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Prediction of key structural features responsible for aromaticity of single-benzene ring pollutants and their photooxidative intermediates

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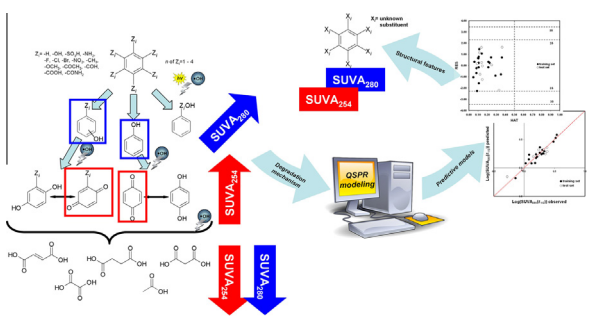
HIGHLIGHTS

- Established SUVA parameters of aromatics and their photooxidative intermediates.
- Quantitative models for aromaticity of single-benzene ring water pollutants.
- Key structural features influencing aromaticity of studied aromatics.
- Key structural features influencing aromaticity of formed photooxidative intermediates.

GRAPHICAL ABSTRACT



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ABSTRACT

The study was aimed at the prediction of structural factors influencing the aromaticity of typical single-benzene ring water pollutants, as well as their photooxidative intermediates, using structure–activity relationship modeling. UV absorbance (*A*) at 254 nm and 280 nm, along with the total organic carbon (TOC) values, were determined for 30 compounds structured of single benzene ring possessing different types, numbers, and positions of substitutes. These single-benzene ring pollutants were afterwards submitted to photooxidative treatment by UV-C/H_2O_2 process, where *A* and TOC values in reference treatment periods (RTPs) were determined in order to estimate the aromaticity of formed intermediates. The aromaticity of both parent pollutants and their photooxidative intermediates formed in RTPs were expressed by means of specific UV absorbance (SUVA) values. Such calculated SUVA values were taken as response values in QSPR modeling in order to establish key structural features of studied single-benzene ring pollutants contributing to the aromaticity changes during applied UV-C/H_2O_2 process. Within QSPR modeling, a genetic algorithm and multiple linear regression analysis were applied for the selection of descriptors representing structural characteristics of the studied compounds, and to generate the correlation models. The 3- and 4-variable models were found to be most predictive for $SUVA_{254}$ and $SUVA_{280}$ values, clearly reflecting contributing structural characteristics of the studied compounds toward aromaticity and corresponding changes occurring during their photooxidative treatment.

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1. Introduction

Clean and plentiful water resources provide the foundation for prosperous communities. Water supplies are challenged by the population growth, rapid industrialization, climate changes, and increased pollution, which are all closely correlated. According to the US Clean Water Act and the EU Water Framework Directive [1,2] water should be considered as a heritage which must be protected and conserved. In spite of these initiatives, vast array of chemical substances are introduced into the natural recipients on daily basis worldwide, presenting a serious threat to the quality of aquatic ecosystem and consequently, to human health. Although benzene ring is the most widely distributed unit of chemical structure in nature, many man-made environmental pollutants and/or their intermediates pertain to single-benzene-ring pollutants possessing various types and numbers of functional groups. Such functional groups determine the chemical properties, and consequently the environmental fate and behavior of single-benzene ring pollutants. Single-benzene ring aromatics are generally characterized with moderate to high solubility, low biodegradability, and toxicity toward aquatic organisms and humans [3–6]. Hence, their presence in natural reservoirs, although documented [7–9], is highly undesired, and logically waste streams containing such aromatics should be adequately treated to preserve natural water resources.

The effective treatment of refractory organics can be achieved by advanced oxidation processes (AOPs); highly reactive species generated within, primarily hydroxyl radicals ($HO^{\cdot}$), are capable of oxidizing organic contaminants into biodegradable products or ultimately to CO_2 and H_2O [10,11]. According to the type of energy used for the generation of $HO^{\cdot}$, AOPs can be broadly classified into: chemical; photochemical and photocatalytic, electrical, and mechanical processes. The effectiveness of UV-C/H_2O_2 process, the most studied photochemical AOP, for the treatment of a vast array of organic pollutants, either simple- (e.g. single benzene ring) or complex-structured, is well documented [11–17], as well as its full-scale applications [18–20]. Since the complete mineralization of organic contaminants by AOPs might be costly, their application can be aimed at the elimination of targeted refractory organics (mainly of aromatic structures), thus increasing biodegradability and lowering toxicity and aromaticity of the treated water, which are often cross-correlated [21].

