

# Adsorption of BTEX from Amine Solution by Activated Carbon

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## Abstract

In the present study, some experiments were performed on the adsorption of benzene, toluene, ethylbenzene and xylene (BTEX) from amine solution by granular activated carbon. Isotherm studies were conducted to evaluate the adsorption behavior of the activated carbon. The Langmuir, Freundlich and Redlich-Peterson isotherm models were used to describe the equilibrium data. A mathematical model was proposed for describing the BTEX transfer between the amine solution and solid particles. To evaluate the validity of the proposed model, a pilot – plant was constructed, in which the breakthrough curve for different component were investigated practically. The results predicted by the proposed model were compared with the experimental results and a satisfactory agreement was observed between them. The effects of the different operating parameters on the rate of adsorption were also discussed. The results of fixed bed column tests showed that the activated carbon was very effective in removing the BTEX from amine solution.

Keywords: BTEX; Activated carbon; Adsorption; Amine solution; Mathematical model

## **1. Introduction**

Several aromatic compounds including benzene, toluene, ethylbenzene and xylene, collectively known as BTEX, were included on a list of 189 hazardous air pollutants (HAP) [1]. The clean air act limits the amounts of total BTEX compounds which may be emitted from a facility to 25 tons per year and 10 tons per year of any individual compound. In amine process, heavy hydrocarbons and aromatics are absorbed from natural gas streams in addition to the acid gas components [2]. These dissolved hydrocarbons are ultimately released in

the overhead of the regenerator. If the overhead of the regenerator is vented to the atmosphere, BTEX emissions may be of concern. If the overhead of the regenerator is fed to a burner such as in a Claus plant, the BTEX components are more difficult to destroy relative to other hydrocarbon. These BTEX components tend to deactivate the Claus catalysts, severely limiting the catalyst life [3].

BTEX components are typical toxic organic compounds that appear very often in chemicals and petrochemical wastewaters. They are designated by the US EPA as priority chemicals that need to be reduced to a very low level in those wastewaters for safe discharge because of their toxicity to human and marine life [4].

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Liquid-phase adsorption is shown to be effective for collection of suspended solids, odors, organic matter, and oils. Powder or granular activated carbon is the most widely used adsorbent for this purpose also it has high adsorption Adsorption process capacity [5]. involves the selective transfer of solute onto the surface or onto the bulk of the solid material. This solute transfer process is found to occur through varied mechanisms such as external mass transfer, intraparticle diffusion and adsorption at sites [6].

Fixed-bed operations are widely used in chemical processes and pollution control processes such as separating ions by an ion-exchange bed or removing toxic organic compounds by a carbon adsorption bed [7]. In order to properly design and operate fixed-bed adsorption processes, the adsorption isotherm and the fixed-bed dynamics must be known. In the present study, the effects of the different operating parameters such as: flow rate, inlet BTEX concentration and particle size on the rate of adsorption is investigated.

## 2. Theory and Model

Consider a fixed-bed adsorber packed column, randomly fresh or just regenerated with adsorbent particles. An aqueous solution containing organic component (BTEX) is fed to the bottom of the bed at a constant flow rate. The governing equation for predicting the fixed-bed column dynamics can be described by the following differential mass balance equation:

$$e\frac{\partial C}{\partial t} + u_0 \times e\frac{\partial C}{\partial t} + (l - e)r_P\frac{\partial q}{\partial t} = 0 \quad (1)$$

Eq. (1) is basically the unsteady- state mass balance of the adsorbate. The assumptions associated with Eq. (1) are:

- **§** No chemical reactions occur in the column.
- **§** Only mass transfer by convection is significant.
- **§** Radial and axial dispersions are negligible.
- **§** The flow pattern is the ideal plug flow.
- **§** The temperature in the column is uniform and invariant with time.
- **§** The flow rate is constant and invariant with the column position.

The mass balance in the solid phase can be described by the following equation:

$$(1-e)r_P \frac{\partial q}{\partial t} = K_c a(C-C^*)$$
 (2)

The adsorption isotherm relates the liquid- and solid-phase concentration at equilibrium is given by:

$$\boldsymbol{C}^* = \boldsymbol{g}(\boldsymbol{q}) \tag{3}$$

In the terms of the constant-pattern wave approach theory [7, 8, 9], the wave move at a constant flow velocity,  $u_W$ :

$$u_W = \left(\frac{\partial z}{\partial t}\right)_c \tag{4}$$

Where z is the linear distance in the flow direction and t is time.

