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Analytical model for chemisorption of cyanogen chloride on impregnated carbon

Tek Sutikno*

Apt. 13101, 5555 New territory Blvd., Sugar Land, TX 77479, USA

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Abstract

An analytical model has been derived for chemisorption of cyanogen chloride in ASC carbon. This model, derived from the mass balance differential equation, uses simplified rate expressions for both the external diffusion and the reaction each with a decay function. Agreements between the calculated and experimental breakthroughs of cyanogen chloride are reasonably good. However, the selected values for transfer coefficients and rate constants require additional data for further verifications of the rate controlling steps assumed in the model. © 1999 Elsevier Science S.A. All rights reserved.

1. Introduction

A mathematical model has been derived from the mass balance equation with simplified rate expressions for the time-dependent chemisorption process of cyanogen chloride in ASC carbon filter. This model can be solved analytically and gives pretty good agreements with the experimental data.

Metal-impregnated carbons have been used for removing small amounts of toxic agents (contaminants) in air and used in canisters for breathing protection against these agents. Cyanogen chloride (CK) is a toxic agent commonly used for performance evaluation of metal impregnated carbon. The ASC formulation for metal impregnation of carbon offers significant protection against toxic agents with high vapor pressures such as CK and became the standard for metal impregnation of military carbon filter [1].

Removal of (CK) from air by ASC carbon has been reported to involve chemisorption – combined adsorption and chemical reaction. While investigations and characterization of this phenomena have been reported in numerous references, they involved a wide variety of solute–sorbent systems. Chemisorption characteristics may vary from one system to another, and sometimes from one set of experimental conditions to another [6]. For example, the rate controlling step for the transfer of a solute to the carbon surface may depend on the system variables such as fluid velocity and other physiochemical characteristics such as intra-pore mass transfer coefficients, reaction rate constant, and others such as the equilibrium adsorption isotherm. Mathematical modeling normally assumes some forms of algebraic expression to represent the rate controlling step out of the complex transport mechanism in chemisorption. A model providing satisfactory representation of a particular solute–sorbent system may fit poorly to the experimental data from another type of chemisorption system, even after all coefficients and constants have been optimized to best fit the experimental data. One primary reason is that the assumed algebraic expressions in the model do not adequately represent the chemisorption behaviors of the different system.

Friday [1] reported a mathematical model for chemisorption of CK on ASC carbon. This model includes expressions for external and internal (pore) diffusions in addition to second order reaction terms and Langmuir equilibrium adsorption isotherm. This model required numerical solution and was compared with the experimental data. This paper presents the use of simplified, lumped expressions coupled with a decay function in the mass balance equations for describing the chemisorption (both the adsorption and reaction) of CK on ASC carbon. The simplification enables an analytical solution to these equations and gives reasonable agreement with the experimental CK breakthrough data.

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*Tel.: +1-281-277-8698

E-mail address: teksutikno@aol.com (T. Sutikno)

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2. Mathematical equation

The mass balance equation below describes gas chemisorption in a cylindrical, fixed bed of activated carbon.

$$\frac{\delta C}{\delta t}+\nu\frac{\delta C}{\delta x}-D\frac{\delta^2 C}{\delta x^2}=R-\frac{(1-\varepsilon)}{\varepsilon}\frac{\delta S}{\delta t} \qquad (1)$$

where C is the CK concentration in the gas phase (g/ml); t the time (s); x the axial distance; υ the gas velocity (m/s); D is the diffusivity (cm^2/s); R the rate of CK reaction (g/ml/s); ε void fraction (dimensionless) and S is the g of sorbate/ml of solid carbon

The reaction term R for CK is expressed as first order kinetics below

$$R=-k_r C \qquad (2)$$

Eq. (2) assumes that reaction of CK on the metal surface is fast, and CK concentration in gas phase is the limiting concentration while k_r is the effective rate constant. This is one of the simplifications made to solve Eq. (1) analytically.

The third term (axial dispersion) on the left of Eq. (1) is assumed negligible as the gas flow velocity in this chemisorption case is assumed sufficiently high. Soares et al. [7] evaluated the effects of axial dispersion for CK-ASC system, and empirical correlations were used to estimate the bed Peclet number. Although one of the estimated Peclet numbers suggests that dispersion is significant, they concluded that the estimated Peclet number varies depending on which correlation is used and the presence of axial dispersion does not appear to alter the general behavior of the system. Nevertheless, the dispersion term is assumed negligible in this model to obtain an analytical solution.

