PER- AND POLYFLUOROALKYL SUBSTANCES ON MODIFIED CLAY

A COMBINED EXPERIMENTAL AND MOLECULAR SIMULATION STUDY

Dr. Jinxia Liu, McGill University, studied the performance of FLUORO-SORB® 200 adsorbent to adsorb per- and polyfluoroalkyl substances (PFAS) from an aqueous film-forming foam (AFFF) contaminated groundwater. In this study, batch adsorption experiments demonstrated that FLUORO-SORB 200 adsorbent can effectively remove PFAS pollutants in real impacted groundwater via strong adsorption. The performance of FLUORO-SORB 200 adsorbent was superior to granular activated carbon (for 11 of 13 PFAS compounds) and comparable to an ion exchange resin. FLUORO-SORB 200 adsorbent removal efficiency was not significantly impacted by organic co-contaminants (diesel, BTEX, TCE, and 1,4 dioxane) or inorganic water chemistry ($CaCl_2$ and NaCl).

Analysis indicated the AFFF-contaminated groundwater contained total PFAS of 64.9 ±1.0 µg/L, with PFOA (5.99 ±0.11 µg/L) and PFOS (14.2 ±0.3 µg/L) present. Analysis also indicated the presence of COD (7.9 mg/L) and TOC (2.4 mg/L). Other non-PFAS contaminants detected were diesel (C 10 -C 28, 0.43 mg/L) and acetone (8.3 mg/L). Mineral concentrations of calcium (50 mg/L), magnesium (6.6 mg/L), sodium (2.6 mg/L) and potassium (0.77 mg/L) were measured.

Batch adsorption experiments were carried out with varying adsorbent to solution ratios; 400.0 mL of the AFFF-impacted groundwater and 5.0 - 40.0 ±0.1 mg of the adsorbents were mixed for 168 hours in 500 mL HDPE bottles. Removal efficiencies for 40.0 mg tests, run in triplicate, are illustrated in Figure 1. For PFOA, FLUORO-SORB 200 adsorbent achieved 88% removal compared to 97% for ion exchange resin and 58% for granular activated carbon (re-agglomerated bituminous type). For PFOS, FLUORO-SORB 200 adsorbent achieved 94% removal compared to 89% for ion exchange resin and 59% for granular activated carbon. Biochar performed poorly for both PFOA and PFOS with 10-15% removal.

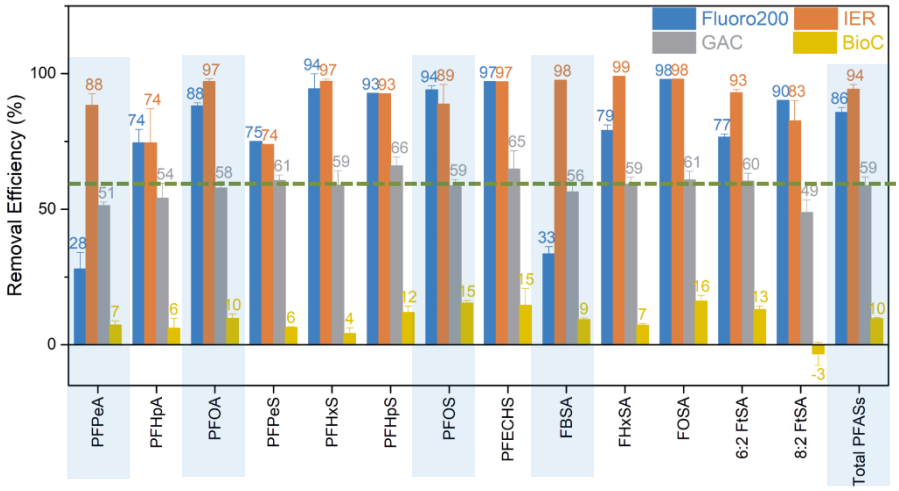

Figure 1. Efficiency of adsorbents for removal of PFOA and PFOS from AFFF-impacted groundwater; adsorbent:liquid ratio of 40 mg:400 mL (Yan et al. 2020).

