## COMMUNICATION

# Highly selective removal of perfluorinated contaminants by adsorption on all-silica zeolite Beta

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**Abstract:** Perfluorinated alkylated substances (PFASs) are widely used in industrial and commercial applications, leading to a widespread occurrence of these persistent and harmful contaminants in our environment. Removal of these compounds from surface and waste waters is being mandated by European and U.S. governments. Currently, there are no treatment techniques available that lower the concentrations of these compounds for large water bodies in a cost- and energy-efficient way. We hereby propose a hydrophobic, all-silica zeolite Beta material that is a highly selective and high-capacity adsorbent for PFASs, even in the presence of organic competitors. Advanced characterization data demonstrate that the adsorption process is driven by a very negative adsorption enthalpy and favorable steric factors.

Perfluorinated compounds (PFASs) have seen extensive industrial use over the past 40 years, but are now considered top priority pollutants, due to their chemical persistence, and their pervasive presence in (drinking) water, food products, animals and even humans.[1,2] Exposure to PFASs entails serious health risks like liver and kidney cancer, and may affect fetus and child growth.[3–5] Current PFAS regulations range from restricting production to imposing threshold PFAS concentrations in tap, surface and waste water.[6,7] Most regulation focuses on perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), two of the most spilled PFASs.

Conventional waste water treatment plants are unable to remove PFASs in low concentration from complex waste and surface waters. Sonolysis and electro- or photocatalysis have been explored, but these suffer from high energy demand and require pretreatment steps, impeding treatment of large water volumes.[8–10] Adsorption may be a better, lower cost approach.[11–16] So far, most PFAS adsorption studies use solutions of individual compounds, without the non-fluorinated organics that are present in real situations. A single study exploring the impact of organic matter on PFAS adsorption reports a drastic decline of capacity for PFASs on conventional adsorbents like activated carbon.[17] Even though a large variety of different adsorbent types has been screened so far, not many adsorbents are known that selectively accumulate PFOA or PFOS in the presence of competing organics. A particular and promising adsorbent type are macrocyclic, polymeric adsorbents that possess a cavity that can be highly selective for specific guest molecules. Recent examples are a β-cyclodextrin polymer network and a guanidinocalix[5]arene network, both showing high adsorption capacity and selectivity for PFOA and PFOS.[18,19] However, these materials are expensive, difficult to recover from aqueous streams and hard to regenerate. In a study of Na-exchanged Y zeolites, a higher Si/Al ratio appears to enhance the PFOS adsorption, but the nature of the zeolite sorbent and the role of the Na+ are unclear, and more importantly, no competitive sorption data are given.[15] Since zeolites, as crystalline microporous materials, present a multitude of pore architectures and compositions, we initiated a detailed search into the best zeolite adsorbent for adsorptive PFAS removal. Here, we report direct experimental and spectroscopic evidence that all-silica zeolite Beta is a highly-selective and high-capacity adsorbent for removing PFOA and PFOS from water, even in the presence of organic competitors.

All-silica zeolite Beta was synthesized using fluoride as the mineralizing agent. The resulting zeolite framework is almost free of local defects, as proven by the very weak intensity of the silanol $\nu_{OH}$ vibration at 3733 cm$^{-1}$ in the FTIR spectrum (Figure S1).[20,21] It exhibits high pore volumes of 0.21 cm³/g and high surface areas of 624 m²/g (calculated by the t-plot and Brunauer-Emmet-Teller equations, respectively via nitrogen physisorption isotherms, see Figure S2). The lack of defects and Al in the zeolite framework (i.e. the absence of silanol groups) renders the interior surface extremely hydrophobic, as can be seen on water vapor adsorption isotherms, when compared to a more hydrophilic zeolite Beta type (Figure S2). Besides Beta, other all-silica and high-silica

