

# JES

JOURNAL OF  
ENVIRONMENTAL  
SCIENCES

April 1, 2015 Volume 30  
[www.jesc.ac.cn](http://www.jesc.ac.cn)

ISSN 1001-0742  
CN 11-2629/X



## MBR in Wastewater Reclamation



Sponsored by  
Research Center for Eco-Environmental Sciences  
Chinese Academy of Sciences

**Highlight articles**

- 129 Rice: Reducing arsenic content by controlling water irrigation  
Ashley M. Newbigging, Rebecca E. Paliwoda and X. Chris Le
- 132 Apportioning aldehydes: Quantifying industrial sources of carbonyls  
Sarah A. Styler

**Review articles**

- 30 Application of constructed wetlands for wastewater treatment in tropical and subtropical regions (2000-2013)  
Dong-Qing Zhang, K.B.S.N. Jinadasa, Richard M. Gersberg, Yu Liu, Soon Keat Tan and Wun Jern Ng
- 47 Stepwise multiple regression method of greenhouse gas emission modeling in the energy sector in Poland  
Alicja Kolasa-Wiecek
- 113 Mini-review on river eutrophication and bottom improvement techniques, with special emphasis on the Nakdong River  
Andinet Tekile, Ilho Kim and Jisung Kim

**Regular articles**

- 1 Effects of temperature and composite alumina on pyrolysis of sewage sludge  
Yu Sun, Baosheng Jin, Wei Wu, Wu Zuo, Ya Zhang, Yong Zhang and Yaji Huang
- 9 Numerical study of the effects of local atmospheric circulations on a pollution event over Beijing-Tianjin-Hebei, China  
Yucong Miao, Shuhua Liu, Yijia Zheng, Shu Wang and Bicheng Chen, Hui Zheng and Jingchuan Zhao
- 21 Removal kinetics of phosphorus from synthetic wastewater using basic oxygen furnace slag  
Chong Han, Zhen Wang, He Yang and Xiangxin Xue
- 55 Abatement of SO<sub>2</sub>-NO<sub>x</sub> binary gas mixtures using a ferruginous active absorbent: Part I. Synergistic effects and mechanism  
Yinghui Han, Xiaolei Li, Maohong Fan, Armistead G. Russell, Yi Zhao, Chunmei Cao, Ning Zhang and Genshan Jiang
- 65 Adsorption of benzene, cyclohexane and hexane on ordered mesoporous carbon  
Gang Wang, Baojuan Dou, Zhongshen Zhang, Junhui Wang, Haier Liu and Zhengping Hao
- 74 Flux characteristics of total dissolved iron and its species during extreme rainfall event in the midstream of the Heilongjiang River  
Jiunian Guan, Baixing Yan, Hui Zhu, Lixia Wang, Duian Lu and Long Cheng
- 81 Sodium fluoride induces apoptosis through reactive oxygen species-mediated endoplasmic reticulum stress pathway in Sertoli cells  
Yang Yang, Xinwei Lin, Hui Huang, Demin Feng, Yue Ba, Xuemin Cheng and Liuxin Cui
- 90 Roles of SO<sub>2</sub> oxidation in new particle formation events  
He Meng, Yujiao Zhu, Greg J. Evans, Cheol-Heon Jeong and Xiaohong Yao
- 102 Biological treatment of fish processing wastewater: A case study from Sfax City (Southeastern Tunisia)  
Meryem Jemli, Fatma Karray, Firas Feki, Slim Loukil, Najla Mhiri, Fathi Aloui and Sami Sayadi

