OZONE AND AOP REACTORS DESIGN

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Contents

Summary

Fundamentals of ozone mass transfer from gas into water and in aqueous systems have briefly been discussed. Special emphasis has been put on mass transfer with accompanying chemical reactions pointing out kinetic aspects that characterize the AOPs. The role of major factors that are responsible for generation of hydroxyl radicals in ozone-based AOPs has been described. Final sections are devoted to design principles of the ozone-based AO reactors and some remarks on practical applications of the AOPs.

1. Introduction

Vast majority of the ozone technical applications concerns its activity within the liquid phase. Historically the earliest one was the treatment of drinking water. In this case ozone has mainly been used for disinfection purposes and because of its supreme ability in inactivation of microorganisms that usage of ozone has still remained an important step in drinking water treatment as well as in wastewater treatment. As it has been pointed in the previous sections of this chapter, ozone belongs to the most powerful oxidants. Its oxidative ability can frequently be enhanced by combining it with other oxidants or physical agents (e.g. hydrogen peroxide, UV radiation, catalysts, activated carbon), especially when synergistic effects occur, giving rise to more efficient generation of hydroxyl radicals, the feature essential to all processes of advanced oxidation. By increasing the rate of reactions by 2 or 3 orders of magnitude than that with either oxidants or UV applied separately many organic compounds that are normally resistant to powerful oxidants can be destroyed in a relatively short time.

First practical applications of AOP (UV/O_3) concerned water purification, while in wastewater treatment this technology was developed for removal of cyanides in wastewaters from electroplating and color photographic processes. Full-scale installations based on AOPs have been used in both military and industrial sites for remediation of groundwater and industrial wastewaters. The AOPs enable to effectively destroy toxic pollutants originating from petroleum products, industrial solvent-related organics, e.g. trichloroethylene (TCE), dichloromethylene (DCE), trichloroethane (TCA), PCBs (polychlorinated biphenyls) or explosive wastes. In water purification major concern as priority pollutants because of their potential toxicity and health hazards involve phenols, polyaromatic hydrocarbons (PAHs), pesticides (*s*-triazine compounds), volatile organochlorine compounds (VOC), 1,4-dioxane etc.

In general, for ozone-based AOPs ozone is expected to act within the liquid (mainly aqueous) phase, therefore it should effectively be introduced there from the gaseous phase. Ozone transfer from the gas phase into the liquid one and dissolving there corresponds to the widely known case of absorption process. Therefore, design of ozone transfer from gas into water should be considered based on the principles and rules that govern the effective absorption process. Possibly high effectiveness of the ozone absorption process (> 90%) is required since ozone generation is accomplished by direct using of electric energy (typically corona discharge process) and residual (unabsorbed) ozone must not be released to the atmosphere (environmental and health issues).

2. Fundamentals of Ozone Mass Transfer into Water and in Aqueous Systems

Theoretical background of ozone transfer from the gas phase into the liquid phase (water and/or aqueous solutions) is described in Chapter 5. In most cases two-film model of mass transfer is commonly assumed when considering processes that involve ozone absorption into the aqueous systems. The fundamental equations describing the mass transfer rate are as follows:

$$N_{\mathrm{O3}} = k_{\mathrm{G}} A\left(C_{\mathrm{G}} - C_{\mathrm{Gi}}\right) = k_{\mathrm{L}} A\left(C_{\mathrm{Li}} - C_{\mathrm{L}}\right) \tag{1}$$

$$N_{\mathrm{O3}} = K_{\mathrm{G}} A\left(C_{\mathrm{G}} - C_{\mathrm{G}}^{*}\right) = K_{\mathrm{L}} A\left(C_{\mathrm{L}}^{*} - C_{\mathrm{L}}\right) \tag{2}$$

