

Adsorption into the MFI zeolite of aromatic molecule of biological relevance. Investigations by Monte Carlo simulations

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Abstract Adsorption of paracresol and water into the silicalite-1 (MFI) zeolite has been investigated using canonical and grand-canonical Monte Carlo simulations. The most stable sites of adsorption of paracresol are found to be located at the channel intersections. Grand-canonical simulations have shown that at low loading, water molecules adsorb preferably at the vicinity of paracresol molecules, whereas they are also located in the sinusoidal channels as the loading increases. In order to explain the experimental adsorption isotherm observed for the coadsorption of water and paracresol in the MFI zeolite we propose a new concept of apparent adsorption enthalpy that varies with the concentration of the solution. The mathematical expression for the apparent enthalpy is introduced in an adsorption isotherm model. We shall refer to this theoretical isotherm as a non-langmuirian isotherm. The non-linear expression for the apparent adsorption enthalpy accounts for a variable accessibility of the sites of adsorption with respect to the concentration of the solution.

Keywords Adsorption in porous materials · Adsorption isotherm · Coadsorption · Molecular simulations · Monte Carlo simulations · Non-langmuirian adsorption isotherm model · Paracresol · Uremic toxins · Zeolites

Introduction

Paracresol ($\text{CH}_3\text{C}_6\text{H}_4\text{OH}$) is a well-known uremic toxin. It is part of the protein-bound class of toxins and as a consequence, it is not efficiently eliminated during a dialysis treatment. In spite of continuous efforts to improve membranes used in the dialysis processes, the problem posed by protein-bound toxins is still far from solved using conventional materials.

Recently we have initiated a study [1, 2], both experimentally and theoretically, on the potential use of zeolites in the process of dialysis as an additional setup that could be able to eliminate protein-bound toxins. It has already been shown that the silicalite-1 zeolite (also known as MFI) is a good candidate for adsorbing large quantity of sorbates [1, 2].

From a theoretical point of view, the adsorption of paracresol into the MFI zeolite is a challenging task. First, because the size of the molecule is similar to the pore size of the zeolite, configurational-biased Monte Carlo algorithms have to be used to obtain significant probabilities of adsorption. Second, paracresol is dissolved into liquid water, and co-adsorption simulations should be undertaken to match as close as possible to the experimental conditions. For these two reasons it has not yet been possible to simulate the coadsorption into MFI, and an alternative strategy has been developed, as described in the next section.

One of the objectives of this work is to understand the interaction of paracresol with its environment (silicalite and water) when confined in the silica structure. In addition, we aim to explain the process of the coadsorption. This paper is divided into two parts that detail the theoretical approach we have used and the results we have obtained.

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Theoretical details

Method and force fields

Silicalite-1 (or MFI) is a pure silica zeolite with unit cell stoichiometry defined by the formula $(\text{SiO}_2)_{48}$. It belongs to the symmetry group Pnma (group number 62) [3]. The MFI zeolite is made of a three-dimensional network of interconnected pores. The pore network is composed of straight channels that are intercepted by sinusoidal ones, as depicted in Fig. 1. The experimental cell parameters [4, 5] are reported in Table 1. A model of ideal structure of MFI zeolite that contains 12 unit cells were built from both the experimental cell parameters of the corresponding primitive lattice and the crystallographic positions of the silicon and oxygen atoms. This model of zeolite was used throughout our simulations and the atom positions were frozen.

The mechanism of adsorption of water and paracresol into MFI is explained on the basis of experimental data obtained from measurements of two different MFI zeolite samples. The first one that we hereafter refer to as MFI was prepared by hydrothermal synthesis at high pressure and was calcined twice to remove hydroxyl species. Hence, this treatment made the zeolite very hydrophobic. The second sample, that we call modified-MFI, was prepared under low pressure and is more hydrophilic than MFI.

