Predicting the Adsorption Capacity of Activated Carbon for Emerging Organic Contaminants from Fundamental Adsorbent and Adsorbate Properties

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1. Introduction

Activated carbon adsorption is a powerful technology for removing organic contaminants from water. Information about adsorption isotherms is important to select the most effective activated carbon for water treatment applications. Many activated carbons with different physical and chemical characteristics are manufactured, and only few isotherm data are available for the more than 100,000 chemical substances and mixtures that have been or are currently being produced. As a result, the selection of the most cost-effective activated carbon presents a challenge to water treatment professionals. In addition, collection of adsorption isotherm data can be difficult because of a compound's toxicity, analytical challenges (instrument availability, cost), and time requirements to complete the experiments. Therefore, the development of a model capable of predicting the adsorption capacity of activated carbons from fundamental adsorbent and adsorbate properties would be of great benefit to the water treatment industry.

2. Objectives

The objectives of this research were (1) to identify a set of molecular descriptors that define the affinity of organic contaminants for activated carbon and (2) to incorporate the resulting quantitative structure-property relationship (QSPR) into the Polanyi-Dubinin-Manes (PDM) model to predict single-solute adsorption isotherms for emerging contaminants (pharmaceutically active compounds, endocrine disrupting compounds, chemical warfare agents, fluorotelomer alcohols, and brominated flame retardants).

3. Overview of Modeling Approach

The Polanyi-Dubinin-Manes (PDM) model served as the basis for adsorption isotherm predictions. The PDM model is based on two postulates (*1-8*): (1) adsorption is described as a (micro)pore filling process and (2) the volume occupied by the adsorbed compound (V) is a temperature-independent function of the adsorption potential (ε). To apply the PDM model, a reference curve is constructed from adsorption isotherm data for a reference compound, such as benzene, that establishes the relationship between V and ε for a given activated carbon. It is then assumed that affinity coefficients (β) exist such that the relationship between V and ε/β for

compounds other than the reference compound coincides with the reference curve. Thus, β is a measure of an adsorbate's affinity for the activated carbon surface relative to the reference compound, for which a β-value of one (1) is assigned.

To apply the PDM model to aqueous contaminants, the affinity of water for the activated carbon surface needs to be known as well (7-9). The affinity coefficient for water was estimated from the adsorbent oxygen content using a correlation developed previously in our research group (9). Affinity coefficients of individual adsorbates were estimated from adsorption isotherm data collected by the U.S. EPA for 62 neutral organic contaminants. These affinity coefficients were used to develop a poly-parameter QSPR that permits the estimation of a contaminant's affinity coefficient from molecular descriptors. Molecular descriptors were calculated with the semi-empirical quantum mechanics software MOPAC.

4. Materials and Methods

4.1. Adsorption Isotherm Data

Adsorption isotherm data for 62 neutral organic contaminants were obtained from the U.S. EPA. The adsorption isotherm data were collected for contaminants that are currently regulated or are of regulatory interest. Compound classes that were represented in the data set included halogenated aliphatic hydrocarbons, benzene and substituted benzenes (including halogen- and nitro-substituents), triazines, carbamates, chloroacetanilides, organochlorine compounds, ketones, and one ether.

4.2. Adsorbents

Three activated carbon samples [F400(old), F400(new) and Norit1240], with which adsorption isotherm data had been collected, were obtained from the U.S. EPA and characterized at NC State University (Table 1). Five additional activated carbon samples were characterized (Table 1); these adsorbents were used in external model validation tests.

4.3. Adsorbent Characterization

To characterize adsorbents, both N_2 and CO_2 adsorption isotherm data were collected (Autosorb-1-MP, Quantachrome Corporation, Boynton Beach, FL). Prior to analysis, adsorbent samples were outgassed overnight at 473 K. N_2 adsorption was studied at 77 K over a relative pressure range from 10^{-6} to 1. CO_2 adsorption was studied at 273 K over a relative pressure range from 10^{-6} to 10^{-2}. Oxygen contents were measured according to ASTM D5622 (Huffman Laboratories, Golden, CO). Ash contents of GACs were determined by combusting about 5 g of adsorbent in a muffle furnace at 550°C for 2 hours. The hydrophilicity of activated carbon surfaces was expressed in units of mmol O/g dry, ash-free [daf] adsorbent.

