

## Adsorption of Benzaldehyde on Granular Activated Carbon: Kinetics, Equilibrium, and Thermodynamic

R. K. Rajoriya, B. Prasad, I. M. Mishra, and K. L. Wasewar\*

Chemical Engineering Department, Indian Institute of Technology (IIT),  
Roorkee – 247667, Uttarakhand, India

Email: k\_wasewar@rediffmail.com, klw73fch@iitr.ernet.in

Phone: +91-1332-285347; Fax: +91-1332-276535

Original scientific paper

Received: September 19, 2006

Accepted: March 1, 2007

Adsorption isotherms of benzaldehyde from aqueous solutions onto granular activated carbon have been determined and studied the effect of dosage of granular activated carbon, contact time, and temperature on adsorption. Optimum conditions for benzaldehyde removal were found adsorbent dose  $\gamma \approx 4 \text{ g l}^{-1}$  of solution and equilibrium time  $t \approx 4 \text{ h}$ . Percent removal of benzaldehyde increases with the increase in adsorbent dose for activated carbon, however, it decreases with increase in benzaldehyde mass concentration. Adsorption capacity of activated carbon for benzaldehyde removal decreases with increase in temperature, the adsorbent showing the exothermic nature of adsorption. The adsorption of benzaldehyde by granular activated carbon followed pseudo-second order kinetics. Diffusion is not the only rate-controlling step. Adsorption equilibrium data were analyzed by Langmuir, Freundlich and Temkin isotherm equation using regression analysis. Temkin found to best represent the data for benzaldehyde adsorption onto granular activated carbon. Value of the change in entropy ( $\Delta S^\circ$ ) and heat of adsorption ( $\Delta H^\circ$ ) for benzaldehyde adsorption on activated carbon were negative. The high negative value of change in Gibbs free energy ( $\Delta G^\circ$ ) indicates the feasible and spontaneous adsorption of benzaldehyde on granular activated carbon.

*Key words:*

Adsorption, benzaldehyde, activated granular carbon, kinetics, equilibrium, thermodynamics

### Introduction

Numerous techniques have been developed in recent years to remove contaminants such as toxic organic or inorganic chemicals from drinking or waste water. Among these techniques, active carbon adsorption, a process in which the molecules of the contaminants are transferred from a dissolved state in the aqueous phase to the surface of active carbon, has become one of the most effective means for this purpose.

Benzaldehyde ( $\text{C}_6\text{H}_5\text{CHO}$ ) is the simplest and the most industrially useful member of the family of aromatic aldehydes. Benzaldehyde exists in nature, primarily in combined form such as glycoside in Almond, apricot, cherry and peach seeds. The characteristic benzaldehyde odour of oil of bitter almond occurs because of trace amounts of free benzaldehyde formed by hydrolysis of the glycoside amygdalin. It is used in the food, beverage, pharmaceutical, perfume, soap, and dyestuff industries.

Its more than 98 % is used as an intermediate in production of pharmaceuticals, aromatic alcohols, photographic chemicals, dyes, benzoic acid

and cinnamic acid. Purified benzaldehyde used as an intermediate (60 % on site and 38 % off site) in closed systems and 1–2 % is used as a food and fragrance additive. It is used as a solvent for oils, resins, some cellulose ethers, cellulose acetate, and nitrate and is a useful pharmaceutical vehicle for administering bromides and other salts, especially when a low salt content is desired. Benzaldehyde is widely used in flavors such as almond and cherry in various fragrances for soap and toiletries.

Benzaldehyde is released to the environment in emissions from combustion processes such as gasoline and diesel engines, incinerators and wood burning. It is formed in the atmosphere through photochemical oxidation of toluene and other aromatic hydrocarbons. It occurs naturally in various plants. It is affected by light and it oxidizes in air to benzoic acid. In view of environmental aspects, it is essential to remove the benzaldehyde to desired concentration from wastewater. In present paper, equilibrium, kinetics, and thermodynamics for the adsorption of benzaldehyde on activated carbon were studied. Also the error analysis was studied for various kinetic models. The data presented here are useful for the further study of adsorption of benzaldehyde using other adsorbents.

\* Corresponding author

## Material and methods

### Adsorbate

The adsorbate, benzaldehyde (molar mass 106.16 g mol<sup>-1</sup>, chemical formula = C<sub>6</sub>H<sub>5</sub>CHO) was supplied by Qualigens Fine Chemicals, Mumbai, India. It was used without any treatment. Experimental solutions of the desired mass concentrations ( $\gamma = 100, 200, 300 \text{ mg l}^{-1}$ ) were obtained by successive dilutions with distilled water. The pH values of the solution used are in the range of 6.5 to 6.9. Granular activated carbon was supplied by Hi-media Research Laboratory, Mumbai, India. The detail characteristics of granular activated carbon used are mentioned in Table 1.

