On the need for engineering models of integrated chemical and biological oxidation of wastewaters

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Abstract
Experimental examples of sequential chemical and biological oxidation treatment have been previously reviewed by Scott and Ollis, and economic estimates proposed by Esplugas and Ollis. Despite the prevalence of examples evident in these reviews and in recent conferences, very little use of kinetic models to codify and rationalize results on complex or simulated wastewaters has appeared. In consequence, models are not widely available nor have they yet received widespread acceptance as a method of analysis and reporting. To ameliorate this situation we here report a summary of important kinetic behaviors characteristic of individual chemical and biological kinetics, and provide experimental examples from recent works which illustrate the utility of such simple kinetic forms to construct two step treatment engineering models for complex wastewater and waters.

Keywords
Chemical oxidation; biological oxidation; process integration

Introduction
With more than 100 literature examples now available over the last decade to indicate the plausibility, and at times, the utility of sequential chemical and biological oxidation for recalcitrant wastewaters, the basic principle is clearly visible in the research community, and by now demonstrated over a variety of single compounds (e.g., chlorophenols, nitroaromatics, pesticides, synthetic dyes, etc) and multicomponent feed streams (effluents from textile mills, paper mills, tannery, vinasse and olive mills, pesticide wastewaters, etc.). See the reviews by Scott and Ollis (1995, 1997) of experimental examples and the economic estimates proposed by Esplugas and Ollis (1997).

To move this suggestive literature into a form more susceptible for use in chemical and bioreactor design, as well as in formulation of associated process control and integration strategies, and process economics, the development of an acceptable and rational set of rate equations is required. Just as the reaction mechanism provides to the chemist an indication of structure versus reactivity patterns to be expected, so kinetic equations provide to the design engineer a basis for projecting kinetic expectations as reactor configurations and size, feed stream composition, and flow rates are varied.

The art of engineering kinetic choices has always been to select rate forms which reflect the important kinetic characteristics which are exhibited over the range of interest of the target pollutant. Here it is important to distinguish among rate models in common use for the target compounds, \( C_T \).

(a) Fundamental: derivable from an intimate knowledge of the sequence of elementary reactions occurring during reaction of \( C_T \).

(b) Empirical, but based on target compound \( C_T \) of known structure.

(c) Lumped or global variable model, in which all or a subgroup of compounds are treated in combinations as a single pseudo-compound in the rate equation(s). Examples here include conventional wastewater measures, such as BOD\(_5\), COD, TOC, and DOC.

As the destruction and mineralization by chemical and/or biological means is found to follow one or other kinetic law, the choice of reactor configurations and of process design...
suggests itself naturally, as noted in standard texts on chemical, biochemical and sanitary engineering.

It is time for the emerging field of sequential chemical and biological oxidation of biorecalcitrant feedstreams to move to this next important step of kinetic characterization. The acceptance of engineering modelling in new areas has always been problematic until a general range of workable models is demonstrated and found to reasonably describe existing studies in sufficient detail. We provide here examples of recent advances in this regard.

**Methods**

We now illustrate the arrival of this state by use of a two step approach:

1. statement of a brief summary of rate forms expected to commonly apply under appropriate circumstances, and
2. provision of satisfying examples which confirm or extend one or more such models.

Before beginning, identification of the real or pseudo-compound which is the target, \( T \), of the treatment is necessary in order to formulate rate equations to reduce its concentration, \( C_T \). Examples represented by the variable \( C_T \) in a kinetic rate equation might include:

- (a) a *specific compound* in a mixture (e.g., a legislated compound (carcinogen, mutagen, etc., known toxin to aquatic life, etc).
- (b) a *group of compounds* having a particular characteristic, e.g., absorbance in visible wavelengths (objectionable color), odor, biotoxicity, etc.
- (c) a *global variable* including up to all compounds, e.g., BOD, COD, etc.

**Table 1** Simple reaction engineering models for chemical oxidation

<table>
<thead>
<tr>
<th>( C_T ) = “target” compound</th>
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</thead>
<tbody>
<tr>
<td><strong>First order</strong></td>
</tr>
<tr>
<td>rate = ( r_T = k(C_T)^{1.0} )</td>
</tr>
<tr>
<td>(example UV-ozone or UV-peroxide at low ( C_T ) values)</td>
</tr>
<tr>
<td><strong>Zero order</strong></td>
</tr>
<tr>
<td>( r_T = k ) (not a function, ( f(C_T) ), of ( T ) concentration)</td>
</tr>
<tr>
<td>example: (ozonation at moderate ( C_T ); physical mass transfer limited)</td>
</tr>
<tr>
<td><strong>Half order</strong></td>
</tr>
<tr>
<td>( r_T = k(C_T)^{0.5} )</td>
</tr>
<tr>
<td>example: (ozonation at high ( C_T ); reaction enhancement of film mass transfer)</td>
</tr>
<tr>
<td><strong>Saturation</strong></td>
</tr>
<tr>
<td>( r_T = k C_T / (K_T + C_T) )</td>
</tr>
<tr>
<td>example: photocatalysis</td>
</tr>
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</table>