Table 1. Adsorbent characteristics

Carbon	BET Surface Area (m²/g)	DFT Micropore Volume[a] (cm³/g)	BJH Mesopore Volume[b] (cm³/g)	%O	%Ash	$\beta_{w/benzene}$
F400(old)	953	3.45×10^{-1}	1.62×10^{-1}	1.95	5.00	0.0756
F400(new)	932	3.35×10^{-1}	1.58×10^{-1}	2.10	4.90	0.0760
Norit 1240	902	3.23×10^{-1}	1.64×10^{-1}	2.09	5.50	0.0760
OAW15	1350[c]	4.27×10^{-1}	4.33×10^{-1}	11.34[c]	N/A[c]	0.0961
G219	1270[c]	4.29×10^{-1}	3.24×10^{-1}	4.90[c]	2.82[c]	0.0822
F600	820[c]	2.66×10^{-1}	3.05×10^{-1}	2.60[c]	1.84[c]	0.0769
Picazine	1680[c]	4.96×10^{-1}	6.55×10^{-1}	15.88[c]	3.37[c]	0.1093
CC-602	1157	4.37×10^{-1}	6.01×10^{-2}	3.75	3.14	0.0796

[a] Micropore volume calculated by density functional theory (DFT) for pores with widths less than 20 Å

[b] Mesopore volume calculated by Barrett, Joyner, and Halenda (BJH) method for pores with widths ranging from 20 to 500 Å.

[c] From Quinlivan et al. (*10*).

4.4. Reference Curve

Reference curves were obtained for the 8 adsorbents shown in Table 1. Reference curves were constructed from N_2 and CO_2 adsorption isotherm data, and adsorption potentials $\varepsilon_{l,i}$ for the two gases were computed using Equation 1,

$$\varepsilon_{l,i} = RT \ln\left(\frac{p_{sat}}{p}\right) \tag{1}$$

where $\varepsilon_{l,i}$ is the adsorption potential (J/mol) of adsorbate i (N_2 or CO_2), R is the universal gas constant (8.314 J/mol-K), T is the equilibrium temperature (K), P_{sat} is the vapor pressure of the adsorbate (1 atm for N_2, 34.28 atm for CO_2), and P is the equilibrium pressure. The adsorbed gas volume (V_{gas}, cm³ at STP/100g activated carbon) was transformed to condensed adsorbate volume ($V_{adsorbed}$, cm³/100g) using Equation 2, where molar volumes (V_m) of N_2 and CO_2 were calculated from their respective densities in the adsorbed state ($\rho = 0.808$ g/cm³ for N_2 at 77 K and $\rho = 1.023$ g/cm³ for CO_2 at 273 K (*11*).

$$V_{adsorbed} = V_{gas}V_m\left(\frac{1\,mol}{22414\,cm^3(gas\,at\,STP)}\right) \tag{2}$$

Using Equation 3, the adsorption potential of benzene ($\varepsilon_{l,benzene}$), the reference compound, was computed from the adsorption potential of N_2 and CO_2 at any $V_{adsorbed}$ using the affinity coefficients $\beta_{l,N2/benzene} = 0.33$ and $\beta_{l,CO2/benzene} = 0.40$ (*5, 11*).

$$\varepsilon_{l,i/benzene} = \frac{\varepsilon_{l,i}}{\beta_{l,benzene}} \tag{3}$$

3

The reference curve for each activated carbon was then obtained by obtaining the best fit of a third-order polynomial (*8*) that relates $V_{adsorbed}$ to $\varepsilon_{benzene}$ (Equation 4):

$$log\ (V_{adsorbed}) = a\ (\varepsilon_{l,benzene})^3 + b\ (\varepsilon_{l,benzene})^2 + c\ (\varepsilon_{l,benzene}) + d \tag{4}$$

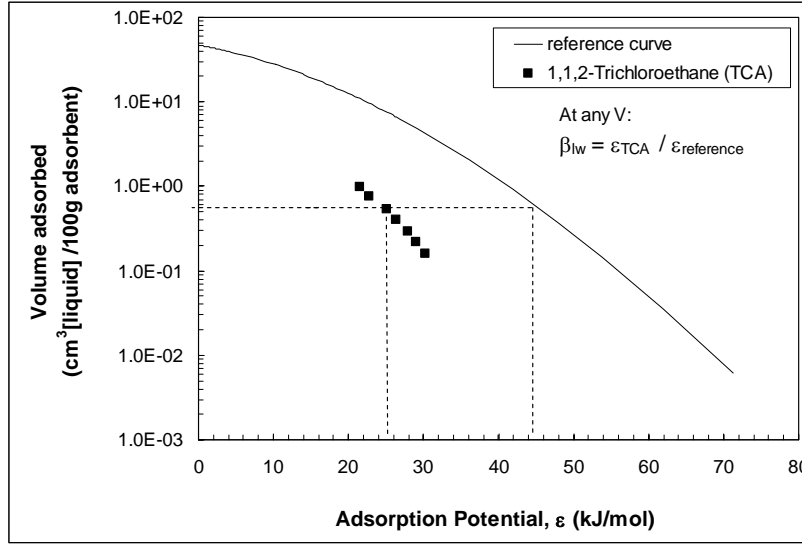where, *a - d* are regression coefficients. Figure 1 shows an example reference curve for activated carbon F400(old).