Table 1 – Characteristics of granular activated carbon

Characteristic	Values
Proximate analysis (sample as received)	
moisture, %	6.07
ash, %	8.73
volatile matter, %	7.49
fixed carbon, %	78.08
Bulk density, kg m <sup>-3</sup>	785
Ultimate analysis (dry basis)	
C	79.16
H	5.185
N	0.045
S	0.541
Chemical analysis of ash, %	
insoluble matter	3.2
silica	2.9
ferric & alumina	3.6
CaO	88.0
Mg	2.5
Specific surface area, m <sup>2</sup> g <sup>-1</sup>	
BET	807.57
Langmuir	1045.43
t-plot micropore	985.29
t-plot external	56.14
single point	883.19
BJH adsorption cumulative	79.16
Specific pore volume, cm <sup>3</sup> g <sup>-1</sup>	
single point pore volume	0.59
t-plot micropore volume	0.36
BJH adsorption cumulative	0.08
Pore size, nm	
BET Adsorption average pore width	2.867
BJH adsorption average pore diameter	4.50

### Analytical measurements

Concentrations of benzaldehyde were determined by finding out the absorbance characteristic wavelength using UV-spectrophotometer. A standard solution of the benzaldehyde was taken and

the absorbance was determined at different wavelengths to obtain a plot of absorbance vs. wavelength. The wavelength corresponding to maximum absorbance ( $\lambda_{\text{max}}$ ) as determined from this plot was 258 nm. This wavelength was used for preparing the calibration curves between absorbance and the mass concentration of the benzaldehyde solution. The calibration plot of absorbance versus concentration for benzaldehyde showed a linear variation.

### Batch Adsorption

Batch experiments were carried out to study the effect of important quantities like dose, concentration, time and temperature. For each experimental run, 100 ml of benzaldehyde solution of known concentration and a known amount of the adsorbent were taken in a 100 ml conical flask. This mixture was agitated in a temperature-controlled orbital shaker at a constant speed of  $n = 160 \text{ min}^{-1}$  at  $T = 30 \text{ }^\circ\text{C}$ . Samples were withdrawn at appropriate time intervals. Some activated carbon particles remain suspended and do not settle down easily. Therefore, all the samples were centrifuged (Research Centrifuge, Remi scientific works, Mumbai) at  $n = 8000 \text{ min}^{-1}$  for 10 min and analyzed by UV-spectrophotometer for the residual benzaldehyde concentration. For the optimum amount of adsorbent per unit mass of adsorbate, a 100 ml of benzaldehyde solution was contacted with different amounts of activated carbon respectively till equilibrium was attained. The kinetics of adsorption was determined by analyzing adsorptive uptake of the benzaldehyde from the aqueous solution at different time intervals. For adsorption isotherms, benzaldehyde solution of different mass concentrations were agitated with the known amount of adsorbent till the equilibrium was achieved. The effect of temperature on the sorption characteristics was investigated by determining the adsorption isotherms at 293 K, 303 K, and 313 K for benzaldehyde mass concentration of 50 mg l<sup>-1</sup> to 1000 mg l<sup>-1</sup>.

## Results and discussion

### Process parameters

#### Effect of adsorbent dose

The effect of activated carbon dose on the extent of solute adsorption was investigated by varying the dose from 0.05 to 1.2 g per 100 ml under the selected initial solute mass concentration (100 mg l<sup>-1</sup>) with agitation speed of  $n = 160 \text{ min}^{-1}$  and temperature 293 K. It is observed from Fig. 1 that as the dose increases the amount of solute adsorbed increases and reaches a maximum value corresponding to a certain dose. The minimum amount

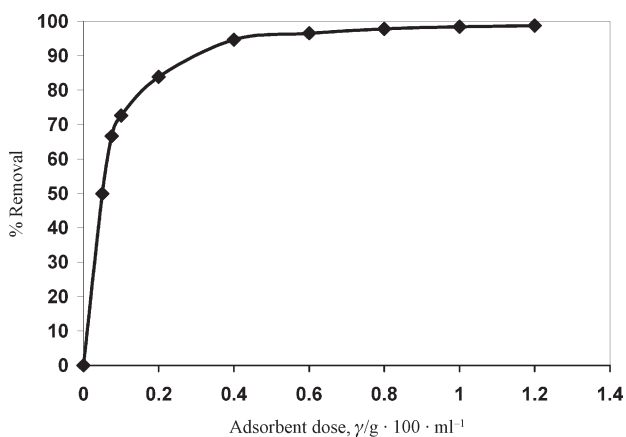


Fig. 1 – Effect of adsorbent mass (per 100 ml of solution) on adsorption of benzaldehyde for activated carbon

of adsorbent corresponding to the maximum adsorption is declared as the optimum dose. The optimum dose observed in the present study is 0.4 g per 100 ml of the solution of adsorbent dosage for activated carbon for 100 mg l<sup>-1</sup> of initial solute concentration.

