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GCMC Simulations in Zeolite MFI and Activated Carbon for Benzene Removal from Exhaust Gaseous Streams

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Keywords:	GCMC simulation, benzene removal, adsorption, zeolite, activated carbon

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Table1. 3D periodic cells characteristics.

Structure	Dimensions x, y, z [Å]	Composition [% in weight]	Density [kg/m^3]
Zeolite MFI	40.044, 39.798, 26.766	Si 46.7%, O 53.3%	1796
Zeolite FAU (NaY)	25.104, 25.104, 25.104	Si 30.1%, O 48.3%, Al 11.7%, Na^+ 9.9%	1337
Cs1000a	25.000 x 25.000 x 25.000	C 99.2%, H 0.8%	728

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Table 2. Isosteric heats for multicomponent adsorption in zeolite MFI and activated carbon cs1000a.

		Benzene [kcal/mol]	H_2O [kcal/mol]	CO_2 [kcal/mol]	N_2 [kcal/mol]	O_2 [kcal/mol]
MFI (101.3 kPa)	500 K	24.46 (0.12)	10.46 (0.63)	10.99 (0.34)	[-]	[-]
	750 K	24.30 (0.17)	7.98 (0.16)	9.64 (0.15)	[-]	[-]
	1000 K	24.27 (0.17)	7.68 (0.17)	9.68 (0.10)	[-]	[-]
MFI (202.6 kPa)	500 K	24.59 (0.13)	10.32 (0.52)	10.91 (0.40)	[-]	[-]
	750 K	24.35 (0.06)	8.22 (0.26)	9.67 (0.18)	[-]	[-]
	1000 K	24.29 (0.19)	7.75 (0.11)	9.71 (0.06)	[-]	[-]
MFI (506.5 kPa)	500 K	24.39 (0.12)	7.65 (0.12)	9.30 (0.07)	[-]	[-]
	750 K	24.30 (0.15)	8.49 (0.36)	9.96 (0.32)	[-]	[-]
	1000 K	24.03 (0.14)	7.64 (0.07)	9.27 (0.07)	6.45 (0.01)	5.65 (0.04)
Cs1000a (101.3 kPa)	500 K	19.75 (0.20)	3.47 (0.05)	5.32 (0.14)	3.14 (0.05)	2.71 (0.05)
	750 K	16.80 (0.23)	3.38 (0.04)	4.64 (0.03)	3.26 (0.02)	2.97 (0.03)
	1000 K	14.26 (0.49)	3.59 (0.04)	4.62 (0.06)	3.51 (0.01)	3.31 (0.03)
Cs1000a (202.6 kPa)	500 K	19.50 (0.33)	3.53 (0.04)	5.18 (0.14)	3.12 (0.06)	2.68 (0.05)
	750 K	16.98 (0.18)	3.37 (0.04)	4.66 (0.04)	3.27 (0.02)	2.97 (0.02)
	1000 K	14.11 (0.48)	3.60 (0.03)	4.62 (0.04)	3.51 (0.01)	3.30 (0.02)
Cs1000a (506.5 kPa)	500 K	19.21 (0.43)	3.53 (0.07)	5.17 (0.06)	3.08 (0.05)	2.64 (0.03)
	750 K	16.95 (0.16)	3.40 (0.02)	4.67 (0.04)	3.26 (0.01)	2.96 (0.01)
	1000 K	14.26 (0.29)	3.60 (0.02)	4.61 (0.05)	3.52 (0.01)	3.30 (0.02)

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GCMC Simulations in Zeolite MFI and Activated Carbon for Benzene Removal from Exhaust Gaseous Streams

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Additional information

In this additional section we provide some of the intermediate results for the data fitting with the Sips model; in Table 1 fitting coefficients for pure gas adsorption (Langmuir-Freundlich model) are given.

Table 1: Langmuir-Freundlich coefficients obtained from GCMC simulations for pure gases.

	Component	q_0	b	α
MFI 500 K	C_6H_6	0.694891	1720.402	1.697132
	CO_2	2.256095	0.004879	0.996195
	H_2O	2.50333	0.000924	1.157638
	N_2	2.996174	0.001264	0.794164
	O_2	2.167964	0.000162	1.081247
MFI 750 K	C_6H_6	0.5777	0.4892	1.201978
	CO_2	2.619929	0.0016	0.708732
	H_2O	4.010516	0.000431	0.778028
	N_2	3.094037	0.000141	0.855976
	O_2	2.624987	5.62E-05	0.948991
MFI 1000 K	C_6H_6	0.6124	0.030372	0.635486
	CO_2	2.181992	0.000131	0.88384
	H_2O	2.744951	1.64E-05	1.061462
	N_2	3.171256	4.56E-05	0.87837
	O_2	2.598625	1.98E-05	0.970649
Cs1000a 500 K	C_6H_6	5.548263	0.160656	0.49089
	CO_2	15.15991	0.000329	0.785837
	H_2O	19.56613	2.11E-06	1.376407
	N_2	13.38064	4.68E-05	0.959993
	O_2	16.36275	2.76E-05	0.954396
Cs1000a 750 K	C_6H_6	3.862232	0.002408	0.970701
	CO_2	18.62218	9.5E-07	1.254696
	H_2O	19.6067	0.0007	1.036259
	N_2	13.2514	1.89E-05	0.946193
	O_2	18.18576	1.78E-05	0.89834
Cs1000a 1000K	C_6H_6	4.052317	2.69E-05	1.188316
	CO_2	1.026116	1.11E-05	1.059579
	H_2O	2.582858	4.34E-06	1.048639
	N_2	5.546026	8.37E-06	0.858746
	O_2	2.145528	7.38E-06	0.9716

In Figure 2 - 7, adsorption isotherms for all adsorbed gases in the mixtures and for zeolite MFI and activated carbon cs1000a are given; loading is expressed as a function of benzene partial pressure. It can be seen how the coverage of the other components is very limited. In Figure 8 adsorption isotherms for the mixture at 500 K, 101.3 kPa (1 atm) for zeolite NaY are given; loading is expressed as a function of benzene partial pressure. It can be noticed how benzene loading is significantly lower than water or oxygen.

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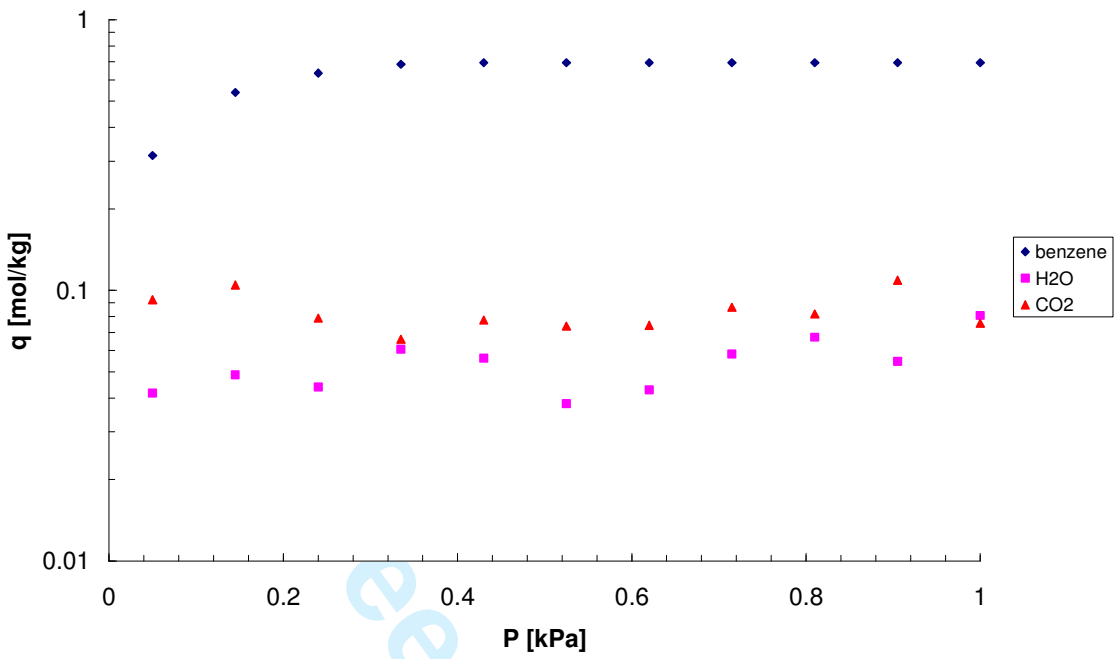
(a)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P [kPa]
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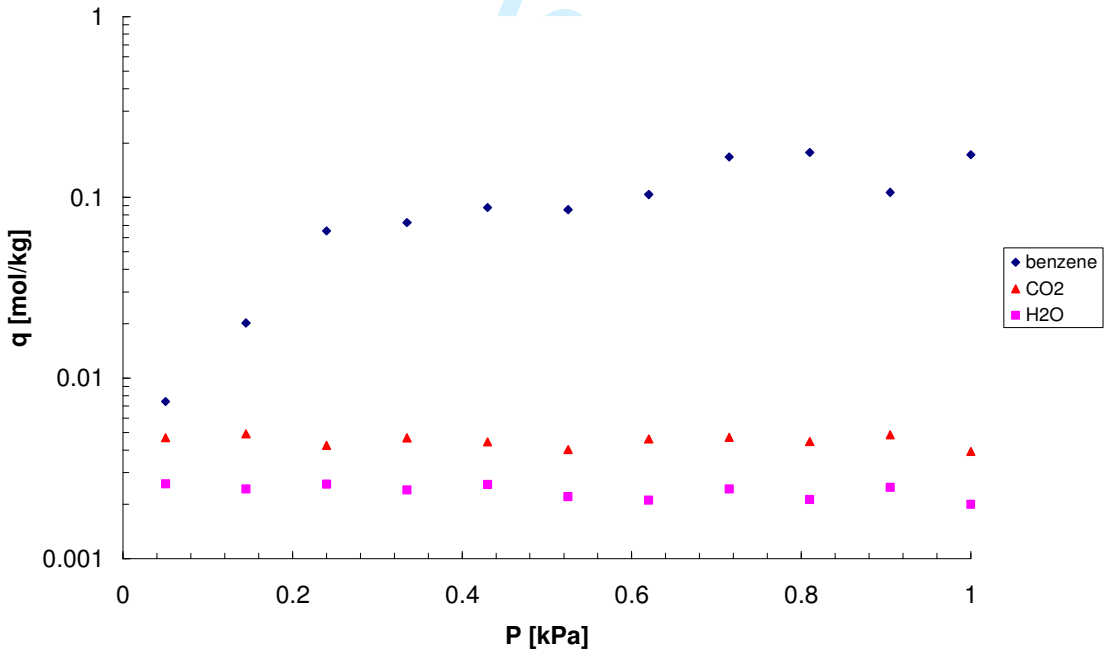
CO2

