Quantitative Structure-Adsorbability Relationships for the Adsorption of Organic Chemicals by Carbon Nanotubes

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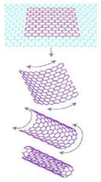
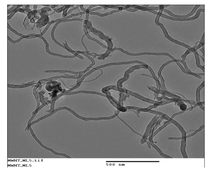
INTRODUCTION

- Carbon nanotubes (CNTs) are tubular graphitic sheets with very high length to diameter ratios.
- This unique 1-D structure gives CNTs remarkable physical, thermal, electrical properties, making CNTs favorable in various industries leading to a rapid growing market.
- The rapid growing CNT market increases serious concerns over their environmental and health effects.
- In addition, CNTs have hydrophobic surface areas and they exhibit strong adsorption affinities to organic contaminants.
- CNTs may exhibit increased toxicity and environmental harms due to the adsorbed organic contaminants.
- Despite the voluminous research in literature, the available adsorption data for CNTs still covers only a small portion of anthropogenic pollutants.





MOTIVATION AND OBJECTIVE

Obtaining experimental adsorption data for pollutants can be laborious, costly and time consuming. Predictive models for the adsorption of organic chemicals by CNTs are of great significance to researchers and practitioners. ***The objective of this study was to develop predictive models for adsorption of organic contaminants by CNTs using linear solvation energy relationship (LSER) and quantitative structure-activity relationship (QSAR) modeling techniques***.

DATA COMPILATION

- CNT adsorption data was collected from 24 different studies from literature and combined with the data produced in our lab.
- A database of 46 compounds was created for adsorption on CNTs.
- Data was filtered by compiling adsorption descriptors of aromatic compounds with molecular weight less than 200 g/mol.
- Since the type and surface chemistry of CNTs impact the adsorption of organic compounds, data for adsorption on multi-walled CNTs with less than 5% of oxygen content were used in modeling.

Training Dataset

	Compound	Log K_∞
1	Phenanthrene	3.29
2	Pyrene	4.01
3	Naphtalene	1.63
4	1-naphtol	0.76
5	Biphenyl	2.05
6	2-phenylphenol	1.63
7	Benzene	-0.45
8	Chlorobenzene	-0.33
9	1,2,4-trichlorobenzene	1.17
10	Nitrobenzene	0.33
11	2,4-dinitrotoluene	2.38
12	Phenol	-0.54
13	Catechol	0.21
14	Pyrogallol	1.18
15	2,4,6-trichlorophenol	1.43
16	3-nitrotoluene	1.03
17	4-nitrophenol	0.77
18	Aniline	-0.77
19	4-chloroaniline	-0.66
20	2-nitroaniline	1.60
21	3-nitroaniline	0.72
22	4-nitroaniline	0.95
23	4-methylphenol	0.06
24	2-chlorophenol	0.08
25	4-chlorophenol	0.74
26	2,4-dichlorophenol	0.96
27	2-nitrophenol	0.56
28	3-nitrophenol	0.92
29	1,3-dinitrobenzene	1.46

Validation Dataset

	Compound	Log K_∞
1	Ethylbenzene	0.19
2	4-xylene	0.26
3	Bromobenzene	0.50
4	Propylbenzene	0.76
5	4-chlorotoluene	0.82
6	Benzonitrile	0.04
7	4-fluorophenol	-0.32
8	Benzyl alcohol	-0.90
9	Iodobenzene	0.88
10	Acetophenone	0.26
11	3-methylphenol	0.08
12	Methyl benzoate	0.70
13	4-chloroanisole	1.07
14	Phenethyl alcohol	-0.46
15	3-methylbenzl alcohol	-0.15
16	4-ethylphenol	0.62
17	3,5-dimethylphenol	0.49
18	Ethyl benzoate	1.14
19	Methyl 2-methylbenzoate	1.12
20	3-chlorophenol	0.62
21	4-nitrotoluene	1.44
22	4-chloroacetophenone	1.28
23	3-bromophenol	0.79
24	1-methylnaphtalene	1.89
25	2-dichlorobenzene	0.56
26	3-dichlorobenzene	0.65
27	4-dichlorobenzene	0.51
28	Isophorone	0.01
29	2-chloronaphthalene	2.73
30	Azobenzene	2.72

- Final training dataset was consisted of single point adsorption descriptors (Log K) for 29 low molecular weight aromatic compounds.
- Validation dataset (30 low molecular weight aromatic compounds) was obtained from the data reported by Xia et al. (2010).