#### Effect of contact time

The effect of contact time for the adsorption of benzaldehyde by activated carbon was studied for a period of 10 h for initial benzaldehyde mass concentrations of 100, 200, 300 mg l<sup>-1</sup> at 293 K. Activated carbon dosage was 4 g l<sup>-1</sup> of benzaldehyde. The effect of contact time on removal of benzaldehyde is shown in Fig. 2. As concentration of benzaldehyde increases efficiency (%) removal decreases for same contact time. The uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a

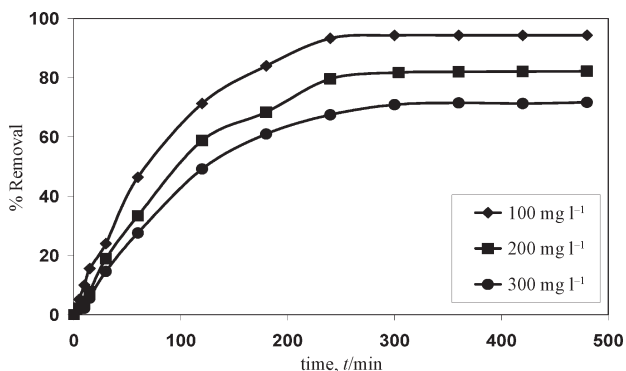


Fig. 2 – Effect of contact time on adsorption of benzaldehyde by activated carbon

lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

#### Effect of initial benzaldehyde concentration

The effect of initial benzaldehyde mass concentration on the removal of benzaldehyde by granular activated carbon is shown in Fig. 2. Efficiency benzaldehyde removal decreased with increase in initial benzaldehyde mass concentration. The necessary driving force to overcome the resistance to the mass transfer of benzaldehyde between the aqueous and the solid phases is provided by initial benzaldehyde concentration. The increases in initial benzaldehyde mass concentration also enhance the interaction between benzaldehyde and activated carbon. The rate of adsorption also increases with the increase in  $\gamma_0$  due to increase in driving force.

#### Kinetics

In order to investigate the kinetics of adsorption processes of benzaldehyde on granular activated carbon, pseudo-first-order, pseudo-second-order, Bangham and intraparticle diffusion kinetic models were used.

#### Pseudo-first-order model

The pseudo-first-order equation is given as:

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \quad (1)$$

Where,  $q_t$  is the amount of adsorbate adsorbed at time  $t$  (mg g<sup>-1</sup>),  $q_e$  is the adsorption capacity at equilibrium (mg g<sup>-1</sup>),  $k_f$  is the pseudo-first-order rate coefficient (min<sup>-1</sup>), and  $t$  is the contact time (min). The integration of eq. (1) with the initial condition,  $q_t = 0$  at  $t = 0$  leads to following equation.<sup>1</sup>

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \quad (2)$$

The values of adsorption rate coefficient ( $k_f$ ) for benzaldehyde adsorption on activated carbon at  $\gamma_0 = 100, 200$  and 300 mg l<sup>-1</sup> were determined from the plot of  $\log(q_e - q_t)$  against  $t$ . the values of  $k_f$  (min<sup>-1</sup>) are shown in Table 2. These values are almost same.

#### Pseudo-second-order model

The pseudo-second-order model is represented as:<sup>2</sup>

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \quad (3)$$

Where,  $k_s$  is the pseudo-second-order rate coefficient ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

Integrating eq. (3) and  $q_t = 0$  at  $t = 0$ , the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad (4)$$

The initial sorption rate,  $\Gamma$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ), at  $t \rightarrow 0$  is defined as

$$\Gamma = k_s q_e^2$$

Fig. 3 shows the plot of  $t/q_t$  vs.  $t$  at  $\gamma_0 = 100, 200$  and  $300 \text{ mg l}^{-1}$ . The  $q_e$  is obtained from the slope of the plot and the  $\Gamma$  value is obtained from the intercept. Since  $q_e$  is known from the slope,  $k_s$  can be determined from the  $\Gamma$  value. The  $k_s$  and  $\Gamma$  values as calculated from the figures are listed in Table 2. It can be seen from the Table 2 that the calculated correlation coefficients are also closer to unity for pseudo-second-order kinetics than that for the pseudo-first-order kinetic model. Therefore, the sorption of benzaldehyde can be approximated more appropriately by the pseudo-second-order kinetic model.

