

# Innovative reactor technology for selective oxidation of toxic organic pollutants in wastewater by ozone

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**Abstract** Ozonation can be a suitable technique for the pre-treatment of wastewater containing low concentrations of toxic or non-biodegradable compounds that cannot be treated with satisfactory results when only the traditional, less expensive biological techniques are applied. In this case, the oxidation process has to be made as efficient as possible, in order to reduce the costs of ozone addition and energy use. An efficient oxidation process with ozone can be obtained by focusing the oxidation with ozone selectively on the direct oxidation of toxic pollutants and to minimize ozone losses due to the decay of ozone in water. Supported by data of the rate constants of the reactions involved, a mathematical model was developed. It quantifies the ozone consumption by the process, and the share of ozone consumption by undesired side reactions, in several different reactor systems. Results obtained with this model indicate that a plug flow reactor (PFR) will be the most efficient design for the oxidation reactor. As an alternative, the cascaded tank reactor system (CTR), in which the ozone feed may be realized with less practical problems, might be considered. The traditional continuous flow stirred tank reactor (CFSTR) is shown to be the least efficient system.

**Keywords** Organic pollutants; ozonation; reactor optimization; selectivity

## Introduction

During the last two decades an increasing interest in advanced physical–chemical processes for wastewater treatment has been observed. There are several reasons for this increasing interest. First, with conventional aerobic and anaerobic biological wastewater treatment technologies many industrial wastewater streams can not be treated to a high effluent quality at low costs (Gulyas, 1997). Physico–chemical wastewater treatment systems are often considered as an appropriate alternative or can be applied as an additional treatment system (Scott and Ollis, 1995; Heinzle *et al.*, 1995; Kayser, 1996; Esplugas *et al.*, 1996). When the presence of strongly toxic organic compounds in the wastewater will disturb the biological treatment process completely this physico–chemical treatment step has to be applied as a pre-treatment process (Wang *et al.*, 1989). A lot of research is directed at solving problems optimizing such physico–chemical pre-treatment or post-treatment processes.

The second reason for the increased interest in the physico–chemical processes is that the water management approach within the industry is focusing more and more on closed-loop systems, including the reuse of treated wastewater streams. However, in this case very often a biological process or a combination of biological processes cannot achieve the required effluent quality. To obtain a water quality sufficient for reuse it will often be necessary to include a physico–chemical treatment step. A large variety of physico–chemical processes or process steps exist which can be applied in practice in combination with biological processes. Such well known processes are: membrane filtration, precipitation, flotation, adsorption, chemical oxidation, electrodialysis and ion exchange. Each process has its own specific field of application. In the case of strongly toxic soluble pollutants, like chlorinated aromatics, phenols, dyes, pesticides, etc., advanced oxidation processes

(AOPs) may be suitable destruction techniques. In general, these AOPs are rather expensive due to the amounts of chemicals that are required and due to the costs of the energy needed for these processes. Especially in the case of wastewaters containing small amounts of such pollutants, in addition to large quantities of other easily oxidizable and biodegradable compounds, the application of only a physico-chemical treatment step to completely remove all pollutants will, in general, not be feasible economically. In that respect there is a strong need for oxidation processes which can selectively oxidize toxic pollutants, prior to a biological treatment step.

This paper deals with the selective partial oxidation of toxic compounds by ozone in wastewater, which also contains large amounts of non-toxic easily biodegradable pollutants. For a technically and economically optimal reactor design three aspects are relevant: reaction kinetics, reactor type and process conditions. The reactor design for the oxidation process can be optimized regarding both the selectivity of the reaction and the use of ozone when the reaction kinetics of the oxidation of the wastewater constituents are known. Data regarding these reaction kinetics have been taken from literature, and were supplemented by experimental data for various organic compounds, such as substituted phenols and benzoic acids (Boncz *et al.*, 1998). Taking these data into account, a model is built which will allow optimization of the process design in such a way that an organic pollutant will be oxidized by ozone selectively with a minimum amount of ozone.

