show that the Redlich-Peterson model is agreement with the experimental data. In addition, the amounts of  $R^2$  are about 0.99 and D. W. T. are more than 1 for all the adsorbates.

**Table 7.** Calculation results of the Redlich-Peterson model constants.

Model	Parameters	1.5mm			2.5mm		
		A	B	BA	A	B	BA
Redlich-Peterson	$K_R$	15.94	18.57	46.36	16.99	19.40	49.99
	$a_R$	0.17	0.13	0.33	0.28	0.12	0.37
	$g$	0.89	0.90	0.89	0.87	0.97	0.93
	MRPE	0.89	1.44	1.93	1.35	1.34	1.22
	$R^2$	0.99	0.99	0.99	0.99	0.99	0.99
	D.W.T	1.55	1.44	1.25	1.26	2.40	1.25
	Average MRPE						

### 3.1.5 Hill isotherm model

Hill's equation was postulated to explain the binding of various species onto homogeneous substrates. The model assumes that adsorption is a cooperative phenomenon, with the ligand binding ability at one site on the macromolecule, may influence different binding sites on the same macromolecule<sup>[12, 18]</sup>. The linear form of the Hill isotherm is shown in Tab. 3 and The calculation results from the Hill model were shown in Tab. 8.

$$q_e = \frac{q_H C_e^{n_H}}{K_D + C_e^{n_H}}, \quad (9)$$

where  $K_D$ ,  $n_H$ , and  $q_H$  are constants.

**Table 8.** Calculation results of the Hill model constants

Model	Parameters	1.5mm			2.5mm		
		A	B	BA	A	B	BA
Hill	$q_H$	205.88	279.58	305.84	139.12	190.29	206.81
	$K_D$	9.76	10.89	5.52	6.79	8.35	3.66
	$n_H$	0.69	0.73	0.60	0.63	0.88	0.69
	MRPE	0.40	0.89	1.20	0.75	1.02	0.60
	$R^2$	0.99	0.99	0.99	0.99	0.99	0.99
	D.W.T	1.84	1.27	1.09	1.09	2.37	1.30
	Average MRPE						

According to Tab. 8, the amounts of MRPE for the Hill model are very good in comparison with previous models (varies from 0.4 to 1.2) and  $R^2$  approximately is 0.99 for all of adsorbates. Furthermore, the D. W. T. is more than 1 for all the adsorbates.

### 3.1.6 Koble-corrigan isotherm model

Koble-Corrigan isotherm is a three-parameter equation which incorporated both Langmuir and Freundlich isotherm models for representing the equilibrium adsorption data. The isotherm has an exponential dependence on concentration in the numerator and denominator. It is usually used with heterogeneous adsorption surfaces. The calculation results from the Koble-Corrigan model were shown in Tab. 9.

$$q_e = \frac{AC_e^D}{1 + BC_e^D}, \quad (10)$$

where A, B, and D are constants and evaluated from the linear plot using a trial and error optimization.

According to Tab. 9, the calculation results show that estimations of the Koble-Corrigan model are in good agreement with the experimental data. Furthermore, the amounts of  $R^2$  are close to 0.99 for all of adsorbates and D. W. T. is more than 1 for all of the solutes. Consequently, according to the amounts of  $R^2$ , D.W.T. and MRPE in Tab. 8 and Tab. 9, the Hill and Koble-Corrigan models are well adapted for the



**Table 9.** Calculation results of the Koble-Corrigan model constants

Model	Parameters	1.5mm			2.5mm		
		A	B	BA	A	B	BA
Koble-Corrigan	A	21.09	249.83	279.55	125.44	178.19	198.02
	B	0.10	0.16	0.29	0.24	0.23	0.48
	D	0.69	0.52	0.38	0.42	0.55	0.36
	MRPE	0.38	0.85	1.24	0.74	1.04	0.62
	$R^2$	0.99	0.99	0.99	0.99	0.99	0.99
	D.W.T	1.84	1.63	1.46	1.31	3.09	1.32
	Average MRPE						

description of A, B, and BA adsorption on both sizes of activated carbon. In these models, the amount of  $R^2$ , D.W.T, and MRPE are suitable and confirm the basic definition of modelling.

In addition, the Koble-Corrigan model's MRPE is the same as the Hill model. On the other hand, the low difference of MRPE between Hill and Koble-Corrigan models, it obtained probably these two models are the same mathematical structure. Therefore, we compared two models with each other (we initiate with Hill's model and received to Koble-Corrigan model):

$$q_e = \frac{q_H C_e^{n_H}}{K_D + C_e^{n_H}} = \frac{q_H C_e^{n_H}}{K_D \left(1 + \frac{1}{K_D} C_e^{n_H}\right)} = \frac{\left(\frac{q_H}{K_D}\right) C_e^{n_H}}{1 + \left(\frac{1}{K_D}\right) C_e^{n_H}}. \quad (11)$$

From comparing Eq. (11) and Koble-Corrigan model, we can define  $A = (q_H/K_D)$ ,  $B = (1/K_D)$ , and  $n_H = D$ . Therefore, it would be concluded that the two models are similar and have the same structure.

