Lumped Kinetic Model for Catalytic Wet Oxidation of Organic Compounds in Industrial Wastewater

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A simplified reaction pathway was proposed to describe the kinetic behavior of catalytic wet oxidation of organic mixture. The oxidation reactions were divided and lumped into two groups: (1) the deep or complete oxidation reactions with formation of CO_2 and H_2O; (2) the partial oxidation reactions with formation of all intermediates in aqueous solution of the industrial wastewater. The concentrations of all reactants in wastewater and those of the intermediates formed during the reaction are also represented by a lumped concentration of total organic carbon (TOC). To test the model, catalytic oxidation of organic pollutants in an effluent from a softwood Kraft pulp mill was investigated in a slurry reactor using a Pd-Pt/Al_2O_3 catalyst. Sodium hydroxide was used to adjust the initial pH of wastewater to 7.3 to avoid the problem of metal leaching and excessive corrosion. The lumped kinetic model developed in this study describes well both our experimental data and those reported in literature. The lumped kinetic model proposed in this study can be used for both catalytic and noncatalytic wet oxidation processes.

Introduction

Wet air oxidation (WAO) has been shown to be useful in treatment of industrial wastewaters (Mishra et al., 1995; Matatov-Meytal and Sheintuch, 1998). Noncatalytic WAO of the effluent streams from pulp mills have been reported (Teletzke and Pradt, 1969; Zimmermann and Diddams, 1960; Yin et al., 1986; Foussard et al., 1989). However, studies on the catalytic wet oxidation of these effluents are meager. The industrial wastewaters often contain many organic compounds in great diversity, for example, effluents from pulp mills contain sulfur compounds, pulping chemicals, organic acids, chlorinated lignins, resin acids, phenolics, unsaturated fatty acids, and terpenes. It is often impossible to monitor the concentration changes of individual organic compounds during oxidation. Hence, the approach of lumping the components has been used to describe the oxidation of multicomponent mixtures in wastewater. Takamatsu et al. (1970) lumped the sludge to four components: (i) solid; (ii) soluble nonevaporative compounds at 298 K; (iii) soluble evaporative compounds at 298 K; (iv) water. Ploos van Amstel and Rietema (1973) divided the sludge as: (a) easily oxidizable; (b) difficult oxidizable; (c) not oxidizable. Foussard et al. (1989) divided the sludge into two groups: (a) easily oxidizable; (b) difficult oxidizable. Li et al. (1991) divided the organics in the effluent of WAO into three groups: (a) organics except acetic acid; (b) acetic acid; (c) oxidation end products (CO_2 and H_2O). The generalized kinetic model developed by Li et al. (1991) shows a slight improvement over Foussard's model in terms of agreement with experimental data obtained for the WAO of biological sludge. However, the point selectivity, as defined by Li et al. (1991), often fails to describe the resistance of the organic pollutants to oxidation in liquid phase (Mishra et al., 1995). Furthermore, the model requires the specific rate constant of acetic acid (assumed as the only intermediate in WAO) to be determined independently. For noncatalytic oxidation, some published rate constants were suggested (Li et al., 1991). However, the generalized kinetic model cannot be used to describe the catalytic wet oxidation process since the activity of the catalyst for acetic acid oxidation is often unknown. To apply the generalized kinetic model to the catalytic oxidation process, additional experimental work on the catalytic wet oxidation of acetic acid solution over the same catalyst has to be carried out. Direct regression of the generalized kinetic model using the experimental data has not been proven successful. Lin et al. (1996) reported that the specific rate constant of acetic acid oxidation

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determined from the generalized model does not follow the Arrhenius equation. Similar problems have been encountered by regression of the generalized kinetic model using experimental data for the catalytic oxidation of the basic bleach plant effluent (Zhang and Chuang, 1998a). Thus, the purpose of this study is to develop a kinetic model to describe the catalytic wet oxidation process for industrial wastewater treatments. Another objective of this study is to evaluate the influences of operating conditions on the catalytic oxidation of acidic bleaching effluent under initial neutral conditions.