MODEL DEVELOPMENT

QSAR Parameters → LASSO → Selected QSAR Parameters → Regression (Multi Parameter Linear Regression) → QSAR Model

LSER Parameters → Regression (Multi Parameter Linear Regression) → LSER Model

RESULTS

QSAR MODEL

$$\text{Log } K_\infty = -(2.98 \pm 0.52) + (0.18 \pm 0.12)\,{}^0\chi + (0.17 \pm 0.15)\,{}^0\chi^v + (0.55 \pm 0.20)\,{}^3\chi_p$$

$$(n = 29,\ r^2 = 0.88,\ r_{adj}{}^2 = 0.87)$$

- QSAR parameters (computed by MolconnZ 3.24) were selected by the Least Absolute Shrinkage Selection Operator (LASSO) method. Three independent variables ($^0\chi$, $^0\chi^v$, $^3\chi_p$) out of 33 QSAR parameters were selected by using the LASSO method.
- The multiple linear regression for the selected parameters against the adsorption coefficients generated the QSAR model. The obtained coefficient of determination ($r^2 = 0.88$) indicated the goodness of the fit.

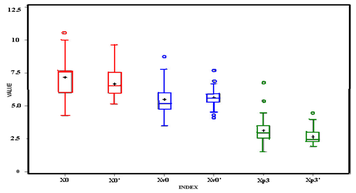


Figure 1. Box and whisker plots for the QSAR descriptors. Xv0, X0, Xp3 and Xp6 represent, $^0\chi^v$, $^0\chi$, $^3\chi_p$ and $^6\chi_p$, respectively. Validation dataset descriptors were marked with (').

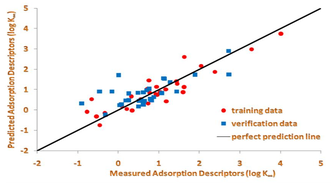


Figure 2. Experimentally measured adsorption descriptors vs. the predicted adsorption descriptors by QSAR model for training and external validation datasets.

- Generated QSAR model was validated by external verification using a new set of compounds. The validation parameter ranges were within the training parameter ranges (Figure 1).
- The external verification indicated the accuracy of the QSAR model. Model predicted adsorption descriptor values and experimentally measured adsorption descriptors were scattering around the perfect prediction line (Figure 2).

LSER MODEL

$$\text{Log } K_\infty = -(4.34 \pm 0.56) + (0.05 \pm 0.32)\,A - (0.48 \pm 0.86)\,B + (4.55 \pm 0.56)\,V + (0.61 \pm 0.34)\,P$$

$$(n = 29,\ r^2 = 0.83,\ r_{adj}{}^2 = 0.80)$$

- The multiple linear regression for the selected parameters against the adsorption coefficients generated the LSER model. The obtained coefficient of determination ($r^2 = 0.83$) indicated that the goodness of the fit is slightly lower than the QSAR fit.
- The data fitting ability of QSAR model was stronger because there were 33 parameters to select the significant independent variables, whereas LSER has only 4 predetermined variables containing physical and chemical information.
- The V term, representing the molar volume, was the most influential parameter in the LSER equation and it represents the adsorbate molar volume, capturing the van der Waals interactions and hydrophobic driven adsorption.
- The A and B terms (H- bonding attraction between the CNT surface and molecules) were not captured as a significant contributor in the LSER equations. Since the selected MWCNTs contain small amounts of oxygen (<5%), H-bonding interactions are mainly contributed to water solubility.
- P term, representing polarizability, might also represent interactions between the compound and the CNT surface since benzene rings of aromatic compound would have more conjugated π electrons to interact with the benzene rings of the graphitic CNT surface.