adsorbents were synthesized and screened for PFOA adsorption in a relevant concentration range (0.1 – 500 mg/L). On most zeolites, such as all-silica silicalite-1 and high-silica chabazite, there was no significant PFOA uptake. Mesoporous materials like SBA-15 and MCM-41, with all-silica composition, but with significant numbers of defect –OH groups, showed no sign of PFOA adsorption. All-silica zeolite Beta, on the contrary, showed both high affinity (in the lower concentration range) and high saturation capacity for PFOA (37 wt%), strongly outperforming the industrial benchmark adsorbent activated carbon (AC) (Figure 1 (A)). Especially the high affinity at lower concentrations, even below 1 mg/l, is highly relevant in an environmental context.[22,23] In similar experiments for adsorption of PFOS (0.1-250 mg/L), the capacity of all-silica Beta (21 wt%) proved to be similar to that of AC, but the affinity at lower concentrations was again much higher (Figure 1 (A)). The fact that all-silica zeolite Beta does not outperform AC on maximum PFOS adsorption capacity is due to AC being a better adsorbent for PFOS than for PFOA; indeed the sulfonic acid group of PFOS is a stronger and more polar acid compared to the carboxyl group of PFOA, which allows a stronger interaction with AC.

Fast adsorption kinetics are essential for efficient PFAS removal in waste water treatment. Kinetic experiments revealed that adsorption equilibrium is reached much faster for PFOA on all-silica zeolite Beta than on AC, while the time profiles for PFOS adsorption are similar for both adsorbents (Figure 1 (B)). Hence, considering kinetics, all-silica zeolite Beta looks very well suited to be used in a flow-through adsorption column.

Even though adsorption might be the best available technique for the low-cost and energy efficient removal of PFASs from water, many adsorbents with good or high capacity (like AC) simply lack the selectivity that is required to be used for real waters. Adsorption selectivity is therefore arguably the most important feature for adsorbent selection, since natural waters contain various organic competitors, often in molar excess. For this study, a series of selectivity experiments were performed, in order to assess the influence of organic competitors on the uptake of PFOA and PFOS. Five non-fluorinated compounds were selected to represent the wide array of organics in real waters: the aromatics phenol and benzoic acid, which carry motives of more complex humic acids; adipic acid, as a representative dicarboxylic acid, and caprylic acid and sodium dodecyl sulfate, being non-fluorinated analogues of PFOA and PFOS, respectively. First, PFOA and PFOS uptakes were measured in the presence of an equimolar amount (100 µM) of each organic compound. The results for all-silica Beta are outstanding: the uptakes of both PFOA and PFOS remain the same as in the reference experiment without organic competitor (see Figure 2). In contrast, PFOA uptake on AC was reduced significantly by other organics, with an average reduction in uptake capacity of 43%. PFOS adsorption on AC in the presence of competing organics proved more resilient compared to PFOA adsorption, but a reduction of PFOS uptake (-17% on average) is still seen (Figure 2). Next, PFOA and PFOS uptakes on all-silica Beta and on AC were measured in the presence of an excess of organic material, like in waste or natural waters. All five organics were added simultaneously in either 1:1 or 3:1 ratio towards 100 µM of PFOA or PFOS, resulting in organics to PFAS ratios of 5:1 and 15:1, respectively. Even in these challenging conditions, PFOA adsorption on all-silica zeolite Beta was not reduced, demonstrating the outstanding PFOA selectivity of Beta (Figure 3). In contrast, PFOA uptake on

AC was cut down dramatically with 43% and 60% in the 5:1 and 15:1 test solutions. Also PFOS adsorption was reduced significantly on AC in the 5:1 (-22%) and 15:1 (-51%) solution. On all-silica zeolite Beta, PFOS adsorption remained relatively stable under excess competition, with only minor reductions in uptake (-9% for the 5:1; -14 % for the 15:1 solution). This shows that the high selectivity of all-silica Beta is not limited to PFOA, but also applies to other PFASs. The adsorbate scope of all-silica zeolite Beta can thus be extended towards other types of perfluoro-compounds like non-functional perfluoroalkanes; it has for instance been found that also perfluorooctane and perfluorodecane are adsorbed in high quantities.

