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Unexpected malformations in  
*Xenopus tropicalis*



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## CONTENTS

## Aquatic environment

Metal composition of layered double hydroxides (LDHs) regulating $\text{ClO}_4^-$ adsorption to calcined LDHs via the memory effect and hydrogen bonding Yajie Lin, Qile Fang, Baoliang Chen .....	493
Limitation of spatial distribution of ammonia-oxidizing microorganisms in the Haihe River, China, by heavy metals Chao Wang, Baoqing Shan, Hong Zhang, Yu Zhao .....	502
Temperature sensitivity of organic compound destruction in SCWO process Yaqin Tan, Zheming Shen, Weimin Guo, Chuang Ouyang, Jinping Jia, Weili Jiang, Haiyun Zhou .....	512
Influence of moderate pre-oxidation treatment on the physical, chemical and phosphate adsorption properties of iron-containing activated carbon Zhengfang Wang, Mo Shi, Jihua Li, Zheng Zheng .....	519
Reduction of DOM fractions and their trihalomethane formation potential in surface river water by in-line coagulation with ceramic membrane filtration Pharkphum Rakruam, Suraphong Wattanachira .....	529
$\text{N}_2\text{O}$ emission from nitrogen removal via nitrite in oxic-anoxic granular sludge sequencing batch reactor Hong Liang, Jiaoling Yang, Dawen Gao .....	537
Influence of stabilizers on the antimicrobial properties of silver nanoparticles introduced into natural water Aleksandra Burkowska-But, Grzegorz Sionkowski, Maciej Walczak .....	542
Addition of hydrogen peroxide for the simultaneous control of bromate and odor during advanced drinking water treatment using ozone Yongjing Wang, Jianwei Yu, Dong Zhang, Min Yang .....	550
Nitric oxide removal by wastewater bacteria in a biotrickling filter Hejingying Niu, Dennis Y C Leung, Chifan Wong, Tong Zhang, Mayngor Chan, Fred C C Leung .....	555
Elucidating the removal mechanism of <i>N,N</i> -dimethyldithiocarbamate in an anaerobic-anoxic-oxic activated sludge system Yongmei Li, Xianzhong Cao, Lin Wang .....	566
Influencing factors of disinfection byproducts formation during chloramination of Cyclops metabolite solutions Xingbin Sun, Lei Sun, Ying Lu, Jing Zhang, Kejing Wang .....	575

## Atmospheric environment

Sources of nitrous and nitric oxides in paddy soils: Nitrification and denitrification Ting Lan, Yong Han, Marco Roelcke, Rolf Nieder, Zucong Cai .....	581
Upper Yellow River air concentrations of organochlorine pesticides estimated from tree bark, and their relationship with socioeconomic indices Chang He, Jun Jin, Bailin Xiang, Ying Wang, Zhaohui Ma .....	593
Mechanism and kinetic properties of $\text{NO}_3$ -initiated atmospheric degradation of DDT Cai Liu, Shanqing Li, Rui Gao, Juan Dang, Wenxing Wang, Qingzhu Zhang .....	601
Sorption and phase distribution of ethanol and butanol blended gasoline vapours in the vadose zone after release Ejikeme Ugwoha, John M. Andresen .....	608

## Terrestrial environment

Effects of temperature change and tree species composition on $\text{N}_2\text{O}$ and $\text{NO}$ emissions in acidic forest soils of subtropical China Yi Cheng, Jing Wang, Shenqiang Wang, Zucong Cai, Lei Wang .....	617
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## Environmental biology

Influence of sunlight on the proliferation of cyanobacterial blooms and its potential applications in Lake Taihu, China Qichao Zhou, Wei Chen, Kun Shan, Lingling Zheng, Lirong Song .....	626
Bioavailability and tissue distribution of Dechloranes in wild frogs ( <i>Rana limnocharis</i> ) from an e-waste recycling area in Southeast China Long Li, Wenyue Wang, Quanxia Lv, Yujie Ben, Xinghong Li .....	636

## Environmental health and toxicology

Unexpected phenotypes of malformations induced in <i>Xenopus tropicalis</i> embryos by combined exposure to triphenyltin and 9- <i>cis</i> -retinoic acid Jingmin Zhu, Lin Yu, Lijiao Wu, Lingling Hu, Huahong Shi .....	643
Expression of sulfur uptake assimilation-related genes in response to cadmium, bensulfuron-methyl and their co-contamination in rice roots Jian Zhou, Zegang Wang, Zhiwei Huang, Chao Lu, Zhuo Han, Jianfeng Zhang, Huimin Jiang, Cailin Ge, Juncheng Yang .....	650

