Study of Binary Adsorption – A Multivariate Data Analysis Approach

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Introduction

Removing volatile organic compounds (VOCs) from air or recovering solvent from tail gas often require the use of fixed beds of granular activated carbon. The service life of such beds depends on the carbon capacity for vapours and the rate of adsorption. In practical applications, environments with more than one volatile chemical contaminant are frequently encountered. Accordingly, the development of a theoretical model to predict the service life in the presence of a mixture of adsorbates is important. Investigations of the breakthrough time in the case of multiple adsorbates are however somewhat limited [1-3], since the adsorption process for mixtures is more complicated. Multiple vapours compete for the adsorption sites and one adsorbate can be displaced by another in the air stream. The effect of multiple adsorbates on the adsorption process is thus dependent on the properties of each compound in the binary mixture.

The objective of this work is to investigate the influence of compound properties on the binary adsorption process, and eventually predict the initial parts of the breakthrough curves. The tool used in this work is Multivariate Data Analysis (MVDA) [4]. It is based on work done previously for a single organic adsorbate. Partial least squares projection to latent structures (PLS) is the MVDA regression method used to connect the information of variables and responses. It has been used in the modeling of the affinity coefficient in the Dubinin-Radushkevich equation [5], in modeling the adsorption capacity [6], and in the development of predictive models for the adsorption rate coefficient in Wheeler-Jonas equation [7]. The strength of applying MVDA in studying the adsorption process has been summarized by Fangmark et al. [8].

Experimental

Strategy for selection of Binary VOCs
By means of statistical experimental design 8 representative compounds were selected from a set of 68 VOCs covering several compound classes. The selected compounds were used as model compounds in the measurements of adsorption isotherm and breakthrough profiles [5-7]. In order to avoid too many time-consuming experiments it was decided to apply a mixture design in the compound property space. Eleven binary mixtures were selected based on distance criteria. Combinations of compounds having as large distance in property space as possible, and some who are similar to each other, i.e. close in the property space, were thus selected.

Breakthrough curves
Clean dry air at a flow rate of 5.46 l/min was challenged with the two organic vapours at a concentration of 1000 ppm. The inlet and outlet concentrations were analyzed by a GC instrument equipped with an automatic sampling loop and FID. From the breakthrough curves, the adsorption capacity W_e and the rate coefficient k_v of the Wheeler-Jonas (W-J) equation were calculated for each vapour. These parameters were obtained from the slope and intercept of a plot of breakthrough time vs. $\ln((C_o-C_x)/C_x)$, which showed good linearity up to about 20% breakthrough ratio. This implies that binary data can be treated with the W-J equation in this region. In this preliminary study values of the W-J parameters are treated as ratios with respect to the single compound values [9]. Accordingly the ratios (R_{we1}, R_{kv1}) are obtained by dividing W_{e1}, k_{v1} of first eluting compound by the corresponding parameters of the single compound. Correspondingly, R_{we2}, R_{kv2} are calculated based on W_{e2} and k_{v2} of the second eluting compound.

Results and Discussion

PLS is employed to correlate the matrix of properties of the two compounds in each binary mixture with the responses (R_{we1}, R_{kv1}, R_{we2}, R_{kv2}). The modelling results show that

- there is no correlation between the physico-chemical properties of the two compounds and R_{kv1}, R_{we2} (with the exception of two binary mixtures of compounds having similar properties),
- k_v on a single compound can be used for the first eluting compound in binary systems,
- R_{we1} and R_{kv2} depend on the properties of both compounds. Quantitative predictive relationships can be developed for both parameters using PLS.

The first eluting compound of the binary mixture should encounter the same environment as if it were a single vapour at the same inlet concentration. This explains why the adsorption rate constant is almost the same for single and binary systems [9]. The capacity of the second eluting compound of the binary system also keeps the same as for the single adsorbate if the compounds are far away from each other in the property space. Compounds that are close in properties behave differently. W_{e1} and k_{v2} depend on the properties of both adsorbates due to displacement and competition mechanisms. Once such property that is important for W_{e1} is polarizability of both compounds, and for k_{v2} the hydrophobicity of the second eluting compound. Predicted 10% breakthrough times for both components of the nine binary VOC mixtures, composed of dissimilar compounds, are compared with the experimental values in Figure 1. The predictions agree very well with the experimental results.

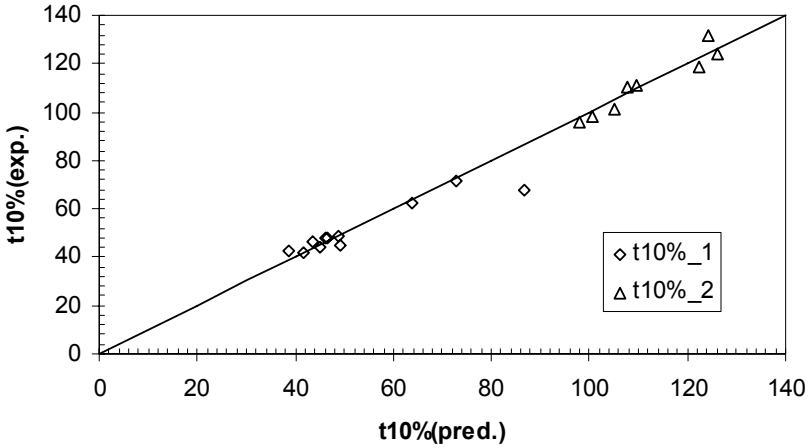

Figure 1. Predicted breakthrough time at 10% breakthrough fraction for both compounds in 9 binary systems.

Conclusions

The breakthrough time of both adsorbates can be predicted even when displacement occurs due to competition between the two components of a mixture. Thus, MVDA is a useful technique to establish a model for prediction of the service life of packed carbon beds when exposed to binary vapour mixtures. The effect of binary adsorbate mixtures on the W-J parameters of each compound can be revealed by MVDA. It is found that k_v of the first eluting compound keeps the same as for the single adsorbate, and that W_e of the second-eluting compound is independent of the first-eluting compound. The ratios R_{we1} and R_{kv2} depend on the properties of both compounds. Quantitative relationships can be built to predict these ratios. The W-J equation can therefore be used to predict the service life of carbon beds for binary adsorbate mixtures.

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