Then the liquid-phase concentration can be expressed as a unique function of the adjusted time  $\tau$ , defined as:

$$t = t - \frac{z}{u_w} \tag{5}$$

Substituting Eq (5) into Eq. (1) leads to:

$$\left(1 - \frac{u_0}{u_W}\right)\frac{dC}{dt} + \frac{r_P}{e}\frac{dq}{dt} = 0$$
(6)

Which can be integrated and writhen as:

$$\int_{0}^{C} \left( 1 - \frac{u_0}{u_W} \right) dC + \int_{0}^{q} \frac{r_P}{e} dq = 0$$
(7)



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Or

$$\left(1 - \frac{u_0}{u_w}\right)C + \frac{r_P}{e}q = 0$$
(8)

Since the boundary condition at  $C = C_0$ ,

 $q = q_0$  must be satisfied, the following equation is also valid:

$$\left(1 - \frac{u_0}{u_w}\right)C_0 + \frac{r_P}{e}q_0 = 0 \tag{9}$$

Combining Eqs. (8) and (9) lead to

$$\frac{q}{q_0} = \frac{C}{C_0} \tag{10}$$

The adsorption rate expressed in terms of the adjusted time is:

$$(1-\varepsilon)\rho_{\rm P}\frac{\mathrm{d}q}{\mathrm{d}\tau} = K_{\rm c}a(C-C^*) \tag{11}$$

Combining Eqs. (10) and (11) lead to

$$(1-\varepsilon)\rho_{\rm P} \frac{q_0}{C_0} \frac{dC}{d\tau} = K_{\rm c} a(C-C^*)$$
(12)

Combining Eqs. (3), (10) and (12), results in:

$$(1-\varepsilon)\rho_{\rm P} \frac{q_0}{C_0} \frac{dC}{d\tau} = K_{\rm c} a [C - g(\frac{C}{C_0} q_0)] \quad (13)$$

Eq. (13) can be rearranged and integrated with the following boundary

condition at  $t = t_{1/2}, \ C = \frac{C_0}{2}$ :

$$\int_{\frac{C_0}{2}}^{C} \frac{dC}{C - g(C\frac{q_0}{C_0})} = \int_{t_{1/2}}^{t} \frac{C_0 K_C a dt}{(1 - e) r_P q_0}$$
(14)

Where  $t_{1/2}$  is the adjusted time when the effluent adsorbate concentration reaches half of the feed concentration. Assuming that the volumetric mass-transfer coefficient K<sub>c</sub>a is constant, Eq. (14) becomes

$$\tau = \tau_{1/2} + \frac{(1-\varepsilon)\rho_{\rm P}q_0}{C_0 K_{\rm c}a} \int_{\frac{C_0}{2}}^{C} \frac{1}{C - g(C\frac{q_0}{C_0})} dC \qquad (15)$$

Since

$$t - t_{1/2} = (t - \frac{z}{u_w}) - (t_{1/2} - \frac{z}{u_w}) = t - t_{1/2}$$

The breakthrough curve at z=L can be calculated by the following equation: t =  $t_{1/2}$ 

$$+\frac{(1-\varepsilon)\rho_{\rm P}q_{\rm 0}}{C_{\rm 0}K_{\rm c}a}\int_{\frac{C_{\rm 0}}{2}}^{C}\frac{1}{C-g(C\frac{q_{\rm 0}}{C_{\rm 0}})}dC \qquad (16)$$

## 3. Experimental

The granular activated carbon was repeatedly washed with deionized water to remove any leachable impurities and adherent powder and then dried at 110  $^{\circ}C$  in an electric oven for over 24 hr. It was then placed in a desiccator for cooling and in order to maintain constant moisture content. Benzene, toluene, ethylbenzene and xylene with purity greater than 99.8 were provided from Merck Corporation (Germany). The stock BTEX solution was prepared by mixing an appropriate quantity of the BTEX with 15 wt % monoethanolamine (MEA). In determining the adsorption isotherms, various amounts of the washed and dried carbon (0.0342- 0.25g) were added to 300- mL (glass-stoppered flasks) Erlenmeyer flasks, each filled with 250 mL of the stock solution. The initial concentration of Benzene and Toluene were 100 mg/L, Ethylbenzene and Xylene were 150 mg/L. The flask was completely sealed. All the flasks were shaken in a temperature- controlled shaker at a constant shaking speed of



