Wet Oxidation of an Azo Dye: Lumped Kinetics in Batch and Mixed Flow Reactors

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Oxidation of a dilute aqueous solution of a model azo dye pollutant (Orange II) was studied in batch and continuous well-mixed (CSTR) reactors. Both reactors operate at 200−250°C, and total pressures up to 50 bar and at oxygen partial pressure from 10 to 30 bar. The model pollutant concentrations were in a range between 100 and 1,000 mg/L, which may be found in industrial wastewaters. The dye oxidation undergoes a parallel-consecutive reaction pathways, in which it first decomposes thermally and oxidatively to aromatic intermediates and via organic acids to the final product carbon dioxide. To develop a kinetic equation capable of predicting organic carbon reduction, all organic species present in solution were lumped by total organic carbon (TOC). The lumped oxidation rate in batch reactor exhibited second-order behavior, whereas in the CSTR it was found linearly proportional to its TOC concentration. The lump behavior in batch reactor was dominated by the refractory low molecular mass aliphatic acids formed during the oxidation.

Introduction

In recent years, the subcritical wet oxidation process (WO) has been demonstrated to be a very efficient technology for treating a variety of dilute aqueous streams polluted by organics. The oxidation takes place in the liquid phase where the organic carbon is oxidized to carbon dioxide. There are two factors that are considered of primary importance in the successful operation of any WO process: efficient transport of the gaseous reactant (oxygen) across the gas-liquid interface and the intrinsic reaction kinetics. The high demand of oxygen is best illustrated by comparing the equilibrium concentration of oxygen in pure water that can be attained at temperatures and pressures used in WO with a typical chemical oxygen demand (COD) of an aqueous medium treated by WO: the equilibrium concentration is below 1 g/L, while the typical COD is in the range between 30 and 100 g/L. Thus, an efficient WO system has to constantly maintain an oxygen flux even up to at least 30 times the equilibrium concentration. To design such gas-liquid reactors, one must know whether the oxidation would occur in the bulk liquid phase ($\mathrm{Ha}^2 \ll 1$), which necessitates a large volume of liquid, or completely in the boundary layer ($\mathrm{Ha}^2 \gg 1$), which calls for contacting devices that provide for a large interfacial area. The Hatta number (Ha) is defined as a ratio of characteristic time for the gas-liquid mass transfer and that for the liquid-phase reaction. For the reactions whose rate equation can be written as

$$r_{\mathrm{org}} = k \cdot C_{\mathrm{org}}^{m} \cdot C_{\mathrm{oxy}}^{n} \tag{1}$$

the Hatta number is given in the following form (Deckwer, 1992)

$$\mathrm{Ha} = \frac{\sqrt{\dfrac{2}{n+1} \cdot k \cdot C_{\mathrm{org}}^{m} \cdot C_{\mathrm{oxy}}^{n-1} \cdot D_{\mathrm{oxy}}}}{k_1}. \tag{2}$$

Wet oxidation reactions are considered to be medium rate gas-liquid reactions ($0.01 < \mathrm{Ha}^2 < 10$) requiring long residence times for the liquid phase. The unique feature of the

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WO reactor design lays in the fact that the Hatta number changes in the direction of flow due to a decrease in the concentration of organics and due to the formation of more refractory compounds (such as aliphatic acids with a few order of magnitude lower rate constants). Consequently, the wet oxidation reactor has to practically be custom designed and optimized for specific stream. However, when searching for an optimal reactor size, which is strongly dictated by a new very expensive corrosion resistant material, one must take into account a proper balance between intensive (back)mixing and plug-flow behavior (Levec, 1998).

In order to use Eq. 2 for the design purposes, it is obvious that the concentration of organic materials (C_{org}) must be expressed by means of a lumped parameter such as total organic carbon (TOC), which accounts for all organic species present in a wastewater, or chemical oxygen demand (COD), which also takes into account oxidizable inorganics. Therefore, the kinetic models that solely predict the disappearance rate of pure compounds are not sufficient: a lumped kinetic model capable of predicting complete conversion of all organic species present in wastewater is needed. Unfortunately, a vast portion of the works reported in the literature deals with the oxidation kinetics for single compounds. Mishra et al. (1995) have extensively reviewed the oxidation mechanism and kinetics obtained with pure organic compounds dissolved in water, and the structure-oxidizability correlation for the WO of carboxylic acids, phenols, cyanides, and nitriles. The kinetics of subcritical wet oxidation is thoroughly discussed in an article by Li et al. (1991). In a broad spectrum of organic compounds, they found that oxidation in a batch system obeys mostly the first-order rate law with respect to both organic compounds and oxygen. They proposed a three-lump generalized kinetic model for wet oxidation of organic compounds. Li et al. (1996) further elaborated this model and have shown by many examples that the lumping technique is a powerful tool for handling experimental wet oxidation data.

All the above mentioned studies deal with the kinetic models that have been developed from the experimental data of batch oxidation systems. So far, there has been no attempt in the open literature to show how these lumped kinetic models predict the performance of a reactor with different residence time distribution (RTD) than that of batch or plug flow. However, Hutchinson and Luss (1970) appear to be the first to show that systems with some degree of backmixing may have to be lumped with a different rate equation than systems with plug-flow behavior. It was later confirmed experimentally by Van Dongen et al. (1980) while studying the kinetics of hydrodemetallization of residual oils: they found that the reaction is first order when carried out in a continuous-stirred tank reactor (CSTR) and 1.5 order in a plug-flow reactor. The same was concluded by Ho (1996) who found that in many cases lumped kinetics are of the power-law form, with the exponent for CSTR being lower than that for a plug-flow reactor (PFR). Although the lumped kinetic equation obtained from the batch reactor data cannot be applied to solve the CSTR case (Luss and Golikeri, 1975; Westerterp et al., 1984) for wet oxidation, it has been overlooked in the open literature. One should be aware that there is a common practice to evaluate oxidation kinetics in a laboratory batch reactor while the commercial wet oxidation units operate mostly as CSTRs (Copa and Gitchel, 1989).

