Encapsulating functional organic molecules in porous solids

Adsorption of pharmaceuticals and personal care products in zeolites studied with density functional theory calculations

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In Short

- Electronic structure calculations are used to study the adsorption of pharmaceuticals, personal care products, and other functional organic molecules in the pores of zeolites.
- Calculations on carbamazepine (CBZ) adsorption in all-silica zeolites have shown that the fit of CBZ into the pores is the main factor determining the affinity. The impact of pore topology is much less pronounced for triclosan.
- The adsorption of two UV filters, octinoxate and avobenzone, in faujasite-type zeolites has been investigated. Future work will focus on the spectroscopic properties.
- Other work planned for the second project phase will address the interaction of contaminants with protonated zeolites.

Pharmaceuticals, personal care products (such as disinfectants or UV filters) and other functional organic molecules (such as herbicides and pesticides) are ubiquitously used in our modern society. Their release into the environment, *e.g.*, via municipal or hospital wastewaters, has become a matter of significant concern due to potential adverse effects on the ecosystem and, potentially, also on human health.[1] Since conventional wastewater treatment plants are not designed for the removal of these "emerging organic contaminants", a variety of advanced treatment technologies are under investigation. One possible option is the adsorption-based removal using inorganic adsorbents, such as zeolites.[2] Zeolites are crystalline porous materials that already find widespread use in catalysis, gas separation, and ion exchange.[3] Besides their potential application in contaminant removal, zeolites could also find use as host materials for the encapsulation of pharmaceuticals or personal care products. Recently, it was shown that the organic UV filters octinoxate (OMC) and avobenzone (AVO), widely used in sunscreen lotions, can be adsorbed in some zeolite structures.[4] The encapsulation into zeolites can reduce their reactivity, enhancing the stability and potentially paving the way towards more effective sunscreens. Moreover, the use of these composite materials dubbed "ZEOfilters" could mitigate the release of the organic UV filters into the environment.

Although a number of experimental studies have addressed the adsorption of some functional organic molecules in zeolites, even advanced experimental techniques can only provide limited insights into the structure of the adsorption complexes and the dominant interactions. Rather surprisingly, computational chemistry methods have scarcely been used in this area, despite their widespread application in other fields of zeolite science.[5] In this project, electronic structure calculations in the theoretical framework of dispersion-corrected density functional theory (DFT) are employed to investigate the adsorption of various organic molecules in different zeolites, anticipating that an in-depth understanding of the adsorption processes at the atomic level will be crucial for the further development of new applications, for example in wastewater treatment, drug delivery, or UV filter encapsulation.

A comprehensive DFT study addressed the adsorption of carbamazepine (CBZ), an anticonvulsant drug that shows very recalcitrant behaviour as environmental contaminant, in eleven all-silica zeolites with different framework types (distinct framework types are abbreviated with three-letter codes like IFR, FAU, MOR).[5] While being expensive to produce, all-silica zeolites are interesting model systems to study the selective adsorption of organics from water due to their hydrophobicity. Despite the identical framework composition, large variations in the adsorption energy occurred among the different frameworks, highlighting the important influence of pore topology on the affinity towards CBZ. The strongest interaction was observed for the IFR framework, where CBZ exhibits an exceptionally good fit into the zig-zag channels (Figure 1). Further calculations were used to study the relative importance of guest-guest interactions among co-adsorbed CBZ molecules, as well as the dynamic behaviour of adsorbed CBZ under confinement. An ongoing study looks at the adsorption of triclosan (TCL), a disinfectant. Here, calculations for six all-silica zeolites revealed a much less pronounced impact of the pore topology on the interaction strength in comparison to CBZ. Further work will study the impact of the presence of framework protons or extra-framework cations on the affinity towards TCL. As the hydrophilicity of the adsorbent will inevitably increase when such heterogenities are introduced, the co-adsorption of water will also be investigated using the same DFT approach.

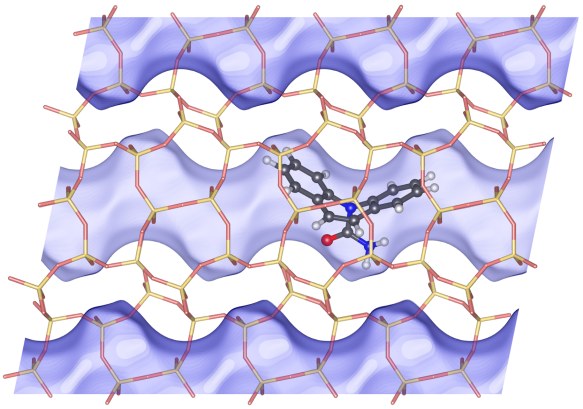

Figure 1: *Low-energy configuration of CBZ adsorbed in the zigzag channels of an IFR-type all-silica zeolite.*

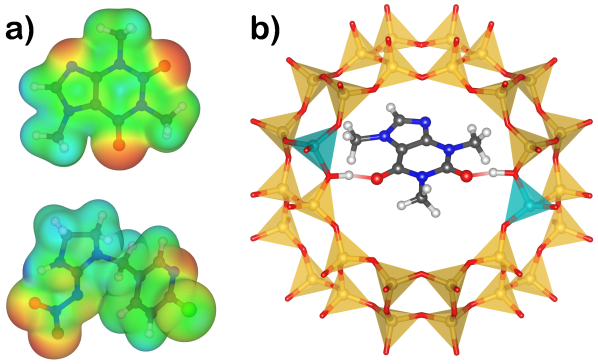

Figure 2: *a) Electrostatic potential of caffeine, a stimulant, and imidacloprid, a pesticide. Negatively polarised areas are shown in red. b) "Multi-site" adsorption complex of caffeine in a FAU-type zeolite.*

Another investigation within the project, conducted in close collaboration with the developers of the "ZEOfilter" composites,[4] deals with the adsorption of OMC and AVO in zeolites with different compositions and topologies. So far, the DFT calculations have focussed on zeolites having the FAU topology. All-silica FAU was compared to zeolite 13X, a FAU-type aluminosilicate (Si/Al ratio = 1) containing Na^+ cations that balance the framework charge. An evaluation of the adsorption energies showed that both OMC and AVO are much more strongly adsorbed in 13X as compared to the all-silica analogue, primarily due to the interaction of negatively polarised areas of the guest molecules with the Na^+ cations. This underlines the beneficial properties of 13X as carrier material for UV filters that had already been observed experimentally. In contrast, the calculations revealed no clear preference for particular isomers (*cis* or *trans* form of OMC, *enol* or *keto* form of AVO). As different isomers of OMC and AVO vary considerably in terms of their UV absorption efficiencies, the elucidation of the molecular structure in the adsorbed state is very relevant for the intended application. This issue will be addressed in future work through a combination of DFT-based predictions of the vibrational spectra and infrared spectroscopy experiments.

Further calculations planned for the second project phase will investigate the interaction of organic contaminants having several negatively polarised areas with protonated FAU-type adsorbents. If there are two or more framework protons in relatively close proximity, "multi-site" interactions could enhance the affinity towards the contaminant. This concept is illustrated for caffeine, one of several organic contaminants that will be considered, in Figure 2. Additional work packages will address the generation of realistic surface models of clinoptilolite, a common natural zeolite, which will be used in future studies of contaminant adsorption.

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More Information

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Project Partners

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