A Comparative study on PFAS removal by Various Adsorbents Using Comprehensive Analytical Methods in Industrial Wastewater

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Introduction

PFASs contamination in drinking water

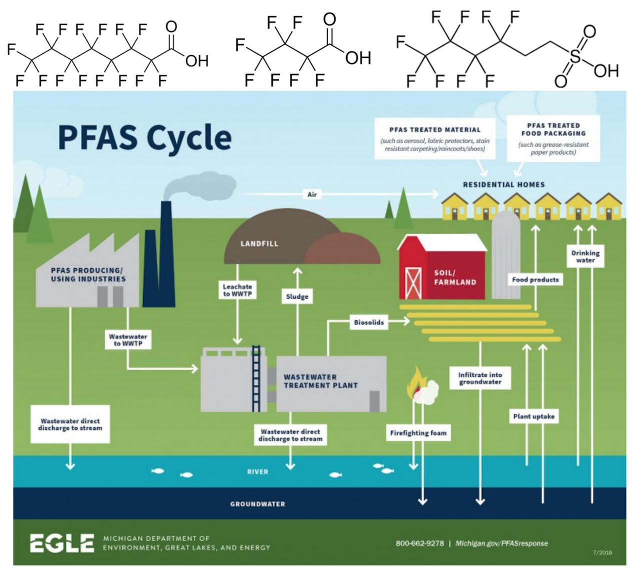


Figure 1.PFAS structures and PFAS cycle.
Michigan.gov/PFASresponse(2023.10.12)

- PFASs represent a large group of organo-fluorine compounds that are widely used as surfactants in consumer products.
- PFASs are persistent chemicals that can accumulate over time in the environment and human body, potentially causing harmful effects.
- Beginning with the Stockholm Convention in 2009, which set a regulatory limit for major PFASs at 0.07 ppb (μg/L), drinking water regulations have become increasingly stringent. More recently, the U.S. Environmental Protection Agency (USEPA) has further tightened these standards to a regulatory limit as low as 0.004 ppb.
- Potential exposure to PFAS can occur through various routes, including non-stick cookware, grease-resistant paper, fast food wrappers, and convenience packaging.
- PFASs can be released into environment when wastewater from industrial facilities or household activities is discharged without sufficient treatment.

PFASs treatment technologies

- Various studies have been conducted to remove PFASs from water using different processes. The treatment processes include physical, chemical, and biological methods. Physical treatment involves adsorption and ion exchange, chemical treatment includes oxidation and coagulation, and biological treatment involves degradation using microorganisms.
- Due to the unique properties of PFASs, which are difficult to remove or degrade, physical treatment processes using adsorbents are proving to be more effective in their removal compared to other processes.
- By applying O_3 treatment, PFAS precursors undergo oxidation, transforming them into compounds that are more amenable to adsorption. This transformation can increase the overall removal efficiency.

Research Objectives and Scope

- Removing various types of PFASs present in actual industrial wastewater effluent.
- Synthesis of chitosan-based adsorbents to enhance removal efficiency, and comparison with commercial adsorbents in PFASs removal.
- Comparison of quantification method; targeted analysis using LC-MS/MS, total quantification using CIC and analysis with and without TOP assay and O_3 treatment.

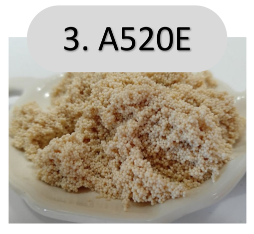
Material & Methods

Adsorbents

Powder- Activated carbon (PAC) · **Ion-exchange resin (IXR)** · **Biosorbent**

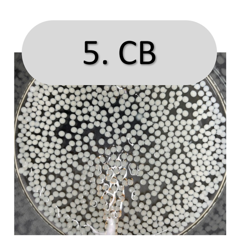
1. Commercial activated carbon
2. Surface area : 1170 m^2/g

