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Quantitative structure–biodegradability relationship of sulfide mineral flotation collectors

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ABSTRACT

12 physicochemical and quantum chemical parameters of 7 kinds of sulfide mineral flotation collectors are calculated. On the basis of the experimental data, a QSBR model including parameters, such as E_{LUMO}, μ, TE, $(E_{LUMO}-E_{HOMO})$ and $(E_{LUMO}-E_{HOMO})^2$ was established for K_b prediction by multiple linear regression. Results showed that the calculated data fitted well with the experimental values, indicating the reliable prediction and good robustness of the developed model, which can be used in K_b prediction of analogs. According to analysis of the model, the electrical parameters were the dominant factors affecting the aerobic biodegradability of sulfide mineral flotation collectors. However, the steric parameters and hydrophobic parameters had a small impact on biodegradability of the collectors.

1. Introduction

For most organic chemicals, biodegradation is the principal abatement process in the environment, hence, biodegradability is the most important parameter influencing the toxicity, persistence, and ultimate fate in aquatic and terrestrial ecosystems (Raymond et al., 2001; Liu et al., 2003).

Quantitative structure–biodegradability relationship (QSBR) is an effective research approach based on quantitative structure–activity relationship (QSAR), with which the biodegradation rule, degradation mechanism and prediction for biodegradation capabilities of toxic organic chemicals can be obtained (Liu et al., 2003). Sulfide mineral flotation collectors have been widely used in flotation (Hope et al., 2001). It has been known that even small concentration of these reagents in water streams is toxic to water life, besides their deleterious influence on end stream processes during recycling (Okibe and Johnson 2002). Serious environmental problems associated with flotation reagents in mineral processing plant wastewater have been well documented (Hissner et al., 1999; Chockalingam et al., 2003).

Studies on the QSBR model of flotation reagents have not been reported. In the present investigation, 12 physicochemical and quantum chemical parameters of sulfide mineral flotation collectors are calculated, and the aerobic biodegradation rate constants ($LogK_b$) are used as observations to develop corresponding QSBR model. On the basis of molecular structure, the dominant influencing factors in aerobic biodegradation of sulfide mineral flotation collectors are discussed. Finally, the general QSBR modeling yield was tested and verified by experiments. Therefore, studies on the QSBRs model are mainly to understand the mechanism of biodegradation and to classify the chemical reagents according to the relative biodegradability and to develop reliable biodegradation assessment methods for sulfide mineral flotation collectors.

2. Materials and methods

2.1. Materials

The analytical grade reagents were purchased from Tianjin Chemical Co., Ltd. (Tianjin, P.R. China). Ethyl xanthate, isopropyl xanthate, n-butyl xanthate, isobutyl xanthate, n-amyl xanthate, ammonium butyldithiophosphate and ethylthionocarbamate were obtained from Zhuzhou Mineral Processing Reagent Plant (Zhuzhou, P.R. China).

2.2. Indexes of aerobic biodegradation

Aerobic biodegradation indexes used in this paper are the first order dynamic constants obtained from the aerobic activated sludge degradation process of sulfide mineral flotation collectors. Before inoculation, the aerobic activated sludge was first filtered through a screen to remove large particles and then transferred into a jar and aerated for 4 h. Activated sludge was characterized by viable cell count. Viable cell counts were determined by plate count agar tests. And a large number of live microbes were found with a cell number of about $(7.0–8.5)\times10^7$ CFU · mL^{-1}. The initial concentration of sulfide mineral flotation collectors was 30 mg · L^{-1}. The biodegradation rate constants are listed in Table 1.

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Table 1
Biodegradation rate constants of sulfide mineral flotation collectors.

