

Zeolites

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Comments on “Highly Selective Removal of Perfluorinated Contaminants by Adsorption on All-Silica Zeolite Beta”

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The study of Van den Bergh et al.^[1] describes a new high performance adsorbent—all-silica zeolite Beta—for removal of perfluorinated alkylated substances (PFAS) from contaminated water. The study combines a number of highly sophisticated techniques which enable a deep insight into the mechanism and driving forces of the adsorption process. The authors compare the new zeolite adsorbent with the most widely used adsorbent, which is activated carbon (AC). The result of a comparison depends on the selection of the chosen benchmark. Due to significant practical implications, this comparison is examined in the following.

The comparison between zeolite Beta and AC refers to adsorption affinity, capacity and selectivity. Indeed, Figure 1 A seems to prove this on hand of adsorption isotherms for perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). The class of ACs is represented here by a single AC (Norit SX 1G from Cabot). It is known, however, that adsorption affinities of ACs for PFAS can differ widely between various AC samples, e.g., by up to 3 orders of magnitude in adsorption coefficients under the same experimental conditions, as described in Saeidi et al.^[2,3] and literature cited therein. Such huge differences have rarely been observed for other organic pollutants: they appear to be specific to perfluorinated acids. Therefore, it may be justified to compare the new zeolite-based adsorbent with other ACs, and also with advanced, “tailor-made”, carbon-based adsorbents as benchmark.


Saeidi et al.^[3] modified a commercial AC felt by a simple thermochemical procedure such that adsorption coefficients


($K_{d,i} = C_{\text{adsorbed},i}/C_{\text{dissolved},i}$) up to 10^6 L kg^{-1} for PFOA and up to 10^8 L kg^{-1} for PFOS were obtained. It is difficult to compare such adsorption coefficients with the data presented in^[1] because adsorption coefficients are neither calculated there, nor can they be directly derived from the presented data. A rough estimation of K_d values from Figure 1 A leads to $K_d \approx 10^{4.7} \text{ L kg}^{-1}$ for PFOA and $10^{4.4} \text{ L kg}^{-1}$ for PFOS on the zeolite Beta at $C_{\text{dissolved,PFAS}} = 5 \text{ mg L}^{-1}$. The corresponding K_d values with the advanced AC adsorbent described in^[3] are $10^{5.6} \text{ L kg}^{-1}$ and $10^{6.5} \text{ L kg}^{-1}$, respectively, at the same PFAS equilibrium concentrations. Thus, this AC appears to be one to two orders of magnitudes “better” than the zeolite Beta.

Another outstanding property of zeolite Beta which was stressed in the study is its high *selectivity* with respect to the n-alkyl perfluorinated acids. However, this may not be an advantage under all circumstances: it could conceivably prove to be a limitation when branched PFAS isomers come into play. It should be noted that technical PFAS products can be mixtures of linear and branched isomers.^[5] According to the mechanistic considerations in^[1] and the derived hypotheses, it remains to be seen whether the “favorable steric factors” and the “tight packing of PFOA in the Beta pores” will apply on the branched isomers. It is likely that AC adsorbents with their broader pore size distribution may prove to have advantages in this regard.

Let us now consider the *adsorption kinetics* as presented in Figure 1 B. Again, the zeolite appears to be superior to the AC, because it adsorbs at least PFOA faster. It is well known, however, that sorption kinetics depend not only on intrinsic material properties such as pore texture, but also on the size of the adsorbent particles. The mathematical description of adsorption kinetics is complex and beyond the scope of this comment. Usually, the adsorbent particle diameter appears in the denominator of rate expressions as its square value.^[4] In other words, no useful conclusions can be drawn from data on sorption kinetics without knowledge of the particle sizes (more precisely particle size distributions). Unfortunately, the particle size data is missing in the addressed study.^[1] When considering practical aspects of PFAS removal from natural waters, groundwater or surface water, the environmental engineer is faced with trace concentrations in the range of a few $\mu\text{g L}^{-1}$ or less.^[7] All adsorption data presented and evaluated in^[1] are with dissolved PFAS concentrations many

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orders of magnitude higher than environmentally relevant ones. This may prove to be a critical factor when building the bridge from science to practice. Still, it is essential to denominate the concentrations correctly: usually these are *equilibrium* concentrations (C_e), as presented in Figure 1. However, in Figure 2, the given solute concentrations (100 μM) appear to be *initial* concentrations rather than equilibrium concentrations; the difference is significant. Unless this is made clear, it may cause problems for the reader.

We have to address some further technical issues of the study^[1] which make a comprehensive evaluation of adsorption data difficult for the reader. Neither pH nor type of cations or ionic strength values are specified. These parameters may play significant roles for adsorption phenomena, in particular of ionic adsorbates such as PFAS. Instead, protonated carboxylates are proposed (Figures 4 and 6), considering that the $\text{p}K_a$ value of PFOA is very low (≤ 1 ^[6]). Although speciation inside the pore space may be different from the aqueous bulk phase, it is hard to accept that the strong acid PFOA is adsorbed in its protonated form in equilibrium with a circumneutral water bulk phase. This issue becomes even more challenging when considering the adsorption of PFOS in zeolite Beta: PFOS is among the strongest acids with a $\text{p}K_a$ value of about -3.3 .^[8] Nevertheless, it is well adsorbed in the zeolite (Figure 1).

Finally, when comparing activated carbon and zeolite Beta as adsorbents from an engineering point of view, the cost aspect comes into play. This may pose a challenge for the zeolite in comparison with ACs. This should not, however,

restrain innovative scientific investigations. The study^[1] has considerable merit and zeolite Beta is definitely a promising candidate for combating PFAS pollution. Our comment aims at a balanced evaluation of different state-of-the-art adsorbents.

Conflict of interest

The authors declare no conflict of interest.

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- [1] M. Van den Bergh, A. Krajnc, S. Voorspoels, S. R. Tavares, S. Mullens, I. Beurroies, G. Maurin, G. Mali, D. E. De Vos, *Angew. Chem. Int. Ed.* **2020**, *59*, 14086–14090; *Angew. Chem.* **2020**, *132*, 14190–14194.
 - [2] N. Saeidi, F.-D. Kopinke, A. Georgi, *Chem. Eng. J.* **2020**, *381*, 122689.
 - [3] N. Saeidi, F.-D. Kopinke, A. Georgi, *Chemosphere* **2020**, 128520.
 - [4] P. Grathwohl, *Diffusion in natural porous media*, Kluwer Academic Publishers, Dordrecht, **1998**, 97-46940 CIP.
 - [5] K. Schulz, M. R. Silva, R. Klaper, *Sci. Total Environ.* **2020**, *733*, 139186.
 - [6] K.-U. Goss, *Environ. Sci. Technol.* **2008**, *42*, 456–458.
 - [7] O. S. Arvaniti, A. S. Stasinakis, *Sci. Total Environ.* **2015**, *524–525*, 81–92.
 - [8] D. Brooke, A. J. Footitt, T. A. Nwaogu, *Environmental risk evaluation report: perfluorooctane sulfonate (PFOS)*, UK Environment Agency, **2004**.

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