**Table 2** Simple reaction engineering models for biological oxidation

<table>
<thead>
<tr>
<th>( X ) = biomass concentration</th>
<th>( A ) = non-biodegradable reactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S ) = biodegradable reactant(s)</td>
<td>( \mu_{\text{max}} ) = max. specific growth rate((\text{time}^{-1}))</td>
</tr>
<tr>
<td><strong>Monod (saturation)</strong></td>
<td>( r_X = \mu_{\text{max}} X C_S / (K_S + C_S) )</td>
</tr>
<tr>
<td><strong>Monod plus endogenous maintenance and/or death</strong></td>
<td>( r_X = \mu_{\text{max}} X C_S / (K_S + C_S) - k_e X )</td>
</tr>
<tr>
<td>(example: activated sludge waste water oxidation)</td>
<td></td>
</tr>
<tr>
<td><strong>Monod with competitive inhibition by ( A )</strong></td>
<td>( r_X = \mu_{\text{max}} X C_S / (K_S + C_S + C_A/K_A) )</td>
</tr>
<tr>
<td><strong>Inhibition by excess biomass (Contois form), with maintenance</strong></td>
<td>( r_X = \mu_{\text{max}} X C_S / (B X + C_S) - k_a X )</td>
</tr>
</tbody>
</table>
Thus, depending on the feed stream, we have interest in conversion of specific compounds (e.g., benzo(a)pyrene, a carcinogen) individually or in a well or poorly defined groups, e.g., a mixture of chlorophenols or simply the COD or BOD₃ value of an initial mixture.

In a few instances where a complex mixture can be characterized by a modest number of biodegradable and non-degradable compounds, it may be possible to transform species concentrations analytically into global variables such as COD and BOD.

Our starting supply of rate equations, the initial tool set for the creation of models, is shown in Table 1 and Table 2 for chemical and biological conversions, respectively.

In a similar way, we may expect that a modest number of reactor configurations may be in use even in research, and thus the demonstration of each rate equation will be for a particular configuration. Its applicability to other configurations is commonly presumed in reactor design, but especially with mixtures, the plausibility of such assumptions needs continuous testing after the fact.

These common configurations appear in Table 3. The biological fill-and-draw sequence provides an alternate to the conventional activated sludge plants in common use for domestic wastewater treatment. In much laboratory work, well stirred batch reactors are common, with recirculation systems a subset of these. Immobilized biofilms provide examples of the final configuration, with mixed cultures in soil columns yet another realization of this last circumstance.

Several of these equations were used by Esplugas and Ollis (1993, 1996) and Scott and Ollis (1996) to demonstrate with sample calculations the existence of regions wherein two operations in sequence gave a kinetic performance superior to that obtained by a single reactor.

Having specified a plausible set of equations and configurations, let us explore some established or recent investigations which have supported this limited set of possibilities.

**Discussion**

**Chemical oxidation kinetics**

While a simple first order rate form was assumed by Esplugas and Ollis (1993, 1996) and Scott and Ollis (1996), other kinetic forms are known which may be non-linear, or even the sum of several terms representing several chemistries. For example, for UV/ozone/peroxide, the direct photolysis, ozone attack, and hydroxyl attack of the reactant have at times been represented as separate reaction rate forms, summed to give the overall rate.

With heterogeneous reactors, other limitations may arise and thereby affect the form of the kinetic rate equation. For photoreactors, light becomes limiting in high optical density feedstreams. Similarly, with ozonation, mass transfer of ozone itself may become a

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**Table 3** Ideal, simple reactor configurations

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Biological reactors</th>
</tr>
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<tbody>
<tr>
<td>continuous stirred tank reactor (CSTR)</td>
<td>CSTR (lab)</td>
</tr>
<tr>
<td>plug flow</td>
<td>recycle</td>
</tr>
<tr>
<td>batch</td>
<td>fill-and-draw sequence</td>
</tr>
<tr>
<td></td>
<td>immobilized biomass</td>
</tr>
<tr>
<td></td>
<td>batch</td>
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limiting factor. The most common example of the latter derives from a nearly zero ozone level in the bulk phase, with a non-reactive, physical mass transfer film limiting ozone dissolution and dispersion. This is described routinely by a rate form of zero order in $C_T$:

$$r_{O_3} = k_L a C^*_{O_3} ,$$

where $^*$ indicates local equilibrium value: $C^* \Leftrightarrow P_{O_3}$

and $r_A = r_{O_3} / Y$ where $Y$ relates ozone absorption to target pollutant disappearance.

