Challenges in the removal of per-fluoroalkyl substances (PFAS) from biosolids

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Abstract

Per- and poly-fluoroalkyl substances (PFAS) represent a persistent group of emerging pollutants that have significant adverse health effects on the human and ecosystem. Due to their extensive use across various industries and their slow degradation, PFAS concentrations in water resources have been on the rise. Numerous methods have been employed to remove PFAS from different matrices, with a strong emphasis on drinking water due to the stringent Environmental Protection Agency (EPA) limits.

However, research on elimination of PFAS from complex matrices such as sewage sludge has been relatively limited due to the challenges presented by the unique properties of sludge. The existing literature on PFAS removal from sludge often faces obstacles and insufficiencies. This paper aims to introduce the existing methods for PFAS removal and degradation from biosolids while reviewing the challenges and inefficiencies associated with these methods.

Keywords: per- and poly-fluoroalkyl substances (PFAS), biosolids, thermal treatment, advance oxidation, adsorption, persistent emerging pollutants

Introduction

Poly- or per- fluoroalkyl substances (PFAS) [1-9]

PFAS characteristics

- Aliphatic fluorinated anionic surfactants
- Hydrophobic: alkyl chain with the C-F bonds that are partially (poly) or fully (per) substituted with fluorine atoms
  Hydrophilic: terminal functional group such as sulfonate, carboxylate, phosphonate, etc.
- High chemical and thermal stability, distinctive wettability, and friction properties
- **Resistivity to degradation methods**

PFAS applications

- Fire-fighting foam and flame-resistant substances
- Adhesives
- Detergents and cleaning products
- Coatings, for water-repellency properties
- Electronics industry
- Metal plating and finishing industries
- Mining, oil, and gas industries
- Packaging, paper, and cardboard

PFAS health hazards

- Endocrine and metabolic disruption : interference with the estrogenic, thyroid and androgenic hormonal pathways
- Immunotoxicity
- Hepatotoxicity
- Tumorigenic effect
- Reproductive/developmental toxicity

While regulations put in place in 2018 by EPA, were limiting the combined concentrations of Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS) in drinking water to 70 ng/L, in March 2023, the USEPA proposed even stricter standards for six PFAS compounds, specifically PFOA and PFOS, setting individual maximum contaminant levels (MCLs) at 0.004 ppt for PFOA and 0.02 ppt for PFOS [10].

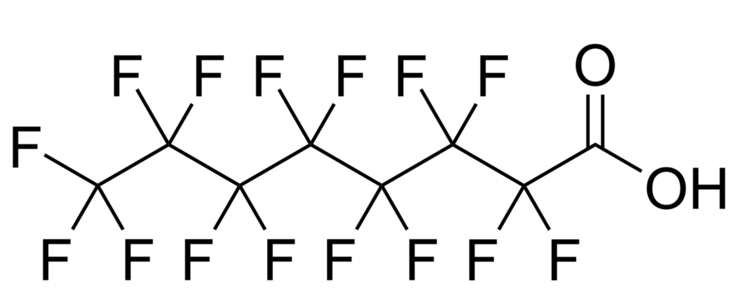

Figure 1. PFOA chemical structure [11]

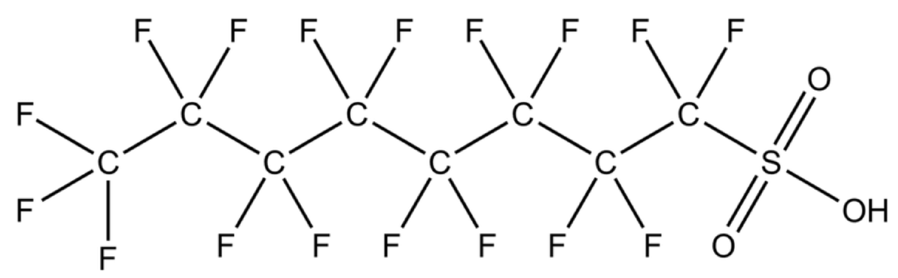

Figure 2. PFOS chemical structure [12]

PFAS occurrence in biosolids

Accumulation of PFAS in biosolids:

The existence of PFAS in biosolids is confirmed With PFOA and PFOS being the most frequently detected ones [13, 14].

Accumulation of PFAS in sludge-amended soils:

Highest concentrations were observed for PFOS (ranging from 2.7 to 18.3 ng. g−1), followed by PFOA (ranging from 0.2 to 2.4 ng. g−1) and PFDA (ranging from 0.1 to 1.01 ng. g−1) in farming lands [15].