### Reaction rate constants

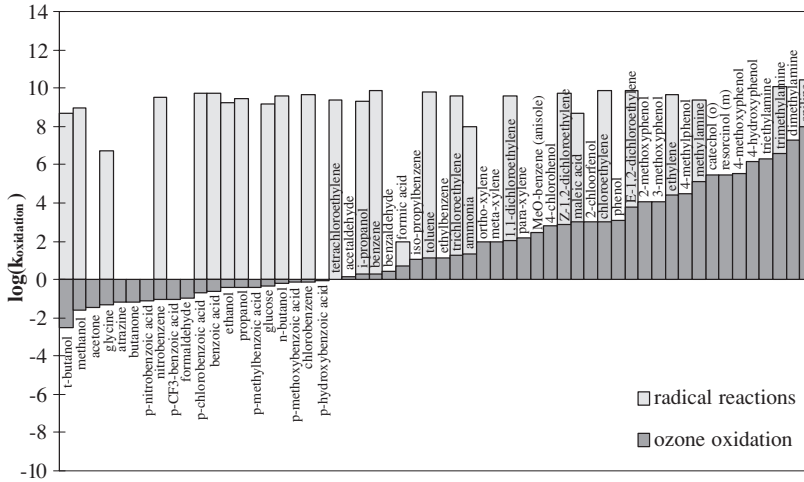
In an ozonisation reactor three reaction types can occur: (1) reactions in which organic compounds are directly oxidized by ozone; (2) reactions in which organic compounds are oxidized by radicals, mainly hydroxyl radicals; and (3) reactions leading to the decomposition of ozone into oxygen, which leads to intermediate radicals.

The process design can be optimized when data concerning the relevant reaction kinetics are available. These include both the reactivity of the organic compounds with ozone and the kinetics of the decay of ozone in water (Staehelin and Hoigné, 1982).

The reactions involved in the decomposition of ozone have been studied in detail by Hoigné and coworkers (Staehelin and Hoigné, 1982; Staehelin, 1983). Numerous reaction rate constants can be found in the literature for the first two categories of reactions (Hoigné and Bader, 1983a, 1983b; Yao and Haag, 1991; De Laat *et al.*, 1996). In addition to these data measurements were performed to further quantify the reaction rates of substituted benzoic acids and phenols, which occur in many industrial wastewaters, under different reaction conditions. A more detailed description of these experiments can be found in Boncz *et al.* (1999). From these experimental data Hammett-relations could be established to quantify the structure-reactivity relationships (Gurol, 2000). These will make it possible to calculate reaction rate constants for compounds of which the reaction rate constants are not presented in the literature.

An overview of a large number of reaction rates, both measured and obtained from the literature, is given in Figure 1. It is clearly visible that the oxidation with ozone will be far more selective than the oxidation with hydroxyl radicals derived from this oxidant. Where the reaction rate constants of the reaction with ozone differ by ten orders of magnitude, the reaction rate constants for the radical reaction only differ by three orders of magnitude. The dominant type of oxidation process (oxidation by molecular ozone or oxidation by hydroxyl radicals) will depend strongly on the relative reactivities of the different compounds present in the wastewater.

When studying these data a few trends can be observed: aliphatic alcohols and acids hardly show any direct reactivity with ozone, aromatic acids are not very reactive. Phenols and amines (both aromatic and non-aromatic) react with ozone at a very high rate, and will

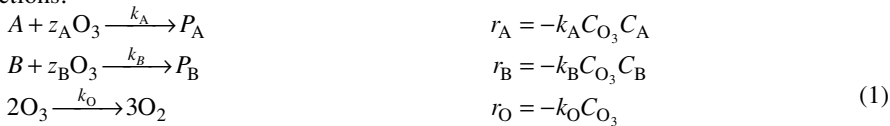


**Figure 1** Reaction rate constants for the reaction rates of 55 organic compounds with ozone or the hydroxyl radical in water. When no reaction rate constant for the rate of the reaction of one of the organic compounds with the hydroxyl radical is known, the bar is omitted

most likely be oxidized by a direct reaction in all situations, even when the reaction conditions are such that a relatively high concentration of radicals should be produced. When these fast reacting compounds are present, the process will most likely be mass-transfer controlled, although this will not significantly affect the selectivity of the process, unless steric factors play a role in the system (Gould, 1987). Here we will only consider the situations where the direct reaction mechanism (oxidation by the ozone molecule) is the predominant degradation route and degradation by the hydroxyl radical can be neglected.

