



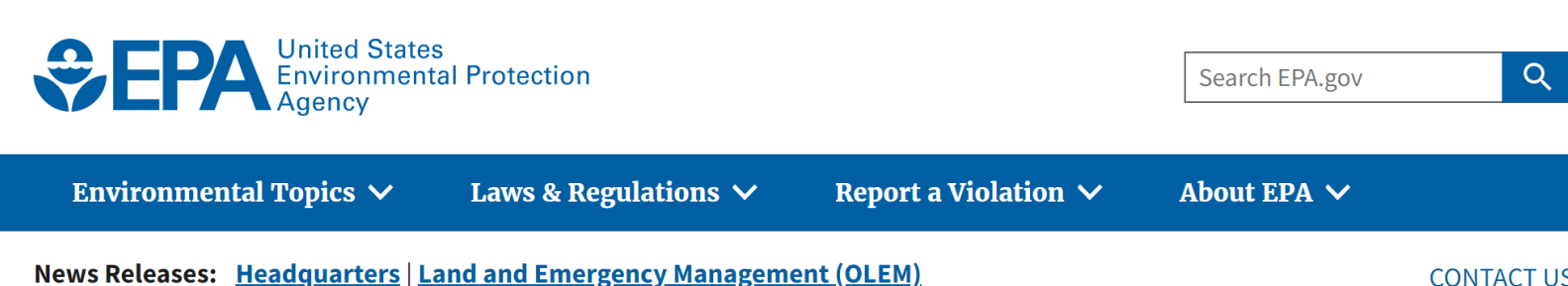
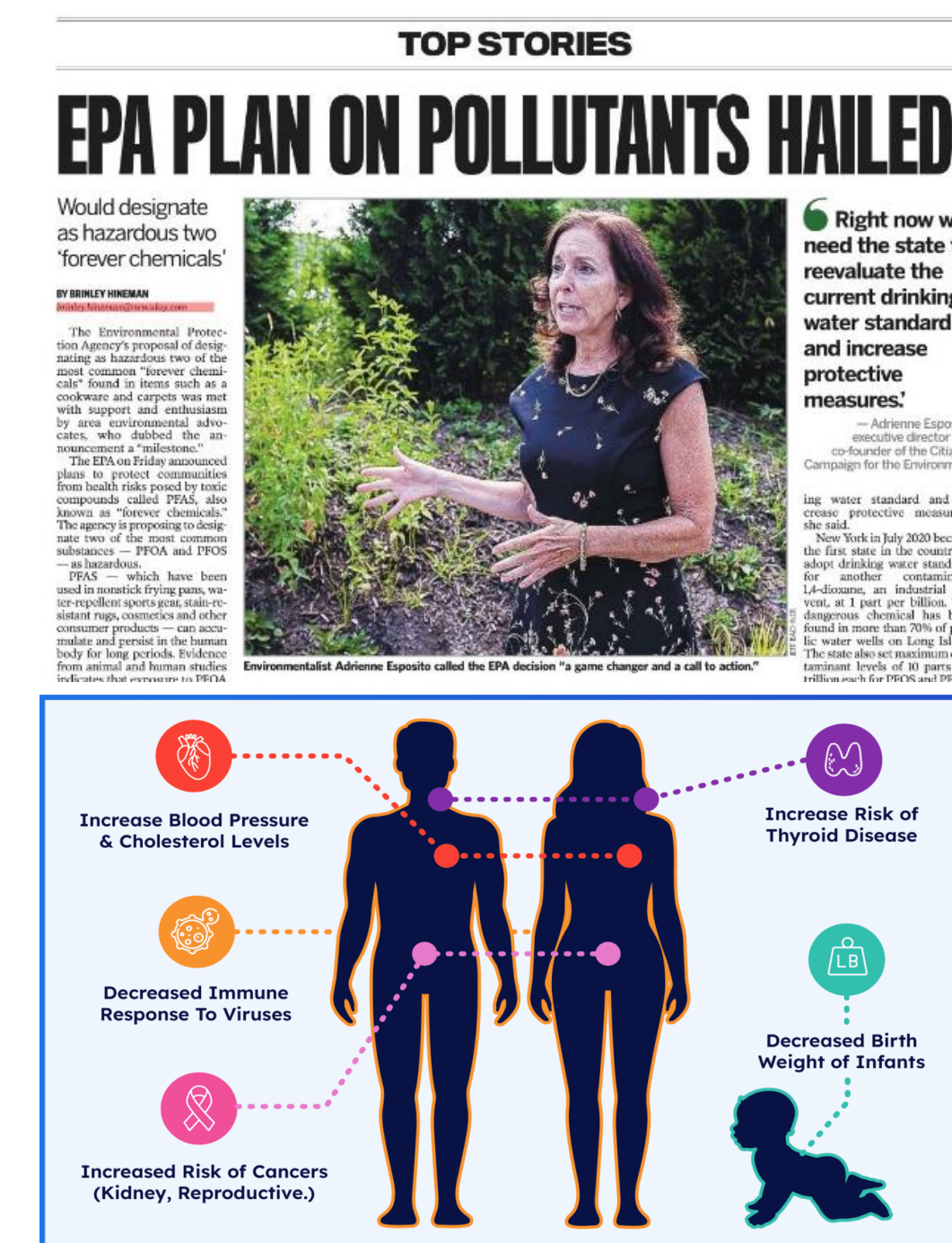
Systematic Investigation of PFOS Adsorption from Water by Metal Organic Frameworks, Activated Carbon, Metal Organic Framework@Activated carbon, and Functionalized Metal Organic Frameworks



