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A high-throughput methodology for liquid phase adsorption experimentation

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Abstract This article describes a novel application of high-throughput experimentation, namely in the field of liquid mixture separation through adsorption. Two separate setups are designed and extensively used to study multicomponent liquid phase adsorption: the first setup performs batch adsorption in static conditions to obtain adsorption isotherms while the latter carries out breakthrough experiments in dynamic conditions, which yield multicomponent breakthrough curves. The obtained data serves as an indicator of the separative qualities of an adsorbent exposed to a particular liquid mixture. The reliability of the obtained measurements is assessed using different validation techniques. Case studies pertaining to the competitive adsorption of binary alkane/alkene/aromatic mixtures on faujasites complete the validation process. A new model for batch adsorption isotherms is proposed based on the equilibrium conditions in liquid phase.

Keywords High-throughput · Batch adsorption · Liquid phase · Breakthrough experimentation · Zeolite

1 Introduction

Numerous applications of adsorption are know in industry, some of them are the separation of xylenes, olefins/paraffins, oxygen/nitrogen, glucose/fructose… (Cavalcante 2000). Many different meso- and microporous materials such as zeolites are used. The diversity in possible adsorbents and the complexity of liquid phase adsorption require a large number of experiments to find a good adsorbent for just one application. Over the past decade, high-throughput experimentation has been widely adopted by the chemical sector (Farrusseng 2008; Maier et al. 2007; Pescarmona et al. 1999), because it allows one to quickly gain insight in a particular system, even where other approaches, such as simulation or modelling, have shown their limits. This is achieved by combining high-throughput equipment with experimental design to determine the kind of experiments to perform. High-throughput experimentation (HTE) is now a tool of choice in specific research areas such as molecular synthesis (Banerjee et al. 2008; Corma et al. 2006; Serra et al. 2003), drug discovery and catalyst discovery and optimization (Hendershot et al. 2006; Kirsten and Maier 2004; Paul et al. 2005; Senkan 2001; Shimizu et al. 1998). In the field of adsorption, no reports have been made on high-throughput methods.

It is also proven to be very useful to derive QSAR models from high-throughput data, thereby obtaining highly predictive models. Such models were previously developed for single component gas phase adsorption in our group (Leflaive et al. 2010), but examples are reported for multicomponent systems in other domains (Ajmani et al. 2006; Sheridan 2000). It is our aim to obtain such predictive models for competitive adsorption on zeolites in liquid phase.

The approach exposed in this article is novel in that high-throughput experimentation is applied to the study of liquid mixture separation through adsorption using zeolites. Zeolites are microporous materials with a wide variety of pore structures and chemical composition and thus specific separation properties. Liquid phase adsorption properties are mainly studied by measuring both adsorption isotherms and

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breakthrough curves. Both techniques are good candidates for automation in a high-throughput environment, as they are both cumbersome to perform manually and easy to parallelize. Liquid phase adsorption itself is an ideal candidate, for its complexity, which is due to the great number of interacting forces, makes it difficult to find a general model describing it adequately (Denayer et al. 2006). By gathering a vast amount of experimental adsorption data, it would be possible to apply data mining techniques to find mathematical relationships between the physicochemical properties of the mixtures and the adsorbent on the one hand and the adsorption behaviour on the other hand. This is already applied in closely related fields such as the prediction of gas-phase adsorption enthalpies (Leflaive et al. 2010) and the optimisation of chromatographic processes (Hubbuch 2009; Susanto et al. 2008). Although high-throughput setups can be used with virtually any liquid and adsorbent, this study is restricted to alkanes, alkenes and aromatics with 6 to 12 carbon atoms and to zeolites from the faujasite family. Two faujasite zeolites were used in this study "NaX" (13X, $\mathrm{Si/Al} = 1.23$) and "NaY" (CBV100, $\mathrm{Si/Al} = 2.79$) as adsorbents, to determine the sensitivity of the high-throughput methods to variations in adsorbent parameters.

2 Methodology and experimental setup

The competitive adsorption of components on meso- and microporous materials is generally studied by two approaches (Table 1). The first one is batch experimentation at adsorption equilibrium. This technique is used at the extremities of the adsorption isotherms (typically 0% to 10–15% of tracer(s) component in a solvent). These results are often fitted to the Langmuir model; a more appropriate model is presented.

Whereas the second one "breakthrough experimentation" is commonly used to study the selectivity of one component over one of more other components at intermediate concentration ranges. A high-throughput methodology is presented for both the techniques.

Table 1 Comparison of the possibilities of batch and breakthrough experimentation

	Batch	Breakthrough
Varying the experimental temperature	± (limited)	+
Experimental pressure		+
Experimental concentration range	0–20 mol%	0–100 mol%
True equilibrium conditions	+	–
Uptake kinetics	+	+
Online sample analysis	–	+

2.1 Batch adsorption experimentation

2.1.1 Theoretical background

The batch adsorption technique is used to study the static aspects of adsorption, at adsorption equilibrium. Concretely, each adsorption isotherm relates the adsorbed amount of a particular component of the liquid mixture (defined as the *tracer*) to the concentration of this component in the liquid mixture at adsorption equilibrium. The adsorption isotherm is measured experimentally by varying the concentration of the tracer component in the liquid adsorptive. At equilibrium, a sample of each mixture is taken and its concentration is measured. Comparing these concentrations to the concentrations of the mixtures before adsorption occurred yields the amount of tracer component adsorbed for every mixture, according to the following formula:

$$q_{\mathrm{sorb}} = \frac{(C_{\mathrm{tracer,t_0}} \cdot M_{\mathrm{tot,t_0}}) - (C_{\mathrm{tracer,t_e}} \cdot M_{\mathrm{tot,t_e}})}{100 \cdot m_{\mathrm{adsorbent}}} \tag{1}$$

with

$$M_{\mathrm{tot,t_e}} = M_{\mathrm{tot,t_0}} - V_{\mathrm{mic}} \cdot m_{\mathrm{adsorbent}} \cdot \rho_{\mathrm{sorbate}} \tag{2}$$

where $M_{\mathrm{tot,t_0}}$ and $M_{\mathrm{tot,t_e}}$ represent the total masses of liquid, respectively at the beginning of the experiment and at equilibrium. V_{mic} corresponds to the microporous volume per unit mass of adsorbent and ρ_{sorbate} is hypothetically taken equal to the density of the bulk liquid phase. $C_{\mathrm{tracer,t_0}}$ and $C_{\mathrm{tracer,t_e}}$ are respectively the tracer concentration before adsorption and at adsorption equilibrium. A schematic overview clarifying the determination of the different parameters is given in Fig. 1.