## CONTENTS

- 122 Bioreduction of vanadium (V) in groundwater by autohydrogentrophic bacteria: Mechanisms and microorganisms  
Xiaoyin Xu, Siqing Xia, Lijie Zhou, Zhiqiang Zhang and Bruce E. Rittmann
- 135 Laccase-catalyzed bisphenol A oxidation in the presence of 10-propyl sulfonic acid phenoxazine  
Rūta Ivanec-Goranina, Juozas Kulys, Irina Bachmatova, Liucija Marcinkevičienė and Rolandas Meškys
- 140 Spatial heterogeneity of lake eutrophication caused by physiogeographic conditions: An analysis of 143 lakes in China  
Jingtao Ding, Jinling Cao, Qigong Xu, Beidou Xi, Jing Su, Rutai Gao, Shouliang Huo and Hongliang Liu
- 148 Anaerobic biodegradation of PAHs in mangrove sediment with amendment of  $\text{NaHCO}_3$   
Chun-Hua Li, Yuk-Shan Wong, Hong-Yuan Wang and Nora Fung-Yee Tam
- 157 Achieving nitrification at low temperatures using free ammonia inhibition on *Nitrobacter* and real-time control in an SBR treating landfill leachate  
Hongwei Sun, Yongzhen Peng, Shuying Wang and Juan Ma
- 164 Kinetics of Solvent Blue and Reactive Yellow removal using microwave radiation in combination with nanoscale zero-valent iron  
Yanpeng Mao, Zhenqian Xi, Wenlong Wang, Chunyuan Ma and Qinyan Yue
- 173 Environmental impacts of a large-scale incinerator with mixed MSW of high water content from a LCA perspective  
Ziyang Lou, Bernd Bilitewski, Nanwen Zhu, Xiaoli Chai, Bing Li and Youcai Zhao
- 180 Quantitative structure-biodegradability relationships for biokinetic parameter of polycyclic aromatic hydrocarbons  
Peng Xu, Wencheng Ma, Hongjun Han, Shengyong Jia and Baolin Hou
- 191 Chemical composition and physical properties of filter fly ashes from eight grate-fired biomass combustion plants  
Christof Lanzerstorfer
- 198 Assessment of the sources and transformations of nitrogen in a plain river network region using a stable isotope approach  
Jingtao Ding, Beidou Xi, Qigong Xu, Jing Su, Shouliang Huo, Hongliang Liu, Yijun Yu and Yanbo Zhang
- 207 The performance of a combined nitrification-anammox reactor treating anaerobic digestion supernatant under various C/N ratios  
Jian Zhao, Jiane Zuo, Jia Lin and Peng Li
- 215 Coagulation behavior and floc properties of compound bioflocculant-polyaluminum chloride dual-coagulants and polymeric aluminum in low temperature surface water treatment  
Xin Huang, Shenglei Sun, Baoyu Gao, Qinyan Yue, Yan Wang and Qian Li
- 223 Accumulation and elimination of iron oxide nanomaterials in zebrafish (*Danio rerio*) upon chronic aqueous exposure  
Yang Zhang, Lin Zhu, Ya Zhou and Jimiao Chen
- 231 Impact of industrial effluent on growth and yield of rice (*Oryza sativa* L.) in silty clay loam soil  
Mohammad Anwar Hossain, Golum Kibria Muhammad Mustafizur Rahman, Mohammad Mizanur Rahman, Abul Hossain Molla, Mohammad Mostafizur Rahman and Mohammad Khabir Uddin
- 241 Molecular characterization of microbial communities in bioaerosols of a coal mine by 454 pyrosequencing and real-time PCR  
Min Wei, Zhisheng Yu and Hongxun Zhang
- 252 Risk assessment of *Giardia* from a full scale MBR sewage treatment plant caused by membrane integrity failure  
Yu Zhang, Zhimin Chen, Wei An, Shumin Xiao, Hongying Yuan, Dongqing Zhang and Min Yang
- 186 Serious BTEX pollution in rural area of the North China Plain during winter season  
Kankan Liu, Chenglong Zhang, Ye Cheng, Chengtang Liu, Hongxing Zhang, Gen Zhang, Xu Sun and Yujing Mu

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

[www.journals.elsevier.com/journal-of-environmental-sciences](http://www.journals.elsevier.com/journal-of-environmental-sciences)

**JES**  
JOURNAL OF  
ENVIRONMENTAL  
SCIENCES  
[www.jesc.ac.cn](http://www.jesc.ac.cn)

# Quantitative structure–biodegradability relationships for biokinetic parameter of polycyclic aromatic hydrocarbons

Peng Xu, Wencheng Ma, Hongjun Han\*, Shengyong Jia, Baolin Hou

State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China. E-mail: [xp12904@126.com](mailto:xp12904@126.com)

## ARTICLE INFO

### Article history:

Received 14 June 2014

Revised 29 July 2014

Accepted 31 July 2014

Available online 31 January 2015

### Keywords:

Leave-one-out cross-validation

Stepwise multiple linear regression

Polycyclic aromatic hydrocarbons

QSBR

## ABSTRACT

Prediction of the biodegradability of organic pollutants is an ecologically desirable and economically feasible tool for estimating the environmental fate of chemicals. In this paper, stepwise multiple linear regression analysis method was applied to establish quantitative structure biodegradability relationship (QSBR) between the chemical structure and a novel biodegradation activity index ( $q_{\max}$ ) of 20 polycyclic aromatic hydrocarbons (PAHs). The frequency B3LYP/6-311+G(2df,p) calculations showed no imaginary values, implying that all the structures are minima on the potential energy surface. After eliminating the parameters which had low related coefficient with  $q_{\max}$ , the major descriptors influencing the biodegradation activity were screened to be Freq,  $D$ ,  $MR$ ,  $E_{\text{HOMO}}$  and  $\text{ToIE}$ . The evaluation of the developed QSBR mode, using a leave-one-out cross-validation procedure, showed that the relationships are significant and the model had good robustness and predictive ability. The results would be helpful for understanding the mechanisms governing biodegradation at the molecular level.

© 2015 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are produced by chemical industry for a variety of applications, including pharmaceuticals, cosmetics, pesticides, disinfectants, agrochemicals, dyestuffs, antifreeze, corrosion inhibitor, coal-tar wastes and creosote wood preservation (Wang et al., 2007; Haritash and Kaushik, 2009). Several PAHs have been reported to display toxic, mutagenic and carcinogenic properties even when present in low concentrations. These compounds pose a serious threat to humans and marine animals and have received increasing awareness in the aquatic environment (Mearns et al., 2009). Their fate in environment includes volatilization, photo-oxidation, chemical oxidation, adsorption on soil particles, leaching, and microbial degradation which are

the major degradation processes for PAHs (Zheng et al., 2007; Augulyte et al., 2009; Kalmykova et al., 2014).