#### 4 A new model for an adsorption isotherm curve

The equilibrium adsorption isotherm is the most important in the investigation of adsorption mechanism. Main adsorption properties such as surface property, the adsorption affinity of adsorbent and the maximum adsorption capacity can be determined from the adsorption isotherm and correlative constants. In this study, a new and modified model has been derived for correlating equilibrium adsorption data. A combination of Langmuir and Jovanovic models were used in order to create a new model with less error in comparison with that of other models. Afterwards, the resulting model is presented in the Eq. (12).

$$q_e = \frac{r C_e}{1 + C_e} [1 - \exp(-p C_e^z)], \quad (12)$$

where  $r$ ,  $p$ , and  $z$  are constants.

Tab. 10 presents the calculated constants of the Eq. (12). According to Tab. 10, the MRPE varies from 0.28 to 1.32 and  $R^2$  is approximately 0.99. Furthermore, D. W. T. for all of adsorbates is more than 1. A comparison between Eq. (12) and other models reveals that the Eq. (12) has a smaller error. Additionally, Eq. (12) has 7.41% smaller MRPE in comparison with that of the Hill and Koble-Corrigan models.

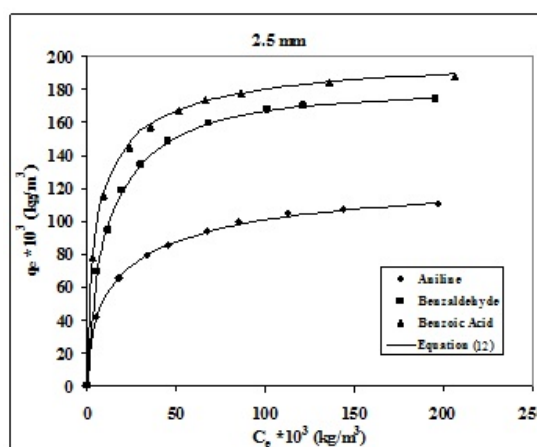
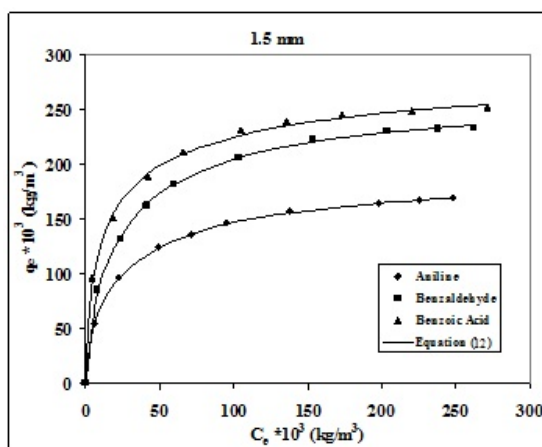
Fig. 3 and Fig. 4 exhibits the isotherm curves for A, B, and BA for two activated carbon sizes. According to Fig. 3 and Fig. 4, it can be concluded that the amount of adsorption for adsorbent with smaller size (1.5 mm) is about 30% higher in comparison with that of other adsorbent (2.5 mm) in which both adsorbents approximately the same area properties have. It can be due to the difference between adsorption amounts is because of size differences. So, the adsorbent with smaller size has a higher area per weight of adsorbent. In addition, BA has been adsorbed more in comparison with that of B and A. Moreover, B has been adsorbed more than A. The main factors which affected the process of adsorption are the solubility in water and hydrophilic characteristics (the effect of hydrogen bond). An increase in the solubility in water and hydrophilic properties causes a decrease in the adsorbed amount. In addition to solubility in water and hydrophilic properties, molecular weight is another parameter which affected the amount of adsorption. Therefore, BA with the least solubility in water and the highest molecular weight was adsorbed more than the other adsorbates.



**Table 10.** Calculation results of constants of Eq. (12)

Model	Parameters	1.5mm			2.5mm		
		A	B	BA	A	B	BA
Eq. (12)	r	184.44	249.83	279.55	125.44	178.19	198.02
	p	0.17	0.16	0.29	0.24	0.23	0.48
	z	0.49	0.52	0.38	0.42	0.55	0.36
	MRPE	0.28	0.68	1.30	0.82	0.75	0.66
	$R^2$	0.99	0.99	0.99	0.99	0.99	0.99
	D.W.T	2.18	1.63	1.46	1.31	3.09	1.32
	Average MRPE						

Furthermore, the molecular weight and the solubility of B in water are higher in comparison with that of A. Consequently, the adsorption of B on activated carbon is more than A.



