nature portfolio

Peer Review File

Integrating redox-electrodialysis and electrosorption for the removal of ultra-short- to long-chain PFAS

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This study presents a nanofiltration membrane-enabled redox-polymer electrodialysis system (Redox-polymer ED) designed for the removal of ultra-short- to long chain PFAS. The manuscript is well-organized, demonstrating significant novelty, and the findings represent important advances in electrochemical PFAS removal, with a notable focus on ultra-short PFAS compounds. Therefore, I consider the manuscript appropriate for publication in Nature Communications with a moderate revision to address the following concerns.

1. Please elaborate on the reasons for using nanofiltration membranes (NF) for the removal of inorganic salt in this present work. Note that NF membranes are typically designed to effectively separate divalent or multi-valent ions, while exhibiting a low reject rate for sodium chloride. Please clarify it.
2. Please provide additional insights into the principal function of NF within the redox-polymer ED system. Additionally, the nanoconfinement of NF membrane could enhance the rate of redox reactions?
3. The author asserts that no additional peaks, such as C=O and C-F, were identified in the FTIR spectra of the NF membrane (Fig. 2c), while distinct peaks are presented in AEM (Fig. 2c). However, the results do not align with the statements. For instance, there are noticeable C=O characteristic peaks shown in the NF membrane. Please carefully revise the statement.
Also, could you clarify the significance of the peak present at 1000 cm-1 in the spectra of the NF membrane?
4. The author states that over 90% loss occurred in Redox-ED with AEMs; however, the irreversible loss seems to be only 80% in Fig. 2b. Please clarify this discrepancy.
5. Similar questions arise regarding the membrane fouling test. If more than 80% of TFA was fouled on the AEM, why did the FTIR spectra of the used NF membrane not show distinct peaks as the one shown in the TFA solution? SEM images (surface and cross-section) of pristine and used AEM, CEM, and NF as well as their EDS analysis are suggested for further identification of membrane fouling.
6. How do we distinguish the distribution % for RC+AC, FC, and electrosorption (Fig. S5.3)? Why do some of the error bars of the distribution exceed 100% (i.e., PFBA and PFHxA)? Is it based on mass balance results? Please provide details.
7. Typo:
(L203, P9) “In the presence of 1 mM TFA, more than 80% of TFA was fouled on the AEM (Supplementary Fig. S1a).” Fig. S1a should be S3.1a.

Reviewer #2 (Remarks to the Author):

Per- and polyfluoroalkyl substances (PFAS) have become major emerging contaminants for clean

water production and environmental remediation, with the efficiency significantly affected by the structural and chemical diversity of these emerging contaminants. To this end, Kim et al. demonstrated the combination of water-soluble redox polymer with NFs for treating a wide range of PFAS, from ultra-short- to long-chain PFAS, in tandem with desalination at low cost. This work is generally well organized, with mechanistic insight given to the electrodialytic and electrosorption contribution to PFAS removal. The outputs would draw wide academic attention in this field. There are a few minor comments that should be addressed.

Lines 36-41. "Recent work has focused mostly on a subset of PFAS (e.g. either long-chain or short-chain),8-10 with relatively few studies targeting simultaneous removal across the entire range,6,11-13 and no emphasis on tandem desalination with PFAS removal. Here, we introduce a nanofiltration membrane-enabled redox-polymer electrodialysis system (Redox-polymer ED) to remove ultra-short- to long-chain PFAS in tandem with desalination within a single process (Schemes 1a and c)." The presentation of the system concept herein is open to discussion. Since the authors have not elaborated the knowledge gap, the significance/novelty of the system is not clearly though the following sections identify the challenges to address. This reviewer would suggest introducing Scheme 1 in the latter part of the introduction.

Lines 130-131. "Over 66% of TMPMA was oxidized to redox-active moiety, TMA. This TMA moiety facilitates the migration of charged species via its reversible redox reaction." Is this conversion process controllable and/or this conversion ratio (66%) purposeful? Why was this ratio used in this work?

Lines 145-149. "To facilitate migration and electrosorption of PFAS, implementing redox-polymer which captures PFAS on the redox-active units, e.g., ferrocene- and cobaltocenium-based polymers,44 makes it challenging to implement within the redox-polymer ED platform as a subsequent desorption step is required to release the bound PFAS before the polymer recycling." This statement is complicated and hard to follow.

Lines 183-185. "the redox ED system with AEMs encountered irreversible fouling of TFA on the AEM, leading to the loss of over 90% of the removed TFA (Fig. 2b)." How the irreversible fouling determined was determined is not clear. The statement indicated the deposition/sorption of TFA on the AEM, rather than irreversible fouling. Fouling should be characterized by increased charger transfer resistance and reduced transfer number. Likewise, the section of "Examination of membrane fouling" further discussed the deposition/sorption issue rather than membrane fouling.

Lines 234-236. "The enhanced removal % is primarily due to the increased availability of PFAS ions compared to chloride (Cl-) as the concentration ratio between PFAS and Cl-changes from 1:10,000 (1 μM:10 mM) to 1:10 (100 μM:10 mM)." It should be "1:10,000 (1 μM:10 mM) to 1:100 (100 μM:10 mM)." The authors should revise throughout.

Lines 287-291. "On the other hand, water-splitting reaction in the conventional ED system generates protons and hydroxides, which can also migrate through NFs in the opposite direction of the intended ion removal. As a result, both salt and PFAS removal performance decreased to 4%

and 43-67%, respectively in comparison to our system (Fig. 4b and Supplementary Fig. S5.2)." While the percentage removal of Cl- and PFAS using conventional ED system was low, a significant separation factor, i.e., obvious higher % removal of PFPrA, PFBA, PFHxA and PFOA compared to Cl-, was noted. The authors should further discuss the implications and its potential contribution to higher separation factor when being delicately integrated with the redox-polymer ED.

Lines 358-360. "With boron-doped diamond (BDD) as an anode, TFA and PFPrA showed complete PFAS degradation and defluorination in 6 hours, while PFHxA exhibited complete degradation, as well as 76% defluorination in 8 hours". Perchlorate can be an important byproduct during defluorination; however, relevant information was not presented in this work.