The quantitative structure–biodegradability relationship (QSBR) developed from the quantitative structure activity relationships (QSAR) is a tool used to describe and predict the biodegradability of organic compounds (Okey and Stensel, 1996). The objectives of QSBR studies are to understand mechanisms of biodegradation, to classify chemicals according to relative biodegradability, and to predict the biodegradability of new organic compounds. It is also valuable for estimating the environmental fate of pollutants and the risk assessment of PAHs (Raymond et al., 2001; Baboshin and Golovleva, 2012). Toward these objectives, much research has been performed to develop reliable QSBR models. Ferreira (2001) performed a structure based study of the

\* Corresponding author. E-mail addresses: [han13946003379@163.com](mailto:han13946003379@163.com) (Hongjun Han).



biodegradation rates of 22 benzene derivatives in aqueous systems. They revealed that the computed averaged dipole polarizabilities and the summation of the Raman activities over vibrational degrees of freedom of benzene derivatives are in excellent linear correlation with the observed first-order biomass-normalized rate coefficient of benzene derivatives. A negative correlation (correlation coefficient 0.99) between denitrification rate and molecular connectivity index  $^1\chi^v$  reflected that the degradation of aromatic heterocyclic compounds in activated sludge was substantially influenced by molecular size and the electronic properties (Wammer and Peters, 2005). Meanwhile, during  $O_3$ /UV degradation process, a QSAR model was established which revealed that the degradation rate depended on the highest occupied molecular orbital and delocalization energy (Chen et al., 2001).

Currently, in the model development process of the QSBR, the half-lives, theoretical oxygen demand (ThOD) and biological oxygen demand (BOD) were commonly used as the biodegradability indexes (Okey and Stensel, 1996). Although some models are available for the %BOD predictions, their applicability is limited to specific classes (Philipp et al., 2007). No attention has been paid to the theoretical considerations of the relationship between biokinetic parameters of compound and the descriptors. The objective of the present study was to develop valid QSBR for appropriate parameter expressing the kinetics of bacterial biotransformation of PAHs. The relationship between specific biodegradation rate ( $q_{\max}$ ) and molecular structure

descriptors was gradually established using multiple linear regression analysis.

## 1. Materials and methods


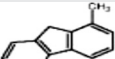

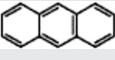
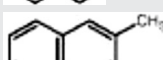
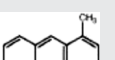


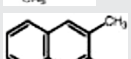
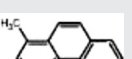
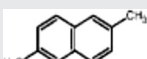
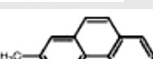
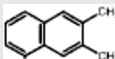


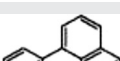


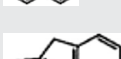

### 1.1. Biodegradation data

Experiments were designed to measure biodegradation rates of 20 PAHs in aqueous systems. These experiments were performed individually for each PAH at a concentration significantly below its aqueous solubility to ensure that no separate PAH phase was present. Experimental measurement of the biokinetic parameters was based on the Andrews model, an extension of the Monod model that accounts for substrate inhibition (Wammer and Peters, 2005):

$$q = \frac{q_{\max} \times C}{K_s + C + C^2/K_i} \quad (1)$$

where,  $q$  (mg/(L·hr)) is the specific biotransformation rate,  $C$  (mg/L) is the substrate concentration,  $q_{\max}$  (mg/(L·hr)) is the maximal specific biotransformation rate,  $K_s$  (mg/L) is the biotransformation affinity coefficient, and  $K_i$  (mg/L) is the substrate inhibition coefficient. The fitting parameters in the above equation are presented in Table 1. The biokinetic of  $q_{\max}$  was used as the biodegradability index. The values of

**Table 1 – Structure and biodegradation activity value of 20 PAHs.**

Compound	Structure	$q_{\max}$ (mg/(L·hr))	Compound	Structure	$q_{\max}$ (mg/(L·hr))
Naphthalene		61.36	1-Methylfluorene		161.54
1-Methylnaphthalene		210.52	Anthracene		178.19
2-Methylnaphthalene		240.97	1-Methylanthracene		76.33
1,5-Dimethylnaphthalene		152.63	Phenanthrene		108.94
2,3-Dimethylnaphthalene		101.49	1-Methylphenanthrene		72.85
2,6-Dimethylnaphthalene		172.23	2-Methylphenanthrene		138.39
2,3,5-Trimethylnaphthalene		92.28	3,6-Dimethylphenanthrene		159.64
Acenaphthene		89.59	Fluoranthene		95.48
Acenaphthylene		189.41	Pyrene		61.41
Fluorene		81.47	1-Methylpyrene		32.75

