Enhanced Adsorption of Perfluorooctanoic Acid (PFOA) from Aqueous Solution by Oak Sawdust Derived Activated Carbon (OSAC)

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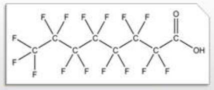
Introduction

What are Perfluorooctanoic Acids (PFOA)



Perfluorooctanoic Acid | $C_8HF_{15}O_2$

History/ Timeline of PFOA

- 1940's — First discovered in Lab
- 1946 — First used in manufacturing
- 1960 — Found in Dupont workers bloodstream
- 1969 — PFOA used in Firefighting foam Linked to liver damage
- 1970 — Research by 3M finds that the PFOA and PFOS are toxic
- 1980 — U.S. Navy study find firefighting foam" kills aquatic life"
- 2019 — Banned globally under the Stockholm Convention
- 2021 — PFAS Action Act of 2021

PFOA Have Been Widely Used in Applications

- Water Proof Jackets
- Fast Food Wrappers
- Electronic manufacturing
- Stain Resistant Furniture
- Firefighting foam
- Nonstick Cooking Appliances

What Happens to PFOA After Usage?

Lakes and Streams → Drinking Water → Himalayan Mountains → Bloodstreams of Nearly all humankind

What are the Environmental Impacts of PFOA

Soluble in water | Extremely Slow Degradation → Bioaccumulation | Biomagnification

Research Need

EPA United States Environmental Protection Agency — Group A3 Carcinogen Perfluorooctanoic Acid

H. R. 2467 — IN THE SENATE OF THE UNITED STATES — PFAS Action Act of 2021

Possible Health Impacts of Exposure

- Cancer
- Alter the immune system
- Low infant birth weights
- Thyroid hormone disruption

Pros and Cons of PFOA Removal Technologies

Reverse Osmosis (RO)	Degradation	Adsorption
Expensive	Expensive	More Affordable
High pressure	High temperature and pressure	Atmospheric temperature and conditions
Breaks easily	Strong Oxidation chemicals	Materials common and affordable
Low yield	High yield	High yield
Needs maintenance	Unreliable/ inconsistent results	Consistent results

Abstract

Perfluorooctanoic acid (PFOA) was first manufactured in 1946 and was dubbed as the "modern miracle of chemistry" because of its ability to "repel" water and oil. These properties have given PFOA vast applications in various products, including everyday items, namely nonstick cooking appliances and fast-food wrappers. However, decades after PFOA's initial production, researchers began linking its exposure to serious health impacts in humans, such as cancer, thyroid disease, ulcerative colitis, and congenital disabilities. Hence, the United States Environmental Protection Agency established health advisory levels which currently stand at 70 ppt. Scientists and engineers have been researching approaches to remove PFOA from water, and adsorption has been one of the best-suited technologies among current methods for PFOA removal. In this study, oak sawdust derived activated carbon (OSAC) was developed to remove PFOA from an aqueous solution. The pore structure of the OSAC was optimized through carbonizing under different temperatures (500°C-1100°C). The surface was chemically functionalized by adding modifying compounds, including boric acid, urea, and polyethyleneimine. The adsorption capacity of OSAC was determined through liquid chromatography-mass spectrometry, and the maximum adsorption capacity of OSAC prepared at 900°C was found to be 83.7 mg/g. In addition, kinetic and isotherm studies were conducted to evaluate the adsorption behavior. Various background ions effects on the adsorption were also studied to explore the possible adsorption mechanism. Moreover, this adsorbent's effectiveness, abundance, and potential low cost may provide a practical solution to reduce PFOA exposure to communities and ecosystems.