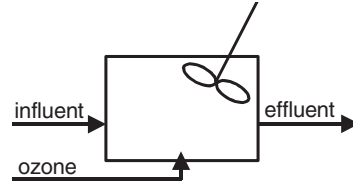
**Reactor systems optimization**

The oxidation process in a wastewater containing small amounts of a toxic component *A* and a high concentration of a non-toxic easily biodegradable pollutant *B* involves three reactions:



in which *z<sub>A</sub>* and *z<sub>B</sub>* are stoichiometric coefficients, *C<sub>A</sub>*, *C<sub>B</sub>* and *C<sub>O<sub>3</sub></sub>* are the concentrations of compound *A*, *B* and ozone respectively, and *P<sub>A</sub>* and *P<sub>B</sub>* are the oxidation products. *r<sub>A</sub>*, *r<sub>B</sub>* and *r<sub>O</sub>* are the reaction rates of the three reactions, in which *k<sub>A</sub>*, *k<sub>B</sub>* and *k<sub>O</sub>* are the reaction rate constants. As already mentioned, the selectivity which can be reached and thus the amount of ozone used in a continuous reactor system depends both on differences in chemical reaction kinetics of the compounds present, the reactor design and the applied process conditions.

Regarding the process design several reactor types and reactor configurations may be considered. In this paper we will discuss three different reactor systems: the continuous flow stirred tank reactor (CFSTR), the plug flow reactor (PFR) and the cascaded tank reactor (CTR). Diagrams of these reactor systems are shown in Figures 2, 3 and 5, respectively. For all these three reactor systems it is assumed that the ozone is fed as a gas, optimal gas–liquid mass transfer occurs, and there is no loss of ozone via the gas phase. It is further assumed that the liquid phase mixing conditions and the ozone distribution are optimal and that all reactions occur in the bulk liquid. Component *A* has to be converted to reach a



**Figure 2** Schematic view of a CFSTR

certain effluent concentration  $C_{Ae}$ , defined by the maximum allowed concentration of this compound in the effluent that is fed to a bioreactor system. The reaction is selective with  $k_A > k_B$ . The third reaction, the spontaneous decay of ozone, is assumed to be first order according to the literature (Staelin, 1983).

### Continuous flow stirred tank reactor (CFSTR)

We first consider the continuous flow stirred tank reactor (CFSTR). The ozone consumption per unit time  $\Phi_{\text{ozone}}$  is given by:

$$\Phi_{\text{ozone}} = z_A Q (C_{Ai} - C_{Ae}) + z_B Q (C_{Bi} - C_{Be}) + (Q + k_O V) C_{O_3e} \quad (2)$$

in which  $Q$  is the flow through the reactor,  $C_{Ai}$ ,  $C_{Ae}$ ,  $C_{Bi}$ , and  $C_{Be}$ , are the influent and effluent concentrations of component  $A$  and component  $B$  respectively.  $C_{O_3e}$  is the effluent concentration of ozone and  $V$  is the volume of the reactor.  $\Phi_{\text{ozone}}$  can be expressed in kinetic constants and influent composition. From mass balances over the reactor and the conversion rate equations (Eq. (1)) it can be calculated that with a given residence time  $\theta = V/Q$  the conversion of component  $A$  and component  $B$  are given by:

$$\frac{C_{Ae}}{C_{Ai}} = \varepsilon = \frac{1}{1 + k_A C_{O_3e} \theta}$$

$$\frac{C_{Be}}{C_{Bi}} = \frac{1}{1 + k_B C_{O_3e} \theta} \quad (3)$$

The value of the conversion factor  $\varepsilon$  is determined by the required efficiency of the conversion of component  $A$ . By substituting Eq. (3) into Eq. (2) we find the ratio of the total ozone consumption to the amount of ozone needed for the oxidation of component  $A$ , defined as the ozone consumption factor (OF):