Reviewer #3 (Remarks to the Author):

This manuscript demonstrates an innovative approach of redox-polymer electrodialysis which was tested for desalination in combination with PFAS removal. I consider the novelty aspect as high and the study has certainly implications for the research field. IT demonstrates the effect of desalination on PFAS which are ubiqiutous at trace level in the water environment. However, in terms of implications for solving the challenge of PFAS removal, this study is still not convincing. In this respect, the authors need to improve their manuscript in order to provide a clear evaluation of the advantages and realistic chances for real-world application on the one side and unsolved questions and disadvantages on the other side. Comparison to the state of the art in literature for PFAS removal also needs to be done with more emphasis.

Detailed comments:
Abstract: 'demineralized' is not the right word. It is 'mineralized'.
lines 504-509: Which amounts of ACC and polymer were applied in the cell?
A scheme showing the solution reservoirs (volumes) and flow directions of the setup (in-circuit through the unit?) should be placed in the supporting information.
Line 52: not only long-chain PFAS in carboxylic form are regulated but also the sulfonic acids and precursors of long-chain PFAS
Lines 53 to 55: replacement products are in some cases short-chain PFAS but not really ultra-short chain PFAS (as they would not have the same function). However, polyfluorinated compounds as replacements can release upon degradation all of these (ultra-)short-chain perfluorinated compounds.
Line 60 and below: TFA is not a typical PFAS and some regulators even exclude it from the definition. This is due that a major source of TFA is cooling agent atmospheric loss and transformation into TFA which is contained than in rain water. Maybe this should be added here.
Line 78: There are indeed literature studies on TFA removal by adsorption and even adsorption with electro-stimulated desorption which should be mentioned here. See e.g.
https://doi.org/10.1016/j.jhazmat.2022.129051
Lines 153-155: Please improve language. 'more redox reactions' is not scientific language.

Line 162: Why this high TFA concentration in the mg/L range while µg/L is mentioned as relevant range above. The ratio of TFA to chloride in such cases would be even worse.
Figure 2 caption contains errors.
In the section on membrane fouling for anion exchange membranes, the authors should refer to the extensive literature on PFAS anion removal by ion exchange resins. Based on this knowledge it is not surprising that PFAS anions adsorb on AEMs.
Line 269: Please improve language kJ/mmol_PFAS is not describing PFAS removal but energy consumption related to PFAS removal.
Fig. S3.2 Important information on experimental conditions should be added in figure captions. If loss is reported than the adsorbent concentration as well as PFAS concentration added should be provided.
Lines 300 to 308: The concentration of sorption-active material needs to be mentioned here as well. Otherwise, reporting reduction values is not meaningful.
Line 323-324: The reader cannot evaluate the performance of the system from removal percentages alone. Operation parameters are needed here. Neither the text nor the figure caption does contain such information.
Line 337-339: Obviously, the polymers have a a considerable sorption affinity towards PFAS. This needs to be quantified, e.g. by sorption isotherms or at least a sorption coefficient.
What are the consequences of this sorption effect for reusing the system? It is impossible to use solvent to clean the polymer in real applications.
Lines 384-386: “We successfully treated ultra-short-chain PFAS simultaneously with desalination down to potable water standards..” This statement is ambiguous. Desalination to potable water was for sure achieved but the challenge is to remove PFAS to finally reach ng/L concentrations. This was not shown in this study.
The authors should discuss the advantages and disadvantages of the suggested one-step desalination and PFAS removal process compared to sequential treatment. Please not that the aspect of sequential desalination and PFAS electrosorption was discussed in a recent review on electrosorption for removal of micropollutants: https://doi.org/10.1016/j.cej.2023.144354
Electrooxidation using BDD electrodes is known to mineralize PFAS but it is also known to oxidize chloride to hazardous chlorate species. Please discuss this issue in relation to the simultaneous up-concentration of chloride and PFAS.
Line 438-439: Please explain in detail how the fluoride release during electrooxidation of the PFAS using the activated carbon electrode was determined. For which purpose was the combustion method described in lines 438-439 applied? Electrooxidation of PFAS by carbon electrodes would be a real breakthrough. IF you want to claim this, you need to provide much stronger evidence than what is described so far in the manuscript. This needs a mass balance of fluorine, as starting compound, all shorter-chain products and fluoride. In the best case all fluorine is released as fluoride into the solution phase (alkaline washing of solids to release fluoride is usually done).
Overall, the required residence/treatment time appears to be rather high. What is the ratio of treated water flow (m^3/h) per active area of the electrodialysis unit (m^2) for achieving a certain removal degree and how does this compare to the state-of-the art? It is not sufficient to just discuss removal degrees without using parameters to quantify the effort spent.

Reviewer #4 (Remarks to the Author):

This manuscript reports on an NF-enabled redox polymer electrodialysis system to remove both ultra-short-chain and regular perfluorocarboxylates. This study is comprehensive and the characterizations are of high quality. The system design followed general mechanisms but showed effective removal of ultra-short-chain PFCAs. With the help of redox-responsive polymer, the PFCA removal by the new ED system is better than the conventional system. The removal section is OK to go.

However, I do not find an effective connection to the PFAS destruction with BDD in the last paragraph (Line353-369). First, the BDD treatment configuration is different from the proposed ED system. It is a separate topic but the authors tried to mix it to oversell the ED system. Second, it is not clear how the electrosorbed PFHxA was defluorinated. I do not find any information on whether the PFHxA was desorbed from the polymer/membrane by some solvent washing before the BDD oxidation. Third, the solution contained chloride, and BDD oxidation is known for converting chloride into other harmful species such as chlorate and perchlorate. Although the authors could argue that this problem is not in the scope of this study, I would then point out that the entire defluorination section is also out of the scope of the study because BDD is not an integrated component in the ED system. So I would suggest the authors remove the defluorination section because it is oversold. However, if the authors choose to keep the BDD oxidation step in this study as an important treatment for PFAS destruction, a comprehensive profile of chlorine oxidation products must be provided. So, either no report or a comprehensive information profile is recommended. Partially reporting the favorable aspect will not help solve the PFAS issue.

We thank the reviewers for their invaluable suggestions and feedback. In response, we have carefully revised our manuscript to address both high-level concerns and technical details.

In particular, we have added additional discussions to explain the defluorination mechanisms and the generation of perchlorate resulting from defluorination side reactions. To explore these phenomena further, we conducted kinetic experiments to monitor changes in chloride and perchlorate concentrations using ion chromatography. Additionally, for a more thorough examination of membrane fouling, we performed detailed analytical investigations employing scanning electron microscopy, energy-dispersive X-ray spectroscopy, and electrochemical impedance spectroscopy to investigate membrane characteristics. These findings have been integrated into a new main figure (**Fig. 3**). Moreover, we have thoroughly revised our introduction to incorporate the latest literature and elucidated the physicochemical mechanisms more effectively.