Canonical and grand canonical Monte Carlo (MC) simulations were carried out [6]. For paracresol in the zeolite, canonical simulations were performed at 310 K. The simulations were run for at least one million of iterations to equilibrate the system, and an additional one million of MC steps were done to collect the data. For the adsorption isotherm of water in the silicalite (in presence of paracresol) a configurational-biased algorithm was used [7] in order to increase the probability of adsorption of the molecule in the confined environment. Simulations were performed at 310 K. Five to ten millions iterations were

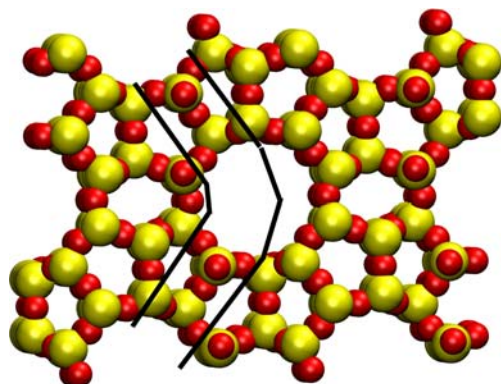


Fig. 1 MFI zeolite depicted in the direction of the straight channels. An example of a sinusoidal channel is delimited by black lines. Yellow: silicon atoms; Red: oxygen atoms

Table 1 MFI structural characteristics (from Ref. [4, 5])

MFI	a (Å)	b (Å)	c (Å)	α	β	γ	Symmetry group number
	20.0220	19.8990	13.3830	90.0°	90.0°	90.0°	Pnma #62

needed to equilibrate the system and an additional five millions of MC steps were performed to collect the data. Simulations of water adsorption were also performed at 310 K.

The ClayFF force field of Cygan *et al.* was used to model the interaction of the zeolite with adsorbed molecules [8]. Only the atomic charges and van der Waals parameters were used. The internal contributions (bonds, angles,...) to the total energy were not accounted for since the zeolite were rigid in the simulations. Concerning the Van der Waals energy, the mixed interaction parameters were calculated using the Lorentz-Berthelot rules. For paracresol and water the Amber force field were used [9]. In this force field the TIP3P parameterization is implemented for water [10].

As already mentioned, the zeolite atom framework was rigid during all the simulations (canonical and grand-canonical ones). It is expected that such approximation is suitable to simulate adsorption in microporous materials such as zeolite and does not significantly affect the results. First, it is well-known that the whole zeolite framework is able to expand up to about 10%. To account for this behaviour a volume change should be allowed during the Monte Carlo simulations (isothermal-isobaric ensemble) but the computational efforts would be prohibitive in regards to the benefit for the simulation results. Second, when adsorbates diffuse into the channels the zeolite framework locally deforms. Although this behaviour can be naturally accounted for in molecular dynamics simulations, again the use of a flexible zeolite, (*i.e.* zeolite atom move) is useless in Monte Carlo simulations. In effect, the probability that paracresol translates towards a region of the zeolite where its atoms are concomitantly relaxing (translation move) is likely to be zero. In conclusion, molecular dynamics is a more appropriate technique to simulate flexible frameworks.

For the NVT simulations of paracresol in the MFI translation, rotation and intramolecular moves were performed. The latter move permits internal relaxations of the molecule within the zeolite channels and therefore allows it to find a favourable conformation for adsorption. The same moves were applied for paracresol in the case of the μ VT simulations of water in the MFI in the presence of aromatic molecules. For water molecules rotation, translation, creation and deletion moves were applied. Since the TIP3P

constraints water molecules to be rigid, intramolecular relaxations are not permitted.

Finally, the Towhee MC code was used to perform the simulations [11], visualization was done with VMD [12] and graphs were drawn with Grace [13].

Justification of the procedure

We know from experiments [2] that four molecules of paracresol per unit cell of silicalite are adsorbed at full loading, and that the molecules are located at the intersections of the straight and sinusoidal channels. This information was used as a starting point for the NVT (canonical) Monte Carlo simulations. In this way, we avoided some difficulties of grand-canonical MC simulation of the adsorption isotherm of the toxin. Such procedure, undertaken on the basis of both available experimental results and simulations allowed us to obtain easily numerical distributions of the energy of adsorption and the orientation of the molecules in the cavities (channel intersections).

