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Here we present the combination of our adsorption process simulator with a hybrid optimisation strategy for the automated analysis of a series of ZLC experiments.

The Zero Length Column (ZLC) method is an established technique for the measurement of the kinetic and equilibrium properties of adsorption systems. Briefly, in the ZLC method the desorption curve of a small amount of adsorbent previously equilibrated with a known gas mixture is measured. By changing the experimental conditions, i.e. flow rate of the purge gas, the system can be operated under equilibrium or kinetic control; thus equilibrium and kinetic properties can be investigated in the same series of experiments. The reliable measurements for fast and slow kinetics combined with the small required sample quantity (less than 10mg) make the ZLC method a very useful and flexible tool for kinetic and equilibrium measurements for a wide range of materials.

In order to automate and improve the analysis of the experimental data we have applied our in-house adsorption simulator to the simulation of the ZLC system. The process simulation is built from units representing the separate parts of the system: feed, purge, zero length column and detector. This representation allows the explicit description of the ZLC and the surrounding parts of the system. For example, the dead volume of the system and the detector response are included through fitting of the blank experiments. The used full-scale column model facilitates the direct application of the estimated parameters in complex, large-scale PSA cycles. Furthermore, the column unit implements different adsorption isotherms, different mass transfer models as well as isothermal and non-isothermal models. Thus the simulator provides an accurate description of the dynamics in the ZLC system.

By linking the ZLC simulation to a hybrid optimisation strategy (combining a global Multi-Objective Genetic Algorithm with a local optimisation routine) we generate an automated tool for the estimation of the kinetic and equilibrium parameters from several experimental runs. The optimisation algorithm tries to minimise the least square error between the experimental data and the simulation output. In the first step the parameters of the empty system, i.e. no adsorbent in the ZLC, are fitted with empty system experimental runs. Then in the second step only the kinetic and equilibrium parameters in the ZLC are fitted. The combination of the adsorption simulator and the hybrid optimisation allows us to fit the parameters with greater certainty compared to the previously used simplified analytical models. Specifically

the simultaneous fitting of several experimental curves at different flow rates and temperatures provides a robust estimation for both the equilibrium and kinetic parameters of the adsorbent.

The flexibility of the adsorption simulator, i.e. different kinetic and equilibrium models, allows the investigation of the dominant physical mechanisms. For example, the error in the parameter estimation from kinetically controlled zeolite 13X experiments using the single-site Langmuir isotherm is much larger than the error obtained using the dual-site Langmuir isotherm. Subsequent comparison of the fitted isotherms to the isotherm obtained from equilibrium controlled experiments shows that the large error for the single-site Langmuir fit corresponds to a large error in the fitted adsorption isotherm.