Collector	K_b	$LogK_b$
Ethyl xanthate	0.3748	−0.4587
Isopropyl xanthate	0.1322	−0.8788
n-Butyl xanthate	0.2168	−0.6639
Isobutyl xanthate	0.1199	−0.9212
n-Amyl xanthate	0.1758	−0.7550
Sodium diethyldithiocarbamate	0.4512	−0.3456
Ethylthionocarbamate	0.0557	−1.2541

2.3. Quantum chemical descriptors and statistical analysis

In this paper, physicochemical and quantum chemical parameters included the most representative electrical parameters, such as the highest energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), dipole moment (μ), electronic energy (EE), and total energy (TE). Steric parameters were Diameter, Molecular Topological Index ($TIndex$) and Conolly Accessible Area (SAS). Hydrophobic parameters, such as $CLogP$, were selected as factors for QSBR study. In addition, three combination electrical descriptors parameters were also considered as independent. They were $(E_{LUMO}-E_{HOMO})$, $(E_{LUMO}+E_{HOMO})$ and $(E_{LUMO}-E_{HOMO})^2$. The $(E_{LUMO}-E_{HOMO})$ and $(E_{LUMO}+E_{HOMO})$ can be related to absolute hardness and electronegativity, respectively (Zhou et al., 2010; Dai et al., 2006; Yang et al., 2006a, 2006b), which can be used to characterize the reactivity of a molecule based on the theory of a molecular frontier orbital (Yang et al., 2006a, 2006b). The parameters were calculated using the AM1 contained in the quantum chemical computation software of ChemOffice 2004. The method of AM1 was selected in MOPAC (2004), because it was a recently developed semi-empirical molecular orbital algorithm and the computational time was much shorter than needed by the ab initio methods (Li and Xi, 2007; Dai et al., 2006). This method can automatically optimize the bond length, the bond angle and the twist angle, and yield a lot of structural information (Lu, et al., 2003).

All statistical analyses were carried out by ORIGIN software (version 7.5). The regression analysis was used to establish the model. The model quality was characterized by the correlation coefficient (R), the standard deviation (SD), the number of observations (n), and the significance level (P) (Li and Xi, 2007).

3. Results and discussion

The quantum structural parameters of sulfide mineral flotation collectors are listed in Table 2 and the quantum structural parameters related to $LogK_b$ are shown in Table 3.

Table 3 shows that, E_{LUMO}, μ, TE, $(E_{LUMO}-E_{HOMO})$ and $(E_{LUMO}-E_{HOMO})^2$ have more important impact on $LogK_b$, so the QSBR model including those five parameters were established by multiple linear regression, as shown below:

$$\begin{aligned} Log\,K_b = {} & 0.3242E_{LUMO} - 0.08653\mu + 7.228\times10^{-4}TE \\ & +316.1784\times(E_{LUMO}-E_{HOMO}) - 20.7715\times(E_{LUMO}-E_{HOMO})^2 \\ & -1210.496\left(n=7, R^2=0.970, SD=0.134, P<0.0001\right) \end{aligned}$$

where, R^2 is the square of the correlation coefficient,

SD is the standard deviation,
P is the significant level,
n is the number of compounds.

It can be concluded that a good linear relationship can be found among $LogK_b$, E_{LUMO}, μ, TE, $(E_{LUMO}-E_{HOMO})$ and $(E_{LUMO}-E_{HOMO})^2$.

Table 2
Quantum structural parameters of sulfide mineral flotation collectors.

Collector	E_{HOMO}/eV	E_{LUMO}/eV	μ/Debye	TE/eV	EE/eV	D	$TIndex$	SAS/A^2	$CLogP$	$(E_{LUMO}-E_{HOMO})$/eV	$(E_{LUMO}+E_{HOMO})$/eV	$(E_{LUMO}-E_{HOMO})^2$/eV^2
Ethyl xanthate	−7.363	0.172	13.915	−1167.09	−4119.99	5	303	298.188	1.018	7.535	−7.191	56.776
Isopropyl xanthate	−7.304	0.151	13.538	−1322.70	−5373.86	5	444	313.893	1.100	7.455	−7.153	55.577
n-Butyl xanthate	−7.349	0.144	13.423	−1478.52	−6467.41	7	702	341.439	2.076	7.493	−7.205	56.145
Isobutyl xanthate	−7.363	0.115	13.405	−1478.53	−6505.52	6	663	338.859	1.946	7.478	−7.248	55.920
n-Amyl xanthate	−7.315	0.212	13.456	−1634.29	−7792.33	8	992	361.514	2.605	7.527	−7.103	56.656
Sodium diethyldithiocarbamate	−7.478	0.125	13.319	−1314.61	−6284.54	5	642	356.174	2.385	7.603	−7.353	57.805
Ethylthionocarbamate	−7.467	−0.109	4.462	−1668.68	−8064.00	6	773	345.365	2.099	7.358	−7.576	54.140