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TWO-STAGE KINETIC MODEL FOR THE NON-ISOTHERMAL DECOMPOSITION OF PHENOL ADSORBED ON ACTIVATED CARBON

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ABSTRACT

Samples of activated carbon loaded with different amounts of phenol from aqueous solutions were regenerated in an atmosphere of argon at a constant rate of increase in temperature of 7.6 K min^{-1}. Heating to 385°C caused a 49% loss in phenol, after which the rate of decomposition decreased markedly. A residue of 32.6% of the phenol originally adsorbed, remained on the carbon at temperatures higher than 800°C. The amount of residue left by the decomposition reactions showed a linear dependence on the initial amount of phenol loaded. A two-stage first order thermal cracking model was applied successfully to the decomposition of phenol loaded on activated carbon.

INTRODUCTION

Adsorption on activated carbon has been used widely for removal of organic pollutants from effluents owing to its excellent affinity to hydrophobic matter. For the process to be economically feasible the loaded carbon has to be regenerated and reused. The cost of thermally regenerating carbon constitutes such a large percentage of the treatment costs that research on this aspect is necessary before it can be fully accepted [1,2].

Recently, activated carbon has also been used in the carbon-in-pulp process for the adsorption of gold and silver cyanides from cyanide leached slurries [3,4]. Some organic impurities loaded during the adsorption cycle are not removed by the elution and acid washing, and should be eliminated by thermal reactivation in order to restore the adsorptive capacity of the activated carbon.

Suzuki et al. [5] suggested that organics such as phenol, β-naphthol and lignin which leave high residuals on activated carbons after heating up to

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800°C are critical to ordinary thermal regeneration. The objective of this paper is to explain the application of a two-stage kinetic model to the non-isothermal decomposition of phenol loaded on activated coconut carbon.

KINETIC MODEL

Suzuki et al. [5] derived a first order thermal cracking model for a single reaction to predict the decomposition of various organics loaded on activated carbon. Matsui et al. [6] used the same model and thermogravimetric analysis (TGA) to study steam gasification rates of various activated carbons. The principles of this model were extended to a two-step process by Chihara et al. [7] and applied to the decomposition of sucrose loaded on powdered activated carbon. Sucrose was removed easily and only 9% remained as residue after heating to 500°C. Hashimoto et al. (8) analysed the kinetics of thermal regeneration of activated carbon loaded with *p*-nitrophenol and a surface active agent on the basis that decomposition consisted of multiple first order reactions, each of which had a different activation energy and frequency factor.

It is proposed here that phenol, A, first decomposes irreversibly into a nonvolatile, adsorbed fragment, B, and a volatile fragment, C, which is subsequently desorbed into the gas stream. The number and structure of the desorbed products are not known exactly. Wang and Smith [9] identified water, carbon dioxide and very small amounts of phenol and diphenyl ether as some of the desorption products in the temperature range between 393 and 673 K. Additional heating to 1073 K resulted in the desorption of cracked products which could not be identified [9]. The first decomposition step is written as

$$\mathrm{A(ads)} \xrightarrow{k_\mathrm{A}} b\mathrm{B(ads)} + c\mathrm{C(ads)} \tag{1}$$

$$\mathrm{C(ads)} \xrightarrow{k_C} \mathrm{C(g)} \tag{2}$$

If the desorption process (2) is rapid with respect to the decomposition reaction (1), i.e., $k_\mathrm{C} \gg k_\mathrm{A}$, the total amount, q, adsorbed at any time is

$$q = q_\mathrm{A} + q_\mathrm{B} \tag{3}$$

The intermediate product B starts to decompose at a higher temperature into an adsorbed char residue R and easily desorbed cracked products C′. This second step is represented by

$$b\mathrm{B(ads)} \xrightarrow{k_\mathrm{B}} r\mathrm{R(ads)} + c'\mathrm{C'(ads)} \tag{4}$$

$$\mathrm{C'(ads)} \xrightarrow{k_{C'}} \mathrm{C'(g)} \tag{5}$$

where $k_{C'} \gg k_B$. Consecutive reactions (1) and (4) occur independently, which means that reaction (1) is complete when reaction (4) starts. Therefore, when reaction (4) is in progress