To study the impact of framework aluminum and silanol groups on PFAS uptake, a comparison was made with two Al-containing Beta samples, with $SiO_2/Al_2O_3$ ratios of 22 (Beta-22) and 300 (Beta-300). These have an identical pore architecture, but were prepared via templated synthesis in $OH^-$ medium (for Beta-22), eventually followed by dealumination (for Beta-300). At $SiO_2/Al_2O_3 = 300$, the zeolite would be considered hydrophobic. However, PFOA uptakes on Beta-300 and Beta-22 are similar, and much lower than on all-silica Beta: a maximum uptake of 78 mg PFOA/g was measured, 79% lower than the maximum uptake on the all-silica analogue (Figure S4). A similar trend was seen for PFOS adsorption, with all zeolites based on an Al-containing synthesis being poor adsorbents. This indicates that not only Al, but also the silanol defects formed during dealumination have a detrimental effect on PFAS adsorption, even in very small amounts. Also the stability and reusability of all-silica zeolite Beta were assessed by a performing a thermal treatment. This revealed that after complete saturation with PFOA, all adsorbed molecules can be removed at 350 °C without any damage to the zeolite's framework and its crystallinity (Figure S2 and S3). The possibility of a thermal regeneration is a significant asset for all-silica zeolite Beta, because such a simple treatment cannot be applied for organic adsorbents like the aforementioned macrocyclic polymers or ion-exchange resins.

An intriguing question is why all-silica zeolite Beta has such a high affinity and selectivity for PFASs. Calorimetric experiments were performed to resolve whether the adsorption process is mostly driven by enthalpy or entropy. One may expect an entropy-driven process, given the very hydrophobic nature of both the all-silica zeolite Beta and the perfluorinated chains of the surfactants; many hydrophobic effects are indeed entropic phenomena. Moreover, perfluorinated carbon chains hardly engage in Van der Waals interactions, due to the extremely low polarizability of the fluorine-carbon bonds. However, calorimetry shows that PFOA adsorption on the different zeolite Beta types is associated with a negative adsorption enthalpy, both at low and at higher occupation of the zeolite surface (Figure S5). Adsorption enthalpies for all-silica zeolite Beta are much more negative, at -30 to -40 kJ mol$^{-1}$, than for the aluminated zeolite Beta types, where the enthalpy increases from -20 to 0 kJ mol$^{-1}$ at higher concentrations (Beta-22 and Beta-300, see Figure S5).

Given the estimated dimensions of PFOA (ca. 13Å x 6.5Å x 6.5Å) and zeolite Beta (channel diameter of 5.95 Å, intersection spacing of 12.62 Å), the packing of PFOA in the Beta pores must be tight. The fluorous tails of PFOA may assume a helical or a zig-zag conformation; and the PFOA surfactant may be packed in a head-head, tail-tail or head-tail conformation.[24,25] Through Density Functional Theory (DFT) simulations, the total energy of different optimized conformations of PFOA and caprylic acid

molecules in zeolite Beta was calculated. These DFT calculations demonstrate a strong preference of PFOA for head-head interactions, with a total energy difference of -16.5 kJ mol$^{-1}$ and -76.8 kJ mol$^{-1}$ over the head-tail and tail-tail conformations, respectively (Figure 4 (A)). The stability of the head-head interactions results from the formation of carboxylic acid dimers, driven by H-bonding.[26,27] The same scenario is observed for caprylic acid (Figure S6), associated, however, with a guest/zeolite Beta interaction energy (-181.1 kJ mol$^{-1}$) that is much lower than that obtained for the head-head conformation of PFOA (-264.6 kJ mol$^{-1}$). This observation shows that the observed selectivity of all-silica zeolite Beta for PFOA is enthalpy-driven, confirming the calorimetry results. DFT simulations also show that a helical conformation of PFOA is slightly more favourable than the zig-zag one; the corresponding total energy difference between the two is -4.2 kJ mol$^{-1}$, in contrast to caprylic acid for which a zig-zag structure is more stable (Figure S7). Since the helical conformation is slightly shorter than the zig-zag one, PFOA might also have a steric advantage over caprylic acid when the zeolite is fully packed. The PFOA molecules are aligned according to the straight channels in the *a*- and *b*-directions; DFT calculations show a total energy penalty of 19.7 kJ mol$^{-1}$ for the PFOA in the tortuous channels along *c* (Figure 4 (B)).