As to the adsorption of water, the relatively small size of the molecule allowed us to easily simulate the adsorption isotherm. Therefore, μ VT (grand-canonical) Monte Carlo simulations were performed. Since the location of the water molecules in the channels network is still a question of debate for the system {MFI + paracresol + water}, our simulations are able to provide, for the first time, some informations on the mechanism of coadsorption.

Results

We first present the results of the adsorption of paracresol and water into MFI and then we discuss the elaboration of a new analytical expression for a non-langmuirian isotherm that models the experimental isotherms in order to explain the process of coadsorption.

Paracresol and water adsorption

As have been mentioned before, the canonical simulations were performed to study the interaction of paracresol with the zeolite. In Fig. 2 three paracresol molecules adsorbed into the channels of MFI are depicted. Figure 2(a) shows that although paracresol is able to has some rotational freedom in the channel, the molecule is not able to diffuse easily because of the similar size of both the molecule and the channel. In fact, the canonical simulations showed that it was not possible for paracresol to move neither towards the sinusoidal channels nor along the straight channels. As a consequence the only sites of adsorption are those located at the intersection of the straight and sinusoidal channels, as

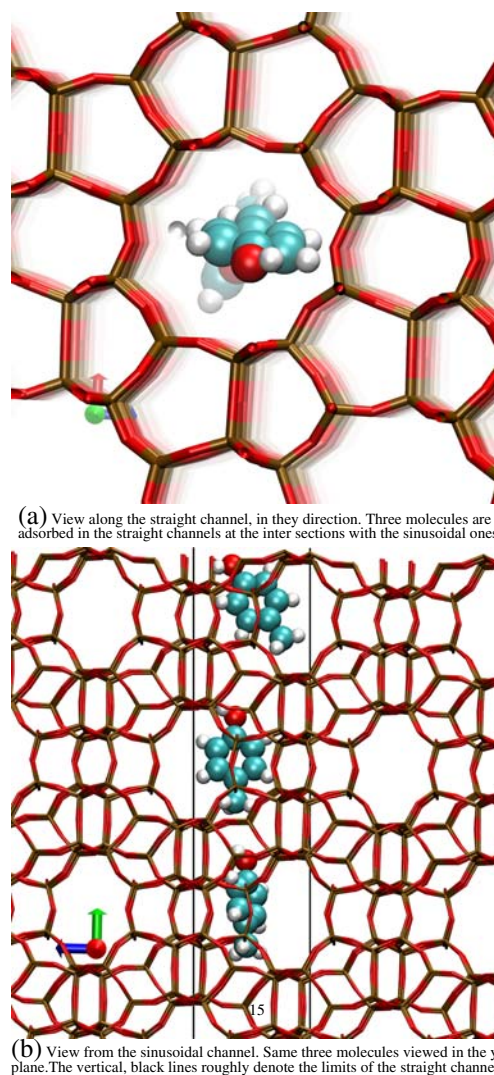


Fig. 2 Paracresol adsorbed within the MFI channel. Configuration obtained from NVT simulations. Red: oxygen; Brown: Silicon; Blue: carbon; white: hydrogen. 2(a) View along the straight channel, in the y direction. Three molecules are adsorbed in the straight channels at the intersections with the sinusoidal ones. 2(b) View from the sinusoidal channel. Same three molecules viewed in the yz plane. The vertical, black lines roughly denote the limits of the straight channel

depicted in Fig. 2(b). This result confirms and explains the experimental observation that only four molecules per unit cell can be adsorbed in full loading.

