Removal of Per- and Polyfluoroalkyl Substances (PFAS) Using Polyaniline-Grafted Chitosan Bio-adsorbent (PG-CB)

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Introduction

PFAS contamination in water

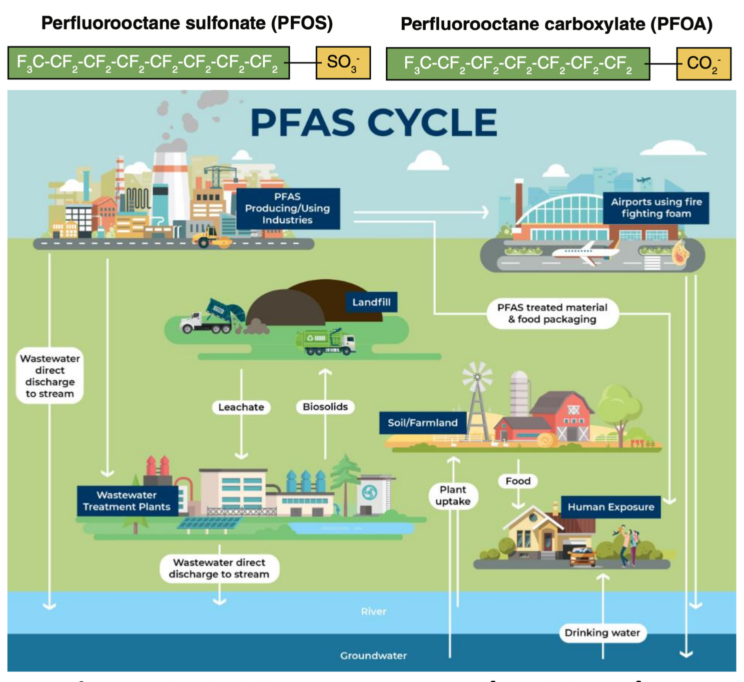
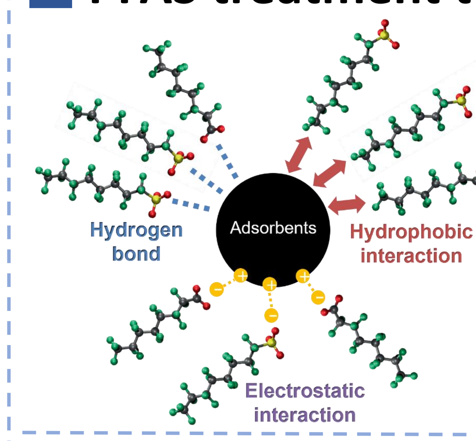


Figure 1. PFAS structures and PFAS cycle.
McAlisterGeoScience (2020.06.24)

- ❖ Per- and Polyfluoroalkyl Substances (PFAS) represent a large group of organofluorine compounds widely used as surfactants.
- ❖ PFAS are persistent and can accumulate over time in the environment and human body, indicating harmful effects.
- ❖ PFAS can be released into environment when wastewater is discharged without sufficient treatment.
- ❖ The U.S. Environmental Protection Agency (USEPA) has tightened the regulatory limit for PFAS to 4 ppt and expanded to 6 PFAS (PFOA, PFOS, PFNA, PFHxS, PFBS, and GenX).

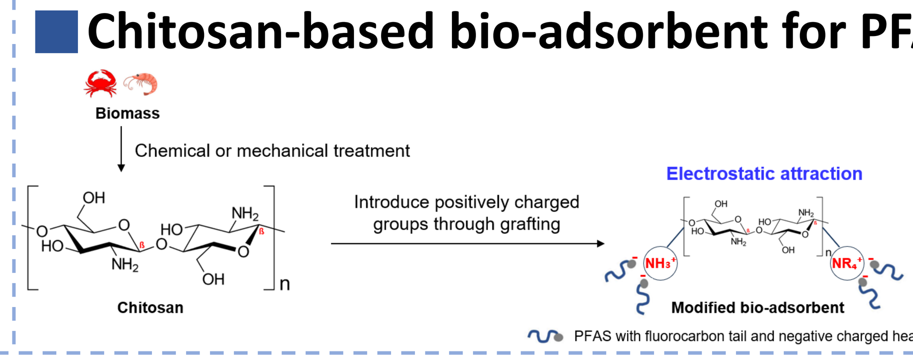
PFAS treatment technologies



- ❖ PFAS treatment technologies include adsorption and ion exchange, oxidation and coagulation, and degradation using microorganisms.
- ❖ PFAS are difficult to remove or degrade due to their high chemical stability, so physical treatment processes using adsorbents are more effective than other processes.
- ❖ In particular, biomass-based adsorbents are cost-effective and eco-friendly, and are suitable for the removal of a full range of PFAS, including short-chain PFAS, by functionalizing functional groups.

