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Short communication

Degradation mechanism study of organic pollutants in ozonation process by QSAR analysis

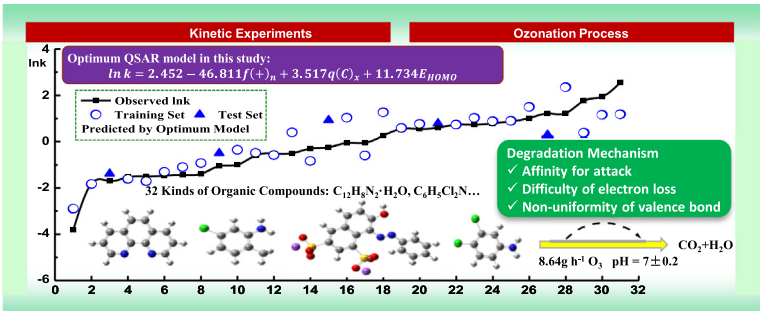
Huicen Zhu, Zhemin Shen *, Qingli Tang, Wenchao Ji, Lijuan Jia

School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

HIGHLIGHTS

- Degradation rules are explored in an organic system containing various compounds.
- We study the kinetics of each molecule to find predictable and propagable models.
- Fukui indices are considered as research emphasis in QSAR analysis.
- Optimum QSAR model exactly reveals determinant factors related to ozonation process.

GRAPHICAL ABSTRACT



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ABSTRACT

It is of great significance to find a universal relationship between reaction rates and molecular parameters of diverse organic pollutants by ozonation process. In this study, quantitative structure activity relationship (QSAR) models were developed in an organic system with 32 substances, including azo dyes, heterocyclic compounds and ionic compounds. Quantum chemical parameters were conducted by Gaussian 09 and Material Studio 6.1 for each organic compound, such as μ, $q(C)_x$ and E_{HOMO}. Fukui indices, one of the research emphases, have contained the electron density on main-chain atoms of both carbon and nitrogen. The favorable model is $\ln k = 2.452 - 46.811f(+)_n + 3.517q(C)_x + 11.734E_{HOMO}$ with squared regression coefficient $R^2 = 0.723$ and standard deviation SD = 0.789. Nearly all the compounds could obtain accurate predictions of their degradation rates, with slight differences. Besides, the model is validated by internal and external validations, and the statistical data suggest optimum stability and reliability. Optimum QSAR model exactly reveals three determinant factors, which are directly related to degradation rules. Specifically, the lowest $f(+)$ value of main-chain atoms ($f(+)_n$) indicates the degree of affinity for nucleophilic attack. E_{HOMO} refers to the electron energy of the highest occupied molecular orbital, representing the difficulty of electron loss. $q(C)_x$ shows the non-uniformity of electric charge on main chain, which indicates the ease or complexity of valence-bond breakage of organic molecules. Coincidentally, these three aspects are consistent with degradation mechanism. Together with all the above factors, the degradation mechanism could reasonably be illustrated from each perspective, providing a deeper insight of universal and propagable ozonation rules.

* Corresponding author. Tel.: +86 21 54741065.
E-mail address: zmshen@sjtu.edu.cn (Z. Shen).

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1. Introduction

A variety of highly toxic organic pollutants are released into the environment mostly through industrial effluents. They are often hardly degraded by microorganism owing to their complex structures, such as double bonds and activated aromatic rings [1–3]. Meanwhile, better water quality and more strict emission laws have been proposed worldwide, forcing people to seek more efficient wastewater treatments [4]. Many advanced oxidation processes (AOPs) have been conducted to degrade hazardous organic compounds into CO_2 and H_2O [5,6]. Ozonation, one of common AOPs, has gained increasingly attention due to its stronger oxidability and less selectivity [7,8].

Theoretical predicted methods are considered as a rapid and cost-effective alternative to experimental evaluations [9,10]. Among them, quantitative structure activity relationship (QSAR) analyses are widely used to evaluate and predict reaction rate constants [11–13]. Several QSAR models have been reported to estimate the relationship between structures of pollutants and degradation behaviors by quantum chemical parameters in wastewater [14,15]. Jiang et al. [16] have pointed out that ozonation process is greatly influenced at the molecular orbital level. However, Fukui indices are seldom taken into considerations, which are key indicators of affinity for attack in degradation reactions [17,18]. They have been applied to predict whether a chemical reaction or the synthesis of certain organic substances can be carried out [19].

Since each structure of organic pollutants is complex and distinctive, it is our emphasis to figure out a common rule available to oxidation systems. In this study, the impact of Fukui indices on ozonation process was prioritized in QSAR analysis. Primarily, kinetic experiments for the ozone degradation of a complex organic system were explored. Later, QSAR models were developed using multiple linear regression. Finally, validations were performed to testify the optimum model was robust to make predictions.