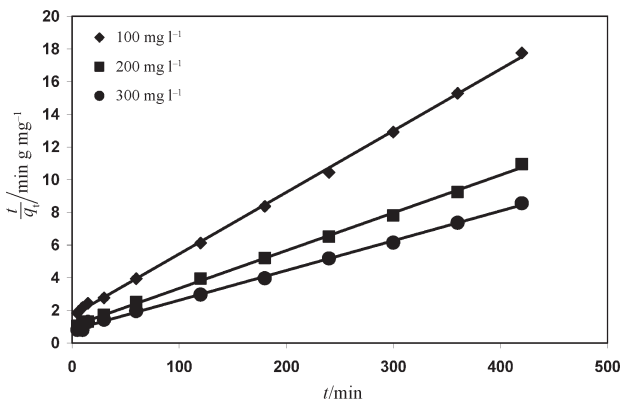


Fig. 3 – Pseudo second order plot for the removal of benzaldehyde by activated carbon for various initial concentration of benzaldehyde

**Bangham’s equation**

Bangham’s equation is given as:<sup>3</sup>

$$\log \log \left( \frac{\gamma_0}{\gamma_0 - q_t m} \right) = \log \left( \frac{k_0 m}{2.303 V} \right) + \alpha \log(t) \quad (5)$$

Where,  $V$  is the volume of the solution (ml), and  $\alpha$  ( $<1$ ) and  $k_0$  are coefficients. The double logarithmic plot, according to eq. (5) did not yield satisfactory linear curves for the benzaldehyde removal by the adsorbents shown in Fig. 4. This shows that the diffusion of adsorbate into the pores of the sorbent was not the only rate-controlling step.<sup>4</sup> The film and pore diffusion both were important to different extents in the removal process.

Table 2 – Kinetic parameters for the removal of benzaldehyde by activated carbon ( $\gamma_0 = 100\text{--}300 \text{ mg l}^{-1}$ ,  $m = 4 \text{ g l}^{-1}$ )

Pseudo-first-order model				
$\frac{\gamma_0}{\text{mg l}^{-1}}$	$\frac{q_{e,\text{exp}}}{\text{mg g}^{-1}}$	$\frac{q_{e,\text{calc}}}{\text{mg g}^{-1}}$	$\frac{k_f}{\text{min}^{-1}}$	$R^2$
100	23.70	3.79	0.014	0.995
200	39.02	4.69	0.013	0.849
300	49.93	4.85	0.013	0.973
Pseudo-second-order model				
$\frac{\gamma_0}{\text{mg l}^{-1}}$	$\frac{q_{e,\text{calc}}}{\text{mg g}^{-1}}$	$\frac{h}{\text{mg g}^{-1} \text{min}^{-1}}$	$\frac{k_s}{\text{g mg}^{-1} \text{min}^{-1}}$	$R^2$
100	26.52	0.0009	1.21E-06	0.999
200	43.29	0.0005	2.76E-07	0.999
300	54.94	0.0004	1.38E-07	0.998
Bangham model				
$\frac{\gamma_0}{\text{mg l}^{-1}}$	$\frac{k_0}{\text{g}}$	$\alpha$	$R^2$	
100	0.97	0.75	0.991	
200	1.12	0.61	0.980	
300	1.07	0.57	0.969	
W-M Intra-particle diffusion model				
$\frac{\gamma_0}{\text{mg l}^{-1}}$	$\frac{k_{id}}{\text{mg g}^{-1} \text{min}^{-1/2}}$	$\frac{I}{\text{mg g}^{-1}}$	$R^2$	
100	1.23	2.28	0.920	
200	2.00	3.76	0.935	
300	2.55	4.85	0.927	

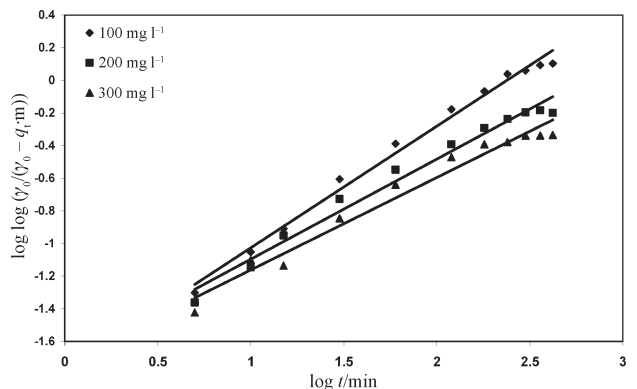


Fig. 4 – Bangham plot for the removal of benzaldehyde by activated carbon for various initial concentration of benzaldehyde