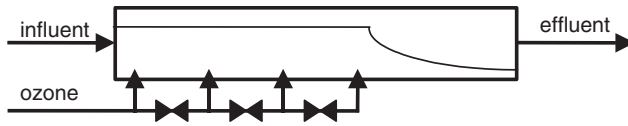
$$\text{OF} = \frac{\Phi_{\text{ozone}}}{Q z_A (C_{Ai} - C_{Ae})} = 1 + \frac{(z_B C_{Bi} / z_A C_{Ai})}{1 + \varepsilon (k_A / k_B - 1)} + \frac{k_O}{z_A k_A C_{Ai} \varepsilon} + \frac{1}{z_A k_A C_{Ai} \varepsilon \theta} \quad (4)$$

With given flow  $Q$  and influent concentrations  $C_{Ai}$  and  $C_{Bi}$ , and the required efficiency  $\varepsilon$  the reactor volume and ozone consumption can be optimized from this equation.

### Plug flow reactor (PFR)

In a plug flow reactor (PFR) the process can be further optimized by taking into account the spatial distribution of ozone. In the case of a PFR the ozone consumption rate  $\Phi_{\text{ozone}}$  can be given by an equation comparable to that for the CFSTR:

$$\Phi_{\text{ozone}} = Q z_A (C_{Ai} - C_{Ae}) + Q z_B (C_{Bi} - C_{Be}) + V k_O (C_{O_3}) + Q C_{O_3e} \quad (5)$$



**Figure 3** Schematic view of a PFR. The line in the reactor indicates the ozone concentration as a function of the reactor length

Here,  $\langle C_{O_3} \rangle$  is the average ozone concentration in the PFR. From the conversion rate equations and mass balances it can be derived that:

$$\begin{aligned}
 u \frac{dC_A}{dx} + k_A C_{O_3} C_A &= 0 \\
 u \frac{dC_B}{dx} + k_B C_{O_3} C_B &= 0
 \end{aligned}
 \tag{6}$$

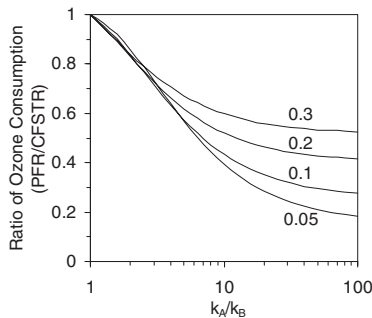
in which  $u$  is the linear flow velocity. These differential equations (Eq. (6)) can be solved by substituting the independent variable  $\mu = \int_0^x C_{O_3} dx$  resulting in:

$$\begin{aligned}
 \frac{C_{Be}}{C_{Bi}} &= \varepsilon^{k_B/k_A} \\
 \langle C_{O_3} \rangle &= \frac{1}{k_A \theta} \ln\left(\frac{1}{\varepsilon}\right)
 \end{aligned}
 \tag{7}$$

Substitution of Eq. (7) into Eq. (5) yields the ozone consumption factor (OF) for the PFR:

$$OF = \frac{\Phi_{\text{ozone}}}{Q z_A (C_{Ai} - C_{Ae})} = 1 + \frac{z_B C_{Bi}}{z_A C_{Ai}} \left( \frac{1 - \varepsilon^{k_B/k_A}}{1 - \varepsilon} \right) + \frac{k_O \ln(1/\varepsilon)}{z_A k_A C_{Ai} (1 - \varepsilon)} + \frac{C_{O_3e}}{z_A C_{Ai} (1 - \varepsilon)} \tag{8}$$