The mass transfer coefficients $k_{\mathrm{G}}, k_{\mathrm{L}}, K_{\mathrm{G}}, K_{\mathrm{L}}$ are reciprocal to the mass transfer resistances, i.e. local in each phase ($k_{\mathrm{G}}, k_{\mathrm{L}}$) or overall ($K_{\mathrm{G}}, K_{\mathrm{L}}$). At the interface a thermodynamic equilibrium between the contacting phases is assumed, cf. Eq. (3).

$$C_{\mathrm{Li}} \cong \frac{C_{\mathrm{G}}^{*}}{H} = C_{\mathrm{L}}^{*} \tag{3}$$

The values of C_{G}^{*} and C_{L}^{*} are also estimated from Eq. (3) using the corresponding bulk concentrations, C_{L} and C_{G}, respectively.

Since ozone is slightly soluble in water and ozone mass transfer is controlled by the liquid phase, in ozone – aqueous systems $K_{\mathrm{L}} \cong k_{\mathrm{L}}$, and also $C_{\mathrm{Gi}} \cong C_{\mathrm{G}}$.

Equations (1) and (2) contain the mass transfer area (A), usually of an unknown parameter. Therefore, it is more feasible to operate with the liquid phase volume and to combine the interfacial area with the mass transfer coefficient to obtain the so-called volumetric mass transfer coefficient $k_{\mathrm{L}}a$. Now Eq. (1) can be expressed by:

$$N_{\mathrm{O3}} = \left(k_{\mathrm{L}}a\right)\left(C_{\mathrm{L}}^{*} - C_{\mathrm{L}}\right) V_{\mathrm{L}} \tag{4}$$

Eq. (4) is the basis of the mass transfer rate estimation when designing of any mass exchanger (absorber or contactor) is considered. In order to apply such an equation in practice one needs to know the following parameters:

- $k_{\mathrm{L}}a$ - the volumetric mass transfer coefficient (its value depends on the hydrodynamic conditions in the liquid phase),
- C_{L} - the concentration profile (distribution) in the liquid phase in a contactor which depends on the mixing conditions in that phase,
- C_{L}^{*} - the equilibrium concentration in the liquid phase (it depends on the gas phase concentration, temperature, pressure and the liquid phase matrix).

When ozone absorption is accompanied by irreversible chemical reactions, depending on the system conditions different reaction regimes will take place. Typically, the molecular reaction of ozone with dissolved compound B can be assumed as bimolecular reactions, where ν is the stoichiometric ratio. The resulting reaction kinetics scheme can be formulated as follows.

$$\mathrm{O_3} + \nu\,\mathrm{B} \rightarrow \text{products} \tag{5}$$

$$r_{\mathrm{O3}} = k_2\,[\mathrm{O_3}][\mathrm{B}] \tag{6}$$

$$r_{\mathrm{B}} = \nu\,k_2\,[\mathrm{O_3}][\mathrm{B}] \tag{7}$$

In these equations k_2 is the second-order reaction rate constant of ozone with the compound B. The values of k_2 for many chemical compounds can be found in the references (e.g. Beltrán, 2004; Hoigné, 1998; Von Gunten and Laplanche, 2000).

The film theory of mass transfer (also for the penetration models) accompanied by chemical reactions in the liquid phase has been subject to numerous studies resulting in derivation of the expressions or graphs for the mass transfer rate in the case of a first-order, pseudo first-order or second-order reactions kinetics. For practical considerations the concept of the enhancement factor, *E*, has been introduced, defined by the following relation

$$E = \frac{k_{\mathrm{L,chemical\ absorption}}}{k_{\mathrm{L,physical\ \ absorption}}} \tag{8}$$

As it is seen from Eq. (8) the enhancement factor expresses how much the physical mass transfer coefficient is increased by the presence of chemical reaction. The value of the enhancement factor depends on the reaction regime and the process parameters such as concentrations and diffusivities of ozone and compound B in the liquid phase, k_{L}, a, k_2, ozone concentration at the gas-liquid interface ($C_{\mathrm{LA,i}}$).