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# Environmental catalysis and materials

Reaction mechanism and metal ion transformation in photocatalytic ozonation of phenol and oxalic acid with  $\text{Ag}^+/\text{TiO}_2$   
Yingying Chen, Yongbing Xie, Jun Yang, Hongbin Cao, Yi Zhang ..... 662

Effect of  $\text{TiO}_2$  calcination temperature on the photocatalytic oxidation of gaseous  $\text{NH}_3$   
Hongmin Wu, Jinzhu Ma, Changbin Zhang, Hong He ..... 673

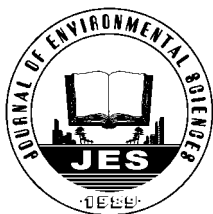
Effects of synthesis methods on the performance of Pt + Rh/ $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  three-way catalysts  
Zongcheng Zhan, Liyun Song, Xiaojun Liu, Jiao Jiao, Jinzhou Li, Hong He..... 683

Catalytic combustion of soot over ceria-zinc mixed oxides catalysts supported onto cordierite  
Leandro Fontanetti Nascimento, Renata Figueredo Martins, Rodrigo Ferreira Silva, Osvaldo Antonio Serra ..... 694

Effects of metal and acidic sites on the reaction by-products of butyl acetate oxidation over palladium-based catalysts  
Lin Yue, Chi He, Zhengping Hao, Shunbing Wang, Hailin Wang ..... 702

Mechanism of enhanced removal of quinonic intermediates during electrochemical oxidation of Orange II under ultraviolet irradiation  
Fazhan Li, Guoting Li, Xiwang Zhang..... 708

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## Temperature sensitivity of organic compound destruction in SCWO process

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### ABSTRACT

To study the temperature sensitivity of the destruction of organic compounds in supercritical water oxidation process (SCWO), oxidation effects of twelve chemicals in supercritical water were investigated. The SCWO reaction rates of different compounds improved to varying degrees with the increase of temperature, so the highest slope of the temperature-effect curve ( $i_{\max}$ ) was defined as the maximum ratio of removal ratio to working temperature. It is an important index to stand for the temperature sensitivity effect in SCWO. It was proven that the higher  $i_{\max}$  is, the more significant the effect of temperature on the SCWO effect is. Since the high-temperature area of SCWO equipment is subject to considerable damage from fatigue, the temperature is of great significance in SCWO equipment operation. Generally, most compounds ( $i_{\max} > 0.25$ ) can be completely oxidized when the reactor temperature reaches 500°C. However, some compounds ( $i_{\max} > 0.25$ ) need a higher temperature for complete oxidation, up to 560°C. To analyze the correlation coefficients between  $i_{\max}$  and various molecular descriptors, a quantum chemical method was used in this study. The structures of the twelve organic compounds were optimized by the Density Functional Theory B3LYP/6-311G method, as well as their quantum properties. It was shown that six molecular descriptors were negatively correlated to  $i_{\max}$  while other three descriptors were positively correlated to  $i_{\max}$ . Among them, dipole moment had the greatest effect on the oxidation thermodynamics of the twelve organic compounds. Once a correlation between molecular descriptors and  $i_{\max}$  is established, SCWO can be run at an appropriate temperature according to molecular structure.

## Introduction

Supercritical water (SCW) is an ideal medium for catalyzing many chemical reactions and has been the subject of numerous experimental studies. As a non-polar solvent of high diffusivity and complete miscibility with organic compounds and even gases (like O<sub>2</sub>), SCW provides a perfect oxidation medium with excellent transport properties (Calzavara et al., 2004, Guan et al., 2011). With high enough temperature, all organic pollutants can be oxidized in the supercritical water oxidation process (SCWO) to

primarily simple, environmentally clean products such as water, carbon dioxide, nitrogen and metal oxides (Houser et al., 1996; Nunoura et al., 2002; Fang et al., 2005; Shin et al., 2009). However, high temperature can not only result in a rapid destruction effect, but also can lead to high corrosion, low solubility of inorganic salts, and weak tensile strength of reactor walls (Rice and Steeper, 1998; Kritzer and Dinjus, 2001). The high-temperature area of SCWO equipment is subject to considerable damage from fatigue and corrosion. Therefore, it is important to choose an appropriate temperature in SCWO.