(b)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0.001
q [mol/kg]
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0.8
1
P [kPa]
benzene
CO2
H2O

(c)

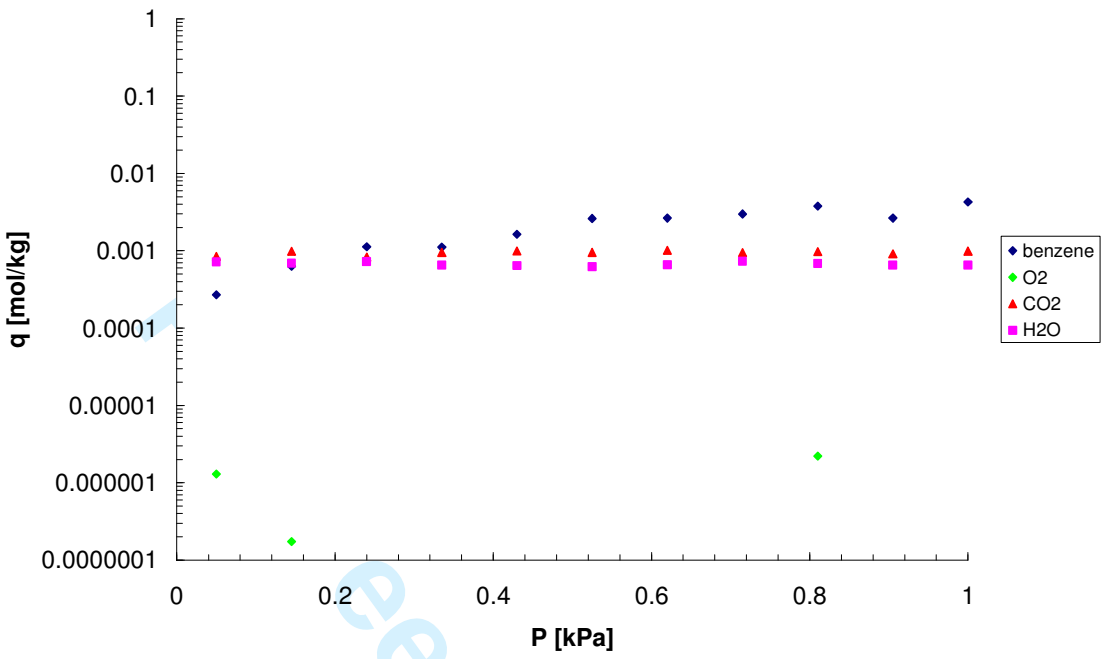
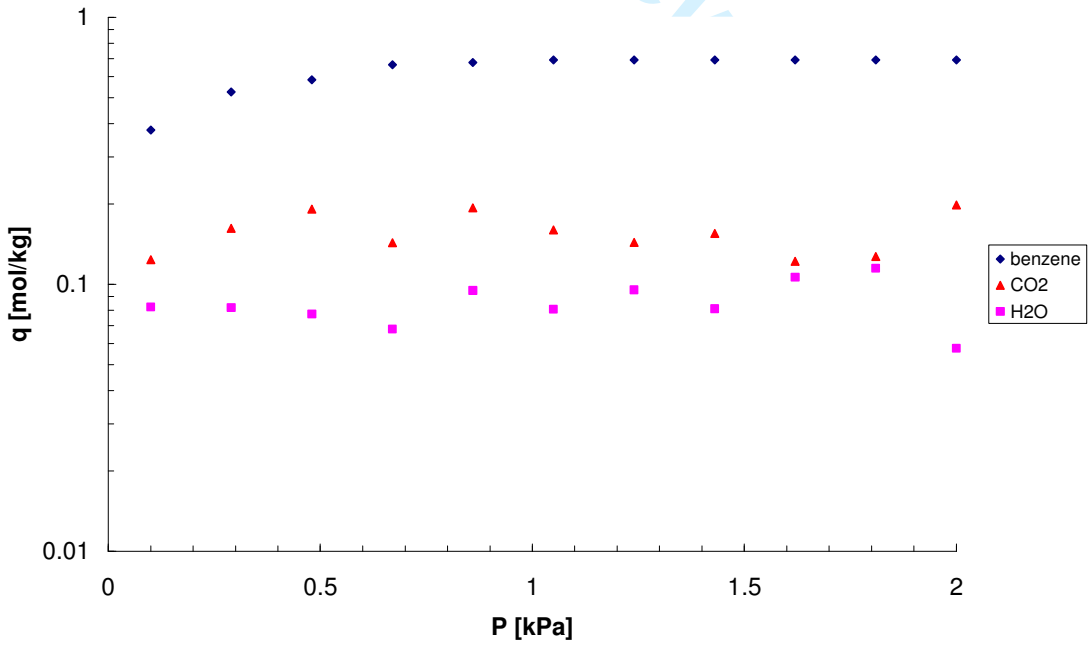


Figure 2. Adsorption isotherms for all components in zeolite MFI at a total pressure of 101.3 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO_2, pink: H_2O, green: O_2.

(a)



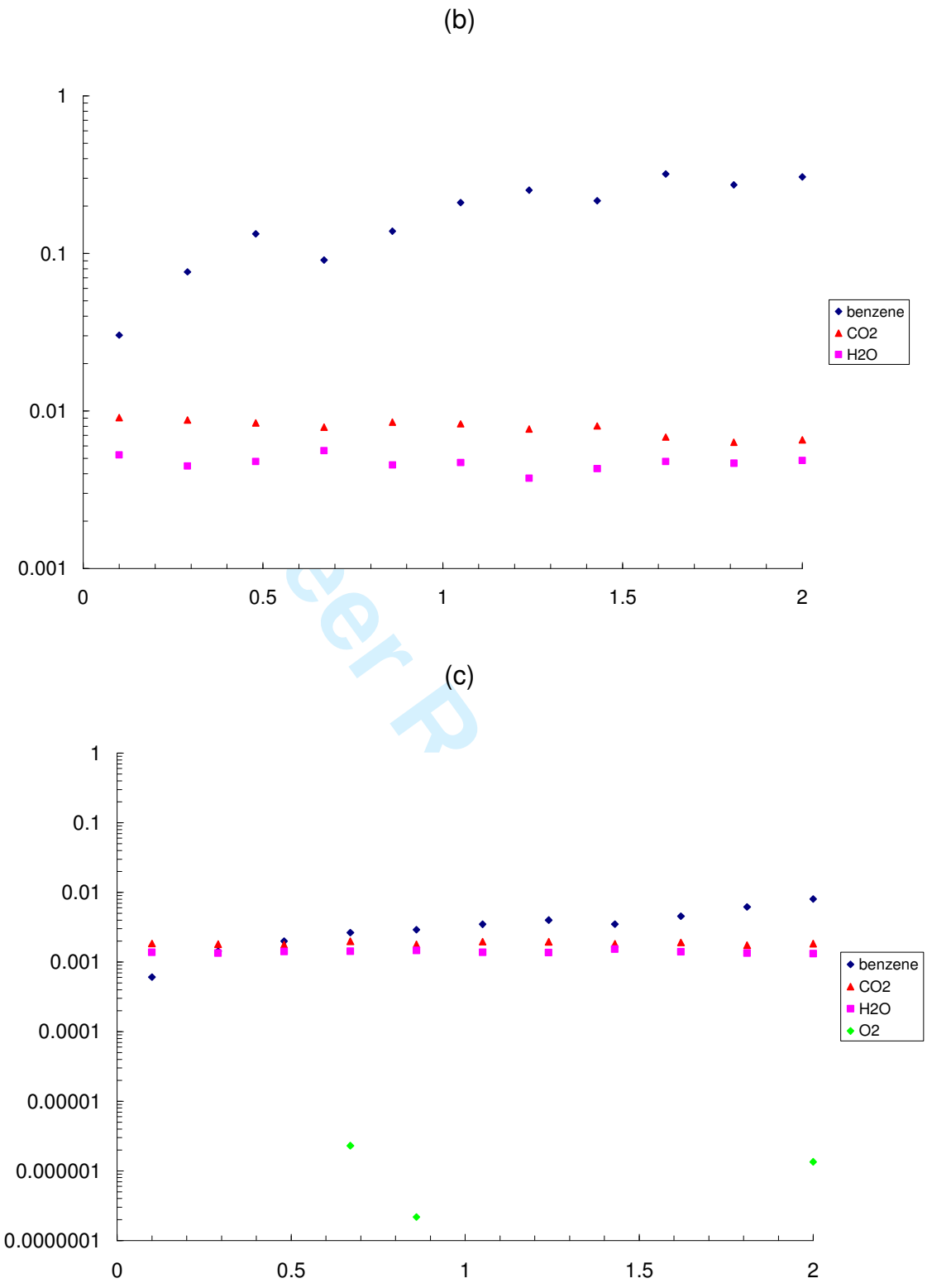
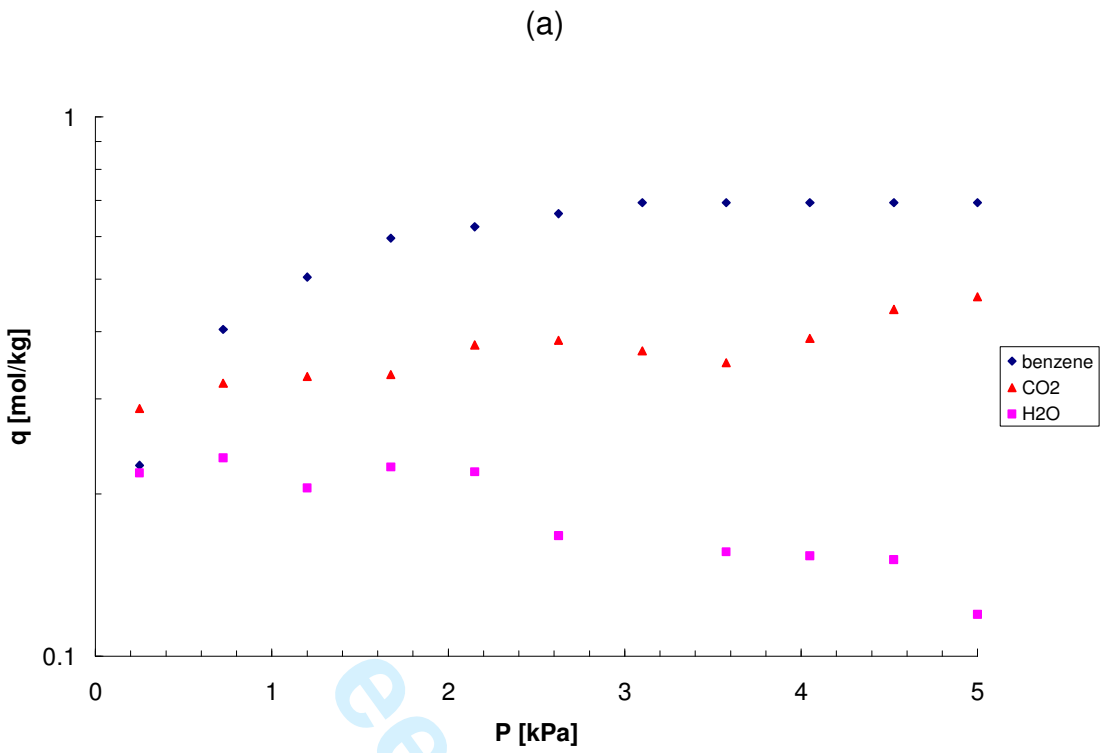


Figure 3. Adsorption isotherms for all components in zeolite MFI at a total pressure of 202.6 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO_2, pink: H_2O, green: O_2.