$$q = q_B + q_R \tag{6}$$

Furthermore, it is assumed here that the decomposition of phenol loaded on activated carbon is independent of the simultaneous decomposition of the base activated carbon. As a first approximation it is assumed that the decomposition reactions are first order such that

$$-\frac{d(q - q_B^0)}{dt} = k_A(q - q_B^0) \tag{7}$$

with initial conditions

$$q_A = q_A^0;\ q_B = 0;\ q_R = 0 \text{ at } t = 0 \tag{8}$$

and

$$-\frac{d(q - q_R^\infty)}{dt} = k_B(q - q_R^\infty) \tag{9}$$

with initial conditions

$$q_A = 0;\ q_B = q_B^0;\ q_R = 0 \text{ at } t = t_B \tag{10}$$

The yield of intermediate product B at $t = t_B$ is given as

$$\alpha_B = q_B^0/q_A^0 \tag{11}$$

The final yield of residue R is given as

$$\alpha_R = q_R^\infty/q_A^0 \tag{12}$$

It is supposed that k_A and k_B follow the Arrhenius equation

$$k_A = k_A^0 \exp(-E_A/R_0T) \tag{13}$$

$$k_B = k_B^0 \exp(-E_B/R_0T) \tag{14}$$

By setting the linear rise in temperature $\beta = \frac{dT}{dt}$ the following equations are obtained

$$\frac{q - q_B^0}{q_A^0 - q_B^0} = \exp\left\{-\frac{k_A^0}{\beta}\int_0^T \exp(-E_A/R_0T)\, dT\right\} \tag{15}$$

and

$$\frac{q - q_R^\infty}{q_B^0 - q_R^\infty} = \exp\left\{-\frac{k_B^0}{\beta}\int_0^T \exp(-E_B/R_0T)\, dT\right\} \tag{16}$$

The integral at the right hand side of eqns. (15) and (16) cannot be integrated analytically. Lee and Beck [10] and Li [11] developed approximation formulae for this integral by assuming moderate temperatures and high activation energies. These assumptions do not hold for the conditions used here. An approximate graphical solution presented by Suzuki et al. [5] will be used here for the evaluation of these integrals. These authors have defined and evaluated a function $\psi(x)$

$$\psi(x) = 1 - x\exp(x)\cdot\int_x^{\infty}\frac{\exp(-x)}{x}\mathrm{d}x \tag{17}$$

Camby [12] used this function to simplify the integrals on the right hand side of eqns. (15) and (16), which may be rewritten as

$$\frac{q - q_{\mathrm{B}}^0}{q_{\mathrm{A}}^0 - q_{\mathrm{B}}^0} = \exp\left\{-\frac{k_{\mathrm{A}}^0}{\beta}T\exp\left(-\frac{E_{\mathrm{A}}}{R_0T}\right)\psi\left(\frac{E_{\mathrm{A}}}{R_0T}\right)\right\} = \phi_{\mathrm{A}}(T) \tag{18}$$

and

$$\frac{q - q_{\mathrm{R}}^{\infty}}{q_{\mathrm{B}}^0 - q_{\mathrm{R}}^{\infty}} = \exp\left\{-\frac{k_{\mathrm{B}}^0}{\beta}T\exp\left(-\frac{E_{\mathrm{B}}}{R_0T}\right)\psi\left(\frac{E_{\mathrm{B}}}{R_0T}\right)\right\} = \phi_{\mathrm{B}}(T) \tag{19}$$

The loading on the carbon may be expressed in dimensionless form by substitution of expressions (11) and (12) into eqns. (18) and (19)

$$\frac{q}{q_{\mathrm{A}}^0} = \alpha_{\mathrm{B}} + (1 - \alpha_{\mathrm{B}})\cdot\phi_{\mathrm{A}}(T) \text{ when } t < t_{\mathrm{B}} \tag{20}$$

$$\frac{q}{q_{\mathrm{A}}^0} = \alpha_{\mathrm{R}} + (\alpha_{\mathrm{B}} - \alpha_{\mathrm{R}})\cdot\phi_{\mathrm{B}}(T) \text{ when } t \geq t_{\mathrm{B}} \tag{21}$$