Operating temperature has a great influence on the destruction of organic compounds in SCWO. As a continuing effort to extend the understanding of the destruction

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behavior of organic compounds in SCWO environments, optimizing temperature design is very important in the application and development of SCWO. This design mainly depends on determining an effective removal temperature under which the compounds can be completely oxidized. The required temperature for SCWO depends on the desired compounds' destruction extent, which is greatly affected by the nature of the organic molecules. Many works have been carried out to determine appropriate temperature ranges for SCWO as applied to a variety of tested organic compounds (Rice and Steeper, 1998; DiNaro et al., 2000; Pinto et al., 2006; Veriansyah and Kim, 2007; Al-Duri et al., 2008). The influence of temperature on the oxidation of various organic compounds is different. Some compounds are sensitive to temperature and are oxidized dramatically during a certain temperature-rise period, while others are insensitive to temperature and need a high temperature to be completely oxidized. Clearly, their sensitivity to temperature is due to the diversity of molecular structures, but little is known about the relationship between temperature effect and the molecular descriptors. In this article, the sensitivity of twelve organic compounds to temperature in the SCWO process is studied for the first time. A new parameter, the highest slope of the temperature-effect curve ( $i_{\max}$ ), is defined. It is an effective indicator for designing and running SCWO. The removal effect of these compounds was monitored using total organic carbon concentrations.

## 1 Experimental apparatus and methods

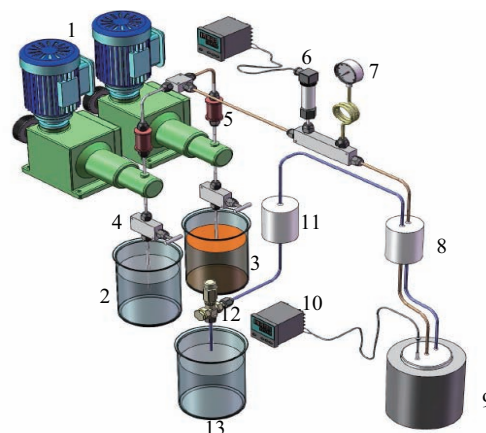
### 1.1 Apparatus

All the oxidation experiments were conducted using our supercritical flow reactor (SFR). This equipment was designed to mix two separate flows at a known temperature and fixed flow rate. The schematic of the SFR is shown in Fig. 1. It is similar to reactors described elsewhere (Houser et al., 1996; Shin et al., 2009). The reactor is constructed of inconel-625. All other parts such as tubes, fittings, and valves are stainless steel-316.

The designed maximum operating temperature and operating pressure are 600°C and 40 MPa respectively, with a volume of 200 mL. Hydrogen peroxide (30 wt%) was used as the oxidant in the SCWO experiments and all reagents were analytically pure grade. A TOC analyzer (TOC/TN Analyzer multi N/C 3000 (ChD), Analytik Jena AG, Germany) was used to monitor the total organic carbon (TOC) of the samples, at both inlet and outlet of the SFR.

### 1.2 Quantum chemical methods

The quantum chemical software Gaussian09 (Frisch et al., 2010), which is a well known powerful quantum



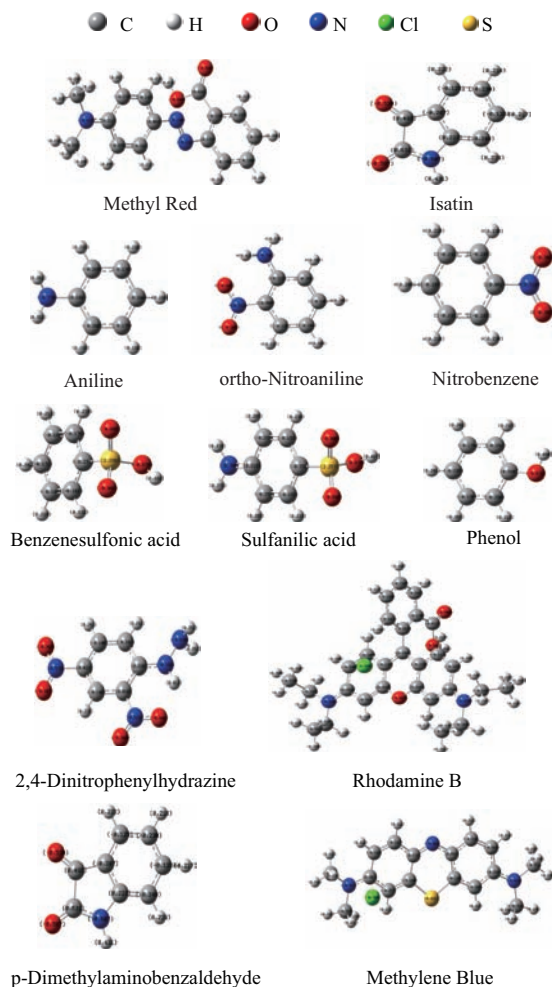
**Fig. 1** Scheme of supercritical water oxidation (SCWO) apparatus. (1) high-pressure plunger pump; (2) hydrogen peroxide tank; (3) waste water tank; (4) gas release valve; (5) check valve; (6) thermometer (7) pressure gage; (8) heat exchanger; (9) heater and reactor; (10) temperature recording controller; (11) condenser; (12) back pressure regulator; (13) effluent tank.

