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# Thermodynamic and Kinetic Behaviors of Trinitrotoluene Adsorption on Powdered Activated Carbons

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# Thermodynamic and Kinetic Behaviors of Trinitrotoluene Adsorption on Powdered Activated Carbons

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**Abstract:** Regulations on the removal of trinitrotoluene (TNT) from wastewater have become increasingly more stringent, demanding faster, less expensive, and more efficient treatment. This study focuses on the adsorption equilibrium and kinetics of TNT on powered activated carbons (PAC). Three types of PACs (i.e., wood based, coal based, and coconut-shell based) were studied as functions of temperature and pH. Thermodynamic properties including Gibbs free energy, enthalpy, and entropy, were evaluated by applying the Van't Hoff equation. In addition, the adsorption energy distribution functions which describe heterogeneous characteristics of porous solid sorbents were calculated by using the generalized nonlinear regularization method. Adsorption kinetic studies were carried out in batch adsorber under important conditions such as PAC types, temperature, pH, and concentration. We

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found that fast and efficient removal of TNT dissolved in water can be successfully achieved by PAC adsorption.

**Keywords:** Adsorption, trinitrotoluene, powdered activated carbons, equilibrium, kinetics

## INTRODUCTION

TNT has been classified by EPA as a toxic and mutagenic pollutants (1, 2). Environmental regulations have steadily become more stringent for the removal of TNT from wastewater and groundwater (3). The EPA has set the ambient criteria of 0.06 mg $l^{-1}$ for TNT and the drinking water criteria of 0.049 mg $l^{-1}$(4). The conventional treatment techniques such as incineration, detonation, biodegradation, and solvent extraction have been found unsuitable for the reduction of TNT to the low discharge limit required (5–8). It has been suggested that the treatment of TNT requires a fast, inexpensive, and efficient treatment technique (9). Naturally, researchers have been considering powdered activated carbon (PAC) adsorption as an alternative technique for the removal of TNT from wastewater. Unfortunately, however, experimental and theoretical studies of the equilibrium and kinetic studies of TNT on PAC have been very limited to date.

The objective of this study is to investigate the feasibility of treating TNT contaminated water by powdered activated carbon adsorption. For this purpose, the adsorption equilibrium, thermodynamic properties, and kinetic studies were systematically conducted using PACs (i.e., wood based (WB), coal based (CB), and coconut-shell based (HA)). The adsorption energy distribution functions of TNT obtained as functions of temperature and solution pH were calculated on the basis of a generalized nonlinear regularization method (10) since the surface energy heterogeneity offers the fundamental and informative data required in understanding the adsorption properties. In addition, adsorption kinetic data were analyzed by employing the pseudo-second-order model and intraparticle diffusion models (11, 12).

## EXPERIMENTAL

### Materials

The adsorbents used in this study are three different PACs; namely, wood based (WB), coconut-shell based (HA), and coal based (CB) PACs supplied by James Cumming & Sons PTY Ltd. (Australia). For the equilibrium isotherm experiment, the adsorbents were boiled in distilled water for 12 h, dried at 378.15 K for 24 h in a thermostatic oven, and kept on a dessicator. The nitrogen adsorption apparatus (Micromeritics, model ASAP-2010) measured the surface area and pore size distribution. The surface area was calculated by using the BET method, and the pore size distribution was measured by BJH (Barrett, Joyner and Halenda) method using the nitrogen desorption data. The surface area was found to be in the range from 882 to 1200 $m^2\ g^{-1}$. The physical properties of PACs are listed in Table 1. All experiments were carried out with the solutions of TNT (from industrial production) in distilled water. The important chemical properties of TNT are listed in Table 2.

## Procedure

The equilibrium data were obtained by introducing a given amount of PAC into an aqueous solution of TNT with a known concentration (within the range of $1 \sim 50\ mgl^{-1}$), shaking the adsorbates in a constant temperature incubator (298.15, 313.15, 323.15 K) sufficiently for 46 h until the equilibrium was reached. The solution pH (3, 4, 5, 7, 9) was adjusted by using HCl and NaOH. After shaking in a constant temperature incubator at constant temperature to give sufficient contacting time for equilibrium, samples were taken from the flask and filtered through 150 mm filter paper (ADVANTEC, Japan). The filtrate was then measured for the TNT concentration. The adsorption capacity of TNT was calculated using

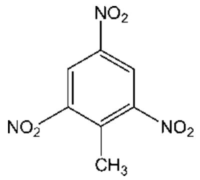
$$q = \frac{(C_0 - C)}{w} V, \tag{1}$$

where $q(\mathrm{mg\ g^{-1}})$ is the equilibrium capacity, and $C_0$ are $c$ the initial and equilibrium concentration $(\mathrm{mg\ l^{-1}})$ of TNT in solution, $V(\mathrm{l^{-1}})$ is the volume, and $w$(g) is the weight of the adsorbent.

