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A Quantitative-Structure-Activity-Relationship (QSAR) model for the reaction rate constants of organic compounds during the ozonation process at different temperatures

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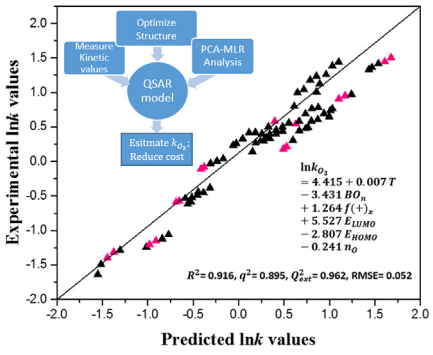
HIGHLIGHTS

- Organic compounds with various structures were degraded by ozonation.
- Temperature was an important parameter influencing the reaction rate constants.
- A high-quality QSAR model was developed for the reaction rate in ozonation process.
- The model could accurately predict reaction rate over a temperature range 25–60 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

The ozonation process is an effective method for removing hazardous wastes in water. To better characterize and understand the factors influencing the reaction rate constants of organic compounds during the ozonation process, a quantitative-structure–activity-relationship (QSAR) model was developed using the principal component analysis and multiple linear regression (PCA-MLR) method. In principal component analysis, five of the seven components were found to mechanistically and statistically affect the reaction rate constants. Component 1 was represented by the number of oxygen atoms (n_O) and minimum value of bond order (BO_n), component 2 was represented by the energy of the highest occupied molecular orbital (E_{HOMO}), and component 3 and 4 were dominated by the largest change in the charge of each atom during nucleophilic attack ($f(+)_x$) and the energy of the lowest unoccupied molecular orbital (E_{LUMO}), respectively. The temperature (T) was the most important factor for component 7. The optimal model was $\ln k_{O_3} = 4.102 + 0.007T - 3.419BO_n + 1.765f(+)_x + 5.698E_{LUMO} - 4.016E_{HOMO} - 0.241n_O$, with the following evaluation index values: squared correlation coefficient (R^2) = 0.916, internal validation (q^2) = 0.895 and external validation (Q^2_{ext}) = 0.962. Based on these evaluation indices, Y-randomization validation and the definition of the applicability domain, the optimal model was stable, robust and predictive. We anticipate that our work will provide a credible theoretical foundation for estimating the reaction rate constants for degradation of high-molecular weight organic compounds during ozonation over a temperature range from 25 to 60 °C.

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1. Introduction

The elimination of excess organic pollutants in water has recently drawn the interest of researchers because the increase in the number and concentration of organic pollutants is recognized as environmental threat [1], particularly in the densely populated areas [2]. Most of these organic contaminants come from industrial processes, agriculture effluents, and domestic activities such as the discharge of sewage and end up back in the environment [3]. Wastewater produced by these organic contaminants has become a serious global environmental issue due to the high toxicity and stability of these pollutants [4]. In addition, there are many different types of organic pollutants, including phenolics, dyes, pharmaceuticals, etc. [5]. The negative effects of organic pollution include increasing levels of chemical and biochemical oxygen, adverse effects on aquatic organisms, destruction of ecosystems and so on [6–8].

Biological techniques and traditional physicochemical processes are widely used to treat wastewater. However, these methods are often inadequate in the face of industrial effluents since they are expensive, ineffective or cause secondary pollution [9,10]. Advanced oxidation processes (AOPs), such as Fenton reaction, ozonation and wet oxidation, generate the hydroxide radical, and its powerful oxidative potential can be used to remove organic compounds that are not easily degraded [11]. AOPs have the potential to treat or pretreat organics, generating CO_2, H_2O and inorganics, or to transform them into harmless products [12].

The AOP ozonation, in which ozone molecules break down recalcitrant organic pollutants into smaller molecules, has proven to be a promising treatment technology [13–15]. Some published studies have revealed that ozonation is an effective method for the removal of organics. Snyder et al. (2008) reported that an ozone dose of 2.5 mg/L was highly effective for pharmaceutical and personal care product removal [16]. Kusvuran et al. (2013) showed that bisphenol A (BPA) could be completely degraded by ozonation under optimal conditions (pH = 3.0; t = 25 min) [17]. Bourgin et al. (2018) found that an ozone dose of 0.97 g O_3/g DOC was sufficient to remove more than 80% of the molecules of 38 organic substances [18].