Figure 1. Reference curve and aqueous-phase 1,1,2-Trichloroethane (TCA) adsorption isotherm data. Adsorbent: F400(old).

4.5. Affinity Coefficients of Water

From the oxygen and ash content data obtained for each adsorbent, the affinity coefficient of water, $\beta_{w/benzene}$, was computed using a correlation developed by Li *et al*. (*9*). Equation 5 relates $\beta_{w/benzene}$ to the adsorbent oxygen content:

$$\beta_{w/benzene} = 0.00353x + 0.0711 \qquad (r^2 = 0.950, n=12) \tag{5}$$

where x is the adsorbent oxygen content in mmolO/g dry, ash-free [daf] carbon. Table 1 summarizes $\beta_{w/benzene}$ values obtained for the adsorbents evaluated in this study.

4.6. Composite water/contaminant affinity coefficients

Adsorption potentials for 62 neutral organic contaminants, for which isotherm data were obtained from the U.S. EPA, were computed from Equation 6,

$$\varepsilon_{lw,i} = RT \ln\left(\frac{c_S}{c_e}\right) \tag{6}$$

4

where $\varepsilon_{lw,i}$ is the adsorption potential of the aqueous target compound, and c_S and c_e are the aqueous solubility and liquid phase equilibrium concentration of the adsorbate, respectively.

The aqueous solubility of contaminants was obtained from four sources: 1) the database of Mackay *et al.* (*12*), which recommends a most probable c_s value from a range of experimentally determined solubility values; 2) the database of Horvath *et al.* (*13*), which also provides a comprehensive review of published aqueous solubility data and proposes a recommended c_s value for many contaminants; 3) the PhysProp database (*14*); and 4) The Pesticide Manual (*15*). For contaminants that were solids at 24°C, the temperature at which isotherm experiments were conducted at the U.S. EPA, the subcooled liquid solubility, $c_{s.liquid}$ was used instead of c_s. Values for $c_{s.liquid}$ were computed following the procedure of Prausnitz et al. (*16*).

The adsorbed volume of aqueous contaminants was obtained from equilibrium solid phase concentration data (q_e) using Equation 7,

$$V_{adsorbed} = \frac{q_e V_m}{MW} \tag{7}$$

where $V_{adsorbed}$ is the adsorbed volume, cm^3 (condensed adsorbate)/100g; q_e (g/100g) were obtained from U.S. EPA isotherm data, and values of molar volume and molecular weight were obtained with ChemSketch (*17*).

To determine the composite water/contaminant affinity coefficient of a given compound, $\beta_{lw,i/benzene}$, a regression analysis was conducted, in which the sum of squares of the absolute difference between the scaled abscissa values (i.e., $\varepsilon_{lw,i}/\beta_{lw,i/benzene}$) and the reference curve abscissa values at each experimental $V_{adsorbed}$ were minimized as shown in Figure 1.

4.7. Affinity Coefficients of Organic Compounds

The affinity coefficients of individual adsorbates, $\beta_{l,i/benzene}$, were computed from the composite water/contaminant affinity coefficient, $\beta_{lw,i/benzene}$, and the affinity coefficient for water, $\beta_{w/benzene}$ (shown in Table 1), using Equation 8,

$$\beta_{lw,i/benzene} = \frac{\varepsilon_{lw,i}}{\varepsilon_{l,benzene}} = \frac{\varepsilon_{l,i} - \varepsilon_w (V_m / V_w)}{\varepsilon_{l,benzene}} = \beta_{l,i/benzene} - \beta_{w/benzene}(V_m / V_w) \tag{8}$$

where V_m and V_w are the molar volumes of adsorbate i and water, respectively.