***Table 1.*** Characteristics of powdered activated carbon (PAC)

| Specification | PAC-WB | PAC-CB | PAC-HA |
|---|---|---|---|
| Raw material | Wood-based | Coal-based | Coconut-based |
| BET surface area, $m^2\ g^{-1}$ | 882 | 915 | 1200 |
| Moisture content, % | 5 | 8 | 10 |
| Bulk density, $kg\ m^{-3}$ | 340 | 200 | 425 |
| Mean pore diameter, Å | 31 | 24 | 31 |
| Mean particle diameter, μm | 20 | 11 | 34 |

*Table 2.* Properties of TNT

| | |
|---|---|
| Chemical structure |  |
| Chemical formula | $C_7H_5N_3O_6$ |
| MW | 227.13 |
| Color | Yellow-white |
| Odor | Odorless |
| Solubility at 293.15 K (mg $l^{-1}$) | 130 |
| Melting point (K) | 353.25 |
| Boiling point (K) | 513 |
| Partition coefficients Log $K_{ow}$ | 1.60 |
| Vapor pressure at 293.15 K (atm) | $2.618 \times 10^{-2}$ |
| Henry's law constant at 293.15 K (atm $m^3$ $mol^{-1}$) | $4.57 \times 10^{-7}$ |

To obtain the concentration decay curves, batch experiments were conducted in a carberry-type batch adsorber of $2.0 \times 10^{-3}$ $m^3$. The PAC particles were loaded into the batch adsorber and rotated to permit good contact with the solution. All the experiments were carried out at approximately 300 rpm under varying temperatures (298.15, 313.15, 323.15 K) and pH (3, 4, 5, 7, 9).

### Analysis

The concentration of TNT in the solution was analyzed by a Shimadzu model LC-6AD HPLC system (Japan) equipped with a UV detector at 254 nm and Eurospher RP-18 (Fa. Knauer, Berlin, Germany) under the flow rate of 1.5 ml $min^{-1}$ and at 303.15 K. Deionized water, analytical grade methanol, and acetonitrile were mixed at a ratio of 50:38:12 (v/v), filtered, and degassed to use as a mobile phase.

## RESULTS AND DISCUSSION

### Equilibrium Study

The adsorption characteristics of the three PACs were evaluated on the basis of adsorption equilibrium and kinetic studies. Adsorption equilibrium is the most fundamental data on an adsorption system. It is also very important in model prediction for analyzing and designing an adsorption process. As stated in the experimental section, the surface area of PACs (wood based, coal based, and coconut-shell based) used in this work was found to be 882 to 1200 $m^2\ g^{-1}$, and the average pore diameter was 24 to 31 Å. Figure 1a shows the adsorption of TNT on different powdered activated carbons. The adsorption capacity mainly depends on the properties of the adsorbate and adsorbent. As expected, the adsorption capacity of TNT was in the order of PAC-HA > PAC-CB > PAC-WB. It is evident that comparatively PAC-HA exhibited better adsorption capacity among the three. The greater affinity of coconut shell-based PAC-HA can be attributed to its higher surface area (Table 1).

Figures 1b and 1c show the adsorption isotherms of TNT on PAC-HA in terms of temperature (298.15, 313.15, 323.15 K) and pH (3, 4, 5, 7, 9). The adsorption capacity increased with increasing temperature (Fig. 1b), which indicates chemisorption (13, 14). The rate of adsorption is an important criterion for the determination between physisorption and chemisorption. The chemisorption usually requires activation energy which increases with increasing temperature. Similar results have been reported by Marinovic et al. (2). They investigated the adsorption capacity of granular activated carbon under wide temperature ranges from 283.15 K to 333.15 K. At temperatures up to 293.15 K, physical adsorption predominates while the contribution of chemisorption becomes increasingly large within the temperature region from 298.15 K to 333.15 K because of the positive temperature coefficient of the rate of chemisorption (13, 14). To compare the influence of solution pH, the adsorption isotherm data as shown in Fig. 1c were obtained in terms of pH (3, 4, 5, 7, 9) at higher temperature (323.15 K). The adsorption capacity increased with decreasing pH (i.e., increasing hydrogen concentration), and the isotherm data showed more concave (i.e., favorable adsorption). This result implies that the effective removal of TNT can be achieved at lower pH and higher temperature. Adsorption equilibrium data of TNT on PAC were correlated well with the Langmuir-Freundlich equation:

$$\text{Langmuir-Freundlich} \quad q = \frac{q_m b C^{1/n}}{1 + bC^{1/n}} \tag{2}$$

The solid lines in Fig. 1a, 1b and 1c are the results predicted by the Langmuir isotherm parameters (Table 3). The isotherm parameters were determined by minimizing the mean percentage deviations between experimental and predicted amounts adsorbed. The values of the correlation coefficients ($R^2$) are listed in Table 3.