Figure 2. Adsorption mechanism between PFAS and adsorbents.

Chitosan-based bio-adsorbent for PFAS removal



- ❖ Chitosan can be extracted from biomass and easily modified for PFAS adsorption.
- ❖ Cross-linking the amine group of chitosan enhances its PFAS adsorption ability.
  → This increases reactivity with anionic PFAS by modifying the cationic groups, enhancing adsorption efficiency.

Figure 3. Interaction between modified chitosan and PFAS.

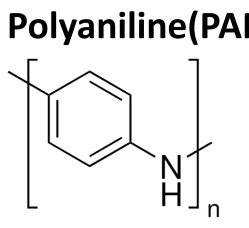
Research Objectives

- ❖ To synthesize Polyaniline-Grafted Chitosan Bio-adsorbent (PG-CB) and compare its performance with other commercial adsorbents.
- ❖ To evaluate the removal efficiency of 6 newly regulated PFAS (PFOA, PFOS, PFNA, PFHxS, PFBS, and GenX) by the EPA using the PG-CB.

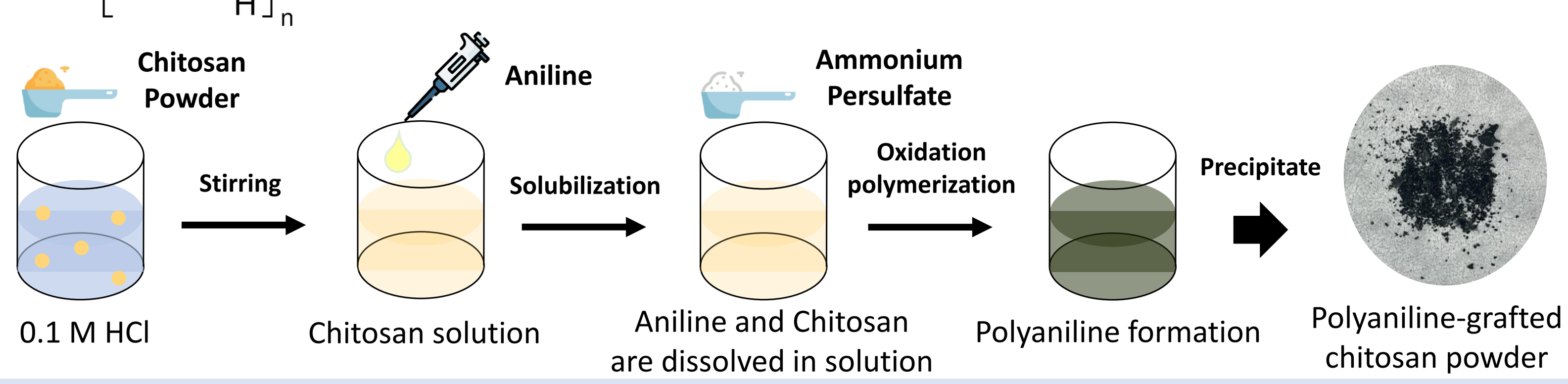
Methods

Synthesizing Polyaniline-Grafted Chitosan Bio-adsorbent (PG-CB)

❖ **Polyaniline(PANI)-grafting**



- Aniline's benzene ring (hydrophobic) and amino group (NH_2, hydrophilic) support cross-linking and polyaniline formation.
- Polyaniline provides large active sites effective for removing anionic PFAS.



PFAS adsorption tests

1. Evaluate the removal efficiency of 6 regulated PFASs using PG-CB

- Reaction time : 30 min, 1 hour
- Target PFAS : PFOA, PFOS, PFNA, PFHxS, PFBS, GenX
- PG-CB dosage : 0.5 g/L
- PFAS analysis : HPLC-MS/MS

2. Adsorption performance comparison in real water with other commercial adsorbents

❖ **Target PFAS and industrial wastewater information**

Industrial wastewater effluent from Daegu
General equipment manufacturing industry (e.g., metal sheeting and automobile devices)
Capacity : 17,304 m³
DOC of industrial wastewater : 6000 mg/L

- PFAS detection reported in the Nakdong River basin.
- A total of 11 compounds were detected, including PFBA, PFPeA, PFHxA, GenX, PFOA, PFHpA, PFHxS, PFMOPrA, PFOS, and PFDA.