2. Materials and methods

2.1. Reaction system

All experiments were carried out at pH = 7 ± 0.2 in 2000 mL reactors at 298.15 K. Most database of QSAR analysis was performed under universal pH and temperature, providing conformity experimental conditions in model-building process. Beltrán [20] has reported that under pH 7 the kinetic regime corresponds to a slow reaction and, hence the concentration profile of ozone is nearly uniform through the film layer. In this case, the reaction takes place completely in the bulk water. The initial concentration of each organic compound was determined by oxygen demand, as listed in Table 1. The oxidized time could be figured out by stoichiometric relationship theoretically when organic pollutants were completely oxidized by ozone. During degradation reactions, ozone was generated by an ozone generator (Op-10 g, Qingdao Guolin Industry Co., Ltd., China). It was continuously introduced into the reactors and maintained at a constant concentration (8.64 g h^{-1}). Theoretically, ozonation process was in accordance with second-order reaction equation. Since the amount of ozone was far excess, the degradation process could be considered as first-order kinetic reaction [2]. Excess ozone in the outlet gas was absorbed by 10% sodium thiosulfate solution. After different residence time, the solution concentrations were detected by UV spectrophotometer at their maximum

Table 1
Tested and three predicted ln$k$ values of 32 organic pollutants.

No.	Molecule	Initial conc. (mg L^{-1})	Tested	1		2		3	
				Pred.	Diff.	Pred.	Diff.	Pred.	Diff.
1[a]	2,6-Dinitrotoluene	38.8	−5.521	0.184	5.705	−0.524	4.998	−1.627	3.895
2	*m*-Trihydroxybenzene	100	−3.817	−2.991	0.826	−2.982	0.834	−2.900	0.916
3[b]	Nitrobenzene	80	−1.808	−0.174	1.634	−0.899	0.909	−1.831	−0.023
4	2,4-Dichlorophenol	120	−1.698	−1.068	0.630	−1.179	0.519	−1.379	0.320
5	*o*-Chlorophenol	90	−1.532	−1.337	0.196	−1.448	0.084	−1.611	−0.078
6	Phenol	65	−1.496	−1.650	−0.154	−1.696	−0.199	−1.710	−0.214
7	Aniline	50	−1.470	−1.113	0.357	−1.530	−0.061	−1.308	0.162
8	3,4-Dichloroaniline	95	−1.444	−0.755	0.689	−1.132	0.312	−1.099	0.345
9 [b]	Isatin	75	−1.390	−0.264	1.127	−0.581	0.809	−0.926	0.464
10	*o*-Cresol	65	−1.053	−0.532	0.521	−0.550	0.502	−0.493	0.560
11	2-Nitrophenol	98	−0.997	−0.129	0.868	−0.039	0.957	−0.353	0.644
12	5-Chloro-2-Methylbenzylamine	70	−0.591	−0.264	0.327	−0.612	−0.022	−0.487	0.103
13	*o*-Nitroaniline	80	−0.503	−0.129	0.373	−0.453	0.050	−0.577	−0.075
14	2-Nitroso-1-Naphthol	100	−0.496	0.005	0.501	0.276	0.772	0.403	0.899
15 [b]	1,10-Phenanthroline Monohydrate	60	−0.294	−0.219	0.076	−0.598	−0.303	−0.836	−0.542
16	Orange G	115	−0.241	0.452	0.693	0.509	0.750	0.929	1.170
17	Chromotropic Acid	150	−0.058	0.407	0.465	0.584	0.641	1.034	1.092
18	*p*-Phthalic Acid	34.5	−0.053	−1.605	−1.552	−0.399	−0.346	−0.597	−0.544
19	*m*-Cresol Purple	74	0.262	1.123	0.861	1.884	1.622	1.271	1.009
20	*p*-Dimethylaminobenzaldehyde	60	0.544	0.094	−0.450	0.300	−0.244	0.596	0.051
21 [b]	Eriochrome Blue Black R	85	0.554	0.854	0.300	1.196	0.642	0.765	0.211
22	Metanil Yellow	75	0.606	0.854	0.248	0.522	−0.084	0.793	0.186
23	Fuchsin Basic	60	0.730	0.631	−0.100	0.307	−0.424	0.740	0.009
24	Cresol Red	75	0.735	0.810	0.074	1.555	0.820	1.028	0.292
25	Bromophenol Blue	160	0.791	1.257	0.466	1.183	0.392	0.884	0.094
26	Methylene Blue Trihydrate	60	0.876	0.497	−0.380	0.308	−0.569	0.903	0.027
27 [b]	Crystal Violet	55	1.018	0.810	−0.208	0.644	−0.373	1.502	0.484
28	Azure I	65	1.216	0.362	−0.854	0.751	−0.466	0.297	−0.919
29	Rhodamine B	65	1.231	1.078	−0.153	1.388	0.157	2.359	1.129
30	Methyl Red	25	1.774	0.452	−1.322	0.143	−1.631	0.391	−1.383
31	Bromocresol Green	145	1.944	1.436	−0.508	1.379	−0.565	1.160	−0.784
32	Indigo	65	2.568	0.273	−2.295	0.737	−1.831	1.188	−1.380

[a] Outlier whose Diff. is larger than 2.303 ln units.
[b] Samples in external test set.