4.8. Poly-parameter QSPR development

Molecular descriptors were obtained for each of the 62 adsorbates using the semi-empirical quantum mechanics software MOPAC (CAChe WorkSystem Pro v. 6.1.8, Fujitsu Computer Systems Corp., Westwood, MA). To obtain molecular descriptors, all molecules were initially built in the ProjectLeader[TM] table (CAChe). Ten descriptors were calculated, and the four that were most highly correlated with $\beta_{l,i/benzene}$ were chosen for QSPR development. The following

list provides brief definitions of and methods of calculation for the four QSPR variables:

- *V_s, Surface Volume* ($Å^3$/mol). The surface volume of a molecule is the volume enclosed by the molecular surface (*18*). The molecular geometry was optimized using MOPAC with PM3 parameters.

- *E_d, Dielectric Energy* (kcal/mol). The dielectric energy is a portion of the total energy of a molecule surrounded in a dielectric. It is the stabilizing portion that results from screening the charges in the molecule by a dielectric (*19*). The dielectric energy is calculated at an optimized geometry in water. The water geometry is obtained from optimization using MOPAC with PM3 parameters and the Conductor-like Screening Model (COSMO).

- *ε_{HOMO}, Highest Occupied Molecular Orbital Energy* (eV). The energy required to remove an electron from the highest occupied molecular orbital (HOMO) is expressed by ε_{HOMO}. The HOMO energy was determined after optimizing the molecular geometry using MOPAC with PM3 parameters.

- *q_- , Electrostatic Hydrogen Bond Basicity*, which is represented by the most negative atom charge (acu) in the molecule (*20*).

The QSPR relating $\beta_{l,i/benzene}$ to the four molecular descriptors listed above was obtained with the multiple linear regression option in CAChe. The molecular descriptors V_s and ε_{HOMO} were scaled by factors of 100 and 10, respectively prior to QSPR development to assure that statistical weights associated with each QSPR variable were similar. QSPR quality was assessed by comparing experimental $\beta_{l,i/benzene}$ values with calculated $\beta_{l,i/benzene}$ values. Metrics used to assess QSPR quality were the coefficient of determination, R^2, the root mean square error (RMSE) and the cross-validation coefficient, r_{CV}^2. Cross-validation coefficients, r_{CV}^2, were obtained from CAChe using a 3-fold cross-validation technique, in which two thirds of the $\beta_{l,i/benzene}$ values were used to develop a QSPR, which was then used to predict the remaining third of the $\beta_{l,i/benzene}$ values. This procedure was repeated for each third, and the coefficient of determination obtained from the relationship between experimental and predicted $\beta_{l,i/benzene}$ values for all compounds in the data set was computed to obtain r_{CV}^2.

5. Results

5.1. Adsorbent Characterization

Table 1 summarizes physical and chemical characteristics of the tested activated carbons. The results in Table 1 illustrate that the activated carbons used to collect the isotherm data for QSPR calibration [F400(old), F400(new) and Norit1240] were similar in terms of their physical structure (BET surface area, micropore and mesopore volumes) and chemical character (oxygen and ash contents). On the other hand, the five adsorbents used for external QSPR validation showed a broad range of physical and chemical characteristics (Table 1). Oxygen contents of the five adsorbents used for external QSPR validation ranged from 2.6 to 15.9%. As shown by a number of research groups (e.g. *9, 21-23*), the oxygen content of activated carbons is important for the adsorption of aqueous organic contaminants because oxygen-containing functional groups enhance water adsorption and thus negatively affect organic contaminant removal.

5.2. QSPR

Equation 9 shows a new QSPR that relates the affinity coefficient of a contaminant to the four molecular descriptors surface volume (V_s), dielectric energy (E_d), highest occupied molecular orbital (HOMO) energy (ε_{HOMO}), and electrostatic hydrogen-bond basicity (q_-).

$$\beta_{l,i/benzene} = 6.146\text{x}10^{-1} * (V_s/100) - 3.123\text{x}10^{-1} * E_d + 1.160 * (\varepsilon_{HOMO}/10) + 1.869\text{x}10^{-1} * q_- + 1.616 \quad (9)$$

The QSPR was developed with a training set of 62 contaminants. Figure 2 illustrates that predicted $\beta_{l,i/benzene}$ values closely matched experimental $\beta_{l,i/benzene}$ values for the training set (R^2 = 0.90), and the RMSE associated with $\beta_{l,i/benzene}$ predictions was 0.16 (experimental $\beta_{l,i/benzene}$ values ranged from 0.74 and 2.65). The cross-validation coefficient r_{CV}^2, which quantifies the predictive power of the QSPR, was 0.85.