The CK concentration in the gas phase is small, and its change due to chemisorption does not affect the density of the gas phase. With these assumptions and by introducing dimensionless variables, Eq. (1) can be rewritten to dimensionless Eq. (5).

$$z=\frac{x}{dp} \qquad (3)$$

$$t'=\frac{Q_m}{\varepsilon\rho_a A\,dp}t \qquad (4)$$

$$\frac{\delta y}{\delta t'}+\frac{\delta y}{\delta z}=-a\,k_r\,y-m\frac{\delta S'}{\delta t'} \qquad (5)$$

where a is equal to ($\varepsilon\rho_a A\ dp/Q_m$), s; A is the cross-sectional area, cm^2; dp is the average carbon granule size, cm; m equals (ρ_b MWa/ε ρ_a MWe), dimensionless; MWa and MWe are the molecular weights of air and CK, respectively; while ρ_a and ρ_b are the air density (g/cm^3) and density of bulk carbon in bed, respectively. Q_m is the mass flowrate of air, g/s; S' g of adsorbed CK/g of carbon; y the mole fraction of CK in gas phase and k_r is the reaction rate constant of CK, 1/s.

For physical gas adsorption, the pseudo first-order kinetics has been shown to agree with the beginning region of the breakthrough curve exiting from a packed sorbent bed [2]. If first order kinetics is used, $\delta S'/\delta t'$ can be expressed as

$$\frac{\delta S'}{\delta t'}=a\,k_a y \qquad (6)$$

where k_a (s^{-1}) is the effective adsorption rate constant of CK on the carbon, Eq. (5) becomes

$$\frac{\delta y}{\delta t'}+\frac{\delta y}{\delta z}=-a\,k_r\,y-ma\,k_a y \qquad (7)$$

As chemisorption proceeds in the carbon bed, the vacant sites available for adsorption and the active metal surface for reaction are gradually diminishing. If N_0 represents the initial active sites (both adsorptive and catalytic) of the carbon and N the active sites after the chemisorption has started, N can be expressed in term of N_0 in the following forms to describe the decay function of the active sites.

$$k_a=k'_a N=\frac{k'_a N_0}{(1+KS')}=\frac{k_a^o}{(1+KS')} \qquad (8)$$

$$k_r=k'_r N=\frac{k'_r N_0}{(1+KS')}=\frac{k_r^o}{(1+KS')} \qquad (9)$$

where k_a^o and k_r^o are the initial reaction and adsorption rate constants, respectively, when the carbon is new and unused. K is the decay coefficients. This implies that both the rates of chemical reaction on the active site of metal impregnants and physical adsorption rate on the carbon surface reduce as cyanogen chloride content of the carbon bed increases. In reality, the chemical species remaining on the active metal site are some of the products from the catalytic reaction of CK, and these species are different from the reactant CK which is $CNCl_2$. Although S' does not differentiate between these species and CK, the adsorption and reaction processes occur in parallel. As solid diffusion of sorbed CK from the adsorptive site to the active metal site is not considered, the increase in S' is assumed to correspond to the increase in the decay of the metal site. The expression 1/(1 + KS') is used to represent the metal decay reducing the reaction rate to the same extent as this expression reduces the adsorption rate.

By defining is $y'=y/y^o$ where y^o the mole fraction of CK at the inlet to the carbon bed, Eqs. (6) and (7) become

$$\frac{\delta y'}{\delta t'}+\frac{\delta y'}{\delta z}=\frac{-a\,k_r^o y'-ma\,k_a^o y'}{(1+KS')} \qquad (10)$$

$$\frac{\delta S'}{\delta t'}=\frac{a\,k_a^o y^o y'}{(1+KS')} \qquad (11)$$

Eqs. (10) and (11) are a pair of coupled, hyperbolic partial differential equations. Solution to these equations can be derived more easily by using as independent variables, z and η, rather than z and t', where

$$\eta=t'-z \qquad (12)$$

In mathematical terms η is the variable along a characteristic of Eq. (7) and equals to 0 when $t'=z$. For practical purpose, $\eta = t'$ when $t' > z$ except for very short time. With η, Eqs. (10) and (11) may be written as:

$$\frac{\delta y'}{\delta z} = \frac{-a\,k_{\mathrm{r}}^{\mathrm{o}} y' - ma\,k_{\mathrm{a}}^{\mathrm{o}} y'}{(1+KS')} = \frac{-\psi_1 y'}{(1+KS')} \tag{13}$$

$$\frac{\delta S'}{\delta \eta} = \frac{a k_{\mathrm{a}}^{\mathrm{o}} y^{\mathrm{o}} y'}{(1+KS')} = \frac{\psi_2 y'}{(1+KS')} \tag{14}$$

where ψ_1 and ψ_2 are constants and equal to $ak_{\mathrm{r}}^{\mathrm{o}} + mak_{\mathrm{a}}^{\mathrm{o}}$. and $ak_{\mathrm{a}}^{\mathrm{o}}y^{\mathrm{o}}$, respectively. At the inlet to the carbon bed, y' equals to 1.0, or y equals to y^{o}.

