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Article / Book Information

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著者(和文)	DWINANDHADhimas
Author(English)	Dhimas Dwinandha
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	土木・環境工学 系 土木工学 コース	申請学位（専攻分野）： Academic Degree Requested	博士 (Philosophy) Doctor of
学生氏名： Student’s Name	Dhimas Dwinandha	審査員主査： Chief Examiner	

要旨（和文 2000 字程度）
Thesis Summary（approx.2000 Japanese Characters ）

Organic compounds in the water environment exist in many forms, from anthropologically-derived micropollutants to the complex mixture of natural organic matter. The presence of organic compounds in the water is commonly undesirable due to risk possession of being harmful substances, therefore several techniques have been studied and implemented for their removal. One of the progressive removal techniques currently is advanced oxidation process (AOP). AOP treatments, especially OH·-based process, have been proven as an effective method to eliminate organics in the water while also being easy to implement at a low cost. However, recent studies suggested AOP treatments may not remove the organics completely–the organics are merely transformed into transformation products (TP). In addition, the TPs itself have a potential of being more toxic than their parent compounds. Thus, assessment of TPs from AOPs treatment of organic compounds are significantly needed, particularly assessment of transformation mechanism and resulting products. In this thesis, in silico and experimental methods were employed to give information about: (i) reactivity of organic compounds in OH·-based process; (ii) transformation mechanism from parent compounds to their TPs and its key reaction pathways. The outcomes of this study have significant implications for water treatment strategies, enabling the design of more efficient Advanced Oxidation Processes (AOPs) and providing insights into the dynamics of organic compound degradation in water systems. Furthermore, the findings contribute to the assessment of environmental transformation products, assisting in the mitigation of potential risks associated with the production of toxic substances in water.

Part 1: Theoretical investigation of phenol oxidation mechanism during OH radical-mediated process using quantum chemical calculation

Understanding the reaction mechanism of OH·-mediated oxidation of organic micropollutants (OMPs) contributes to the assessment and development of advanced oxidation processes (AOPs) for removal of OMPs in water environment. In this study, a theoretical approach using quantum chemical calculation (QCC) was employed to investigate the prediction accuracy of the reaction mechanism (i.e., reaction site and rate) for OH·-mediated oxidation of phenol, where the hydroquinone and catechol are generated as transformation products (TPs) via radical and electrophilic reactions. We compared three different levels of theory (Hartree-Fock, B3LYP, and M06-2X) with 6-311 + G (2d,2p)/SMD, and the reaction site and rate constants were predicted by the Fukui function and transition state theory, respectively. Overall, the prediction accuracy of the TPs formation mechanism was the highest in the calculations using M06-2X. For example, the initial OH· addition to phenol was predicted to occur with a probability of 77% for the ortho position and 23% for the para position, which was consistent with the experimental observation. By applying the transition state theory, the rate constants toward TPs formation pathway can be reasonably reproduced, suggesting that M06-2X has an effective function for polycyclic reactions. However, the observed discrepancies in rate constants are inferred from dispersion effects and the multi-reference property in the computational system or derived from mismatch of target reactions between theoretical calculations and experiments. Overall, this study provides an insight into QCC application for investigating the formation mechanism of TPs in AOPs for removal of OMPs in water environment.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。
Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	土木・環境工学 土木工学	系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	(Philosophy)
学生氏名： Student's Name	Dhimas Dwinandha		審査員主査： Chief Examiner		

要旨（英文300語程度）
Thesis Summary（approx.300 English Words ）

Part 2: Machine learning assisted isotopically labelled FT-ICR-MS for exploring natural organic matter reactivity and its molecular changes during UV photolysis

Isotopically labelled FT-ICR-MS combined with multiple post-analyses including interpretable machine learning (IML) and paired mass difference (PMD) network, were employed to unravel the reactivity and transformation of natural organic matter (NOM) during UV irradiation. FT-ICR-MS analysis was used to assign formulas, which were classified based on their molecular compositions and structural categories. Isotope (D) labelling was utilized to unequivocally determine the photochemical products and examine the development of OD radical-mediated NOM transformation. Regarding the reactive molecular formulas, CHOS-formulas exhibited the highest reactivity (86.5% of precursors disappeared) followed by CHON (53.4%) and CHO (24.6%). Regarding structural categories, degree of reactivity was in order of tannins > condensed aromatics > lignin/CRAMs. The IML algorithm demonstrated that the crucial features governing the reactivity of formulas were molecular weight, DBE-O, NOSC and the presence of heteroatoms (i.e., N and S), suggesting that the large-size and unsaturated compounds containing S and N are more prone to photodegradation. Reactomics approach using PMD-network further indicated that 11 specific molecular formulas in CHOS and CHO class served as hubs, implying a higher photo-reactivity and participation in a range of transformations. The isotope labelling analyses also found that, among reactions observed, hydroxylation reaction (i.e., +OD) is dominant for lignin/CRAMs and condensed aromatics, and formulas containing up to 10 D atoms were developed. Overall, this study, by adopting rigorous and interpretable techniques, could provide in-depth insights into the molecular-level dynamics of NOM under UV irradiation.

Part 3: Exploring Lignin Reactivity and Transformations as a Model Compound for Natural Organic Matter during UV Photolysis

FT-ICR-MS was utilized to decipher the mineralization process and the reactivity of lignin under UV irradiation. The relationship between the molecular composition with the reactivity and transformations was analysed using interpretable machine learning (ML) and paired mass distance (PMD). After UV irradiation, the transformation products were more oxidized and less saturation formulas which were featured by NOSC, O/C and DBE of -0.048, 0.570, and -0.519 compared with -0.562, 0.315, and 2.398. Based on ML, the most influential molecular features that govern the lignin reactivity under UV exposure were molecular weight and properties linked to oxygen and oxidation state (nO, O/C, and NOSC). Furthermore, aliphatic hydroxyl groups were proposed as the most reactive functional groups in the early stage of UV exposure (48 hours), while phenolic hydroxyl groups were the most reactive in the prolonged stage (72 hours). Furthermore, PMD analysis revealed that dominant reactions in the early stage of UV irradiation were hydroxylation and ketonization/quinone production, while dealkylation and deformylation reactions were dominated the prolonged stage of 72 hours, indicating aromatic ring oxidation and cleavage. Overall, this research is expected to shed light on the alteration of lignin molecules after UV exposure, as well as the elements that influence their reactivity. These discoveries help to improve our understanding of natural organic matter and its degradation in photo-oxidation system.

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