## Evaluation of Thermodynamic Properties

According to the thermodynamic relationship, the equilibrium constant ($b$) is related to the change of Gibbs free energy ($\Delta G$), the entropy change ($\Delta S$), and

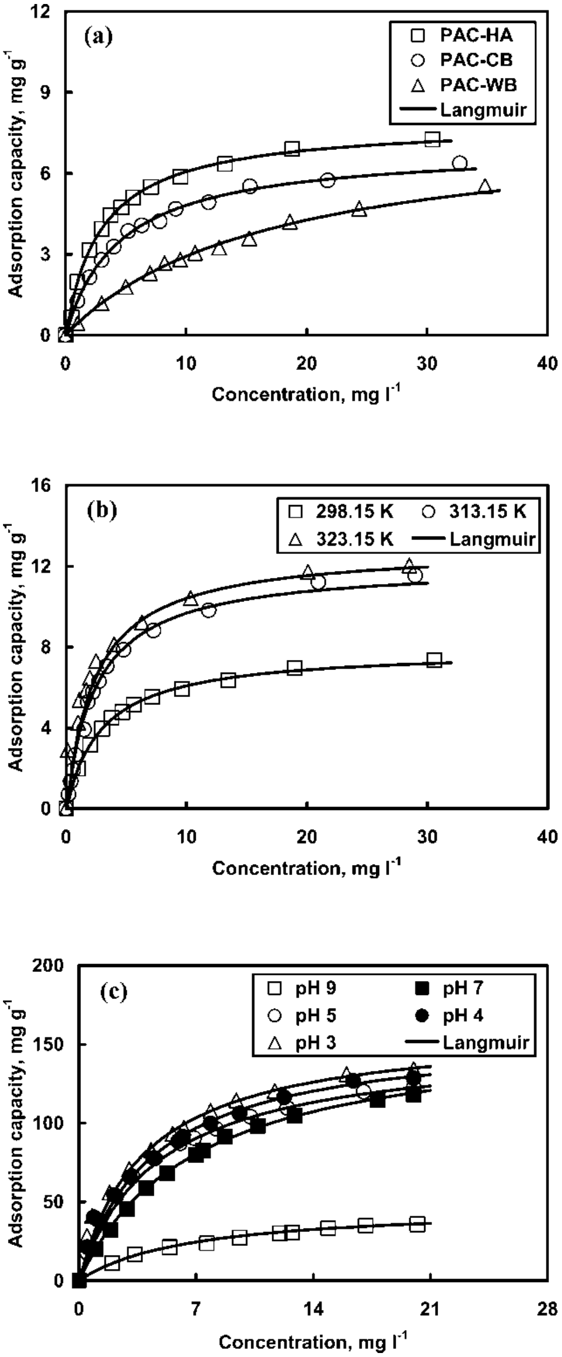


***Figure 1.*** Adsorption isotherm in terms of TNT: (a) PAC types at 298.15 K and pH 9, (b) temperatures at pH 9 on PAC-HA, and (c) pH at 323.15 K on PAC-HA.

***Table 3.*** Langmuir isotherm parameters of TNT on PAC

| Adsorbent | Temperature (K) | pH | Parameters | | |
|---|---|---|---|---|---|
| | | | $q_m$(mg g$^{-1}$) | $b$(l g$^{-1}$) | $R^2$ |
| PAC-WB | 298.15 | 9 | 7.880 | 0.058 | 0.939 |
| PAC-CB | 298.15 | 9 | 6.978 | 0.221 | 0.970 |
| PAC-HA | 298.15 | 9 | 7.874 | 0.333 | 0.994 |
| PAC-HA | 313.15 | 9 | 12.438 | 0.399 | 0.985 |
| PAC-HA | 323.15 | 9 | 12.919 | 0.416 | 0.993 |
| PAC-HA | 323.15 | 3 | 161.290 | 0.255 | 0.995 |
| PAC-HA | 323.15 | 4 | 158.730 | 0.223 | 0.994 |
| PAC-HA | 323.15 | 5 | 151.515 | 0.210 | 0.998 |
| PAC-HA | 323.15 | 7 | 161.290 | 0.141 | 0.991 |
| PAC-HA | 323.15 | 9 | 48.076 | 0.149 | 0.959 |

the heat of adsorption ($\Delta H$) at a constant temperature:

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

$$\ln(q_m b) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{4}$$

where $R = 8.314$ J mol$^{-1}$ K$^{-1}$ is the gas constant and $T$ is the temperature in Kelvin. The enthalpy of adsorption ($\Delta H$) and the entropy change ($\Delta S$) were determined from the slope and intercept of the linear plot, namely $\ln(q_m b)$ vs. $1/T$. The correlation coefficients ($R^2$) of the linear plot is 0.92. The determined values of $\Delta H$, $\Delta G$, and $\Delta S$ at 313.15 K are $23.963 \times 10^3$ J mol$^{-1}$, $-3.841 \times 10^3$ J mol$^{-1}$, and 88.79 J mol$^{-1}$ K$^{-1}$. The positive standard enthalpy change suggests that the interaction of TNT adsorbed by PAC is endothermic which is supported by the increasing adsorption of TNT with the increase in temperature. In addition, the negative value of $\Delta G$ and the positive values of $\Delta S$ indicate that the adsorption of TNT on PAC is a spontaneous process (11, 12). The positive $\Delta S$ may be attributed to the release of water molecules produced by ion exchange reactions between the adsorbate and the functional groups on the surface of PAC.