Initially, the cyanogen chloride content in the carbon bed is 0. These lead to the following conditions for solving Eqs. (13) and (14).

$$y'(0, \eta) = 1.0 \tag{15}$$

$$S'(z, 0) = 0.0 \tag{16}$$

The set of Eqs. (13)–(16) can be solved analytically to give the solution below [3].

$$y' = \exp\left[-\psi_1 z + (1 + 2K\psi_2\,\eta)^{0.5} - 1 - KS'\right] \tag{17}$$

$$KS' \exp(KS') = \left[(1 + 2K\psi_2\,\eta)^{0.5} - 1\right] \times \exp\left[-\psi_1 z + (1 + 2K\psi_2\,\eta)^{0.5} - 1\right] \tag{18}$$

3. Experimental data

Cyanogen chloride breakthrough data reported by Friday [1] were used to evaluate the model. Activated carbon (12 × 30 Mesh) bed with the ASC impregnant formulation was used in the reported experiments for generating the breakthrough data. The breakthrough time was defined as the time when the cyanogen chloride concentration in the effluent reaches 0.008 mg/l.

The carbon bed (2.0 cm ID) was initially in equilibrium with clean air at 80% relative humidity. The feed to the bed was contaminated ambient air at 80% relative humidity and 294–298 K with cyanogen chloride concentration of 4.0 mg/l.

Table 1 summarizes the breakthrough times at four air velocities at various bed depth. As shown in the table, the experimental breakthrough data have significant variation spans indicating a duplicate run may not give the same breakthrough point. As an example, four runs at a carbon bed depth of 1.0 cm with 5.9 cm/s air velocity results in breakthrough times from 1.7 to 3.5 min. Because of these variations, the averages of the breakthrough data from sets of identical runs are arbitrarily used to verify the chemisorption model Eqs. (13) and (14).

Table 1
Experimental breakthrough data

Air velocity (cm/s)	Carbon bed depth (cm)	Mean breakthrough time (min)	Number of breakthrough data and spans (min)
5.9	1.0	2.6	4: 1.7–3.5 min
	1.39	7.95	4: 6.5–9.4
	1.74	23.15	4: 20.3–26
	2.2	46.8	4: 43.5–50
9.6	2	9.1	2: 8.8–9.4
	2.5	19.68	4: 16.7–22.65
	3.0	31.15	4: 27.3–35
	3.26	42.65	4: 39.4–45.9
14.7	2.25	3.37	2: 2.94–3.8
	3.27	9.38	4: 7.05–11.7
	4.08	25.25	4: 24.0–26.5
	5.0	53.55	4: 50–57.1
24.8	2.78	1.79	2: 1.78–1.8
	4.2	5.59	4: 4.12–7.05
	5.57	12.94	4: 10.88–15.0
	7.0	30.37	4: 28.23–32.5

4. Results and discussions

Figs. 1–4 plot the calculated breakthrough times versus the experimental data at four air velocities −5.9, 9.6, 14.7, and 24.8 cm/s. A bulk density (r_{b}) of 0.6 g/ml [1] was used in the calculations. As shown, the agreements are reasonably well. The values for constants and mass transfer coefficients are arbitrarily selected after several trials. Much better prediction accuracy may still be achieved with Eqs. (17) and (18) by using the best fitting values of the coefficients or constants. This may require additional experimental data with better repeatability.

The values of K and $k_{\mathrm{r}}^{\mathrm{o}}$ used in Figs. 1 to 4 are 85 and 0.5/s, respectively. These values are assumed constant for all runs in these figures. The reaction rate constant, $k_{\mathrm{r}}^{\mathrm{o}}$ is typically a function of temperature. All breakthrough data in the figures were generated at the same ambient temperature, and $k_{\mathrm{r}}^{\mathrm{o}}$ should be the same for all runs in the figures. The decay coefficient K is also held constant, as all runs were also conducted at the same total pressure and the same inlet cyanogen chloride concentration of 4.0 mg/l.