Lumped Kinetic Model

The mechanism of wet oxidation of organic compounds is very complex. Even with a pure compound such as phenol, the exact mechanism or reaction pathway has not been established. In many cases, the oxidation goes through a very complicated pathway and leads to the formation of many different intermediates, such as lower carboxylic acids. In the case of industrial wastewater such as the effluent from pulp mills, many compounds are present in the waste stream. The oxidation of such a mixture is much more complex than that of oxidation of a single compound solution. The reactivity of each component is different, and so are the intermediates formed from these compounds during the oxidation process. To model such a complicated process, the rate equation may be based on the lumped reactions and the lumped concentrations of all organic pollutants in industrial wastewater streams, that is, TOC or COD in wastewater streams.

The overall oxidation of the organic compounds in the wastewater stream can be represented by the following reaction equation

$$\mathrm{A} + \gamma_i \mathrm{O}_2 \longrightarrow \mathrm{B} + \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \tag{1}$$

where the organic compounds in wastewater are lumped as a single compound A, and the stream's concentration is represented as total organic carbon (TOC). Similarly, the intermediates formed during the oxidation process are lumped as compound B, and its concentration is expressed in TOC. The following two parallel reaction schemes are thus proposed to describe the catalytic wet oxidation process

For Complete or Deep Oxidation

$$\mathrm{A} + \gamma_1 \mathrm{O}_2 \xrightarrow{k_1} \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \tag{2}$$

For Partial Oxidation

$$\mathrm{A} + \gamma_2 \mathrm{O}_2 \xrightarrow{k_2} \mathrm{B} + \mathrm{H}_2\mathrm{O} \tag{3}$$

Considerable investigations on wet oxidation of different types of single organic compounds have revealed the multistep first-order kinetic behavior in respect to various organic compounds (Mishra et al., 1995). Previous studies on wet air oxidation of the bleach plant effluents also indicated first-order kinetic behaviors in respect to TOC concentration during initial reaction and final steps (Prasad and Joshi, 1987; Zhang and Chuang, 1998a). Hence, the first-order kinetic behavior was assumed for both complete oxidation and partial oxidation reactions in respect to the lumped compound A. The rate equation for the oxidation of lumped organic pollutants in liquid phase in a semi-batch slurry reactor can be expressed by Eq. 4 or 5.

$$-r_A = -\frac{dN_A}{V dt} = k_1'[\mathrm{A}][\mathrm{O}_2]^a + k_2'[\mathrm{A}][\mathrm{O}_2]^b \tag{4}$$

that is,

$$-r_A = -\frac{d[\mathrm{A}]}{dt} = k_1'[\mathrm{A}][\mathrm{O}_2]^a + k_2'[\mathrm{A}][\mathrm{O}_2]^b \tag{5}$$

Similarly, for the lumped intermediate compound B, we obtained

$$r_B = \frac{dN_B}{Vdt} = k_2'[\mathrm{A}][\mathrm{O}_2]^b \tag{6}$$

$$\frac{d[\mathrm{B}]}{dt} = k_2'[\mathrm{A}][\mathrm{O}_2]^b \tag{7}$$

Equations 5 and 7 can be rewritten as Eqs. 8 and 9

$$-\frac{d[\mathrm{A}]}{dt} = (k_1 + k_2)[\mathrm{A}] \tag{8}$$

$$\frac{d[\mathrm{B}]}{dt} = k_2[\mathrm{A}] \tag{9}$$

where

$$k_1 = k_1'[\mathrm{O}_2]^a \tag{10}$$

$$k_2 = k_2'[\mathrm{O}_2]^b \tag{11}$$

When excess oxygen is used, [O] changes little during the oxidation process. Therefore, the oxygen terms in Eqs. 10 and 11 may be assumed to be constant.

At time $t = 0$, $[\mathrm{A}] = [\mathrm{A}]_0 = [\mathrm{TOC}]_0$, $[\mathrm{B}] = 0$. At time $t = t$, $[\mathrm{A}] = [\mathrm{A}]$, $[\mathrm{B}] = [\mathrm{B}]$ and $[\mathrm{A}] + [\mathrm{B}] = [\mathrm{TOC}]$. If we integrate Eqs. 8 and 9 from $t[0, t]$, we obtain

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]}\right) = (k_1 + k_2)t \tag{12}$$

$$[\mathrm{B}] = \frac{[\mathrm{A}]_0 k_2}{k_1 + k_2}\{1 - \exp[-(k_1 + k_2)t]\} \tag{13}$$

Combining Eqs. 12, 13 and $[\mathrm{A}] + [\mathrm{B}] = [\mathrm{TOC}]$, $[\mathrm{A}]_0 = [\mathrm{TOC}]_0$, we obtain

$$\frac{[\mathrm{TOC}]}{[\mathrm{TOC}]_0} = \left\{\frac{k_2}{k_1 + k_2} + \frac{k_1}{k_1 + k_2}\exp[-(k_1 + k_2)t]\right\} \tag{14}$$

where $[\mathrm{TOC}]_0$ and [TOC] represent the initial and the time-dependent TOC concentration (mol/m^3), respectively.