## Adsorption Energy Distribution

It is well-known that activated carbons have strongly heterogeneous surfaces. Chemical and geometrical heterogeneities show the unique sorption properties of activated carbons. Geometrical heterogeneity comes from the differences in size and shape of pores while chemical heterogeneity is associated with different functional groups and various surface contaminants on a surface. The heterogeneity properties of solid adsorbents can be described by their so-called adsorption energy distribution functions (15). Adsorption energy distributions have been extensively applied for characterizing the numerous adsorption systems and understanding the surface energy heterogeneities. The fundamental adsorption integral equation of the dilute solutions on energetically heterogeneous solid surfaces is given as follows (16–18):

$$\theta_T = \int_{E_{12\min}}^{E_{12\max}} \frac{\Phi\omega \exp(E_{12}/RT)}{1 + \Phi x \exp(E_{12}/RT)} F(E_{12}) dE_{12} \tag{5}$$

where $\theta_T$ is the total fractional coverage, $E_{12} = E_1 - E_2$ is the energy difference of components (i.e., TNT and water), $\Phi = \Phi(c, \theta_T)$ is a model dependent function (i.e., the molecular interactions between bulk and surface phases), $F(E_{12})$ is the normalized energy distribution function, $\omega = c/c_{sol}$, $c_{sol}$ is the solubility of adsorbate, $R$ is the gas constant, and $T$ is the absolute temperature. The adsorption integral equation (i.e., Eq. (5) is the well-known linear Fredholm integral equation of the first kind, and the calculation of adsorption energy distribution is an ill posed problem (16). For the current work, we investigated the generalized nonlinear regularization method based on smoothness constraint (i.e., Tikhonov regularization) and edge preserving regularization methods. The generalized nonlinear regularization method can avoid the difficulties that result from the ill-posed nature of an adsorption integral equation (17). Figure 2 shows the flow chart for the general calculation of adsorption energy distribution. Here, proper selection of local adsorption isotherm equation for the calculation of energy distribution is very important in analyzing the heterogeneous adsorption systems. In general,

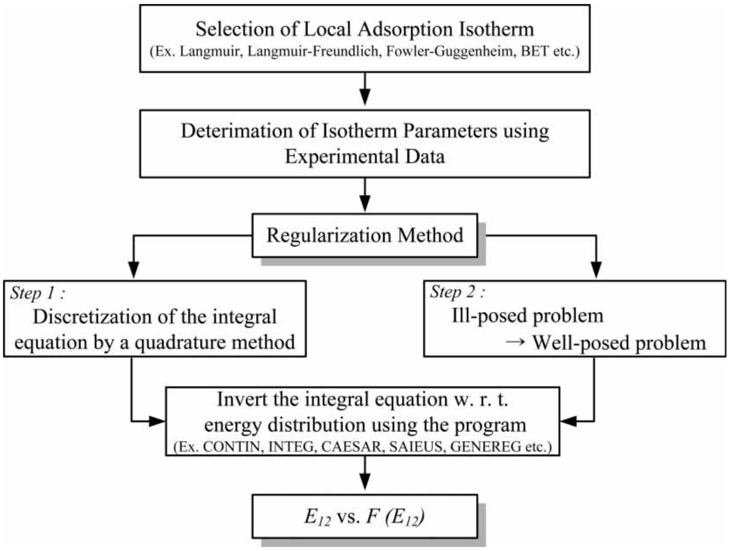


***Figure 2.*** Flow chart for the general calculation of adsorption energy distribution.

the Langmuir isotherm has been extensively used to determine the monolayer amount in aqueous adsorption systems. However, Podkoscielny et al. (18). have reported that the Langmuir-Freundlich isotherm equation is more reasonable for estimating the monolayer capacity of liquid sorption and for correlating experimental adsorption data. The Langmuir-Freundlich isotherm parameters were used in this study to describe the adsorption isotherm data and surface heterogeneity because the Langmuir-Freundlich equation seems to be suitable for approximating most of the adsorption systems having quasi-Gaussian energy distribution.