100 rpm for 168 h to attain equilibrium. A packed gas chromatograph (Varian model 3700) equipped with FID detector and Carbopack SP-1000 packed column was used for the BTEX concentration determination. The adsorbed amounts of BTEX were calculated by mass balance relation:

$$q = (C_0 - C^*) \times \frac{V}{W} \tag{17}$$

The experimental apparatus which is constructed for this study is mainly composed of an adsorption column. The fixed-bed adsorption column is a Pyrex glass tube of 2.1 cm inside diameter and 31 cm length. The column is packed with 15 g of Coconut based activated carbon with a volume of 22.5 cm<sup>3</sup>. A solution with known concentration of BTEX is fed to the bottom of the column and its flow rate is regulated by a precise flow meter. The exiting aqueous solution is sampled periodically and its BTEX concentration is determined using a gas chromatograph system.

#### 4. Results and Discussion

#### 4.1. Adsorption isotherm

The three general adsorption isotherms can be represented by the monolayer Langmuir, Redlich-Peterson and the empirical Freundlich models:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e}$$
(18)

$$q = K_F C^{*^n}$$
(19)

$$q_e = \frac{AC_e}{1 + BC_e^{\ g}} \tag{20}$$

The adsorption isotherms of the BTEX at  $27^{\circ}C$  are shown in Figures 1 and 2,

respectively. The models Parameters were determined from non-linear regression of experimental data and the results are shown in Table 1. The Freundlich model gives satisfactory fit to the experimental data.



Fig.1. Experimental and Freundlich adsorption isotherm of Benzene and Toluene at  $27 °_{\rm C}$ 



Fig.2. Experimental and Freundlich adsorption isotherm of Ethylbenzene and Xylene at  $27^{\circ}C$ 

# 4.2. Effects of the different operating parameters on Breakthrough

Combining Eq. (19) with (16) lead to:



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$$t = t_{1/2} + \frac{(1-\varepsilon)\rho_{p}K_{F}C_{0}^{n-1}}{K_{c}a}(\ln 2x - \frac{1}{1/n-1}\left(\ln\left(\frac{1-x^{1/n-1}}{1-2^{1-1/n}}\right)\right)$$
(21)

Table 1-	Adsorption	model	parameter	for	BTEX
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Model	parameter	Benzene	Toluene	Ethylbenzene	Xylene
Langmuir	K <sub>L</sub>	-0.0025	0.013	0.0202	0.0254
	$q_{\rm m}$	-739.4646	476.0174	955.4667	1277.6
Freundlich	K <sub>F</sub>	1.13371	13.6291	43.4290	59.8990
	n	1.1565	0.6711	0.6067	0.6380
Redlish-Petersor	n A	2	3.1777	6.3854	0.0192
	В	16065	-657.1443	-234.3163	-0.9999
	g	-3	-2.2017	-10.514	-0.0003

Eq. (21) can be used to predict the breakthrough curve of fixed-bed adsorption processes whit the Freundlich adsorption isotherms. Where x is the normalized effluent concentration  $(x=C/C_0)$ . The values of  $t_{1/2}$  and  $K_La$  were determined from the intercept and slope of the

$$\ln 2x - \frac{1}{1/n - 1} \left( \ln \frac{1 - x^{1/n - 1}}{1 - 2^{1 - 1/n}} \right)$$

versus t curve. The experimental and predicted breakthrough curves calculated by Eq.(21) are shown in Fig.3-8. Fig. 3 and Fig .4 show the breakthrough curves of Toluene and Xylene at different particle size of activated carbon. The  $t_{1/2}$  values decreases and  $K_ca$  increases with decreasing particle diameter. Fig. 5 and Fig. 6 show the the breakthrough curves of Toluene and Xylene at different feed concentration. The  $t_{1/2}$  values decreases with increasing  $C_0$ , on the other hand  $K_ca$  increases with increasing  $C_0$ . On the other hand  $K_ca$  increases with increasing  $C_0$ . This means the breakthrough curve is steeper at higher  $C_0$ . It is likely that the driving force of mass-transfer in the liquid-film is enhanced when  $C_0$  is increased. Fig. 7 and Fig 8 show different feed flow rate.  $t_{1/2}$  decreases and  $K_ca$  increases with increasing feed flow rate.