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Introduction



EPA Proposes Designating Certain PFAS Chemicals as Hazardous Substances Under Superfund to Protect People's Health

Designating PFOA and PFOS under CERCLA would improve transparency, accountability, and deliver on Administrator Regan's PFAS Strategic Roadmap

With the introduction of Per- and Polyfluoroalkyl Substances (PFAS) in the early '90s for various applications such as firefighting foams, non-stick cookware, and stain-resistant fabrics, there has been growing concern about its existence in water due to its harmful health effects on human and animals over time. The chemical and thermal stability of PFAS makes the breakdown difficult and PFAS environmental persistence makes the removal challenging. Among all techniques, the adsorption methodology has shown effective performance in removing PFAS from water. Different adsorbents, including classical powder activated carbon (AC) and metal-organic frameworks (MOFs) as a new generation of adsorbents have been used for the removal of short-chain (C<6) and long-chain (C>7) PFAS.

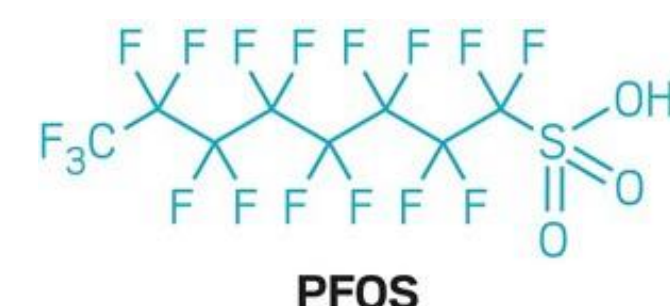


Figure 1. PFOS Structure

Adsorption mechanisms & Characterization after PFOS adsorption

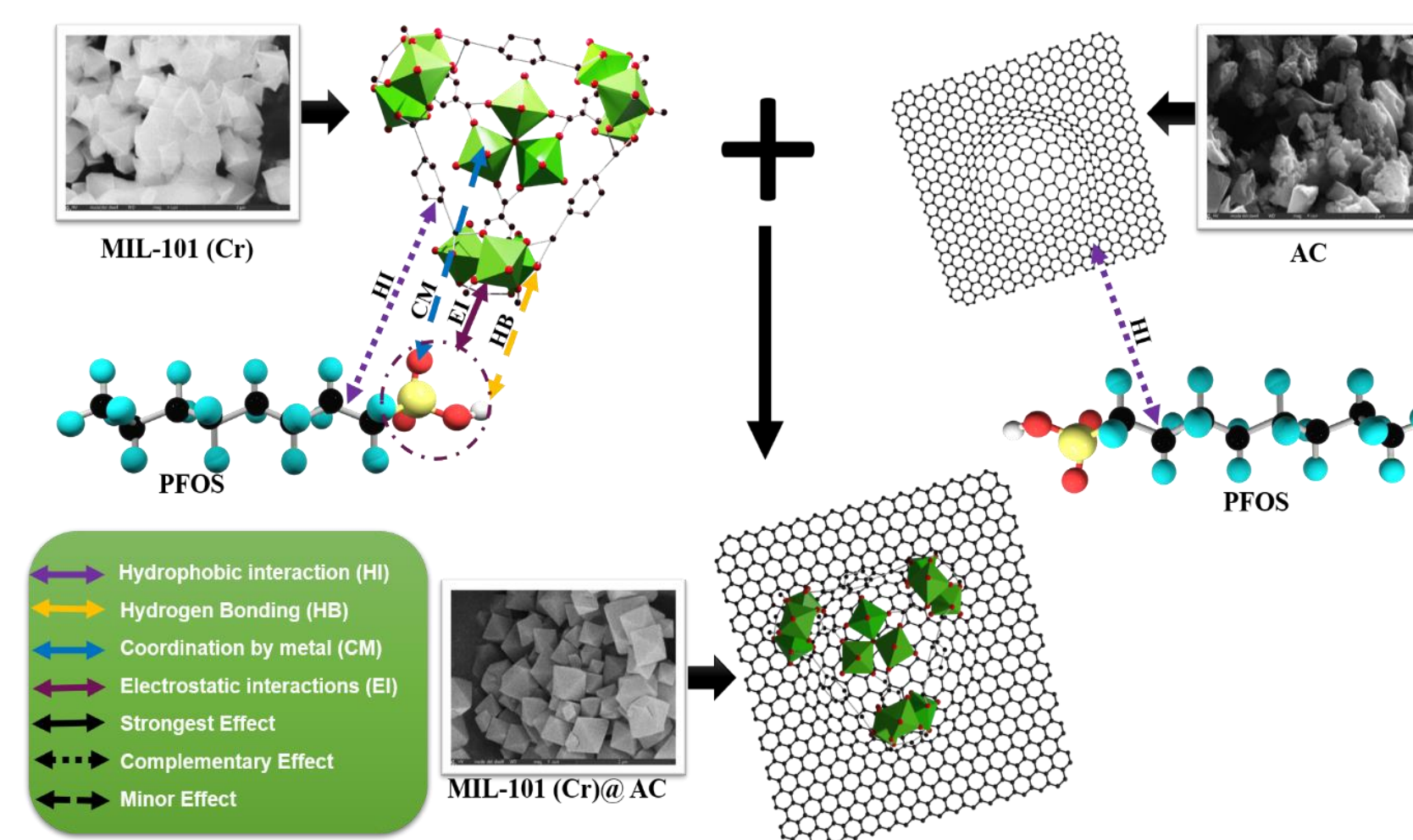
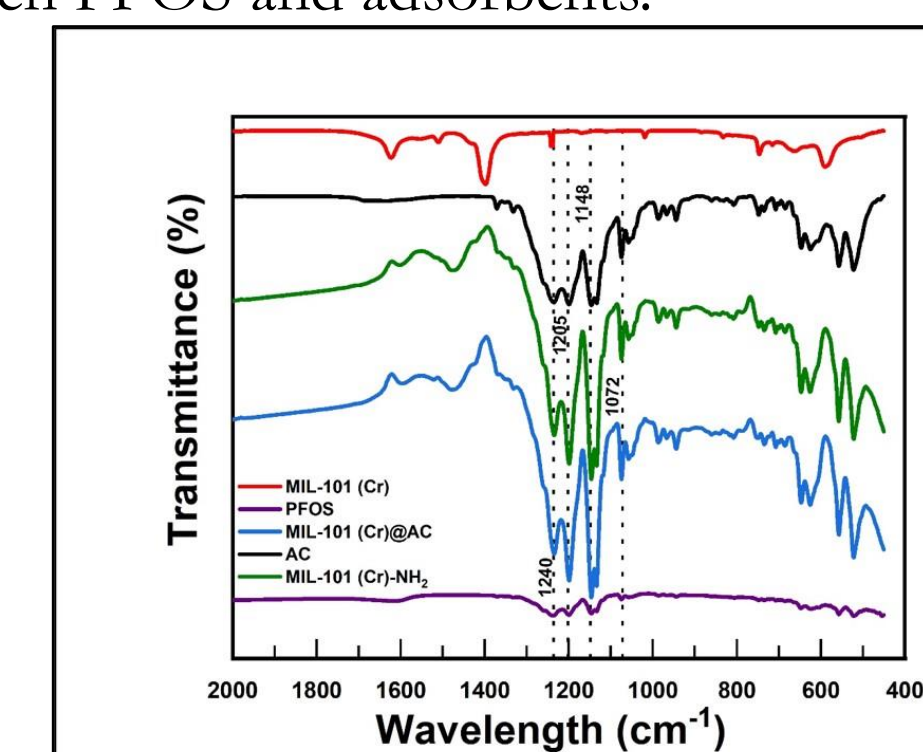
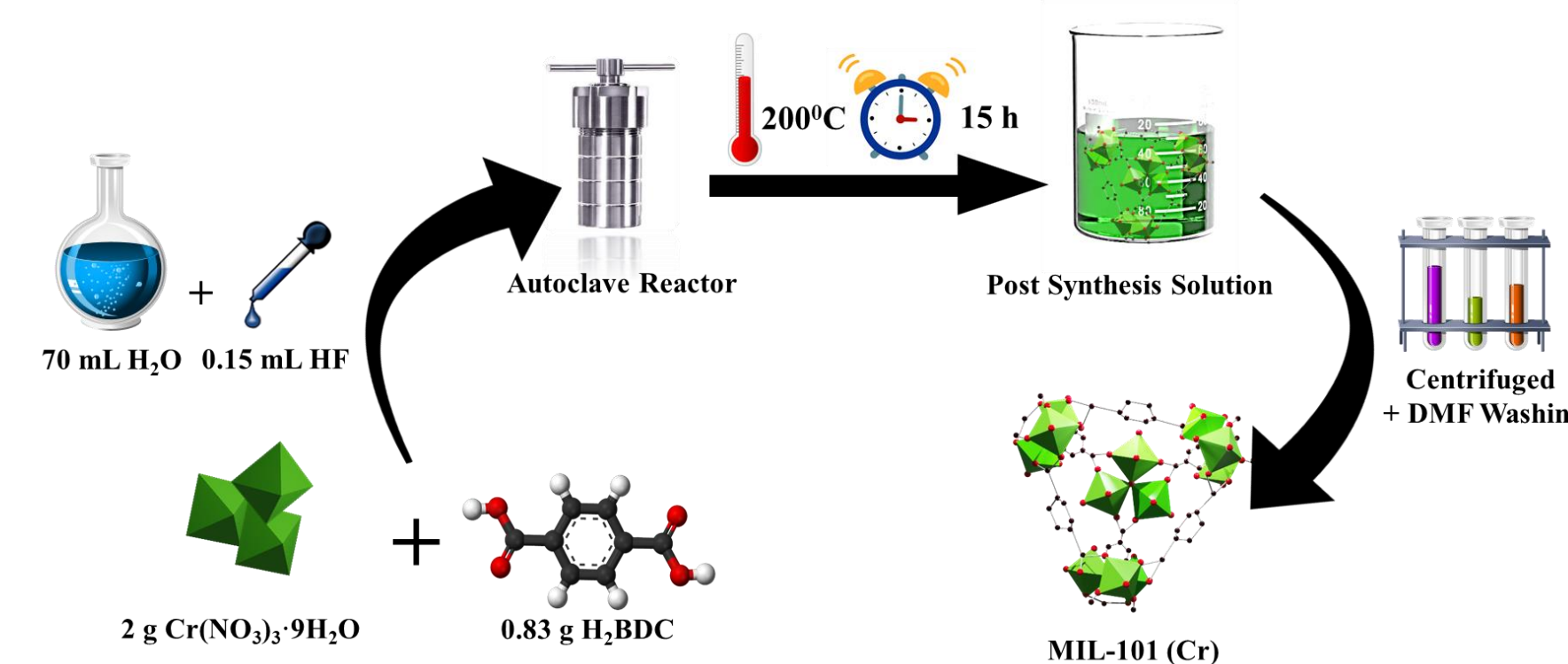