chemical software package, was used in this study. Complex quantum chemical calculations can be programmed by Gaussian 09. The Density Functional Theory (DFT) method is one of the quantum chemical methods developed on the basis of the Thomas-Fermi model. It attempts to describe many-electron systems on the foundation of electronic density instead of wave functions.

To study the relationship between temperature effect and molecular descriptors, twelve organic compounds were selected in this work, which were Methyl Red, isatin, aniline, ortho-nitroaniline, nitrobenzene, benzene-sulfonic acid, sulfanilic acid, 2,4-dinitrophenylhydrazine and p-dimethylaminobenzal, Methylene Blue, phenol, and Rhodamine B. Their structures were optimized by the DFT B3LYP/6-311G method using Gaussian 09, as listed in Fig. 2. In the calculation process of Gaussian 09, exchange and correlation terms are considered with a B3LYP function based on the 6-311G basis set (B3LYP/6-311G) to optimize the molecular structures. Meanwhile, the natural population analysis of atomic charge was performed by the same method. Other descriptors include dipole moment ( $\mu$ ), heat of formation (HOF), most positive partial charge on a hydrogen atom ( $q_{H^+}$ ), most positive partial charge of a hydrogen atom connected to a carbon atom ( $q_{C-H^+}$ ), and most negative partial charge on a carbon atom ( $q_{C^-}$ ), energy of highest occupied molecular orbital ( $E_{HOMO}$ ), energy of the lowest unoccupied molecular orbital ( $E_{LUMO}$ ), surface area grade (SAG), and volume. These descriptors were selected to describe the molecular structural characteristics.

### 1.3 Experiment analysis

Experimental variables for the SCWO of the twelve organic compounds were temperature and residence time. There were two types of errors affecting the overall accuracy of



**Fig. 2** Optimized molecular structures and natural population analysis atomic charges of nine organic matters.

the experimental results presented in this article. One is associated with the accuracy of the analytical methods. The other one is the control of operating conditions, such as temperature, pressure, residence time and sample collection techniques. Operation of the SFR is simple and routine, but there are design limitations governing the precision of its control. The chemical analysis methods also have an effect on the accuracy of experimental results. Total organic carbon was measured using the TOC/TN Analyzer multi N/C 3000 (ChD).

## 2 Results and discussion

### 2.1 Destruction effects of organic compounds in supercritical water

The SCWO simulation equipment was operated in a fashion consistent with industrial working conditions. The experiments were conducted at 24 MPa pressure, 300% excess oxygen and varying reaction temperature.