The kinetic parameters in the lumped kinetic model can be estimated by fitting experimental data to the model using the

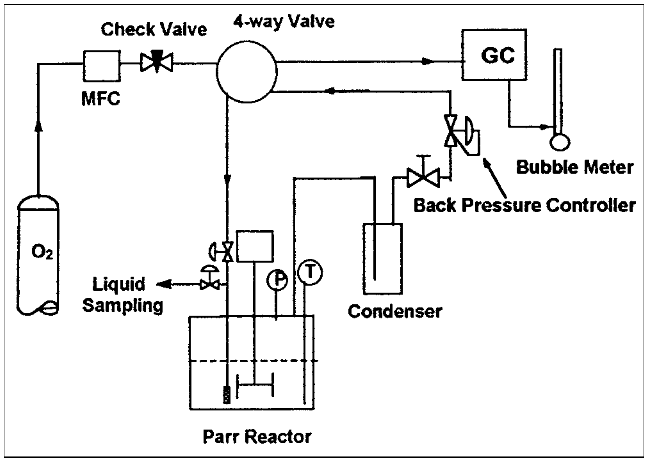

Figure 1. Experimental apparatus.

nonlinear Marquardt method (Marquardt, 1963). Statistical analysis of the data and evaluation of the model were carried out using a commercially available statistics software SigmaStat (Jandel Scientific Software, 1995).

Catalytic Wet Oxidation of Pollutants in Pulp Mill Effluent

Alumina supported Pd-Pt catalyst (Pd: 7.05 wt. %, Pt: 0.82 wt. %) was used for oxidation. Details for catalyst preparation were given elsewhere (Zhang and Chuang, 1998b). The original wastewater sample (TOC: ~ 700 mg/L, pH 2.2) was supplied by Weyerhaeuser Canada Ltd. A desirable amount of sodium hydroxide (Fisher) was added to adjust pH of the original wastewater sample to about 7.3 to avoid excess corrosion.

Experimental procedures

The experimental setup is shown in Figure 1. The reaction vessel is a high-pressure Parr reactor (Model 4653, Parr Instrument Inc.). It is made of SS-316 stainless steel with a Pyrex glass liner. The reactor, equipped with a glass impeller, has an effective volume of 300 mL. A thermal sensor and an external heating element are also provided in the reactor for temperature control to an accuracy of ± 1 K. The operating pressure of the oxidation reaction was controlled by a back-pressure controller in the exit line.

In the experiments, typically 1 g of catalyst powder (<120 mesh) was charged into the reactor. This was followed by the charge of a 140 mL wastewater sample (pH 7.3). The reactor was pressurized using helium to the designated pressure level before heating in order to keep the wastewater in liquid phase. Then, the reactor was heated to the designated temperature. The reactions during the pressurization and heating period can be neglected. As soon as the set temperature was achieved, helium flow was stopped and oxygen was fed continuously to the reactor at a flow rate of 80 mL/min (NTP).

Liquid samples were taken periodically during the reaction and analyzed using a Shimadzu 5050 TOC Analyzer. A gas sample was analyzed using an on-line GC (HP 5890 Series II) equipped with a 3-m-long column (1/8 in. OD) packed with Porapak T and a thermal conductivity detector (TCD). The pH of wastewater samples was determined using a Mettler DL 21 pH meter. Leaching of Pt, Pd, and Al in the reaction mixture was measured using the ICP-MS method. Detailed sampling and analytical procedures were given elsewhere (Zhang and Chuang, 1998b).

Experimental Results

To test if the oxidation was limited by the dissolved oxygen concentration, experiments were performed at various oxygen pressures, flow rates, and stirring speeds. These experiments showed that the reaction was not limited for oxygen at a pressure above 1.2 MPa and a stirring speed above 600 rpm. No improvement in TOC removal was observed by increasing the oxygen flow above 80 mL/min. Hence, kinetic data was measured at pressure of 1.5 MPa and stirring speed of 800 rpm. On-line GC analysis of the effluent gas indicated that carbon dioxide is the only gas-phase product.