The value for the initial adsorption rate coefficient, $k_{\mathrm{a}}^{\mathrm{o}}$ varies with the gas velocity. As shown in the figures, the values are 0.20, 0.218, 0.241 and 0.25/s for the respective four velocities – 5.9, 9.6, 14.7, and 24.8 cm/s. While these agree with the typical adsorption behavior which gives higher external diffusion rates at higher velocities, the values selected for K, $k_{\mathrm{r}}^{\mathrm{o}}$, and $k_{\mathrm{a}}^{\mathrm{o}}$ in Eqs. (13) and (14) do not quite agree with those evaluated from previous studies [1]. This is mainly due to the present model which uses simplified mathematical representations for the adsorption and reactions of cyanogen chloride on ASC carbon. These representations differ from those used in the previous study which required numerical solutions. The present simplifications are necessary to solve the mass balance equations analytically and discussed as follows.

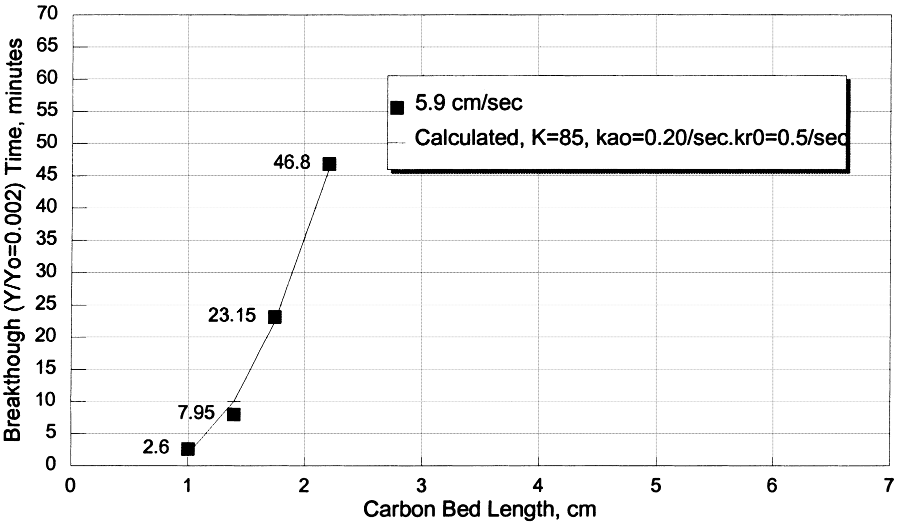

Fig. 1. Calculated versus experimental breakthroughs at 5.9 cm/s.

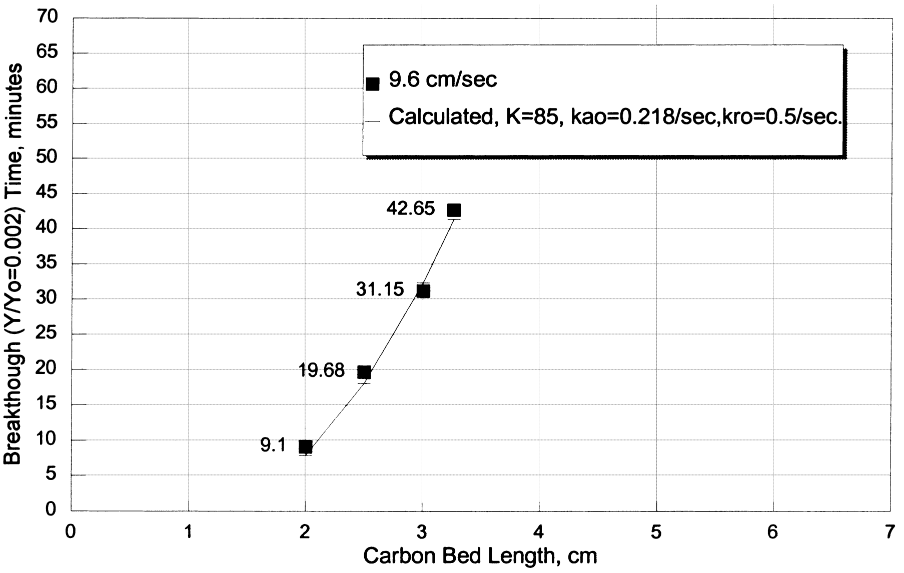

Fig. 2. Calculated versus experimental breakthroughs at 9.6 cm/s.