❖ **Adsorption experiment method (Jar test)**

- Reaction time : 30 min
- Adsorbents : Powder-Activated carbon (F400, SG), Ion-exchange resin (A520E, MIEX), Bio-adsorbent (PG-CB)
- Adsorbents dosage : 0.05, 0.1, 0.2, 0.5 g/L

Results & Discussion

Characterization with SEM-EDS

→ To investigate the surface characteristics and elemental composition of the adsorbent.

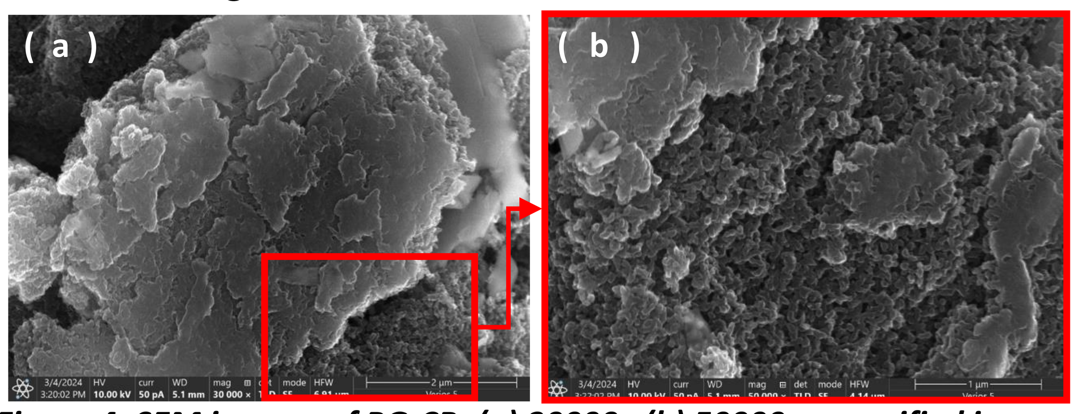


Figure 4. SEM images of PG-CB. (a) 30000x (b) 50000x magnified images.

Table 1. Elemental composition of PG-CB.

Element	PG-CB (wt.%)
C	65.5
N	16.4
O	18.1

- ❖ Irregular surface → Enhances the interaction between surface of the adsorbent and PFAS.
- ❖ Porosity → Increases surface area and promotes molecular diffusion within the adsorbent, enhancing adsorption efficiency.
- ❖ Higher N content than Chitosan (6 wt.%) → PANI modification of chitosan introduces amine group effect.

Characterization with FT-IR

→ To examine the atomic bonds present on the adsorbent surface.

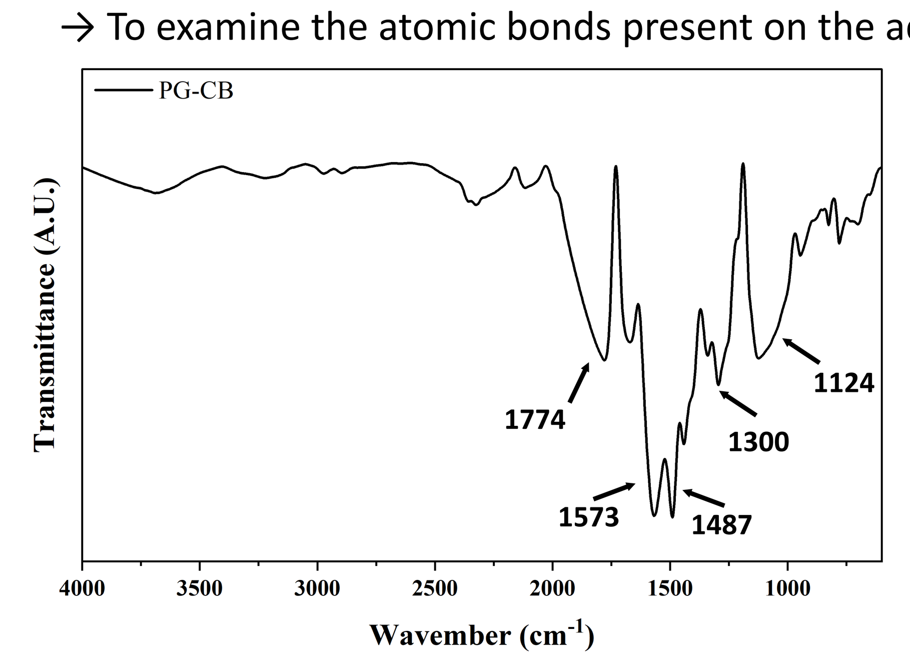


Figure 5. FT-IR spectra of PG-CB.