Sampling time was designed as 140, 190, 240, 330 and 460 sec. **Figure 3** shows that the TOC concentration changed with time and temperature from subcritical to supercritical conditions. It is generally believed that supercritical reactions are complete within a few seconds to 1 minute. In this study, the minimum residence time of the twelve compounds was 140 sec. Rice and Steeper (1998) has studied seven common organic compounds including methanol, phenol, methyl ethyl ketone, ethylene glycol, acetic acid, methylene chloride, and 1,1,1-trichloroethane. Their results indicate that most compounds can be oxidized completely when temperature is over 550°C and residence time is 20 sec. Ahn et al. (1998) has carried out research on the oxidation characteristics of phthalic and adipic acids by supercritical water. It was found that more than 99% decomposition can be easily accomplished for both acids in SCWO. Generally, when the temperature is above 450°C, most of the twelve organic compounds exhibited a high TOC removal effect in a short residence time (140 sec). Extending reaction time had little influence on the removal ratio when the temperature was above 450°C. As for aniline, ortho-nitroaniline and Methylene Blue, a high TOC removal effect could be obtained only when the temperature was above 480°C. Extending reaction time had little influence. At low conversion temperatures (250–290°C), the TOC concentration of the twelve compounds decreased linearly with the increase of the residence time, and its removal ratio was less than 60% in 460 sec. These compounds were partially oxidized during the time from 140 to 460 sec, and extending residence time could appreciably decrease the TOC concentration of the outlet samples. To conclude, in subcritical reactions, extending the residence time will noticeably improve the removal ratio, while in supercritical reactions, the oxidation will be complete within a short time and the extension of residence time has no significant effect on the decomposition of organic compounds.

### 2.2 Influence of temperature on destruction effect

At pressure 24 MPa, with 300% excess oxygen and residence time of 460 sec, the destruction effects of the twelve organic compounds at different temperatures were analyzed and compared. As shown in **Fig. 4**, the conversion percentages of organic compounds increased with the rise of temperature from 300 to 530°C. However, the influence of temperature on the oxidation of various organic compounds was greatly different. In sum, the curves' slopes changed dramatically in the conversion percentage range of 60%–90%. During this stage, the compounds were almost completely oxidized. The highest slope of the temperature-effect curve ( $i_{\max}$ ) is defined in Eq. (1), suggesting the temperature sensitivity effect on SCWO.