The purpose of this work is to demonstrate experimentally that the lumped kinetics of an oxidation process obtained in batch reactor appreciably differs from that obtained in a CSTR. Therefore, the former cannot be used for the prediction of TOC concentration in CSTR effluents. A typical model pollutant from textile industry (azo dye Orange II), which undergoes a complex oxidation pathway with many intermediates, is chosen for the kinetic study in both reactor types.

Experimental Studies

Apparatus and procedure

Wet oxidation experiments were carried out in a 2-L stainless steel autoclave reactor (Parr Instr. Company) equipped with a magnetically driven turbine type impeller, and temperature and pressure control units. The setups used for batch and continuous oxidation experiments as well as the experimental procedure for Orange II oxidation are described in detail elsewhere (Donlagic, 1998; Donlagic and Levec, 1997).

Figure 1 shows the apparatus for continuous oxidation experiments. The reactor vessel was the same as used in the batch mode of operation. Contrary to the batch experiments, continuous experiments called for some specific experimental arrangements. For example, because an aqueous solution of the dye undergoes thermal degradation (Donlagic and Levec, 1997), it was not possible to preheat the dye feed solution to the reactor operating temperature and, thus, to ensure a stable operation of CSTR. To avoid thermal degradation of the dye prior to entering the reactor, the reactor feed was divided into two parts: a concentrated solution of the dye (5.0 and 10.0 g/L) and water. The dye solution was fed into the reactor by means of a positive displacement pump (Beckman, 114M) without being preheated. Water was preheated to the reactor operating temperature in a stainless steel coil (5 m long, 6 mm OD) placed into an electric heater and fed into the reactor by means of a diaphragm metering pump (Orlita, S-30). The desired dye concentration in the feedstream was thus adjusted by a ratio of the flow rates of water and dye solution. The conditions employed in both modes of operation are given in Table 1.

Since wet oxidation is a two-phase reaction, oxygen transfer across the gas-liquid interface may retard its intrinsic rate. At the conditions employed, the gas-side mass-transfer resistance was estimated to be negligible due to high diffusivity of oxygen in the gas phase and due to its low solubility in water. To verify the absence of the liquid-side mass-transfer resistance, the impeller speed on the rate of the dye decay and TOC reduction, respectively, was studied. It was found out that the rates were independent of the impeller speed in a range of 500–1,250 rpm, thus indicating there were no limitations associated with the oxygen transfer. However, in both modes of operation the oxidation experiments were performed with the impeller speed of 1,000 rpm (Table 1).

The need to know the actual residence time of the liquid phase in the two-phase operating CSTR created another problem to solve. The overflow installed in the reactor kept the level of the gas-liquid dispersion constant, but not the amount of the liquid. The amount of the liquid present in the reactor depends on the gas holdup. Because the gas holdup changes with the operating temperature and pressure, as well as with dye concentration and impeller speed (however, these