- ❖ 1774 cm^{-1} : aromatic C-H
- ❖ 1573 cm^{-1} : N-H stretching
  → Enhances electrostatic interaction with PFAS
- ❖ 1487 cm^{-1} : C-H stretching
- ❖ 1300 cm^{-1} : C-N of aromatic amines
  → Successful grafting of PANI onto the chitosan, enhancing functional properties.
- ❖ 1124 cm^{-1} : C-O stretching

Characterization with XPS

→ To confirm the elemental composition and chemical bonding states.

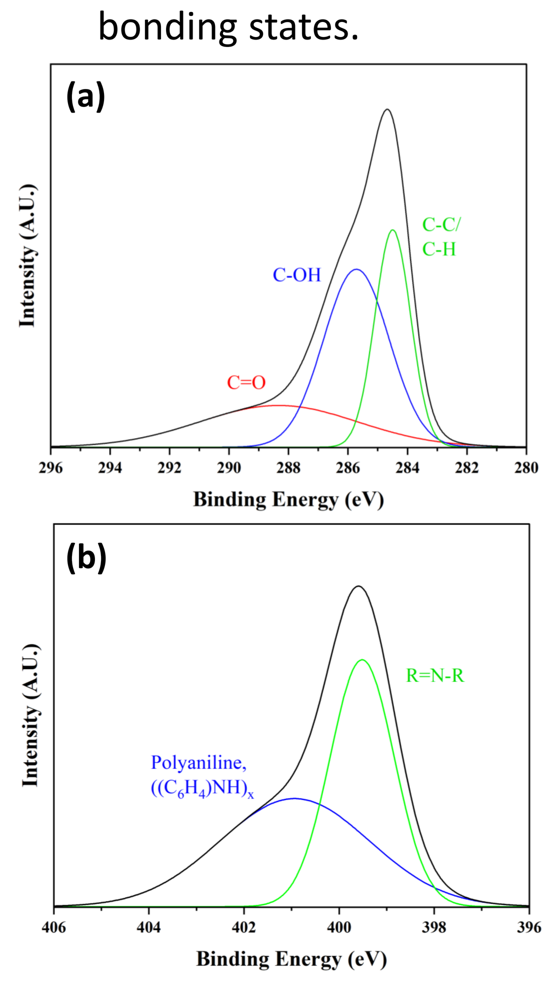


Figure 6. XPS spectra of PG-CB. (a) C1s (b) N1s.

C1s

- ❖ 284.5 eV : C-C/C-H
- ❖ 285.7 eV : C-OH
- ❖ 288.4 eV : C=O

N1s

- ❖ 399.5 eV : R=N-R
- ❖ 400.9 eV : Polyaniline $((C_6H_4)NH)_x$

→ **Grafting PANI on chitosan**

Removal efficiency of 6 regulated PFASs by PG-CB.