1. Used in Busan (Sin-gwang)
2. Surface area : 1150 m^2/g

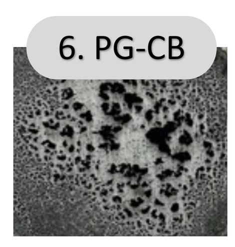


1. Polystyrenic
2. Surface area : 36 m^2/g

1. Magnetic
2. Surface area : 2 m^2/g



1. Chitosan Biosorbent (CB)
2. Glutaraldehyde Crosslinked chitosan beads
3. Surface area : 3 m^2/g



1. Polyaniline-Grafted Chitosan Biosorbent (PG-CB)
2. Preparation :
   1) Chitosan powder + polyaniline in acidic solution
   2) Add Ammonium persulfate(APS) as catalyst
3. Surface area : 63 m^2/g

Reaction condition

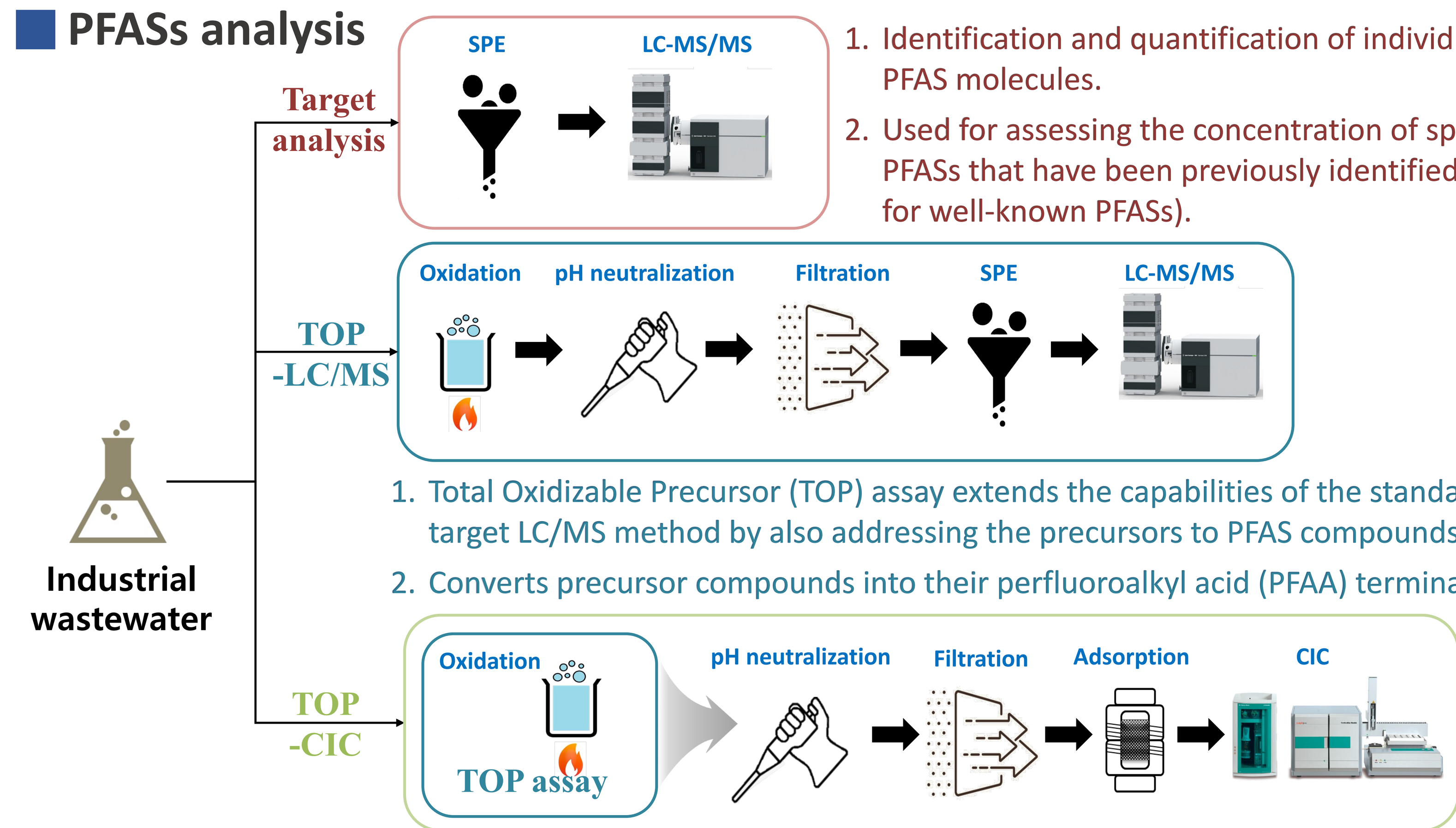
Adsorption Experiment Method (Jar test)