Figure 6. Schematic showing possible interactions during the adsorption of PFOS on MIL-101 (Cr) including electrostatic interaction followed by hydrophobic interaction, metal coordination bonding and H₂ bonding and adsorption of PFOS on AC by hydrophobic interaction. The coupling of MIL-101 (Cr) and AC led to the formation of MIL-101 (Cr)@AC, which will involve all the interactions possible for MIL-101 (Cr) and AC individually. The arrows between the chemical structure qualitatively represent the strength of the interaction between PFOS and adsorbents.

Figure 7 represents the FTIR of all the adsorbents after adsorption. The peaks at 1240, 1205, and 1148 cm⁻¹ correspond to the CF₂ and CF₃ of PFOS groups, while the band at 1073 cm⁻¹ shows that the adsorbents contain a PFOS sulfonic group.



MOFs and their synthesis method



- ❖ 3D crystalline structure
- ❖ Extensive porosity
- ❖ Large surface area
- ❖ Selectivity
- ❖ Shape tunability
- ❖ Potential reusability

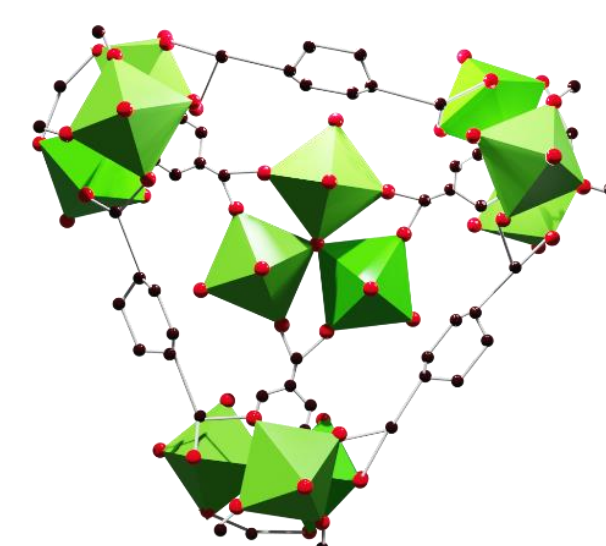


Figure 3. Structure of MIL-101 (Cr) MOF

We will be Synthesizing MIL-101 (Cr), MIL-101 (Cr)@AC & MIL-101 (Cr)-NH₂

Figure 2. Synthesis approach of MIL-101 (Cr) through hydrothermal synthesis.