(a)
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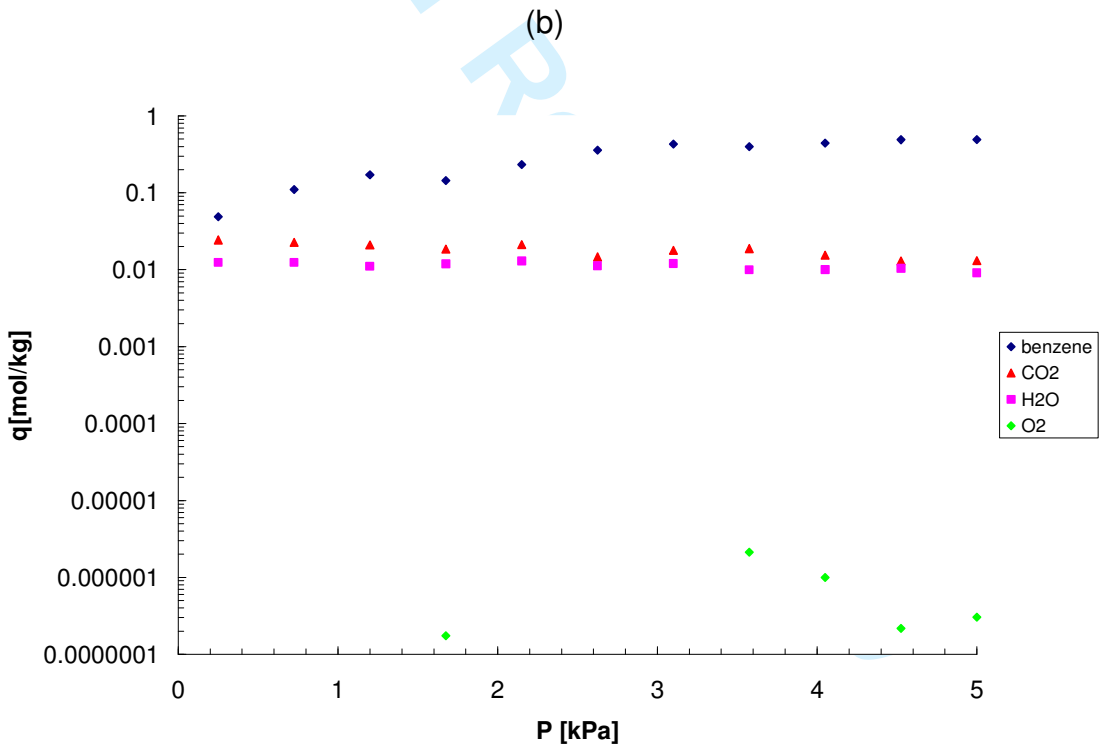
0.1
q [mol/kg]
0
1
2
3
4
5
P [kPa]
benzene
CO2
H2O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q[mol/kg]
0
1
2
3
4
5
P [kPa]
benzene
CO2
H2O
O2

(c)

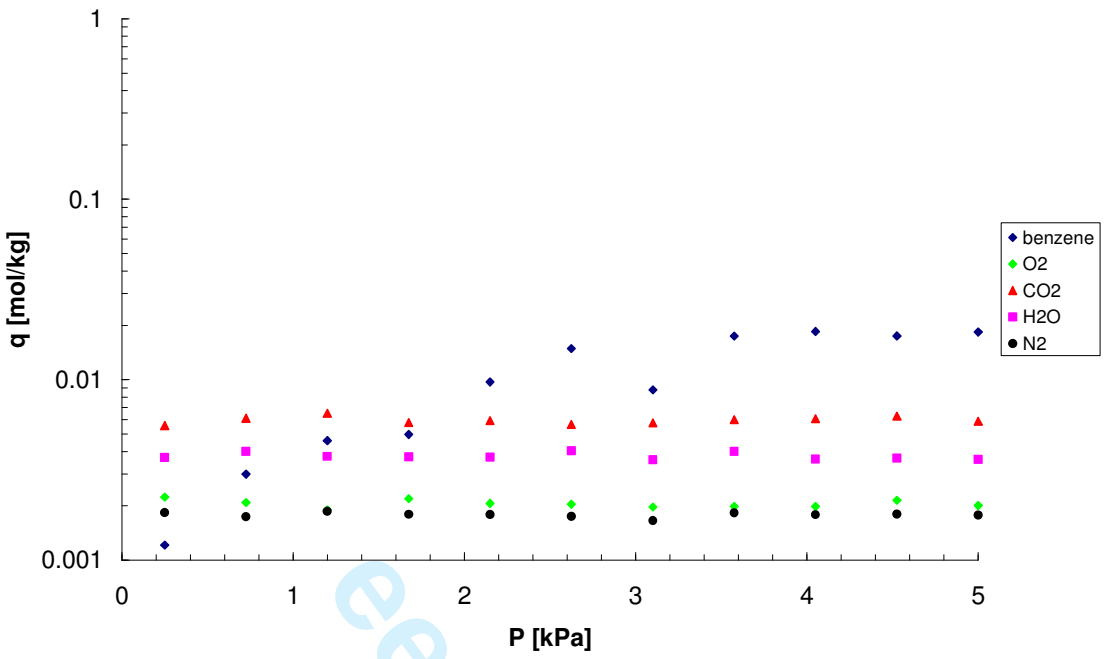
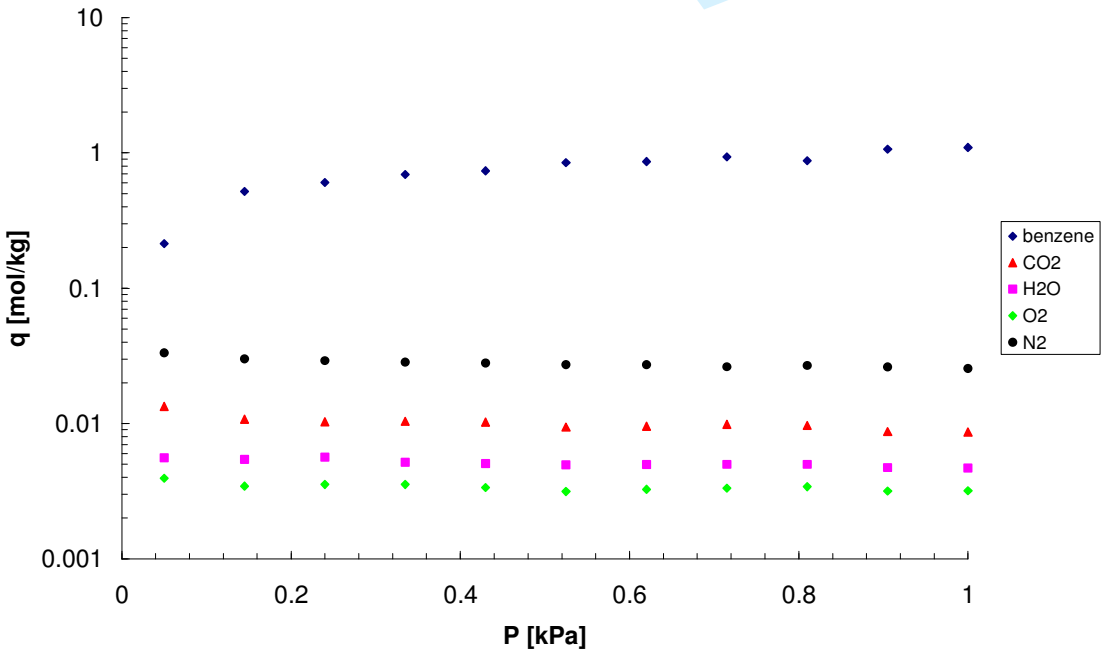


Figure 4. Adsorption isotherms for all components in zeolite MFI at a total pressure of 506.5 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO_2, pink: H_2O, green: O_2, black: N_2.

(a)



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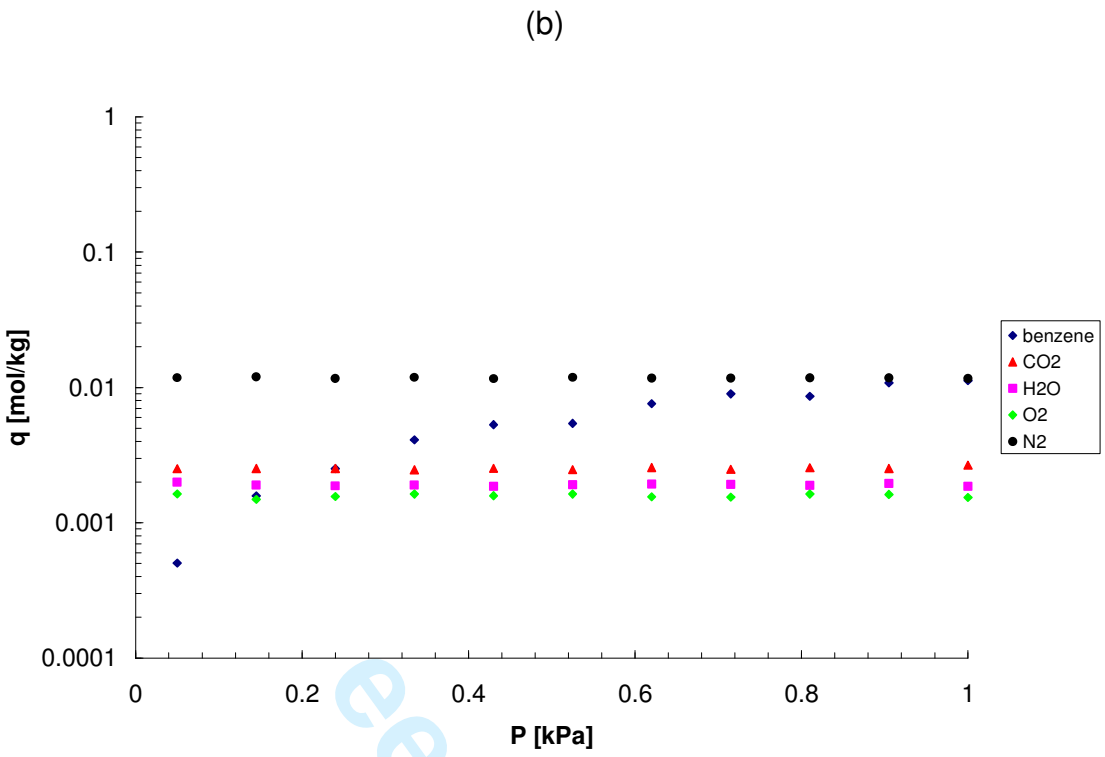