The data points of each of the individual experiment are then fitted individually using the following equation (5). This model is derived from a classical equilibrium between component 1 and 2 competing to adsorb on a fixed number of identical sites, where c_1 and c_2 are respectively the concentration of the component 1 and 2 in the external phase and where Q_1 and Q_2 are respectively adsorption sites occupies by component 1 and 2. The exchange of a molecule of component i on the adsorption site by another molecule of component i is not taken in account as it does not change the distribution of compounds 1 and 2 over the adsorption sites.

$$c_1 + Q_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Q_1 + c_2 \tag{3}$$

At equilibrium, a so-called steady state is reached where adsorption (v_{ads}, given by (4a)) and desorption (v_{des}, given by (4b)) velocities cancel out each other.

$$v_{\mathrm{ads}} = k_1[C_1]\theta_2, \tag{4a}$$

$$v_{\mathrm{des}} = k_2[C_2]\theta_1 \tag{4b}$$

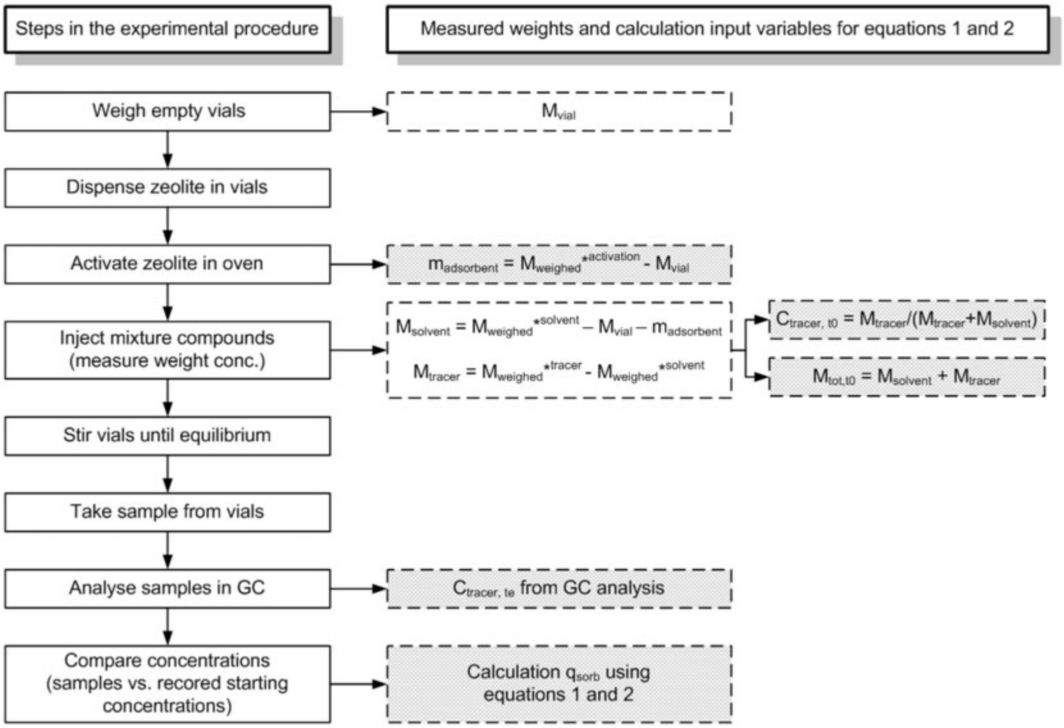


Fig. 1 Schematic overview of the determination of parameters (*shaded boxes*) needed to calculate the adsorbed amount of tracer using (1) and (2). The corresponding stages in the high-throughput batch adsorption methodology (Fig. 4) are shown on the *left*

with θ_1 and θ_2 respectively the fraction of adsorption sites occupied by component 1 and 2, as the number of sites is contact "$\theta_1 = 1 - \theta_2$" is valid. Defining the amount of adsorbed tracer q as "$q_s \cdot \theta_1$", (5) can be found by substitution of (4a) and (4b) in (3).

$$q = q_s \frac{K \cdot c_1}{c_2 + K \cdot c_1} \tag{5}$$

where c_1 and c_2 are now respectively the concentration of the tracer and solvent liquid in the external phase at equilibrium and q is the amount of tracer adsorbed, as calculated using (1); q_s represents the tracer's theoretical maximum adsorption capacity and K the equilibrium constant k_1/k_2 in (3); the value of K is an indication of the slope of the adsorption isotherm, while q_s represents the value at which the plateau of the isotherm is reached.

2.1.2 High-throughput device

Since batch adsorption experiments consist mainly of simple liquid handling operations, they can easily be automated using a general-purpose liquid handling robot. A dedicated setup was designed for batch adsorption experiments based on the Tecan Freedom Evo liquid handler. Figure 2 schematizes the liquid handling part of the robot. The workbench is schematized in Fig. 3. 196 samples can be prepared by mixing of different liquids. Half of this number of samples (98) can be thermostated between 0 °C and 70 °C (higher temperatures are avoided to limit evaporation), at low temperature to limit evaporation of volatile components after septum piercing of the sealed vials or at high temperature to determine the effect of temperature on the adsorption equilibrium. This device is equipped with a thermostatic shaker, a precision balance (0.1 mg) and a set of racks which can accommodate up to 4 × 49 20 ml vials and 2 × 98 1.5 ml sample vials. Furthermore, the robot possesses a robotic arm capable of transporting 20 ml vials as well as a liquid handling arm mounted with eight syringe tips (7 × 1 ml and 1 × 5 ml) capable of aspirating and dispensing liquids from and to any vial on the robot's bench. Moreover, the first syringe (5 ml) is capable of aspirating large amounts of liquids from six external liquid containers. All other needle tips are filled with a user-definable system liquid drawn from a separate external liquid container; the role of this system liquid is twofold: it serves both as a fluid to fill the tubing between the syringes and the tips and as a tip washing liquid to remove the remainders of previous liquids from the inside and outside surface of the tip.

The batch adsorption high throughput device is operated through the Evoware application: when the user inputs a series of commands written in a special purpose high-level scripting language, the software transforms each command into a sequence of low-level operations which are sent to the robot for execution. A custom made interface *Emoware*