*Intra particle diffusion study*

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model:<sup>5</sup>

$$q_t = k_{id}t^{1/2} + I \tag{6}$$

Where,  $k_{id}$  is the intra-particle diffusion rate coefficient and  $I$  is the intercept. Plot of  $q_t$  vs.  $t^{1/2}$  should be a straight line with a slope  $k_{id}$  and intercept  $I$  when adsorption mechanism follows the intra-particle diffusion process. Fig. 5 presents a plot of  $q_t$  versus  $t^{1/2}$  at  $g_0 = 100, 200$  and  $300 \text{ mg l}^{-1}$  for benzaldehyde adsorption. The values of  $I$  (Table 2), gives an idea about the thickness of the boundary layer, i.e., the larger the intercept the greater is the boundary layer effect.<sup>6</sup> The deviation of straight lines from the origin may be because of the difference between the rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step.<sup>7</sup> The values of intraparticle diffusion rate parameters are given in Table 2.

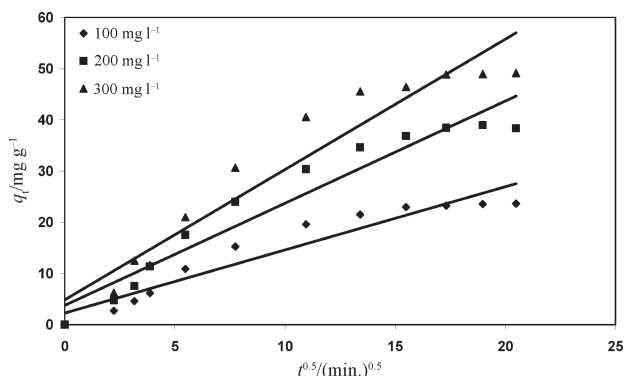


Fig. 5 – *Weber and Morris intra-particle diffusion plot for the removal of benzaldehyde by Activated carbon for various initial concentration of benzaldehyde*

**Equilibrium**

Various isotherm equations like Freundlich, Langmuir and Temkin have been used to describe the equilibrium characteristics of adsorption. The Freundlich isotherm<sup>8</sup> is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Whereas in the Langmuir theory<sup>9</sup> basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. Temkin isotherm contains a factor that explicitly takes into the account adsorptive-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the

adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.<sup>10</sup>

*Freundlich and Langmuir isotherms*

Linearised form of Freundlich and Langmuir isotherm equations are given as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln \gamma_e \text{ (linear form)} \tag{7}$$

$$\frac{\gamma_e}{q_e} = \frac{1}{K_L q_m} + \frac{\gamma_e}{q_m} \text{ (linear form)} \tag{8}$$

Fig. 6 shows the Freundlich isotherm plots ( $\ln q_e$  vs.  $\ln \gamma_e$ ) for adsorption of benzaldehyde onto activated carbon at  $T = 293, 303$  and  $313 \text{ K}$ . Langmuir isotherm plot ( $\gamma_e/q_e$  vs.  $\gamma_e$ ) are shown in Fig. 7 for adsorption onto activated carbon. Freundlich isotherm constants and Langmuir isotherm constants are given in Table 3.

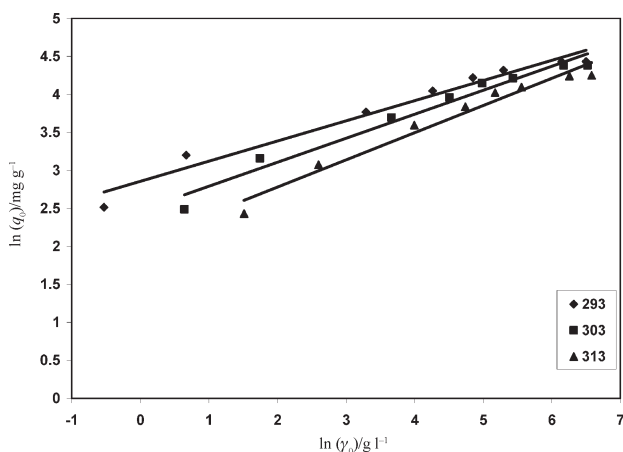


Fig. 6 – *Freundlich isotherm for removal of Benzaldehyde by activated carbon for various temperatures*