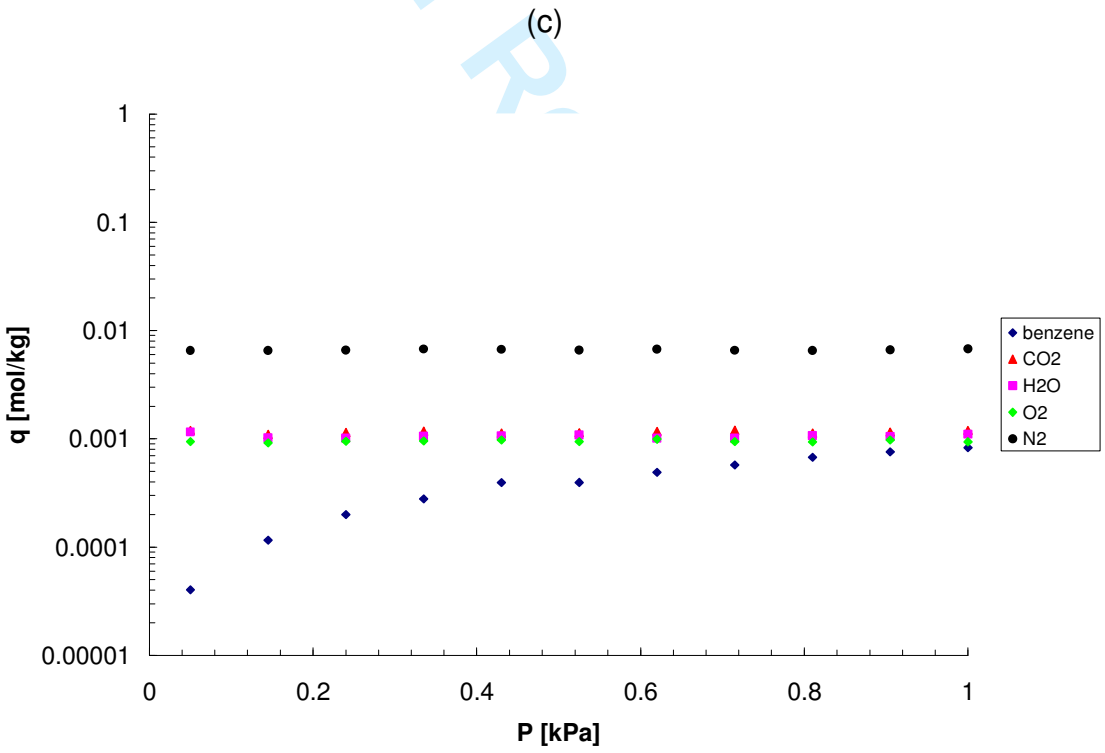
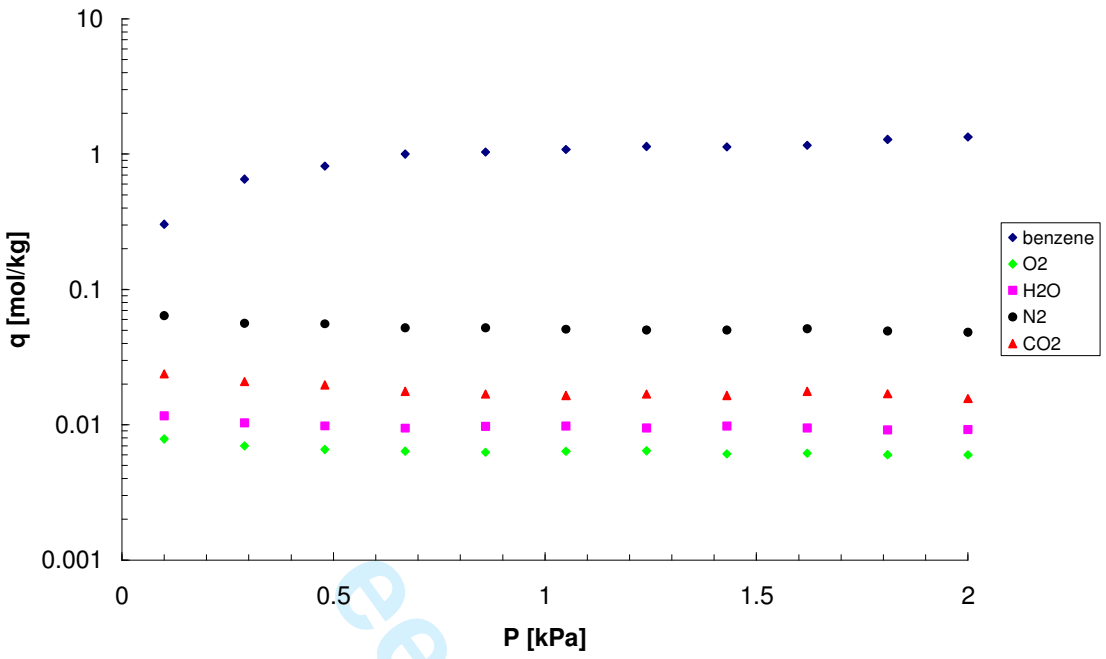


Figure 5. Adsorption isotherms for all components in cs1000a at a total pressure of 101.3 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO_2, pink: H_2O, green: O_2, black: N_2.

(a)


10
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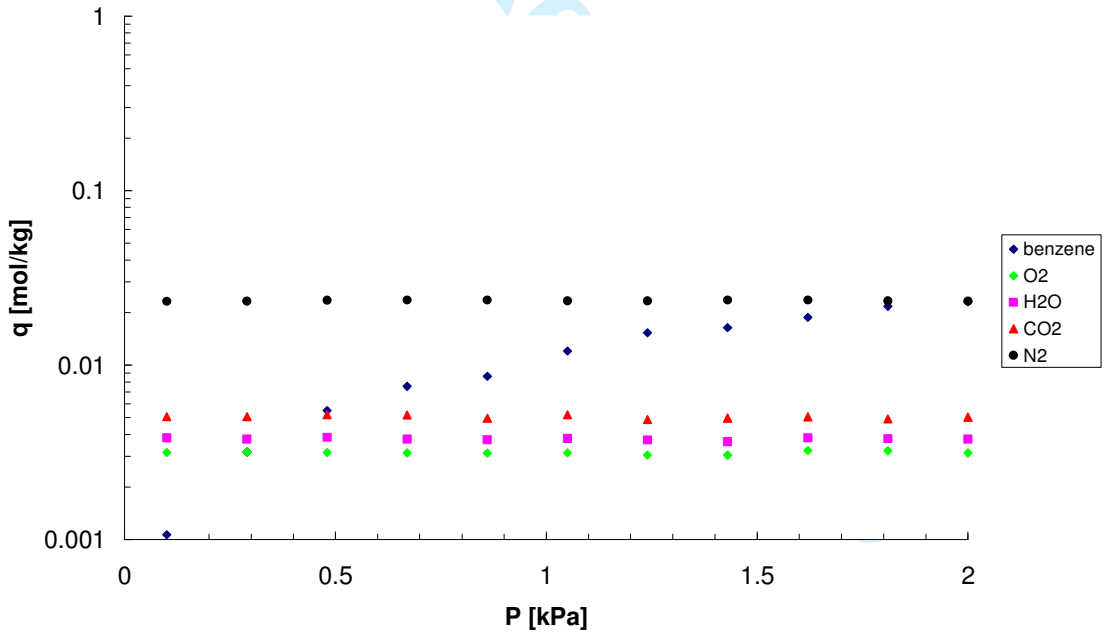
0.1
0.01
0.001
q [mol/kg]
0
0.5
1
1.5
2
P [kPa]
benzene
O2
H2O
N2
CO2

(b)


1
0.1
0.01
0.001
q [mol/kg]
0
0.5
1
1.5
2
P [kPa]
benzene
O2
H2O
CO2
N2

(c)