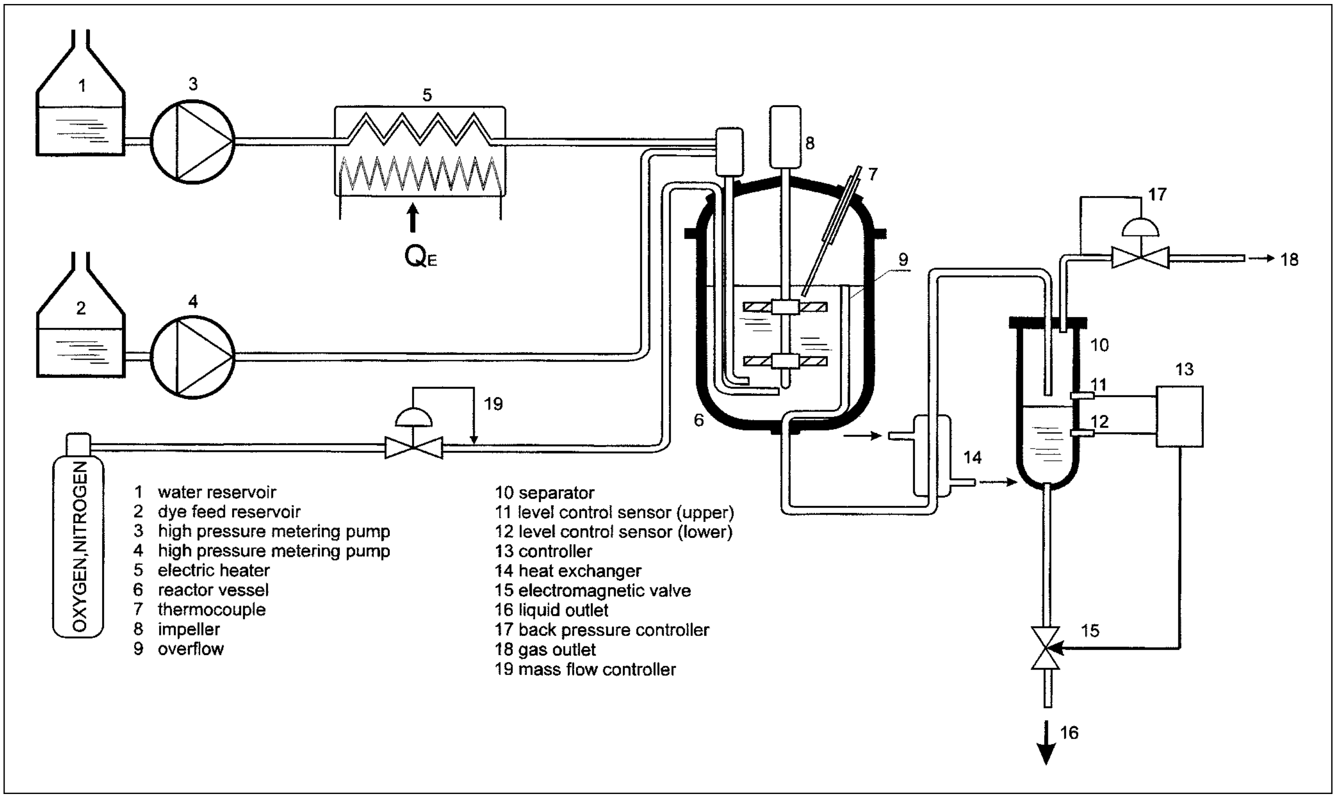

Figure 1. Apparatus for continuous oxidation.

variables were kept constant), it was necessary to determine the volume of the liquid in the reactor for each operating conditions separately. For this purpose, the dynamic experiments were performed in an inert atmosphere (nitrogen) with the dye as a tracer. In the range of temperatures used and nitrogen atmosphere, the dye decomposes into benzenesulfonic acid and naphthol (Donlagic and Levec, 1997), thus retaining the total organic carbon (TOC) in the solution constant. This made it possible to follow TOC in the reactor effluent after the dye in the feedstream was cut off. Typical responses to the stepdown input function at different operating conditions are shown in Figure 2. However, the residence time distribution can be presented with the following relation

$$F(t) = \frac{C(t)}{C_0} = e^{-t/\bar{t}}. \qquad (3)$$

Table 1. Operating Conditions for Batch and Continuous Oxidation Experiments

Batch Operation	
Initial dye concentration (mg/L)	100–1,000
Oxygen flow rate (L/min; 20°C, 1 bar)	1.0
Oxygen partial pressure (bar)	10.0–30.0
Total pressure (bar)	25.0–50.0
Temperature (°C)	180–240
Impeller rpm (1/min)	1,000
Continuous Operation (CSTR)	
Dye concentration in feed reservoir (g/L)	5 or 10
Dye solution flow rate (L/min $\times 10^3$)	1.5–9.8
Water flow rate (L/min $\times 10^2$)	1.2–8.8
Dye concentration in reactor feed solution (mg/L)	500 and 1,000
Oxygen flow rate (L/min)	1.0
Oxygen partial pressure (bar)	10.0–28.0
Total pressure (bar)	25.0–50.0
Temperature (°C)	180–250
Impeller rpm (1/min)	1,000

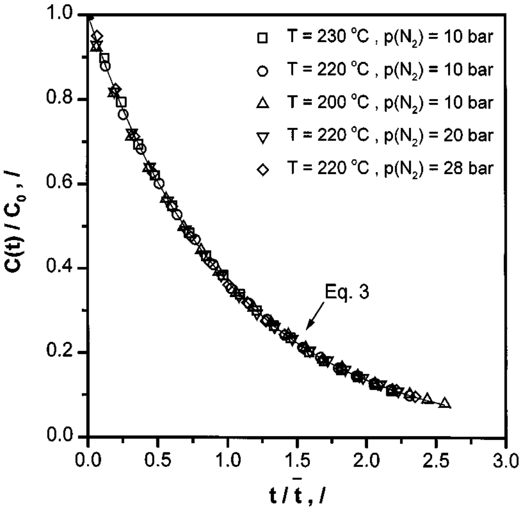

Figure 2. Typical experimental responses to the stepdown input function.

From the data of Figure 2, one can calculate the mean residence time according to the equation

$$\bar{t} = \int_0^1 t\,dF = \frac{V}{Q} \qquad (4)$$

and, further from it, the amount of the liquid present in the reactor. The average amount of the liquid phase was evaluated to be 1.03 L for all oxidation experiments carried out in CSTR. Practically the same liquid content (1.06 L) was determined after the reactor was calmed down and dismantled. The liquid content (that is, gas holdup) in the reactor was found practically independent on pressure and temperature most probably due to the narrow range of operating conditions. However, the exponentially distributed residence times shown in Figure 2 undoubtedly speak for the well-mixed liquid phase.

Constant concentrations in the CSTR effluents (steady-state operation) were attained after at least three times the mean residence time. For example, at the residence time of 70 min, the reproducible results with the reactor effluent concentrations were assured after 210 min. All data points presented in the work are averages of at least three samples taken from the effluents.

Analysis

The analytical methods employed in this work are described in detail in recent articles of Donlagic and Levec (1997, 1998), therefore, they are only briefly mentioned here. The quantity of residual Orange II in solution was determined by a reversed-phase HPLC using a Hewlett Packard 1100/DAD system. To achieve satisfactory separation of the breakdown products from the mother compound, a gradient elution was used. The residual organic carbon concentration in the samples were measured by an advanced HTCO Rosemount/Dohrmann DC-190 TOC analyzer equipped with a nondispersive infrared (NDIR) CO_2 detector. Low molecular mass organic acids were quantitatively evaluated by means of ionic chromatography (Dionex 4000I).