1. Reaction time : 30 min
2. Adsorbents dosage : 0.05, 0.1, 0.2, 0.5 g/L
3. O_3 concentration : ~ 1mgO_3/mgDOC

Target PFAS and Industrial Wastewater information

1. Industrial wastewater effluent from Daegu
2. LC-MS analysis was conducted for 32 different PFASs, only 11 PFASs are detected.

PFASs analysis



Target analysis:
1. Identification and quantification of individual PFAS molecules.
2. Used for assessing the concentration of specific PFASs that have been previously identified (only for well-known PFASs).

TOP-LC/MS:
1. Total Oxidizable Precursor (TOP) assay extends the capabilities of the standard target LC/MS method by also addressing the precursors to PFAS compounds.
2. Converts precursor compounds into their perfluoroalkyl acid (PFAA) terminals.

TOP-CIC:
1. Focuses on the total ionizable PFAS present in the sample, following the oxidation of precursors.
2. Effective for detecting a wide range of PFAS compounds, including unknown PFASs, while excluding non-PFAS compound.

Results & Discussion

Occurrence and composition of PFASs in industrial wastewater

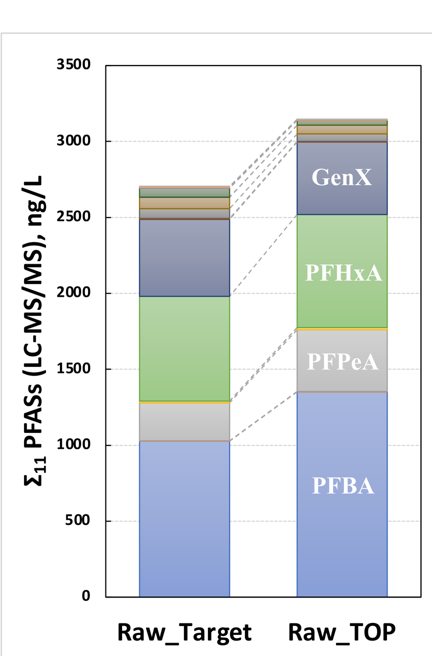


Figure 2. PFAS concentration of industrial wastewater

- The total PFAS concentration(Σ11 PFASs) in the industrial wastewater effluent was in the range of 2.6 to 2.7 ppb.
- Analysis was conducted for 32 different PFASs, only 11 PFASs are detected.
- 11 compounds were detected, including PFBA, PFPeA, PFHxA, GenX, PFOA, PFHpA, PFHxS, PFMOPrA, PFOS, and PFDA. The highest concentration was observed for PFBA, at approximately 1 ppb.
- 17 compounds were not detected. Additionally, four compounds were found at concentrations within 10 times the limit of quantification (LOQ) and were excluded from the removal efficiency evaluation.
- After TOP oxidation, the total concentration increased by approximately 1.2 times.