From this analysis we see that the selectivity is independent of the spatial distribution of the ozone concentration. Minimal ozone dosage can be obtained when  $C_{O_3e} = 0$ . This can be achieved by dividing the PFR into two zones (see Figure 3): the first zone, to which the influent is fed and in which ozone is introduced up to the solubility, and a second zone without introduction of ozone in which the ozone concentration will decrease to  $C_{O_3e} = 0$ . The consumption of ozone by component  $B$  is lower when using a PFR instead of a CFSTR, as can be calculated from the second terms in the right-hand side of Eqs (4) and (8). In Figure 4 the ratio of the ozone consumption by the conversion of component  $B$  in a PFR and a CFSTR is given in dependence on the ratio  $k_A/k_B$  and  $\varepsilon$ . When a high conversion of component  $A$  is desired ( $\varepsilon \ll 1$ ) and the  $k_A$  and  $k_B$  differ by more than one order of magnitude,



**Figure 4** Ratio of the ozone consumption by the conversion of component  $B$  (second term in the right-hand side of Eqs (4) and (8)) in a PFR and a CFSTR as a function of  $k_A/k_B$ . The parameter is  $\varepsilon = C_{Ae}/C_{Ai}$

which is mostly the case when only oxidation by molecular ozone is considered (Figure 4), the ozone losses due to the conversion of component *B* can be reduced by more than 90%.

The absence of mixing (PFR) leads to an optimal ozone usage. If it is assumed that in the PFR the concentration at the exit approaches 0 (optimal conditions) then the amount of ozone self-decomposition in the PFR can be compared to that in the CFSTR using the third term in the right-hand side of Eqs (4) and (8). From this comparison it is clear that in the CFSTR more ozone will be lost due to self-decomposition than in the PFR.

#### Cascaded tank reactor (CTR)

To get more insight into the effects of mixing we consider a third design: the cascaded tank reactor (CTR) (Figure 5). This design consists of a series of CFSTRs, which can differ in size and ozone concentration. For this reactor system the ozone consumption is given by Eq. (9):

$$\Phi_{\text{ozone}} = Qz_A(C_{Ai} - C_{Ae}) + Qz_B(C_{Bi} - C_{Be}) + \sum_{i=1}^n V_i k_O C_{O_3i} + QC_{O_3n} \quad (9)$$

in which  $n$  is the number of tanks and  $V_i$  and  $C_{O_3i}$  are the volume and the ozone concentration of tank  $i$ . From a mass balance over each tank it can be derived that:

$$\varepsilon = \frac{C_{Ae}}{C_{Ai}} = \prod_{i=1}^n \frac{1}{1 + k_A C_{O_3i} \theta_i}$$

$$\frac{C_{Be}}{C_{Bi}} = \prod_{i=1}^n \frac{1}{1 + k_B C_{O_3i} \theta_i} \quad (10)$$

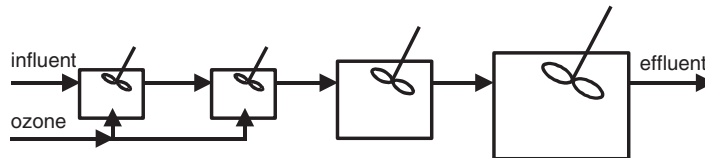
After substituting Eq. (10), giving the removal efficiencies of the components *A* and *B* after a series of  $n$  reactors into Eq. (9),  $\Phi_{\text{ozone}}$  can be optimized by differentiation with respect to  $\theta_i$  and  $C_{O_3i}$ . From symmetry arguments we find that minimal ozone consumption is reached when the following condition is met for each tank:

