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Chemical Engineering Journal

Modeling of photooxidative degradation of aromatics in water matrix; combination of mechanistic and structural-relationship approach

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HIGHLIGHTS

- Photooxidative degradation of aromatics predicted by mechanistic modeling (MM).
- Introduced structurally dependent kinetic parameters in MM.
- Kinetic parameters predicted by QSPR modeling.
- Developed robust and flexible model simulating degradation of aromatics by UV/H$_2$O$_2$ process.

GRAPHICAL ABSTRACT
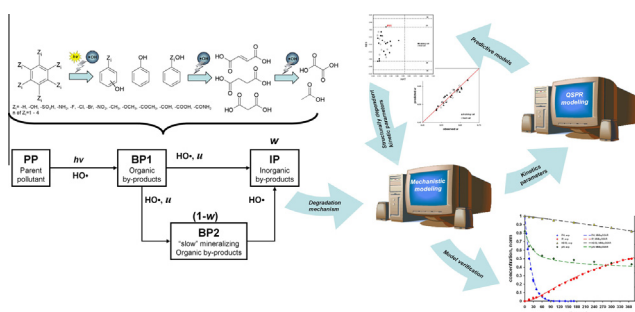
ARTICLE INFO

ABSTRACT

The study was aimed at developing a model simulating the photooxidative degradation of single-benzene ring typically water pollutants. In that purpose, 30 aromatics with different types, numbers and positions of substitutes were treated by UV/H$_2$O$_2$ process. The hypothesis of structural dependence of degradation kinetics was tested by combined mechanistic and structural-relationship modeling approach. The treatment is simulated by mechanistic model (**MM**) based on simplified degradation scheme. QSPR models were developed to predict the parameters of **MM** in dependence of parent pollutant structure. The applied combined approach yielded high accuracy in simulating the overall system behavior, accurately predicting the effectiveness of UV/H$_2$O$_2$ process by the means of parent pollutant conversion and mineralization of overall organic content, as well as describing the pH changes and consumption of oxidant during the treatment.

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1. Introduction

Water is not a commercial product like any other but, rather, a heritage which must be protected, defended and treated as such [1]. Introduction of various chemical substances into water may arise harmful effects to human health and the quality of aquatic ecosystem. A vast array of toxic and refractory aromatic compounds is generated and used in a variety of industrial sectors such as chemical, agriculture, pharmaceutical, food, dyestuff, and petrochemical. The benzene ring is the most widely distributed unit of chemical structure in nature, but many of major environmental pollutants pertain to the group of single-benzene ring compounds [2,3]. They possess various types and numbers of functional groups determining their chemical properties, as well as their environmental fate and behavior. Generally, such aromatics are mainly associated with (i) moderate to high solubility, (ii)

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low biodegradability, and (iii) suspected toxic effects toward aquatic organisms and humans [3,4]. As a consequence of inadequate treatment of industrial and urban effluents and low removal potential by natural occurring processes, single-benzene ring pollutants are often detected in natural reservoirs [3,5,6]. Their potential toxic effects are usually associated with various health issues, mutagenicity and carcinogenicity of all members in aquatic food chain including tertiary consumers; humans [2,3,7].

Advanced oxidation processes (AOPs) are characterized by the capability to oxidize refractory organics present in water into biodegradable products or ultimately to CO_2 and H_2O [5,8]. Among AOPs, photochemical processes proved their high capacity for the treatment of various single- and multi-benzene ring-structured pollutants [9–18]. The efficiency of UV/H_2O_2 process, the most studied photochemical AOP, depends on several key process parameters [8,19]. Operating pH determines the yield of radicals generated due to undesired dissociation of H_2O_2. The concentration of H_2O_2 determines the yield of radicals generated taking into account scavenging effect in excess. Radiant power at wavelength applied determines the yield of generated radicals in respect to H_2O_2 concentration. Reactor geometry determines the effective length path, which is inversely proportional to the yield of radical generation, and flow regime, whereas turbulent flow is preferable in order to overcome the mass transfer limitations. The characteristics of wastewater, i.e. the pollutants' structure, presence of HO˙ scavengers and suspended solids, play important role due to the competitive kinetics, scavenging reactions, and photon-shielding effect.