Experimental evidence supporting the computational prediction is offered by solid-state NMR spectroscopy. $^{19}$F MAS and $^{1}$H-$^{13}$C CPMAS NMR spectra of pure, crystalline PFOA and of PFOA loaded into all-silica zeolite Beta show large similarity and confirm the presence of PFOA inside the zeolite (Figure S8 and Figure S9). With increasing concentration of PFOA in the zeolite, the NMR linewidths become smaller, meaning that the molecular arrangement becomes more ordered. In the carbon spectrum there is a slight difference in the chemical shift of the carboxylate carbon signal between pure PFOA and PFOA in the zeolite, suggesting that the polar heads experience different environments in both cases. The 2D $^{1}$H-$^{1}$H homonuclear correlation spectrum of the zeolite Beta loaded with the highest concentration of PFOA exhibits a strong diagonal signal at about 8 ppm, proving that hydrogen atoms of the PFOA carboxyl groups see identical hydrogen atoms in their proximity (Figure 5 (A)). This strongly suggests that PFOA within the zeolite forms head-to-head hydrogen-bonded dimers. The chemical shift of the hydrogen nuclei involved in these bonds is different from the

chemical shifts of the hydrogen nuclei within the crystalline PFOA, indicating that the geometries of bonds between the PFOA molecules within the zeolite and the molecules within the pure PFOA are different. Indeed, molecules in pure PFOA are involved in a network of hydrogen bonds; they cannot be regarded as isolated head-to-head bonded dimers (Figure S10). The $^{1}$H-$^{1}$H homonuclear correlation spectrum also shows that the PFOA carboxyl groups do not interact with the hardly detectable hydroxyl groups of the zeolite framework (resonating between 3 and 5 ppm). The latter groups are rare in the all-silica zeolite Beta; they most probably only appear at defects on the surface of the crystals. The $^{29}$Si NMR spectrum of the all-silica zeolite Beta exhibits several partly overlapped signals (Figure 5 (B)). The signals can be grouped into three chemical shift ranges, one between -111 and -113 ppm, one between -113 and -114 ppm, and one around -116 ppm. According to DFT/GIPAW calculations the first and the third groups of signals belong to framework silicon atoms that form the straight channels of zeolite Beta, whereas the second group of signals belongs to silicon nuclei at the channel intersections. Close inspection of the $^{19}$F-$^{29}$Si heteronuclear correlation spectrum suggests that the hydrophobic part of the molecule (fluorine atoms F3-F6) is located within the straight channels, since the corresponding $^{19}$F-$^{29}$Si cross peaks emphasize the $^{29}$Si resonances between -111 and -113 ppm and the resonances around -116 ppm. The tail of the molecule, with fluorine atoms F8, is closer to the channel intersections (the corresponding $^{19}$F-$^{29}$Si cross peaks emphasize the $^{29}$Si resonances between -113 and -114 ppm). All these findings are in line with the computational predictions.