As the feed concentration move to higher levels, reaction will occur even within the ozone liquid-side diffusion film. This case for sequential chemical plus biological oxidation has been noted recently by Beltran et al. (1999). Now, the physical ozonation mass transfer rate above is augmented by substrate presence in the ozone mass transfer layer, leading to a reactant concentration (e.g., COD) dependent enhancement factor (in square brackets below):

$$r_{COD} = k_L a C^*_{O_3} \left[ D_{O_3} (COD)^{0.5} / k_L \right].$$

As a result, integrating a plug flow gas bubble over its transit time through a presumably well mixed CSTR liquid phase produces a predicted behavior of

$$\log \left[ P_{out} / P_{in} \right] \text{ proportional to } (COD)^{0.5}$$

as was indeed demonstrated experimentally.

Hence at least three chemical reaction regimes are now demonstrated for chemical oxidations of biorecalcitrant mixtures leading to subsequent bioreactor feeds: first order (chemical reaction limit: slow reaction), zero order (physical mass transfer limit: faster reaction), and half order (mass transfer film enhancement; very fast reaction). This set of behaviors corresponds well to that established in other more studied areas of gas–liquid mass transfer with simultaneous liquid phase reaction.

**Biological rate equations**

Esplugas and Ollis (1996) first examined two CSTRs in series, assuming a first order reaction for the first, chemical CSTR, and a Monod form for the second, biological CSTR. Their equations analyzed the model network $A$(non-biodegradable) $\Rightarrow S$(biodegradable) $\Rightarrow CO_2,$ and allowed therefore for $A$ conversion only in reactor 1 and for $S$ conversion in reactor one and two. Their model exploration established regimens where two step performance eclipsed than of a single operation. They demonstrated as well the existence of two bioreactor washout criteria, the first, conventional value represented an excessive flow rate in the bioreactor which would washout or dilute out the resident bioculture, and the second, novel one arising from an excessively short residence time in the chemical reactor, thus producing insufficient biodegradable material to sustain a biomass culture in the second reactor. Their reaction network for two steady state CSTRs in series was thus

$$r_{cA} = k_A C_A$$

$$r_{cS} = -k_S C_S$$

$$r_{bS} = Y_{max} C_S / (K_S + C_S)$$

where subscripts c and b indicated chemical and biological reactors, respectively.

The Monod form (Table 2) was used successfully by Ledakowicz and Solecka (1999) for a relatively high COD system, arising from oxidation of a synthetic dye wastewater containing anthraquinone dye Acid Blue 40 C.I., an anionic detergent, a softening agent and mineral salts. These authors found two important results: first that using COD to represent biodegradable substrate and VSS as biomass measure, the simple Monod equation fit their data satisfactorily, and second, the same Monod form could also represent bioconversion of
the same synthetic feed when subjected either to prior ozonation or to UV-peroxide-oxygen pre-treatment (Table 4).

Their experimental results are reminiscent of those of earlier reports for ozonation followed by biotreatment. The difference is that here the authors went one step further, and reduced their data to easily transportable rate equations. Moreover, inspection of the three rate parameters shows the kinetics of the integration story: with increased oxidative pretreatments, a faster biomass growth occurs (increased $\mu_{max}$), accompanied by a larger biomass yield (more efficient biocatalyst production).

For moderate COD systems, the Monod equation with endogeneous maintenance and/or cell death has been found to fit kinetics of activated sludge treatment of domestic wastewater (Bailey and Ollis (1986), as well as other mixed wastes such as dissolved milk solids.

Where industrial wastewater are concerned, inhibitory behavior may be observed. The classic competitive inhibition of biodegradable intermediates $S$ being inhibited by a non-degradable compound (Table 2) has been noted often.

Biomass itself may appear to be self inhibiting, possibly because excess biomass takes up some unknown limiting factor for further biomass production (even perhaps simply diminishing dissolved oxygen levels), and such effects may be modelled empirically by the Contois equation of Table 2. This latter equation has recently been invoked by Beltran et al. (2000a, b) in their study of agroindustrial-domestic mixed wastewaters.

### Kinetic models of integrated system

No comparison of model versus experiment for the steady state sequential treatment of an actual or simulated effluent has yet been published. However, Esplugas and Ollis (1993, 1996), Scott (1994) and Scott and Ollis (1996) have explored the steady state performance predicted from simple models combining first order oxidation (Table 1) with various models of biological reaction including that of Monod (Table 2) and of competitive inhibition (Table 2). We therefore search for example experimental systems from the literature in which two step sequential batch or semi-continuous systems from laboratory scale have been obtained. While batch residence time in a lab stirred tank reactor (STR) and hydrodynamic holding time in continuous flow stirred tank reactors (CSTR) do not correspond exactly, due to the distribution of residence times in the flow configuration, the kinetics similarity can be striking, and suggestive of further study.

