



Adsorption of paracresol in silicalite-1 and pure silica faujasite. A comparison study using molecular simulation

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ABSTRACT

This paper presents the results on the Grand-Canonical Monte Carlo simulations of the adsorption of the paracresol uremic toxin and water into the silicalite-1 and pure silica faujasite zeolites. The co-adsorption of water and paracresol seems to proceed along a cooperation effect between the toxin and the solvent. A model of adsorption that accounts for the effect of the solvent has been elaborated and verified using experimental isotherms. The model is based on the Langmuir isotherm in which an apparent adsorption enthalpy is used that changes with the concentration of the solute. The new expression for the isotherm reproduces the experimental isotherm with good accuracy and physical interpretation is given to justify the model.

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1. Introduction

Zeolites are microporous crystalline materials with the diameter pores size of the order of the nanometer [1]. A common application of zeolites is for purification purposes [2–4]. Another possible application is the removal of uremic toxins during the hemodialysis process: zeolites would be used for the storage of the toxins instead of conventionally used polymer membranes [5].

The necessity of the zeolite usage in dialysis arises from the inefficient removal of paracresol (1,4-methylphenol) in conventional dialysis method. Contrary to water bound solutes (e.g. urea and creatinine), protein bound solutes (e.g. paracresol) are not efficiently removed in conventional dialysis. The high toxicity of paracresol (hereafter called *p*-cresol) is responsible for the intoxication of patients, ultimately causing heart attack because of its increased serum concentration during renal failure [6–9].

The need to gather detailed insights into the behavior of zeolite with the sorbate molecules on the molecular scale has influenced the usage of molecular simulation studies. The Monte Carlo techniques have been used to complement experimental information on adsorption problems [10–16].

The present work is devoted to the adsorption of *p*-cresol and water in pure silica faujasite and silicalite-1 zeolites. Although pure silica faujasite is unstable; this work has been carried out to better understand properties of both zeolites in view of possible applications in dialysis. The report is categorized as follows. The methodology used in the simulation studies is first emphasized

which includes the molecular models for adsorbates and frameworks. In the further part of the report, we discuss the results on the adsorption of *p*-cresol and water in silicalite-1 and siliceous faujasite, and the development of a new adsorption isotherm that accounts for the effect of the solvent during the adsorption of the toxin.

2. Simulation details

2.1. Zeolite models

Only pure siliceous silicalite-1 and faujasite models of zeolite were used in our simulations. The structure of silicalite-1 has been built according to IZA database [17].

The silicalite-1 zeolite ((SiO₂)₉₆) belongs to orthorhombic, Pnma space group [18] with the lattice parameters $a = 20.02 \text{ \AA}$, $b = 19.98 \text{ \AA}$ and $c = 13.38 \text{ \AA}$. Two straight channels intercept two sinusoidal channels forming a cavity larger in size than the channels. The porous network of faujasite is made up of cuboctahedral sodalite cages which are linked together in a tetrahedral manner by six oxygen atoms forming cavities called supercages. These supercages are interconnected in the same tetrahedral manner by windows. A single unit cell of faujasite consists of 192 SiO₂ units having eight supercages and eight sodalite cages belonging to Fd3m space group with the lattice parameters $a = b = c = 25.03 \text{ \AA}$.

2.2. Simulation techniques

2.2.1. Monte Carlo simulations

All the Monte Carlo (MC) simulations were carried out using the simulation package “Towhee version 5.21-6.0.2” [19]. In this study

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Table 1

Atomic charges used in the simulations to calculate the electrostatic interaction energy.

Molecules	Atom type	Charges in unit of electrons
<i>p</i> -Cresol	Ring carbon	-0.25
	Methyl carbon	-0.30
	Carbon holding methyl group	0.20
	Carbon holding hydroxyl group	0.35
	Ring hydrogen	0.20
	Methyl hydrogen	0.10
Water	Hydrogen	0.40
	Oxygen	-0.80
Faujasite and silicalite-1	Silicon	2.4
	Oxygen	-1.2

we have used Grand-Canonical Monte Carlo (GCMC) method using configurational-biased algorithm at 310 K [20,21].

The Amber force field [22] for the adsorbate molecules (*p*-cresol and water) and the ClayFF [23] one for the zeolites were used in the simulations. The zeolite atoms were kept fixed during simulations, therefore only the Van der Waals and electrostatic energies were accounted for in the calculations of the interaction energies. The TIP3P model was used for the parameterization of water. Intramolecular energetic terms were accounted for in the case of *p*-cresol molecules, the functional forms of which have already been presented elsewhere [24].

Regarding the coulombic energy, the charges for *p*-cresol were obtained using the Density Functional Theory methods [25,26] (PBE functional [27] with the 6-311G** basis set [28]) by fitting the electrostatic potential created by the electron density. The Gaussian03 package was used [29]. The charges are presented in Table 1.