Results and Discussion

Lumped kinetics from batch reactor

It has been found by Donlagic and Levec (1997) that the dye oxidation undergoes a parallel-consecutive reaction scheme: it decomposes thermally and oxidatively to aromatic intermediates, and via organic acids to the final product carbon dioxide. A simplified reaction scheme is presented in Figure 3. The known (that is, identified) intermediates are benzenesulfonic acid, 2-naphthol, 1,2-benzene-dicarboxylic acid, 4-hydroxybenzenesulfonic acid, 2-(hydroxymethyl)-benzoic acid, 1,3-iso-benzofurandione, acetic acid, formic acid, oxalic acid, and glycolic acid.

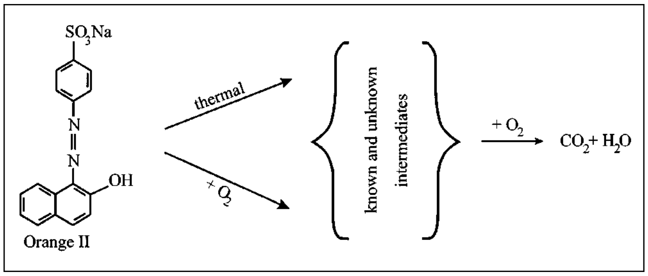

Figure 3. Simplified reaction scheme for Orange II oxidation.

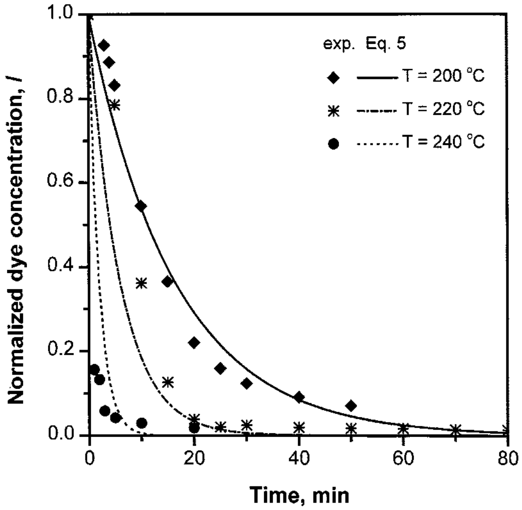

Figure 4. Normalized experimental and predicted dye concentrations from batch reactor operated at 10 bar of oxygen partial pressure with different temperatures.

However, in order to develop a lumped kinetics equation for the prediction of TOC reduction, organic carbon that appears in all species present in the solution was lumped by means of the TOC concentration. Typical dye decay curves are shown in Figure 4 for different temperatures with the exception of a constant oxygen partial pressure, while the TOC concentration profiles are depicted in Figure 5. Aimed at the development of a power-law kinetic equations for the

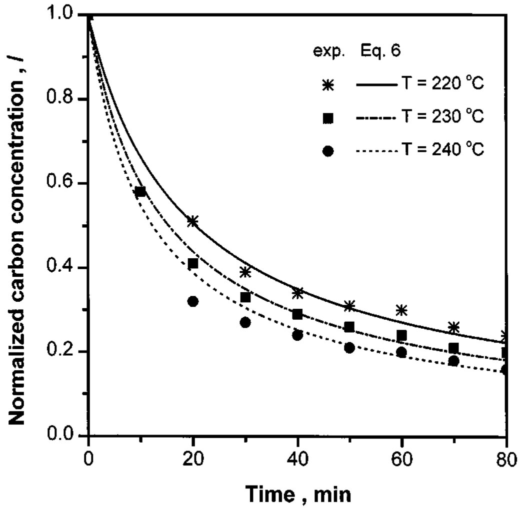

Figure 5. Normalized experimental and predicted TOC concentration from batch reactor operated at 10 bar of oxygen partial pressure with different temperatures.

dye decay and TOC reduction, a multivariable nonlinear regression technique was employed (Marquardt, 1963). However, the optimized parameters (that is, the pre-exponential factor, the activation energy, and partial orders with respect to dye and TOC, and oxygen, respectively) constitute the following rate equations:

For the dye decay

$$-\frac{dC_{\text{dye}}}{dt} = -r_{\text{dye}} = 5.9\times10^{6}\exp\left(-\frac{68\ \text{kJ/mol}}{RT}\right)C_{\text{dye}}C_{O_2} \quad (5)$$

For the lumped TOC reduction

$$-\frac{dC_{\text{TOC}}}{dt} = -r_{\text{TOC}} = 1.7\times10^{12}\exp\left(-\frac{154\ \text{kJ/mol}}{RT}\right)C_{\text{TOC}}^{2}C_{O_2} \quad (6)$$

Since the dye concentrations were very low, the oxygen concentration in the above equations is assumed equal to the solubility of oxygen in water (Donlagic, 1998). Although Eq. 5 accounts for the thermal as well as for the oxidative dye decomposition, it indicates a linear dependence of the dye disappearance rate on its concentration. Thus, Eq. 5 is in agreement with Donlagic and Levec (1997), who found that the oxidative and thermal decomposition are both first-order processes. On the other hand, Eq. 6 shows that the lumped TOC concentration reduces by a second-order rate process with respect to the TOC concentration. It is interesting to note that the same order with respect to the TOC lump would result if one lumps parallel first-order oxidation reactions in a continuous mixture with an exponential initial carbon distribution (that is, the distribution parameter in the gamma function equals one). This further implies that many intermediates were already formed in the first few minutes of the oxidation process. However, by introducing the TOC lump, essential first-order oxidation processes are converted into an overall second-order process. The same transition in the rate order was found in supercritical wet oxidation (SCWO) of phenol carried out in a plug-flow reactor when organic species were lumped by TOC (Krajnc and Levec, 1996), while the example with crude oil cracking has been known for many years (Weekman, 1979). Second-order kinetic behavior of a lump is usually attributed to a wide range of reactivity of the lumped species, which appears to be the case also with Orange II oxidation.