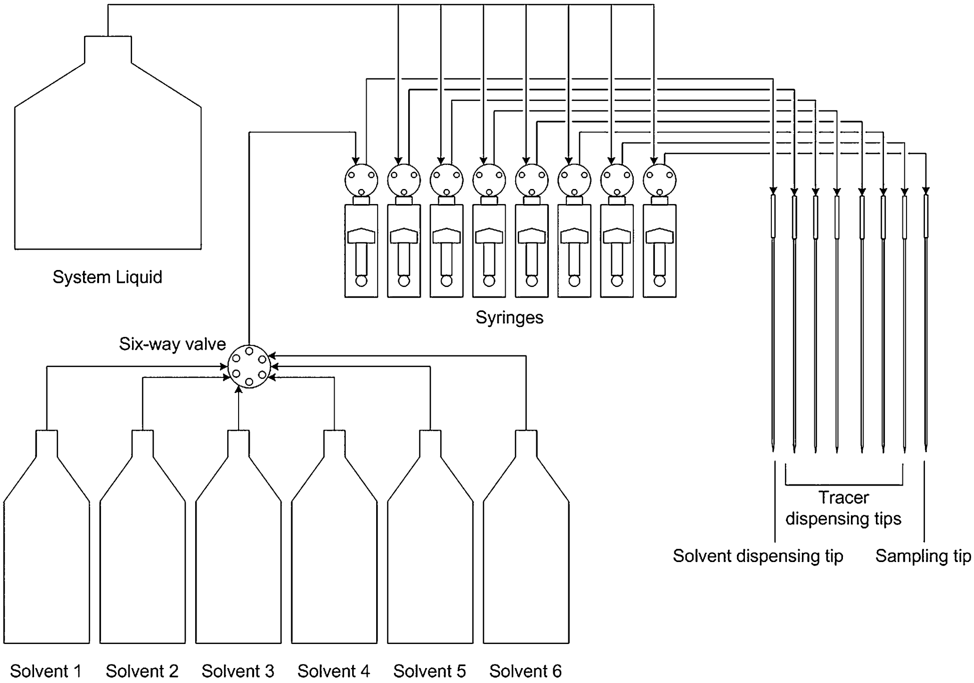


Fig. 2 Paths followed by the different liquids in the batch high-throughput adsorption device. The first syringe (5 ml) connected to the solvent flasks by a six-way valve; where as the next 6 syringes (1 ml) are used to transport liquids between positions on the workbench (Fig. 3). The last syringe is used to take samples. The system liquid is needed to fill the tubing at all times; this is done by use of a three-way valve for syringes 2–8

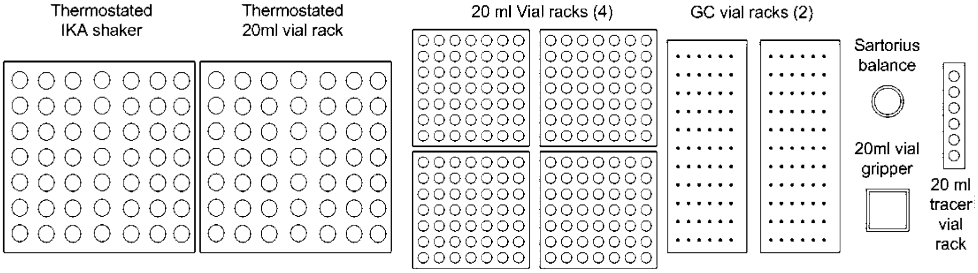


Fig. 3 Schematic overview of the Tecan liquid handling robot's workbench containing from *left* to *right*: a thermostated (0–150 °C) IKA shaker (0–360 rpm) for 49 × 20 ml vials, a thermostated 20 ml vial rack (49), four removable 20 ml vial racks (49), two removable GC vial racks (98), a Sartorius balance (0.0001 g), a 20 ml vial gripper and enclosed 20 ml vial rack (7)

was designed to perform up to 12 binary batch adsorption experiments during a single run; Emoware's working principle is schematically shown in Fig. 4. A single automated binary batch adsorption experiment in which the adsorption of 1 tracer from a solvent in the pores of the adsorbent is measured consists of a sequence of manual and automated tasks. The shaded boxes in Fig. 5 represent the steps that are performed by the high-throughput robot. First, a set of 14 empty 20 ml vials is weighed using the robot's integrated balance, after which each vial is filled with a small amount of adsorbent; the vials are then manually placed in a pulsed air oven to regenerate the adsorbent. After regeneration the vials are removed from the oven and immediately sealed with a septum; the vials are then weighed again using the robot. Next, the Emoware application calculates the amounts of tracer and solvent to be injected in each vial in order to vary the concentration of the tracer in the 0–20 mol% range; both the tracer and the solvent are subsequently added di-

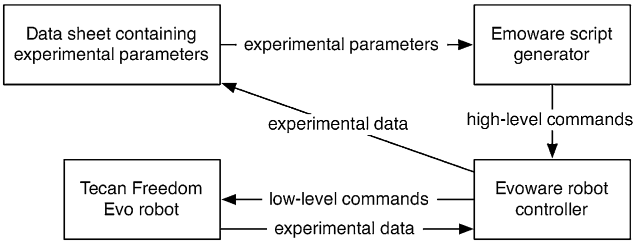


Fig. 4 Flowchart representing the data-flow in high-throughput batch adsorption experiments

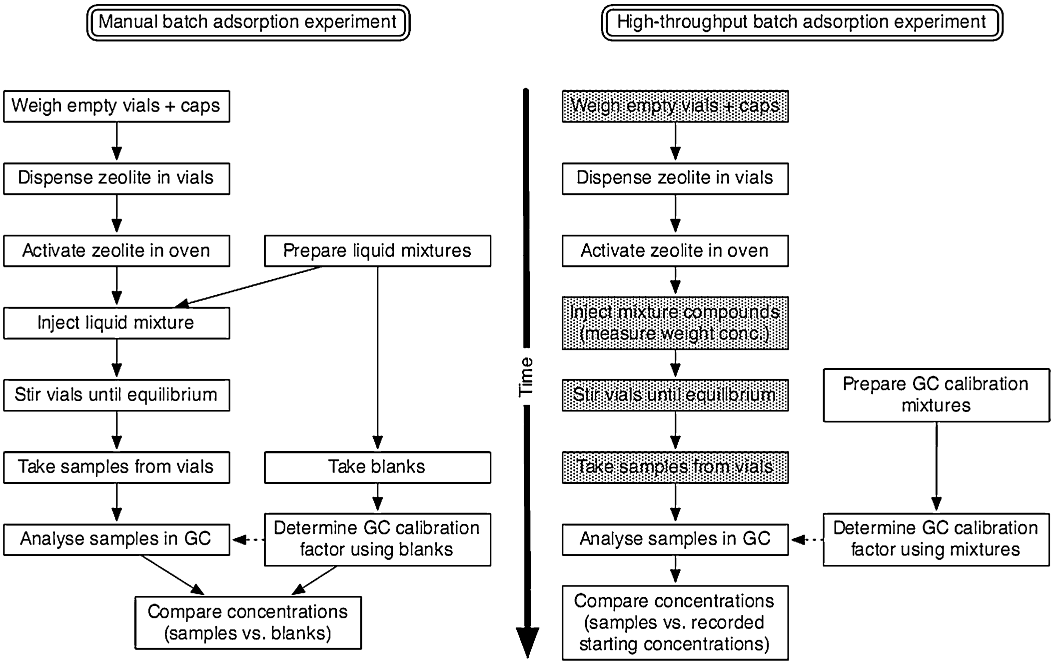


Fig. 5 Comparison of the steps required to perform both manual and automated batch adsorption experiments. The *shaded boxes* represent the steps that are performed by the robot

rectly to each vial via the septum piercing needles. All vials are weighed again after each injection to register the exact amount of liquid that was injected; the vials are then stirred on the robot's shaker for 24 hours to ensure that the adsorption equilibrium is reached; after that, the robot takes a sample of the liquid phase of each vial and injects it into a 1.5 ml vial for analysis in the gas chromatograph. Using a calibration curve, the peak areas resulting from gas chromatography are translated to tracer concentrations, which, following (1), produces 14 data points of the measured adsorption isotherm. The adsorption isotherm can then be fitted from the 14 experimental data points using a theoretical isotherm model. Multiple batch adsorption experiments can be arranged efficiently to increase the number of experiments that can be run at once.