A single unit cell of silicalite-1 and siliceous faujasite with periodic boundary conditions was used for the simulation of the adsorption of *p*-cresol. Adsorption of water molecules in silicalite-1 and faujasite holding *p*-cresol, were studied using 8 unit cells of zeolite. Each simulation was run for 2 million steps for attaining the equilibrium and also for the acquisition of data.

2.2.2. Molecular dynamics simulations

Molecular dynamics simulations for the diffusion of *p*-cresol in silicalite-1 were performed using the Discover module of Accelrys Materials Studio 4.4 simulation package [30].

The CVFF [31] forcefield was used for all the species and both the zeolite and the sorbates are considered to be flexible. The simulations were carried out in the NVT ensemble and the temperature (310 K) was kept constant using the Berendsen thermostat. A time step of 1 fs was adopted. The system was first equilibrated and the simulations were then run for 1 ns to collect data.

3. Simulation results

3.1. *p*-Cresol

Fig. 1a shows the adsorption isotherm of *p*-cresol in silicalite-1. Four *p*-cresol molecules are adsorbed per unit cell exclusively at the channel intersections, in agreement with the experimental observations (0.65 mmol g^{-1}) [5]. Fig. 1b shows that there are 38 *p*-cresol molecules per unit cell of faujasite, mostly located at the supercages. Examination of the structures evidences that, for both zeolites, the adsorption is due to the hydrogen bonding between the sorbate hydroxyl groups and the zeolite oxygen atoms. The

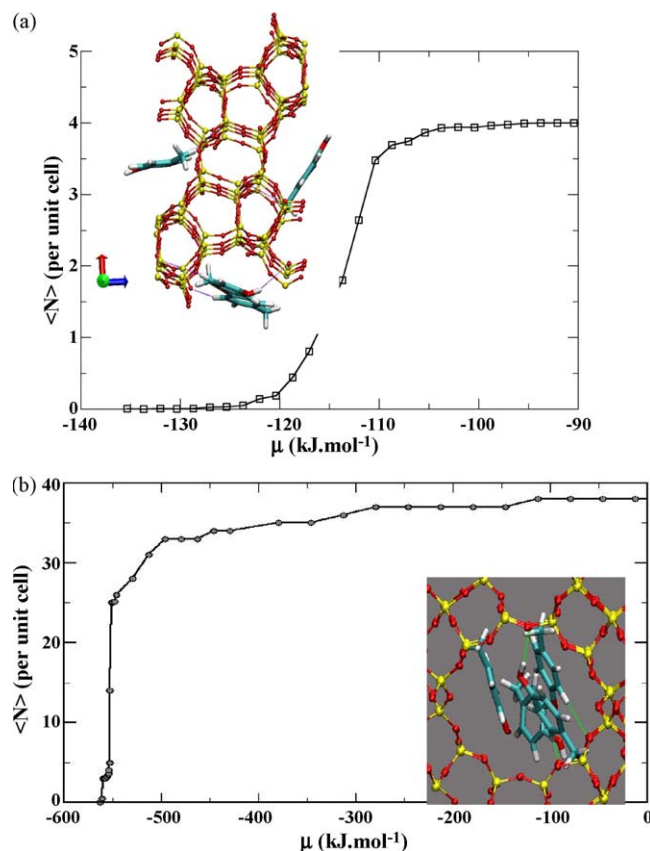


Fig. 1. Simulated adsorption of *p*-cresol in (a) silicalite-1 and (b) faujasite. (N) is the amount of molecules adsorbed per unit cell. Insets: structures of the equilibrium state. Color legend: silicon atoms in yellow; oxygen atoms in red; carbon atoms in cyan; hydrogen atoms in white (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

high amount of adsorption in faujasite can be attributed to the large pore size diameter. In addition, the sorbate molecules possessing high dipole moment exhibit strong interactions among themselves through hydroxyl groups.

A schematic view of the adsorbed molecules in faujasite along the crystallographic (1 0 1) plane is also shown in Fig. 2. It can be seen that the adsorbed molecules form a regular pattern of faujasite framework giving insights into the location of the molecules. It appears that 35 molecules of *p*-cresol are adsorbed at supercages ($\sim 4.37/\text{supercage}$) while the rest are found to be at the windows.

3.2. Co-adsorption phenomena of *p*-cresol and water in silicalite-1 and faujasite

The adsorption isotherms of water follow a similar pattern both in silicalite-1 and faujasite with and without the presence of *p*-cresol as shown in Fig. 3a and b. In the absence of *p*-cresol, the amount of adsorbed water in faujasite is approximately four times higher than in silicalite-1. This is solely attributed to the large pore size diameter of pure silica faujasite in comparison with silicalite-1. From Fig. 3a and b, it is observed that at the chemical potential below -38 kJ mol^{-1} no water is adsorbed for both zeolites. Upon increasing the chemical potential of water, there is some adsorption of water seen in both zeolites and slightly more significant water adsorption is seen when the chemical potential is -24 kJ mol^{-1} . This small increase in water content obviously results from the hydrophobic nature of siliceous faujasite and silicalite-1 framework. However, when the chemical potential is

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