To further evaluate the quality of the QSPR, results of an internal validation test are depicted in Figure 3, which shows scaled isotherm data (i.e., $\varepsilon_{scaled,i} = \varepsilon_{lw,i}/\beta_{lw,i/benzene}$) for the 46 neutral organic contaminants, for which adsorption isotherm data were collected on F400(old). Using $\beta_{l,i/benzene}$ values that were predicted with the QSPR and the $\beta_{w/benzene}$ values shown in Table 1, $\beta_{lw,i/benzene}$ values were calculated with equation 8 and used to scale the isotherm data. A RMSE of 4.57 was obtained, which represents the average difference between $\varepsilon_{scaled,i}$ and $\varepsilon_{l,benzene}$ at any experimental $V_{adsorbed}$.
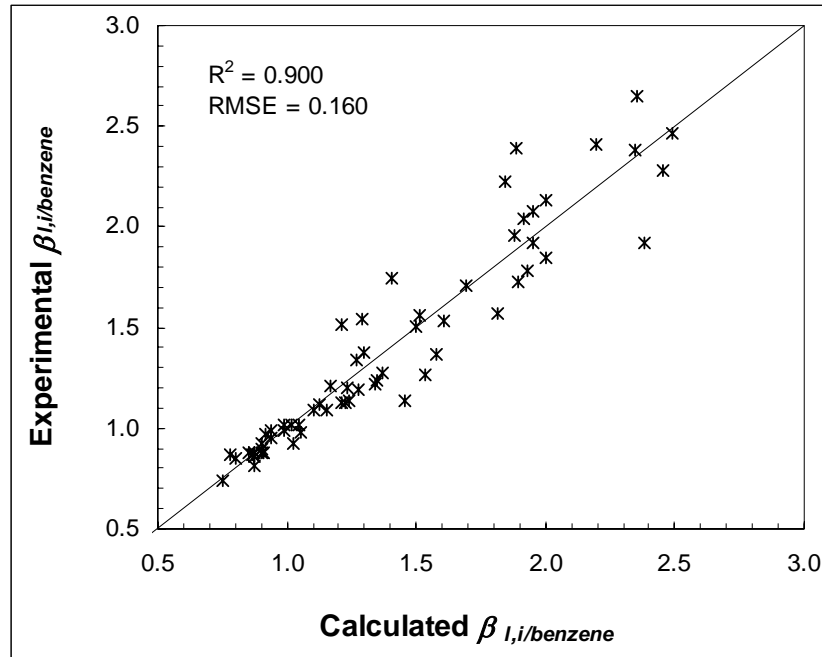
Figure 2. Relationship between experimental $\beta_{l,i/benzene}$ values and $\beta_{l,i/benzene}$ values calculated with the QSPR model. Straight line depicts 1:1 relationship.
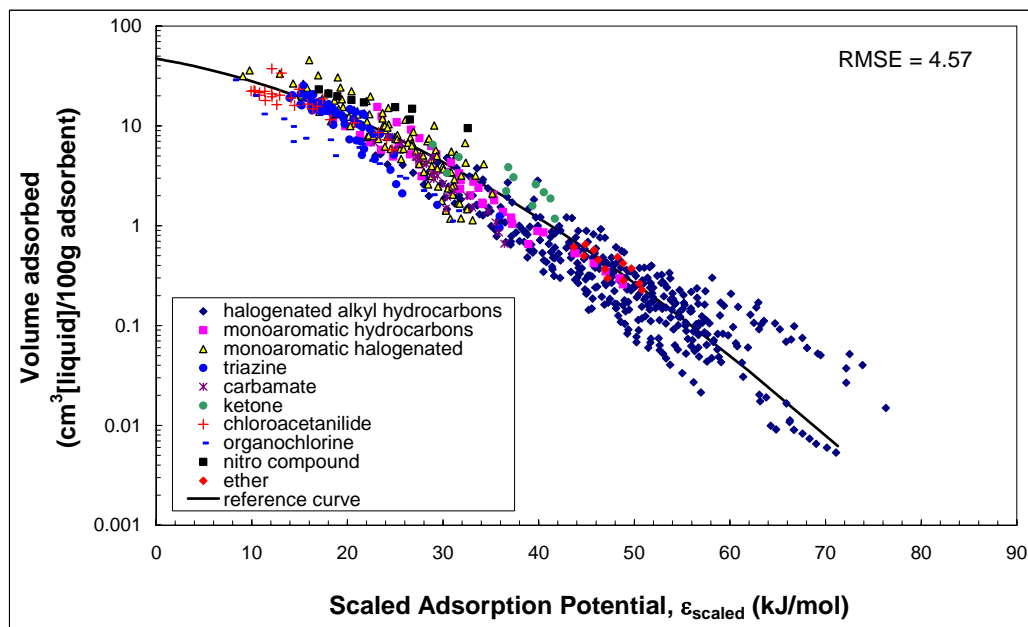

