An Agent-Based Stochastic-Probability Simulation Modeling for Chemical Reactions in Advanced Oxidation Processes – A Case Study

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Abstract: Advanced Oxidation Processes (AOPs) have been defined as emerging wastewater treatment technologies with the generation of highly radicals (esp. hydroxyl radical). These processes can effectively handle various hazardous organics in wastewater and groundwater. This study developed a novel agent-based stochastic-probability simulation modeling to reflect the interactive reactions from a microscopic perspective and predict the outcomes under different chemical concentrations. The developed method simulated the chemical reaction networks of AOPs within a spatial resolution to molecule size scale. Each molecule was treated as a point-like particle that diffused freely in a three-dimension space. When a pair of reactive molecules collided, a reaction occurred based on the reaction probabilities and kinetic parameters, the simulated reactants were then replaced by products. More than 20 basic reactions in AOPs system were considered and the input to the simulation are from NRPOP experimental data and previous journal papers. The model can simulate AOPs with more than 200,000 particles (including reactants and intermediates) within both short-term (hours) and long-time (days) periods. The preliminary results showed approximate trends (e.g., Organic matter, hydroxyl radical) in the comparison with the experimental result curves. The capacities of the proposed method will be subsequently demonstrated with the case studies considering five types of AOPs are considered: ozone, ozone with hydrogen peroxide, UV photolysis of ozone, UV photolysis of hydrogen peroxide, and UV photolysis of ozone and hydrogen peroxide. The simulated results will be further compared with experimental data by correlation analysis.

Keywords: Advanced oxidation processes; simulation modeling; agent-based modeling

1. Introduction

Advanced oxidation processes (AOPs) have been stated as suitable technologies for the elimination of organic contaminants. Strong radical oxidants are utilized to accelerate or facilitate the removal of many organic contaminants (Jing et al., 2018). Hydroxyl radical ($OH\cdot$) is one of the strongest reactive and reacts with organic matters non-selectively. AOPs usually combine multiple oxidation technologies in terms of ozonation-derived, peroxide-derived or UV-derived oxidations (e.g., O_3, O_3 /H_2O_2, UV/ O_3, UV/ H_2O_2, UV/ O_3/ H_2O_2, etc.) (Salimi et al., 2017). However, the effectiveness of different combinations can only be detected through a number of high-cost and time-consuming tests. How to transfer current laboratory data to a simulation model is a challenge to be conquered. In this study, a novel simulation and prediction modeling was developed regarding agent-based modeling with consideration of stochastic probabilities. The model can represent the interactive reactions with a bottom-up order

to reflect the whole reaction processes from a microscopic perspective. It can also predict the outcomes under difference chemical concentrations as well as combined types of oxidation technologies after a comprehensive training with previous experimental data.

2. Methodology

In this study, agent-based modeling (ABM) was used as the foundation theory to develop the proposed AOPs system. ABM was a type of microscale models for the simulation of the actions and interactions of autonomous agents with an assessment of the integrated effects as a whole system. It reflected the responses from lower (individual) levels to a higher (systematic) level (Ye et al., 2019b). Thus, ABM could be a preferred technology for complex chemical reaction processes, such as AOPs. In the ABM-based AOPs modeling, five major elements are included as:

1) Numerous agents with specific characteristics at various scales;

2) Decision-making criteria for selections and judgements;

3) Learning rules or adaptive processes, such as empirical equations, kinetics models, probabilities for the occurrence of reactions, and stochastic programming;

4) An interaction topology for chemicals reactions. Such as, the processes of, $HO_2^- + O_3 \rightarrow OH\cdot + O_2 + O_2^-$ and $H_2O_2 + hv \rightarrow 2OH\cdot$.

5) An environment for stable or environmental properties, such as UV light intensity or w/o catalyst, TiO_2.

ABM had four advantages compared with other traditional simulation tools, which included, self-identification, autonomy, reactivity and pro-activeness. An agent was an identifiable, discrete, or modular, individual with a set of characteristics and rules governing its behaviors and decision-making capability. The discreteness requirement implied that an agent had a boundary and one can easily determine whether something was a part of an agent or not or a shared environment characteristic. Agents operated without direct intervention from the user and had some sort of control over their actions (Ye et al., 2019a). An agent can function independently in its environment and in its interactions with other agents for the limited range of situations that were of interest.

The figure showed the framework of the proposed ABM-based AOPs simulation system with consideration of stochastic probability. The system had three major aspects: initialization, calibration/training and prediction. In this case study, only the first aspect, initialization was completed. Further tests will be done with regard to train the system with abundant experimental data from NRPOP Lab to enhance the simulation performance and increase the reliability and correlation. The trained system can be further validated by other data to test its robustness and used as a prediction model for scenarios with various combinations of AOPs technologies.