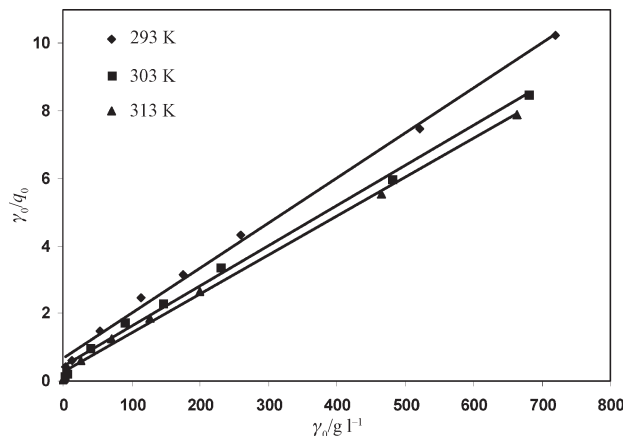


Fig. 7 – *Langmuir isotherm for removal of Benzaldehyde by activated carbon for various temperatures*



Table 3 – Isotherm parameters for adsorption of benzaldehyde onto activated carbon

Langmuir Isotherm			
$\frac{T}{K}$	$\frac{K_L}{l\text{ mg}^{-1}}$	$\frac{q_m}{\text{mg g}^{-1}}$	$R^2$
293	0.047	86.21	0.997
303	0.029	84.03	0.995
313	0.021	74.63	0.996
Freundlich Isotherm			
$\frac{T}{K}$	$\frac{KF}{(\text{mg g}^{-1})/(\text{l mg}^{-1})^{-1/n}}$	$1/n$	$R^2$
293	17.37	3.76	0.967
303	11.85	3.16	0.969
313	7.87	2.79	0.966
Temkin Isotherm			
$\frac{T}{K}$	$\frac{K_T}{l\text{ mg}^{-1}}$	$B_1$	$R^2$
293	4.45	10.57	0.981
303	1.15	12.05	0.984
313	0.46	12.29	0.990

#### Temkin isotherm

Temkin isotherm<sup>10</sup> for adsorption is given as

$$q_e = \frac{RT}{b} \ln(K_T \gamma_e) \quad (9)$$

which can be linearized as

$$q_e = B_1 \ln K_T + B_1 \ln \gamma_e \quad (10)$$

Where

$$B_1 = \frac{RT}{b}$$

A plot of  $q_e$  versus  $\ln \gamma_e$  enables the determination of the isotherm constants  $B_1$  and  $K_T$  from the slope and the intercept, respectively.  $K_T$  is the equilibrium binding constant ( $l\text{ mol}^{-1}$ ) corresponding to the maximum binding energy and constant  $B_1$  is related to the heat of adsorption. Fig. 8 shows the Temkin isotherm plot for activated carbon. The Temkin isotherm quantities listed in Table 3 activated carbon.

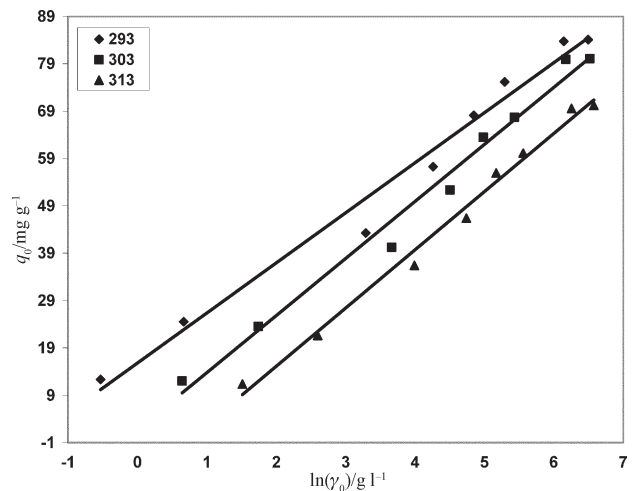


Fig. 8 – Temkin isotherm for removal of Benzaldehyde by activated carbon for various temperatures

#### Error analysis

Five different error functions of non-linear regression basin were employed in this study to find out the most suitable kinetic and isotherm models to represent the experimental data

The sum of the squares of the errors (SSE)

This error function, SSE<sup>11</sup> is given as

$$\text{SSE} = \sum_{i=1}^n (q_{e,\text{calc}} - q_{e,\text{exp}})_i^2 \quad (11)$$

Here,  $q_{e,\text{cal}}$  and  $q_{e,\text{exp}}$  are, respectively, the calculated and the experimental value of the equilibrium adsorbate solid concentration in the solid phase ( $\text{mg g}^{-1}$ ) and  $n$  is the number of data points. This most commonly used error function.

The sum of the absolute errors (SAE)

The sum of the absolute errors (SAE)<sup>11</sup> is given as

$$\text{SAE} = \sum_{i=1}^n |q_{e,\text{calc}} - q_{e,\text{exp}}|_i \quad (12)$$

The isotherm parameters determined by this method provide a better fit as the magnitude of the errors increase, biasing the fit towards the high concentration data.