4.1. External and internal diffusions

While several algebraic expressions have been reported for diffusional steps of gases in the carbon bed, the external and pore diffusion steps are typically expressed as Eqs. (19) and (20), respectively.

$$\frac{\delta S'}{\delta t'} = -a\,k_{\mathrm{a}}(y - y^*) \tag{19}$$

$$\frac{\delta S'}{\delta t'} = -a\,k_{\mathrm{p}}(S'^* - S') \tag{20}$$

where y^* is the gas phase concentration at adsorbent surface, S'^* the solid phase concentration in equilibrium with y^*, and k_{p} pore diffusion coefficient. Both S'^* and y^* can be related by the adsorption isotherm, most gases with carbon show Langmuir type isotherm. The external diffusion is normally the rate determining step for gas adsorption breakthroughs at high velocities. Moreover, the external diffusion will tend to predominate at low extents of breakthrough and internal diffusion will have more of a retarding effect as full saturation is approached. For carbon filters used for military protection against toxic agents, the breakthrough is defined at low effluent concentration, and the present model considers only the external diffusion and assumes y^* is negligible relative to y. However, a decay function is added to account for the decreasing rate of chemisorption as the carbon becomes saturated or fouled with the sorbate.

For gas–solid adsorption without chemical reactions, the literature [2,4,5] indicates that the external diffusion coefficient in Eq. (19) is proportional to the square root of the gas velocity, or $k_{\mathrm{a}} \cong v^{0.5}$. The values of $k_{\mathrm{a}}^{\mathrm{o}}$ (Eq. (6)) used in Figs. 1–4 indicates that external diffusion coefficient in chemi-

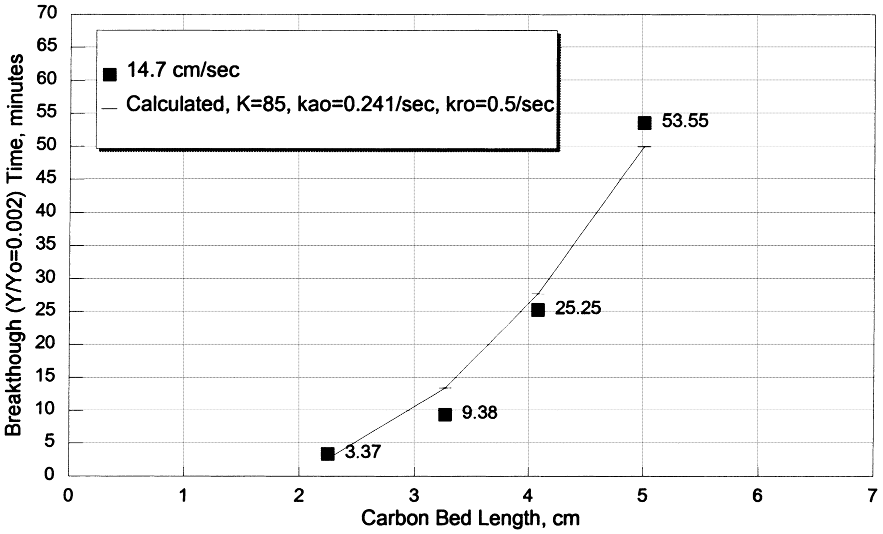

Fig. 3. Calculated versus experimental breakthroughs at 14.7 cm/s.

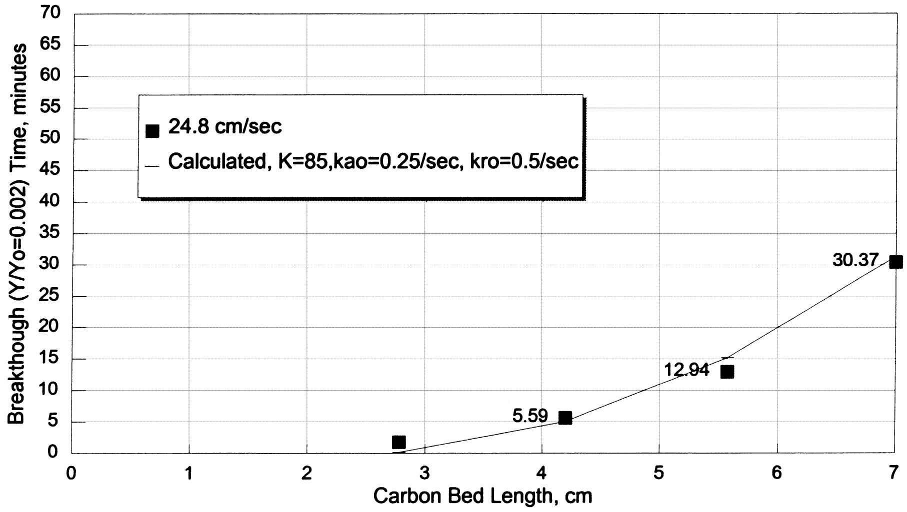

Fig. 4. Calculated versus experimental breakthroughs at 24.8 cm/s.