Figure 3 shows the adsorption energy distribution functions of PACs with employing Lagnmuir-Freundlich isotherm parameters listed in Table 4. The adsorption energy distribution curves exhibited single peaks. The shape and the intensity of the adsorption energy distribution curve were highly related with the microporosity of the adsorbent (i.e., geometrical heterogeneity). The highest adsorption energy peaks for HA, CB, and WB were observed around 9.08, 7.06, and 4.03 kJ mol$^{-1}$, respectively. As expected, the energy distribution peaks proceeded to higher energy with the increase of surface area because of micropore volumes (Table 1). On the other hand, Fig. 4 shows the influence of pH on the adsorption energy distribution functions of PAC-HA. The adsorption energy distribution curves are highly sensitive to the chemical heterogeneity of PAC depending on the solution pH. For the evaluation of chemical heterogeneity, zeta potential measurements of PAC-HA are measured in terms of solution pH ($3 \sim 9$) with PAC-HA dose (5, 10, 20 mg L$^{-1}$). The zeta potential values ranged approximately between

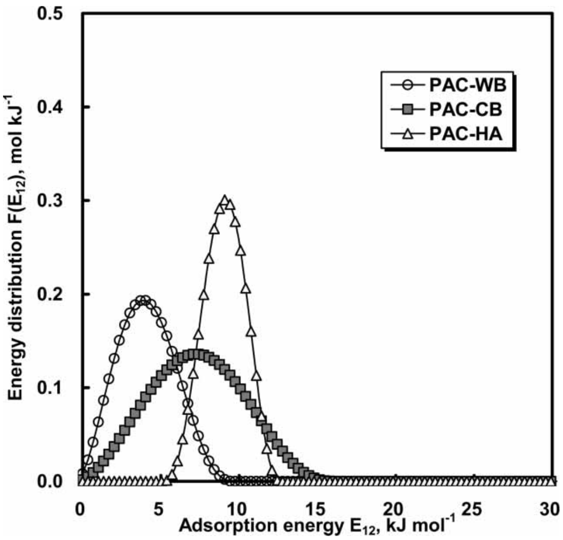


***Figure 3.*** Adsorption energy distributions of TNT for different PACs.

*Table 4.* Langmuir-Freundlich isotherm parameters

| | | | Parameters | | |
|---|---|---|---|---|---|
| Adsorbent | Temperature (K) | pH | $q_m$(mg g$^{-1}$) | $b$(l g$^{-1}$)1/n | $n$ |
| PAC-WB | 298.15 | 9 | 9.916 | 0.037 | 0.894 |
| PAC-CB | 298.15 | 9 | 7.469 | 0.188 | 0.915 |
| PAC-HA | 298.15 | 9 | 7.750 | 0.335 | 1.073 |
| PAC-HA | 323.15 | 3 | 245.128 | 0.081 | 0.620 |
| PAC-HA | 323.15 | 4 | 233.250 | 0.080 | 0.658 |
| PAC-HA | 323.15 | 5 | 162.930 | 0.194 | 0.832 |
| PAC-HA | 323.15 | 7 | 154.841 | 0.154 | 1.062 |
| PAC-HA | 323.15 | 9 | 131.923 | 0.014 | 0.684 |

+30 to −25 mV as shown in Fig. 5. The zeta potential decreased with an increasing PAC dose and pH. Isoelectric point of PAC-HA was present around the pH 7. We found from Figs. 3 and 4 that the adsorption energy distribution functions can be essentially applied in evaluating the heterogeneous sorbent properties (i.e., chemical and geometrical heterogeneities).

## Kinetic Study

Adsorption kinetics is one of the most important properties that determines the potential applications of PACs. The adsorption kinetic experiments were carried

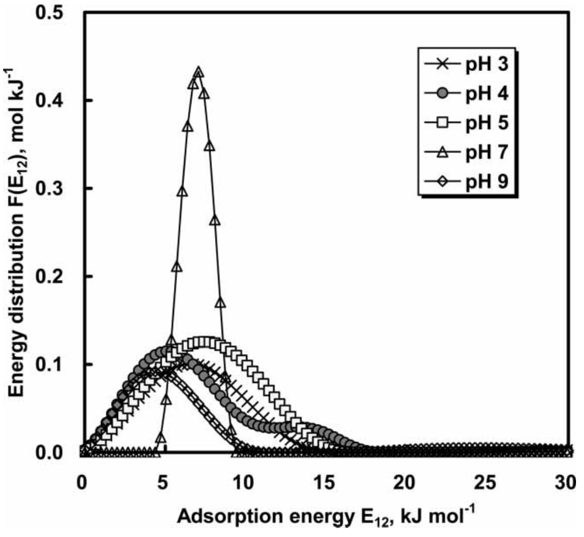


*Figure 4.* Adsorption energy distributions of TNT on PAC-HA in terms of solution pH.