Accordingly, the system behavior needs to be optimized and described by appropriate simulative model in order to assess the potential application of proposed wastewater treatment technology. Modeling strategies based on artificial neural networks (ANN) and response surface methodology (RSM) can be used for the optimization and robust prediction of system response(s) in dependence of input parameters [20–22]. However, ANN and RSM based models do not encompass underlying chemical phenomena influencing the degradation kinetics within AOPs. On the other hand, phenomenological approach used in mechanistic modeling allows capturing the relevant interactions within the system. The degradation of parent pollutants, the generation of species (either radical, ionic or molecular), and their interactions through chain mechanism influencing the overall kinetics are specific for the type of present pollutants and AOP, and are described by chemical reactions. They are represented by the set of differential equations providing concentration *vs.* time relationship [12,15,23,24]. In such manner, not only the prediction within studied system boundaries, but extrapolation of applied AOPs behavior can be accomplished as well. However, the accurate simulation requires the involvement of numerous chemical reactions based on detailed degradation mechanisms, as well as specific reactions for AOP applied, which may significantly increase the complexity of developed model. It should be noted that such models developed on detailed mechanism, specific for the studied system, are not flexible regarding the type of present pollutants, thus cannot be applied for the same AOP treating wastewaters with different characteristics. In order to overcome the above limitations, we applied the combined mechanistic/structural-relationship modeling approach for the prediction of photooxidative degradation of single-benzene ring pollutants in water by UV/H_2O_2. The prediction of system behavior was accomplished using mechanistic modeling basics, while the important model parameters determining the rate of parent pollutant degradation and mineralization of overall organic content are assumed to be depended on the structure of parent pollutant. In such manner, they can be determined using structural-relationship modeling. Several publications described development of QSAR/QSPR (quantitative structure–activity/structure–property relationship) models for the prediction of respective reaction rate constants between aromatic

and aliphatic compounds and HO˙ [25–28], capturing the HO˙ reactivity toward a wide range of organics. In such manner, the important knowledge on kinetics of specific reactions within AOPs treatment is accumulated. The objective of this study was to develop a flexible model providing a relationship between process parameters and kinetics, as well as the structural characteristics of present pollutants. This is accomplished by novel approach combining mechanistic and structural-relationship modeling, and introducing the generalized kinetic parameters in order to bridge the complex degradation schemes.

2. Materials and methods

2.1. Chemicals

Thirty single-benzene ring aromatic compounds (Sigma–Aldrich, USA or Acros Chemicals, USA) are used as model pollutants. Their names, abbreviations, chemical formula, CAS numbers and purities are summarized in Table 1, while their structures are given in Fig. 1. Methanol (CH_3OH, HPLC grade, Sigma–Aldrich, USA), and *ortho*-phosphoric acid (o-H_3PO_4, $w \approx 85\%$, Sigma–Aldrich, USA), are used as mobile phases in HPLC analyses. Hydrogen peroxide (H_2O_2, $w = 30\%$), sulfuric acid (H_2SO_4, >96%), sodium hydroxide (NaOH, p.a.), and ammonium metavanadate (NH_4VO_3, p.a.), were purchased from Kemika, Croatia.

2.2. Experimental procedure

All experiments were performed with the model solutions ($c_0 = 1$ mM and $V = 1.4$ L) in a glass water-jacketed ($T = 25.0 \pm 0.2$ °C) batch photoreactor equipped with UV-C lamp ($I_0 = 5.12 \times 10^{-6}$ Einstein s^{-1}) and magnetic stirrer (Fig. S1, Supplementary material). Initial pH values (adjusted by 0.1 M NaOH and H_2SO_4) and H_2O_2 concentrations were determined as optimal within the investigated range for each studied pollutant in the previous studies using RSM modeling approach [13,29–33] and are summarized in Table S1 (Supplementary material). The duration of each experiment depended on the pollutant structure and ranged from 192 to 609 min. Samples were taken periodically from the reactor and thereafter immediately analyzed. All experiments were performed in triplicates and averages were reported; the reproducibility was >95%.

2.3. Analyses

The conversion of studied aromatics was monitored by HPLC, Shimadzu, Japan, with UV-DAD, SPD-M10A$_{VP}$, Shimadzu, Japan, using either 5 μm, 25.0 cm × 4.6 mm, Supelco Discovery C18 column, USA, or EC 250/4.6 120-5 C18 column, Macherey–Nagel Nucleosil, Germany, and mobile phase $H_2O/CH_3OH/o$-H_3PO_4 (ratio depended on the type of pollutant, i.e., its structure) operating at 1.0 mL min^{-1} flow. Mineralization of model solutions of studied aromatics was monitored by Total Organic Carbon analyzer, TOC-V$_{CPN}$, Shimadzu, Japan. Handylab pH/LF portable pH-meter, Schott Instruments GmbH, Mainz, Germany, was used for pH measurements. UV/VIS spectrophotometer, Lambda EZ 201, Perkin Elmer, USA, was used for spectrometric determination of H_2O_2 consumption during the treatment using modified metavanadate method [34].

3. Calculations

3.1. Mechanistic model formulation

The mechanistic model (**MM**) is originally developed, verified and validated in our previous studies focused on degradation of