Summarizing, the PFOA molecules are positioned in the straight *a*- and *b*-channels of the zeolite, with the hydrophobic chains in the channels and the carboxylic heads, forming hydrogen bonded pairs, in the intersections. This results in a very favourable adsorption enthalpy. The helical conformation of the perfluorinated chains makes a very tight packing at maximal capacity sterically possible, as shown in Figure 6. This explains the exceptionally high affinity and selectivity of all-silica zeolite Beta for PFOA and similar perfluorinated compounds. These properties position this unusual zeolite as the lead candidate for combating PFAS pollution.
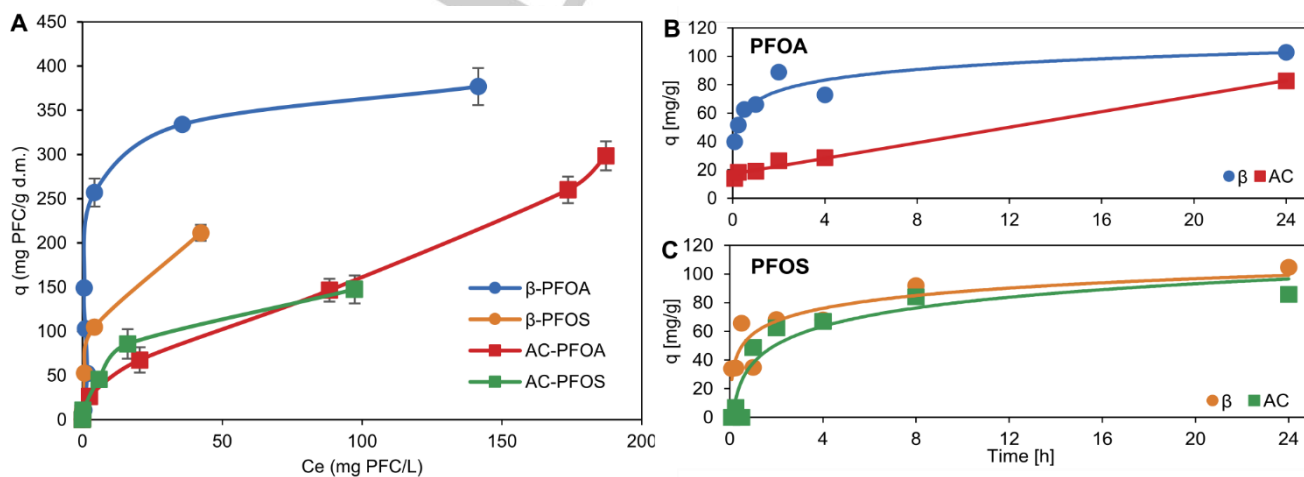
**Figure 1.** (A) Adsorption isotherms (293 K) for PFOA and PFOS on all-silica Beta (β) and activated carbon (AC). $q$ = mg PFAS adsorbed per g of dry matter; $C_e$ = equilibrium concentration in water. (B) Adsorption kinetics for PFOA and (C) PFOS on all-silica Beta (β) and activated carbon (AC).
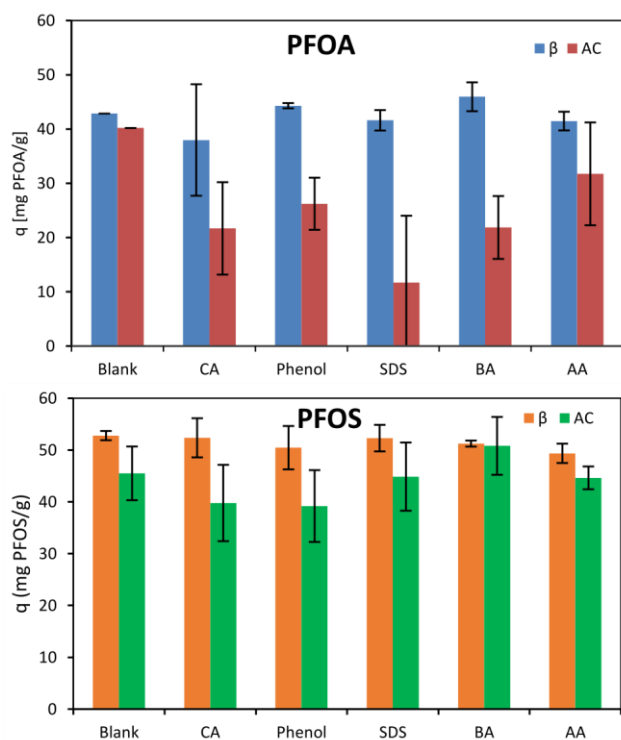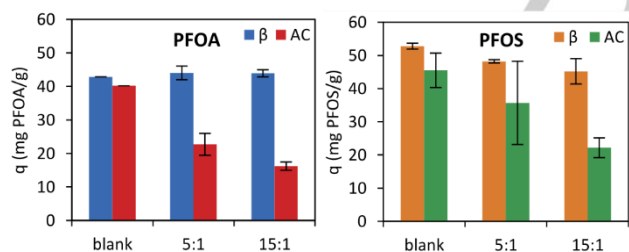


**Figure 2.** PFOA (top) and PFOS (bottom) adsorption on all-silica Beta (β) and activated carbon (AC) under competitive conditions (100 µM of PFOA or PFOS and 100 µM of a single organic competitor). CA = caprylic acid, SDS = sodium dodecyl sulfate, BA = benzoic acid, AA = adipic acid.