**Table 2 – Descriptors of PAHs used in QSBR study.**

Compound	LogK <sub>OW</sub>	D (Å)	<sup>0</sup> X <sup>v</sup>	<sup>1</sup> X <sup>v</sup>	MR (m <sup>3</sup> /mol)	NRB	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	ToIE (eV)	Freq (cm <sup>-1</sup> )	DE (kJ/mol)
Naphthalene	1.37	2	9.342	3.114	4.0418	4	-8.7429	-2.8212	-1473.2851	867.125	89.384
1-Methylnaphthalene	0.19	2	8.903	2.945	5.5604	3	-6.9381	-1.9214	-987.0517	743.439	95.527
2-Methylnaphthalene	1.24	2	9.013	3.048	6.1983	3	-6.5742	-1.5890	-926.1428	698.381	82.018
1,5-Dimethylnaphthalene	2.19	3	6.438	1.917	4.3195	4	-8.4719	-2.3461	-1293.4271	723.014	103.284
2,3-Dimethylnaphthalene	0.73	3	5.189	1.482	3.0873	4	-7.7943	-1.8472	-1738.0924	807.725	64.893
2,6-Dimethylnaphthalene	1.68	4	6.724	2.049	4.2981	5	-10.3725	-2.9425	-1095.3758	715.293	71.582
2,3,5-Trimethylnaphthalene	1.35	3	4.024	1.273	2.9946	5	-6.9318	-1.8219	-1437.4978	791.785	87.017
Acenaphthene	1.87	2	2.571	0.842	3.4571	6	-9.5321	-2.0481	-1631.8567	780.269	60.491
Acenaphthylene	0.94	3	5.617	1.891	5.0278	6	-7.8736	-1.7832	-1037.2154	738.153	79.279
Fluorene	0.57	3	3.506	1.139	2.9012	5	-12.6981	-4.2704	-1537.2803	803.942	93.493
1-Methylfluorene	0.81	2	1.783	0.582	4.1254	6	-8.8364	-2.4378	-1358.0874	758.236	81.572
Anthracene	1.48	4	2.946	0.947	2.5031	6	-7.1734	-2.0941	-2088.6796	705.293	76.249
1-Methylantracene	1.09	4	6.178	2.014	2.7988	6	-11.8942	-3.8926	-1948.1732	805.179	99.027
Phenanthrene	3.04	5	8.934	3.173	3.1806	7	-9.9576	-3.4123	-1703.9718	772.895	82.687
1-Methylphenanthrene	2.95	5	3.016	0.927	4.3189	7	-12.5638	-4.9831	-1439.0267	791.073	94.284
2-Methylphenanthrene	0.79	4	5.284	1.893	3.7923	7	-9.4932	-3.0874	-1580.2693	772.038	103.912
3,6-Dimethylphenanthrene	0.18	6	5.013	1.378	2.6847	6	-8.4271	-2.4892	-1274.3281	718.386	127.103
Fluoranthene	2.84	4	4.820	1.694	3.0956	8	-10.4831	-3.0461	-1892.5286	829.591	86.268
Pyrene	2.41	5	1.849	0.593	3.2153	8	-15.2911	-4.9783	-2105.3924	815.675	93.891
1-Methylpyrene	1.58	6	7.135	2.439	2.8539	8	-13.9804	-4.2935	-2379.5871	873.248	110.392

the kinetic parameters for Andrews equation were obtained using nonlinear regression analysis in MINITAB 14.0

### 1.2. Geometry optimization and molecular descriptors

The equilibrium geometries of all PAHs were fully optimized using the density functional theory (DFT) method. The DFT calculations were run using a moderate basis set size (6-311+G(2df,p)) In all optimizations, the initial structures were pre-minimized using a force-field in Gaussian 09 program. Since the structures are relatively rigid, the precise starting geometries were not considered to be particularly important. We performed the optimizations in the framework of the C1 and C2 point groups. The frequency B3LYP/6-311+G(2df,p) calculations showed no imaginary values, implying that all the structures are minima on the potential energy surface.

There are 11 molecular descriptors used in this article. Six descriptors such as octanol/water partition coefficient ( $K_{OW}$ ), zero molecular connective index ( $^0X^v$ ), first molecular connective index ( $^1X^v$ ), molecular diameter ( $D$ ), molar refractivity (MR) and number of rotatable bonds (NRB) were calculated by Algorithms Builder 1.0. The quantum chemical descriptors of the highest occupied molecular orbital ( $E_{HOMO}$ ), the energy of lowest unoccupied molecular orbital ( $E_{LUMO}$ ), total energy of electronics (ToIE), the wagging vibration frequency of the whole molecule (Freq) and delocalization energy (DE) were calculated by using the software of Chemoffice 6.0. on energy-minimized structures at a semi-empirical level (AM1). The related chemical descriptors of 20 PAHs are listed in Table 2.

### 1.3. Development of QSBR equation

The stepwise regression analysis was carried out by MINITAB 14.0, including dependent variable  $q_{max}$  and independent variables mentioned above obtained from calculating results. Procedures for stepwise regression analysis were described by Xu et al. (2012). The goodness of the established model was accessed by the following statistical parameters: R (correlation coefficient),  $R^2$  (coefficient of determination), S.E. (standard error of regression estimation), F (Fisher check value) and RMSE (the root mean squared error).

## 2. Results and discussion

### 2.1. Unitary linear regression

Prior to stepwise multiple linear regression analysis, the monadic linear correlation between 11 chemical descriptors and  $q_{max}$  was studied respectively. The related coefficients are shown in Table 3. As can be seen in Table 3, there is the highest linear correlation coefficient ( $R = -0.844$ ) between  $q_{max}$  and Freq. Meanwhile there is the lowest linear correlation coefficient ( $R = 0.368$ ) between  $q_{max}$  and DE. The scatter diagram of Freq and DE with  $q_{max}$  was shown as Fig. 1. After eliminating the parameters which had low related coefficient ( $|R| < 0.5$ ) with  $q_{max}$ , we found that the major descriptors influencing the biodegradation activity were Freq,  $D$ , MR,  $E_{HOMO}$  and ToIE.