Figure 2 shows the TOC removal vs. time profiles for different catalyst charges at 443 K and 1.5 MPa. The final pH values of the solution after 3 h reaction increased from 7.3 to about 8, depending on the mass of catalyst charged into the reactor. It is evident that total organic carbon removal increases with the mass of catalyst charged into the reactor. Hence, further tests on the influence of pH on the rate of catalytic oxidation were carried out at a catalyst charge of 1.0 g. After a 3 h run with a 1 g catalyst, no leaching of Pd or Pt was detected by ICP-MS analysis to the detection limits of Pd <0.05 mg/L and Pt <0.005 mg/L, respectively. The lumped kinetic model described the data well (Figure 2).

The pH values of the solution increased to about 8 after 3 h oxidation in the temperature range of 393–443 K (Figure 3). TOC removal increased with temperature (Figure 3). The lumped kinetic model describes the experimental data well. The specific rate coefficients derived from the lumped kinetic model can be presented well using an Arrhenius equation (Figure 4). The apparent activation energies are determined to be 18.28 kJ/mol and 2.62 kJ/mol for the lumped deep and partial oxidation reactions, respectively.

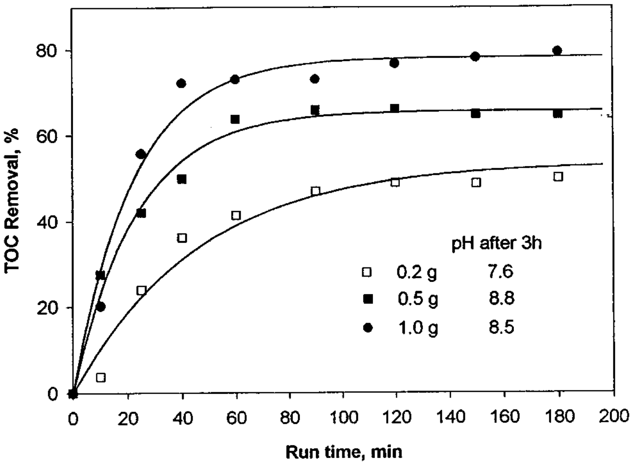

Figure 2. Influence of mass of catalyst charged into reactor on TOC removal at 443 K and 1.5 MPa.

■, □, ●: Experimental data; ——: lumped kinetic model.

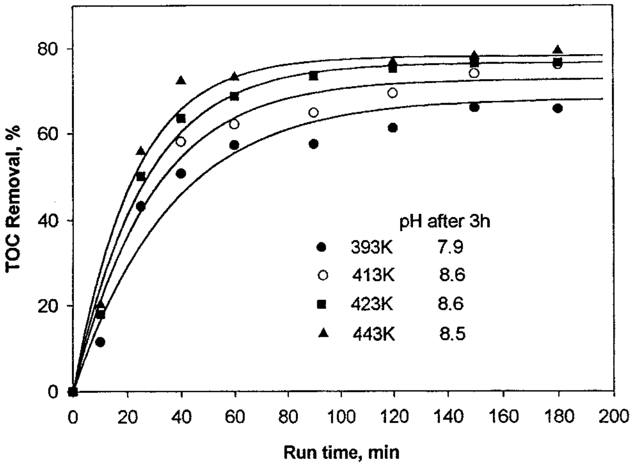

Figure 3. Influence of temperature on TOC removal with catalyst charge of 1.0 g.

●, ○, ■, ▲: Experimental data; ——: lumped kinetic model.

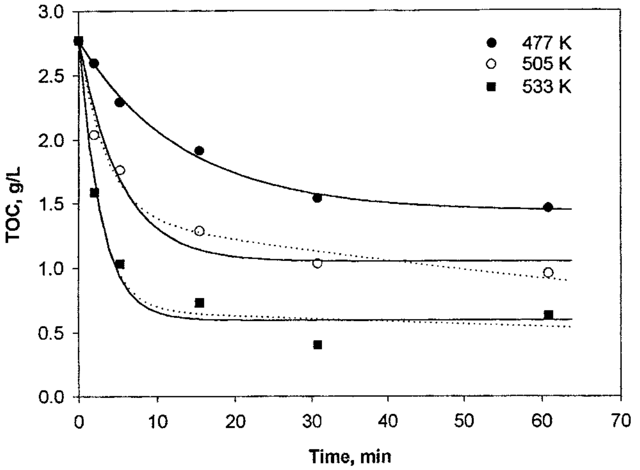

Figure 5. Wet oxidation of 2-chlorophenol: Comparison of the generalized kinetic model with the lumped kinetic model.