Figure 3. Scaled isotherm data for 46 neutral organic contaminants on F400(old). RMSE is for ε_{scaled}.

5.3. External Validation of the developed QSPR

Adsorption isotherm predictions were validated with TCE adsorption isotherm data on activated carbons OAW15, F600, G219 and Picazine. The results in Figure 4 show that the predicted isotherms are in excellent agreement with the experimental data, both for adsorbents with low (F600 and G219) and high (OAW15 and Picazine) oxygen contents. It should be noted that neither TCE nor the adsorbents, for which adsorption isotherms were predicted, were part of the QSPR calibration.

To further validate the developed QSPR, adsorption isotherm prediction for the antimicrobial compound trimethoprim and the pesticides acifluorfen and methomyl were compared with experimental isotherm data (Figure 5). Good agreement between predicted isotherms and experimental isotherm data was obtained for all three adsorbates.
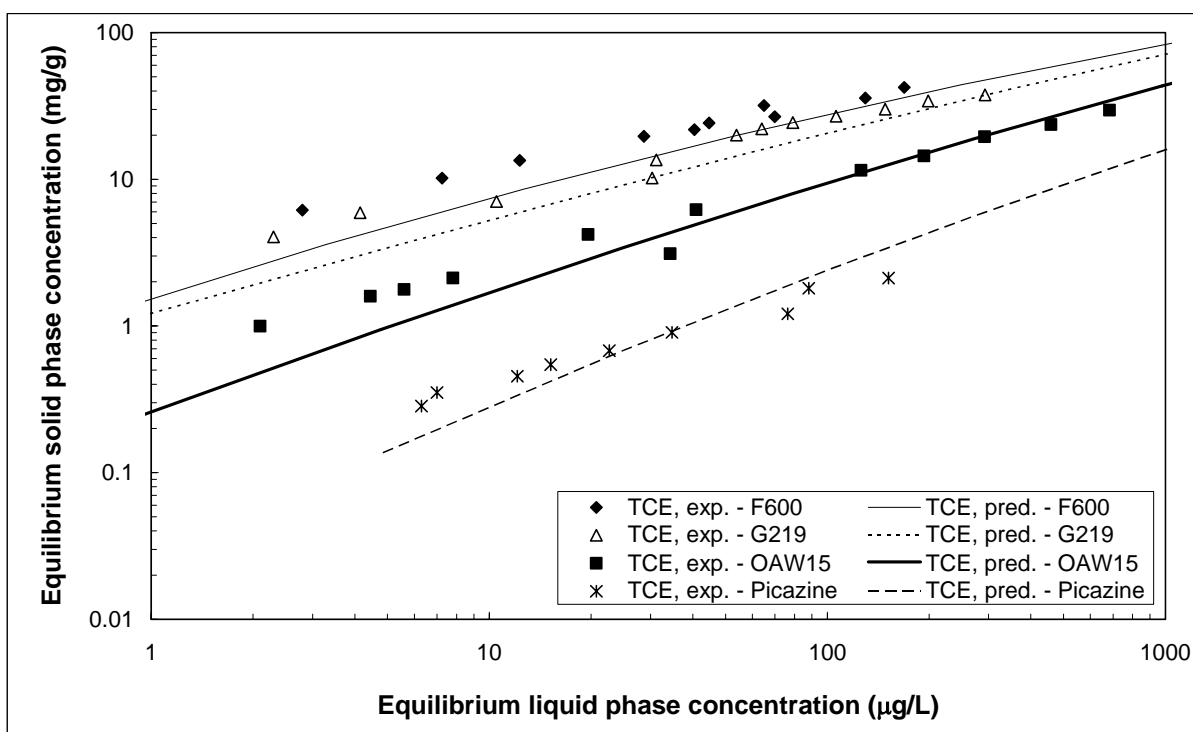