Detailed revisions to the manuscript, along with point-by-point responses, are provided below:

Reviewer #1 (Remarks to the Author):
This study presents a nanofiltration membrane-enabled redox-polymer electrodialysis system (Redox-polymer ED) designed for the removal of ultra-short- to long chain PFAS. The manuscript is well-organized, demonstrating significant novelty, and the findings represent important advances in electrochemical PFAS removal, with a notable focus on ultra-short PFAS compounds. Therefore, I consider the manuscript appropriate for publication in Nature Communications with a moderate revision to address the following concerns.

We express our thanks to the reviewer for the valuable insights. In response to the comments, especially regarding membrane characteristics and fouling, we have revised our manuscript and conducted further analytical investigations using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

1. Please elaborate on the reasons for using nanofiltration membranes (NF) for the removal of inorganic salt in this present work. Note that NF membranes are typically designed to effectively separate divalent or multi-valent ions while exhibiting a low reject rate for sodium chloride. Please clarify it.

Response: In response to the reviewer's suggestion, we provided a detailed explanation of our motivation for integrating NF for the removal of both inorganic and organic salts in the revised manuscript. Our current research is not primarily focused on the selectivity among inorganic salts but rather on treating bulkier charged organic species, which poses challenges for ion-exchange membranes. Various electrochemical and pressure-driven studies have shown selective separations between monovalent and multivalent species using functionalized NF membranes (e.g., modified polyethersulfone and polyamide) with molecular weight cutoffs of 200-800 Da.[1-4] In contrast, we utilized a non-functionalized cellulose-based NF membrane with a MWCO of 1 kDa, which allows for transport of PFAS under an electric field. Due to the lack of functionalization, our membrane does not exert strong charge repulsion against multivalent ions. We elaborated on the rationale for our choice of NF membranes more thoroughly as follows:

Revision (pg. 3-4): To address these intrinsic challenges in PFAS removal, we introduce an NF-enabled redox-polymer electrodialysis system (redox-polymer ED) (**Scheme 1a**). Our redox-polymer ED system replaces expensive and sensitive anion-exchange membranes (AEMs) with affordable size-exclusion NFs for the removal of a wide range of charged species, from inorganic salts to organic substances. In particular, we employed a non-functionalized cellulose-based NF with a 1 kDa molecular-weight cut-off (MWCO). This membrane enables the electric field-driven removal of PFAS without experiencing fouling.

AND

Revision (pg. 15-16): Although multiple electrochemical and pressure-driven studies have demonstrated selective separation of monovalent ions from multivalent species using functionalized NF membranes (e.g., modified polyethersulfone and polyamide) with a MWCO of 200-800 Da,[53-56] our approach employs non-functionalized cellulose-based NF membranes with a larger MWCO of 1 kDa. Consequently, the membrane does not experience significant charge repulsion against multivalent ions.

2. Please provide additional insights into the principal function of NF within the redox-polymer ED system. Additionally, the nanoconfinement of NF membrane could enhance the rate of redox reactions?

Response: We provided additional insights into the mechanism of the redox-polymer ED system and the role of NF within it. Our NF is not in contact with the current collector, so we believe that the NF membrane does not directly impact the rate of redox reactions. Instead, it influences the overall ion flux based on its physicochemical properties, such as hydrophilicity, pore structure, functional groups, and surface potential. Investigating the physicochemical properties of NF in relation to PFAS removal performance could be a potential avenue for future research.

Revision (pg. 18): Further optimization of the molar ratio of P(TMA-*co*-TMPMA-*co*-METAC), exploration into the physicochemical attributes of NF concerning PFAS removal efficiency, and judicious systematic engineering for the up-concentration process are necessary for improving both the molecular-level electrochemical properties and the overall system performance. Nonetheless, our study signifies the first stride towards process-intensified electrochemical PFAS removal from ultra-short-chain all the way to long-chain PFAS. This approach opens avenues to simultaneously target multiple PFAS within a single system and process, while also addressing water scarcity.

3. The author asserts that no additional peaks, such as C=O and C-F, were identified in the FTIR spectra of the NF membrane (Fig. 2c), while distinct peaks are presented in AEM (Fig. 2c). However, the results do not align with the statements. For instance, there are noticeable C=O characteristic peaks shown in the NF membrane. Please carefully revise the statement. Also, could you clarify the significance of the peak present at 1000 cm-1 in the spectra of the NF membrane?

Response: NF membrane exhibits characteristic C=O peaks in its pristine cellulose structure. The peak at 1000 cm^{-1} in the NF corresponds to the C-OH stretching (1015 cm^{-1}) and C-O-C stretching of pyranose rings (1100 cm^{-1}) from cellulose.[5,6] When comparing the FTIR spectra between pristine and after redox-ED experiments or fouling tests, we did not observe any significant changes in the C=O peak, nor did we observe any notable C-F peaks on the NF membrane. Furthermore, there were no notable changes in PFAS concentrations following fouling tests. This spectroscopic analysis supports our conclusion that NF can

mitigate the irreversible adsorption of PFAS that occurs in AEM. We have revised the original sentences to provide a more comprehensive discussion of the pristine NF structures and to avoid any confusion.

Revision (pg. 5): Upon the applied voltage, both inorganic anions and PFAS undergo ion migration facilitated by redox reactions and an electric field, crossing over the size-exclusive NF membrane, whereas cations pass through the cation-exchange membrane (CEM) (**Scheme 1a**). Subsequently, the carbon electrodes within the anodic chamber electroadsorb hydrophobic long-chain PFAS, while ultra-short to short-chain PFAS migrate to the cathodic chamber and cross over the NF membrane to be concentrated in the accumulating channel.

AND

Revision (pg. 8): We conducted Fourier transform infrared spectroscopy (FTIR) analysis to assess the adsorption of TFA on the NF membrane. Given that our NF membrane comprises cellulose, distinct cellulose peaks appear in the pristine FTIR spectrum, notably the C-OH stretching (1015 cm^{-1}), C-O-C stretching of pyranose rings (1100 cm^{-1}), and O-H stretching (3350 cm^{-1}).[54,55] After conducting 7-hour redox-ED experiments, we analyzed the membranes using FTIR and found no notable peak developments corresponding to TFA, such as the C-F peak (1200 cm^{-1}), nor any significant changes in the C=O peak (**Fig. 2c).** This spectroscopic analysis aligns with the mass balance calculated in the concentration profiles, emphasizing that the removal of PFAS in our redox-polymer ED platform relies on PFAS migration rather than their irreversible binding to the membranes.