Removal behaviors of individual PFAS evaluated using LC-MS/MS (without & with) TOP analysis

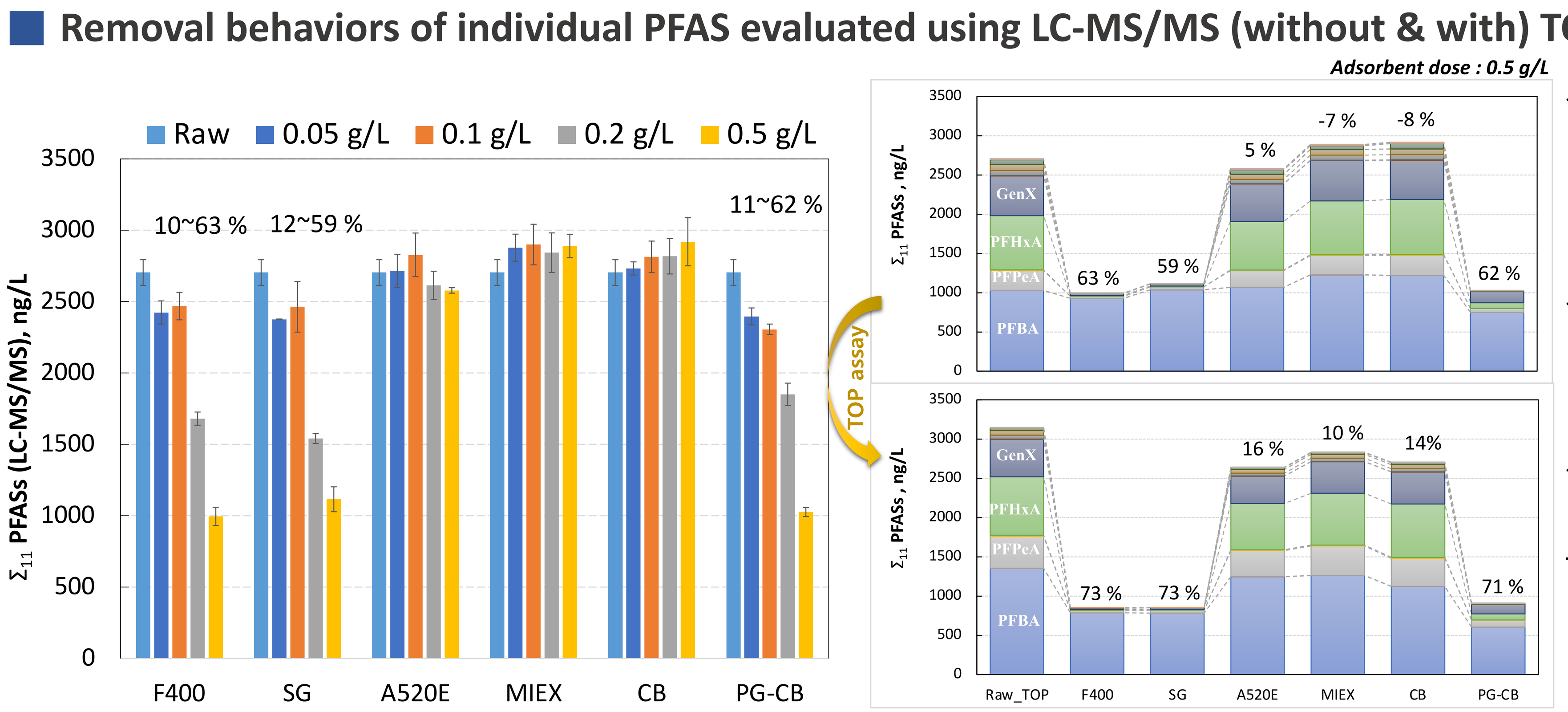


Figure 3. PFAS removal evaluated using LC/MS

- PAC and PG-CB show a high removal efficiency of 59-73 % at a dose of 0.5 g/L. And as the dose increases, the removal efficiency increases
- Despite the low removal rates for PFBA (0~10 %), PG-CB demonstrates higher removal efficiency for PFBA at 27 %.
- With TOP assay, an increase in removal efficiency was observed.

→ The increase in initial concentration following TOP leads to an improved removal rate. This indicates that some precursors are removed by the adsorbent.