Comparison of the carbon profiles from the batch experiments and those calculated by Eqs. 5 and 6 is shown in Figure 4 for the dye decay and in Figure 5 for the TOC reduction, respectively. In a parity plot one would find more than 90% of the rate data points calculated by Eq. 5 within the confidence interval of ±10%, whereas in the case with Eq. 6 all data points lay within this interval. A disagreement shown in Figure 3 at 240°C is mainly due to the sampling difficulties, whereas deviations at 200° and 220°C can be ascribed to the phenomenon called induction period, which is a characteristic phenomenon for the reactions involving free-radicals. It should also be pointed out that much better agreement between the experimental and calculated data is obtained when thermal and oxidative decomposition rates are compared separately (Donlagic and Levec, 1997).

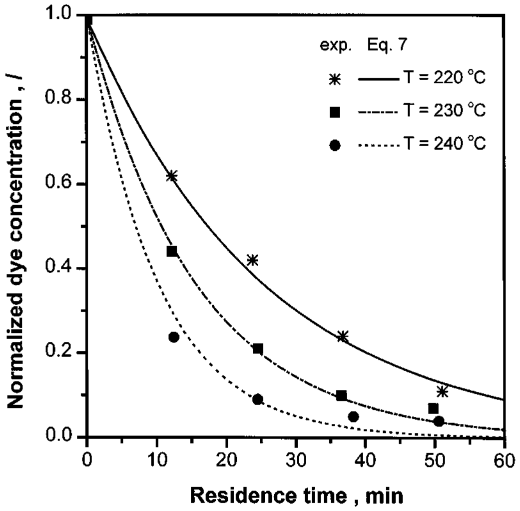

Figure 6. Normalized experimental and predicted dye concentrations from CSTR operated at 10 bar of oxygen partial pressure with different temperatures.

Lumped kinetics from CSTR

The concentration profiles of the dye obtained in the CSTR oxidation experiments are shown in Figure 6. As found out in a batch reactor, the dye concentration decreases very rapidly with the residence time, whereas the total carbon in solution (TOC) reduces much more slowly. In Figure 7 the dye disappearance rate vs. concentration is shown on the logarithmic plot at a constant concentration of oxygen in the solution. According to the batch reactor results, a linear dependence is expected. A close inspection of the data in Figure 7 shows that the slope increases with both the conversion (the outlet concentration decreases) and temperature, and that the linearity in a whole range of conversions is obtained only at the highest temperature (250°C). It seems that a constant value

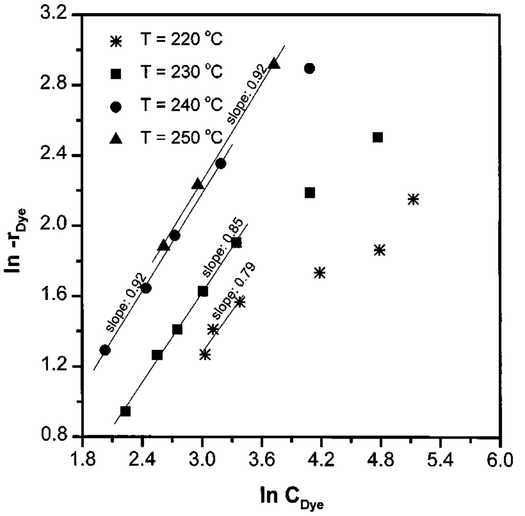

Figure 7. Differential method of analysis of CSTR data for dye decomposition.

of the order with respect to the dye concentration is reached already at 240°C (0.92). Departure from the linearity can be again ascribed to the induction period, which is more pronounced at low temperatures and short residence times (low conversions). This retardation effect seems to be hidden in the concentration vs. residence time plot (Figure 6), but is well displayed in Figure 7. The order less than one with respect to the dye concentration may also be due to accounting for the thermal and oxidative decomposition in a single rate equation. However, when assuming a linear dependence on the dye concentration, the following simplified rate equation for the dye decay in CSTR is obtained

$$-r_{\text{dye}} = 2.3\times 10^{5}\exp\left(-\frac{60\ \text{kJ/mol}}{RT}\right)C_{\text{dye}}C_{O_2}. \tag{7}$$

The dye concentrations calculated by Eq. 7 are presented in Figure 6 by solid curves. As can be seen, the agreement is reasonably good even though the order of 1.0 instead of 0.92 was used; the calculated data points lay well inside the confidence limits of ±10%.