The determination of E depends on the reaction regime and requires the evaluation of the process parameters such as the film mass transfer coefficient, k_{L}, the reaction rates constants, k_2, diffusivity coefficients, ozone solubility in the liquid phase. The knowledge of chemical regimes can be deduced from the Hatta dimensionless number, Ha. For a second-order irreversible reaction it is defined by

$$Ha = \frac{\sqrt{D_{\mathrm{O3}}.k_2.[\mathrm{B}]}}{k_{\mathrm{L}}} \tag{9}$$

Other dimensionless numbers that can be useful for the characterization of the kinetic regime are as follows:

$$R = \frac{k_2[\mathrm{B}]}{k_{\mathrm{L}}a}; \quad \text{Damköhler number } Da = k_{\mathrm{L}}a \cdot \tau; \quad E_{\mathrm{i}} = 1 + Z \; ; \quad Z = \frac{D_{\mathrm{B}}[\mathrm{B}]}{\nu \, D_{\mathrm{O3}} \, C_{\mathrm{L}}^*}$$

where τ is the hydraulic residence time of the liquid inside the contactor; E_{i} is the instantaneous enhancement factor, and C_{L}^* is the ozone concentration at the gas-liquid interface (equilibrium value with respect to the gas phase concentration in the bulk). In terms of the range of the Hatta number values, typical conditions can be summarized as follows:

- $Ha < 0.02$ No reaction occurs in the liquid film. The reaction is very low and takes place into the bulk of the liquid. The enhancement factor E is equal to 1.The ozone concentration C_{L} is given by the relation: $C_{\mathrm{L}}{=}C_{\mathrm{L}}^*/(1+R+1/Da)$. If the condition $R+1/Da \ll$ is fulfilled ($R<0.1$ or $Da>100$), then the dissolved ozone concentration is nearly equal to the saturation value, C_{L}^*. The liquid film offers no resistance and the gas absorption rate is determined by the chemical kinetics alone.
- $0.02 < Ha < 0.3$ The reaction takes place into the bulk of the liquid. Mass transfer rate is slow compared to the reaction rate. If the condition $R+1/Da \gg$ is fulfilled, the concentration C_L can reach a very small value, close to zero. However, the reaction is too slow to enhance the rate of absorption, and $E = 1$.
- $0.3 < Ha < 3$ A part of the reaction takes place in the liquid film and another part in the bulk of the liquid, E is greater than 1.
- $Ha > 3$ The reaction is very fast and occurs entirely in the liquid film; no gas reaches the bulk fluid. The concentration of ozone is zero in the bulk of the liquid, and E is greater than 1.The gas absorption rate is given by

  $$N_{\mathrm{O3}} = E \, k_{\mathrm{L}} a \, C_{\mathrm{L}}^* \, V_{\mathrm{L}} \tag{10}$$
- $Ha > 3$ and $E_{\mathrm{i}} > 2Ha$ The second order reaction can be considered as a pseudo first order reaction, the concentration of the compound B can be considered as constant everywhere. In these conditions $E = Ha$.

Graphical representation for a dependence of $E = f(Ha, E_{\mathrm{i}})$ published by Van Krevelen and Hoftijzer in 1948 for an irreversible second-order chemical reaction and some approximations are given in Chapter 5.

When using these expressions or graph it is important to realize that the Hatta number depends on the concentration of component B. In a batch reactor this concentration varies with time, thus during a batch mode experiment different reaction regimes are encountered. In the case of a first-order irreversible reaction

- for $Ha < 0.3$ $E = 1$,
- for $0.3 < Ha < 3$ $E = \sqrt{1 + \mathrm{Ha}^2}$,
- for $Ha > 3$ $E = Ha$.

In a number of papers numerical or even analytical solutions for predicting simultaneous chemical ozone mass transfer and removal of organic pollutants from water (cf. for example, Muroyama et al., 1999; Qiu, 1999; Chen et al., 2003; Cheng et al., 2003; Benbelkacem et al., 2003 a,b; Munter, 2004).