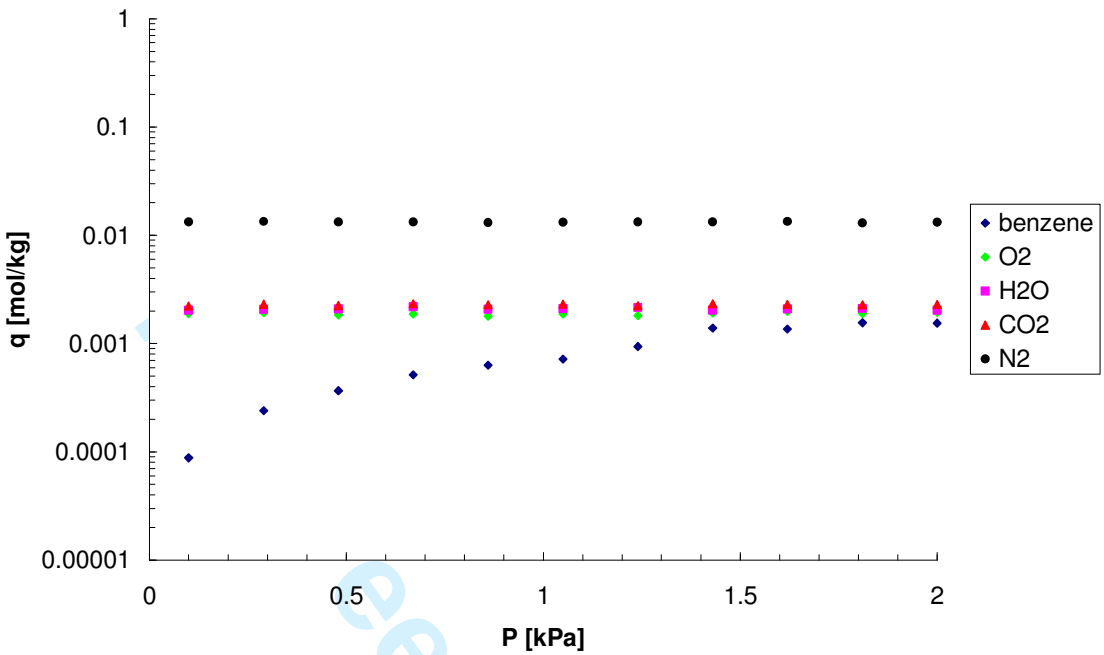
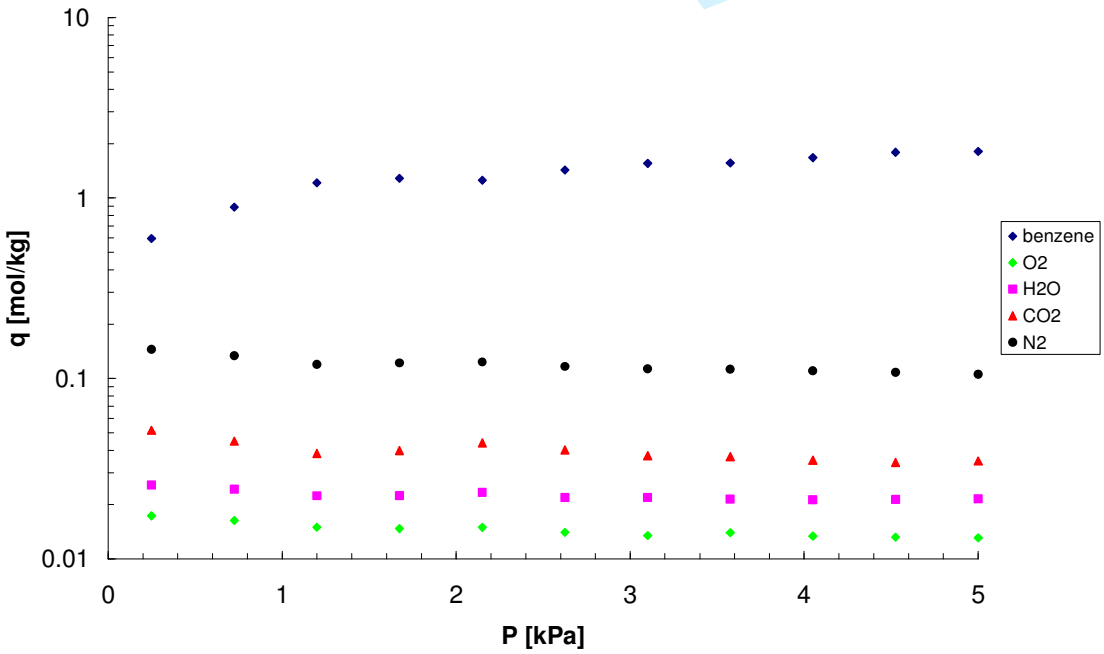
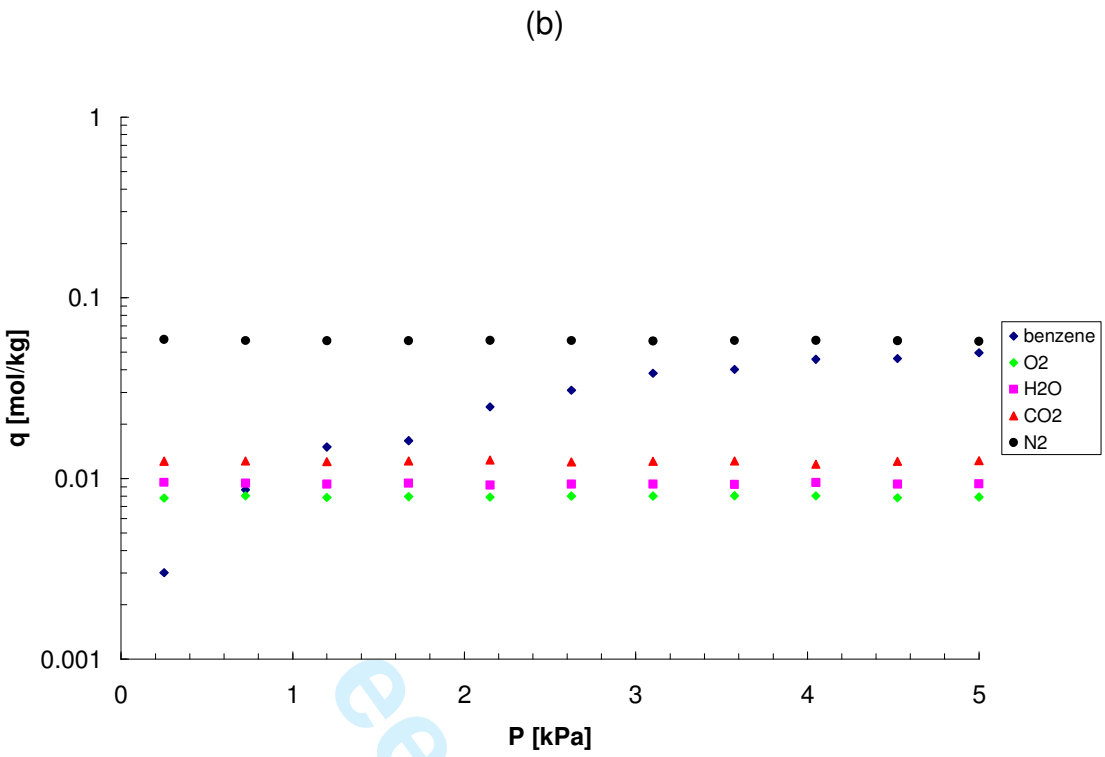


Figure 6. Adsorption isotherms for all components in cs1000a at a total pressure of 202.6 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO_2, pink: H_2O, green: O_2, black: N_2.

(a)





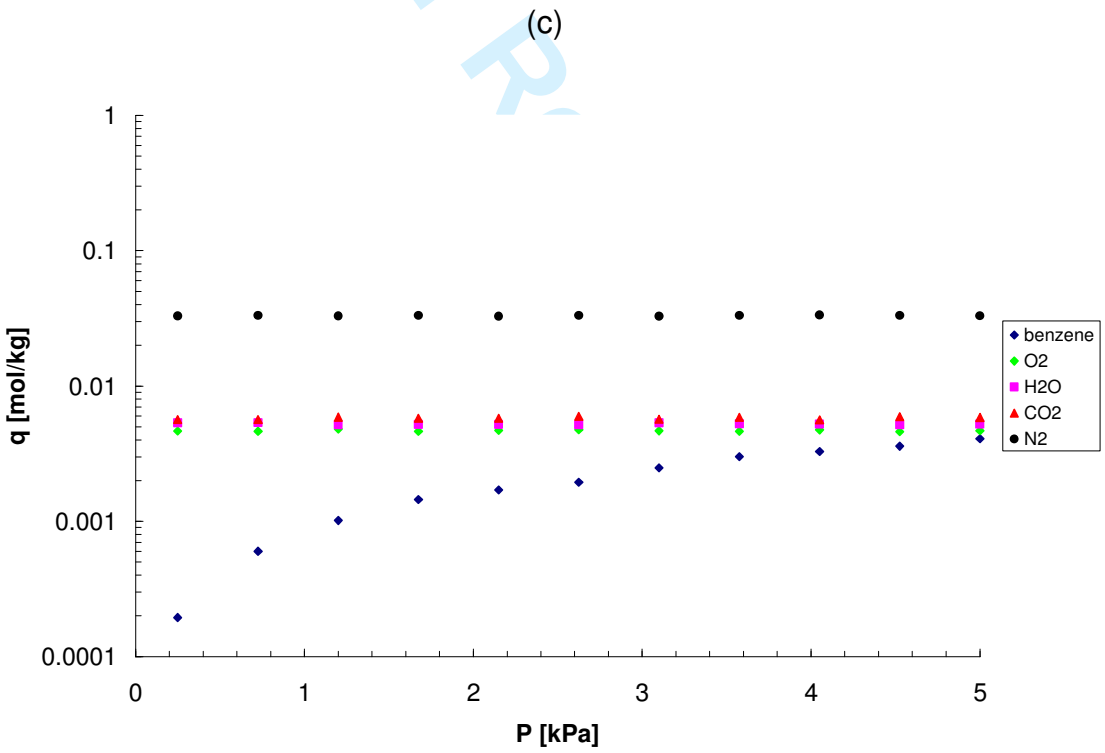


Figure 7. Adsorption isotherms for all components in cs1000a at a total pressure of 506.5 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO_2, pink: H_2O, green: O_2, black: N_2.

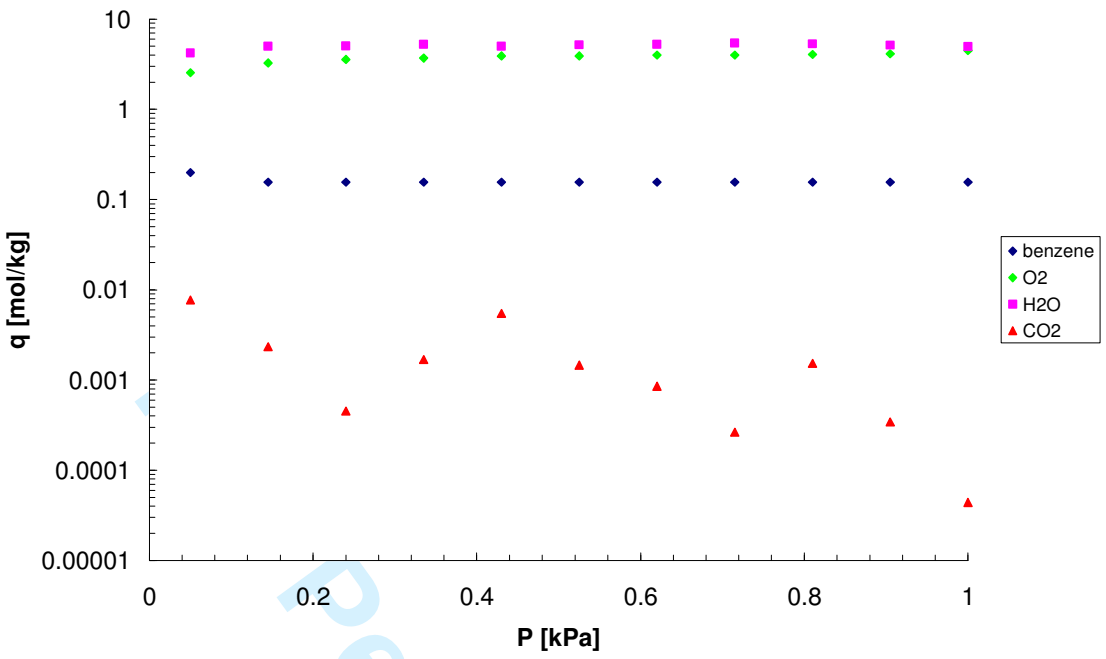


Figure 8. Adsorption isotherms for all components in NaY at a total pressure of 101.3 kPa and 500 K. Blue: benzene, red: CO_2, pink: H_2O, green: O_2.