**Table 3 – Correlation coefficients of descriptors used in this study.**

	LogK <sub>OW</sub>	D	<sup>0</sup> X <sup>v</sup>	<sup>1</sup> X <sup>v</sup>	MR	NRB	E <sub>HOMO</sub>	E <sub>LUMO</sub>	ToIE	Freq	DE
$q_{max}$	0.493	0.601	-0.402	-0.398	0.573	-0.389	0.837	-0.413	0.701	-0.844	0.368

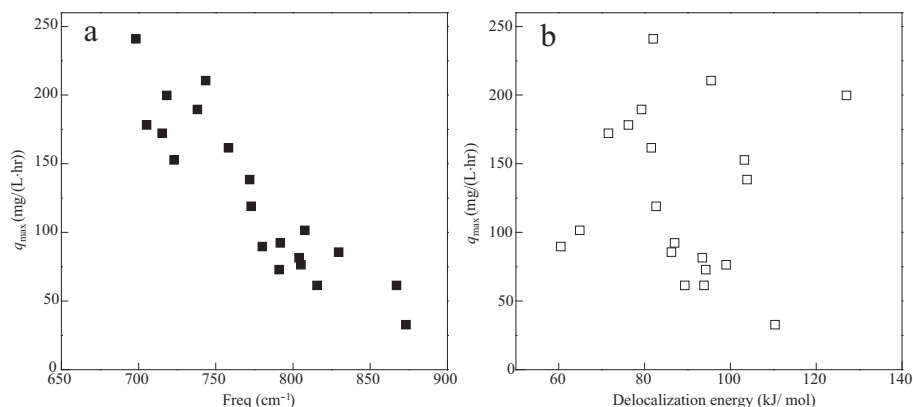


Fig. 1 – Scatter diagram of (a) vibration frequency and (b) delocalization energy with  $q_{\max}$ .

## 2.2. Quantitative structure–biodegradability relationship

In order to get the best QSBR model, Freq and  $D$  were initially taken as independent variables to carry out linear regression analysis, and we got Eq. (2):

$$q_{\max} = 147.2 - 0.11 \text{ Freq} + 31.6 D \quad (2)$$

$n = 20$ ,  $R = 0.871$ ,  $R^2 = 0.703$ , S.E. = 10.18,  $F = 27.69$ , RMSE = 7.89.

To investigate the influence of adding variables to QSBR, we added MR as an independent variable and got Eq. (3) based on Eq. (2). Moreover, by adding  $E_{\text{HOMO}}$  as an independent variable we got Eq. (4) based on Eq. (3), and by adding ToIE as an independent variable we got Eq. (5) based on Eq. (4).

$$q_{\max} = 109.3 - 0.15 \text{ Freq} + 27.5 D + 4.52 \text{ MR} \quad (3)$$

$n = 20$ ,  $R = 0.921$ ,  $R^2 = 0.852$ , S.E. = 5.084,  $F = 23.51$ , RMSE = 3.782

$$q_{\max} = 172.9 - 0.31 \text{ Freq} + 19.6 D + 8.97 \text{ MR} + 3.82 E_{\text{HOMO}} \quad (4)$$

$n = 20$ ,  $R = 0.951$ ,  $R^2 = 0.901$ , S.E. = 4.72,  $F = 25.38$ , RMSE = 2.23

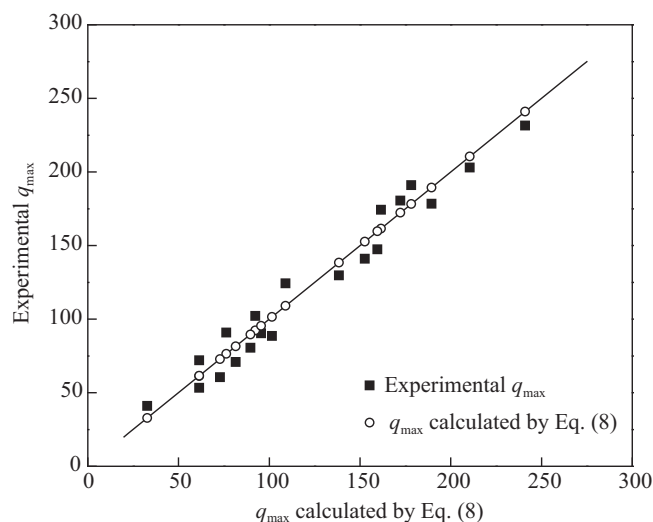
$$q_{\max} = 382.1 - 0.57 \text{ Freq} + 13.4 D + 6.08 \text{ MR} + 13.24 E_{\text{HOMO}} + 0.017 \text{ ToIE} \quad (5)$$

$n = 20$ ,  $R = 0.969$ ,  $R^2 = 0.946$ , S.E. = 2.73,  $F = 34.38$ , RMSE = 1.032.

By comparing the various parameters in Eqs. (3) to (5), it can be found that Eq. (5) is an ideal QSBR model. This is because with the increase of the variable, correlation coefficient  $R$ , determination coefficient  $R^2$  and Fisher check value  $F$  become bigger; while standard deviation S.E. and root mean squared error RMSE become smaller. In order to validate the predictive ability of different models, predicted values calculated by different models and experimental values were listed in Table 4. The relationship between experimental results and predicted values calculated by Eq. (5) was shown as Fig. 2. The results show good agreement between predictions and experimental data. Validation is a crucial aspect of any QSBR modeling. It is the process by which the reliability and

Table 4 – Experimental and predicted biodegradabilities.