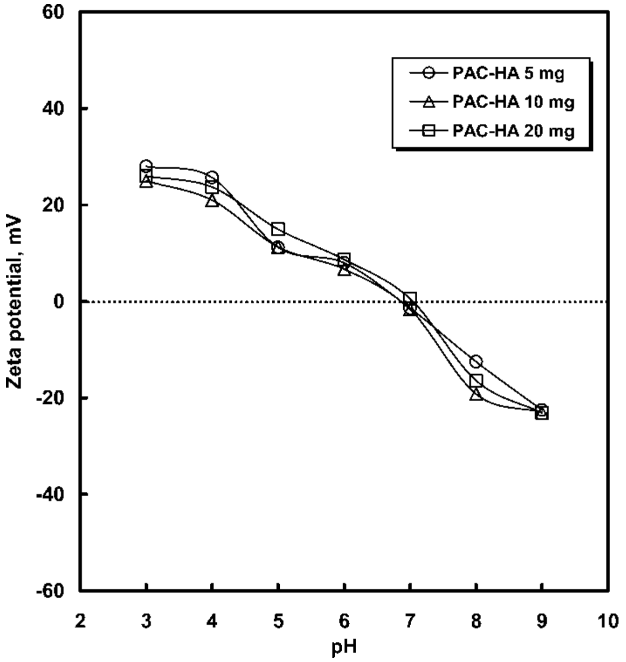


***Figure 5.*** Variation of zeta potential as functions of solution pH and PAC-HA dose.

out at different types of PAC (HA, WB, CB), temperatures (298.15, 313.15, 323.15 K), pH (3, 4, 5, 7, 9), and concentrations (15, 30, 60 mg $l^{-1}$). It was observed that the pseudo-first-order model explains the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Thus, the kinetic data were analyzed with the pseudo-second-order model (11, 12) and intraparticle diffusion models (19, 20).

## Pseudo-Second-Order Model

The adsorption kinetic data was tested using the pseudo-second-order model (11, 12).

$$\frac{dq}{dt} = K_2(q_e - q)^2 \tag{6}$$

Integrating Eq. (8) for the boundary conditions $q = 0$ to $q = q_t$ at $t = 0$ to $t = t$, gives

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}, \tag{7}$$

$$h = k_2 q_e^2, \tag{8}$$

where $k_2$ (g mg$^{-1}$ min$^{-1}$) is the second-order rate constant determined by the plot of $t/q_t$ vs. $t$. Figures 6a and 6b show the typical examples of the effect of initial pH (run 5, 6, 7, 8, 9) and initial concentrations (run 7, 10, 11). Note that the correlation coefficients ($R^2$) of the pseudo-second-order model for the linear plots of PAC-HA are very close to 1. This result implies that adsorption kinetics can be successfully described by the pseudo-second-order model. The rate constant, $k_2$ determined in this study was in the range of $0.028 \sim 5.041$ g mg$^{-1}$ min$^{-1}$ (Table 5).

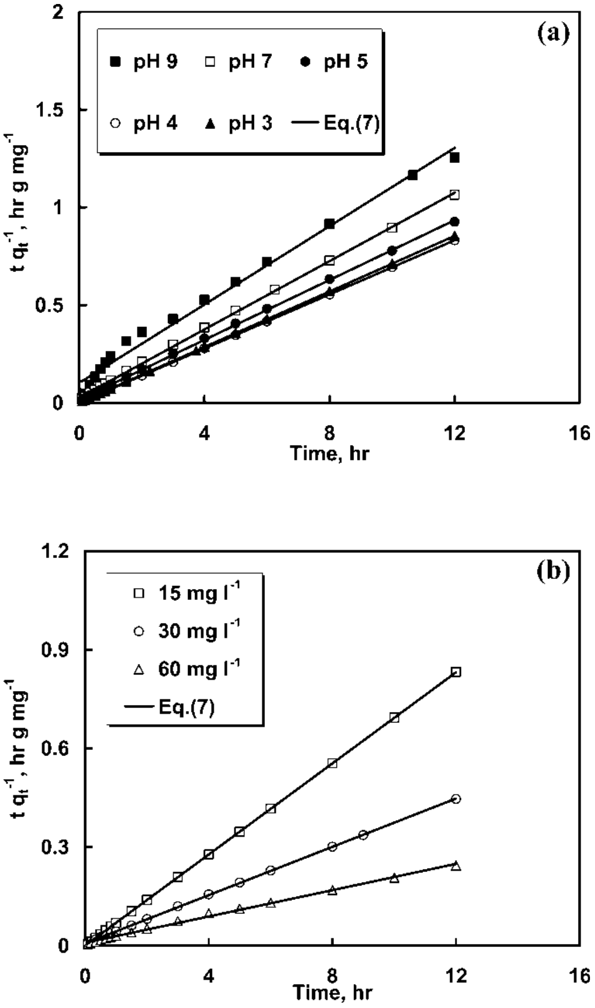


***Figure 6.*** The pseudo-first-order kinetics for TNT adsorption on PAC-HA at: (a) initial pH (run 5, 6, 7, 8, 9) and (b) initial concentrations (run 7, 10, 11).