Recently, for steady-state mass transfer with reversible reaction Meldon et al. (2007) presented an approximate analytical technique for solving nonlinear differential equations that govern such a case. The technique is based on linearization of the kinetics assuming small local departures from equilibrium. It yields precise estimates of enhancement factors for absorption and effectiveness factors for catalysis over complete ranges of operating regimes, from exceedingly slow reaction to instantaneous reaction.

For simple ozonation of a pollutant quite often modeling of the process is based on a mechanistic approach, i.e. taking into account possible reaction pathway and intermediates as well as simultaneous mass transfer enhanced by chemical reaction (cf. for example, Carini, 1999; Beltrán et al., 2000; Beltrán et al., 2002; Beltrán–Heredia et al, 2001; ,Beltrán, 2004; Kuosa et al., 2007; Sung and Huang, 2007; Wu and Masten, 2002).

When ozonation or AOP are considered for wastewaters kinetic considerations are often made with respect to surrogate parameters representing carbon content in water such COD, DOC, TOC, IC (inorganic carbon), UV_{254} (absorptivity at 254 nm) or color. The depth of oxidation may be expressed by means of MOC (mean oxidation number of carbon). Since in both water and, especially in wastewater the concentrations of many compounds (pollutants) are not known, MOC can be estimated from the following relationship:

$$\mathrm{MOC} = 4 - \frac{4M_{\mathrm{C}}}{M_{\mathrm{O2}}}\frac{\mathrm{COD_{org}}}{\mathrm{TOC}} = 4 - 1.5\frac{\mathrm{COD_{org}}}{\mathrm{TOC}} \qquad (11)$$

Basically, description of ozonation process kinetics of wastewaters is similar to that for a known compound (pollutant), however, parameters that are used in this description should refer to the actual wastewater matrix, i.e. accounting for different ozone solubility, mass transfer coefficients, ozone diffusivity etc. Here, most likely preliminary experiments carried out in a laboratory scale equipment should be made in order to establish these differences. Details of the necessary steps and the rules of scale up are available elsewhere (Beltrán, 2004). Examples of modeling ozonation process kinetics using surrogate parameters can be found in the following references: Chiang et al. (1999), Andreozzi et al. (2000), Esplugas et al. (2002), Lackey et al. (2006).

Modeling of mass transfer with radical reactions involved was considered by Hoorn and Versteeg (2006). They discussed three types of model systems, all of which concerned a gaseous component A being transferred to the liquid phase where it reacted with a component B to form product P. The reactions differed in the reaction pathways. Assuming a number of simplifications and the penetration mass transfer model according to Higbie, the authors performed numerical simulations using a finite-differencing technique. From these simulations they concluded that the diffusion coefficients of radical intermediates can significantly influence the profiles of concentrations and reaction rates near the gas-liquid interface. Also, for very fast reactions differences in diffusion coefficients of the intermediates affects the by-product formation. The values of the enhancement factor, E, which is required in the gas-liquid reactor design can be estimated with the simplified models where the reaction intermediates do not occur in the expression for the reaction rates.

In ozone-based AOPs other oxidants or physical agents are involved, so their contribution in the overall reaction kinetics can be expressed by the following expression

$$r_{\mathrm{T}} = r_{\mathrm{d}} + r_{\mathrm{OH}} + r_{\mathrm{UV}} \tag{12}$$

where r_{T} refers to the disappearance rate of a component of interest (a pollutant), and the remaining terms of the RHS of Eq. (12) represent the contributions of direct ozonation (r_{d}), indirect oxidation by hydroxyl radicals (r_{OH}), and photolysis resulting from UV irradiation (r_{UV}), respectively. The term, r_{d}, is typically expressed by Eq. (6), while indirect ozonation by hydroxyl radicals is usually given as

$$r_{\mathrm{OH}} = k_{^\bullet\mathrm{OH/B}}\left[{}^\bullet\mathrm{OH}\right][\mathrm{B}] \tag{13}$$