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Experimental condition	Run1	Run2	Run3	Run4	Run5	Run6	Run7
Feed concentration(mg/L)	90	90	90	90	90	70	55
Flow rate(L/hr)	12	12	12	9	7	12	12
particle diameter (cm)	0.0707	0.14	0.16	0.14	0.14	0.14	0.14
Bed void fraction	0.33	0.33	0.33	0.33	0.33	0.33	0.33
Bed density(g/L)	999	999	999	999	999	999	999
Bed depth(cm)	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Temperature(°C)	27	27	27	27	27	27	27
$K_{ca}(Min^{-1})$ Toluene	269.76	172.52	125.67	145.99	135.16	156.5	142.47
K <sub>c</sub> a(Min <sup>-1</sup> ) Xylene	323.72	183.84	153.13	159.91	151.68	170	142.87
t <sub>1/2</sub> (calculated) (Toluene)	72.4	91.679	105.49	118.6	143.37	127.3	171.8
t <sub>1/2</sub> (calculated)(Xylene)	82.85	116.10	132.5	158.33	202.27	156.07	192.91

 Table 2- Experimental conditions for column tests



Fig.3. Effect of the particle size on the breakthrough curve of Toluene adsorption onto activated carbon ( $C_0=90$ mg/L, Q=12 L/hr, w=15g).

Fig.4. Effect of the particle size on the breakthrough curve of xylene adsorption onto activated carbon ( $C_0=90mg/L$ , Q=12 L/hr, w=15g)



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Fig.5. Effect of the concentration on the breakthrough curve of Toluene (dp=1.4mm, Q=12 L/hr, w=15g)



Fig.6. Effect of the concentration on the breakthrough curve of xylene adsorption onto activated carbon (dp=1.4mm, Q=12 L/hr, w=15g)

## 5. Conclusions

1-The adsorption of BTEX by granular activated carbon from amine solution was studied experimentally and theoretically. The column test results showed that the activated carbon was very effective in removing the BTEX from amine solution.



Fig.7. Effect of the flow rate on the breakthrough curve of Toluene adsorption onto activated carbon (C0=90mg/L,  $d_p$ =1.4mm, w=15g)



Fig.8. Effect of the flow rate on the breakthrough curve of xylene adsorption onto activated carbon  $(C_0=90 \text{mg/L}, d_p=1.4 \text{mm}, w=15 \text{g})$ 

2-Three adsorption isotherm models, Langmuir, Freundlich and Redlich- Peterson were used to fit the batch isotherm data at 27°C. The empirical Freundlich isotherm describes the equilibrium adsorption data better than other isotherms.

3-A mathematical model was proposed for BTEX adsorption by activated carbon. The model



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involves only one parameter (the overall mass transfer coefficient) which can be conveniently estimated using the experimental mass transfer data.

4-Results predicted by the proposed model were compared with experimental results. A relatively good agreement was observed between these results.

#### Nomenclature

- A the Redlish-Peterson isotherm constant (L/g)
- a mass-transfer area per unit volume of the bed  $(m^2/m^3)$
- B the Redlish-Peterson isotherm constant  $(L/mg^{1-1/A})$
- C adsorbate concentration in the liquid phase (mg/L)
- C<sub>0</sub> Initial feed concentration in the liquid phase (mg/L)
- C<sup>\*</sup> Equilibrium feed concentration in the mobile phase (mg/L)
- g the exponent in the Redlish-Peterson isotherm.
- K<sub>c</sub> overall liquid-phase masstransfer coefficient (m/Min)
- $K_c a$  The volumetric coefficients in the liquid-phase (Min<sup>-1</sup>)
- $K_F$  Freundlich model parameter  $(Lit)^n mg^{1-n}/g$
- K<sub>L</sub> Langmuir model parameter (Lit/mg)
- n Freundlich model parameter
- q adsorbate concentration in the solid phase(mg/g)
- q<sub>0</sub> Constant solid phase loading of adsorbate(mg/g)
- $\begin{array}{ll} q_m & \mbox{maximum adsorption capacity} \\ & \mbox{for the solid phase loading} \\ & (mg/g) \end{array}$

- $\varepsilon$  void fraction of the bed
- $\rho_p$  the carbon bed density(g/L)
- t Time(h)
- $u_w$  Wave velocity(m/s)
- u<sub>0</sub> the interstitial fluid velocity(m/s)
- V the volume of solution
- W Weight of dry carbon(g)
- x the normalized effluent concentration, x = C/CF
- z linear distance in the flow direction (m)
- $\tau$  adjusted time (Min)
- $\tau_{1/2}$  half adjusted time at x= 1/2 (Min)

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