**Figure 3.** PFOA (left) and PFOS (right) adsorption on all-silica Beta (β) and activated carbon (AC) under competitive conditions. The 5:1 solution has a 5-time molar excess of organic competitors, the 15:1 solution has a 15-time molar excess.
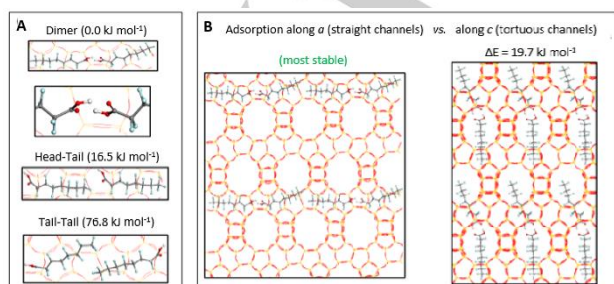


**Figure 4**: Optimized binding geometry of all-silica zeolite Beta and PFOA. (A) Snapshots of DFT-optimized conformations of PFOA molecules, adsorbed on all-silica zeolite Beta, and the associated total energy differences with respect to the head-head dimer taken as reference. (B) Snapshots of the PFOA dimers, adsorbed in the straight channels (along $a$) vs. tortuous channels (along $c$) of all-silica zeolite Beta.
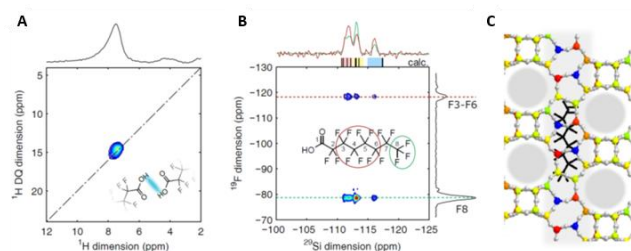
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**Figure 5**: NMR-based inspection of the arrangement of PFOA molecules within the all-silica zeolite Beta. (A) 2D $^1$H-$^1$H DQ-SQ homonuclear correlation and (B) $^{19}$F-$^{29}$Si heteronuclear correlation NMR spectrum. In (B) traces through cross-peaks that describe correlations (proximities) between F8 and Si atoms and F3-F6 and Si atoms are shown above the 2D spectrum with green and red line, respectively. Below the traces, vertical black solid lines mark the values of $^{29}$Si chemical shifts calculated by GIPAW. Location of Si atoms with specific chemical shift within the framework of zeolite Beta can be read from the scheme in (C): Si atoms with chemical shifts between -111 and -113 ppm are plotted in red and orange, atoms with shifts between -113 and -114 ppm are shown in yellow and green, and atoms with shifts around -116 ppm are presented in blue.
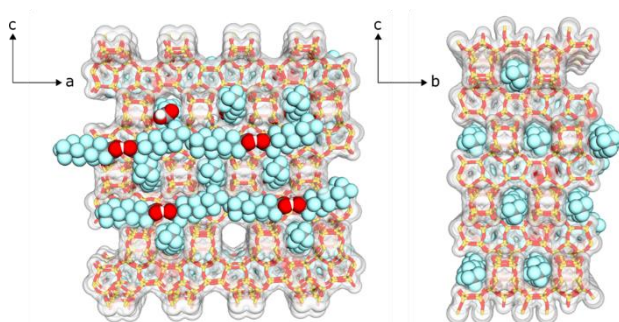


**Figure 6**: Crystallographic structure of all-silica zeolite Beta with adsorbed PFOA molecules. The PFOA molecules are positioned in the *a* and *b* channels and the helical conformation of the perfluorinated chains makes a very tight packing at maximal capacity sterically possible.

**Keywords:** Perfluorinated Compounds • Zeolites • Adsorption • NMR spectroscopy • Computational chemistry

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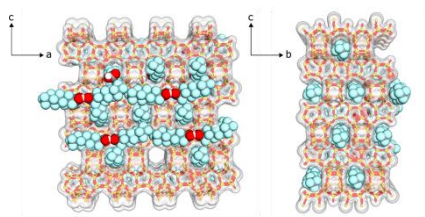


Perfluorinated compounds have found wide application but have adverse effects on health and environment. There is a need to selectively recover them from process and surface waters. We now show that a microporous zeolite Beta, in its all-silica form, shows outstanding capacity and affinity for the uptake of PFCs like perfluorooctanoic acid and perfluorooctanesulfonic acid, even in the presence of other organics.