4. The author states that over 90% loss occurred in Redox-ED with AEMs; however, the irreversible loss seems to be only 80% in Fig. 2b. Please clarify this discrepancy.

Response: Our initial statement referred by reviewer is "*Despite achieving comparable capabilities for TFA removal (89% TFA removal) and desalination (65% reduction in conductivity), the redox ED system with AEMs encountered irreversible fouling of TFA on the AEM, leading to the loss of over 90% of the removed TFA (**Fig. 2b**).*" We intended to convey that more than 90% of the removed TFA was fouled, equivalent to 80.1% (89% $removed\ TFA \times 0.9$). Recognizing the potential confusion highlighted by the reviewer, we have revised the sentence to improve clarity as follows:

Revision (pg. 8): Although the redox-ED with AEMs achieved similar capability in removing TFA (89% TFA removal) and desalination (65% reduction in conductivity), it experienced irreversible adsorption of TFA on AEM, resulting in the loss of over 80% of the initial TFA (**Fig. 2b**).

5. Similar questions arise regarding the membrane fouling test. If more than 80% of TFA was fouled on the AEM, why did the FTIR spectra of the used NF membrane not show distinct peaks as the one shown in the TFA solution? SEM images (surface and cross-section) of pristine and used AEM, CEM, and NF as well as their EDS analysis are suggested for further identification of membrane fouling.

Response: The AEM membrane experienced irreversible TFA adsorption, with 80% of the initial TFA concentration (1 mM) being fouled on the membrane. Despite the distinct changes in solution concentrations, we still observed a weak signal of C=O and C-F signals on FTIR spectra because of the dispersion of TFA molecules onto the active membrane surface (3.5 × 3.5 cm^2). In response to the reviewer's suggestion, we conducted SEM and EDS characterizations and introduced new Figured (**Fig. S3.2-3.4** and **Fig. 3**) to provide a comprehensive examination of membrane fouling through SEM, EDS, XPS, and EIS

in the section titled "*Investigating membrane fouling by irreversible PFAS adsorption.*" The following lines and figures represent the changes we made.

Revision (pg. 10-11): In the presence of 1 mM TFA, more than 80% of the TFA was undetectable in the solution following the immersion of AEM into the TFA solution (Supplementary **Fig. S3.1a**). Notable C=O and C-F peak formations on the FTIR spectrum indicate the presence of TFA on the AEM membrane surface (Supplementary **Fig. S3.1b**). Moreover, energy-dispersive X-ray spectroscopy (EDS) mappings show a distinct fluoride presence, while scanning electron microscopy (SEM) images reveal increased roughness and non-uniformity compared to pristine AEM, indicating alterations in surface morphology and the formation of aggregates (Supplementary **Fig. S3.2**). For NF and CEM, on the other hand, there were negligible changes observed in the concentration of TFA (Supplementary **Fig. S3.1a**), the FTIR spectrum (**Figs. S3.1c** and **d**), the surface morphology in SEM images, and the fluoride content in EDS mappings (**Figs. S3.3** and **S3.4**). This comprehensive analysis supports the successful removal of TFA without any fouling formation on the NF and CEM membranes in the redox-polymer ED system, as discussed in **Fig. 2a**. (*Omitted*) Furthermore, the X-ray photoelectron spectroscopy (XPS) spectrum reveals significant CFx peaks in both the C1s and F1s spectra following the immersion of AEM in PFAS solutions (**Figs. 3a** and **b**). Notable changes in the surface roughness and fluoride content were also observed on SEM images and EDS mappings, respectively (**Figs. 3c** and **d**). (*Omitted*) Across membrane characterizations, including XPS, SEM, and EDS, no notable indications of PFAS adsorption were observed for NF (**Figs. 3f-I**, Supplementary **Figs. S3.5**, and **S3.8**). Moreover, both charge transfer and membrane resistance remained unchanged after the immersion in the PFAS solution (**Fig. 3e**), highlighting the remarkable durability of NFs against fluorinated organic compounds. Similar to NF, CEM exhibited no membrane fouling when exposed to a broad range of PFAS, including ultra-short- to long-chain PFAS (Supplementary **Figs. S3.5-3.7**).

AND

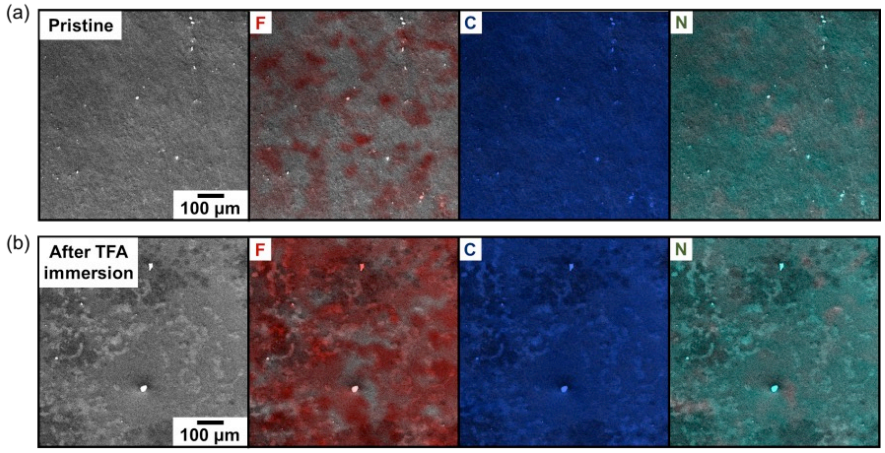

Fig. S3.2: SEM images and EDS mappings (F, C, N) for (a) pristine AEM and (b) after a fouling test with a 2.0 × 2.0 cm^2 membrane immersed in 1 mM TFA and 10 mM NaCl for 24 hours. Note the distinct fluoride presence and the rougher, non-uniform surface in the SEM image after immersion in the TFA solution, indicating changes in surface morphology and the formation of aggregates.