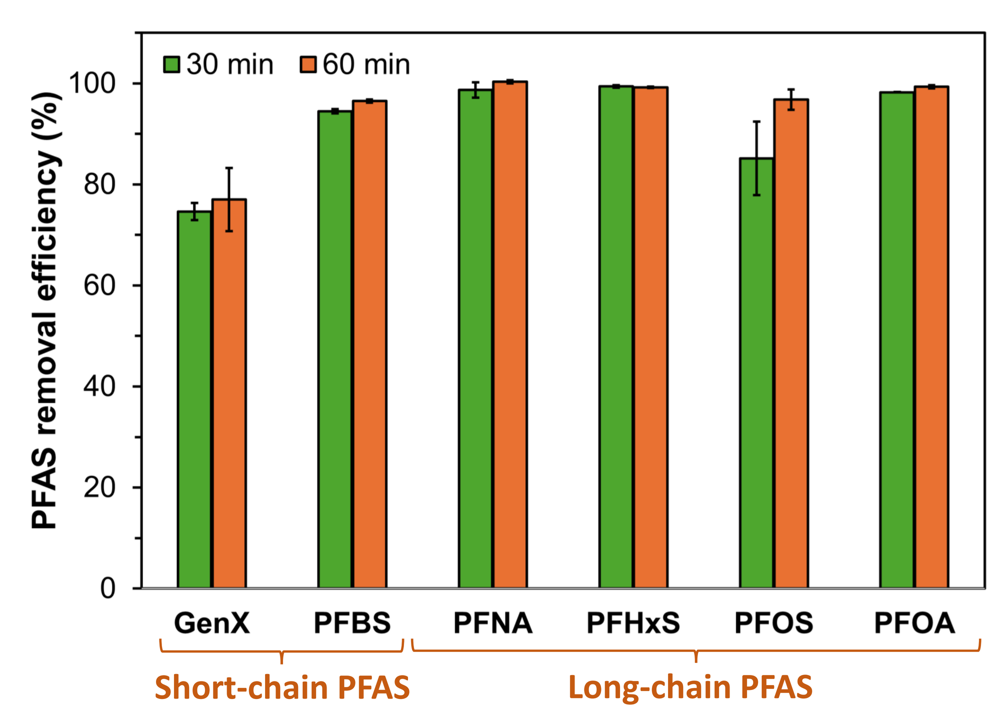


Figure 7. Removal efficiency of different PFAS in a mixture by PG-CB at an initial concentration of 100 ppb for each PFAS.

- ❖ High removal efficiency observed for long-chain and short-chain PFAS.
- ❖ Relatively lower removal efficiency for **GenX**.
  → GenX bindings with active sites are unstable, more hydrophobic PFAS replace the adsorbed GenX.

Adsorption performance comparison in real water with other commercial adsorbents.

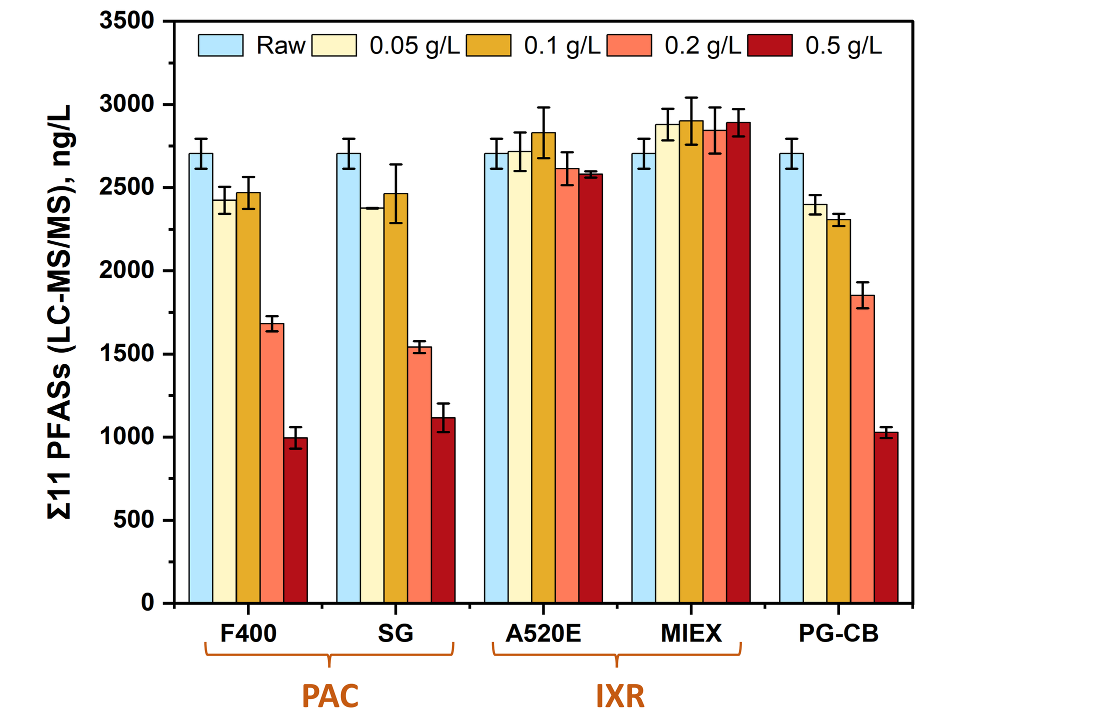


Figure 8. Summary of PFAS removal trend by adsorbents dosage evaluated using LC-MS/MS.

- ❖ PAC, PG-CB : Exhibited high total removal rates, approximately 59-76%.
- ❖ IXR : Relatively lower removal rates, ranging from -8-29%.

Conclusions

- ❖ Characterization of the synthesized Polyaniline-Grafted Chitosan Bio-adsorbent (PG-CB) confirmed its suitability for PFAS adsorption.
- ❖ Adsorption experiments on 6 newly regulated PFAS by the EPA confirmed that, unlike activated carbon, PG-CB effectively remove both long-chain and short-chain PFAS.
- ❖ PG-CB showed comparable PFAS removal efficiency to Powder-Activated carbon when compared with other commercial adsorbents (F400, SG, A520E, MIEX).
- ❖ Future work can evaluate adsorption capacity of PG-CB across various water matrices.

Acknowledgement

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