The average relative error (ARE)

The average relative error (ARE)<sup>11</sup> is given as

$$\text{ARE} = \frac{100}{n} \sum_{i=1}^n \left| \frac{(q_{e,\text{exp}} - q_{e,\text{calc}})}{q_{e,\text{exp}}} \right| \quad (13)$$

This error function attempts to minimize the fractional error distribution across the entire concentration range. The values of ARE are given in Table 4 for activated carbon.

Table 4 – Isotherm error analysis for adsorption of benzaldehyde onto activated carbon

Temperature Isotherm	HYBRID	MPSD	SSE	SAE	ARE
293K					
Langmuir	16.32	85.28	691.95	0.92	26.11
Freundlich	-3.05	33.78	260.82	9.82	9.44
Temkin	-0.75	30.76	169.72	7.22	8.60
303K					
Langmuir	12.47	62.66	310.56	0.90	19.18
Freundlich	-0.89	35.01	258.54	2.60	9.78
Temkin	1.91	22.45	63.00	-0.29	6.27
313K					
Langmuir	-1.38	44.66	214.04	18.82	13.67
Freundlich	-0.74	35.87	263.30	3.32	10.02
Temkin	1.82	22.03	47.39	-0.46	6.15

#### The hybrid fractional error function (HYBRID)

The hybrid fractional error function (HYBRID) is given as

$$\text{HYBRID} = \frac{100}{n-p} \sum_{i=1}^n \left[ \frac{(q_{e,\text{exp}} - q_{e,\text{calc}})}{q_{e,\text{exp}}} \right] \quad (14)$$

This error function was developed<sup>12</sup> to improve the fit of the ARE method at low concentration values. Instead of  $n$  as used in ARE, the sum of the fractional errors is divided by  $(n-p)$  where  $p$  is the number of quantities in the isotherm equation.

#### Marquardt's percent standard deviation (MPSD)

MPSD<sup>13</sup> has been used by a number of researchers in the field<sup>14</sup> to test the adequacy and accuracy of the model fit with the experimental data. It has some similarity to the geometric mean error distribution, but was modified by incorporating the number of degrees of freedom. This error function is given as:

$$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left( \frac{(q_{e,\text{meas}} - q_{e,\text{calc}})}{q_{e,\text{meas}}} \right)^2} \quad (15)$$

The values of MPSD error functions are given in Table 3.

The values of the five error functions SSE, SAE, ARE, HYBRID and MPSD are presented in Table 4. By comparing the results of the values of the error functions, it is found that Temkin model best-fits the benzaldehyde adsorption isotherm data for the activated carbon at  $T = 293$  K, 303 K and 313 K.

#### Thermodynamics

The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classic van't Hoff equation

$$\Delta G^0 = -RT \ln K \quad (16)$$

According to thermodynamics, the Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (17)$$

Combining above two equations, we get

$$\ln K = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T} \quad (18)$$

Where  $\Delta G^0$  the free energy change ( $\text{kJ mol}^{-1}$ ) is,  $\Delta H^0$  is the change in enthalpy ( $\text{kJ mol}^{-1}$ ),  $\Delta S^0$  is the entropy change ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ),  $T$  is the absolute temperature (K) and  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{K}^{-1}$ ). Thus  $\Delta H^0$  can be determined by the slope of the linear van't Hoff plot i.e. as  $\ln K$  vs.  $(1/T)$ , using equation:<sup>14</sup>

$$\Delta H^0 = \left[ R \frac{d \ln K}{d(1/T)} \right] \quad (19)$$

$\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  as calculated are given in Table 5 for adsorption of benzaldehyde onto activated carbon. The negative  $\Delta H^0$  value confirms the exothermic nature of the overall-adsorption process.

Table 5 – Thermodynamics study

Isotherm	$\Delta G^0$ , $\text{J mol}^{-1} \text{K}^{-1}$			$\Delta H^0$ , $\text{kJ mol}^{-1}$	$\Delta S^0$ , $\text{kJ mol}^{-1} \text{K}^{-1}$
	293 K	303 K	313 K		
Langmuir	-20.76	-20.22	-20.00	-32.01	-38.56
Temkin	-31.83	-29.51	-28.11	-86.51	-187.12
Freundlich	-18.32	-17.98	-17.51	-30.13	-40.26

## Conclusion

The present study shows that the granular activated carbon is an effective adsorbent for the removal of benzaldehyde from aqueous solution. The optimum adsorbent dose was 4 g l<sup>-1</sup> of solution and 4 h is time taken by system to achieve equilibrium. Adsorption kinetics was found to follow second order rate expression. The diffusion is not the only rate controlling step. Equilibrium data for adsorption of benzaldehyde on granular activated carbon were best represented by Temkin isotherm. Adsorption of benzaldehyde on granular activated carbon is favorable influenced by decrease in the temperature of the operation. The negative values of  $\Delta G^0$  indicate spontaneous adsorption of benzaldehyde on granular activated carbon.

