

Adsorption of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) emerging contaminants on Y and silver-Y exchanged zeolites using thermal analysis and X-ray diffraction facilities.

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Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are two highly representative per- and polyfluoroalkyl substances (PFAS) recognized as environmental persistent organic contaminants [1-2]. Adsorption on zeolites is a reliable alternative to eliminate these compounds from water and wastewaters because of their framework flexibility, high organic contaminant selectivity, high specific capacity, rapid kinetics, excellent resistance to chemical, biological, mechanical or thermal stress [3-4]. Ag-exchanged zeolites show unique physical, chemical, and antibacterial properties along with strong absorption property and good stability thus working synergistically in removal of PFAS from water. Consequently, a deep investigation of these materials with exceptional performances must be explored beside their effectiveness for PFAS removal. In this work, the interactions between PFOA and PFOS and Y zeolites (FAU-topology) with different SiO₂/AlO₂ (SAR) were systematically investigated for the first time, in order to evaluate the role of hydrophobic and electrostatic forces in the interaction between polyfluoroalkyl substances and the adsorbents. A careful characterization of Y zeolites (with SAR= 30, 60 and 500, respectively) loaded with PFOA and PFOS, respectively, was carried out before and after silver functionalization in order to: i) investigate the effectiveness of synthetic Y and Ag-Y zeolites with a different SAR ratio towards PFAS, ii) characterize their structure; iii) localize the host species in the zeolites channel system, iv) investigate the thermal stability and their crystallinity degree, v) probe the interaction between PFAS molecules, water molecules, Ag ions and framework oxygen atoms. X-ray powder diffraction patterns (XRD) of the as-synthesized and Ag-loaded Y samples before and after PFAS adsorption, were collected at room temperature by using Bruker D8 Advance Diffractometer with a Sol-X detector, Cu K α 1, α 2 radiation. Rietveld structure refinements were performed using the GSAS package with EXPGUI graphical interface in the Fd-3m space group. The zeolites crystallite sizes were achieved by both the Scherrer and Williamson-Hall approaches. TG and DTA measurements of all samples were performed in constant air flux conditions from room temperature up to 1400 °C using an STA 409 PC LUX[®] - Netzsch (10 °C/min heating rate). After PFOS and PFOA adsorption, the selected materials maintain a high crystallinity degree. PFAS adsorption on Y and AgY samples was evidenced by differences in both the positions and intensities of the powders diffraction peaks, which are indicative of structural variations in terms of nature and concentration of the extraframework species, unit cell dimensions and framework geometry. The PFOA and PFOS adsorption was accompanied by deformations of the framework, evidenced by the value of the crystallographic free area of the zeolites channel systems. In all samples, PFOA and PFOS molecules were localized at the centre of Y-supercage, thus assuming six different orientations. The bond distances indicated strong interactions mediated via water molecules between zeolite framework and PFASs reactive carboxylic and sulfonyl functional groups. The structure refinements gave an extraframework content corresponding to ~26.0 and 22.0% wt. of PFOA and PFOS, respectively, in good agreement with the weight loss given by the thermogravimetric analyses. Our results highlighted that Ag-exchanged zeolites with high SAR were the most efficient adsorbents thus representing selective tools for PFOS and PFOA abatement as environmentally friendly, bactericidal and low-cost materials.

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