The concentration profiles of TOC from the CSTR data are shown in Figure 8, whereas the disappearance rate of TOC is shown in Figure 9 as a function of TOC concentration. As can be seen, the TOC data exhibit very similar behavior to that found with the dye. The order (slope) with respect to the total carbon concentration increases again with conversion; at 230°C, for example, it starts from a negative value (low carbon conversions) and ends with a positive value (high conversions). This behavior diminishes as temperature increases, and, at 240°C, the slope reaches a value of 0.93. Further temperature increase up to 250°C yields the order of 0.99. However, one may speculate that a first-order dependence with respect to the TOC lump is already attained at 250°C. Unfortunately, due to the temperature limitations of the apparatus, it was not possible to safely perform oxidation experiments above this temperature limit. Assuming the slopes of the lines in Figure 8 to be the same and equal to 1.0, one can evaluate the rate constant at three different operating temperatures and further the activation energy. The expression for the lump disappearance rate can then be written as

$$-r_{\text{TOC}} = 114.8\exp\left(-\frac{37\ \text{kJ/mol}}{RT}\right)C_{\text{TOC}}C_{O_2}. \tag{8}$$

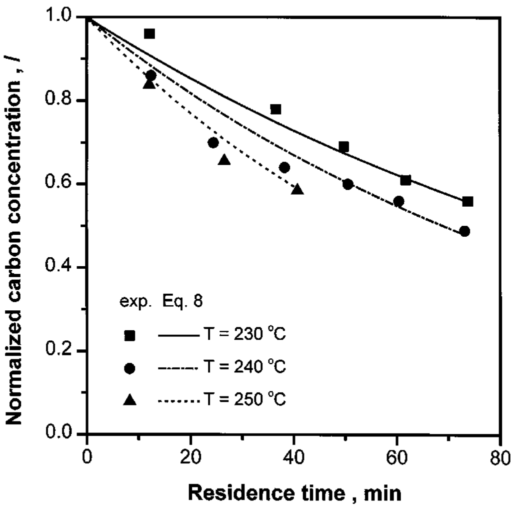

Figure 8. Normalized experimental and predicted TOC concentrations from CSTR operated at 10 bar of oxygen partial pressure with different temperatures.

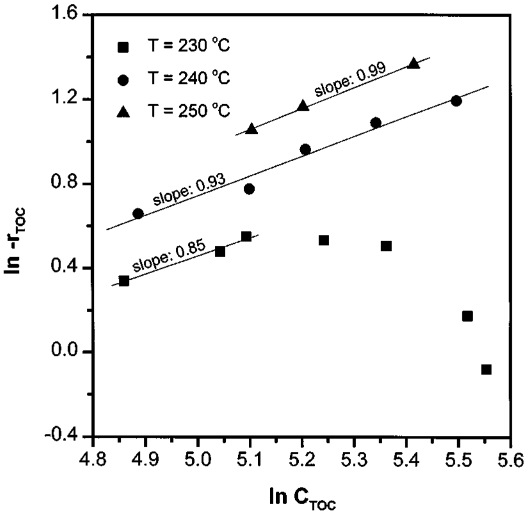

Figure 9. Differential method of analysis of CSTR data for TOC reduction.

Equation 8 undoubtedly reveals that the rate of TOC reduction in CSTR is a first-order process, in contrast to a second-order process found in batch reactor. Similar results have been obtained by Van Dongen et al. (1980) with the hydrodemetallization reaction: in CSTR the lump order was found to be 1 while in plug-flow reactor it was 1.5 order. However, the calculations made by Eq. 8 are shown in Figure 8 by solid curves while in a parity plot one would find all calculated data points well within the confidence interval of ±10%.

The kinetic behavior of a mixture with irreversible reactions in a plug-flow (or batch) reactor is usually governed by the most refractory fraction of the feed (Ho, 1996). Accordingly, the refractory low molecular mass organic acids must play an important role in the batch oxidation of the dye. Figure 10 shows the formation of low molecular mass organic acids as a function of the TOC conversion. In the CSTR the amount of acids increases much more steeply with the TOC conversion than in batch reactor. Furthermore, at 54% of TOC conversion in the CSTR, about 61% of the total amount of acids is contributed by the refractory acetic acid; at this conversion in the batch reactor, the acidic lump consists only of 45% of acetic acid. At the maximum TOC conversion obtained in the batch reactor (84%), the acidic lump already consists of 85% acetic acid. However, it is obvious from Figure 10 that in the batch reactor more refractory acids are further converted than in the CSTR. In the batch system the reaction thus slows down, apparently because more refractory acids (with lower oxidation rates) take place in the overall oxidation. By slowing down the reaction rate with conversion, the behavior of a second-order reaction is simulated

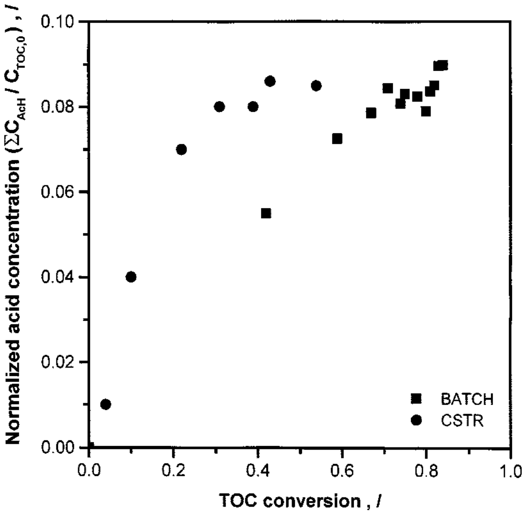

Figure 10. Normalized sum of carbon concentration in aliphatic acids as a function of TOC conversion for both reactors operated at 230°C and 10 bar of oxygen partial pressure.