When combining multiple experiments, it is possible to substantially reduce the running time if all experiments are properly interleaved. To do so, the actions performed by the system are divided in three groups: adding the liquid mixture, shaking the vials and taking samples. The experiments are then interleaved as follows: first, all mixtures are added to the vials; next, all vials are alternately agitated on the shaker; finally, a sample is taken from each vial for later analysis. Using this order, the running time of 12 combined experiments is not significantly longer than the time required to run a single experiment. Moreover, multiple optimisations were added to the Emoware script generation engine. For example, when several experiments require the same solvent, the solvent injections are automatically grouped together so that less solvent is wasted since the syringe tip must only be washed once with the solvent in question. Additionally, the Emoware application can further be optimized by properly configuring the experimental parameters, as shown next.

To configure an experiment, the user enters the experimental parameters into a special purpose data sheet, containing a section related to the liquids manipulated in the experiment as well as sections related to the shaking of the vials and to the sample taking process. Furthermore, the data sheet is used as an output port by the Evoware application. Lastly, the data sheet includes a number of validation procedures preventing the experiment from being started when incoherencies are detected in the experimental parameters entered by the user.

2.1.3 Contamination

One important issue to consider in high-throughput experimentation is sample contamination. Contamination can occur every time a needle tip enters a vial if the tip contains remainders of previous liquids. In the case of batch adsorption experiments, this can occur in three situations: when injecting the solvent, when injecting the tracer, and when taking a sample. Each case is dealt with in a separate manner: contamination of the solvent is avoided by first flushing the entire liquid path between the six-way selection valve and the tip with an appropriate cleaning solvent (e.g. acetone); the same operation is then repeated using the solvent required for the next experiment.

The situation is different in the case of tracer injection, because the tracer liquid is drawn from a regular 20 ml vial

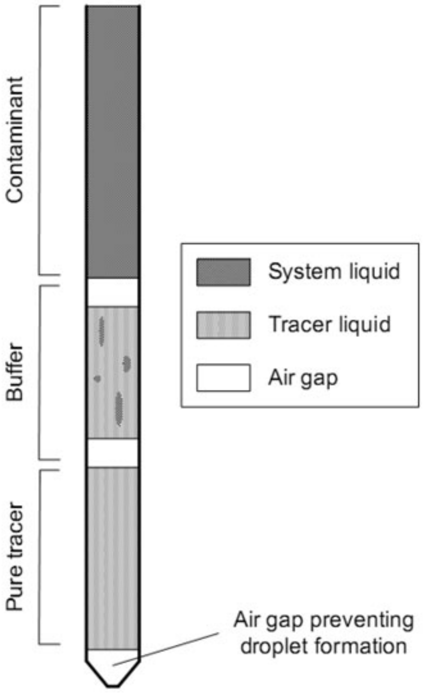


Fig. 6 Schematic representation of the filling of a tracer dispensing tip. The buffer zone comprising air gaps and tracer liquid serves to reduce the contamination of the tracer by the system liquid

on the robot's workspace, and because the tracer tips are filled with the system liquid, which serves as the fluid between the syringes and the tips, as shown in Fig. 2. Hence, when the tracer liquid is aspirated, the retracting system liquid will leave a thin film on the inside surface of the tip, thus contaminating the aspirated tracer liquid. Therefore, to limit the amount of contamination, a small air gap is aspirated between the system liquid and the tracer liquid; furthermore, an excess volume of tracer liquid is aspirated as an additional buffer between the system liquid and the aspirated tracer liquid (see Fig. 6); this excess volume is then discarded to the waste after one or more injections.

The final case in which contamination can occur is during the sampling process: a sample could potentially be contaminated by the remainders of previously taken samples, as all samples are taken with the same tip. To preclude this, the tip is washed with the system liquid after each injection. To limit contamination of the samples by the system liquid itself, the same stratagem is used as for aspirating the tracer liquid. The impact of the different forms of contamination on the experimental results is discussed below.

2.2 Breakthrough experimentation

2.2.1 Theoretical background

Liquid phase breakthrough experiments are used to study the separation of mixtures in dynamic conditions. A mixture of two or more components is pumped through a column packed with adsorbent particles and the effluent concentration profile of each component is recorded in time. This allows quantification of the selectivity of one component over another and the uptake kinetics. The experimental results are analyzed by drawing a so called breakthrough curve, i.e. a curve showing the evolution of effluent concentration as a function of time. Mathematical integration of the breakthrough curve yields the amount of component that was adsorbed by the column (Malek and Farooq 1997):

$$q_i = \left(\frac{\upsilon \cdot \tau_i}{L} - 1\right)\left(\frac{\varepsilon \cdot C_i}{(1-\varepsilon)\cdot \rho_P}\right), \tag{6}$$

$$\tau = \int_0^{t_\infty} \left(1 - \frac{x_e}{x_i}\right) dt \tag{7}$$

q_i = amount adsorbed of component i (mmol/g); τ_i = mean residence time of component i (s); $x_{e,i}$ = molar fraction at exit (e) or inlet (i); L = length of the column (cm); C_i = concentration of solute i (mol/cm^3); ε = porosity of the column; υ = interstitial velocity (cm/s); ρ_P = particle density of the adsorption bed (g/cm^3); t = time (s).

Injecting mixtures introduces competitive adsorption effects amongst the different components of the mixture, causing every component to be adsorbed with a specific selectivity; the most selectively adsorbed component is eluted last, gradually displacing the other, less strongly adsorbed components inside the pores of the adsorbent. An average selectivity for each pair of components (c_1, c_2) can be calculated using the formula:

$$\alpha_{1,2} = \frac{q_1 \cdot c_2}{q_2 \cdot c_1} \tag{8}$$

2.2.2 High-throughput device

Liquid phase breakthrough experiments are less straightforward to implement into a high-throughput environment. To perform parallel breakthrough experiments in liquid phase conditions, the number of pumps should be equal to the number of adsorption columns. In our approach, a different strategy is followed to limit costs. The setup is designed to perform experiments in a sequential order.