Compound	$q_{\max}$ (exp.)	$q_{\max}$ (calcd.)					
		By Eq. (3)	Residual	By Eq. (4)	Residual	By Eq. (5)	Residual
Naphthalene	61.36	49.32	12.04	82.69	−21.33	53.24	8.12
1-Methylnaphthalene	210.52	199.84	10.68	227.59	−17.07	202.98	7.54
2-Methylnaphthalene	240.97	262.04	−21.07	253.61	−12.64	231.42	9.55
1,5-Dimethylnaphthalene	152.63	172.42	−19.79	133.4	19.23	141.02	11.61
2,3-Dimethylnaphthalene	101.49	111.44	−9.95	114.64	−13.15	88.48	13.01
2,6-Dimethylnaphthalene	172.23	158.17	14.06	152.38	19.85	180.48	−8.25
2,3,5-Trimethylnaphthalene	92.28	114.05	−21.77	77.36	14.92	102.11	−9.83
Acenaphthene	89.59	94.28	−4.69	84.15	5.44	80.53	9.06
Acenaphthylene	189.41	218.24	−28.83	191.71	−2.3	178.42	10.99
Fluorene	81.47	102.18	−20.71	70.78	10.69	70.84	10.63
1-Methylfluorene	161.54	206.85	−45.31	150.74	10.8	174.32	−12.78
Anthracene	178.19	202.98	−24.79	163.2	14.99	191.05	−12.86
1-Methylanthracene	76.33	88.45	−12.12	86.62	−10.29	90.84	−14.51
Phenanthrene	108.94	139.83	−30.89	94.67	14.27	124.23	−15.29
1-Methylphenanthrene	72.85	82.94	−10.09	59.37	13.48	60.53	12.32
2-Methylphenanthrene	138.39	108.24	30.15	119.43	18.96	129.74	8.65
3,6-Dimethylphenanthrene	159.64	176.54	−16.9	138.66	20.98	147.43	12.21
Fluoranthene	95.48	104.28	−8.8	86.09	9.39	90.34	5.14
Pyrene	61.41	83.93	−22.52	39.6	21.81	72.04	−10.63
1-Methylpyrene	32.75	46.03	−13.28	43.46	−10.71	40.95	−8.2



**Fig. 2 – Plots of experimental  $q_{\max}$  versus those predicted by Eq. (8).**

relevance of a procedure are established for a specific purpose. It is now being accepted that validation is an important process that includes assessment of issues such as data quality, applicability of the model and mechanistic interpretability in addition to statistical assessment (Nandy et al., 2013). A common method for internally validating a QSBR model is leave-one-out cross-validation. This has the advantage that each data point is used for both training and validation on each trial (Zhang et al., 2014). Leave-one-out cross-validation is normally restricted to applications where the amount of training data available is severely limited, such that even a small perturbation of the training data is likely to result in a substantial change in the fitted model. In the present study, it makes good sense to adopt a leave-one-out cross-validation strategy as it minimizes the perturbation to the data in each trial. The outcome from this procedure is a cross-validated correlation coefficient ( $Q^2_{\text{LOO}}$ ), which is usually smaller than the overall  $R^2$  for a QSBR mode (Kar and Roy, 2011). Frequently,  $Q^2_{\text{LOO}}$  is used as a criterion of both robustness and predictive ability of the model. Many authors consider high  $Q^2_{\text{LOO}}$  (for instance,  $Q^2_{\text{LOO}} > 0.5$ ) as an indicator or even as the ultimate proof of the high predictive power of the QSBR mode. For Eq. (5), the  $Q^2_{\text{LOO}}$  of validation results is 0.927, which was significantly larger than 0.5. So the established QSBR model performed well with the aspects of goodness-of-fit, robustness and predictivity.

### 2.3. Mechanisms interpretation for the established QSBR mode

Freq is a parameter reflected the chemical bond strength. Biodegradation of PAHs included the fracture of the benzene ring. Therefore, chemical bond strength of the benzene ring must be closely correlated with biodegradation activity (Xu et al., 2012).  $E_{\text{HOMO}}$  is a parameter associated with the ability to donate electrons. All  $E_{\text{HOMO}}$  values are negative; therefore, smaller  $E_{\text{HOMO}}$  values indicate electrons that are more strongly bound to the system, which weakens the biodegradability of such compounds (Yang et al., 2004). TolE was the total energy of

all electrons energy and repulsion energy between atomic nucleuses in a molecule. It was in direct proportion to the biodegradability of the compounds. When a PAH compound had lower TolE, the biodegradability would be poorer (Yang et al., 2006). Molecular diameter ( $D$ ) indicated the spatial scale in where electrons in the molecule moved, and characterized the size of a molecule. Larger diameter molecules may interact with an enzyme more readily, thus increasing the biodegradability of this organic compound (Yang et al., 2006). Finally, MR was directly associated with its electronic property. If an aromatic compound had bigger MR, the electrons in this molecule was easier to be lost to form stronger electrostatic, so the biodegradability of this aromatic compound was better.