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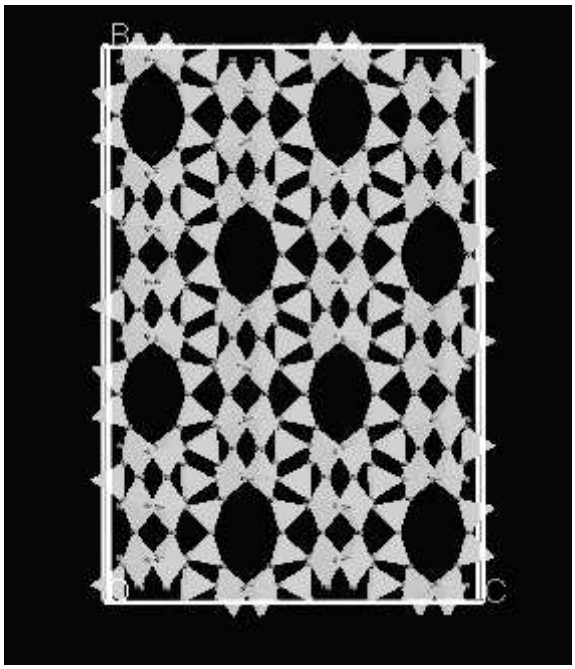

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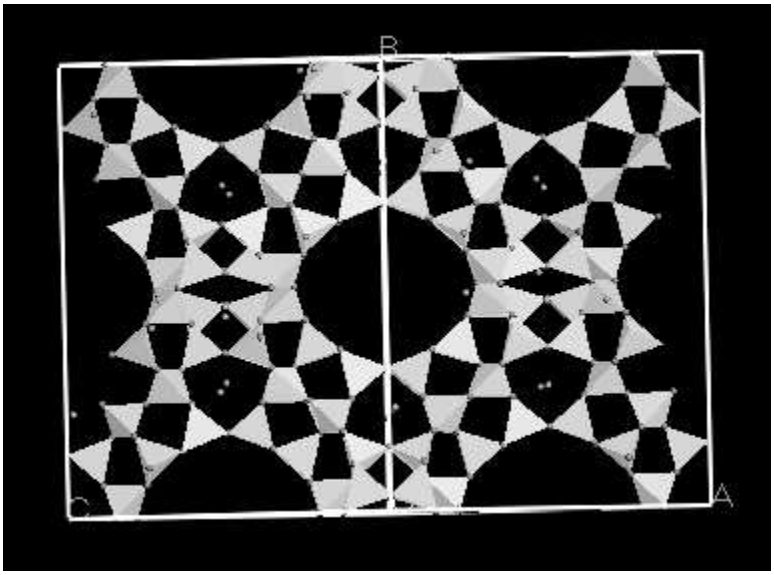

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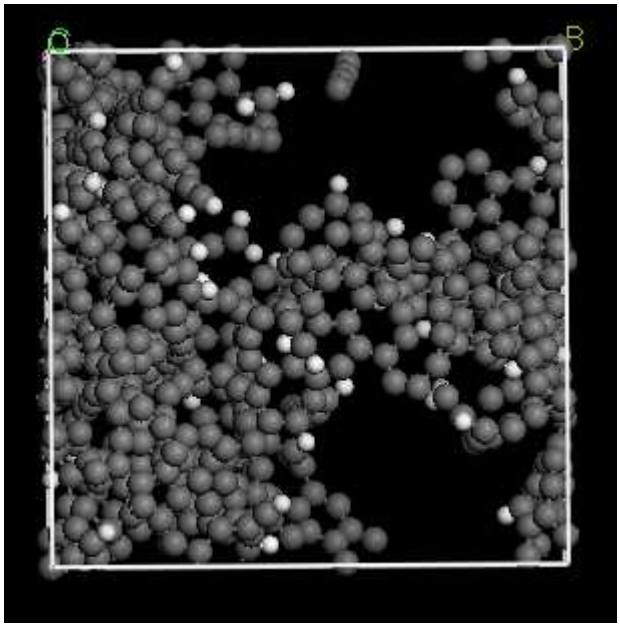

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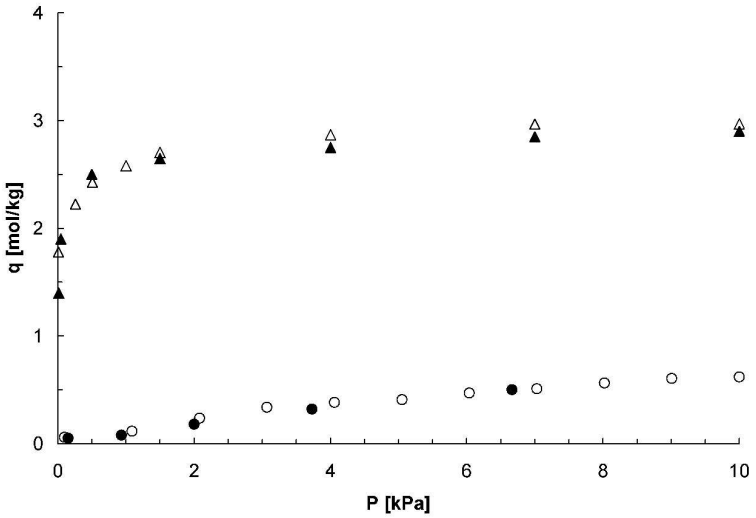

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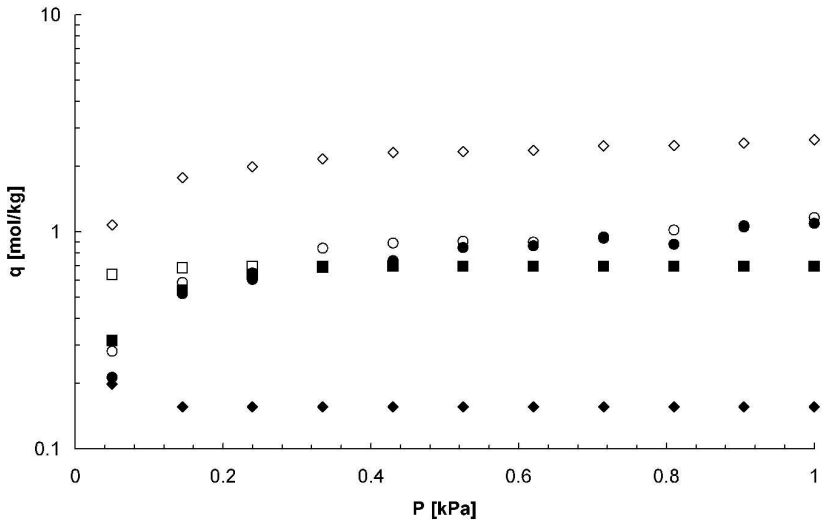

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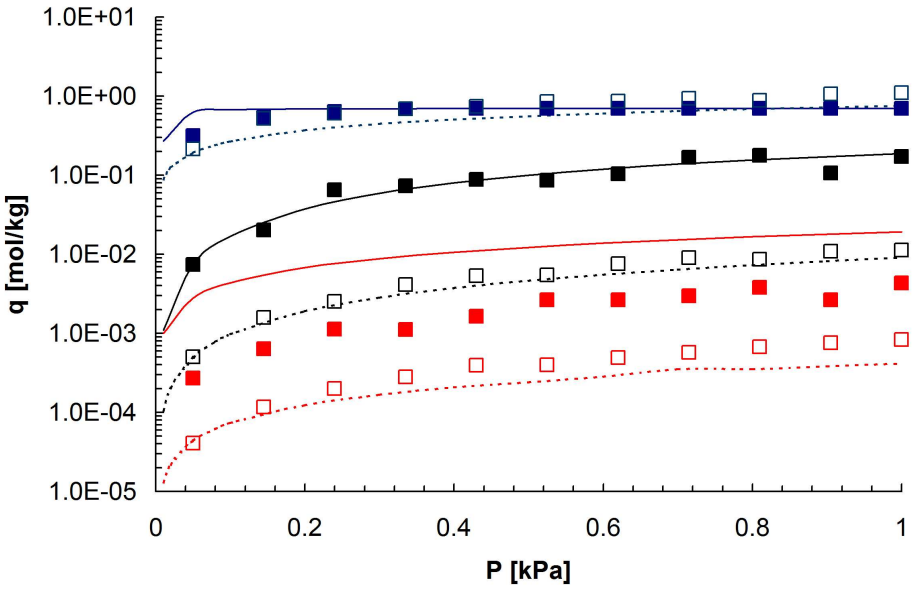

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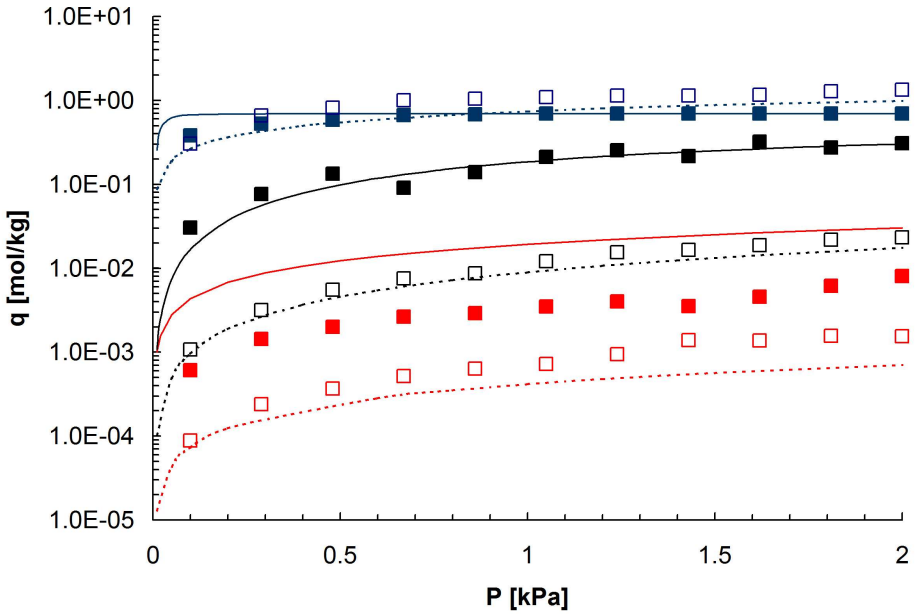

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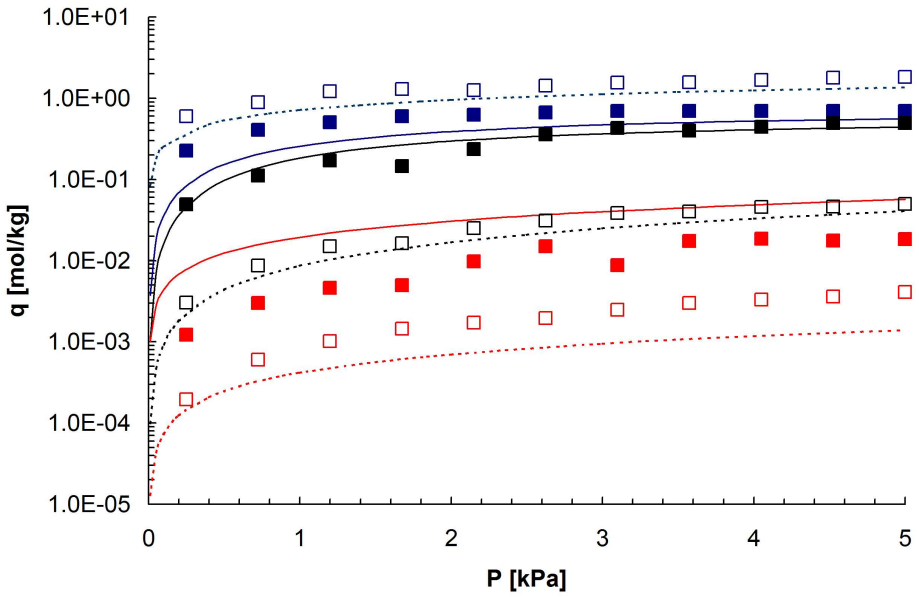