The setup is built from multiple independent devices, as schematized in Fig. 7. The heart of the system consists of 2 ovens, each containing 10 adsorption columns. While adsorption experiments are running in the first oven, columns are being regenerated in the second oven, allowing continuous operation. A number of valves allow one to specify the path that is followed by a fluid between the inlet and the outlet of the setup. At the inlet, the setup is equipped with three high pressure syringe liquid pumps, two of which serve to pump the liquids used in the experiments through the system allowing mixture generation of different compositions,

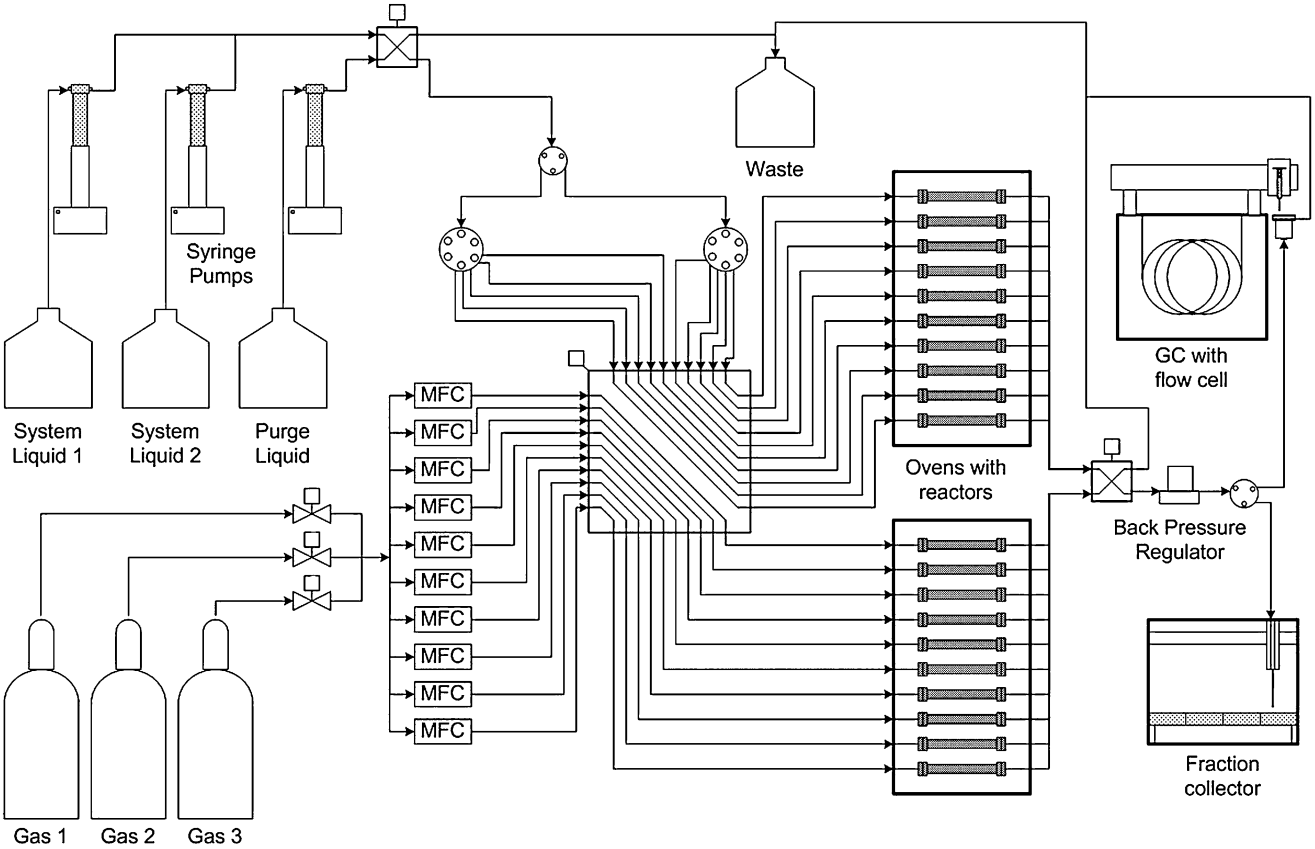


Fig. 7 Schematic overview of the automated high-throughput breakthrough setup. The device is equipped with 3 liquid pumps (500 ml capacity, flow rate < 50 ml/min), 3 gas pumps connected to 10 mass flow controller, two ovens (each containing 10 parallel reaction or adsorption beds) allowing experimental condition between 20–400 °C at pressures 150 bar, direct injection valve on GC for online sample analysis of the flow cell (Fig. 8) or sample collector (5 × 98) for offline analysis

while the third one is used to pump a purge liquid through the setup. Each pump has a capacity of 500 ml and is able to maintain a very stable flow over its entire domain of operation. Additionally, three different gases can be sent through the system to activate and regenerate the adsorbents. Unlike the liquids, which only flow through one channel at the time, the gas flow is split over 10 channels, each of which is equipped with an independent mass flow controller to precisely control the gas flow through the adsorption bed. Since the adsorption columns are often packed with small zeolite crystals of 1 µm or less, a very high resistance to gas flow and thus a large pressure drop occurs. Mass flow controllers which can operate at a broad range of pressures are thus required, better used.

Next, the system possesses two ovens, which can be independently heated or cooled to a maximum of 450 °C. Each oven can accommodate up to 10 columns with a maximal length of 25 cm. A valve allows the experimenter to specify what oven is traversed by liquid; the columns in the other oven are then automatically traversed by gas. After passing through the ovens, a set of valves allow one to redirect the output flow to a gas chromatograph for online analysis, or to a fraction collector for offline analysis or a combination of both.

The online analysis is done by means of a gas chromatograph: the liquid effluent from the experiment passes through a flow cell which is integrated in an autosampler (Fig. 8); the autosampler is then programmed to continually aspirate samples from the flow cell and inject them directly in the chromatograph. This implies that the time between two consecutive concentration determinations is determined by the duration of the chromatographic method used to analyze the samples. The analysis time is easily reduced to less than 1 minute by using a resistively-heated ultra fast capillary column module with a GC column of 5 m. This allows for very short heat up and cool down cycles times. The setup is operated using special purpose control software, which allows controlling each individual entity of the setup; this way, one can reroute the path of every gas or liquid through the setup in order to obtain the desired results. The software also comprises a number of “operational modes” allowing the setup to run in a fully automatic manner. For example, a feedback control loop between GC-analysis and the high-throughput setup allows to stop the experiment on one col-

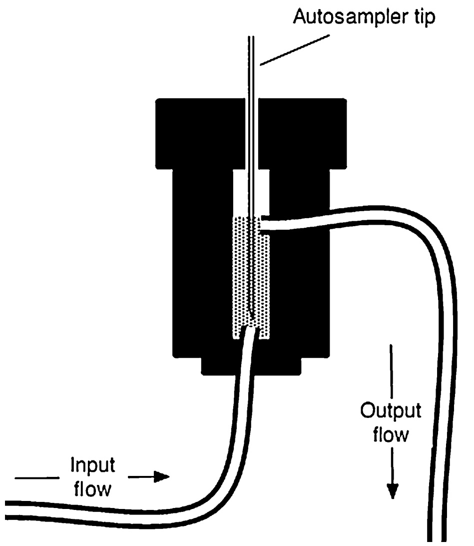


Fig. 8 Schematic representation of the flow cell used in the automated high-throughput breakthrough setup