## 3. Conclusions

The theoretical relationship between biokinetic parameter ( $q_{\max}$ ) and molecular descriptors has been investigated based on stepwise multiple linear regression analysis. According to the experimental results, the major descriptors influencing the biodegradation activity were screened to be Freq,  $D$ , MR,  $E_{\text{HOMO}}$  and TolE. Assessment based on leave-one-out cross-validation indicated that the established QSBR model had good robustness and predictive ability. Interpretation of the descriptors responsible for biodegradation activity can be useful tools for designing new biodegradable chemicals and/or predicting the biodegradability of new chemicals in the environmental hazard assessment.

## Acknowledgments

This work was supported by the State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (No. 2013DX10), the Sino-Dutch Research Program (No. zhmhgfs2011-001), and the Sino-American Coal Chemical Industry Program (No. ZMAGZ 2011001).

## REFERENCES

- Augulyte, L., Kliugaite, D., Racys, V., Jankunaite, D., Zaliauskiene, A., Bergqvist, P., Andersson, P.L., 2009. Multivariate analysis of a biologically activated carbon (BAC) system and its efficiency for removing PAHs and aliphatic hydrocarbons from wastewater polluted with petroleum products. *J. Hazard. Mater.* 170 (1), 103–110.
- Baboshin, M.A., Golovleva, L.A., 2012. Biodegradation of polycyclic aromatic hydrocarbons (PAH) by aerobic bacteria and its kinetics aspects. *Mikrobiologiya* 81 (6), 639–650.
- Chen, J.W., Peijnenburg, W., Quan, X., Chen, S., Martens, D., Schramm, K.W., Kettrup, A., 2001. Is it possible to develop a QSPR model for direct photolysis half-lives of PAHs under irradiation of sunlight. *Environ. Pollut.* 114 (1), 137–143.
- Ferreira, M., 2001. Polycyclic aromatic hydrocarbons: A QSPR study. *Chemosphere* 44 (2), 125–146.
- Haritash, A.K., Kaushik, C.P., 2009. Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. *J. Hazard. Mater.* 169 (1–3), 1–15.
- Kalmykova, Y., Moona, N., Strömval, A.M., Björklund, K., 2014. Sorption and degradation of petroleum hydrocarbons, polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A



- and phthalates in landfill leachate using sand, activated carbon and peat filters. *Water Res.* 56, 246–257.
- Kar, S., Roy, K., 2011. Development and validation of a robust QSAR model for prediction of carcinogenicity of drugs. *Indian J. Biochem. Bio.* 48 (2), 111–122.
- Mearns, A.J., Reish, D.J., Oshida, P.S., Buchman, M., Ginn, T., Donnelly, R., 2009. Effects of pollution on marine organisms. *Water Environ. Res.* 81 (10), 2070–2125.
- Nandy, A., Kar, S., Roy, K., 2013. Development and validation of regression-based QSAR models for quantification of contributions of molecular fragments to skin sensitization potency of diverse organic chemicals. *Sar Qsar Environ. Res.* 24 (12), 1009–1023.
- Okey, R.W., Stensel, H.D., 1996. A QSAR-based biodegradability model-A QSBR. *Water Res.* 30 (9), 2206–2214.
- Philipp, B., Hoff, M., Germa, F., Schink, B., Beimborn, D., Mersch-Sundermann, V., 2007. Biochemical interpretation of quantitative structure-activity relationships (QSAR) for biodegradation of N-heterocycles: a complementary approach to predict biodegradability. *Environ. Sci. Technol.* 41 (4), 1390–1398.
- Raymond, J.W., Rogers, T.N., Shonnard, D.R., Kline, A.A., 2001. A review of structure-based biodegradation estimation methods. *J. Hazard. Mater.* 84 (2–3), 189–215.
- Wammer, K.H., Peters, C.A., 2005. Polycyclic aromatic hydrocarbon biodegradation rates: a structure-based study. *Environ. Sci. Technol.* 39 (8), 2571–2578.
- Wang, L., Wang, I.C., Chang, J., Lai, S., Chang-Chien, G., 2007. Emission of polycyclic aromatic hydrocarbons (PAHs) from the liquid injection incineration of petrochemical industrial wastewater. *J. Hazard. Mater.* 148 (1–2), 296–302.
- Xu, X., Li, X., Sun, S., 2012. A QSAR study on the biodegradation activity of PAHs in aged contaminated sediments. *Chemom. Intell. Lab. Syst.* 114, 50–55.
- Yang, H.W., Jiang, Z.P., Shi, S.Q., 2004. Anaerobic biodegradability of aliphatic compounds and their quantitative structure biodegradability relationship. *Sci. Total Environ.* 322 (1–3), 209–219.
- Yang, H.W., Jiang, Z.P., Shi, S.Q., 2006. Aromatic compounds biodegradation under anaerobic conditions and their QSBR models. *Sci. Total Environ.* 358 (1–3), 265–276.
- Zhang, X., Xie, J., Sun, F., 2014. Effects of three polycyclic aromatic hydrocarbons on sediment bacterial community. *Current Microbiol.* 68 (6), 756–762.
- Zheng, X., Blais, J., Mercier, G., Bergeron, M., Drogui, P., 2007. PAH removal from spiked municipal wastewater sewage sludge using biological, chemical and electrochemical treatments. *Chemosphere* 68 (6), 1143–1152.