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GCMC Simulations in Zeolite MFI and Activated Carbon for Benzene Removal from Exhaust Gaseous Streams

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GCMC Simulations in Zeolite MFI and Activated Carbon for Benzene Removal from Exhaust Gaseous Streams

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ABSTRACT

A set of GCMC molecular simulations has been performed over zeolite MFI and disordered, activated carbon structures, to determine adsorption isotherms and thermodynamic characteristics of a gaseous mixture adsorbed into porous structures, activated carbon, all-silica MFI and hydrophilic FAU-NaY zeolites. Simulations have been carried out over a multicomponent mixture, in order to mimic a more realistic gaseous emission, when benzene has to be removed. Validation of the model has been obtained by comparison with available experimental data. Different conditions, as temperature and total pressure of the stream have been taken into account. Results give a ranking for the most appropriate process conditions, and for the best materials to be employed for the separation process. Data fitting with the Sips thermodynamic model has also been provided for benzene isotherms. Our procedure is simple and may be adapted to different temperature and pressure conditions, adsorbate or adsorbent characteristics, and gas composition.

KEYWORDS

GCMC simulation, benzene removal, adsorption, zeolite, activated carbon.

INTRODUCTION

Volatile organic compounds (VOC) removal is a necessary operation to respect imposed standard limits in exhaust gaseous streams [1, 2]. It is well known how the presence of even small amounts of these components can be detrimental to environment and human health. VOC are chemical compounds

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with a high vapour pressure to vaporise at normal conditions, and usually have a low water solubility. A large amount of carbon-based compounds, such light hydrocarbons, aldehydes, ketons, are considered as VOC.

VOC can originate from different sources, such as petrochemical processes, vehicle emissions, combustions and, in general, from all kinds of industrial processes [3]. Among all the others VOC, one of the most hazardous ones is the benzene, as its effects, even at typical very low concentrations in emissions, are nowadays well documented [4, 5]. One possible way of VOC removal is the selective adsorption into porous media [6].

In this work we aim at examining possible ways of benzene removal from gaseous streams by adsorption into zeolites or activated carbons, taking into account different operation conditions, such as temperature and pressure, which may be encountered in gaseous streams exiting from a plant. This has been done with the aid of molecular simulation techniques, in particular the well known Grand Canonical Monte Carlo method [7].

Two kinds of zeolites, hydrophobic, dealumined MFI and hydrophilic FAU NaY (Si/Al= 2.5) [8] have been tested in our work, and then dealumined MFI was used. We also tested and used one disordered structure, called cs1000a, which reproduces an activated carbon fibre, obtained from the pyrolysis of pure saccharose at 1000 ℃ for 20 hours in a CO_2 atmosphere. This was one of the disordered structures obtained by the group of Keith Gubbins using the Hybrid Reverse Monte Carlo method (HRMC), and is now freely available in literature [9, 10]. In Figure 1 the 3D structures used in this work are shown: zeolites MFI and NaY, and disordered, activated carbon cs1000a. Both activated carbon and zeolites have been commonly

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investigated, and frequently employed, in processes of purification technologies, in particular for VOC and benzene separation [11 – 22].

The aim of the work is mainly to establish a flexible and simple procedure to estimate the efficacy of different adsorbents in different conditions, to give more insights to the adsorption process at molecular level, and to understand how the presence of a gaseous mixture, which is usually encountered in these kinds of processes, will affect the predicted adsorption isotherms. In fact adsorption experiments have been performed in different conditions and for a huge kind of matrices and adsorbates, as there is a considerable interest in adsorption processes and technologies, as testified by a huge literature [23]. Nevertheless, in the case complex multicomponent mixtures, especially when the component to be separated is very dilute, data are absent or still very scarce [24], due to the difficulties of experimental procedures. Experimental sessions are often tedious and rather expensive; moreover, difficulties for multi-component adsorption experiments and very low partial pressure of some components increase. Although, it is known how competition for pore sites in multi-component adsorption may substantially affect the adsorption mechanism [25].

In our example, we decided to mimic in a simplified way a composition which can be an example of a stream from waste incinerator processes, or from combustions due to industrial processes, or from residual streams of chemical plants. In this way the choice of benzene as pollutant and the specific gaseous composition, are merely exemplificative, and should be intended as a specific case study to explore the effectiveness of the

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procedure, which may be also adapted to different conditions or changed in the case of a different pollutant removal.

This work is organized as follows: in the materials and methods section we define Hardware and Software characteristics, we briefly describe the GCMC method and then we give computational details of our simulations. In the Results and discussion section, we provide a validation of our procedure against available data; then we compare results of pure benzene adsorption isotherms at 500 K with the ones in the multicomponent gaseous mixture, and, finally, we analyze and discuss the results for multicomponent mixtures at different total pressures and temperatures, comparing the obtained results with a simple thermodynamic model for gaseous mixtures.

COMPUTATIONAL DETAILS

Calculations were carried out on an Intel quad-core bi-processor Xeon x5355 with a 6GB RAM.

The Sorption module of *Materials Studio®* (v. 4.2, Accelrys, San Diego, CA, USA) has been employed in this work [26]. It is a Monte Carlo method which is particularly suitable for adsorption phenomena estimation over defined adsorbents.

A mixture of O_2, N_2, H_2O, CO_2 and benzene has been used to approximate and mimic an exhaust gaseous stream from a combustion process. Due to the relatively low pressures considered for all simulations, and accordingly to the aim of our work, we decided to approximate fugacity with partial pressure.

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The frameworks of the chosen zeolites, MFI and FAU (NaY, Si/Al= 2.5), are available in the database of the platform; the Na^+ ions added to balance the total charge have been placed into the NaY cell with a cation locator option, provided in the Sorption module. This allows performing a Metropolis Monte Carlo location of the ions in the cell, according to the lowest energy configuration; acceptance criteria are similar to the ones used for Canonical Monte Carlo simulations [7] but in this case a specified number of annealing cycles (called simulated annealing) is used to slowly freeze the system, in order to repetitively explore the configurational space determined by the adsorbate (sorbent) and adsorbate (Na^+) system, and to avoid local minima [27, 28].

The atom positions of the disordered structure cs1000a, have been obtained with the HRMC method [9, 10]. This method uses an algorithm which attempts to simultaneously minimize the error in the radial distribution function and also the total energy of the system, thus matching the experimental data obtained for the real structure, such as structure factor, porosity and density. Further, a simulated annealing minimization method is also employed to avoid the system to be trapped in local minima.

The core of this work is the GCMC application with the stochastic Metropolis method [29] for multicomponent gas adsorption. The method is well known and described in several books, as in [7]; references to some specific applications both to pure gases and to mixtures can be found elsewhere, thus in this paper we provide a short description.

Generally speaking, the stochastic Monte Carlo (MC) method, which uses statistical mechanical principles to calculate properties of a given

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system, has been employed to perform the simulations. In brief, MC simulations generate configurations of a system by making random changes to the positions of the present species, together with their orientation and conformations, where appropriate [30]. The Metropolis sampling method generates chains of configurations with the ensemble probability. Transforming a configuration involves a random displacement of each atom in the system from its actual position. A trial move is accepted if it lowers the configuration energy of the system. If the configuration energy is increased, trials are accepted with a probability proportional to a Boltzmann factor: $P = e^{-\Delta U/kT}$, where ΔU is the configuration energy difference. Sampling techniques [31] are used to generate states of low energy, and enabling accurate property calculations. In this work, the simulations were carried out using the Grand Canonical Monte Carlo ensemble (GCMC), which creates, destroys, translates, and rotates molecules in order to obtain thermodynamic equilibrium in an open system. Accordingly, in a GCMC calculation the system chemical potential μ, volume V, and temperature T are kept constant, as if the framework is in open contact with an infinite adsorbate reservoir at a given temperature. The reservoir is completely described by temperature and fugacity (or partial pressure) of all components, and does not have to be simulated explicitly. Chemical potential μ is transformed into the partial pressure (or fugacity) of each component. Equilibrium is achieved when the temperature and the chemical potential of the gas inside the framework are equal to the temperature and chemical potential of the free gas outside the framework. The adsorption isotherms were computed by calculating the mean loading of the adsorbate in the framework at a specific vapour pressure.

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The probability of a configuration, m, in the grand canonical ensemble is given by:

$$\rho_m = C \cdot F(\{N_m\}) e^{-\beta E_m} \tag{1}$$

Where

$$\beta = \frac{1}{k_B T} \tag{2}$$

C is an arbitrary normalization constant; E_m is the total energy of configuration m:

$$E_m = E_m^{SS} + E_m^{SF} + U_m^{S} \tag{3}$$

where E_m^{SS} is the intermolecular energy between the adsorbate molecules, E_m^{SF} is the interaction energy between the adsorbate molecules and the framework, and U_m^{S} is the total intramolecular energy of the adsorbate molecules (which is equal to 0 if only translational and rotational degrees of freedom are present). The set of adsorbate loadings of all components in configuration m is denoted by $\{N\}_m$. For a single component, the function *F(N)* is given by:

$$F = \left[\frac{(\beta f V)^N}{N!} \right] e^{-\beta N \mu_{\text{int}}} \tag{4}$$

where *f* is the fugacity (equal to the partial pressure for ideal gases), μ_{int} is the intramolecular chemical potential, and *N* is the loading of the component. For

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a mixture of components, $F(\{N\}_m$ factorizes to a product of functions (1) for each component. The intramolecular chemical potential in (4) follows from

$$\exp[-\beta\mu_{\text{int}}] = <\exp[-\beta\mu_{\text{int}}]>_u \tag{5}$$

The average is taken over a uniform ensemble, which means that every configuration has the same probability. If the adsorbate has one conformation with no degrees of freedom other than translation and orientation, the intramolecular chemical potential reduces to the intramolecular energy.