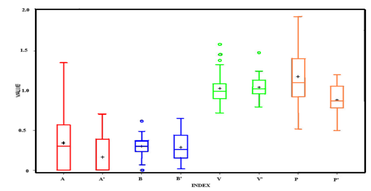


Figure 3. Box and whisker plots for the LSER descriptors. Validation dataset descriptors were marked with (').

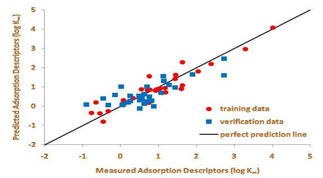


Figure 4. Experimentally measured adsorption descriptors vs. the predicted adsorption descriptors by LSER model for training and external validation datasets.

- Generated LSER model was validated by external verification using a new set of compounds. The validation parameter ranges were within the training parameter ranges (Figure 3).
- The external verification indicated the accuracy of the LSER model. Model predicted adsorption descriptor values and experimentally measured adsorption descriptors were scattering around the perfect prediction line (Figure 4).

ONGOING AND FUTURE WORK

- Our current work in progress extends this work to other classes of organic compounds and other adsorbents.
- 17 chlorinated aliphatic organics with varying hydrophobicities and molecular sizes were selected and their adsorption by CNTs are currently being tested in our laboratories (see table below).
- Single-walled CNTs and graphene nanosheets as an extension to already developed multi-walled CNT model are also being tested with the selected aliphatic compounds.
- After testing adsorption of selected aliphatic compounds on selected adsorbents, a statistical model will be generated using the QSAR approach.
- Predictive models will be obtained for adsorption of both aromatic and aliphatic compounds by single-walled CNTs , multi-walled CNTs and graphenes nanosheets.

List of aliphatic compounds that are currently being tested

	Compound	MW (g/mol)	Solubility (mg/L)	A	B	V	P
1*	Dichloromethane (2/11)	85	13000	0.10	0.05	0.4943	0.57
2*	carbon tetrachloride (2/11)	154	793	0.00	0.00	0.7391	0.38
3*	1,2-dibromoethane	188	3910	0.10	0.17	0.7404	0.76
4**	1,1-dichloroethane (2/11)	99	5040	0.10	0.11	0.6352	0.64
5*	1,2-dichloroethane (2/11)	99	8600	0.10	0.11	0.6352	0.64
6*	1,1,1-trichloroethane	133	1290	0.00	0.09	0.7576	0.41
7*	1,1,2-trichloroethane	133	4590	0.13	0.13	0.7576	0.68
8**	1,1,1,2-tetrachloroethane	168	1070	0.16	0.12	0.8800	0.76
9*	1,2-dichloropropane (2/11)	113	2800	0.00	0.15	0.7761	0.68
10**	1,2,3-trichloropropane (2/11)	147	1750	0.03	0.31	0.8985	0.65
11*	1,2-dibromo-3-chloropropane	236	1230	0.00	0.17	1.0037	0.78
12*	1,1-dichloroethylene	97	2420	0.00	0.05	0.5922	0.34
13*	*cis*-1,2-dichloroethylene	97	6410	0.11	0.05	0.5922	0.61
14*	*trans*-1,2-dichloroethylene	97	4520	0.09	0.05	0.5922	0.41
15*	Trichloroethylene (2/11)	131	1280	0.08	0.03	0.7146	0.37
16*	tetrachloroethylene (2/11)	166	206	0.00	0.00	0.8370	0.44
17	trans-1,4-Dichloro-2-butene	125	850	0.00	0.10	0.8740	0.57

*PDW: Primary drinking water contaminant.
**CCL3: Candidate contaminants list 3 (i.e. CCL3 compounds).
2/11: list 2/11 for regulated and unregulated carcinogenic volatile organic compounds.

- Finally, impact of background solution on adsorption will be investigated by testing the presence of natural organic matter (NOM) in water.
- The data obtained from adsorption in the presence of NOM will also be employed for model development.

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