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As shown in Figure 2, isotherms were created from the batch adsorption tests to show the uptake of PFAS by FLUORO-SORB® 200 adsorbent. Isotherms showed an initial linear isotherm followed by a Langmuir-type isotherm in the adsorption of anionic (PFOA, PFPeS, PFHxS, PFHpS, PFOS, and 6:2 FtSA) and neutral (FHxSA and FOSA) PFAS that have relatively higher concentrations in the groundwater. Based on molecular dynamics simulations, the anionic PFAS first occupy the highly polarized bare interlayer edge sites leading to a linear isotherm (Step I) and then sorb onto the interlayer surface sites resulting in a Langmuir isotherm (Steps Ⅱ + Ⅲ). Such results demonstrated that the adsorption behaviors of anionic and neutral PFAS compounds on FLUORO-SORB 200 adsorbent were significantly influenced by small changes in concentration at the ug/L level. PFOA, for example, displayed a linear isotherm in the relatively low concentration range (i.e., Step I from 0.55 µg/L to 1.59 µg/L), and a Langmuir -type isotherm at slightly higher concentration range (i.e., Step Ⅱ and Ⅲ from 1.59 µg/L to 2.73 µg/L).

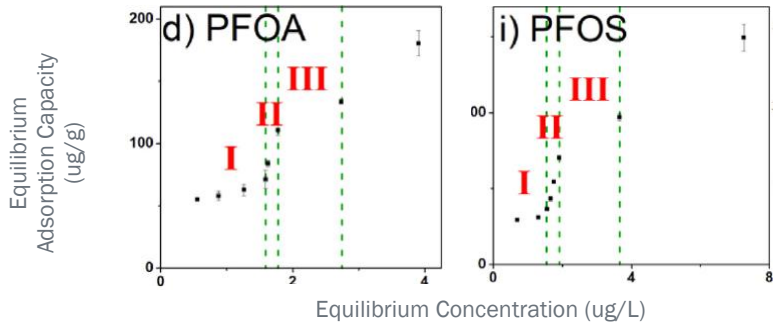

Figure 2. Adsorption isotherms of PFOA and PFOS on Fluoro-sorb® 200 (Yan et al. 2020).

Organic co-contaminants typically are present with PFAS in AFFF-impacted groundwater. Organic co-contaminants can foul granular activated carbon thus reducing efficiency. Saltwater can adversely affect the removal efficiency of ionic exchange resin. In a separate test, the effect of higher levels of organic co-contaminants and inorganic water chemistry were conducted through the spiking of the AFFF-impacted groundwater with diesel (C10- C28), a mixture of benzene, toluene, ethylbenzene, xylene (BTEX), trichloroethylene (TCE), 1,4-dioxane, CaCl2 and NaCl. For BTEX, TCE, and 1,4-dioxane present at 0.01 and 1.0 mg/L, the removal efficiency of PFAS was almost identical at both concentrations, suggesting no or minimal impact from these co-contaminants. Diesel at 1.0 mg/L either mildly reduced the removal of PFAS or had no impact. Interestingly, a higher diesel concentration of 100 mg/L slightly improved the removal efficiency for several PFAS, including PFOA. Additionally, the addition of NaCl and CaCl2 to simulate saltwater intrusion, had little effect on the removal efficiency of most PFAS.

The results show that among commercially available adsorbents, FLUORO-SORB® 200 adsorbent represents a highly effective option for PFAS removal. Also, FLUORO-SORB 200 adsorbent can tolerate the presence of organic co-contaminants (i.e., BTEX, diesel, 1.4 dioxane) and saltwater. Together, these experimental and molecular simulation studies reveal the adsorption mechanism of PFAS onto FLUORO-SORB 200 adsorbent and provide important information for evaluation of FLUORO-SORB 200 adsorbent for PFAS groundwater treatment.

A copy of the full paper, which includes data on other PFAS compounds, is available to consultants upon request.

Reference:
Yan, B., Munoz, G., Sauvé, S., and Liu, J., 2020, “Molecular mechanisms of per- and polyfluoroalkyl substances on a modified clay: a combined experimental and molecular simulation”, Water Research, 184, 116166.

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