$$i_{\max} = \left( \frac{\partial R}{\partial T} \right)_{\max} \quad (1)$$

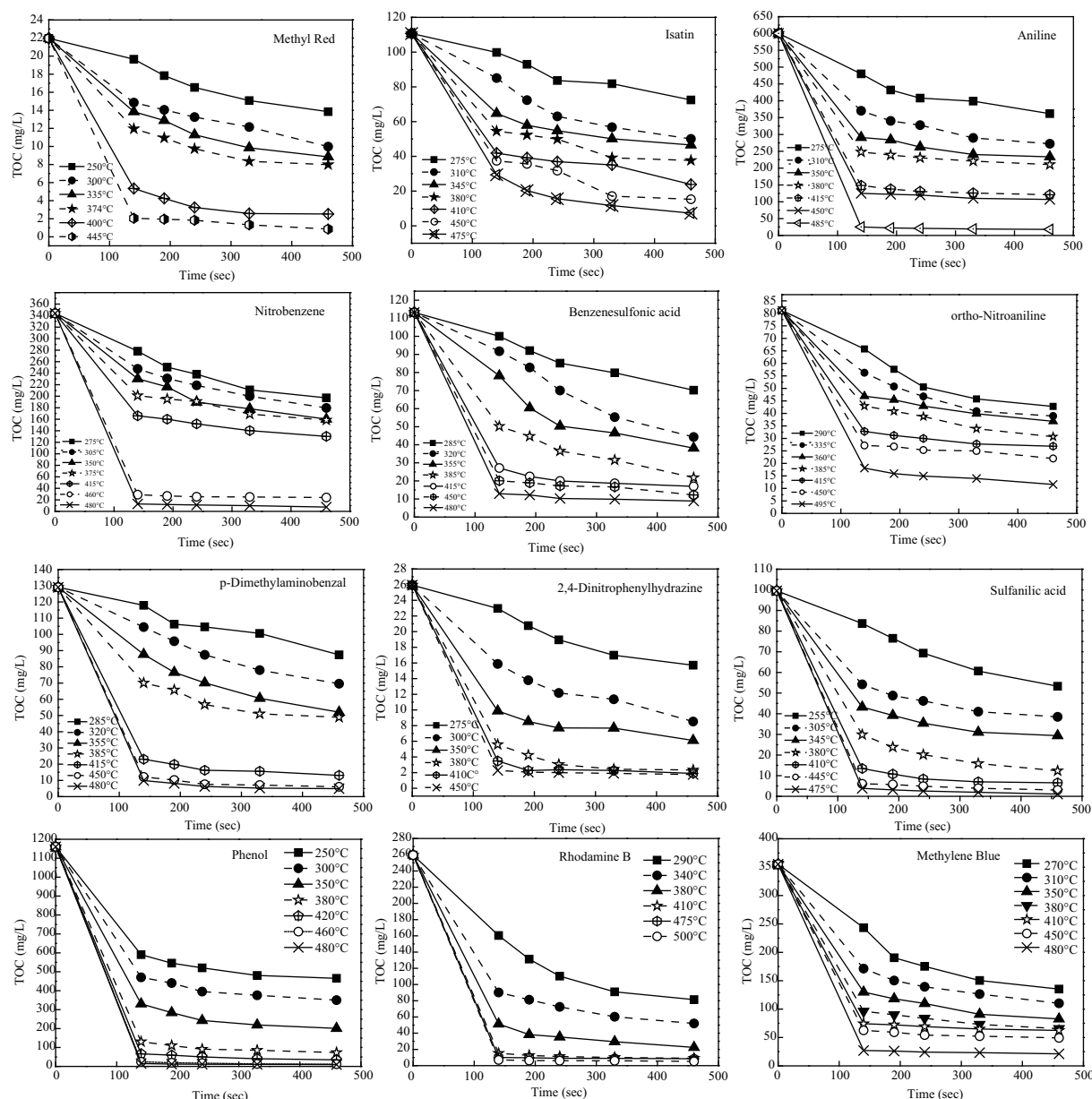


Fig. 3 TOC concentration over the time and temperature in SCWO.

where,  $i_{\max}$  (%/°C) is the highest slope of the temperature effect curve,  $R$  (%) is the removal ratio of organic molecules,  $T$  (°C) is the SCWO working temperature.

The value of  $i_{\max}$  is a key thermodynamic indicator of organic pollutants in the SCWO process. It can be achieved by linearly simulating the middle stage of the  $s$ -curves, as shown in Fig. 4 and Table 1. It is clearly shown that the  $i_{\max}$  value of various compounds during SCWO follows the order: aniline (0.6086) > nitrobenzene (0.4375) > Methyl Red (0.416) > isatin (0.3836) > p-dimethylaminobenzaldehyde (0.3016) > sulfanilic acid (0.2827) > phenylsulfonic acid (0.2782) > Rhodamine B (0.2608) > phenol (0.2542) > 2,4-dinitrophenylhydrazine (0.2517) > ortho-nitroaniline (0.2187) > Methylene Blue

(0.1545). The higher the  $i_{\max}$  values are, the more influence temperature has on degrading organic compounds. A high  $i_{\max}$  value for an organic compound indicates that it is oxidized dramatically during a certain temperature-rise period. Consequently, the proper operating temperature for SCWO equipment can be selected for different pollutants based on their  $i_{\max}$  to avoid unnecessary damage resulting from high temperature. However, a low  $i_{\max}$  value for a compound means that it is not sensitive to temperature increase. Therefore, such compounds need a higher temperature to be completely oxidized. Figure 4 indicates that the  $i_{\max}$  value of aniline is the largest while that of Methylene Blue is the lowest. Aniline begins to oxidize when the reaction temperature reaches 400°C. When the

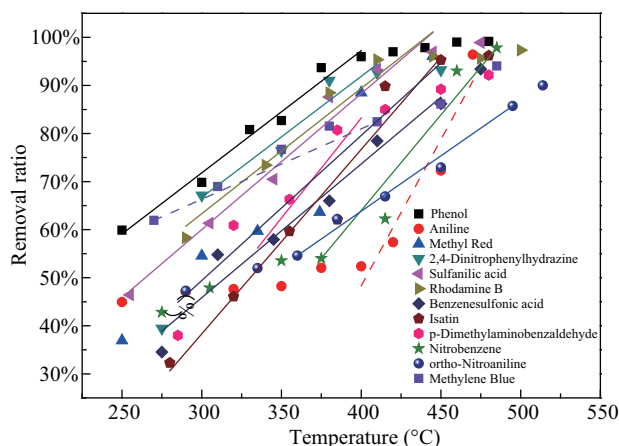


Fig. 4 Temperature effect of organic compounds destruction efficiency in SCWO.

temperature rises up to 475°C, the destruction effect is approximately 100%. Methylene Blue has the lowest  $i_{\max}$  value among the twelve tested compounds. It needs a long temperature-rise period to be oxidized. This implies that Methylene Blue is not sensitive to temperature increase. Ortho-nitroaniline has almost the same temperature insensitivity as Methylene Blue. It needs a high temperature (almost 560°C) for complete destruction. As for the other ten compounds, they are completely oxidized when the temperature reaches 500°C. Generally, most compounds ( $i_{\max} > 0.25$ ) can be completely oxidized when the reactor temperature reaches 500°C. On the contrary, some other compounds ( $i_{\max} < 0.25$ ) need a higher temperature, as high as 560°C.