***Table 5.*** The pseudo-second-order kinetic parameters of TNT adsorption on PACs (w $V^{-1} = 1$ g $l^{-1}$, 300 rpm)

| | | | | | Pseudo-second-order-kinetics | | | |
|---|---|---|---|---|---|---|---|---|
| Run | Adsorbent | Concentration (mg $l^{-1}$) | Temperature (K) | pH | $k_2$ (g $mg^{-1}$ $hr^{-1}$) | $h$ (mg $g^{-1}$ $h^{-1}$) | $R^2$ | $q_e$ (cal) (mg $g^{-1}$) |
| 1 | PAC-HA | 15 | 298.15 | 9 | 0.028 | 3.759 | 0.909 | 11.520 |
| 2 | PAC-WB | 15 | 298.15 | 9 | 0.095 | 4.464 | 0.965 | 6.8335 |
| 3 | PAC-CB | 15 | 298.15 | 9 | 0.042 | 2.783 | 0.898 | 8.051 |
| 4 | PAC-HA | 15 | 313.15 | 9 | 0.039 | 5.376 | 0.918 | 11.737 |
| 5 | PAC-HA | 15 | 323.15 | 9 | 0.083 | 10.752 | 0.998 | 11.363 |
| 6 | PAC-HA | 15 | 323.15 | 3 | 5.041 | 1000 | 1.000 | 14.084 |
| 7 | PAC-HA | 15 | 323.15 | 4 | 0.149 | 2500 | 1.000 | 14.450 |
| 8 | PAC-HA | 15 | 323.15 | 5 | 0.376 | 64.102 | 0.999 | 13.054 |
| 9 | PAC-HA | 15 | 323.15 | 7 | 0.297 | 39.910 | 0.999 | 11.441 |
| 10 | PAC-HA | 30 | 323.15 | 4 | 0.201 | 149.254 | 0.999 | 27.248 |
| 11 | PAC-HA | 60 | 323.15 | 4 | 0.045 | 114.943 | 0.996 | 50.000 |

## Intraparticle Diffusion Models

The determination of the rate-limiting step is an important step in the adsorption process. For a liquid-phase adsorption, the mass transfer is generally governed by boundary layer diffusion (film diffusion) and intraparticle diffusion. The most commonly used technique for identifying the mechanism involved in the adsorption process is an intraparticle diffusion plot. The relationship between the adsorption capacity ($q_t$) at time $t$, versus $t^{0.5}$ can be written as (19)

$$q_t = D_1 t^{0.5} + \delta \tag{9}$$

where $D_1$ is the intraparticle diffusion constant and $\delta$ is the intercept of the line which is proportional to the boundary layer thickness. The calculated values of $D_1$ and $\delta$ are summarized in Table 6.

The adsorption kinetic data were further analyzed by the intraparticle diffusion model (11, 12) (20). Assuming the adsorbent particle to be a sphere of radius and also assuming that the diffusion follows Fick's law, the resultant equation is:

$$F(t) = \frac{C_0 - C_t}{C_0 - C_e} = \frac{q_t}{q_e} = \left[1 - \exp\left(-\frac{\pi^2 D_2 t}{r^2}\right)\right] \tag{10}$$

or

$$\ln[1 - F(t)^2] = \frac{\pi^2 D_2}{r^2} t \tag{11}$$

where $F(t)$ is the fractional uptake at time $t$, $C_0$ is the initial TNT concentration (mg $l^{-1}$), $C_e$ is the TNT equilibrium concentration (mg $l^{-1}$), $D_2$ is the effective diffusion coefficient (m$^2$ s$^{-1}$), and $r$ is the particle radius (m). From the linear plot of ln[1-$F(t)$] vs. $t$, the effective diffusion coefficient was obtained under various conditions such as PAC types, pH, temperature, and concentration. The effective diffusion coefficients determined are in the range from 0.035 to $3.999 \times 10^{-11}$ m$^2$ s$^{-1}$ (Table 6). On the other hand, Figure 7 shows the linear plot of ln[1-$F(t)$] vs. $t$ for different initial concentration (15, 30, 60 mg $l^{-1}$). At the lower concentration of 15 mg $l^{-1}$, the plot does not pass the origin (i.e., the film diffusion is the rate-controlling step). However, it was observed that the concentration of 30 and 60 mg $l^{-1}$ increases, the linear plot moves toward the origin indicating that the particle diffusion is a rate-controlling step (11). TNT adsorption on PAC was found to be controlled by the film diffusion at lower concentrations and shifted to particle diffusion at higher concentrations.