AND

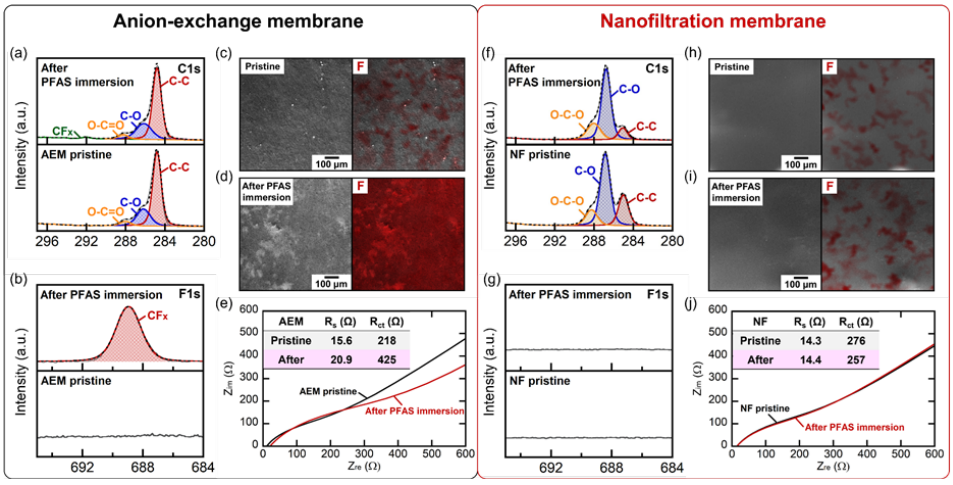

Fig. 3: Membrane fouling examination. Characterization of AEM: XPS spectra of (a) C1s and (b) F1s. SEM images and EDS mappings (fluoride) for (c) pristine AEM and (d) after fouling test. (e) Nyquist plots of pristine AEM and after PFAS immersion. Characterization of NF: XPS spectra of (f) C1s and (g) F1s, SEM images and EDS mappings (fluoride) for (h) pristine AEM and (i) after fouling test. (j) Nyquist plots of pristine NF and after PFAS immersion. Membranes (2.0 × 2.0 cm^2) were immersed for 24-hour 1 mM TFA, PFPrA, PFBA, PFHxA, and PFOA. R_s and R_{ct} correspond to system and charge-transfer resistances, respectively, and were calculated based on the equivalent circuit of R(Q(RW))).

6. How do we distinguish the distribution % for RC+AC, FC, and electrosorption (Fig. S5.3)? Why do some of the error bars of the distribution exceed 100% (i.e., PFBA and PFHxA)? Is it based on mass balance results? Please provide details.

Response: Chloride and PFAS concentrations for each compartment were assessed using IC and LCMS, respectively. We analyzed the distribution of chloride and different chain lengths of PFAS in different components (e.g., FC, AC, RC, electrodes) based on the mass balance. Percent distribution was determined by dividing the concentrations in each component by the initial concentration in the feed channel. Thus, distributions may exceed 100% due to a combination of measurement and sampling errors in each component, indicating higher sums of PFAS concentrations compared to the initial concentrations found in the feed. Detailed experimental methodologies are outlined in the *Supplementary section* titled "*Examination of the mechanism of PFAS removal in the redox-polymer ED system*."

Revision (pg. SI 15): To distinguish between migration and electrosorption mechanisms clearly, we increased the initial concentration of PFAS and employed an equimolar concentration (2 mM) of chloride and PFAS as a feed channel. Chloride and PFAS concentrations for each compartment were assessed using IC and LC-MS, respectively. We analyzed the distribution of chloride and different chain lengths of PFAS in different components (e.g., FC, AC, RC, electrodes) based on the mass balance. Percent distribution was determined by dividing the concentrations in each component by the initial concentration in the feed channel.

7. Typo: (L203, P9) "In the presence of 1 mM TFA, more than 80% of TFA was fouled on the AEM (Supplementary Fig. S1a)." Fig. S1a should be S3.1a.

Response: We corrected the typo.

Reviewer #2 (Remarks to the Author):
Per- and polyfluoroalkyl substances (PFAS) have become major emerging contaminants for clean water production and environmental remediation, with the efficiency significantly affected by the structural and chemical diversity of these emerging contaminants. To this end, Kim et al. demonstrated the combination of water-soluble redox polymer with NFs for treating a wide range of PFAS, from ultra-short- to long-chain PFAS, in tandem with desalination at low cost. This work is generally well organized, with mechanistic insight given to the electrodialytic and electrosorption contribution to PFAS removal. The outputs would draw wide academic attention in this field. There are a few minor comments that should be addressed. We appreciate the reviewer for your valuable feedback. Our manuscript has undergone a thorough revision in response to the specific comments provided.

1. Lines 36-41. "Recent work has focused mostly on a subset of PFAS (e.g. either long-chain or short-chain),8-10 with relatively few studies targeting simultaneous removal across the entire range,6,11-13 and no emphasis on tandem desalination with PFAS removal. Here, we introduce a nanofiltration membrane-enabled redox-polymer electrodialysis system (Redox-polymer ED) to remove ultra-short- to long-chain PFAS in tandem with desalination within a single process (Schemes 1a and c)." The presentation of the system concept herein is open to discussion. Since the authors have not elaborated the knowledge gap, the significance/novelty of the system is not clearly though the following sections identify the challenges to address. This reviewer would suggest introducing Scheme 1 in the latter part of the introduction.

Response: In response to the reviewer's suggestion, we rearranged the introduction, presenting the system design in the latter part (specifically, in the 4th paragraph), while emphasizing the motivation behind the development of our redox-mediated electrodialysis system in the 1st paragraph.

Revision (pg. 2): Recent work has focused mostly on a subset of PFAS (e.g. either long-chain or short-chain),[8-10] with relatively few studies targeting simultaneous removal across the entire range,[6,11-13] and no emphasis on tandem desalination with PFAS removal. Here, we present a single electrochemical process for the removal of ultra-short- to long-chain PFAS, coupled with desalination via the advancement of the redox-mediated electrodialysis system (**Scheme 1a**). Our approach relies on both ion migration through a reversible redox reaction and electrosorption onto the carbon electrodes to effectively remove PFAS across a wide range of chain lengths. The combination of a redox polymer with a cost-effective nanofiltration membrane (NF) within a redox-mediated electrodialysis platform enables the treatment of a broad range of charged species, from inorganic salts to organic contaminants, while mitigating membrane fouling and improving economic viability, thereby expanding the applicability of our system across various water treatment processes.
AND
Revision (pg. 4): To address these intrinsic challenges in PFAS removal, we introduce an NF-enabled redox-polymer electrodialysis system (redox-polymer ED) (**Scheme 1a**). Our redox-polymer ED system replaces expensive and sensitive anion-exchange membranes (AEMs) with affordable size-exclusion NFs for the removal of a wide range of charged species, from inorganic salts to organic substances.