Transformation of precursors:

The concentration of some selected PFAS has increase in the sewage sludge compared to the influent of wastewater treatment plant. The increase is attributed to the transformation of PFAS precursors in wastewater treatment process [16].

PFAS treatment methods in biosolids

Thermal destruction methods

Thermal treatment methods generally use heat to transform materials. An oxidation reaction is involved where the pollutant is oxidized in presence or absence of oxygen. Combustion process, same thing that happens in incinerators, uses oxygen as the oxidant to oxidize the pollutants. Other thermal treatment methods such as pyrolysis and gasification take place in absence of oxygen and been widely used for stabilization of sludge. Most of methods studied for treatment of PFAS in sludge are thermal methods [17, 18].

Incineration [19, 20]

- 81 to 97% removal efficiency
- High energy demand
- Complex and expensive emission control process: alkaline, urea, coke dosing, and textile filtration
- Temperature: 1000-1200°C
- ✓ PFAS containing gaseous emissions
  ✓ Hazardous intermediates and by-products formation
- **Main research gap:** Production of Target and non-target PFAS compounds during the process, fate of PFAS in gas phase

Pyrolysis and gasification [21, 22]

- Decomposition of PFAS by keeping them within the reactor's hot zone before they volatilize and exit.
- **Main research gap:** Fate of PFAS in pyrolysis process; destruction or volatilization

Hydrothermal liquefaction (HTL)

- high pressure and temperature: 10-25 MPa, 250-350°C [23]
- ✓ **PFOA** removal: 96 to 99% [24]
  ✓ **PFOS** removal: 34% [24] enhanced to 86% with addition of KOH [25]
  ✓ Not totally successful for many other PFASs
- Production of crude oil from solid waste and sludge
- **Main research gap:** Fate of PFAS precursors (increase in concentration of PFOS has been evidenced in a few studies.

Smoldering combustion

- Thermal oxidation by diffusion of an oxidant air through the surface of a condensed liquid or solid fuel
- Uncomplete mineralization of PFAS
  Production of fluorinated by-products [26]
- High PFAS removal from biosolids are reported by a few studies
- **Main research gap:** Efficiency acknowledgement; Gas emissions analysis

Supercritical Water Oxidation (SCWO)

- high pressure and temperature: 22.1 MPa, >374°C
  Supercritical state of water where insoluble inorganic compounds dissolve in water and organic pollutants breakdown chemical reaction are possible [27].
- The initial external energy kickstarts the reaction, but the subsequent heat generated drives the process forward.
- Effective in treating various matrices like water-associated waste streams, slurries, and sludges [28]
- high fluorine conversion rate of up to 78.2% at 500°C after 60 minutes is reported [29].
- **Challenges:** Corrosive gas evolution, By-products like trifluoromethane formation [18]
  Relatively high energy demand

Electrochemical Oxidation (EO)

- Utilization of electricity to create oxidative species at the anode electrode, which then react with PFAS and degrade it [30].
  Effective performance in water and wastewater treatment [31]
- **Weakness:**
  ✓ Generation of hazardous by-products such as organic halides, HF, chlorine gas, and perchlorate [18]
  ✓ Usage of heavy metal electrode: potential release of toxic substances
- Performance in soil treatment: 51.7% PFOA and 33% PFOS removal [32]
- **Research gap:**
  ✓ Analysis of method's efficiency in the removal of PFAS from biosolids
  ✓ By-products formation
  ✓ Energy consumption
  ✓ Electrode material consumption rate
  ✓ Costs evaluations

Conclusions

PFAS has emerged as a significant global concern due to its persistence and ability to bioaccumulate. Treating this pollutant in unique matrices like sludge presents a crucial challenge, given its presence in biosolid-amended agricultural soils and groundwater.

In conclusion, thermal treatments are widely used commercially for sewage sludge degradation showing acceptable degradation efficiencies. However, they are associated with drawbacks such as the generation of by-products, transformation of precursors into PFAS, high energy requirements, and harmful emissions. Moreover, the research is limited on their performance and side reactions and products. Other methods such as EO have been used for water and wastewater treatment successfully. Water and wastewater treatment has seen successful application of EO. However, when it comes to treating PFAS from biosolids, EO remains relatively unexplored, to the best of author's knowledge. Researchers must be prepared to address potential challenges, such as high energy requirements, generation of by-products, extensive electrode usage, and incomplete mineralization of PFAS and other organic pollutants found in sludge.

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