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

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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_{HOMO} and 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.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are produced by chemical industry for a variety of applications, including pharmaceuticals, cosmetics, pesticides, disinfectants, agro-chemicals, 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

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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 $^{1}X^{v}$ 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

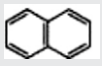
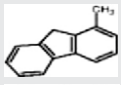
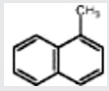
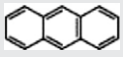
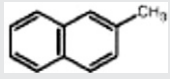
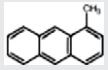
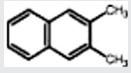
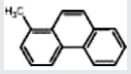
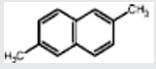
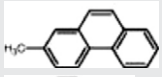
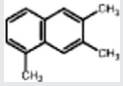
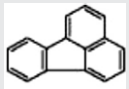
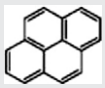
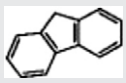
1.1. Biodegradation data

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