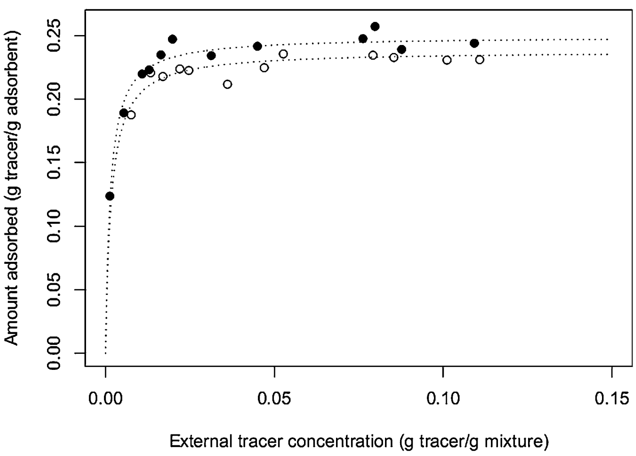


Fig. 9 Comparison of the adsorption of toluene from n-heptane on a NaX faujasite, at room temperature. The hollow data points represent a manual experiment while the filled data points represent the same experiment executed on the Tecan robot

umn when breakthrough has occurred and to switch to the next adsorption column. This allows a much more efficient operation, when running experiments in a continuous way overnight. The presence of two independent ovens and two pumps for system liquids allows uninterrupted breakthrough experimentation, since one liquid pump can be refilled while the other one is actively being used in an experiment; similarly, one oven can be used to perform the experiments while the adsorbents in the other oven are being regenerated concurrently.

2.3 Experimental validation

2.3.1 Batch adsorption experimentation

Contamination occurs in three cases when performing automated batch adsorption experiments: when dispensing the solvent and the tracer, and when taking samples. When dispensing the solvent, contamination should be eliminated by washing the solvent tip as described earlier. This was verified by dispensing different volumes of solvent to empty 20 ml vials using the robot, after which the composition of the liquid in the vials was determined via manual sampling. No contamination by the system liquid was detected in any case. In the second case, the amount of contamination that occurs when dispensing the tracer is measured by performing an automated adsorption experiment without zeolite powder. GC analysis of these samples reveals the presence of system liquid in the samples, at concentrations ranging between 0.01 and 0.10 vol% of the total injected volume when taking the necessary precautions as described above.

In the third case, the 20 ml vials are contaminated by the system liquid every time a sample is taken. The tip containing the contaminant (i.e. the system liquid) is only very briefly brought in contact with the mixture, hence the contaminant is not given sufficient time to be adsorbed by the adsorbent in the vial. Because the sample is aspirated by the contaminated tip, the contamination of the sampled liquid in GC vials can reach up to 2 wt% in this case. However, this last form of contamination is not considered harmful as this peak is easily identified in chromatograms. It can then be discarded from later calculations by normalizing the concentrations of the tracer and the liquid so that their sums equal 100%. The only drawback to this approach is that one cannot perform automated batch experiments in which the tracer liquid is identical to the system liquid.

The influence of the different types of contamination is illustrated by comparing a fully automated batch adsorption experiment to a manually performed one. Figure 9 shows the isotherm of toluene in n-heptane on a 13X zeolite determined using both techniques. The automated experiment yields a slightly higher maximal adsorption capacity. This is the result of dilution of the injected toluene by the system liquid, resulting in an overestimation in the amount adsorbed. Nevertheless, the automated method gives reliable isotherm data.

2.3.2 Breakthrough experimentation

On the high-throughput breakthrough setup, the majority of pipes are traversed by both gases and liquids. This could cause important contamination problems. When examining the contamination in this setup, we discriminate between two cases: contamination before and after the column.

Contamination before the adsorption column leads to foreign components (from previous experiments) entering the reactor and potentially disrupting the adsorption experiment. This type of contamination can be difficult to detect if the contaminant molecules are adsorbed in the column

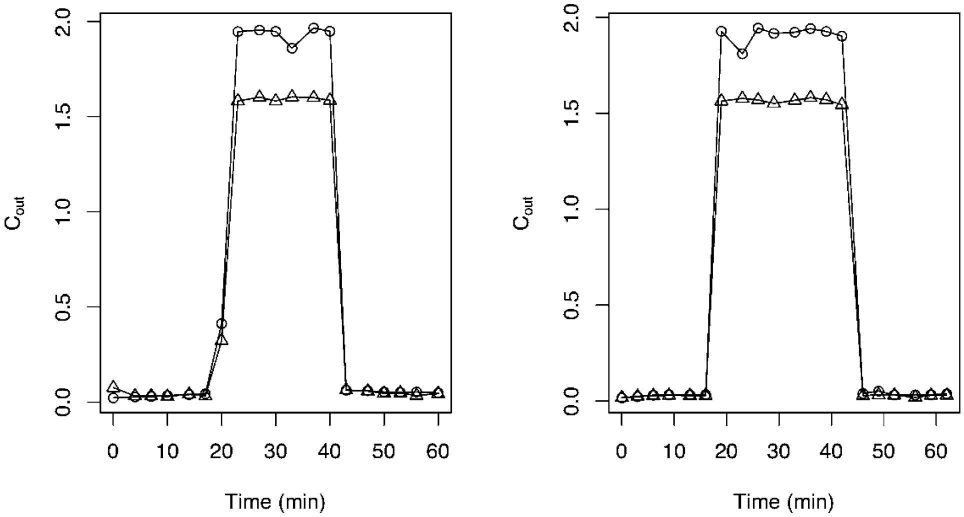


Fig. 10 Blank breakthrough experiments, at a flow rate of 0.5 ml/min (*left*) and 1.0 ml/min (*right*). The data points represent the mass concentration of 1-octene (*circles*) and toluene (*triangles*) at a given time

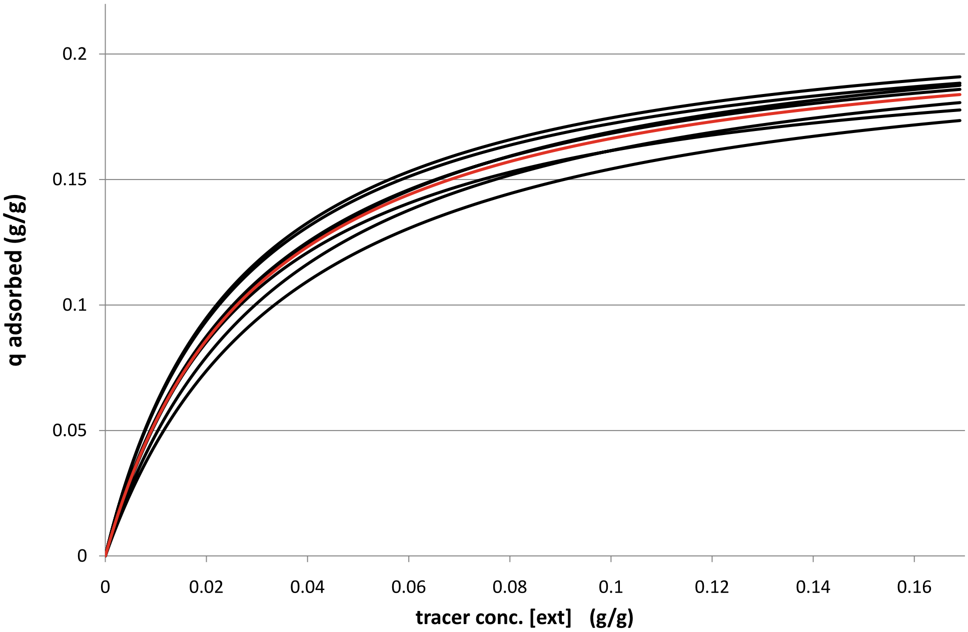


Fig. 11 Repeatability analysis (1-octene in n-heptane on 13X); overlay of the fitted isotherms (*black lines*) and the average isotherm (*red dotted line*)

and hence fail to be detected as they are retained in the column. Contamination after the adsorption column is caused by residues of liquids used in previous adsorption experiments, between the column and the gas chromatogram or the fraction collector. Contrarily to contamination before the column, the contaminants do not interfere with the adsorbent in this case. Additionally, they do reach the analysis step at the end of the experimental chain, such that their presence can be detected and their concentration be quantified.