Results

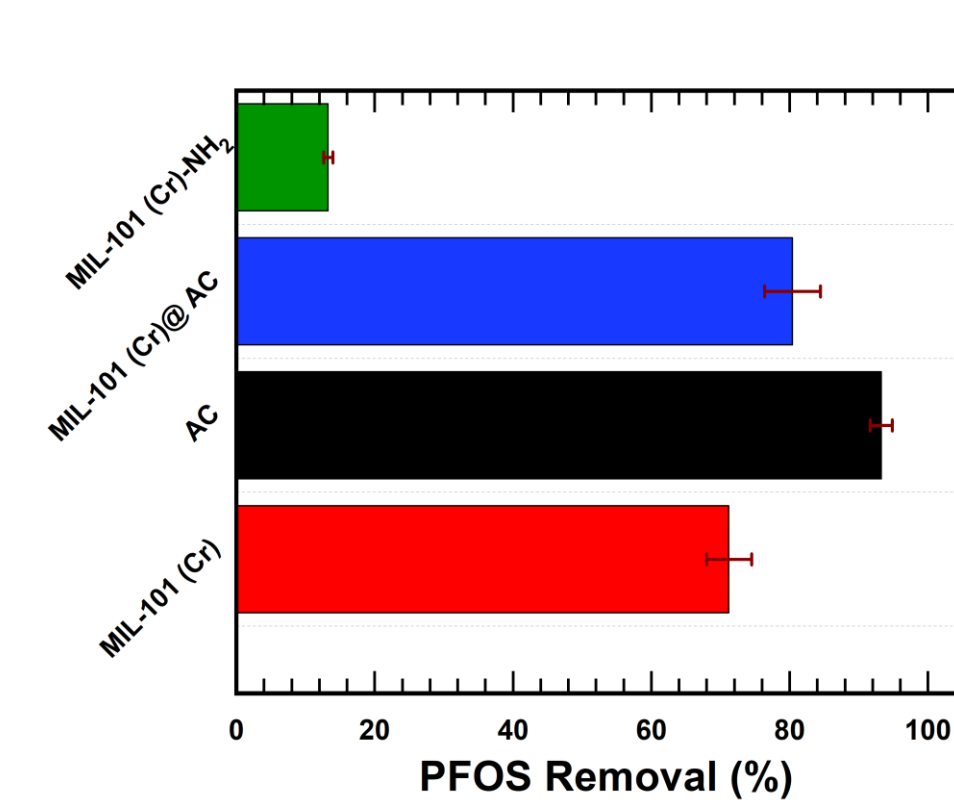


Figure 8. AC had the highest PFOS removal (93%) followed by MIL-101 (Cr)@AC (81%), MIL-101 (Cr) (71%) and MIL-101 (Cr)-NH₂ (16%).

Note

- ❖ All the adsorbents followed pseudo 2nd order reaction.
- ❖ MIL-101 (Cr) and MIL-101 (Cr)-NH₂ fitted Langmuir model while AC and MIL-101 (Cr)@AC fitted Freundlich model.

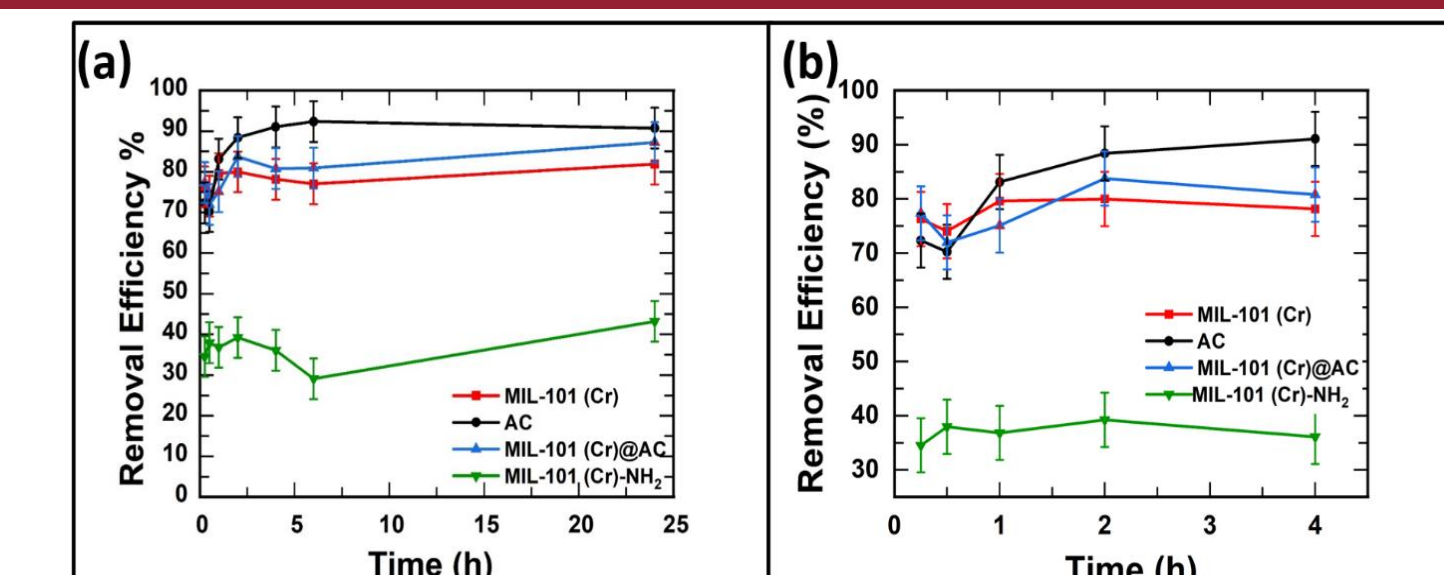


Figure 9. (a) PFOS Adsorption kinetics by (a) MIL-101 (Cr), AC, MIL-101 (Cr)@AC and MIL-101 (Cr)-NH₂ at 15 min, 30 min, 1h, 2h, 4h, 6h, and 24h, (b) The same kinetic data from 1h to 4h.