2. Lines 130-131. "Over 66% of TMPMA was oxidized to redox-active moiety, TMA. This TMA moiety facilitates the migration of charged species via its reversible redox reaction." Is this conversion process controllable and/or this conversion ratio (66%) purposeful? Why was this ratio used in this work?

Response: The conversion ratio of TMPMA oxidation can be regulated by the amount of the oxidizing agent (hydrogen peroxide in this study), as demonstrated in our previous study.[7] We aimed to maximize the molar ratio of TMA without using an excessively large amount of the oxidizing agent. Increasing the TMA ratio in the terpolymer enhances charge transfer reactions, while partially remaining unoxidized TMPMA enhances the overall solubility of the terpolymer. While further investigation is needed to optimize the molar ratio of P(TMA-TMPMA-METAC) in the future, the terpolymer ratios utilized in this study were thoughtfully evaluated, taking into account various factors such as synthesis efficiency, electrochemical performance, solubility, as well as PFAS removal and desalination performance in the redox-polymer ED platform. In the revised manuscript, we provided a more comprehensive discussion of the rationale behind our oxidation ratio and the characteristics of each moiety.

Revision (pg. 6): To prevent potential crossover within NFs (with the molecular-weight cut-off, MWCO, of 1.0 kDa) during the experiment, we dialyzed the synthesized polymer using NF with an MWCO of 3.5 kDa. Then we oxidized TMPMA to TMA to introduce the redox-active moiety into the polymer. We aimed to maximize the molar ratio of TMA to enhance overall charge transfer reactions within the terpolymer without using an excessively large amount of the oxidizing agent. Consequently, with the oxidizing agent of 1.5 eq. H_2O_2, over 66% of TMPMA was converted into the redox-active moiety, TMA. The unreacted TMPMA moiety (17 mol% in our terpolymer) enhances the overall solubility of the polymer as it becomes protonated in neutral solution (pK_a of TMPMA: 11.28),[9] as illustrated in **Scheme 1a**, along with the METAC which provides water solubility to the polymer.[48]

AND

Revision (pg. 18): Further optimization of the molar ratio of P(TMA-*co*-TMPMA-*co*-METAC), exploration into the physicochemical attributes of NF concerning PFAS removal efficiency, and judicious systematic engineering for the up-concentration process are necessary for improving both the molecular-level electrochemical properties and the overall system performance. Nonetheless, our study signifies the first stride towards process-intensified electrochemical PFAS removal from ultra-short-chain all the way to long-chain PFAS. This approach opens avenues to simultaneously target multiple PFAS within a single system and process, while also addressing water scarcity.

3. Lines 145-149. "To facilitate migration and electrosorption of PFAS, implementing redox-polymer which captures PFAS on the redox-active units, e.g., ferrocene- and cobaltocenium-based polymers,44 makes it challenging to implement within the redox-polymer ED platform as a subsequent desorption step is required to release the bound PFAS before the polymer recycling." This statement is complicated and hard to follow.

Response: We have rephrased the sentence for improved clarity.

Revision (pg. 7): Redox-active units, containing ferrocene- and cobaltocenium, have demonstrated highly effective electrosorption, especially for long-chain PFAS molecules.[49] Consequently, integrating them into our redox-polymer ED platform poses a challenge, as a subsequent desorption step is necessary to release the bound PFAS before the polymer recycling. In this regard, the redox-active moiety, TMA, facilitates

redox reaction without direct interactions with PFAS,[8-10] enhancing the up-concentration of ultra-short- to short-chain PFAS and promoting the electrosorption of long-chain PFAS on the electrodes.

4. Lines 183-185. "the redox ED system with AEMs encountered irreversible fouling of TFA on the AEM, leading to the loss of over 90% of the removed TFA (Fig. 2b)." How the irreversible fouling determined was determined is not clear. The statement indicated the deposition/sorption of TFA on the AEM, rather than irreversible fouling. Fouling should be characterized by increased charger transfer resistance and reduced transfer number. Likewise, the section of "Examination of membrane fouling" further discussed the deposition/sorption issue rather than membrane fouling.

Response: We appreciate the reviewer's insightful comments. To characterize irreversible fouling, we performed the electrochemical impedance spectroscopy (EIS) to compare the charge transfer (R_{ct}) and system (R_s) resistances between pristine and after the membrane fouling test (as shown in **Figure 3** and **Fig. S3.7**). Additionally, we conducted surface characterization using SEM and EDS to provide a more comprehensive analysis of membrane fouling (**Figure 3** and **Figs. S3.2-S3.4**). Furthermore, we updated the section title to "*Investigating membrane fouling by irreversible PFAS adsorption*" to more accurately reflect the focus of our study. The subsequent lines and figures illustrate the changes we implemented.

Revision (pg. 11): The irreversible adsorption observed on the AEM is attributed to the presence of the quaternary ammonium functional group, recognized for its strong affinity towards PFAS.[56,57] In fact, this quaternary ammonium group has been demonstrated to be an effective candidate for ion-exchange resin materials for removing PFAS of various chain lengths, including PFBS, PFHxA, and PFOA.11,[57-59] Due to its irreversible PFAS adsorption, AEM suffers performance deterioration, encountering 1.9-fold and 1.3-fold increases in charge-transfer (R_{ct}) and system resistances (R_s), respectively (**Fig. 3e**).

On the other hand, since both the cellulose-based NF and CEM do not contain ammonium groups, they exhibit a low propensity to interact with anionic fluorinated compounds. Across membrane characterizations, including XPS, SEM, and EDS, no notable indications of PFAS adsorption were observed for NF (**Figs. 3f-i**, Supplementary **Figs. S3.5**, and **S3.8**). Moreover, both charge transfer and membrane resistance remained unchanged after the immersion in the PFAS solution (**Fig. 3e**), highlighting the remarkable durability of NFs against fluorinated organic compounds. Similar to NF, CEM exhibited no membrane fouling when exposed to a broad range of PFAS, including ultra-short- to long-chain PFAS (Supplementary **Figs. S3.5-3.7**).