In order to overcome difficulties with the unknown concentration of very reactive hydroxyl radicals ($\left[{}^\bullet\mathrm{OH}\right]$) Elovitz and von Gunten (1999, 2000) introduced a concept of R_{ct} parameter. It determines a ratio between the concentrations of the hydroxyl radicals and ozone in the natural water and is equal to the ratio of hydroxyl and ozone doses expressed by the time integrals measured during the batch experiments using samples of the water in question.

$$R_{\mathrm{ct}} = \frac{\left[{}^\bullet\mathrm{OH}\right]}{\left[\mathrm{O_3}\right]} = \frac{\int\left[{}^\bullet\mathrm{OH}\right]\mathrm{d}\tau}{\int\left[\mathrm{O_3}\right]\mathrm{d}\tau} \tag{14}$$

The R_{ct} parameter can experimentally be determined using a test (probe) ozone resistant-substance concentration changes with the experimental time (e.g. *p*-chlorobenzoic acid, *p*CBA) according to the following equation

$$\ln\left(\frac{[\mathrm{pCBA}]}{[\mathrm{pCBA}]_0}\right) = -k_{^\bullet\mathrm{OH/pCBA}} R_{\mathrm{ct}} \int [\mathrm{O_3}]\,\mathrm{d}\tau \tag{15}$$

If Eq. (15) is fulfilled a linear plot of the experimental data points is expected using the coordinates $\ln\left(\frac{[\mathrm{pCBA}]}{[\mathrm{pCBA}]_0}\right), \int [\mathrm{O_3}]\mathrm{d}\tau$. From such a plot a value of the R_{ct} parameter can be found provided the value of the rate constant $k_{^\bullet\mathrm{OH/pCBA}}$ is known (= 5×10^9 $\mathrm{M^{-1}s^{-1}}$). The values of the R_{ct} parameter are typically of the order of 10^{-8} and depend on the experimental conditions. The R_{ct} parameter reflects the concentration level of hydroxyl radicals in the ozonated water. The integral $\int [\mathrm{O_3}]\mathrm{d}\tau$ is called ozone exposure. When modeling oxidation of micro-pollutant in natural water the resulting equation describing its decay in a plug flow or batch reactors can be written as follows

$$\frac{[\mathrm{B}]}{[\mathrm{B}]_0} = \exp\left[-\left(k_{^\bullet\mathrm{OH/B}} R_{\mathrm{ct}} + k_2\right)\int [\mathrm{O_3}]\,\mathrm{d}\tau\right] \tag{16}$$

The papers by Acero et al. (2003), Wang et al. (2004) or Rosenfeldt et al. (2006) are good illustrations of such modeling, also when comparison of the efficiency of hydroxyl radical formation using different AOPs is undertaken.

If photolysis by UV of a pollutant of interest is included the appropriate equation of photoreaction rate will take the following form

$$r_{\mathrm{UV}} = -\frac{\mathrm{d}[\mathrm{B}]_{\mathrm{UV}}}{\mathrm{d}\tau} = \phi_{\mathrm{B}} I_0 \left(1-\exp\left(-A_{\mathrm{t}}\right)\right) f_{\mathrm{B}} \tag{17}$$

where ϕ_{B} is the quantum yield of B, I_0 – the incident flux of radiation, A_{t} – is the total absorbance of the solution, and f_{B} - is the ratio of light absorbed by B to that absorbed by other components of the solution:

$$A_{\mathrm{t}} = 2.303 L \sum \varepsilon_i [\mathrm{B}_i] \tag{18}$$

$$f_{\mathrm{B}} = \frac{\varepsilon_{\mathrm{B}}[\mathrm{B}]}{\sum \varepsilon_i [\mathrm{B}_i]} \tag{19}$$

where the subscript i refers to any species present in the solution that absorbs light at a specified wavelength, L is the effective path length of the photoreactor, and ε_i is the molar absorptivity of the i-th species at the lamp wavelength.