To assay the amount of contamination, blank experiments were carried out in which the flow through an empty column is alternated between the purge liquid (pure iso-octane) and a ternary mixture (2 mol% 1-octene and 2 mol% toluene dissolved in iso-octane). Determining the composition of the mixture at the output allows measuring both the response time of the system to a switch from the purge liquid to the system liquid and the amount of contamination when the feed is changed back to the (pure) purge liquid. These experiments were performed at flow rates of 0.5 ml/min and 1 ml/min. The breakthrough curves in Fig. 10 show the concentration of 1-octene and toluene over a period of time during which the feed is switched back and forth between the purge liquid and the system liquid. The concentration of 1-octene and toluene swiftly reach the feed level when the feed is switched. When the feed is changed back to the purge liquid, an equally swift response is noticed, the concentration of 1-octene and toluene drop back to zero. Hence, it can be concluded that no unwanted mixing effects are occurring.

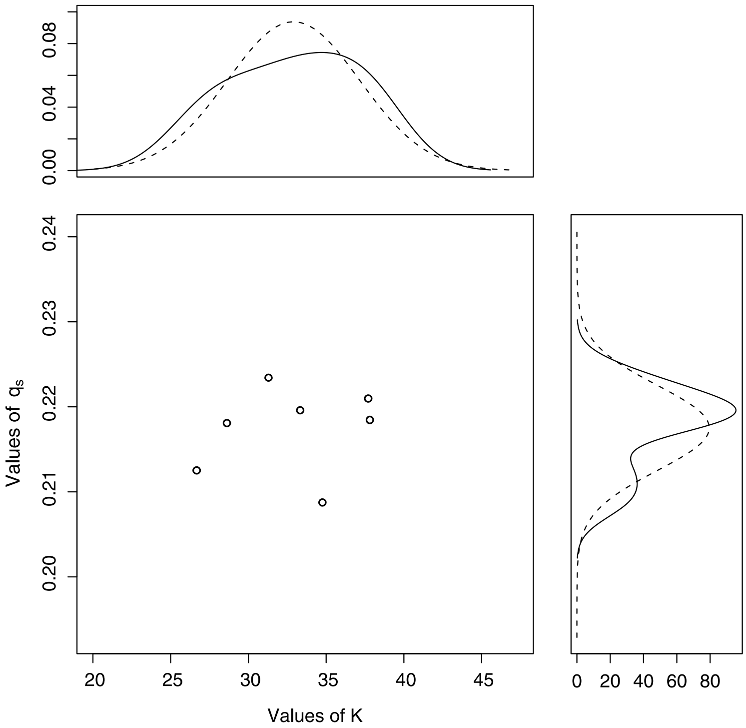


Fig. 12 First repeatability experiment (1-octene in n-heptane on NaX). The *lower left graph* shows the different (K, q_s) couples; the two *other graphs* show density plots of K (*above*) and q_s (*right*). The *dashed curves* show the associated normal distributions

2.4 Repeatability

Repeatability measurements were carried out to quantify the amount of variation between the experimental results of consecutive identical adsorption experiments.

2.4.1 *Batch adsorption experimentation*

The adsorption of 1-octene diluted in n-heptane and toluene diluted in n-heptane was measured on NaX zeolite at room temperature. The choice of mixtures is justified by the difference in adsorption behaviour between both experiments: on NaX, the selectivity of 1-octene over n-heptane is much lower than the selectivity of toluene over n-heptane; this results in a gradual adsorption isotherm for the first system, while the latter has a very steep adsorption isotherm. Figure 11 shows the fittings for 7 repeated experiments with 1-octene/n-heptane as adsorbing mixture, together with the Langmuir fitting for the mean isotherm, which was obtained by dividing the experimental concentration range in 15 segments and taking the average of the experimental values in each segment for the mean isotherm. The values of K and q_s of the individual experiments are then compared to each other in order to quantify the amount of variation between consecutive repeated experiments. The values obtained for the repeated experiments are given in Tables 2 and 3. The different (K, q_s) pairs are also represented graphically in Figs. 12 and 13, together with their density plots.

For both repeatability experiments, the distributions of K and q_s are first tested for normality using the Shapiro-Wilk

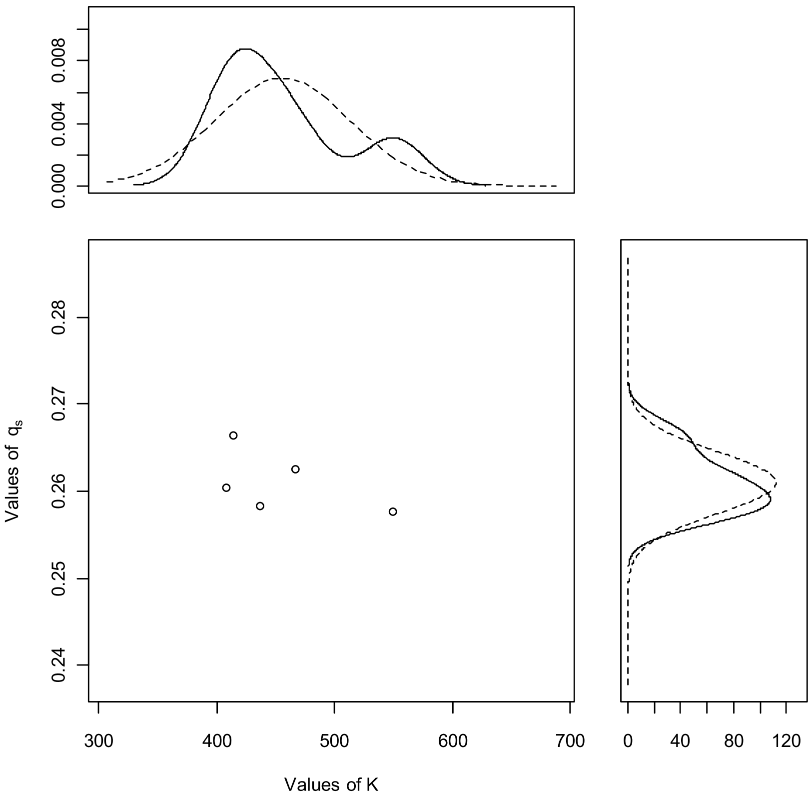
Table 2 First repeatability experiment (1-octene in n-heptane on NaX): values for K and q_s