Removal behavior of total PFAS evaluated using TOP-CIC analysis

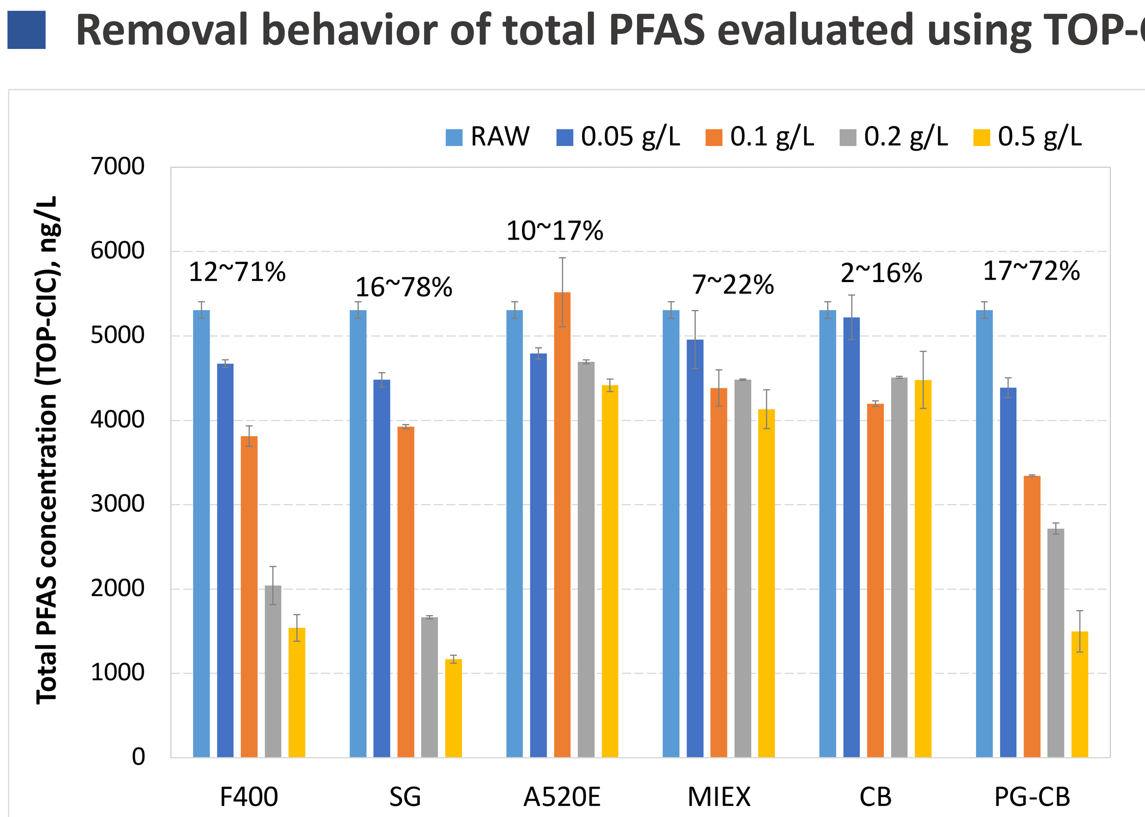


Figure 4. PFAS removal evaluated using TOP-CIC (without O_3 treatment)

- TOP-CIC results for the industrial wastewater effluent were 5.3 ppb before O_3 treatment and 5.0 ppb afterwards.

→ The increase in concentration compared to LC-MS/MS is due to the inclusion of unknown-PFAS compounds.

- PAC and PG-CB achieved a removal efficiency of approximately 70-80% at 0.5 g/L.

→ The overall trends are similar, yet the removal efficiencies were higher compared to those observed with LC-MS/MS.

- The removal efficiency of IXR and CB also increased compared to LC/MS but remained lower that of PAC and PG-CB.
- After O_3 treatment, an overall enhancement in removal were about 10 %.