Very extensive discussion of the assessment of these contributions in terms of the influence of kinetic regime and experimental conditions can be found elsewhere

(Beltrán, 2003, 2004). In the more detailed attempts kinetic models of the AOPs are developed by taking into account possibly all reactions (including radical ones). For the simplest case, a batch CST reactor, this leads to a set of ordinary differential equations describing mass balance of ozone, hydrogen peroxide, hydroxyl and other important radical species. Typically, in case of highly reactive radicals assumption of a steady state concentration is made, thus simplifying further computations. Ozone mass balance equation should include ozone mass transfer from the gaseous into the liquid phase, i.e. the volumetric mass transfer coefficient, $k_L a$, should also be known. In order to apply such a model the values of the reaction rate constants should be known (e.g. from the published data) or estimated from separate experiments.

The set of the ordinary differential equations is numerically solved allowing obtaining the values of the concentration of B as a function of time. The same procedure can be applied when the kinetic constants are to be determined based on batch experiments carried out in a laboratory-scale reactor. Good examples of application of such a procedure are available in the papers of Hautaniemi et al (1998a,b, 1999), Beltrán et al., (2000, 2002) or Latifoglu and Gurol (2003).

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Bibliography

Acero, J.L., Benitez, F.J., Real, F.J., Maya, C. (2003). Oxidation of acetamide herbicides in natural waters by ozone and by the combination of ozone/hydrogen peroxide: Kinetic study and process modeling. *Industrial and Engineering Chemistry Research*, 42, 5762-5769.

Andreozzi, R., Caprio, V., Insola, A., Marotta, R., Sanchirico, R. (2000). Advanced oxidation processes for the treatment of mineral oil-contaminated wastewaters. *Water Research*, 34, 620-628.

Beltrán, F.J. (2003). Ozone-UV radiation-hydrogen peroxide technologies. In: *Chemical Degradation Methods for Wastes and Pollutants. Environmental and Industrial Applications*. Ed. Matthew A. Tarr, Chapter 1, pp. 1-76. Marcel Dekker Inc., New York, 2003.

Beltrán, F.J. (2004). *Reaction Kinetics for Water and Wastewater Systems*. Lewis Publ., Chapters 2, 3, 4, 5, 6, 7, 11.

Beltrán, F.J., González, M., Acedo, B., Rivas, J.F. (2000). Kinetic modeling of aqueous atrazine ozonation processes in a continuous flow bubble contactor. *Journal of Hazardous Materials*, B80, 189-206.

Beltrán, F.J., García-Araya, J.F., Navarrete, V., Rivas, F.J. (2002). An attempt to model the kinetics of the ozonation of simazine in water. *Industrial and Engineering Chemistry Research*, 41, 1723-1732.

Beltrán -Heredia, J., Torregrosa, J., Joaquin r. Dominguez, J.R., Peres, J.A. (2001). Kinetics of the reaction between ozone and phenolic acids present in agro-industrial wastewaters. *Water Research,* 35, 1077-1085.

Biń, A.K. (1993). Gas entrainment by plunging liquid jets. *Chemical Engineering Science*, 48, 3585-3630.

Carini, D. (1999). Treatment of industrial wastewater using chemical-biological sequencing batch biofilm reactor (SBBR) processes. ETHZ, Dissertation ETH Nr. 13431.

Chen, Y.H., Chang, C.Y., Chiu, C.Y., Yu, Y.H., Chiang, P.C., Ku, Y., Chen, J.N. (2003). Dynamic behavior of ozonation with pollutant in a countercurrent bubble column with oxygen mass transfer, *Water Research*, 37, 2583-2594.

Cheng, J., Yang, Z.R., Chen, H.Q., Kuo, C.H., Zappi, M.E. (2003). Simultaneous prediction of chemical mass transfer coefficients and rates for removal of organic pollutants in ozone absorption in an agitated semi-batch reactor. *Separation and Purification Technology*, 31, 97-104.