$$k_A \theta_i C_{O_3i} = \varepsilon^{-1/n} - 1 \quad (11)$$

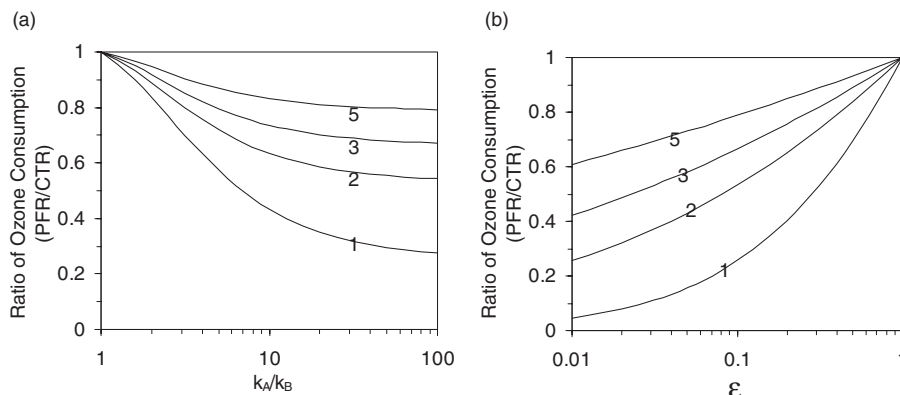
Given the fact that  $k_A$  is a constant this indicates that a CTR will perform optimally when all tanks are characterized by an identical product of  $\theta_i C_{O_3i}$ . The ozone consumption factor for this reactor system is given by:

$$\text{OF} = \frac{\Phi_{\text{ozone}}}{Qz_A(C_{Ai} - C_{Ae})} = 1 + \frac{z_B C_{Bi}}{z_A C_{Ai}} \frac{1 - \left(1 + \left[k_B (\varepsilon^{-1/n} - 1) / k_A\right]\right)^{-n}}{1 - \varepsilon} + \frac{k_O}{z_A k_A C_{Ai}} \frac{n(\varepsilon^{-1/n} - 1)}{1 - \varepsilon} + \frac{C_{O_3n}}{z_A C_{Ai}(1 - \varepsilon)} \quad (12)$$

Optimal ozone usage is reached when  $C_{O_3n}$  approaches 0, which means that the last tank(s) should have a large residence time and no ozone feed. A comparison between the CTR model and the PFR model regarding the ozone consumption is given in Figure 6.



**Figure 5** Schematic view of the cascaded tank reactor



**Figure 6** (a) Ratio of the ozone consumption by the conversion of component B (second term in the right-hand side of Eqs (8) and (12)) in a PFR and a CTR at  $\epsilon = C_{Ae}/C_{Ai} = 0.1$  as a function of  $k_A/k_B$ . (b) The ozone consumption ratio for the spontaneous decay of ozone (third term in the right-hand side of Eqs (8) and (12)) as a function of  $\epsilon = C_{Ae}/C_{Ai}$ . The parameter in both figures is the number of tanks

With a moderate number of tanks the efficient use of ozone for the oxidation of component B in the PFR can be approximated by this set-up. In Figure 6 a comparison is also made between the ozone losses by spontaneous decay in different reactor systems. Minimal losses are obtained in a PFR, while the losses are maximal for a CFSTR. From Eq. (4), it can be derived that in the case of a CFSTR the ratio of the ozone losses by decomposition and losses in the effluent is given by  $k_O\theta$ . Because in most cases  $k_O \ll 1$ , ozone losses in the effluent of a CFSTR are inevitably high.

All three terms which contribute to ozone losses are minimal in a PFR. The relative importance and the absolute values of these terms and the ozone consumption factor can be calculated from Eqs (4), (8) and (12), provided that the reaction rate constants and the reaction conditions are known.

## Conclusions

When toxic compounds are present in wastewaters that further contain relatively high concentrations of biodegradable compounds, ozone can be used as a pre-treatment step for the selective oxidation of toxic pollutants. To keep the process economically feasible, it has to be applied as efficiently as possible. Supported by literature data on reaction kinetics and reactor design, a mathematical model was developed to investigate the efficiency of various reactor configurations. The model predicts that the oxidation process is most efficiently realized by application of a plug flow reactor (PFR) design. As an alternative to the PFR, the cascaded tank reactor (CTR) system may be considered. In this system, the high efficiency of the PFR can be approximated whilst at the same time the ozone can be transferred easily and in a very well controlled way into the wastewater that is being treated. The traditional continuous flow stirred tank reactor (CFSTR) is the least efficient system.

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