## Nomenclature

$\gamma_0$	– initial mass concentration of adsorbate in solution, mg l <sup>-1</sup>
$\gamma_e$	– equilibrium liquid phase mass concentration, mg l <sup>-1</sup>
$\Gamma$	– initial sorption rate, mg g <sup>-1</sup> min <sup>-1</sup>
$I$	– constant that gives idea about the thickness of boundary layer, mg g <sup>-1</sup>
$k_0$	– coefficient in Bangham equation
$k_f$	– rate coefficient of pseudo-first-order adsorption model, min <sup>-1</sup>
$k_{id}$	– intra-particle diffusion rate coefficient, mg g <sup>-1</sup> min <sup>-1/2</sup>
$k_s$	– rate coefficient of pseudo-second-order adsorption model, g mg <sup>-1</sup> min <sup>-1</sup>
$K$	– equilibrium constant
$K_F$	– constant of Freundlich isotherm, (mg g <sup>-1</sup> )/(l mg <sup>-1</sup> ) <sup>1/n</sup>
$K_L$	– constant of Langmuir isotherm, l mg <sup>-1</sup>
$K_T$	– constant of Temkin isotherm, l mg <sup>-1</sup>
$m$	– mass of adsorbent per liter of solution, g l <sup>-1</sup>
$n$	– exponent in Freundlich isotherm model
$n_S$	– agitation speed, min <sup>-1</sup>
$q_e$	– equilibrium solid phase concentration, mg g <sup>-1</sup>

$q_{e,cal}$	– calculated value of solid phase concentration of adsorbate at equilibrium, mg g <sup>-1</sup>
$q_{e,exp}$	– experimental value of solid phase concentration of adsorbate at equilibrium, mg g <sup>-1</sup>
$q_m$	– maximum adsorption capacity of adsorbent, mg g <sup>-1</sup>
$q_t$	– amount of adsorbate adsorbed by adsorbent at time $t$ , mg g <sup>-1</sup>
$R$	– universal gas constant, 8.314 J mol <sup>-1</sup> K <sup>-1</sup>
$R_L$	– separation factor, dimensionless
$t$	– time, min, h
$T$	– absolute temperature, K
$V$	– volume of the solution, l
$\Delta G^0$	– Gibbs free energy of adsorption, kJ mol <sup>-1</sup>
$\Delta H^0$	– enthalpy of adsorption, kJ mol <sup>-1</sup>
$\Delta S^0$	– entropy of adsorption, J mol <sup>-1</sup> K <sup>-1</sup>
$\alpha$	– Bangham coefficient (<1)

## References

1. Lagergren, S., *Ksver Veterskapsakad Handl.* **24** (1898) 1.
2. Ho, Y. S., McKay, G., *Process Biochemistry* **34** (1999) 451.
3. Bangham, D. H., Burt, F. P., *Proceedings of the Royal Society of London. Series A-Containing Papers of A Mathematical and Physical Character* **105** (732) (1924) 481.
4. Tutem, E., Apak, R., Unal, C. F., *Water Res.* **32** (1998) 2315.
5. Weber, Jr. W. J., Morris, J. C., *J. Sanitary Engg. Div. ASCE.* **89** (SA2) (1963) 31.
6. Kannan, K., Sundaram, M. M., *Dyes Pigments* **51** (2001) 25.
7. Poots, V. J. P., McKay, G., Healy, J. J., *J. Water Pollution Control Federation.* **50** (1978) 926.
8. Freundlich, H. M. F., *J. Phys.Chem.* **57** (1906) 385.
9. Langmuir, I., *J. Am. Chem. Soc.* **40** (1918) 1361.
10. Temkin, M. J., Pyzhev, V., *Acta Physiochim URSS* **12** (1940) 217.
11. Kapoor, A., Yang, R. T., *Gas Sep. Purif.* **3** (4) (1989) 187.
12. Porter, J. F., McKay, G., Choy, K. H., *Chem. Eng. Sci.* **54** (1999) 5863.
13. Marquardt, D. W., *J. Soc. (Ind) Appl. Math.* **11** (1963) 431.
14. Wong, Y. C., Szeto, Y. S., Cheung, W. H., McKay, G., *Process Biochemistry* **39** (2004) 693.