EFFECT OF ADSORBATE PROPERTIES ON ADSORPTION RATES IN DRY AND PREHUMIDIFIED ACTIVATED CARBON

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Introduction

The possibility to predict initial break-through performance of active carbon filters is of major importance in order to estimate the level of protection against highly toxic chemicals.

A strategic selection of 16 chemicals from three main classes of organic compounds was characterized by an extensive set of physico-chemical property descriptors. Three types of activated carbon were challenged to vapors of the selected compounds under dry and humid conditions. Since the rate of break-through is inversely related to the rate of adsorption, multivariate data methods were applied to identify important factors influencing adsorption rate. Quantitative structure-affinity relations (QSAfR) were accordingly established between compound properties and initial adsorption rate.

Experimental

The compounds used for carbon testing were selected from 186 high volume industrial chemicals. An optimal spread in physico-chemical property space was provided by using factorial design based on principal component analysis (PCA).[1] The selected compounds, 7 halogenated hydrocarbons, 4 amines, 4 ketones, and one aldehyde are shown in Table 1. About 40 different property descriptors were used to characterize the compounds, 16 of these were experimental data from the literature and the rest were calculated on the basis of chemical structure.

Break-through profiles were determined for Chemviron BPL, Pica and Norit carbons both in a state as received (dry) and preconditioned at 80 % relative humidity, using challenge vapors correspondingly conditioned. Challenge concentrations of vapors were 0.1 mol/m^3 at a flow rate of 1 l/min (5.5 m/s). Carbon beds of 20 mm diameter were packed to 23 mm depth.

The kinetic filter performance was evaluated from points on the early parts of the break-through curve. Adsorption rate was estimated based of the rate constant, defined by the Yoon-Nelson model:[3]

$t_b = \tau + 1/k' \ln [C_b/(C_o-C_b)]$, where
t_b = break-through time,
τ = time of 50 % break-through,
C_o = inlet vapor concentration,
C_b = effluent vapor concentration, and
k' = rate constant

The parameter adopted for modeling initial adsorption rate, the inverse of k' (1/k'), is calculated from times of 1 % and 10 % break-through. The multivariate data set was evaluated by partial least squares analysis (PLS).[2]

In a first model both experimental and calculated property descriptors were used (Model I). Since the accessibility to experimental data is often limited, we were urged to explore the possibility of establishing a model principally based on calculated data. A model was constructed by supplementing calculated data with boiling point and vapor pressure (Model II).

In a first stage of data processing all selected property descriptors were included in the data set and the importance of each variable was evaluated. A stepwise exclusion of less important and highly correlated variables was done which increased the predictive power of the model and eventually ended up in 9 - 12 important physico-chemical descriptors.

Results and Discussion

Irrespective of carbon type, test conditions and model used, boiling point is the most important factor to describe break-through rate. The most volatile compounds show the largest initial rate, and this is even more pronounced for the humid conditions. On going from dry to humidified carbons there is a break-through rate decrease for the high-boiling compounds and this effect is also seen for the low-boiling water miscible compounds.

When we applied Model I to dry and humidified carbons other influential experimental properties identified were vapor pressure, surface tension, viscosity and melting point. Calculated molecular descriptors of importance were areas of high negative electrostatic potential, energy of lowest unoccupied molecular orbital (LUMO), and electric polarizability. Model II involved the same essential calculated descriptors as Model I and in addition the van der Waals volume. Differences between the three types of carbons appeared as differences in relative importance of the parameters mentioned above. The dipole moment

seemed to be of some importance for dry but not for prehumidified carbons.