Comparison of removal efficiency

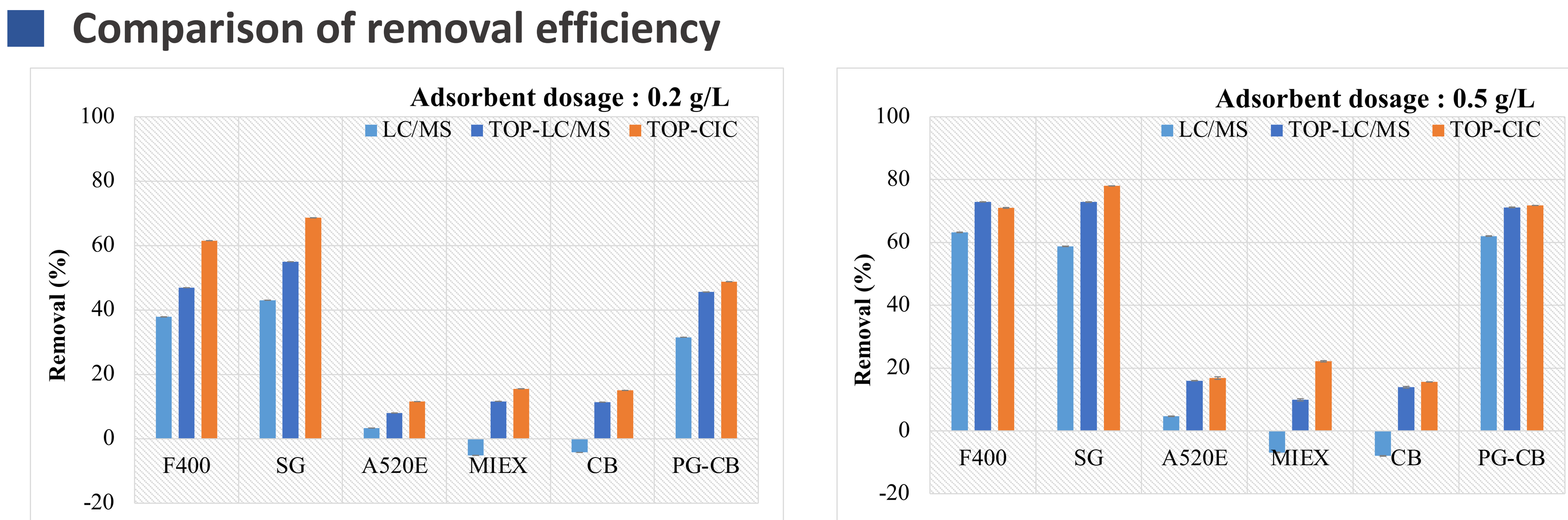


Figure 5. Comparison of removal efficiency

- PAC exhibits a much larger surface area compared to other adsorbents, leading to its higher removal efficiency. The high removal rates for long-chain PFAS suggest that adsorption occurs through hydrophobic interactions.
- Despite its comparatively lower surface area, PG-CB showed high removal rates. This can be attributed to the amine groups in polyaniline and chitosan, which likely facilitate adsorption through electrostatic attraction.
- For IXR and CB, might expect adsorption through ion-exchange or electrostatic interactions with PFAS. However, they exhibited low removal efficiencies, suggesting that these adsorbents may not have sufficient adsorption sites at 0.5 g/L. Consequently, adsorption experiments at higher doses might be necessary.

Conclusions

- The total concentration of PFASs in the industrial wastewater effluent was approximately 2.7 ppb according to target analysis and about 5.3 ppb following TOP-CIC analysis, exceeding guideline limits. The industrial wastewater, originating from an industrial complex near the *Nakdong River*, poses a potential risk as a source of PFAS contamination to drinking water, highlighting the need for effective treatment.
- Six types of adsorbents were utilized to remove various PFASs present in actual industrial wastewater. PAC and PG-CB demonstrated high removal rates about 70~80 %. In contrast, ion exchange resins and CB exhibited lower removal efficiencies about 10~20 %. after TOP assay, the removal efficiency increased due to the adsorption of oxidized precursor.
- Industrial wastewater can significantly contribute to PFAS pollution in the Nakdong River. To effectively remove a wide range of PFAS compounds, including precursors and previously undetected varieties, the development of diverse analytical methods and efficient treatment technologies is essential.

Acknowledgement

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