Chiang, P.-C., Ko, Y.-W., Yang, Y.-M. (1997). Applying mass transfer models for controlling organic compounds in ozonation process. *Environmental International*, 23, 819-828.

Chiang, P.-C., Ko, Y.-W., Liang, C.-H., Chang, E.-E. (1999). Modeling an ozone bubble column for predicting its disinfection efficiency and control of DBP formation. *Chemosphere*, 39, 55-70.

Esplugas, S., Giménez, J., Contreras, S., Esther Pascual, E., Rodríguez, M. (2002). Comparison of different advanced oxidation processes for phenol degradation. *Water Research*, 36, 1034-1042.

Gogate, P.R., Pandit, A.B. (2004a). A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions. *Advances in Environmental Research*, 8, 501–551.

Gogate, P.R., Pandit, A.B. (2004b). A review of imperative technologies for wastewater treatment II: Hybrid methods. Advances in Environmental Research, 8, 553–597.

Gottschalk,C., Libra, J.A., Saupe, A. (2000). *Ozonation of Water and Waste Water*. Wiley-VCH Verlag, Weinham. Part B, Chapters 2-5.

Hautaniemi, M., Kallas, J., Munter, R., Trapido, M. (1998a). Modelling of chlorophenol treatment in aqueous solutions. 1. Ozonation and ozonation combined with UV radiation under acidic conditions. *Ozone Science and Engineering*, 20, 259-282.

Hautaniemi, M., Kallas, J., Munter, R., Trapido, M., Laari, A. (1998b). Modelling of chlorophenol treatment in aqueous solutions. s. Ozonation under basic conditions. *Ozone Science and Engineering*, 20, 283-302.

Hautaniemi, M., Kallas, J., Munter, R., Trapido, M., Veressinina, Y. (1999). Modelling advanced oxidation treatment of polycyclic aromatic hydrocarbons. Proceedins of the Estonian Academy of Sciences. Chemistry, 48, 80-95.

Heyouni, A., Roustan, M., Do-Quang, Z. (2002). Hydrodynamics and mass transfer in gas-liquid flow through static mixers. *Chemical Engineering Science*, 57, 3325-3333.

Hoigné, J. (1998). Chemistry of aqueous ozone, and transformation of pollutants by ozonation and advanced oxidation processes. In: J. Hrubec, editor. *The Handbook of Environmental Chemistry*, vol. 5, Part C, “Quality and Treatment of Drinking Water II”, Spinger Verlag, Berlin, 83-141.

Hoorn, J.A.A., Versteeg, G.F. (2006). Modelling of mass transfer in combination with radical reactions. *Chemical Engineering Science* 61, 5137-5148.

Kosaka, K., Yamada, H., Shishida, K., Echigo, Sh., Minear, R.A., Tsuno, H., Matsui, S. (2001). Evaluation of the treatment performance of a multistage ozone/hydrogen peroxide process by decomposition by-products. *Water Research*, 35, 3587–3594.

Kuosa, M., Laari, A., Solonen, A., Haario, H., Kallas, J. (2007). Estimation of multicomponent reaction kinetics of *p*-nitrophenol ozonation in a bubble column. *Industrial and Engineering Chemistry Research*, 46, 6235-6243.

Lackey, L.W., Mines Jr., R.O., Philip T. McCreanor, Ph.T. (2006). Ozonation of acid yellow 17 dye in a semi-batch bubble column. *Journal of Hazardous Materials* B138, 357–362.

Langlais, Ch. (1998). Etude des mélamgeurs statiques en tant que réacteur chimique utilisant les procédés d’oxidation O_3 et O_3/H_2O_2. Ph.D. Dissertation, University of Poitiers.

Latifoglu, A., Gurol, M.D. (2003). The effect of humic acids on nitrobenzene oxidation by ozonation and O_3/UV processes. *Water Research*, 37, 1879–1889.