The ratios α_{B} and α_{R} may be estimated from the positions of change in shape in the TGA curve. An approximate graphical method similar to that suggested by Suzuki et al. [5] will be used here for the estimation of kinetic

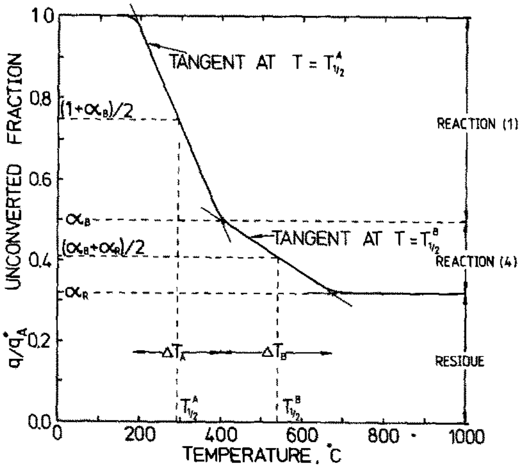

Fig. 1. Graphical estimation of kinetic parameters for a two-stage decomposition reaction.

parameters k_A^0, k_B^0, E_A and E_B. Figure 1 explains the meaning of quantities ΔT_A, ΔT_B, $T_{1/2}^A$ and $T_{1/2}^B$ and how they should be determined graphically from a TGA curve revealing a change in shape. Camby [12] showed that

$$\psi\left(\frac{E_A}{R_0 T_{1/2}^A}\right) = \frac{\Delta T_A \ln 2}{2\, T_{1/2}^A} \tag{22}$$

The activation energy E_A can be determined by making use of the graphical representation of $\psi(x)$ given by Suzuki et al. [5]. The pre-exponential factor k_A^0 is given by Camby [12] as

$$k_A^0 = \frac{2\beta}{\Delta T_A} \cdot \exp\left(\frac{E_A}{R_0 T_{1/2}^A}\right) \tag{23}$$

Similar equations can be written for the determination of E_B and k_B^0.

Having estimated these parameters from experimental data, eqns. (20) and (21) can then be used to predict TGA curves for different operating conditions.

EXPERIMENTAL

The activated carbon used in this study, Le Carbone G210 AS, was made from coconut shells and obtained from Gencor Group Laboratories, Springs. All particles used had an apparent density of 900 kg m^{-3} and were in the sieve size fraction 1.4–1.7 mm. White phenol was obtained from Analyticals Carlo Erba and had a purity of 99.5%. Phenol was a most suitable adsorbate as it does not decompose at drying temperatures under 125°C. Deionized glass-distilled water was used to dissolve the phenol.

A sample of carbon, previously dried to a constant mass for 24 h at 110°C, was weighed accurately before being added to a solution of phenol. These mixtures of carbon and solution were sealed in closed containers and rolled for three days. The sample of carbon was then removed, dried for 24 h at 110°C and weighed. The increase in mass was taken as the loading of phenol.

A Stanton Redcroft Massflow thermobalance was used to heat samples of activated carbon of 1.3 g (virgin carbon) loaded with phenol. The loss of mass was recorded continuously during a heating rate of 7.6 K min^{-1} in an inert atmosphere of argon. To ensure that the argon was pure, it was passed through a de-oxidizing unit, concentrated sulphuric acid, ascarite and calcium chloride. At the argon flow rate of 6 cm^3 s^{-1} used, it was found that variations in the flow rate had no significant effect on the pattern of mass loss. When a sample of high grade graphite powder was heated to 1100°C no loss of mass could be detected, showing that the atmosphere in the furnace was indeed inert.

RESULTS AND DISCUSSION

Decomposition of phenol was considered to occur only after 120°C, when evaporation of moisture had been completed. All calculations are based on the initial amount of virgin activated carbon. Decomposition of the base carbon took place simultaneously with the decomposition of phenol. Figure 2 shows experimental TGA curves for the virgin carbon on its own, and for phenol and carbon where different amounts of phenol were loaded initially. The slopes of all these curves appear to be the same after about 800°C, which suggests that loss of mass at these high temperatures was the result of decomposition of virgin carbon only.