**Fig. 3.** Prediction of isotherm curves by Eq. (12) for A, B, and BA for activated carbon size of 1.5 mm

**Fig. 4.** Prediction of isotherm curves by Eq. (12) for A, B, and BA for activated carbon size of 2.5 mm

Additionally, the isotherm curves of Eq. (12) are obtained and the results are shown in Fig. 3 and Fig. 4. From Fig. 3 and Fig. 4, it is obvious that our model (Eq. (12)) is in a good agreement with the experimental data.

### 5 Conclusions

An experimental investigation was performed to obtain the adsorption isotherm curves for aniline (A), benzaldehyde (B), and benzoic acid (BA) at 293.15 K. GAC with two sizes (1.5 and 2.5 mm) was used as adsorbent. Furthermore, six most recommended models in the literature (Langmuir, Freundlich, Jovanovic, Redlich-Peterson, Hill, and Koble-Corrigan) were utilized in order to correlate experimental data. The results were then analyzed and summarized as follows:

Among six important compatible applicable models about adsorption, the Hill and Koble-Corrigan’s model have best fitting with experimental data of A, B, and BA adsorption from waste water with activated carbon. The percentage of MRPE, for these models are almost 0.81%, and Durbin-Watson Test, D. W. T., for all the curves are more than 1. In addition,  $R^2$  approximately are 0.99 for both models. Consequently, we can conclude that these models can predict experimental data well.

The Hill and Koble-Corrigan models fit well with experimental data and the results of statistical tests are similar. In this investigation, it is obtained that two mentioned models are alike in the structure.

A new and modified empirical model (Eq. (12)) was derived by a combination of the Langmuir and Jovanovic models. The derived model agreed well with the experimental data which MRPE is about 0.75%.

This model was derived for the first time by the authors of this paper and its MRPE are 7.41% smaller than Hills and Koble-Corrigan models.

The adsorption amount of adsorbent with smaller size (1.5 mm) is about 30% higher than the other adsorbent (2.5 mm) in which both adsorbents have approximately the same surface properties. Furthermore, BA has been adsorbed more in comparison with that of B and A because of the effects of solubility in water, hydrophilic properties, and molecular weight. Moreover, B has been adsorbed more than A.

## Nomenclature

$(q_e)_{exp}$	Measured adsorbate concentration at equilibrium ( $mg/g$ ),
$(q_e)_{mod}$	Calculated adsorbate concentration at equilibrium ( $mg/g$ ),
$A$	Koble-Corrigan isotherm constant ( $L^D mg^{1-D}/g$ ),
$a_R$	Redlich-Peterson isotherm constant ( $1/mg$ ),
$B$	Koble-Corrigan isotherm constant ( $L/mg$ ) <sup>D</sup> ,
$b$	Langmuir isotherm constant ( $L/mg$ ),
$C_0$	Adsorbate initial concentration ( $mg/L$ ),
$C_e$	Equilibrium concentration ( $mg/L$ ),
$D$	Adsorption intensity,
$D.W.T.$	Durbin-Watson Test,
$g$	Redlich-Peterson isotherm exponent,
$K_D$	Hill isotherm model constant,
$K_F$	Freundlich isotherm constant ( $mg/g$ )( $L/g$ ) <sup>n</sup> related to adsorption capacity,
$K_J$	Jovanovic isotherm constant ( $mg/g$ ),
$K_R$	Redlich-Peterson isotherm constant ( $L/g$ ),
$m$	Adsorbent mass ( $g$ ),
$MRPE$	Mean relative percent error,
$n$	Adsorption intensity,
$N$	Number of experiments,
$n_H$	Hill cooperativity coefficient of the binding interaction,
$p$	Isotherm constant (Eq. (12)) ( $L/mg$ ) <sup>z</sup> ,
$Q_0$	maximum monolayer coverage capacities ( $mg/g$ ),
$q_e$	Amount of adsorbate in the adsorbent at equilibrium ( $mg/g$ ),
$q_H$	Hill isotherm maximum uptake saturation ( $mg/L$ ),
$q_m$	Jovanovic isotherm constant ( $mg/g$ ),
$q_s$	Theoretical isotherm saturation capacity ( $mg/g$ ),
$r$	Isotherm constant (Eq. (12)) ( $mg/g$ ),
$R$	Universal gas constant ( $8.314J/molK$ ),
$R^2$	Least square parameter,
$T$	Temperature ( $K$ ),
$V$	Solution volume ( $L$ ),
$z$	Isotherm constant (Eq. (12)).

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