●, ○, ■: Experimental data from Baillod et al. (1982); ····: generalized kinetic model; ——: lumped kinetic model.

Further Evaluation of the Lumped Kinetic Model

The applicability of the lumped kinetic model proposed in this study to noncatalytic wet oxidation was evaluated using experimental data published in literature. Figure 5 shows the comparison of the experimental data reported for wet oxidation of 2-chlorophenol with the predictions of both the generalized and the lumped kinetic models. Both models fit the experimental data well. However, the rate coefficients derived from the generalized kinetic model do not follow the Arrhenius equation (Figure 6). On the other hand, the rate coefficients derived from the lumped kinetic model can be well presented using the Arrhenius equation (Figure 7). The apparent activation energies were determined to be 72.73 kJ/mol and 26.43 kJ/mol for the lumped deep and partial oxidation, respectively.

Further evaluation of both models was carried out using experimental data reported by Lin et al. (1996). As shown in Figure 8, the generalized kinetic model fits the data slightly better than the lumped kinetic model. However, Lin et al. (1996) have shown that the rate coefficients determined from the generalized kinetic model did not follow the Arrhenius equation. The lumped kinetic model fits the data, and the specific rate constants derived from the lumped kinetic model can be well described by Arrhenius equation (Figure 9). The apparent activation energies were determined to be 53.54 and 24.02 kJ/mol for deep and partial oxidation, respectively, using the lumped kinetic model. Lin et al. (1996) have reported an activation energy of 50.8 kJ/mol for the oxidation process based on the initial rate of oxidation. The apparent activation energy for deep oxidation determined using the lumped kinetic model is in a very good agreement with that reported by Lin et al. (1996).

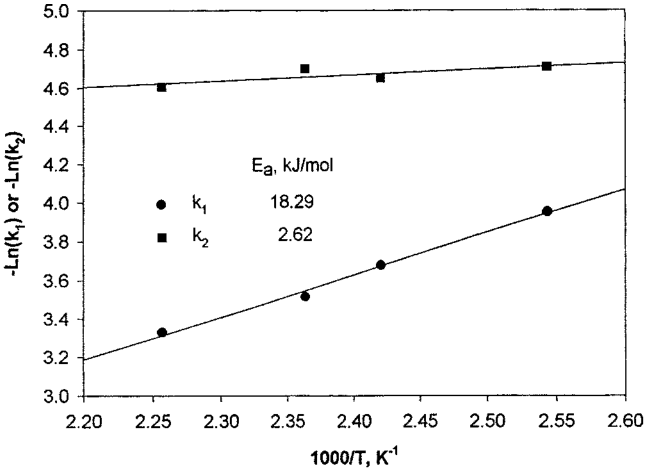

Figure 4. Arrhenius plots of specific rate coefficients derived from the lumped kinetic model.

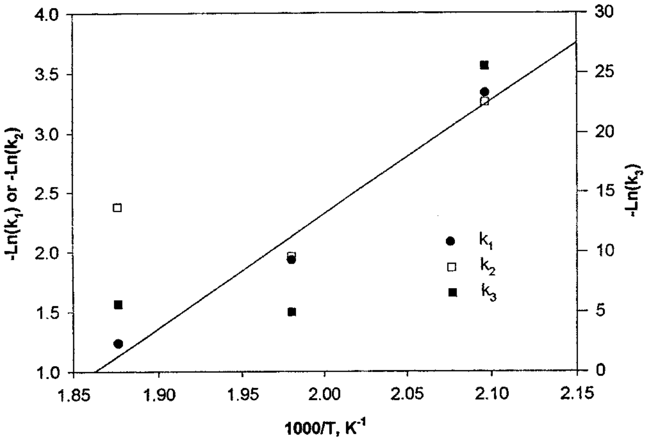

Figure 6. Arrhenius plots of specific rate coefficients derived from the generalized kinetic model based on the experimental data from Baillod et al. (1982).

k_1, k_2, k_3 defined in the generalized kinetic model.