In particular, a recent study by Pulgarin et al. (1999) examined a semi-continuous conversion by photochemical oxidation (Fenton chemistry) of p-nitrotoluene-ortho-sulfonic acid (p-NTS), followed by biological oxidation with an immobilized activated sludge culture. A photo-oxidation treatment time of 50 to 125 minutes, followed by bio-oxidation on a fixed bed operated in recirculating mode (similar to a CSTR) for periods of 1.04 to 2.64 hours produced plots of DOC removal versus photoreactor alone, and versus a combined photoreactor plus bioreactor combination which were very similar to an earlier simulation of Scott (1994) for the continuous process using first order oxidation and Monod rate forms. In a particular instance, the former found that combining the two steps produced the same 76% DOC conversion obtained with photoreaction alone, but gaining a reduction in

### Table 4 Bioreactor monod model values for various chemical reactor pretreatments

<table>
<thead>
<tr>
<th>Treatment</th>
<th>$\text{COD}_i$ (mg O$_2$/dm$^3$)</th>
<th>$\text{COD}_f$ (mg O$_2$/dm$^3$)</th>
<th>VSS$_i$</th>
<th>VSS$_f$</th>
<th>$\gamma$ mgVSS/mg O$_2$</th>
<th>$K_S$ mg O$_2$/dm$^3$</th>
<th>$\mu_{max}$ mg O$_2$/mgVSS-hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>1465</td>
<td>1370</td>
<td>1080</td>
<td>1130</td>
<td>0.53</td>
<td>3378</td>
<td>0.036</td>
</tr>
<tr>
<td>ozone</td>
<td>1150</td>
<td>800</td>
<td>1000</td>
<td>1175</td>
<td>0.45</td>
<td>759</td>
<td>0.055</td>
</tr>
<tr>
<td>UV/H$_2$O$_2$/O$_2$</td>
<td>1400</td>
<td>1080</td>
<td>350</td>
<td>600</td>
<td>1.10</td>
<td>469</td>
<td>0.07</td>
</tr>
</tbody>
</table>
photoreactor holding time (power) of 60%. From similar curves generated by Scott, his simulation example indicates that an approximately 78–80% conversion should be obtained either by photoreactor alone, or by photoreactor plus bioreactor in series, the last configuration giving about a 70% reduction in photoreactor holding time. The overall similarity between the earlier model simulation of continuous flow CSTRs by Scott (1994) for various photoreactor residence times, and the semi-continuous (photoreactor + bioreactor) results of Pulgarin et al. (1999) is striking, and indicative of fresh progress in this intriguing, and emerging area.

**Further motivations for two step treatments**

We have previously argued that a two step treatment is suggested in the following instances.

1. The feedstream is biorecalcitrant, or totally non-biodegradable by intracellular enzymes. Partial oxidation should enhance biodegradability by providing smaller, more oxidized species which resemble natural metabolic intermediates.

2. The feedstream is inhibitory to biocultures. Partial oxidation destroys the (parent) inhibitory compound, and usually produces treated effluents of much reduced toxicity. Additional motivations are provided by recent literature examples, broadening the feedstreams which may be candidates for such process integration.

3. The parent compound is insoluble. Weng et al. (2000) reported that the insoluble carcinogen, benzo[a]pyrene, can be treated with ozone to partially oxidize and thereby produce more soluble products, which again are further processed to reduce molecular weight, open hydrocarbon rings, and produce biodegradable products.

4. Similarly, the parent compound is soluble, but polymeric of molecular weight sufficient to prevent uptake by a bioculture. Thus, thermally catalyzed Wet Air Oxidation of non-biodegradable polyethylene glycol (MW = 10,000) solutions produced substantially biodegradable effluent solutions (Mantzavinos et al., 1999).

**Conclusion**

Progress in design of integrated wastewater systems involving sequential chemical and biological operations will depend centrally upon the creation of demonstrated rate equations to describe the interplay of reactants with oxidants and (bio) catalysts within, and between the reactors. We have here provided a small number of such equations which have been used traditionally in single reactor studies, common in both the chemical and biological reactor literatures. We have further summarized our treatments of situation types previously modelled, including the effects of reactant concentration and biomass inhibition, of flow rate variation, and of biomass recycle and biomass immobilization. Finally, we have shown that more recent literature contains further examples which we argue carries us nicely along the desired path of creating credible rate equations for use in process integration and design.

**Acknowledgement**

The author thanks Ecole des Mines, Centre Poudres et Procedes, Albi, France, for a Visiting Professorship during which this paper was prepared.
References