AND

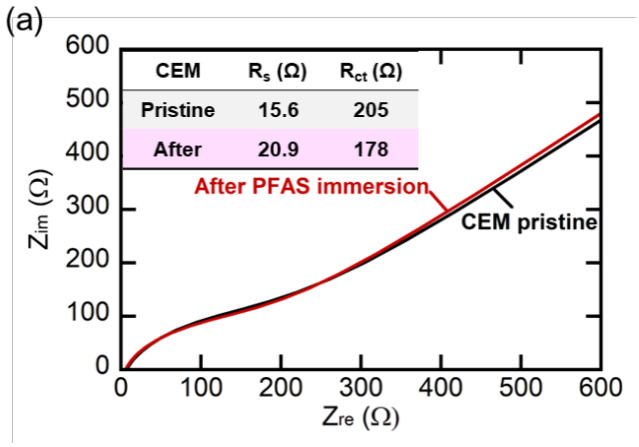

Fig. S3.7: Nyquist plots of pristine CEM and after PFAS immersion. Membranes (2.0 × 2.0 cm^2) were immersed for 24-hour 1 mM TFA, PFPrA, PFBA, PFHxA, and PFOA. R_s and R_{ct} correspond to system and charge-transfer resistances, respectively, and were calculated based on the equivalent circuit of R(Q(RW))).

AND

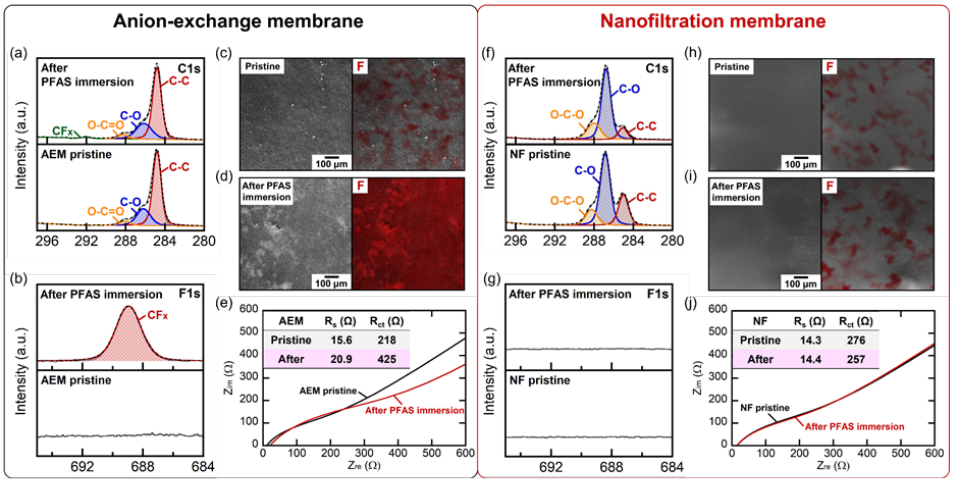

Fig. 3: Membrane fouling examination. Characterization of AEM: XPS spectra of (a) C1s and (b) F1s. SEM images and EDS mappings (fluoride) for (c) pristine AEM and (d) after fouling test. (e) Nyquist plots of pristine AEM and after PFAS immersion. Characterization of NF: XPS spectra of (f) C1s and (g) F1s, SEM images and EDS mappings (fluoride) for (h) pristine AEM and (i) after fouling test. (j) Nyquist plots of pristine NF and after PFAS immersion. Membranes (2.0 × 2.0 cm^2) were immersed for 24-hour 1 mM TFA, PFPrA, PFBA, PFHxA, and PFOA. R_s and R_{ct} correspond to system and charge-transfer resistances, respectively, and were calculated based on the equivalent circuit of R(Q(RW))).

5. Lines 234-236. "The enhanced removal % is primarily due to the increased availability of PFAS ions compared to chloride (Cl-) as the concentration ratio between PFAS and Cl-changes from 1:10,000 (1 μM:10 mM) to 1:10 (100 μM:10 mM)." It should be "1:10,000 (1 μM:10 mM) to 1:100 (100 μM:10 mM)." The authors should revise throughout.

Response: We corrected the typo and revised the manuscript thoroughly.

6. Lines 287-291. “On the other hand, water-splitting reaction in the conventional ED system generates protons and hydroxides, which can also migrate through NFs in the opposite direction of the intended ion removal. As a result, both salt and PFAS removal performance decreased to 4% and 43-67%, respectively in comparison to our system (Fig. 4b and Supplementary Fig. S5.2).” While the percentage removal of Cl- and PFAS using conventional ED system was low, a significant separation factor, i.e., obvious higher % removal of PFPrA, PFBA, PFHxA and PFOA compared to Cl-, was noted. The authors should further discuss the implications and its potential contribution to higher separation factor when being delicately integrated with the redox-polymer ED.

Response: We included lines discussing the favorable diffusion of PFAS and potential directions to improve selectivity and PFAS removal rate through the judicious optimization of operating conditions.
Revision (pg. 14): We believe that the limited salt removal in conventional ED with NFs could be attributed to the presence of a higher concentration of ions in the RC than in the FC, leading to a reduction in the diffusion effect and promoting the migration of protons and hydroxides, as observed in conventional ED with AEMs as well.[42] Unlike chloride, the absence of PFAS in the RC facilitated the preferential migration of PFAS over salt removal. This finding suggests that optimizing operating conditions and controlling both diffusion and electrically-driven migration could enhance the rate and selectivity of PFAS removal. Therefore, further studies on diffusion kinetics are necessary to elucidate the correlation between the concentration gradient across channels and the rate and selectivity of ion removal through diffusion.

7. Lines 358-360. “With boron-doped diamond (BDD) as an anode, TFA and PFPrA showed complete PFAS degradation and defluorination in 6 hours, while PFHxA exhibited complete degradation, as well as 76% defluorination in 8 hours”. Perchlorate can be an important byproduct during defluorination; however, relevant information was not presented in this work.

Response: Taking into account the reviewer's feedback, we evaluated perchlorate production and changes in chloride concentrations over 8 hours of the defluorination test and incorporated relevant details regarding perchlorate generation as a byproduct.
Revision (pg. 19): With boron-doped diamond (BDD) as an anode, TFA and PFPrA showed complete PFAS degradation and defluorination in 6 hours, while PFHxA exhibited complete degradation, as well as 76% defluorination in 8 hours (**Fig. 6f** and Supplementary **Fig. S6.1**). Electrosorbed PFHxA undergoes two steps of the defluorination process: desorption from the ACC and subsequent defluorination in the solution using hydroxyl radicals generated by the BDD (Supplementary **Fig. S6.3**). Consequently, the mineralization of PFHxA requires a longer defluorination period compared to TFA and PFPrA, which are more volatile and do not require a desorption step. Due to high oxidation power, BDD oxidized chloride into perchlorate as a disinfection by-product.[68-70] Over 80% of chloride (20 mM) present in the defluorination test was converted into perchlorate (Supplementary **Fig. S6.2**). Considering the health risks associated with ClO_4^-,[68,69] reducing chlorine oxidation is essential to improve defluorination efficiency and address a pressing topic in U.S. drinking water safety. With further optimization of defluorination conditions and advancements in anode materials, our proof-of-concept defluorination results inspire us to envision a sustainable and energy-efficient PFAS treatment process alongside desalination.