(Weekman, 1979). Thus, the lump order of two found in a batch reactor is not surprising at all. In the CSTR, the residence times of all species are distributed exponentially and, consequently, all reactants are slowed down compared to those in the batch reactor; the fast-reacting ones are hampered more than the slow-reacting ones (Ho, 1996). However, the oxidation process in a CSTR is almost terminated with the formation of refractory acids. A very low value of activation energy (37 kJ/mol) thus results from an easily oxidized intermediate species, while the aliphatic acids were close to not oxidizing further to carbon dioxide. This is in agreement with Ho (1996) who found that the lumped order in a CSTR is taking a value of one when the feed consists of a very reactive species. At this point, one may argue that different RTD in reactors causes different acid distribution, which consequently causes different pH value of the reactive solutions, and therefore different oxidation rates. While the pH effect is very pronounced in ozonation phenolic compounds, where the rate constant may even change for a few orders of magnitude (Hoigné and Bader, 1983), there is no reported change of the concentration-dependent term.

In spite of many experimental and theoretical works that have been published on the lumped kinetics of petroleum feedstock, little information can be used to discuss the results of this study, due to different initial distribution of reactive species. Nevertheless, the results of this work imply that the difference between the lumped orders for the two reactors with different RTD is in agreement with the findings of other investigators of cracking (Hutchinson and Luss, 1970; Luss and Golikeri, 1975; Van Dongen et al., 1980, Westerterp et al., 1984; Ho, 1996).

Prediction of TOC in CSTR

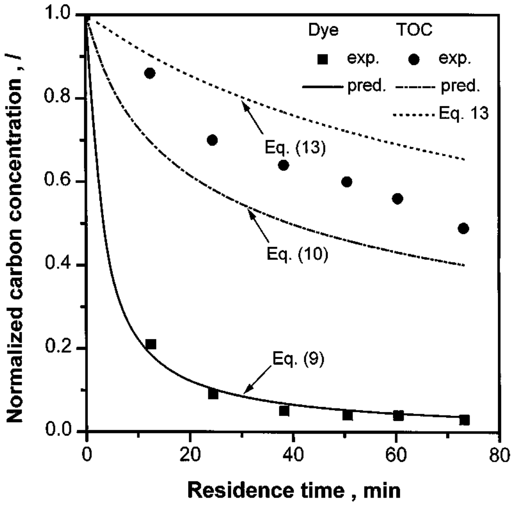

Figure 11. Predicted vs. experimental dye and TOC data from CSTR operated 240°C and 10 bar of oxygen partial pressure.

The results of this work undoubtedly demonstrate that the lumped oxidation kinetics obtained in reactors with different RTD are not identical. A precaution is thus needed when predicting the performance of a reactor from the kinetics that is obtained from a reactor with different RTD. Nevertheless, it is interesting to see how close the rate equations developed from the batch reactor data predict the CSTR performance.

Since Eq. 5 represents a *true* kinetics for the dye decomposition, there should be no problem in predicting the dye concentration in the CSTR effluents. In Figure 11 the experimental CSTR data for the dye are compared with those predicted by Eq. 5 at 240°C. For the prediction of dye concentration in the CSTR effluent, the following equation applies

$$\frac{C_{\text{dye,ex}}}{C_{\text{dye,in}}} = \frac{1}{1 + k^* \bar{t}} \tag{9}$$

where k^* is a pseudo-first-order rate constant (1/min), which includes the oxygen concentration (solubility) at operating temperature $(= k \times C_{O_2})$. As has been expected, the excellent agreement is demonstrated in Figure 11. This can be further considered as a good test for the consistent experimental work in both reactors.

As mentioned above, the prediction of lumped TOC concentration in the CSTR effluent is not a straightforward procedure. There are three possible approaches (Bischoff, 1991): (a) *early luming*, (b) *late lumping*, and (c) *exact lumping*. If one uses the lumped kinetic equation developed from the batch data and solves the usual CSTR mass balance, the following performance equation is obtained (early lumping)

$$\frac{C_{\text{TOC,ex}}}{C_{\text{TOC,in}}} = \frac{1}{2\hat{k}_2 \bar{t} C_{\text{TOC,in}}} + \left[\left(\frac{1}{2\hat{k}_2 \bar{t} C_{\text{TOC,in}}} \right)^2 + \frac{1}{\hat{k}_2 \bar{t} C_{\text{TOC,in}}} \right]^{1/2} \tag{10}$$

where $\hat{k}_2$ is a pseudo-second-order rate constant (L/mg (×min) from Eq. 6, which includes also the oxygen concentration at the operating temperature. As one can see from Figure 11, the early lumped kinetic model largely underestimates the exit TOC concentrations (overestimates the TOC conversions) in the whole range of residence times employed in this study. If Eq. 6 were a *true* kinetic equation, the concentration in the exit stream of CSTR would be given by Eq. 10.

Supposing that oxidation of individual intermediates follows a first-order kinetics, the exit lumped TOC concentration in a batch or plug-flow reactor can then be written as (late lumping)

$$\frac{C_{\mathrm{TOC,ex}}}{C_{\mathrm{TOC,in}}} = \int_0^{\infty} \exp(-kt)\, h(k)\, dk \qquad (11)$$

where $h(k)$ is a distribution function of constituent species, which are all disappearing by parallel reactions. Since the lumped order of 2 was resulted from the batch experiments (see Eq. 6), one can speculate that the reactivities of many intermediate species are exponentially distributed (that is, gamma distribution function with parameter $\alpha = 1$), thus

$$h(k) = \frac{1}{\widehat{k}_1} \exp\left(\frac{k}{\widehat{k}_1}\right) \qquad (12)$$

where $\widehat{k}_1$ is the average pseudo-first-order rate constant (L/min). Knowing the distribution function (Eq. 12), one can calculate the CSTR effluent concentration by rewriting Eq. 11 for the case of CSTR, which after integration yields (Bischoff, 1991)

$$\frac{C_{\mathrm{TOC,ex}}}{C_{\mathrm{TOC,in}}} = \int_0^{\infty} \frac{h(k)}{(1+k\bar{t})} dk = \frac{1}{\widehat{k}_1 \bar{t}} \exp\left(\frac{1}{\widehat{k}_1 \bar{t}}\right) E_1\left(\frac{1}{\widehat{k}_1 \bar{t}}\right) \qquad (13)$$