Figure 4. Adsorption isotherm data and predicted adsorption isotherms for TCE on adsorbents F600, G219, OAW15 and Picazine. Adsorption isotherm data from Li *et al.* (*21*).
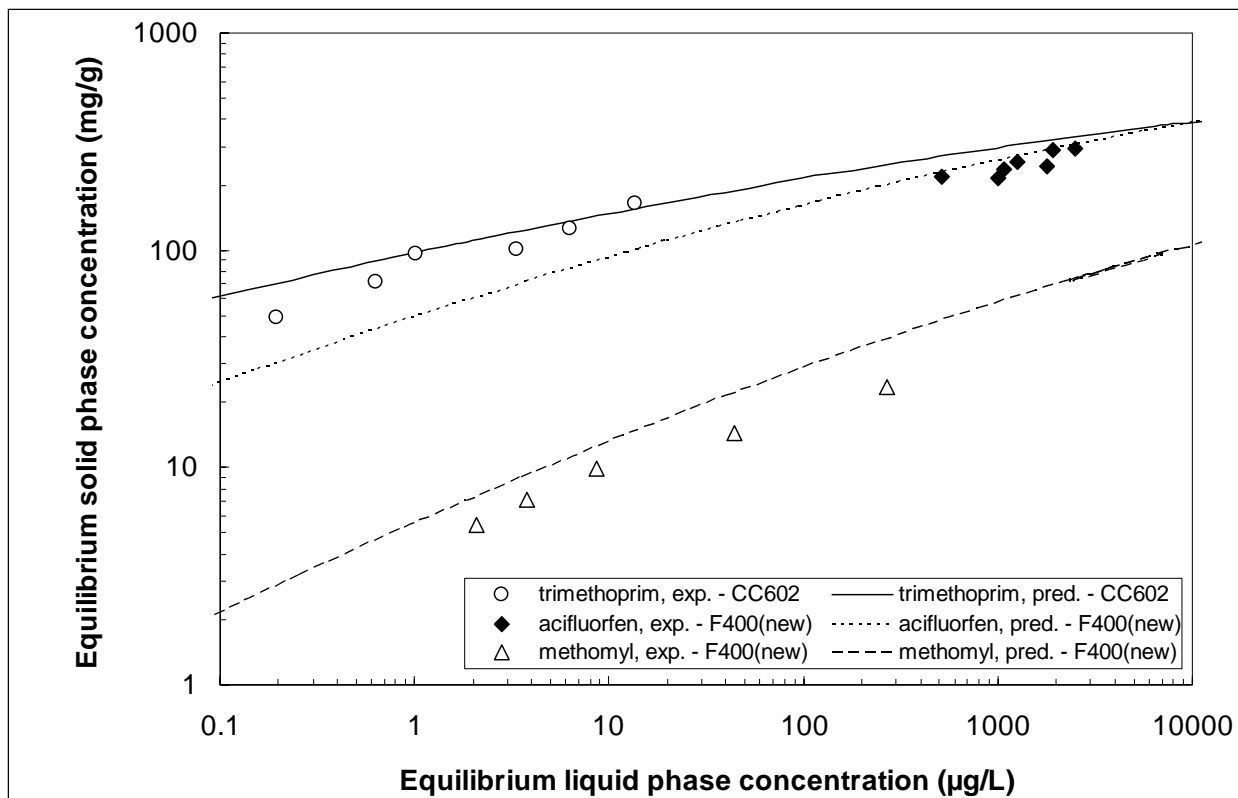
Figure 5. Adsorption isotherm data and predicted adsorption isotherms for trimethoprim, acifluorfen, and methomyl on adsorbents CC602 and F400(new). Adsorption isotherm data for trimethoprim (pK_a for pyridine N is 7.1) were collected at pH 9.1, at which the neutral form is dominant.

5.4. Isotherm Predictions

To illustrate the applicability of the developed QSPR, isotherm predictions were made for representative contaminants in the following emerging contaminant classes: (1) pharmaceutically active compounds (PhACs) - acetaminophen (pK_a of phenol group is about 9.7); triclosan (pK_a of phenol group is ~8); sulfamethoxazole (pK_a of sulfonamide group is ~5.6); and trimethoprim (pK_a of pyridine group is ~7); (2) endocrine disrupting compounds (EDCs) - ethinyl estradiol (pK_a of phenol group is ~10.4); and testosterone; (3) chemical warfare agents (CWAs) - tabun (GA); soman (GD); distilled mustard; nitrogen mustard (pK_a of tertiary amine group is ~6.8); and VX (pK_a of tertiary amine group is ~9); (4) fluorotelomer alcohols (FTOHs) - perfluorohexanol (4:2 FTOH); perfluorooctanol (6:2 FTOH); perfluorodecanol (8:2 FTOH) and perfluorododecanol (10:2 FTOH); and (5) brominated flame retardants (BFRs) – decabromodiphenyl ether (BDE-209); tetrabromobisphenol A (TBBPA); and hexabromocyclododecane (HBCD). For ionizable contaminants, isotherm predictions are for the neutral form.