The thermodynamics of adsorption have been further investigated analyzing the values of the isosteric heat of adsorption h_{RF}, a measure of adsorption capabilities of an adsorbate in an adsorbent framework. h_{RF} is defined as the difference between the partial molar enthalpy of the adsorbate component in the external reservoir (i.e., free gas) and in the framework; accordingly, it is a measure of the enthalpy change involved in the transfer of a solute from the reference state to the adsorbed state at a constant solid phase concentration [32]:

$$h_{RF} = h_R - h_F \tag{6}$$

Evaluation of h_{RF} requires the application of Clausius-Clapeyron equation [31]:

$$h_{RF} = (v_S - v_F)\left[\frac{dp}{d(\ln T)}\right] \cong RT\left[\frac{d(\ln p)}{d(\ln T)}\right] \tag{7}$$

where v_R and v_F are the adsorbate partial molar volumes in the reservoir and in the framework, respectively, p the partial pressure, and T the temperature. In the right-hand side term of equation (7), the partial molar volume of the gas molecules in the framework is neglected with respect to that in the reservoir,

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and the gas behavior in the reservoir is assumed to be ideal. This leads to the expression of h_{RF} in the Grand Canonical ensemble, where the free energy G can be calculated:

$$h_{RF} = RT - G \tag{8}$$

The characteristics of the 3D periodic cells are described in Table 1.

In these simulations we used a slightly modified Augmented Consisted-Valence Force Field (cvff_aug) [33, 34], which is particularly suitable for small molecules adsorption calculations in solid or crystal frameworks. Modifications have been made to take into account the quadrupole moments of some molecules in a more accurate way. Thus, we used the Watanabe-Austin models [35] for N_2, O_2, CO_2, which introduce the presence of dummy atoms to simulate charge displacements. We used the standard TIP3P model for water [36]; the benzene molecule was constructed and then minimized with the cvff_aug Force Field. Finally, in the activated carbon structure, hydrogen parameters have been set to the ones describing hydrogen bonded to sp^3 carbons. Finally, we report the partial charges for adsorbates and frameworks: oxygen: -0.112 (O), 0.224 (dummy atom in the centre); nitrogen: -0.509 (N), 1.018 (dummy atom in the centre); carbon dioxide: 1.04 (C), -0.462 (O), 0.112 (external dummy atoms of Watanabe-Austin model); benzene: 0.1 (H), -0.100 (C), water: 0.417 (H), -0.834 (O); MFI: 2.400 (Si), -1.200 (O); NaY: 2.400 (Si), 1.400 (Al), -1.200 (O), 1.000 (Na^+); Cs1000a: 0.100 (C linked to an H atom), 0.000 (C not linked to H atoms), -0.100 (H).

The representative mixture (N_2 70%, CO_2 10%, H_2O 10% and O_2 11%) contained also a variable amount of benzene (0.05 – 1%). We performed simulations at 500, 750 and 1000 K, and at a total pressure of 101.3, 202.6

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and 506.5 kPa (1, 2 and 5 atm, respectively), with the same mixture composition. In this way we aim to establish the most convenient conditions for benzene removal in terms of adsorption isotherms for the considered structures.

For all simulations, we performed 5000000 of Monte Carlo steps, preceded by 1000000 of equilibration steps. Electrostatic interactions have been taken into account with the Ewald and group summation method [7] with a Ewald accuracy of 0.001 kcal/mol and a cut off distance of 12.5 Å, which is half of the smaller considered cell width. Van der Waals interactions have been described with an atom based summation method, with a cubic spline truncation, splined for 1 Å; the cut off is 12.5 Å.

Finally, we used the common thermodynamic model developed by Sips [37] to reproduce simulated data for mixtures. This is an extension of the Langmuir-Freundlich model to mixtures; the equation for the component i is written as:

$$q_i = q_{0,i} \cdot \frac{b_i \cdot P_i^{\alpha_i}}{1 + \sum_{i=1}^{n} b_i \cdot P_i^{\alpha_i}} \qquad (9)$$

in the case of n components, where $q_{0,i}$ is the saturation value for i, P is the partial pressure of i, α_i and b_i are the coefficients of the Langmuir-Freundlich model [38] which have been obtained from the fitting of simulated adsorption isotherms of pure species (see Additional Information).

We performed a set of simulations to validate our procedure, comparing adsorption isotherms with data available in literature. Then we examined the differences between adsorption isotherms of pure benzene and adsorption isotherms of benzene in the multicomponent mixture, i.e. the

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gaseous emission (N_2 70%, CO_2 10%, H_2O 10% and O_2 11% as partial pressures) to find a reasonable ranking of the most suitable adsorbent and the most convenient thermodynamic conditions.

RESULTS AND DISCUSSION

For validation, we tried to compare adsorption isotherms with data available in literature.

Figure 2 shows the comparison between our data for pure adsorption over MFI zeolite (a) and NaY zeolite (b) and, respectively, the adsorption isotherms of [19] and [39]. As expected, the agreement is fair for all the considered pressure range, bearing in mind the possible presence of impurities in the real zeolite MFI, and the slightly different Si/Al ratio (2.43 in the case of this publication). Analogously, for comparison we report the average isosteric heat of adsorption for pure benzene in MFI, 16.6 (kcal/mol), which is close to the values reported for pure benzene adsorption by Snurr et.al [40], bearing in mind some zeolite structural differences, and the temperature discrepancy (in this case, 328 K). In that case, isosteric heats are plotted as a function of loading and range between 13 and 17 kcal/mol. Finally, for NaY, we find an average isosteric heat value of 18.3 kcal/mol. This is also close to the ones reported by Takahashi and Yang [41], between 16.4 and 18 kcal/mol at the same temperature, and the one proposed by Auerbach et.al. [42] (18.8 kcal/mol at 445 K).

Analogous data for activated carbons, although present in several works, are difficult to compare to our specific structure, due to the huge

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differences which appear in disordered structures with different framework and porosity.

Figure 3 shows a comparison between pure benzene adsorption isotherms and benzene adsorption isotherms in the gaseous mixture (N_2 70%, CO_2 10%, H_2O 10% and O_2 11%) at 500 K and at a total pressure of 101.3 kPa (1 atm). Benzene loading is expressed as a function of the benzene pressure.

Results show several differences, which are due to the adsorption site competition inside the pores. These differences are very pronounced at low benzene pressures and for the hydrophilic zeolite NaY, where the most polar groups and the Na^+ ions favour the adsorption of water and oxygen. Accordingly, benzene adsorption in NaY is very low. As expected, MFI and cs1000a are indicated for the non-polar VOC (in particular, benzene) removal, while NaY zeolite is not.

Thus, we proceeded by examining the isotherms for mixtures (N_2 70%, CO_2 10%, H_2O 10% and O_2 11%) in cs1000a and MFI. Figure 4 show the adsorption isotherms at 500, 750 and 1000 K for MFI and cs1000a, at a total pressure of the system of 101.3, 202.6 and 506.5 kPa (1, 2 and 5 atm, respectively), together with the fitting curves with the Sips model; benzene loading is expressed as a function of the benzene partial pressure. Additional information provides also the adsoption isotherms of all the other components for all structures.

In Table 2 we also show the isosteric heats of adsorption for all effectively adsorbed molecules. Values are averaged over all simulated point,

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standard deviations are in brackets. Empty cells mean no adsorption for the whole pressure range.

Examining isotherms and isosteric heats, it is clear how benzene is favoured over all other components, confirming these structures as suitable for benzene removal. The high benzene loading, even at low partial pressures, corresponds to the other hand to a very low coverage of the other gases (see Additional Information). Nevertheless, higher temperatures influence negatively the adsorption for both structures in a quite dramatic way, as differences are up to 3 orders of magnitude. Isosteric heats are quite constant for all isotherms points; they are slightly temperature dependent, especially for benzene adsorbed in the cs1000a structure.

Higher values for benzene isosteric heats are reached for mixtures. This can be explained invoking the favourable adsorbate-adsorbate interactions that take place in a more confined space. This is particularly evident if we consider the narrow, zig-zag pores of MFI. In the single-component simulations, benzene rings are regularly disposed in a “flat” configuration which is mainly normal to the axe of straight, bigger pores. In multi component simulations, the presence of new adsorbed molecules (mainly CO_2 and H_2O) forces benzene molecules to adsorb in a “close” and mainly randomly oriented disposition, even in zig-zag pores.

In MFI saturation values at low temperatures are reached before the maximum benzene partial pressure. When total pressure increases, benzene adsorption is slightly decreasing, due to the effect of the higher partial pressure of other components; then, at a total pressure of 506.5 kPa and 1000 K, we can observe how in practice the benzene adsorption is very

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limited, and decreasing for a higher total pressure. A similar behaviour can be noticed for cs1000a; in this case saturation values, which are also higher, increase with the total pressure of the system. Generally speaking, both for MFI and cs1000a, adsorption is slightly influenced by total pressure. Although the choice of MFI will be favoured for higher temperatures, and lower total pressures, the most indicate and common situation, (moderate pressure and temperature, 101.3 kPa at 500 K) at the outlet of the stream, seems to suggest the use of the considered activated carbon model, with the exception of a very low benzene fraction. Finally, the considered Sips model show a rather acceptable behaviour, as it is able to reproduce qualitatively (and, with the exception of 1000 K, also quantitatively) the trends for both structures. The use of more sophisticated thermodynamic models to take into account non-idealities or framework heterogeneity for such a complex mixture was out of the scope of our work.

CONCLUSIONS

We used the GCMC molecular simulation technique to evaluate adsorptive potentialities of zeolites and activated carbon structures. We validated our procedure against available adsorption data; then we considered a simplified, ideal gaseous mixture to mimic an outlet stream (e.g. exhaust gas from combustion). Results show how hydrophobic zeolite MFI and the prototype of an activated carbon structure, cs1000a, are indicated for benzene removal. The adsorption isotherms dependence on the total pressure is weak, while it can be suggested to operate at relatively low temperatures, due to the strong influence of this parameter. In this case, the choice of the considered

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activated carbon structure will be generally slightly favoured. Further, the Sips thermodynamic model showed to be able to fit calculated data in an acceptable way. The adopted methods and procedures have shown to be simple and suitable for further applications in the environmental-related fields, providing that porous adsorbent structures are known.

SUPPLEMENTARY MATERIAL

Additional information is freely available as supplementary material.

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CAPTION TO FIGURES

Figure 1. From left to right: 3D structures of (a) zeolite MFI, (b) zeolite FAU (NaY), and (c) activated carbon cs1000a.

Figure 2. Comparison of simulated data (open symbols) with literature data (filled symbols) for benzene adsorption in NaY and MFI zeolites; ▲: NaY, 393 K; ●: MFI, 435 K; q is the loading, P the pressure.

Figure 3. Adsorption isotherms for pure benzene (open symbols) and for benzene in the mixture (filled symbols) at 500 K. ◊: NaY; □: MFI; ○: cs1000a; q is the loading, P is the pressure.

Figure 4. Adsorption isotherms for benzene in the multicomponent mixture at a total pressure of 101.3 kPa (a), 102.6 kPa (b) and 506.5 kPa (c). Filled symbols: zeolite MFI; open symbols: activated carbon cs1000a. Blue: 500 K; black: 750K; red: 1000 K. Continue lines: Sips model for MFI; dotted lines: Sips model for cs1000a; q is the loading, P is the pressure.

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