Experiment	K	q_s (g/g)
1	34.7	0.208
2	33.3	0.219
3	28.6	0.218
4	37.6	0.221
5	26.7	0.212
6	37.7	0.218
7	31.3	0.223
Average	32.8	0.217
Std. Error	4.2	0.005
95% C.I.	32.8 ± 3.9	0.217 ± 0.005

Table 3 Second repeatability experiment (toluene in n-heptane on NaX): values for K and q_s

Experiment	K	q_s (g/g)
1	468	0.262
2	408	0.260
3	414	0.266
4	438	0.258
5	550	0.258
Average	456	0.261
Std. Error	58	0.004
95% C.I.	456 ± 71	0.264 ± 0.004

Fig. 13 Second repeatability experiment (toluene in n-heptane on NaX). The *lower left graph* shows the different (K, q_s) couples; the two *other graphs* show density plots of K (*above*) and q_s (*right*). The *dashed curves* show the associated normal distributions



test: the test yields p-values larger than 0.05 in all four cases, so that it can be concluded with a 95% certainty that the values of K and q_s are normally distributed for both repeatability experiments. This allows constructing confidence intervals for K and q_s, based on the t-distribution: the 95% confidence intervals for K and q_s are given in Tables 2 and 3. It can be noticed that, proportionally, the values of K have a much larger confidence interval than the values of q_s. This is believed to be due to the fact that less data points come into play to estimate the value of the K parameter (typically data points at low concentrations) compared to the q_s parameter.

A case study analyses the adsorption of different aromatics (benzene, xylene, ethylbenzene) from 1-octene on a NaY faujasite. The experimental results of this case study are depicted in Fig. 14. First of all, it shows that all these aromatic molecules are preferentially adsorbed over 1-octene. This is due to the higher interaction of the aromatic ring with the charge compensating cations of the zeolite, compared to the double bond of alkenes. Secondly, the smaller aromatic molecules (benzene, xylenes) are preferentially adsorbed over the larger ones (ethylbenzene). It was shown that this is due to packing effects inside the zeolite's pores (Daems et al. 2005): at high loading, as is the case with liquid phase adsorption, the adsorbent pores are completely saturated. Smaller molecules are able to fill the available space in a more efficient way than their larger counterparts (Serra et al. 2003). Thus, it is shown that high-throughput adsorption experiments yield valuable information, in agreement with manual batch experimentation when adequately dealt with contaminations.

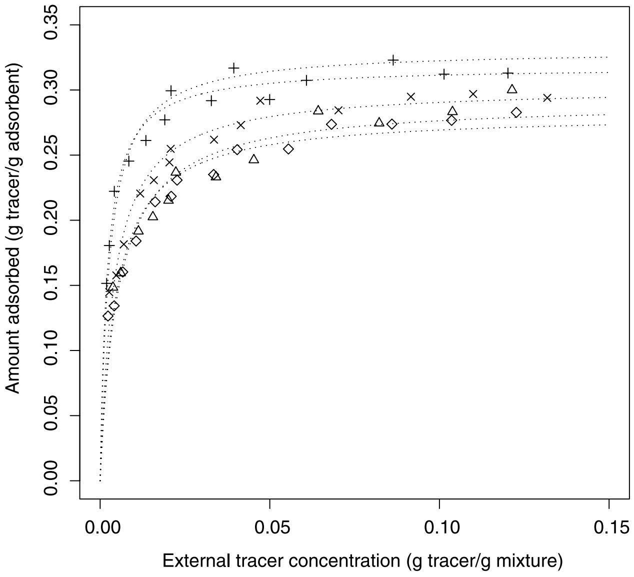


Fig. 14 Comparison of the adsorption of aromatics from 1-octene on a NaY faujasite, at room temperature. From *top* to *bottom*: benzene, m-xylene, p-xylene, o-xylene, ethylbenzene. The *dotted curves* show the fits of the experimental data against the proposed adsorption model (see (5))

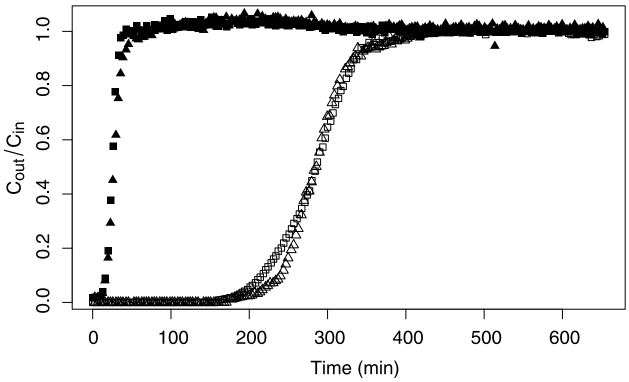


Fig. 15 Repeatability experiment: three separate breakthrough experiments with an equimolar mixture (2 mol% each) of n-octane (*filled shapes*) and toluene (*hollow shapes*) in iso-octane, using NaX beads as the adsorbent. Each of the three shapes represents a different experiment using the same column; deviations can be attributed to weighting errors

2.4.2 Breakthrough experiments

Similarly to the batch adsorption setup, the repeatability of the results obtained with the breakthrough setup was analyzed by performing identical breakthrough experiments. The repeated experiments were carried out with a ternary mixture of 2 mol% n-octane and 2 mol% toluene in iso-octane, on a NaX faujasite. The beads of zeolite were inserted in 20 cm reactors with an inside diameter of 1 cm and regenerated at 450 °C under a nitrogen flow of 50 ml/min. During the experiment, the feed flow was set to 0.75 ml/min; the analysis of the effluent was done online: samples were taken every 3 minutes and analyzed with the gas chromatograph. Figure 15 shows the different experimental breakthrough curves superimposed. n-Octane elutes first, toluene is retained longer due to its stronger adsorption. The separation factor (see (4)) was calculated for each experiment, yielding values of 16.4, 17.6 and 16.4; hence, the coefficient of variation for the three experiments amounts to 4.1%.

3 Conclusion

We have developed a high-throughput methodology to perform static (batch) and dynamic (breakthrough) adsorption experiments. Both experimental setups greatly speed up the amount of experiments that can be performed simultaneously, while relieving the experimenter from the most tedious tasks. The new methodology was validated by multiple experiments: contamination tests were performed; the precision of the setup was assessed using repeatability experiments and several case studies were carried out, yielding results comparable to those obtained by manual experiments. The increased availability of experimental liquid phase adsorption data opens the way for an extensive study of liquid phase adsorption of binary hydrocarbon mixtures in zeolites. The experiments are currently under way. The detailed analysis of the results by using statistical data treatment in the aim to establish quantitative structure-activity relationships will be reported elsewhere.

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