Table 2 summarizes predicted adsorption capacities for the selected emerging contaminants on activated carbon F400(old) at equilibrium liquid phase concentrations of 0.001, 0.01, 0.1, 1.0 and 10.0 µg/L. Among the chemical warfare agents, Table 2 shows that the most adsorbable

compound is VX while the least adsorbable is soman. For the PhACs and EDCs, Table 2 shows that the neutral forms of triclosan, ethinyl estradiol, testosterone, trimethoprim, and sulfamethoxazole are all more adsorbable than the CWAs. Acetaminophen exhibited the poorest adsorbability among the selected PhACs. The adsorption capacities of FTOHs varied over more than 6 orders of magnitude at an equilibrium liquid phase concentration of 1 ng/L (Table 2); among the selected emerging contaminants, 4:2 FTOH exhibited lowest adsorbability while 10:2 FTOH exhibited the largest. Regarding BFRs, Table 2 illustrates that this class of emerging contaminants is well adsorbed by activated carbon.

Table 2. Predicted adsorption capacities of F400(old) for CWAs, PhACs, EDCs, FTOHs and BFRs at selected equilibrium liquid phase concentrations [a]

	$q_{0.001}$	$q_{0.01}$	$q_{0.1}$	$q_{1.0}$	q_{10}
Chemical Warfare Agents (CWAs)					
VX	8.74	14.6	24.4	40.7	67.9
distilled mustard	1.22	3.04	7.61	19.0	47.6
nitrogen mustard	0.234	0.651	1.81	5.04	14.0
tabun	0.0723	0.219	0.666	2.02	6.13
soman	0.0526	0.175	0.582	1.93	6.43
Pharmaceutically Active Compounds (PhACs)					
triclosan	124	165	220	293	391
trimethoprim	18.1	28.3	44.2	69.1	108
sulfamethoxazole	12.3	20.9	35.4	59.9	101
acetaminophen	0.517	1.19	2.74	6.31	14.5
Endocrine Disrupting Compounds (EDCs)					
ethinyl estradiol	44.7	64.9	94.4	137	199
testosterone	27.3	42.6	66.4	103	161
Fluorotelomer Alcohols (FTOHs)					
10:2 FTOH	510	ES[b]	ES[b]	ES[b]	ES[b]
8:2 FTOH	1.51	5.78	22.1	84.5	323
6:2 FTOH	0.0261	0.164	1.03	6.49	40.8
4:2 FTOH	9.45×10^{-5}	8.45×10^{-4}	0.00756	0.0676	0.604
Brominated Flame Retardants (BFRs)					
decabromodiphenyl ether (BDE-209)	466	600	774	ES[b]	ES[b]
hexabromocyclododecane (HBCD)	309	401	519	673	ES[b]
tetrabromobisphenol A (TBBPA)	137	194	275	390	553

[a] Units for q values are mg/g. Subscript on q refers to equilibrium liquid phase concentration in μg/L.
[b] Exceeds solubility.

6. Conclusions

A new procedure was developed that permits the prediction of adsorption isotherms from fundamental adsorbent and adsorbate properties. With respect to adsorbent properties, the procedure requires the development of a reference curve from N_2 and CO_2 isotherm data and knowledge of the adsorbent's oxygen and ash contents. With respect to adsorbate properties, molecular descriptors are required that can be obtained quickly with molecular modeling software packages. Once the affinity coefficient of a target contaminant is calculated from the QSPR model and the affinity coefficient of water is calculated from the adsorbent's oxygen content, a composite contaminant/water affinity coefficient can be obtained for the adsorbate/adsorbent pair of interest. This composite contaminant/water affinity coefficient can then be used to scale the reference curve such that the adsorption isotherm for the desired adsorbate/adsorbent pair is obtained. To date, only a limited external validation of the QSPR developed in this study was conducted. To enhance the confidence in the predictive powers of the developed QSPR, a more comprehensive external validation test should be conducted.

7. Acknowledgment

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