The water quality influenced by organic load can be monitored by detecting and quantifying specific organic pollutants or over global water quality parameters such as total organic carbon (TOC) (or dissolved organic carbon, DOC), chemical and biochemical oxygen demand (COD and BOD_5, respectively), as well as the absorbance at characteristic UV-wavelengths [2,22]. These organic quantifying parameters have their own slightly different biases. For instance, TOC encompasses entire organic content regardless of their structural characteristics, whereas BOD_5 focuses on the biologically active organics. UV absorbance at 254 or 280 nm is the only one of above stated organic tests which has the bias towards the problematic aromatic organics. Namely, aromatics can be easily detected by UV-spectrometry due to the strong absorption properties of these double bond organics at characteristic wavelengths; higher absorption indicates higher organic content in water. The most direct measurement of aromaticity of organic pollutants in water is provided by ^{13}C NMR spectroscopy. However, this method requires expensive sophisticated instrumentation and significant sample preparation. Clearly, a simpler method for estimating aromaticity in water is desirable [23]. Hence, it can be quantified over specific UV absorbance (SUVA, either at 254 or 280 nm) representing the average absorptivity of organics comprised in DOC or TOC. Such simplified global water quality parameter is very useful when complex water matrix is considered (e.g. containing various natural organic matter (NOM) constituents or mixture of vast array of common organic pollutants). It is known that aromaticity is important indicator of DOC reactivity as aromatics combine easily with chemicals used for coagulation and adsorption within the treatment processes affecting their performance. Furthermore, aromatics are usually characterized by lower biodegradability and higher toxicity, influencing the overall water quality. The extensive and detailed analyses of various types of (waste)waters containing a vast array of organics can be time- and money-consuming, especially when the complexity of water matrix is increased during the applied treatment process due to the chemical transformation of parent pollutants (e.g. AOPs) and formation of intermediates. Hence, the simulation of caused changes in water quality by means of above stated parameters would be rather helpful to water specialists, environmental engineers, and decision makers. The prediction of specific pollutant elimination by a particular water treatment process can be successfully simulated by mechanistic modeling taking into account its degradation kinetics within; i.e. knowing specific kinetic parameters such as the reaction rate constant of the pollutant and present reactive species (e.g. $HO^{\cdot}$). Additionally, the mineralization effectiveness can be simulated as well by including (simplified) degradation mechanism into the modeling formulation [17,18]. However, global water quality parameters related to biodegradability, toxicity, and aromaticity are more dependent on structural characteristics of formed intermediates thus may significantly vary during the treatment. One of the modeling techniques that allows the correlation of structural characteristics with various either properties or activities of parent pollutants is QSAR/QSPR (quantitative structure–activity/structure–property relationship). Various different applications of QSAR/QSPR modeling related to water pollution and treatment can be found in the literature [17,24–27], but none of them dealt with the prediction of aromaticity during an applied chemical treatment process, i.e. when the water matrix is significantly changed in comparison to initial ("zero") conditions. Hence, our goal within the study was to apply QSPR modeling for the prediction of key factors responsible for aromaticity of single-benzene ring compounds and their formed intermediates during the photooxidative treatment by UV-C/H_2O_2 process. In such manner, the useful information on aromaticity changes of water matrix by considering only the structure of parent pollutants would be gathered, thus bridging necessity for performing detailed analytical studies.

2. Materials and methods

2.1. Chemicals

Single-benzene ring compounds (Sigma–Aldrich, USA and Acros Chemicals, USA) with various types and numbers of substituents were used as model pollutants. Their structures are provided in Fig. 1, while their names, abbreviations, chemical formula, CAS numbers and purities are summarized in Table S1 (Supplementary material). Other chemicals used in the study are: methanol (CH_3OH, HPLC grade, Sigma–Aldrich, USA), *ortho*-phosphoric acid (o-H_3PO_4, $w \approx 85\%$, Sigma–Aldrich, USA), hydrogen peroxide (H_2O_2, $w = 30\%$, Kemika, Croatia), sulfuric acid (H_2SO_4, >96%, Kemika, Croatia), sodium hydroxide (NaOH, p.a., Kemika, Croatia), sodium sulfite (Na_2SO_3, p.a., Kemika, Croatia) and ammonium metavanadate (NH_4VO_3, p.a., Kemika, Croatia).

2.2. Experimental procedure and analysis

The model solutions of studied single-benzene ring pollutants ($c_0 = 1$ mM) were prepared by dissolving their corresponding

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