Predictive PLS models in most cases showed two significant principal components describing volatility and polarity/polarizability and the predictive power was good. No significant difference was observed in performance of Models I and II. Results for BPL carbon using Model II is illustrated in Figures 1 and 2. Important properties used in modeling of the dry and prehumidified BPL carbons are

- Boiling point
- Vapor pressure
- Electric polarizability
- Energy of lowest unoccupied molecular orbital (LUMO)
- Van der Waals area with high negative electrostatic potential
- Van der Waals volume
- Sum of the absolute values of atomic charges divided by the number of atoms
- Energy of the van der Waals interaction with a model graphite surface

Conclusions

QSAfR models for the estimation of adsorption rate could be established for halogenated hydrocarbons, amines, ketones, and aldehydes. Good predictive power was obtained for dry and prehumidified carbons using calculated property descriptors supplemented with experimental data on boiling point and/or vapor pressure.

Important calculated molecular descriptors are related to charge distribution, polarizability, dispersive forces, size, and electron affinity.

References

[1] Fängmark I, Hammarström L-G, Jönsson P-G, Norman PR, Ness AL, Baker SL, Osmond NM. Selection of halogenated hydrocarbons, amines, aldehydes and ketones for use in structure-affinity modeling of charcoal filter performance. Proceedings of the Scientific Conference on Chemical and Biological Defence Research, Aberdeen Proving Ground, MD, USA 1997.

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Table 1. Set of compounds used for evaluation of break-through performance of activated carbons.

Number	Compound	Boiling point (°C)
44	2,2-Difluoropropane	-0.4
9	Bromomethane	3.6
70	1-Bromopropane	71.0
71	2-Bromopropane	59.4
19	1,2-Dibromoethane	131.3
11	1,2-Dichloroethane	83.5
81	Iodobutane	130.5
2	Allylamine	57.0
28	Diallylamine	112.0
36	Diisobutylamine	139.0
46	N,N-Dimethylethylamine	37.0
1	Acetone	56.0
6	Diisopropyl ketone	125.4
27	Cyclopentanone	130.6
4	Diethyl ketone	101.9
61	Acrolein	52.7

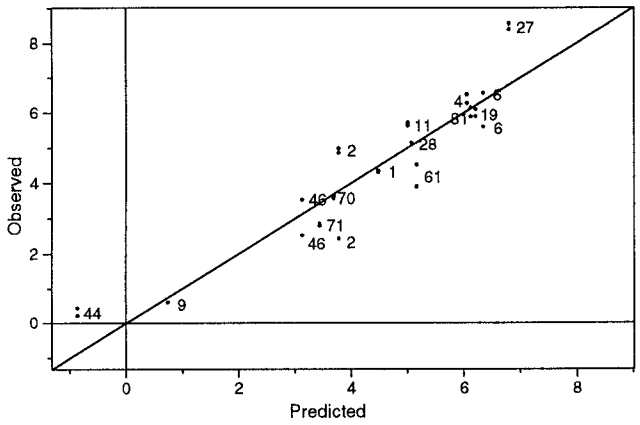

Figure 1. Observed versus predicted 1/k' for initial break-through on prehumidified BPL carbon.

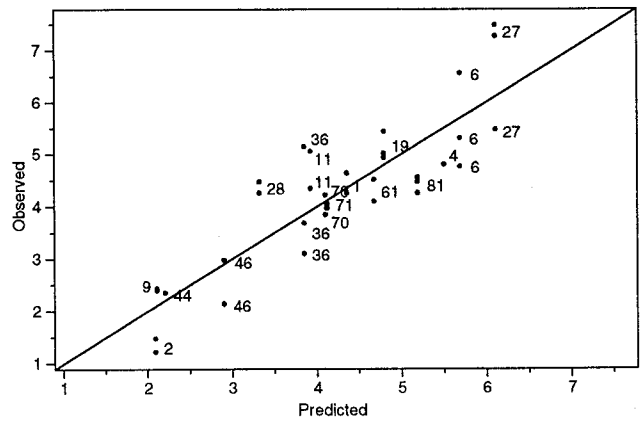

Figure 2. Observed versus predicted 1/k' for initial break-through on BPL carbon as received.