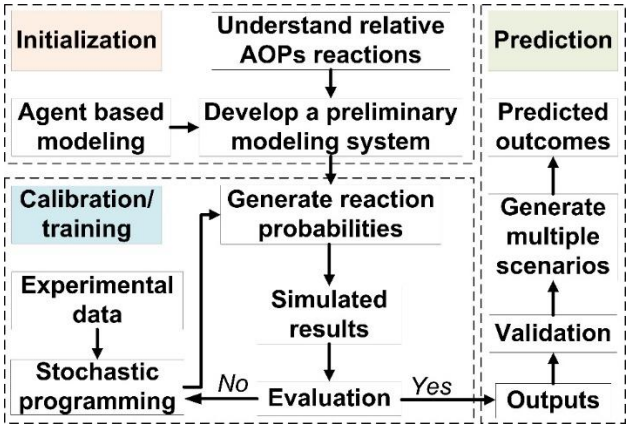

Figure. The framework of proposed AOPs Agent-Based Stochastic-Probability Simulation Modeling

3. Case study

The case study was used to complete to build up a system according to 23 basic reactions in AOPs system (including, $O_3, O_2, cl\cdot, H\cdot, OH\cdot, H_2O, H_2O_2$, organic matter, etc.) (Liu et al., 2017; Zheng et al., 2016). Each molecule (chemical) acted as a point-like particle that diffused freely in a three-dimension space. When a pair of reactive molecules collided, a reaction occurred based on the reaction probabilities and kinetic parameters, the simulated reactants were then replaced by products. In the initialization step, the inputs were hypothetical. The aim was to ensure the system can work successfully and smoothly. The model was developed with a popular ABM software, Netlogo®. In the current version, around 10,000 particles (including reactants and intermediates) were included, but more than 200,000 particles will be considered for both short-term (hours) and long-time (days) periods. The preliminary results showed approximate trends (e.g., Organic matter, hydroxyl radical) in the comparison with the experimental result curves. 75% organic matters can be removed at first 1500 ticks. 40% organic matters have been transferred to reactive compounds by oxidants in first 100 ticks. With the continuous ozone input, free radicals are continuously produced, but at the late reaction stage, they inhibited the removal of organic matters. In the further development, the proposed method capacities will be subsequently demonstrated under different experimental conditions, which contains ozone, ozone with hydrogen peroxide, UV photolysis of ozone, UV photolysis of hydrogen peroxide, and UV photolysis of ozone and hydrogen peroxide. The simulated results will be further compared with experimental data by correlation analysis.

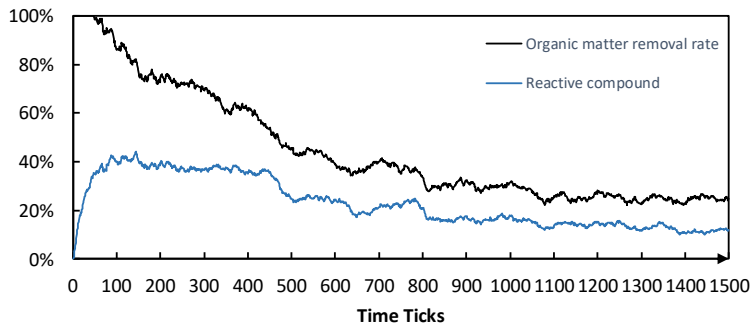

Figure 2. An example of preliminary results from the proposed system

4. Innovations and lessons learned

According to the reviews of previous studies, few studies with AOPs simulation can be found (Mustafa et al., 2014). In this case study, the innovations include: **a)** It is the first time to consider a micro-scale simulation for AOPs technologies under multiple different technical combinations. **b)** It is the first time to utilize ABM to deal with wastewater treatment process problems.

Based on the current version of simulation system and preliminary results, it showed that the proposed modeling can reflect the reasonable trends of organic matters and reactants. However, several drawbacks still exist, which need to be solved in the further research. **a)** Temporal and spatial calibration: the size of simulated reaction space should be scaled down based on real laboratory containers. The time measurement in Netlogo® is ticks, which should be further unified to have same reaction speed with lab testing. **b)** Modeling training: after modeling build-up, the system should be further trained by previous experimental data to find the best probabilities and stochastic number ranges for each reaction. **c)** The consideration of UV and catalyst: the UV light and catalyst (i.e., TiO_2) should be added as environment agents. **d)** Prediction: a prediction process will be done to save time and money for future AOPs experimental designs.

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