Hence, SCWO operating conditions can be configured in accordance with the  $i_{\max}$  values of various target compounds. In most cases, the thermodynamic information of organic compound oxidation can be obtained from experiments under real operating conditions. However, this is limited to temperature measurements inside the reactor

and effluent characterization. The aggressive oxidizing conditions inside the reactor make it difficult to obtain measurement data. Besides, the experimental determination of  $i_{\max}$  value is a time-consuming, inconvenient and expensive process. Therefore, it is necessary to develop a fast and easy-to-do method, and the development of theoretical models is also very interesting as it provides a complement to the experimental information concerning those variables that are difficult to measure (Bermejo et al., 2010).

The  $i_{\max}$  value must be determined by the nature of organic molecules. Nevertheless, the relationship between  $i_{\max}$  and molecular descriptors is still a puzzle to us. Here, an investigation of the relationship between  $i_{\max}$  and the molecular descriptors is helpful to predict the SCWO thermodynamics of various organic compounds.

### 2.3 Correlation coefficients between $i_{\max}$ and molecular descriptors

Many different quantum chemical descriptors such as ionization potential, electron affinity, molecular orbital energies, dipole moment ( $\mu$ ), electro-negativity, electrophilicity etc., have been used to develop a possible quantitative structure-activity and structure-property relationship model for a series of alkanes (Karelson et al., 1996; Thanikaivelan et al., 2000). These descriptors are related to structural, electronic and thermodynamic parameters. Nine theoretical molecular descriptors have been widely used in previous works. They are mass,  $\mu$ , HOF,  $q_{H^+}$ ,  $q_{C-H^+}$ ,  $q_{C^-}$ ,  $E_{HOMO}$ ,  $E_{LUMO}$  (Frisch et al., 2008). Here, to study the relationship of molecular characteristics and the temperature-effect index,  $i_{\max}$ , the above nine theoretical molecular descriptors were selected to describe aromatic compounds.

Correlation coefficients between  $i_{\max}$  and various descriptors were analyzed. The results are illustrated in Table 1.  $\mu$ ,  $q_{H^+}$ ,  $q_{C-H^+}$ ,  $E_{LUMO}$ , volume and SAG are

Table 1  $i_{\max}$  of various organic compounds in SCWO and their quantum characteristics

Organic matters	$i_{\max}$ (%/°C)	$\mu$ (Debye)	HOF (kcal/mol)	$q_{H^+}$ (e)	$q_{C-H^+}$ (e)	$q_{C^-}$ (e)	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	Volume (Å <sup>3</sup> )	SAG (Å <sup>2</sup> )
Sulfanilic acid	0.2827	5.899	−572019	0.487	0.233	−0.332	−0.03811	−0.23664	481.85	320.85
Phenol	0.2542	1.344	−192991	0.46	0.213	−0.291	−0.01158	−0.2286	351.76	248
Rhodamine B	0.2608	15.03	−1180609	0.482	0.28	−0.317	−0.10133	−0.158	1341.95	743.56
2,4-dinitrophenylhydrazine	0.2517	7.628	−471969	0.413	0.272	−0.242	−0.10791	−0.25318	516.19	340.78
Phenylsulfonic acid	0.2782	4.147	−537267	0.493	0.235	−0.274	−0.05907	−0.28708	445.17	302.72
Methyl Red	0.416	5.687	−561947	0.474	0.223	−0.351	−0.07029	−0.19889	798.66	487.97
p-Dimethylaminobenzaldehyde	0.3016	6.425	−300997	0.218	0.218	−0.351	−0.04719	−0.2096	516.03	335.06
Isatin	0.3836	5.912	−322038	0.409	0.219	−0.254	−0.10529	−0.24924	441.57	298.57
Aniline	0.6086	1.715	−180522	0.362	0.199	−0.26	−0.00338	−0.20648	366.21	256.24
Nitrobenzene	0.4375	4.541	−274140	0.238	0.238	−0.191	−0.09666	−0.28751	390.61	272.4
ortho-Nitroaniline	0.2187	4.721	−308885	0.421	0.237	−0.254	−0.08744	−0.23045	417.28	283.04
Methylene Blue	0.1545	12.26	−1031249	0.236	0.222	−0.367	−0.11718	−0.18629	901.8	532.29
Correlation coefficient		−0.496	0.495	−0.077	−0.434	0.364	0.423	−0.114	−0.314	−0.315