Characterization of adsorbents

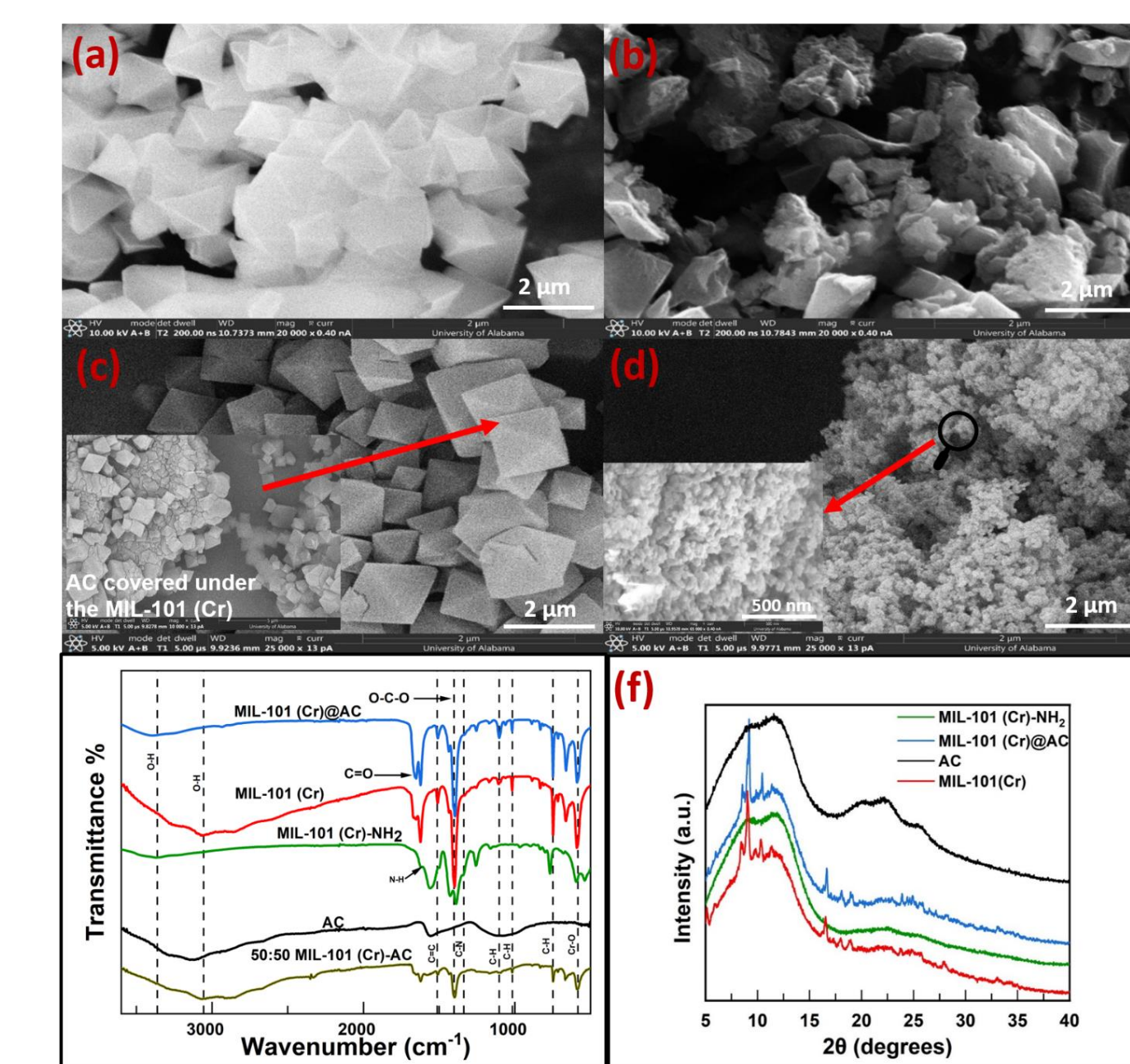


Figure 4. SEM image of synthesized adsorbents: (a) MIL-101 (Cr); (b) AC; (c) MIL-101 (Cr)@AC; (d) MIL-101 (Cr)-NH₂; (e) FTIR spectrum of MIL-101 (Cr), AC, MIL-101 (Cr)@AC, MIL-101 (Cr)-NH₂; (f) XRD pattern of MIL-101 (Cr), AC, MIL-101 (Cr)@AC, MIL-101 (Cr)-NH₂.

Table 1. Z-average size of all the adsorbents at pH 4

Adsorbent	AC	MIL-101 (Cr)@AC	MIL-101 (Cr)	MIL-101 (Cr)-NH ₂
Z-average size (nm)	1070 nm ± 26.16	1274 nm ± 18.72	586.5 nm ± 2.439	316.8 nm ± 0.577

Table 2. Surface area, pore size & pore volume of adsorbents

Adsorbents	Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
AC	1,232.38	5.4568	0.88933
MIL-101 (Cr)@AC	6,955	2.7932	3.44849
MIL-101 (Cr)	2,419.92	2.5995	1.33934
MIL-101 (Cr)-NH ₂	433.1688	12.2019	0.62669