***Table 6.*** Intraparticle diffusion parameters of TNT adsorption on PACs (w $V^{-1} = 1$ g $l^{-1}$, 300 rpm)

| | | | | | Intraparticle diffusion models | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Eq. (9) | | Eq. (11) | |
| Run | Adsorbent | Concentration (mg $l^{-1}$) | Temperature (K) | pH | $D_1$ (mg g$^{-}$1 hr$^{-1}$) | $\delta$ | $D_2 \times 10^{-11}$ (m$^2$ s$^{-1}$) | R$^2$ |
| 1 | PAC-HA | 15 | 298.15 | 9 | 1.686 | 2.297 | 0.373 | 0.933 |
| 2 | PAC-WB | 15 | 298.15 | 9 | 0.711 | 2.299 | 0.083 | 0.849 |
| 3 | PAC-CB | 15 | 298.15 | 9 | 1.127 | 1.869 | 0.035 | 0.884 |
| 4 | PAC-HA | 15 | 313.15 | 9 | 1.873 | 2.326 | 0.525 | 0.989 |
| 5 | PAC-HA | 15 | 323.15 | 9 | 1.195 | 3.659 | 0.528 | 0.943 |
| 6 | PAC-HA | 15 | 323.15 | 3 | 0.258 | 13.340 | 0.969 | 0.588 |
| 7 | PAC-HA | 15 | 323.15 | 4 | 0.149 | 14.057 | 3.999 | 0.935 |
| 8 | PAC-HA | 15 | 323.15 | 5 | 1.705 | 8.187 | 1.089 | 0.929 |
| 9 | PAC-HA | 15 | 323.15 | 7 | 1.796 | 6.169 | 1.124 | 0.963 |
| 10 | PAC-HA | 30 | 323.15 | 4 | 3.784 | 16.811 | 1.368 | 0.932 |
| 11 | PAC-HA | 60 | 323.15 | 4 | 3.706 | 16.898 | 1.011 | 0.981 |

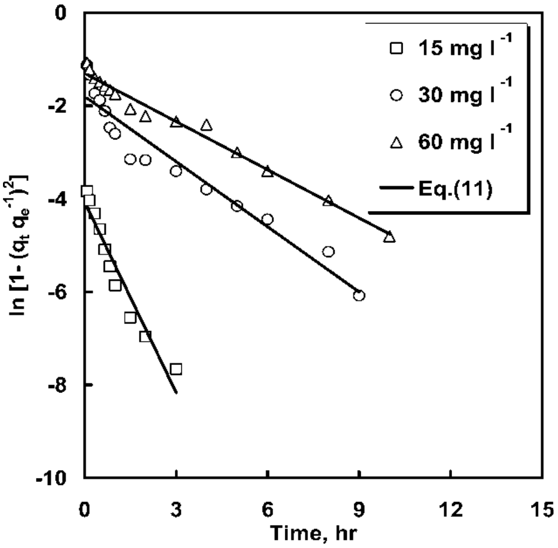


*Figure 7.* Intraparticle diffusion plot for TNT adsorption on PAC-HA at initial concentrations (run 7, 10, 11).

## CONCLUSIONS

Adsorption equilibrium and kinetic studies revealed that the removal of trinitrotoluene (TNT) from wastewater using powdered activated carbon can be successfully achieved. TNT adsorption was found to be temperature-dependent and also pH-dependent, and maximum removal was achieved when PAC-HA was used. The positive value of the standard enthalpy change suggests that the interaction of TNT adsorbed by PAC is endothermic. The negative adsorption standard free energy changes and positive standard entropy changes indicate that the adsorption is a spontaneous process. In addition, the results of the shape and intensity of adsorption energy distribution calculated by the generalized nonlinear regularization method indicated that the adsorption of TNT on PAC showed heterogenous adsorption properties. The adsorption kinetic data are well described by the pseudo-second-order model. Our thermodynamic and kinetic studies revealed that PACs exhibit application potentials that are promising as an adsorbent for the treatment of TNT dissolved in wastewater.

## NOMENCLATURE

| | |
|---|---|
| $b$ | Langmuir-Freundlich isotherm parameter (l mg$^{-1}$) |
| $c_{sol}$ | solubility of adsorbate (mg l$^{-1}$) |

| | |
|---|---|
| $C_0$ | initial concentration of TNT in solution (mg $l^{-1}$) |
| $C_e$ | equilibrium concentration of TNT in solution (mg $l^{-1}$) |
| $D_1$ | intraparticle diffusion constant ($m^2\ s^{-1}$) |
| $D_2$ | effective diffusion coefficient ($m^2\ s^{-1}$) |
| $E_{12}$ | energy difference of components (kJ $mol^{-1}$) |
| $F(t)$ | fractional uptake at time $t$ ($-$) |
| $k_2$ | second-order rate constant (g $mg^{-1}$ $min^{-1}$) |
| $n$ | Langmuir-Freundlich isotherm parameter (l $mg^{-1}$) |
| $q$ | equilibrium capacity (mg $g^{-1}$) |
| $q_m$ | Langmuir-Freundlich isotherm parameter (mg $g^{-1}$) |
| $r$ | particle radius (m) |
| $R$ | gas constant ($=8.314$ J $mol^{-1}$ $K^{-1}$) |
| $R^2$ | correlation coefficients ($-$) |
| $t$ | time (hr) |
| $T$ | temperature (K) |
| $V$ | solution volume ($l^{-1}$) |
| $w$ | weight of the adsorbent (g) |

### Greek Letters

| | |
|---|---|
| $\delta$ | intercept of the line ($-$) |
| $\Delta G$ | change of Gibbs free energy (J $mol^{-1}$) |
| $\Delta H$ | heat of adsorption (J $mol^{-1}$) |
| $\Delta S$ | entropy change (J $mol^{-1}$ $K^{-1}$) |
| $\theta_T$ | total fractional coverage ($-$) |

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