## Editorial Board of Journal of Environmental Sciences

### Editor-in-Chief

**X. Chris Le** University of Alberta, Canada

### Associate Editors-in-Chief

**Jiuhui Qu** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Shu Tao** Peking University, China  
**Nigel Bell** Imperial College London, UK  
**Po-Keung Wong** The Chinese University of Hong Kong, Hong Kong, China

### Editorial Board

#### Aquatic environment

**Baoyu Gao** Shandong University, China  
**Maohong Fan** University of Wyoming, USA  
**Chihpin Huang** National Chiao Tung University, Taiwan, China  
**Ng Wun Jern** Nanyang Environment & Water Research Institute, Singapore  
**Clark C. K. Liu** University of Hawaii at Manoa, USA  
**Hokyong Shon** University of Technology, Sydney, Australia  
**Zijian Wang** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Zhiwu Wang** The Ohio State University, USA  
**Yuxiang Wang** Queen's University, Canada  
**Min Yang** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Zhifeng Yang** Beijing Normal University, China  
**Han-Qing Yu** University of Science & Technology of China, China

#### Terrestrial environment

**Christopher Anderson** Massey University, New Zealand  
**Zucong Cai** Nanjing Normal University, China  
**Xinbin Feng** Institute of Geochemistry, Chinese Academy of Sciences, China  
**Hongqing Hu** Huazhong Agricultural University, China  
**Kin-Che Lam** The Chinese University of Hong Kong, Hong Kong, China  
**Erwin Klumpp** Research Centre Juelich, Agrosphere Institute, Germany

#### Peijun Li

Institute of Applied Ecology, Chinese Academy of Sciences, China  
**Michael Schlöter** German Research Center for Environmental Health, Germany  
**Xuejun Wang** Peking University, China  
**Lizhong Zhu** Zhejiang University, China

#### Atmospheric environment

**Jianmin Chen** Fudan University, China  
**Abdelwahid Mellouki** Centre National de la Recherche Scientifique, France  
**Yujing Mu** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Min Shao** Peking University, China  
**James Jay Schauer** University of Wisconsin-Madison, USA  
**Yuesi Wang** Institute of Atmospheric Physics, Chinese Academy of Sciences, China  
**Xin Yang** University of Cambridge, UK

#### Environmental biology

**Yong Cai** Florida International University, USA  
**Henner Hollert** RWTH Aachen University, Germany  
**Jae-Seong Lee** Sungkyunkwan University, South Korea  
**Christopher Rensing** University of Copenhagen, Denmark  
**Bojan Sedmak** National Institute of Biology, Slovenia  
**Lirong Song** Institute of Hydrobiology, Chinese Academy of Sciences, China  
**Chunxia Wang** National Natural Science Foundation of China  
**Gehong Wei** Northwest A & F University, China

#### Daqiang Yin

Tongji University, China  
**Zhongtang Yu** The Ohio State University, USA

#### Environmental toxicology and health

**Jingwen Chen** Dalian University of Technology, China  
**Jianying Hu** Peking University, China  
**Guibin Jiang** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Sijin Liu** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Tsuyoshi Nakanishi** Gifu Pharmaceutical University, Japan

**Willie Peijnenburg** University of Leiden, The Netherlands  
**Bingsheng Zhou** Institute of Hydrobiology, Chinese Academy of Sciences, China

#### Environmental catalysis and materials

**Hong He** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Junhua Li** Tsinghua University, China  
**Wenfeng Shangguan** Shanghai Jiao Tong University, China  
**Ralph T. Yang** University of Michigan, USA

#### Environmental analysis and method

**Zongwei Cai** Hong Kong Baptist University, Hong Kong, China  
**Jiping Chen** Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China  
**Minghui Zheng** Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
**Municipal solid waste and green chemistry**  
**Pinjing He** Tongji University, China

### Editorial office staff

**Managing editor** Qingcai Feng  
**Editors** Zixuan Wang Suqin Liu Kuo Liu Zhengang Mao  
**English editor** Catherine Rice (USA)

# JOURNAL OF ENVIRONMENTAL SCIENCES

环境科学学报(英文版)

[www.jesc.ac.cn](http://www.jesc.ac.cn)

## Aims and scope

*Journal of Environmental Sciences* is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

## For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via <http://www.elsevier.com/locate/jes>.

## For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: [journal@mail.sciencep.com](mailto:journal@mail.sciencep.com), or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

## Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

## Editorial

Authors should submit manuscript online at <http://www.jesc.ac.cn>. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: [jesc@rcees.ac.cn](mailto:jesc@rcees.ac.cn). Instruction to authors is available at <http://www.jesc.ac.cn>.

## Journal of Environmental Sciences (Established in 1989) Volume 30 2015

<b>Supervised by</b>	Chinese Academy of Sciences	<b>Published by</b>	Science Press, Beijing, China
<b>Sponsored by</b>	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences		Elsevier Limited, The Netherlands
<b>Edited by</b>	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; <a href="http://www.jesc.ac.cn">http://www.jesc.ac.cn</a> E-mail: <a href="mailto:jesc@rcees.ac.cn">jesc@rcees.ac.cn</a>	<b>Distributed by</b>	
		Domestic	Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China
		Foreign	Elsevier Limited <a href="http://www.elsevier.com/locate/jes">http://www.elsevier.com/locate/jes</a>
<b>Editor-in-chief</b>	X. Chris Le	<b>Printed by</b>	Beijing Beilin Printing House, 100083, China

CN 11-2629/X Domestic postcode: 2-580

Domestic price per issue RMB ¥ 110.00

ISSN 1001-0742