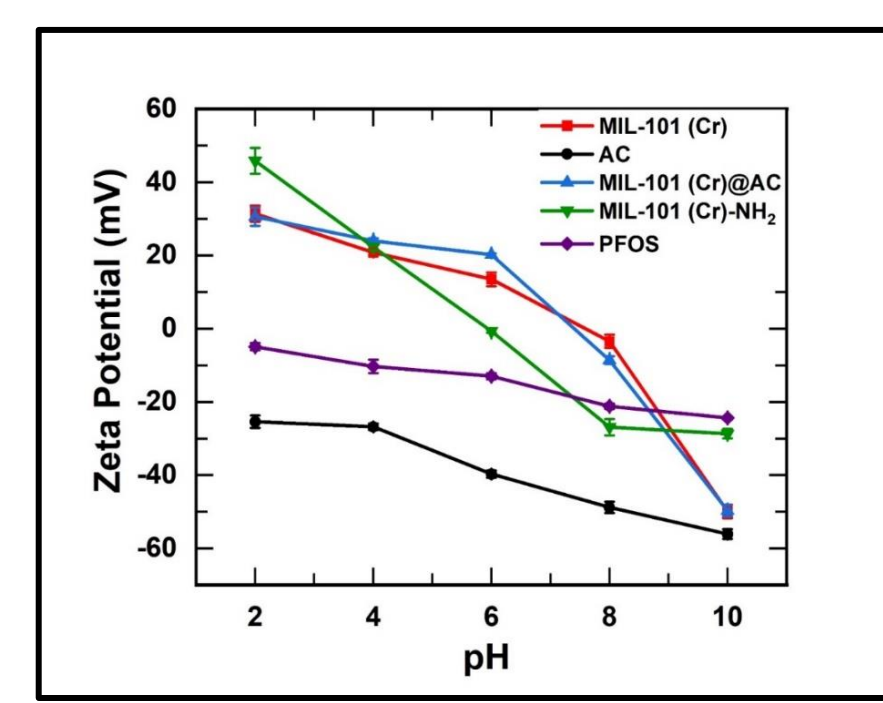


Figure 5. Zeta potential of MIL-101 (Cr); AC; MIL-101 (Cr)@AC; MIL-101 (Cr)-NH₂ at room temperature across pH 2-10 with MOFs concentration 100 ppm and PFOS concentration 2 ppm.



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Regeneration

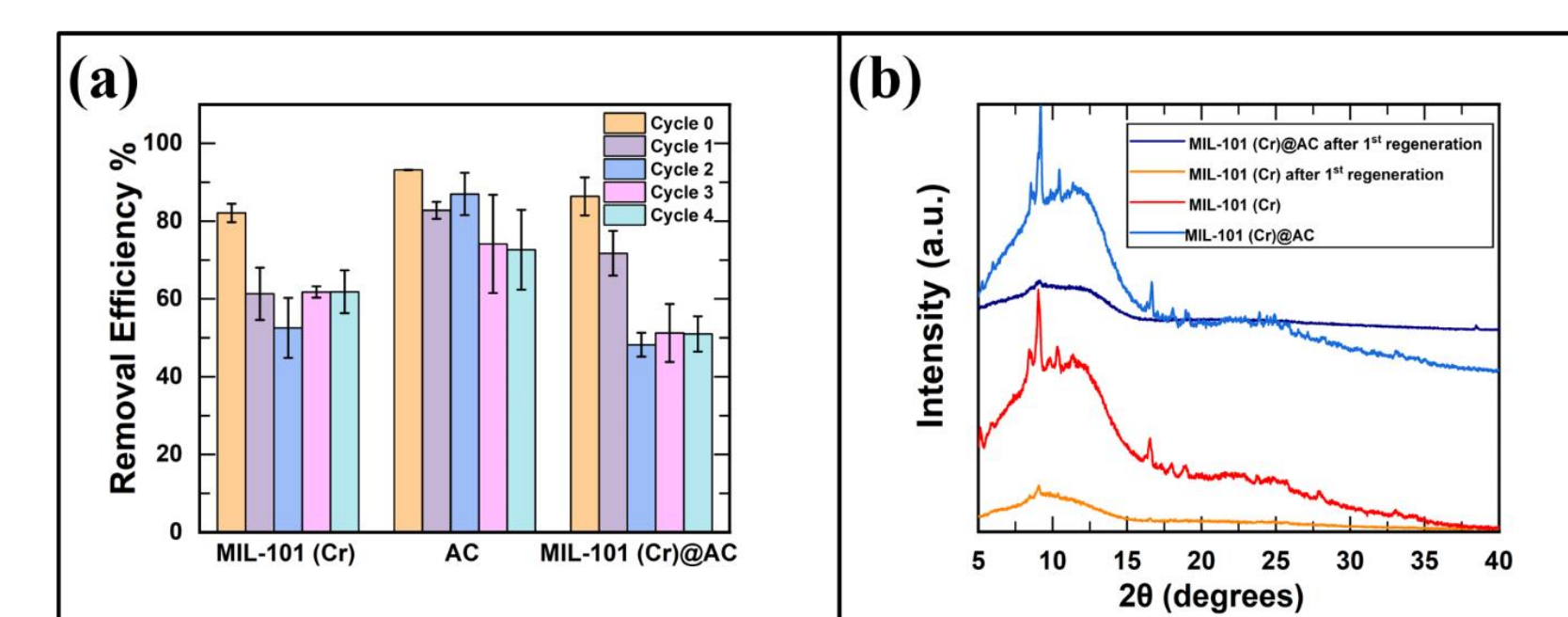
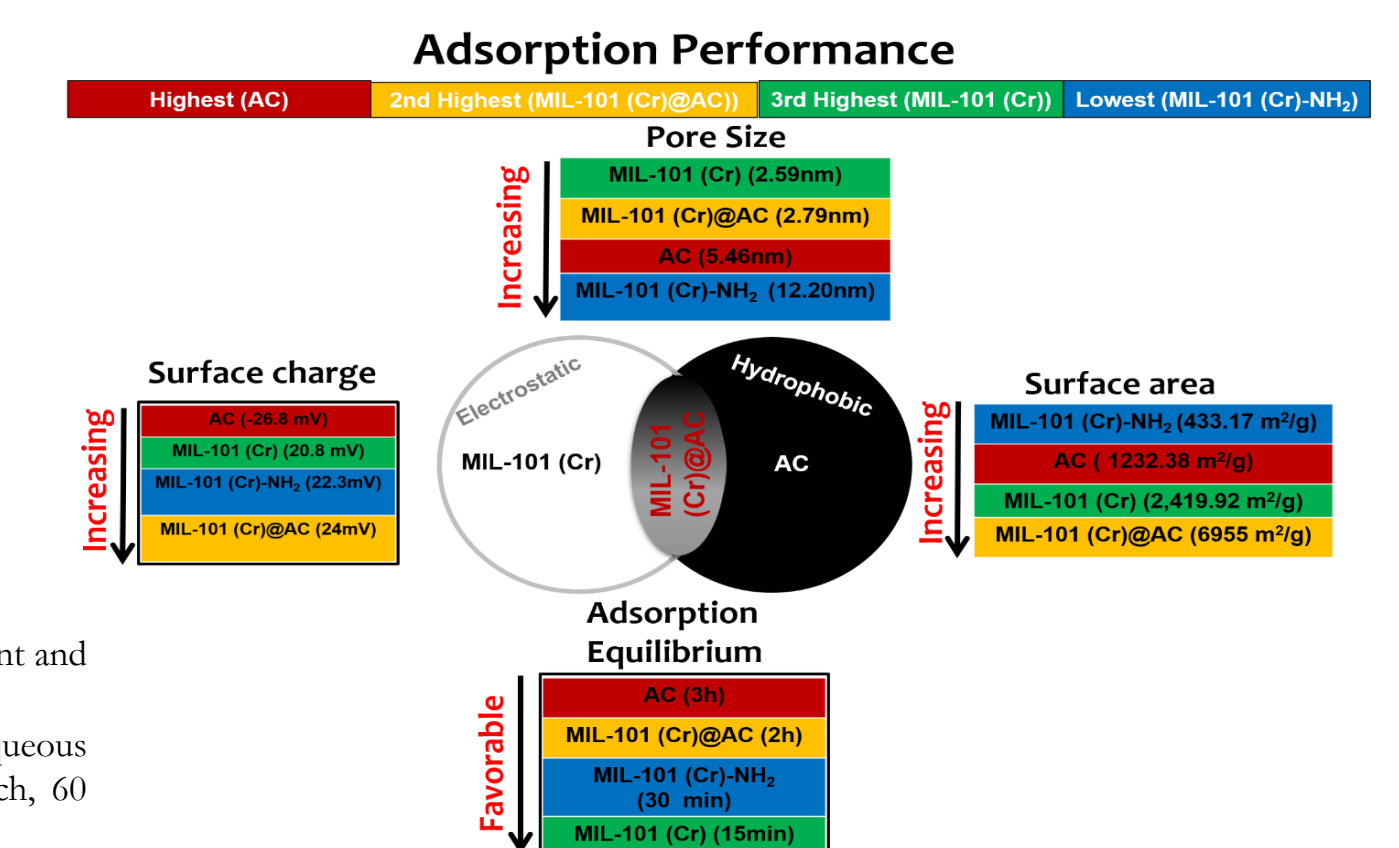