Lee, S.Y., Ruutel, P., Barratt, P.A., Tsui, Y.P. (1999). Impinging zone reactor and its mathematical model for ozonation of wastewater. *Ozone: Science and Engineering*, 21, 501-522.

Meldon, J.H., Olawoyin, O.O., Bonanno, D. (2007). Analysis of mass transfer with reversible chemical reaction. *Industrial and Engineering Chemistry Research*, 46, 6140-6146.

Munter, R. (2004). Mathematical modeling and simulation of ozonation processes in a downstream static mixer with sieve plates. *Ozone: Science and Engineering*, 26, 227-236.

Muroyama, K., Norieda, T., Morioka, A., Tsuji, T. (1999). Hydrodynamics and computer simulation of an ozone oxidation reactor for treating drinking water. *Chemical Engineering Science*, 54, 5285-5292.

Pines, D.S., Min, K.-N., Ergas, S.J., Reckow, D.A. (2005). Investigation of an ozone membrane contactor system. *Ozone: Science and Engineering*, 27, 209-217.

Qiu, Y. (1999). Kinetic and mass transfer studies of the reactions between dichlorophenols and ozone in liquid-liquid and gas-liquid systems. Ph.D. Thesis, Mississippi State University.

Rosenfeldt, E.J., Linden, K.G. Canonica, S., Von Gunten, U., (2006). Comparison of the efficiency of $^{\bullet}$OH radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2. *Water Research*, 40, 3695 – 3704.

Stockinger, H. (1995). Removal of biorefractory pollutants in wastewater by combined ozonation-biotreatment. ETHZ, Dissertation ETH Nr. 11063.

Sung, M., Huang, Ch.-P. (2007). Kinetics of degradation of 2-chlorophenol by ozonation at pH 3. *Journal of Hazardous Materials*, 141, 140-147.

Von Gunten, U., Laplanche, A. (2000). Oxidation and disinfection with ozone, an overview, Proc. Intern. Specialized Symposium IOA 2000, Fundamental and Engineering Concepts for Ozone Reactor Design, 1-3 March, 2000, Toulouse, pp. 39-73.

Von Gunten, U. (2003). Ozonation of drinking water: Part I. Oxidation kinetics and product formation, *Water Research*, 37, 1443-1467.

Wang, X., Huang, X., Zuo, Ch., Hu, H. (2004). Kinetics of quinoline degradation by O_3/UV in aqueous phase. *Chemosphere*, 55, 733–741.

Wright, Ph., C., Meeyoo, V., Soh, W.K. (1998). A study of ozone mass transfer in a co-current downflow jet pump contactor. *Ozone: Science and Engineering*, 20, 17-33.

Wu, J.J., Masten, S.J. (2002). Oxidation kinetics of phenolic and indolic compounds by ozone: application to synthetic and real swine manure slurry. *Water Research*, 36, 1513-1526.

Biographical Sketch

Andrzej K. Biń, was born in Warsaw, Poland, in January 24, 1941. He graduated from the Warsaw University of Technology in 1963 as chemical engineer. His scientific career began in October, 1963, at the Chemical Department of the Warsaw University of Technology, where in 1971 he obtained the Ph.D. degree based on a thesis on air entrainment by plunging liquid jets, then in 1986 at the same University he was granted D.Sc. degree based on a series of papers on mass transfer into turbulent liquid free surfaces. During this period of time he held positions of assistant professor, then associate professor, and in 1995 he was appointed as full professor at the Faculty of Chemical Engineering of the Warsaw University of Technology. His major area of interest and scientific activity is devoted to hydrodynamics and mass transfer in multiphase systems, with special emphasis put on aeration, ozonation, advanced oxidation processes and their applications in environmental protection (water and wastewater treatment). He is a member of the International Ozone Association since 1993, in which he was elected as a Board Member and International Director. He published ca. 170 papers.