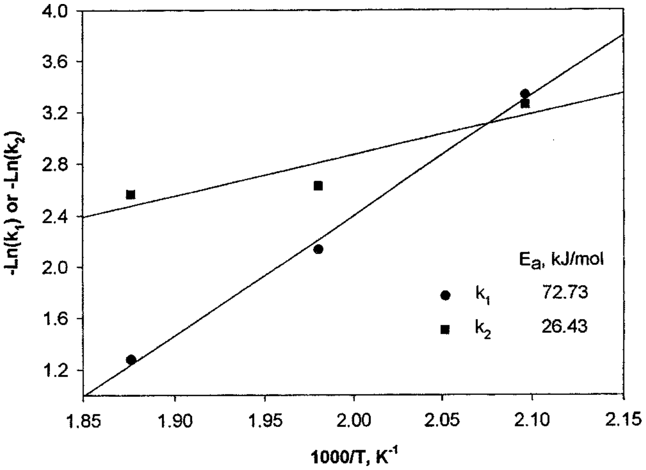

Figure 7. Arrhenius plots of specific rate coefficients derived from the lumped kinetic model based on the experimental data from Baillod et al. (1982).

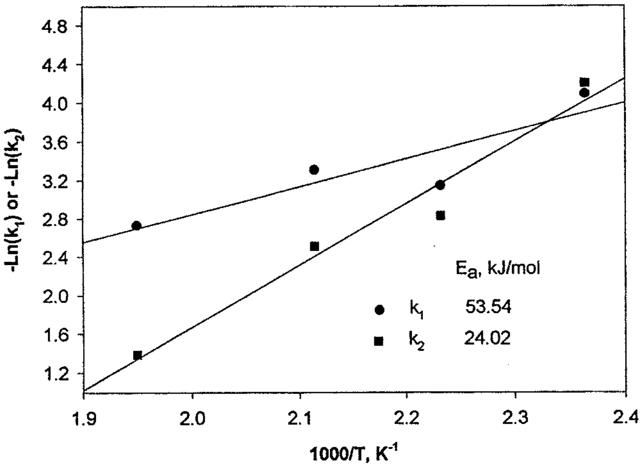

Figure 9. Arrhenius plots of specific rate coefficients derived from the lumped kinetic model based on the experimental data from Lin et al. (1996).

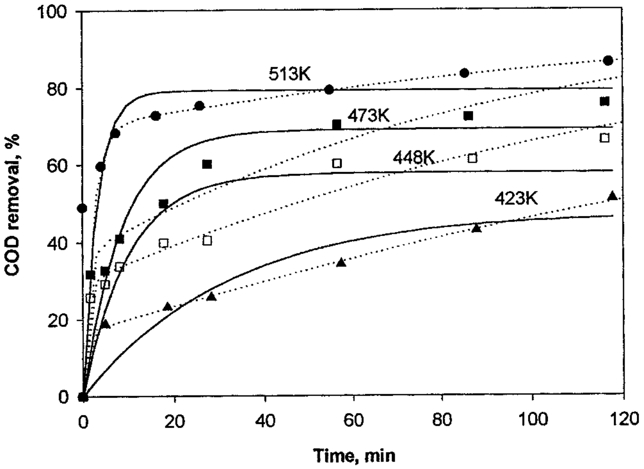

Figure 8. Wet oxidation of the effluent from a petrochemical company: further comparison of the generalized kinetic model with the lumped kinetic model.

●, ■, ▲, □: Experimental data from Lin et al. (1996); · · · ·: generalized kinetic model; ——: lumped kinetic model.

To determine the cause of the discrepancy of the generalized kinetic model in a parameter estimation, statistical analysis of the model and the literature data was carried out using SigmaStat (Jandel Scientific Software, 1995). The variance inflation factor is an important criterion to evaluate the multicolinearity of the model. Generally, the variance factor should be less than 5, and a variance inflation factor greater than 10 is a clear indication of presence of excess adjustable parameters (Winer et al., 1991). When the generalized kinetic model was used to fit the experimental data of Lin et al. (1996), the variance inflation factor reached as high as 2,000. For the experimental data of Baillod et al. (1982), the variance inflation factor reached as high as 52. These results clearly indicate that too many parameters are involved in the generalized kinetic model. This probably explains why the rate coefficients derived from the generalized kinetic model did not follow the Arrhenius equation. Regression of the generalized kinetics in this case becomes a sophisticated curve fitting process. In fact, Li et al. (1991) have suggested that only two of the three parameters can be determined by the oxidation data and the acetic acid oxidation rate coefficient has to be taken from independent studies. Hence, the three-parameter model has been practically converted into a two-parameter model. This also explains why the authors have attached constraints to the generalized model in which an independent acetic acid oxidation rate coefficient has to be used. The generalized kinetic model could not be applied for catalytic wet oxidation since the acetic acid oxidation rate coefficient was often unknown for the catalytic oxidation.