If one further assumes that the CSTR experiments have provided for the value of $\widehat{k}_1$, Eq. 13 should be suitable for predicting the CSTR performance. Figure 11 also shows, however, that Eq. 13 overestimates the exit TOC concentrations (underestimates the TOC conversions) for about the same extent as Eq. 10 underestimates them. Since the assumption of parallel reaction scheme as well as the exponential distribution seems to be somewhat implausible, the discrepancy is expected. In general, the oxidation processes in aqueous media undergo parallel-consecutive reaction pathways and the number of species vary with the oxidation progress. It is obvious in the present case that the distribution parameter (α) changes with time: the oxidation starts with a single compound ($\alpha \to \infty$), which, after a while, decomposes into many intermediates. However, there is no solid experimental evidence that their reactivities are distributed exponentially ($\alpha = 1$).

Assuming that the formation and disappearance rates of all organic species present in solution are first-order processes and with the knowledge of the rate constants, the TOC conversion can be, in principle, calculated by means of the Wei and Kuo (1969) exact (proper) lumping

$$\frac{C_{\mathrm{TOC}}}{C_{\mathrm{TOC,0}}} = \int_0^{\infty} e^{\widehat{K}t} E(t)\, dt \qquad (14)$$

where $\widehat{K}$ is the lumped rate constant matrix (1/min) and $E(t)$ is the residence time distribution for an arbitrary flow reactor (such as a CSTR). It may be sufficient to know the matrix $\widehat{K}$ for the key intermediates, which can be evaluated from the batch experiments as described by Li et al. (1996). In the oxidation of Orange II, the refractory aliphatic acids control the overall oxidation rate; thus, they are the key intermediates. While the present literature allow us to write down the disappearance rates for many of these acids (Li et al., 1991; Mishra et al., 1995; Shende and Levec, 1999a,b), the rates of their production depend primarily on the chemical environment, that is, on the species from which they are produced. Therefore, the complete acid matrix seems to be unattainable at the moment. However, lacking the ability to correctly predict the CSTR performance calls for more carefully planned experimental work with the key TOC lumps in both batch and CSTR systems.

Conclusions

The azo dye oxidation in aqueous solutions undergoes various parallel-consecutive reactions via different intermediates to the final product carbon dioxide. The oxidation kinetics is thus governed by the sum of an immense number of elementary oxidation steps of widely different rates. The dye concentration in the effluent of CSTR can be well predicted by the *true* kinetic model developed from the batch reactor data.

The disappearance rate of total organic carbon can be well expressed by the lumped kinetics of the power-law form without knowing the underlying rate constants for each species constituting the lump. However, it is evident that the lumped kinetics from batch data does not allow us to correctly predict the CSTR performance, since in the batch reactor the lumped kinetics exhibits a second-order behavior, whereas in the CSTR it behaves as a first-order reaction. The lump behavior in the batch reactor is dominated by the refractory low molecular mass aliphatic acids.

It is of practical interest to develop a better understanding of the kinetic behavior of lumps that may undergo wet oxidation in reactors with different residence time distribution. One should bear in mind that wet oxidation reactors operate in a broad spectrum of the Peclet number—the system may approach completely mixed flow on one side when high oxygen transfer rates are needed, or plug flow on the other side when a system calls for moderate/low oxygen transfer rates. Information on the kinetic behavior of key lumps (such as a mixture of aliphatic acids), which frequently dictate the overall TOC/COD reduction, in different two-phase reactor arrangements seems to be of high importance.

Acknowledgment

The authors thank for the financial support provided by the Slovenian Ministry of Science and Technology through Grants J2-6179 and J2-0783.

Notation

$C(t)$ = time-dependent concentration of tracer, mg C/L
C_0 = initial concentration of tracer, mg C/L
C_{dye} = dye concentration, mg C/L
C_{O_2} = concentration of oxygen in solution, g O_2/L
C_{TOC} = concentration of total organic carbon in solution, mg C/L

D = oxygen diffusivity, m^2/s
E_1 = exponential integral of first-order
$F(t)$, $E(t)$ = RTD-residence time distribution function
Ha = Hatta number (Eq. 2)
k = second-order rate constant, $L/g\ O_2 \times min$
$\hat{k}_1$ = average pseudo-first-order rate constant, L/min
k_1 = liquid-side mass-transfer coefficient, m/s
m = order with respect to organic species
n = order with respect to oxygen
r_{dye} = dye disappearance rate, $mg\ C/L \times min$
r_{TOC} = total carbon disappearance rate, $mg\ C/L \times min$
Q = volumetric flow rate, L/min
t = time, min
$\bar{t}$ = mean residence time, min
V = liquid-phase volume, L

Subscripts

in = inlet
ex = exit
org = organic species
oxy = oxygen

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Manuscript received June 4, 1999, and revision received Aug. 16, 1999.