Figure 10. (a) Adsorption-desorption cycles of AC, MIL-101 (Cr) and MIL-101 (Cr)@AC using a 50:50 (V/V) mixture of ethanol and water for 3 h; (b) XRD of MIL-101 (Cr) and MIL-101 (Cr)@AC after 1st regeneration. In the first cycle of adsorption-desorption, there was around 10% decrease in adsorption efficiency for AC followed by MIL 101 (Cr)@AC (approx. 15% decrease) and MIL-101 (Cr) (approx. 20% decrease). This loss in adsorption could be justified based on the alteration in crystallinity of MIL-101 (Cr) and MIL-101 (Cr)@AC after 1st regeneration.

Conclusion

The main overall conclusion of the study is that since each of the adsorbents had specific physicochemical properties controlling the adsorption process and therefore determining the adsorption mechanisms and performance, a more explicit analysis is needed to evaluate the effectiveness of each factor on the adsorption.

Figure 11 illustrates the relative impact of important physicochemical properties, including pore size, surface area, and surface charge, on the adsorption performance of each adsorbent for systematic comparison.



References [1] Le, Esfahani, et al. (2021), "An evolving insight into metal organic framework-functionalized membranes for water and wastewater treatment and resource recovery." Industrial & Engineering Chemistry Research, 60, 19, 6869-6907. [2] H. Shahriyani Far, M. Hasanizadeh, M. Najafi, T.R. Masale Nezhad, M. Rabbani, Efficient Removal of Pb(II) and Co(II) Ions from Aqueous Solution with a Chromium-Based Metal-Organic Framework/Activated Carbon Composites, Industrial & Engineering Chemistry Research, 60 (2021) 4332-4341.

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