The behaviour of water is different. The μ VT simulations of water were performed in the presence of paracresol located at their sites of adsorption (see Fig. 3 for one configuration obtained at intermediate loading of water). The simulations show that, at low loading of water the molecules are preferably located at the vicinity of paracresol molecules, therefore making hydrogen bonds (see Fig. 4). As the content in water molecules increases, these molecules can also be located in the sinusoidal channels. Some MC results (on the base of analysis of

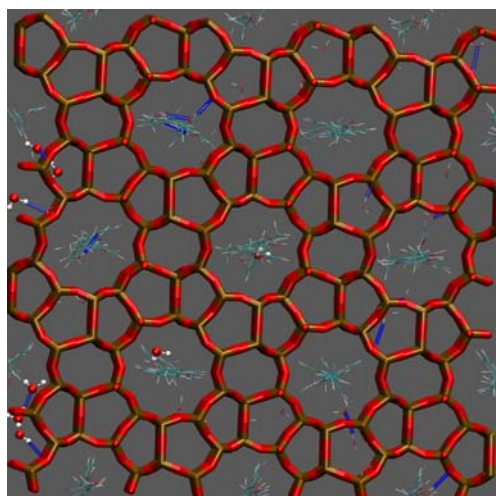


Fig. 3 Adsorption of paracresol and water into the MFI zeolite from μ VT simulations. Configuration taken at intermediate loading of water. Red: oxygen; Brown: Silicon; Blue: car- bon; white: hydrogen; Blue lines: hydrogen bonds

instantaneous configurations) suggest that, before the full loading capacity of the zeolite is reached, clusters of water molecules are formed. These results are obviously in agreement with NMR measurements (not shown here) [14]. As a consequence, as the content of water increases clusters are growing, therefore increasing the network of hydrogen bonds until full loading is reached, which amounts to about 20 molecules per unit cell.

Elaboration of a non-langmuirian adsorption isotherm

Since it has not yet been possible to simulate the coadsorption of paracresol and water by grand-canonical Monte Carlo simulations, we propose an alternative strategy to explain the mechanism of intrusion of the molecules into the MFI. We proceed by finding a new expression of isotherms which is able to reproduce the experimental one. The experimental isotherms are depicted on Fig. 5 for the two samples of zeolites described above. It can be observed that the general shape of the isotherms is typical for adsorbates that are not interacting with each other when they are adsorbed in the zeolites. Considering that there is one paracresol molecule adsorbed at each channel intersection and that these intersections are separated by a distance of at least ten Angstroms the assumption of non-interacting adsorbates is obviously justified. In this case the Langmuir model, which is presented below (see Eq. 2), can be applied to this system and the linear version of this model is plotted at the bottom of Fig. 5 for both zeolite samples.

It can be seen that at high equilibrium concentrations (or high coverage) the system behaves in agreement with the Langmuir model. However, at low concentrations a clear

deviation from the Langmuir model is observed. The question we address now is whether we can model the whole experimental isotherm in a way that may help us to explain the mechanism of coadsorption. At this stage we should stress and recall that, the model we propose concerns the coadsorption of two species from a liquid phase into the zeolite.

The experimental isotherm of paracresol in the MFI zeolite can be interpreted in the range of low concentrations as follows: the isotherm exhibits a convex shape at the origin which is usually attributed to weak interactions between the adsorbant and the adsorbate. As the concentration increases the apparent affinity between the adsorbant and the adsorbate increases. As a consequence, the system seems to behave in a way that the adsorption energy of the sorbate (paracresol in our case) evolves (in fact, increases) with the concentration. We propose to model this behaviour with the following simple, mathematical expression:

$$E_a = \langle E_a \rangle (1 - \lambda e^{-\alpha C}) \quad (1)$$

where E_a is the apparent adsorption enthalpy, $\langle E_a \rangle$ is the “true” adsorption enthalpy, C is the concentration at equilibrium, and α and λ are positive constants to be determined. The “true” adsorption enthalpy can either be an experimental value obtained from calorimetric measurements, or a theoretical value obtained from, e.g. Monte Carlo simulations. In this work, we have chosen to use the experimental data obtained in our laboratory from calorimetric experiments. The measured adsorption enthalpy of paracresol is $11.23 \text{ kJ mol}^{-1}$ and $22.10 \text{ kJ mol}^{-1}$ for the MFI and modified MFI zeolites, respectively.

