Computational studies of zeolites as adsorbents for the removal of pharmaceuticals and personal care products

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Pharmaceuticals and personal care products (PPCPs) have received considerable attention as emerging organic contaminants, with some members of this diverse group of compounds possessing a significant environmental hazard potential (Patel et al. 2019). Conventional wastewater treatment plants are not designed for the removal of these species, and a number of PPCPs show recalcitrant behaviour, entering water bodies and other environmental compartments. Adsorption-based processes constitute one possible technology that can improve the PPCP removal efficiency of wastewater treatment facilities. While carbon-based adsorbents are the most widely studied option, hydrophobic high-silica zeolites could be attractive alternatives due to their good regenerability and reduced co-adsorption of natural organic matter (Jiang et al. 2018). In this contribution, it will be discussed how atomistic modelling methods at different levels of theory can be employed to predict and understand the PPCP adsorption behaviour of these materials.

Given the diversity of zeolite frameworks that are available in highly siliceous form and the even larger number of PPCPs of possible environmental relevance, it is evident that an experimental investigation of all zeolite-PPCP combinations of potential interest would be extremely laborious. In previous work, it could be shown that relatively simple force field simulations deliver host-guest interaction energies that are well correlated with experimental removal efficiencies, providing a pathway to determine zeolite-PPCP combinations of potential interest prior to an experimental characterisation (Fischer 2020). Expanding upon this work, the implementation of a multi-step screening procedure allowed the exploration of a large number of combinations (>10 zeolites, >50 PPCPs) at relatively modest computational cost. Additionally, the capabilities of more sophisticated molecular dynamics simulations to calculate free energies of adsorption were explored. Such simulations allow direct predictions whether a given contaminant will be adsorbed in the zeolite or remain in solution.

Whereas the force field simulations are primarily employed for predictive purposes, dispersion-corrected density functional theory (DFT) calculations enable a more detailed understanding of the interactions that govern PPCP adsorption. Two recent studies dealt with the adsorption of carbamazepine (CBZ, Fig. 1a), an anticonvulsant medication, and triclosan (TCS, Fig. 1a), a disinfectant and preservative agent that is widely used in various products, in different zeolites (Fischer 2023a, Fischer 2023b). It was observed that the topology of the zeolite framework has a significant impact on the CBZ adsorption energy, whereas the interaction with TCS is largely determined by the pore size. This qualitative difference can be explained with the higher flexibility of TCS, which can adjust more readily to different pore shapes than the fairly rigid CBZ molecule. In addition to analysing factors that determine the strength of host-guest interactions, guest-guest interactions between co-adsorbed CBZ molecules were investigated. The study of TCS adsorption also addressed the competitive adsorption of the organic contaminant and water in zeolites having different framework compositions (all-silica zeolites and highly siliceous aluminosilicates, see Fig. 1b), permitting insights into the role of adsorbent hydrophobicity.

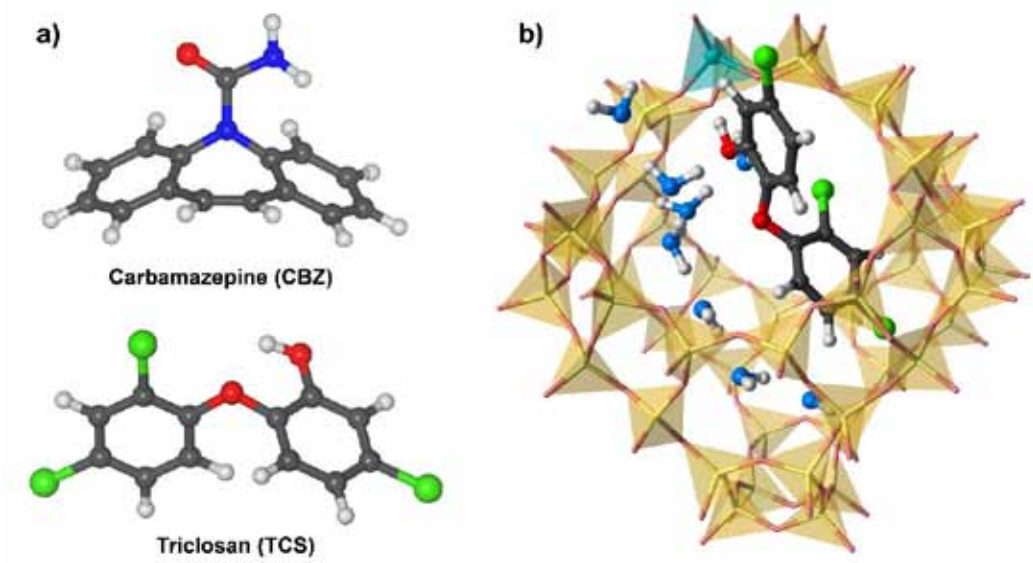

Figure 1. a) Molecular structures of carbamazepine and triclosan. b) Representative snapshot from a DFT-based molecular dynamics simulation addressing the co-adsorption of TCS and H_2O in protonated FAU-type zeolite.

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