It was assumed that the decomposition reactions of phenol and intermediate products formed, and of the base carbon itself were independent. Thus, the decomposition curves for phenol only were obtained by subtracting curve VI from curves I to V in Fig. 2. The resultant TGA curves could then be rendered dimensionless by dividing by the q_A^0 values for curves I to V. Such a dimensionless curve is shown in Fig. 3 for an initial q_A^0 value of 212 mg g^{-1} carbon.

Figure 3 shows that heating to 385°C caused a 49% loss of adsorbed material, after which the rate of decomposition decreased significantly. This

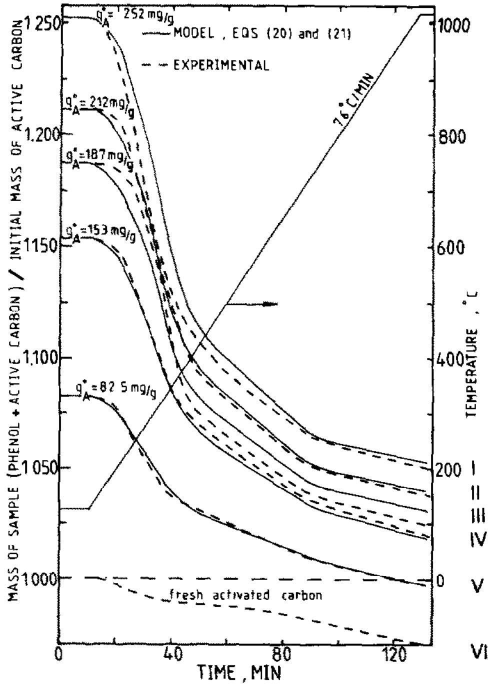

Fig. 2. TGA curves of activated carbon loaded with different amounts of phenol.

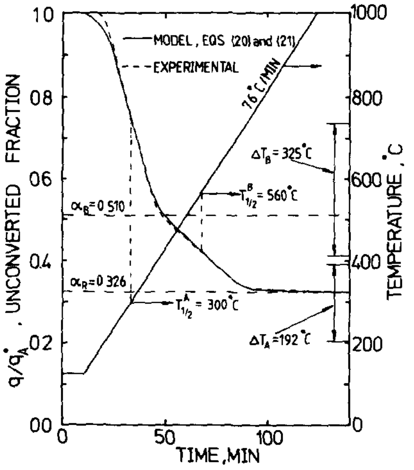

Fig. 3. Dimensionless decomposition curve for phenol loaded on activated carbon at $q_A^0 = 212$ mg g^{-1}.

corresponds to a t_B value of 45 min. A residue of 32.6% of the phenol originally adsorbed, remained on the carbon at temperatures higher than 800°C. The values of parameters α_B and α_R are then taken as 0.510 and 0.326, respectively. Other measurements obtained graphically from Fig. 3 are: $\Delta T_A = 192$ K; $T_{1/2}^A = 573$ K; $\Delta T_B = 325$ K and $T_{1/2}^B = 833$ K.

These values were substituted in eqns. (22) and (23) to yield the following kinetic parameters: $k_A^0 = 77.4$ min^{-1}; $E_A = 32.8$ kJ mol^{-1}; $k_B^0 = 10.2$ min^{-1} and $E_B = 37.3$ kJ mol^{-1}.

Equations (20) and (21) were then used to predict TGA curves for different initial loadings of phenol. Figure 3 shows that the fitted curve differs slightly from the experimental one during the first few minutes of the first stage. The parameters estimated from curve II in Fig. 2 were also used to predict curves I, III, IV and V in Fig. 2. Reasonably accurate predictions of the measured curves were obtained. This indicates that the decomposition reactions were independent of the initial amount of phenol loaded, and that the assumptions of the proposed model are acceptable.

The loss of mass of the virgin activated carbon alone (curve VI in Fig. 2) may be ascribed to the decomposition of the active groups on the surface in the pores of the carbon. Tsuchida et al. [13] suggested that the active sites on activated carbon are carboxylic, phenolic, quinone, chromene type and peroxide groups, all of which contain oxygen. Decomposition took place at all temperatures between 150 and 1025°C in the inert atmosphere of purified argon.