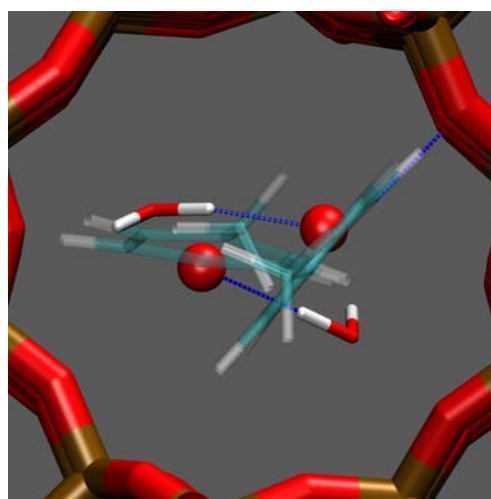


Fig. 4 Details of interactions for the coadsorption of paracresol and water into the MFI zeolite. Red: oxygen; Brown: Silicon; Blue: carbon; white: hydrogen; Blue lines: hydrogen bonds

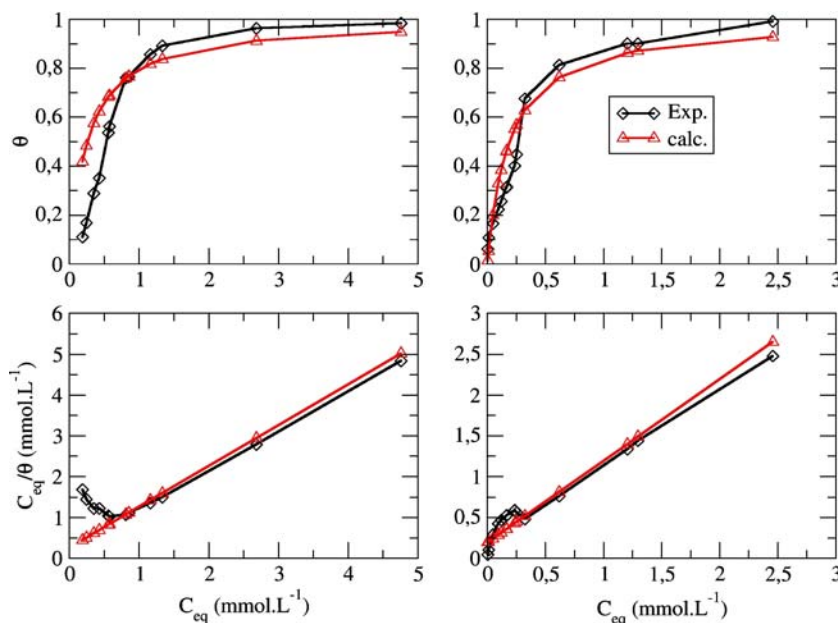


Fig. 5 Experimental and calculated isotherms of the coadsorption of paracresol and water into the MFI (left column) and modified MFI zeolite (right column). For the difference between both samples, see text. The top curves correspond to the plot of the coverage with respect to (w.r.t.) the concentration in paracresol in the solution at

equilibrium. The bottom curves correspond to the plot of the ratio of the equilibrium concentration with the coverage w.r.t. the equilibrium concentration. When systems behave like langmuirian ones, the bottom curves are straight lines as shown by the calculated isotherms (in red)

Be it necessary, let us now recall the expression of the Langmuir isotherm:

$$\theta = \frac{KC}{1 + KC} \tag{2}$$

where θ is the coverage, K is the thermodynamic equilibrium constants and C is the concentration of the solution at equilibrium. From statistical thermodynamics, this expression can be recast as follows:

$$\theta = \frac{z\Lambda^3 e^{-(\beta \langle E_a \rangle)} C}{1 + z\Lambda^3 e^{-(\beta \langle E_a \rangle)} C} \tag{3}$$

where z is the partition function of molecules in energy well of the adsorption site, Λ is de Broglie’s length, $\langle E_a \rangle$ is the experimental adsorption enthalpy (the same as the one in eq. 1) and $\beta = \frac{1}{kT}$, with k the Boltzmann constant and T the temperature. The product $ze^{-\beta \langle E_a \rangle}$ is the Boltzmann factor for the Gibbs free energy: $e^{-\beta \Delta G}$. The linearized form of Eq. 3 reads:

$$\frac{C}{\theta} = \frac{1}{z\Lambda^3 e^{-(\beta \langle E_a \rangle)}} + C \tag{4}$$

As a consequence, from a fit of the linear version of the experimental isotherm, one can obtain the Gibbs free energy ΔG from the value of the intercept. Note that only experimental data pertaining to high concentrations should be retained for this fit. From the knowledge of ΔG and $\langle E_a \rangle$ one can calculate ΔS and z (see Table 2).