In order to improve the efficiency of ozonation, many water quality parameters have been considered, including ozone dose, pH value and temperature. Temperature is typically one of the most important factors influencing the efficiency of oxidation of organic compounds during ozonation. Ramasamy et al. (2001) found that increased temperature caused a decrease in the levels of color, COD and TOC of dye molecules [19]. Zhao et al. (2009) evaluated the degradation of nitrobenzene using the ozone method, and found that the degradation efficiency increased from 5.6% to 62.1% when the reaction temperature was increased from 278 to 318 K [20]. Mehrjouei et al. (2010) used the ozonation system to decolorize wastewater produced by a pyrolysis process, and found that increasing the temperature from 20 to 50 °C, enhanced the color removal rate by 14% over 10 min and decreased the reaction time by nearly half [21]. Therefore, increasing the reaction temperature not only can enhance the degradation efficiency, but also shorten the reaction time.

The kinetic reactions of ozonation are of importance when evaluating degradation rules and behaviors [22,23]. However, determining the reaction rate constants experimentally is time-consuming, and only a limited number of constants have been determined. Given the discovery of new classes of compounds, there is an imperative need for a theoretical model for determining reaction rate constants. In this context, QSAR models have received special attention in the last few years as an impressive alternative to determining reaction rates experimentally. QSAR models are based on the concept that the molecular structure influences the molecular chemical/biological properties [24]. Therefore, QSAR analysis can be used to estimate the reaction rate constants of organic compounds by generating robust, accurate models linked to molecular properties [25].

To date, researchers have established a series of QSAR models to predict the reaction rate constants of organics for ozonation reactions. Zhu et al. (2014 and 2015) developed two optimal QSAR models for estimating the reaction rate constants for ozonation reactions under acidic and neutral conditions. These models successfully estimated the reaction rates of diverse organic compounds, with statistical indices of R^2 = 0.802 and 0.723, respectively. In these two models, the Fukui indices of a molecule significantly influenced the reaction rate constants [26,27]. Sudhakaran et al. (2013) established a QSAR model for ozone oxidation of organic micropollutants. This model included the parameters double bond equivalence, solvent accessible surface area and ionization potential, and had a high regression index of 0.832 [28]. McGillen et al. (2008) used a SAR model to predict the rates of alkyl substituents, and found that there was good agreement between experimental and predicted values [29].

Because temperature is an important factor determining degradation behavior, it is essential to consider this factor as an independent variable in QSAR models to accurately predict the reaction rate constants at different temperatures. In fact, several temperature-dependent QSAR models have been developed recently. Li et al. (2014) developed a room-temperature QSAR model and a temperature-dependent model for the hydroxyl radical oxidation process, and the goodness-of-fit and robustness measures for both models were high [30]. Similarly, Gupta et al. (2016) established room-temperature and temperature-dependent QSAR models for nitrate radical oxidation. Our group recently evaluated a quantitative relationship between the rate of Fenton oxidation and a series of parameters, including temperature and quantum chemical and physical-chemical properties of molecules, and found that temperature was the most important factor influencing the reaction rate constants [31]. Li et al. (2013) built a QSAR model for predicting ozonation reaction rates at different temperatures, and this model showed good predictive ability for 379 reaction rate values [32], though the molecular weights (MWs) of the organics in their study were 200.03 (linalool) or smaller. All of these temperature-dependent QSAR models have improved the applicability domain of traditional QSAR models. However, it is important to note that the measured data are associated with errors, which will affect the reliability of the models, and these errors may be reduced by using data obtained in the same laboratory.

A QSAR model for ozonation of high-molecular weight compounds (MW > 200) at different temperatures is lacking; therefore, in this study, we evaluated the degradation of 16 organic compounds by ozonation at five different temperatures. The reaction rate constants for these 16 organic compounds were evaluated using a pseudo-first-order kinetic model. The quantum chemical parameters were calculated using Gaussian 09 and Material Studio 7.0 software. Based on 80 reaction rate values obtained at different temperatures, the calculated quantum parameters, and the reaction temperatures, a QSAR model was established using the principal component analysis and multiple linear regression (PCA-MLR) method. A series of statistical diagnostics were used to validate the resulting model. We anticipate that this QSAR model will accurately predict the reaction rate constants of high-molecular weight organic compounds at different temperatures, and increase the applicability domain of QSAR models for ozonation.

2. Materials and methods

2.1. Ozonation experiments

Sixteen analytical-grade organic compounds with different structures (Table 1) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). These chemicals covered diverse functional groups (at least three), including $>C=C<$, −OH, −N=N−, $-C_6H_5$, $-C_{10}H_8$, $-SO_3$, $-NO_2$, $-NH_2$, −N=O, −X (Br, Cl), −S− and =O, and represented typical organic pollutants in the water environment. In addition, the structures of organic compounds used in this study are