The intermediates formed during the oxidation are well known to be dependent on the reaction conditions and the catalyst used for the oxidation. However, acetic acid was assumed to be the only intermediate in the generalized kinetic model. Furthermore, the acetic acid oxidation rate coefficient was not included into the "point selectivity" (Li et al., 1991). These might be responsible for the erroneous predictions of the generalized kinetic model on the resistances of organic pollutants to oxidation in liquid phase.

Statistical analysis also indicated that the variance inflation factors of the proposed lumped kinetics model was less than 5 when the model was used to fit our experimental data and those reported by Baillod et al. (1982) and Lin et al. (1996). This indicates that the lumped kinetic model does not contain excess parameters. This was also confirmed by the good agreement between the model prediction and the experimental data, and the excellent linearity of Arrhenius plots of the rate coefficients determined using the model.

Discussion

A kinetic model is useful only if it truly reflects experimental results for given conditions. A common criterion used to evaluate the validity of the model is that the parameter should be determined by experiments and conform to their physical meanings. For wet oxidation, the shortcomings of the generalized model become evident. The acetic acid oxidation rate coefficient cannot be determined using wet oxidation data. Regression of the generalized model results in the parameter not conforming to the Arrhenius equation. The point selectivity defined from the generalized model fails to predict or describe the resistance of the organic pollutants to oxidation in liquid phase.

The lumped kinetic model developed in this study does not contain parameters that are required to be determined by different reaction studies other than wet oxidation. Only the easily determined lumped concentration of TOC or COD is required for parameter estimation. The lumped approach proposed in this article can be readily applied to the model fixed-bed reactor or slurry reactor with continuous operation for both catalytic or noncatalytic wet oxidation of the organic pollutants in industrial wastewater streams or single organic compounds with formation of complex intermediates in the liquid phase.

The activation energies determined using the lumped kinetic model based on the experimental data of Baillod et al. (1982) and Lin et al. (1996) are in good agreement with the range of activation energy (54–78 kJ/mol) reported for noncatalytic wet oxidation of organic compounds (Li et al., 1991; Mishra et al., 1995). With the presence of the Pd-Pt/Al_2O_3 catalyst, lower activation energy was observed (Figure 4). The lower activation energy, particularly for the lumped partial oxidation reaction, is probably caused by the following factors: (1) the complexity of the reactions involving different mechanisms, such as free radical and chain reaction, oxygen transfer reactions, and so on (Zhang and Chuang, 1998b); (2) oversimplification of the reaction pathway; (3) high catalytic activity of the Pd-Pt/Al_2O_3 catalyst. Further study is required to clarify this.

Conclusions

A lumped kinetic model is developed by dividing and lumping the reactions into two groups: (1) the deep or complete oxidation reactions with formation of CO_2 and H_2O; (2) the partial oxidation reactions with the formation of all intermediates in the aqueous solution of the industrial wastewater. The concentrations of all organic reactants in wastewater and that of the intermediates formed during the reaction are also represented by lumped concentrations of total organic carbon (TOC) or chemical oxygen demand (COD). The lumped kinetic model is simpler yet appropriate in describing both catalytic and noncatalytic wet oxidation processes.

Acknowledgments

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Notation

$[A]$ = concentration of lumped compound A, mol/m^3
$[B]$ = concentration of lumped compound B, mol/m^3
r = rate of TOC removal, mol/m^3/s
V = volume of the wastewater, m^3
t = reaction time, s
N = total amount of the lumped compound, mol
k = reaction rate constant, s^{-1}
T = temperature, K
R = gas constant (8.314 J/mol·K)
Ea = activation energy, kJ/mol
γ = stoichiometry factor of oxidation reaction

Subscripts

A = reactant A
B = product B
1, 2 = reactions defined in Eqs. 1 and 2, respectively

Superscripts

a, b = order of reaction with respect to oxygen in Eqs. 1 and 2, respectively

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