As mentioned above, at high equilibrium concentrations the experimental isotherm follows the Langmuir model. Therefore, our model has to account for this observation. Hence, we propose to approximate the whole isotherm using a linear combination of the Langmuir isotherm θ_L and a non-linear one θ_{NL} , the latter one containing our new expression for E_a (Eq. 1) instead of the “true” adsorption energy $\langle E_a \rangle$:

$$\theta = W\theta_L + (1 - W)\theta_{NL} \tag{5}$$

where W is a weight to be determined ($0 \leq W \leq 1$). Note that this expression for θ cannot be linearized, and we shall call this new isotherm a non-langmuirian isotherm. The results of the fits for α , λ and W are given in Table 3 and the calculated isotherms are depicted in Fig. 6. It can be seen that the model we derived for the isotherms reproduces particularly well the experimental ones. Our assumption that the adsorption enthalpy is apparently changing with the concentration is then reinforced. For the MFI zeolite only

Table 2 Thermodynamics data obtained from both the fit of the experimental isotherm and statistical thermodynamics

Zeolite	$\langle E_a \rangle$ (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔS (J mol ⁻¹)	z
MFI	11.23	58.54	152.7	9.55 10 ⁷
modified MFI	22.10	59.31	120.2	1.92 10 ⁶

Table 3 Parameters obtained for the fit of the experimental isotherms by combining eqs. 1 and 5

Zeolite	α	λ	W
MFI	3.59225	1.08378	0.082
Modified MFI	18.64340	21.44816	0.69

8.2% of the Langmuir model accounts for the experimental isotherm whereas in the case of the more hydrophilic zeolite, about 69% of the Langmuir model accounts for the isotherm.

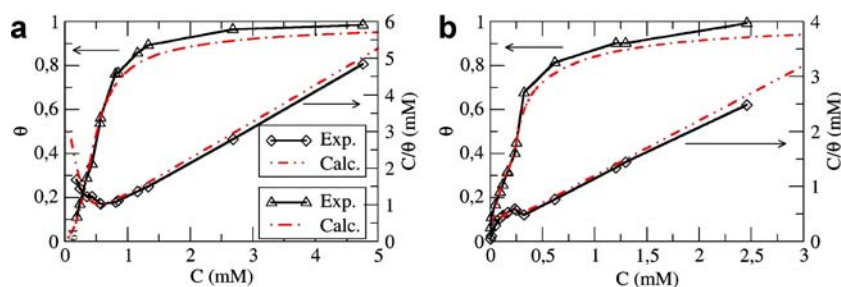
The fitting parameter W deserves a special comment. It is obvious from our model of isotherm that W is related to the affinity between the adsorbent and the adsorbate. In the case of the coadsorption of paracresol and water in silicalite-1, for instance at low concentration of paracresol the prominent interactions are those occurring between the solvent and the zeolite. For the very hydrophobic MFI zeolite, water and MFI tends to repel each other and W is small, whereas for the modified MFI zeolite, water and MFI are both hydrophilic and W is large. One can therefore state that a large coefficient for the non-langmuirian part of the isotherm is an indication of a weak affinity between the adsorbent and the adsorbate, and consequently, a large deviation from Langmuir isotherm at low concentration occurs. W is then a “measure” of the hydrophilic/hydrophobic relation between the adsorbant and the adsorbate. However, at this stage of the work it is not possible to give W a quantitative scale of this relation.

Using this model it is now possible to propose a mechanism of coadsorption of paracresol and water in the zeolites. We first deal with the MFI zeolite.