negatively correlated to  $i_{\max}$  while HOF,  $q_{C^-}$ ,  $E_{\text{HOMO}}$  are positively correlated to  $i_{\max}$ . It is clearly shown that the significance of the descriptors to  $i_{\max}$  during SCWO follows the order:  $\mu$  (−0.496) > HOF (0.495) >  $q_{C-H^+}$  (−0.434) >  $E_{\text{HOMO}}$  (0.423) >  $q_{C^-}$  (0.364) > SAG (−0.315) > Volume (−0.314) >  $E_{\text{LUMO}}$  (−0.114) >  $q_{H^+}$  (−0.077).

It is the dipole moment ( $\mu$ ) that most greatly affects the temperature behavior of organic compounds. Generally, the lower the dipole moment is, the stronger the molecular symmetry is, and the more dramatically the compounds are oxidized. In spite of the fact that SCW has been thought to be a non-polar solvent of high diffusivity and complete miscibility with organic compounds, the compounds are not completely oxidized until the temperature is high enough. Dipole moment reflects the electrostatic attraction ability of molecules, and indicates that the burning of organic chemicals in SCWO is greatly related to their affinity for water molecules and OH radicals. The H-abstraction process is one of the important oxidation mechanisms. Although little is known about the transition state of the oxygen molecule and organic molecules in supercritical water, OH radicals have been considered to be the dominant oxidizing species in the SCWO process (Thomsen, 1998). Since the organic material can function as a fuel in an oxidation reaction (Rice and Steeper, 1998), HOF is also a very important affecting quantum descriptor to reflect the thermo-conversion process. Its importance can be concluded from previous studies of Xantheas and Dunning (1993). They have pointed out that if the HOF was not established, the thermodynamics of reaction are uncertain. Theoretical estimation of the HOF is essential to understanding a reaction. As  $i_{\max}$  indicates the large-scale destruction efficiency of organic compounds, it is strongly related to the rupture of their main chains. Therefore the breaking of C–H bonds should largely occur at these reaction stages. This process should be directly related to the values of  $q_{C-H^+}$ . The higher the  $q_{C-H^+}$  values are, the more easily abstracted the hydrogen atom of C–H bonds is, and the lower the temperature effect is. So the  $q_{C-H^+}$  is another very important factor. In a word, the temperature effect on the destruction of organic compounds in SCWO is more related to  $\mu$ , HOF and  $q_{C-H^+}$  than other quantitative descriptors. Once a correlation between molecular descriptors and  $i_{\max}$  is established, it is useful to predict the appropriate temperature ranges in the SCWO process

### 3 Conclusions

Temperature has a very important significance in SCWO equipment operation. Twelve organic compounds' removal ratios at various temperatures in SCWO were determined. In supercritical conditions, high conversion efficiency for all organic compounds can be obtained. In subcritical conditions, the conversion efficiency is not high enough

for compounds to be completely oxidized. Evidently, temperature increase leads to varying destruction improvement effects on different compounds. The value of  $i_{\max}$ , the highest slope of the temperature-removal ratio curves, was defined and used as a significant index to stand for temperature sensitivity. A high  $i_{\max}$  value for a compound indicates that it is oxidized dramatically during a certain temperature-rise period. Consequently, the high-temperature area of SCWO equipment is subject to extensive damage from fatigue. On the contrary, a low  $i_{\max}$  value for a compound means that it is not sensitive to temperature increase. Therefore, it will need a high temperature to be completely decomposed. Most of the tested compounds ( $i_{\max} > 0.25$ ) could be completely oxidized when the reactor temperature reached 500°C, while some other compounds ( $i_{\max} < 0.25$ ) needed a reactor temperature of 560°C.

In addition, the temperature-effect is closely related to molecular descriptors. Therefore, correlation coefficients between  $i_{\max}$  values and nine molecular descriptors were analyzed in this work. The results reveal that effect of temperature on destruction of organic compounds in SCWO is more related to  $\mu$ , HOF and  $q_{C-H^+}$  than other molecular descriptors. The correlation between molecular descriptors and  $i_{\max}$  is useful to predict the appropriate temperature ranges in the SCWO process.

### Acknowledgments

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