Experimental Section and Results

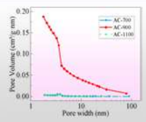
Preparation of OSAC

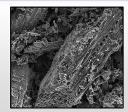
Solid waste + Eco friendly compounds → Carbonize → Undergo Hydrolysis → Activated Carbon Adsorbent

Combine Sawdust and modifier; Grind; Place in Furnace at 500°C, 700°C, 900°C, and 1100°C; Remove modifier

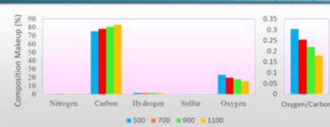
Characterization of OSAC

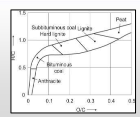
Adsorbent	Specific Surface Area
AC-700°C	649.74 m^2/g
AC-900°C	989.48 m^2/g
AC-1100°C	788.17 m^2/g





Elemental Analysis





Testing Adsorbent Capacity

Activated Carbon Adsorbent + 10 mg/L of PFOA solution → Stir → Test adsorbent capacity (LCMS)

Add PFOA stock solution to oven dried adsorbent; Liquid Chromatography-Mass Spectrometry

Adsorption Behavior

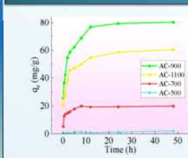


Fig. 1

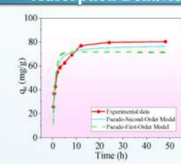


Fig. 2

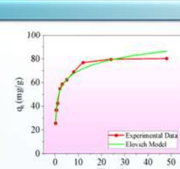


Fig. 3

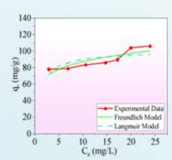


Fig. 4

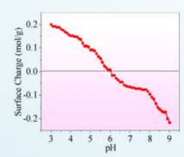


Fig. 5

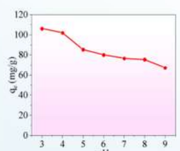
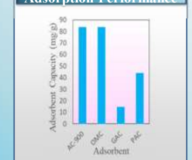
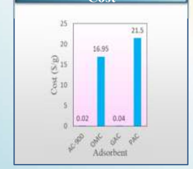


Fig. 6

Discussion

Performance comparison





- **Fig. 1.** AC-900 has the highest adsorbent capacity. The adsorption process for all the activated carbon underwent a steep incline in adsorption capacity in the first 2 hours, followed by a lower adsorption rate from 2 hours to 12 hours. Equilibrium for all activated carbons were reached around 24 hours
- Fig. 2. PFOA-OSAC adsorption reached equilibrium at around 24 hours. The R-squared of the Pseudo First Order is 0.78, while the R-squared of the Pseudo Second Order is 0.92.
- Fig 3. The R-squared of the Elovich model is approximately 0.97, indicating that chemical adsorption may have occurred during this process.
- Fig. 4. The Freundlich Model better describes the experimental adsorption process than the Langmuir Model, which suggests that multilayer adsorption may have occurred during adsorption.
- Fig. 5. The point of zero charge of AC-900 was found at a pH of about 6.0.
- Fig. 6. The adsorption capacity decreases as the aqueous solution becomes more basic.

Environmental Impact Comparison of Activated Carbon

Adsorbent capacity	Oak Sawdust Derived Activated carbon	Ordered Mesoporous Carbon (OMC)	Commercial Granular Activated Carbon (GAC)	Commercial Powdered Activated Carbon (PAC)
Renewable/ nonrenewable	Renewable	Nonrenewable	Nonrenewable	Nonrenewable
Overcome electrostatic force?	Yes	Yes	No	No

Conclusion

- The maximum adsorption capacity of PFOA was 83.7 mg/g for OSAC at a PFOA concentration of 10mg/L.
- The kinetic study demonstrated that the second order reaction model best describes PFOA adsorption, suggesting that this process is chemical adsorption.
- Elemental analysis indicates that as the temperature of carbonization increases, the oxygen to carbon ratio decreases, becoming more hydrophobic.
- The BET test shows that the specific surface area increases with carbonization temperature but begins decreasing after 900°C as the carbon structure starts to collapse.
- Adsorption capacity is higher in acidic aqueous solutions.
- Adsorption is still observed in the presence of negative surface charges. Thus, OSAC's hydrophobic attraction may overcome electrostatic repulsion.

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