As mentioned above, this zeolite is more hydrophobic than the modified-MFI one. At very low concentration of paracresol (below 0.2 mM), the apparent adsorption enthalpy is very small and as a consequence, only a small fraction of the adsorption sites are available to paracresol. Put in other words we can say that, at this stage of the isotherm, since few paracresol molecules are in the solution, mainly water interacts with the adsorbant, therefore creating a sort of screening of the adsorption sites for

the solute, which prevents it from adsorbing. As a consequence, the form of isotherm is convex at low concentration, that is, the adsorption is weaker than it would be in a purely Langmuir-like situation. It can be clearly seen from the linear form of the isotherm where the low concentration points are above the hypothetical line corresponding to ideal Langmuir mechanism (Fig. 5). As the concentration increases (above 0.5 mM), the screening decreases and paracresol molecules are more amenable to adsorb into the zeolite as they both have hydrophobic properties. Concomitantly, the apparent adsorption enthalpy increases. At full coverage, the apparent adsorption enthalpy equals exactly the experimental adsorption enthalpy and all the sites of adsorption are occupied by paracresol molecules.

In the case of the modified-MFI zeolite, which is more hydrophilic than the MFI, the picture is different. At low concentrations (below 0.1 mM), since water interacts more favourably with the zeolite it does not block the paracresol molecules. One could suggest that coadsorption of water and paracresol proceeds by a mutual aid at the penetration into the channels, but Monte Carlo simulations are not suitable to evidence such a mechanism. By contrast, molecular dynamics simulations are more appropriate as information on intermolecular interactions and their changes with time can be obtain. However, very long simulation time might be needed to obtain these data. Therefore, at low concentrations of paracresol in the solution the sites of adsorption are readily available to paracresol, that is, the initial volume accessible to the molecules is bigger than in the previous, strongly hydrophobic situation. At this stage, the shape of the isotherm is concave because the screening of the adsorption sites for paracresol is small, and the apparent enthalpy of adsorption is close to the experimental one. At intermediate concentrations in paracresol (between 0.1 and 0.25 mM) we can observe a small inflexion of the adsorption isotherm. It could be caused by the hydrophobic nature of the zeolites which is weaker than in the first sample but still exists. In such a case, the mechanism is similar as in the first sample, as discussed above but one can also imagine another interpretation. The inflexion can be interpreted by the

Fig. 6 Experimental and calculated isotherms for (a) the MFI; and (b) the modified MFI zeolite

hydrophobic nature of paracresol in the hydrophilic environment of the zeolite: the molecules experience repulsion against the zeolite and an additional increase in the chemical potential (or equally, in the concentration, *i.e.* above 0.3 mM) is necessary for paracresol to reach the remaining sites of adsorption that are located deeper in the volume of the zeolite. At full coverage, the chemical potential is high enough for paracresol to occupy all the sites of adsorption in the zeolite, and the experimental adsorption enthalpy is recovered.

Conclusion

We have presented the results of Monte Carlo simulations of the coadsorption of paracresol and water into the silicalite-1 zeolite. At low loading both water and paracresol molecules are located at the intersection of the straight and sinusoidal channels. It is shown that paracresol molecules cannot adsorb into the sinusoidal channels, at least at the temperature of 310 K. At higher loading of water these molecules occupy both the straight and the sinusoidal channels. A mechanism of coadsorption is proposed in the light of a non-langmuirian expression for the adsorption isotherm for which, a concept of apparent adsorption enthalpy is introduced. The proposed model takes into account the relative hydrophobic/hydrophilic character of zeolite/adsorbent couple. This characteristic modifies the mechanism of adsorption at low concentration of paracresol molecules. The more the opposite characters of the species, the more non-langmuirian form of the adsorption isotherm is observed. This model is able to reproduce the shape of the experimental isotherm with good accuracy. The concept of apparent adsorption enthalpy is

based on the increase of the adsorption enthalpy with the concentration of solute in the liquid and suggests a screening of the sites of adsorption for paracresol.

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