Criteria for ozonation processes modeling and simulation

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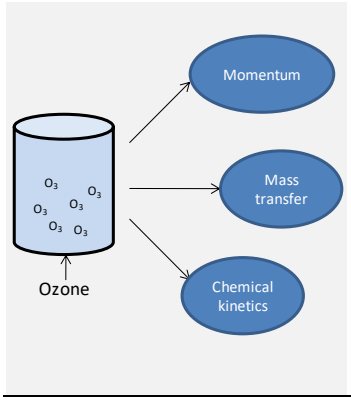

The ozonation is an advanced oxidation process, commonly used in water and wastewater treatments. Recently, many works showed that ozonation could be applied for degradation of drugs, naphtenic acids and biological agents. The reactors for ozonation are multiphase systems, with complex gas-liquid, gas-solid and gas-liquid-solid dynamics. To understand deeply the phenomena involved in these systems and optimize the costs and operation, the researchers are applying CFD (Computational Fluid Dynamics) to couple the governing equations of momentum, mass transfer and chemical kinetics. The present work explains the major criteria adopted in the field.

Introduction

Ozonation is an advanced oxidation process (AOP) using ozone, which is a reactive gas with low solubility, usually generated on-site (to achieve a 1–2 ppm dose) through dry air, or pure oxygen through high-voltage corona discharge [1]. Ozonation is widely employed in water treatment or disinfection [2].

Zhang *et al.* [3] built a three-dimensional model of the ozonation process at the Charles DesBaillets water treatment plant in Montreal, Canada, using CFD and Ansys software. The model proposes the Eulerian-Eulerian model and the standard k-ε turbulence model for multiphase flow.

In a CFD study of the ozonation disinfection process of drinking water in industrial-scale plants, Talvy *et al.*[4] evaluated the coherence of the model obtained through experimental measurements of ozone concentration and the degradation of *Bacillus subtilis* spores. The work was developed using the Ansys Fluent 6.3 software. However, it did not specify the use of a laminar or turbulent model.

Khataee *et al.*[5] carried out numerical CFD simulation of the ozonation process of water containing mebendazole (MBZ), an anthelmintic drug, in a photocatalytic reactor containing TiO_2 nanoparticles. The authors used the Ansys Fluent software to implement the mathematical model, in which the k-ε turbulence model was used.

Li *et al.*[6] numerically modeled the effluent ozonation treatment in an experimental reactor using the Ansys Fluent 17.0 software in 2D. The authors assumed the multiphase fluid volume (VOF) model for multiphase flow and the k-ε turbulence model. The results demonstrated the ozone bubbles formation.

In the study of ozonation of water containing formate (formic acid), Lian *et al.*[7] used the Ansys Fluent software and specified several methodological parameters of the implemented model, such as the use of the Eulerian model for multiphase flow, the RNG k- ε turbulence model and the use of the two-film theory for mass transfer of ozone from the gaseous phase to the aqueous phase, with the implementation of a UDF (User Defined Function).

Schmitt *et al.*[8] developed a fluid dynamic model for the ozonation process of water containing a widely used anti-epileptic drug, carbamazepine (CBZ), by hollow fiber contact, using the Comsol Multiphysics software. In the work, laminar flow was considered, because the authors experimentally used a gas flow of 1 $L.h^{-1}$, which corresponds to a Reynolds number of 55, they also assumed an ideal gas behavior and an isothermal process.

Alam *et al.*[9] coupled the CFD model to the PBM model (Population Balance Model) to evaluate the implementation of a distribution of the average size of ozone bubbles, instead of using just a constant average diameter, in the ozone-water multiphase flow in a reactor with rotating flow for generating nanobubbles. The authors also evaluated the standard k–ω and standard k– ε turbulence models. Li *et al.*[10] also coupled the CFD model to the PBM model for multiphase ozone flow in a venturi containing sludge. The turbulence model adopted was the k–ω SST (Shear Stress Transfer).

The present work aims to explain the major criteria adopted to model and simulate ozonation processes.

Modeling methodology

The main governing equations are the equations of conservation of mass or continuity (Equation 01) and conservation of momentum (Equation 02) [7].

$$\frac{\partial \rho}{\partial t} + \nabla . (\rho \vec{v}) = 0 \qquad (1)$$

$$\frac{\partial}{\partial t}(\rho\vec{v}) + \nabla .(\rho\vec{v}\vec{v}) = -\nabla p + \nabla.\bar{\sigma} + \rho\vec{g} + \vec{F} \quad (2)$$

The multiphase flow can be simulated by the Eulerian-Eulerian, the Eulerian-Lagrange and VOF approaches. However, the model needs to consider an average diameter or population balance model for the ozone bubbles sizes. The average density is calculated according to Equation 03 and the gas-liquid interface between the phases according to Equation 04 [7, 11].

$$\rho = \alpha\rho_g + (1-\alpha)\rho_l \quad (3)$$

$$\frac{\partial}{\partial t}(\alpha\rho_g) + \nabla.(\alpha\rho_g \upsilon_g) = \dot{m}_{lg} - \dot{m}_{gl} \quad (4)$$

The mass transfer of chemical species is modeled and simulated according to the coupling of Equations 06, 07 and 08 in Equation 05 through the implementation of the UDF (User Defined Function) Define_Mass_Transfer in the Ansys Fluent software [7].

$$\frac{\partial}{\partial t}(\rho C_m) + \frac{\partial}{\partial x_i}(\rho u_i C_m) = \frac{\partial}{\partial x_i}\left(\rho D_m \frac{\partial C_m}{\partial x_i}\right) + R_m + S_m \quad (5)$$

$$S^l_{O_3} = -S^g_{O_3} = K_l a(C_l^* - C_l) \quad (6)$$

$$K_l a = 2\sqrt{D_m \frac{|\vec{v}_g - \vec{v}_l|}{d_b}}\frac{6\alpha}{d_b} \quad (7)$$

$$C_l^* = H.P_g \quad (8)$$

The kinetics of the chemical reactions of the ozonization processes depends greatly on the chemical species present in the reaction medium. In some works that evaluated the degradation of simple compounds such as formate [7], studies were developed for the main and secondary reaction mechanisms and the coupling of kinetic constants to the CFD model could happen by the use of standardized tools from the Ansys software or the application of UDFs. In some works, however, the modeling was simplified and did not consider secondary reactions, and the kinetic models were built in Matlab [12, 13].

It is also possible to highlight studies focused on mass transfer carried out to evaluate the global mass transfer coefficient (kla), the diameter of the gas bubbles and the geometry of the reactor [14, 15]. Although most modeling and simulation works applied commercial software, some works had presented significant results for multiphase systems obtained by free softwares, such as OpenFoam [16, 17, 18].

Conclusions

The level of complexity in modeling and simulating ozonation processes will depend on the applied operational conditions, the geometry of the control volumes and the variables aimed to evaluate. Simplified models can be built to evaluate the kinetics of chemical reactions, models of intermediate complexity can be created to evaluate the dynamics of breakage and coalescence of ozone bubbles and finally, complex level models can be created using CFD softwares, which can couple the governing equations of continuity, momentum, mass transfer and kinetics of chemical reactions, enabling a more complete and deep assessment of the phenomena present in ozonation processes.

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