sorption of CK vary with $v^{0.16}$. This discrepancy indicates that external resistance is not the only resistance to be considered. Another possible reason may be the effect of chemical reaction of CK in addition to physical adsorption. More importantly, the model includes only a lumped first-order reaction type expression for the diffusion and does not use the conventional linear driving force model (Eqs. (18) and (19)) for the external and intrapore diffusions. Thus, the model is not sufficiently explicit to be used for identifying the rate controlling step in the diffusional processes. Further investigations may be needed to confirm the rate controlling step.

4.2. Chemical reaction

For chemisorption of CK, Eqs. (19) and (20) should have a reaction term. This is represented as $R = -k_r C$ in the present model, which also assumes that some of the chemical reaction products remain on the active metal site and cause the decay of this site. This decay is empirically expressed in term of $1/(1 + KS')$. This expression keeps the model simple enough to be solved analytically. As both the adsorption and catalytic reaction processes take place simultaneously, the amount of reaction products remaining on the active metal site can be expected to increase as the amount of CK adsorbed on the adsorptive site increases.

5. Conclusions

Analytical model for chemisorption of CK on carbon has been derived from the mass balance equation with modified expressions for both adsorption and chemical reaction steps. The modification neglects the equilibrium gas phase concentration of solute at the carbon surface but adds decay functions to the diffusion transfer coefficient and the chemical rate constant. The analytical solution agrees reasonably well with experimental breakthrough data. These data are limited to breakthroughs at trace effluent concentrations. The analytical model should be evaluated further with additional breakthrough data from experiments designed to verify the rate controlling step and the associated algebraic expression used in the current model.

6. Nomenclature

a	($\varepsilon\ \rho_a\ dp/Q_m$); seconds
A	cross sectional area, cm^2
C	CK concentration in the gas phase, g/ml
dp	average carbon granule size, cm
D	diffusivity, cm^2/s
k_a	effective adsorption rate constant/coefficient of CK, 1/s
k'_a	apparent (before the effect of available active sites on the carbon) adsorption rate constant/coefficient of CK as defined in Eq. (8), 1/s
k^o_a	initial adsorption rate constant/coefficient of CK in new, unused carbon, 1/s
k_p	pore diffusion coefficient, 1/s
k_r	effective reaction rate constant of CK, 1/s
k'_r	apparent (before the effect of available active sites on the carbon) reaction rate constant of CK as defined in Eq. (9), 1/s
k^o_r	initial adsorption rate constant of CK in new, unused carbon, 1/s
K	decay coefficient, dimensionless
m	(ρ_b MWa/$\varepsilon\ \rho_a$ MWe), dimensionless
Mwa	molecular weight of air
Mwe	molecular weight of CK
N_0	available active sites of new, unused carbon for sorption of CK, unity (=1)
N	available active sites after chemisorption has started, fraction/dimensionless
Q_m	mass flow rate of air, g/s
R	rate of CK reaction, g/ml/s
S	g of sorbate (adsorbed CK)/ml of solid carbon
S'	g of adsorbed CK/g of carbon
S'^{*}	solid phase concentration in equilibrium with y^{*}, dimensionless
t	time, seconds
t'	dimensionless time defined in Eq. (4)
x	axial distance, meter
y	mole fraction of CK in gas phase, dimensionless
y°	gas phase mole fraction of CK at the inlet to the carbon bed, dimensionless
y'	y/y°, dimensionless
y^{*}	the gas phase mole fraction of CK at adsorbent surface, dimensionless
z	dimensionless distance defined in Eq. (3)

6.1. Greek letters

υ	gas velocity, m/s
ε	void fraction, dimensionless
η	$t'-z$, dimensionless
ρ_a	air density, g/cm^3
ρ_b	density of bulk carbon in bed, g/cm^3
ψ_1	$a\,k^o_r + ma\,k^o_a$
ψ_2	$a\,k^o_a + y^o$

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