Figure 4 reveals a linear relationship between the initial amount of phenol loaded and the amount of residual material left by the decomposition reactions after heating to 1025°C. This linearity provides further evidence

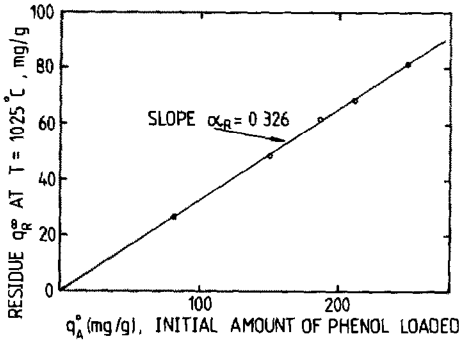

Fig. 4. Residual material adsorbed on carbon after heating to 1025°C as a function of the initial amount of phenol loaded.

that the decomposition of phenol was independent of the initial amount loaded. The 32.6% of residual material left in the pores of the carbon could be removed only by steam regeneration if the activity of the carbon was to be regained. Wang and Smith [9] measured a residue of 47% of the initial mass of phenol adsorbed on a bituminous coal-based carbon. Suzuki et al. [5] observed such a linear relationship for a number of organics, each producing a different slope.

CONCLUSIONS

(1) The two-stage kinetic model proposed here was found to hold for the decomposition of phenol loaded on activated carbon.
(2) The kinetic parameters estimated were found to be independent of the initial amount of phenol loaded.
(3) A residue of 32.6% of the phenol initially adsorbed, remained in the pores of the carbon at temperatures higher than 800°C.
(4) The amount of residue was linearly dependent on the initial amounts of phenol loaded.
(5) Decomposition of the virgin activated carbon took place at all temperatures between 150°C and 1025°C in an inert atmosphere.

ACKNOWLEDGEMENT

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LIST OF SYMBOLS

A	adsorbed phenol.
b	stoichiometric coefficient for intermediate product.
B	intermediate product adsorbed on the carbon.
c, c'	stoichiometric coefficients for volatile fragments.
C, C′	volatile fragments.
E_A	activation energy of decomposition of phenol.
E_B	activation energy of decomposition of intermediate product.
k_A	first order rate constant for loss of mass during the decomposition of phenol.
k_B	first order rate constant for loss of mass during the decomposition of the intermediate product.
k_C, $k_{C'}$	desorption rate constants for volatile fragments.
k_A^0, k_B^0	pre-exponential factors of Arrhenius equations for k_A and k_B, respectively.
q	total mass of adsorbed material per unit mass of initial virgin carbon.
q_A	mass of adsorbed phenol per unit mass of initial virgin carbon.
q_A^0	initial mass of adsorbed phenol per unit mass of initial virgin carbon.
q_B	mass of adsorbed intermediate per unit mass of initial virgin carbon.
q_B^0	initial mass of adsorbed intermediate per unit mass of initial virgin carbon at time t_B.
q_R	mass of adsorbed residue per unit mass of inital virgin carbon.
q_R^∞	maximum loading of adsorbed residue per unit mass of initial virgin carbon.
r	stoichiometric coefficient for adsorbed char residue.
R	adsorbed char residue.
R_0	universal gas constant.
t	time.
t_B	time at which reaction (1) is complete.
T	absolute temperature.
$T_{1/2}^A$, $T_{1/2}^B$	values of T at $\phi_A(T) = 0.5$ and $\phi_B(T) = 0.5$, respectively.
ΔT_A, ΔT_B	equal to $-dT/d\phi_A(T)$ and $-dT/d\phi_B(T)$ at $T_{1/2}^A$ and $T_{1/2}^B$, respectively.

Greek letters

α_B	defined in eqn. (11).
α_R	defined in eqn. (12).
β	constant heating rate.
ϕ_A, ϕ_B	functions defined in eqns. (18) and (19), respectively.
$\psi(x)$	function defined in eqn. (17).

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