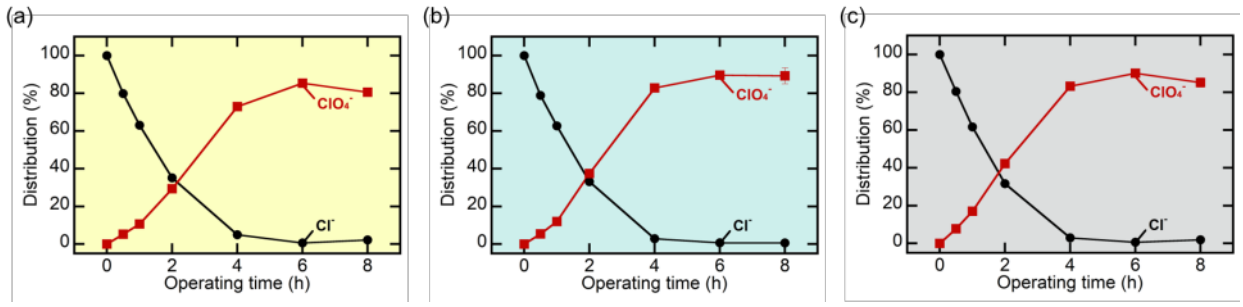

Figure S6.2. Chloride oxidation kinetics during defluorination of (a) TFA, (b) PFPrA, and (c) PFHxA for 8 hours of the oxidation process. The findings indicate that, on average, 98.4% of Cl^- disappeared, with 85.0% of the initial chloride being converted to ClO_4^-. The remaining chloride (%) and perchlorate production (%) were calculated based on the starting NaCl concentrations (20 mM).

Reviewer #3 (Remarks to the Author):

This manuscript demonstrates an innovative approach of redox-polymer electrodialysis which was tested for desalination in combination with PFAS removal. I consider the novelty aspect as high and the study has certainly implications for the research field. IT demonstrates the effect of desalination on PFAS which are ubiqiutous at trace level in the water environment. However, in terms of implications for solving the challenge of PFAS removal, this study is still not convincing. In this respect, the authors need to improve their manuscript in order to provide a clear evaluation of the advantages and realistic chances for real-world application on the one side and unsolved questions and disadvantages on the other side. Comparison to the state of the art in literature for PFAS removal also needs to be done with more emphasis.

We extend our gratitude to the reviewer for the valuable insights and comments. In response to the reviewer's feedback, we have significantly revised our manuscript. Specifically, we have emphasized the advantages and limitations of our current proof-of-concept design of the redox-polymer ED system. Additionally, we have included a table to compare the state-of-the-art PFAS removal performance reported in the literature.

Detailed comments:

1. Abstract: 'demineralized' is not the right word. It is 'mineralized'.

Response: We corrected the word to "mineralized" and revised the entire manuscript thoroughly.

2. lines 504-509: Which amounts of ACC and polymer were applied in the cell? A scheme showing the solution reservoirs (volumes) and flow directions of the setup (in-circuit through the unit?) should be placed in the supporting information.

Response: We utilized 3.0 × 3.0 cm^2 ACC (with a weight of 200-250 mg) as both cathodic and anodic electrodes. As an electrolyte, 20 mL of 30 mM of TMA in P(TMA_{33}-$TMPMA_{17}$-$METAC_{50}$) was dissolved in water. All feed, accumulating, and redox channel solutions were circulated within a closed-loop system. Alongside the requested information from the reviewer, we have incorporated detailed system setup and operational procedures in the Methods section, titled "*Investigation of desalination performance and tandem PFAS removal.*"

Revision (pg. 25): The redox-polymer ED system was composed of a redox channel (RC, 4×4×0.2 cm^3), as well as customized feed (FC, 4×4×0.3 cm^3) and accumulating channels (AC, 4×4×0.3 cm^3). In the RC, Ti-mesh was used as current collectors, and ACC (3.0 × 3.0 cm^2 with a weight of 200-250 mg) was used as both cathodic and anodic electrodes. We arranged these channels in the sequence of RC (cathodic chamber)-*NF*-AC-*CEM*-FC-*NF*-RC (anodic chamber) (as illustrated in **Scheme 1a**). (*Omitted*) Throughout experiments, 20 mL of 30 mM of TMA in P(TMA_{33}-$TMPMA_{17}$-$METAC_{50}$) was used as an electrolyte in the RC. Unless specified, the system was operated at the flow rate of 10 mL/min for all FC, AC, and RC within a closed loop. Also, the system was operated in a two-electrode system at the applied voltage of 1.0 V for 7 hours.

3. Line 52: not only long-chain PFAS in carboxylic form are regulated but also the sulfonic acids and precursors of long-chain PFAS

Response: We have revised the sentence as follows:
Response (pg. 2): Since 2009, global regulations have targeted PFAS, starting from long-chain PFAS (C≥C8 in carboxylic form; C≥C6 in sulfonate form) and their precursors, owing to their potential health effects.[14,16,17]

4. Lines 53 to 55: replacement products are in some cases short-chain PFAS but not really ultra-short chain PFAS (as they would not have the same function). However, polyfluorinated compounds as replacements can release upon degradation all of these (ultra-)short-chain perfluorinated compounds.

Response: We have revised the sentence to elaborate on the major sources of ultra-short-chain PFAS.
Response (pg. 2): Consequently, chemical manufacturing has transitioned from long-chain to short-chain PFAS (C3<C<C8 for carboxylic form). However, recent literature has indicated that shorter-chain PFAS could exhibit persistence and human hazards similar to regulated long-chain PFAS.[1,9,15,18] Moreover, ultra-short-chain PFAS (C≤C3 for carboxylic form) are increasingly prevalent in numerous drinking water sources and wastewater, including seawater, rivers, groundwater, and even bottled water (Supplementary **Table S1**). This is primarily due to the degradation of longer-chain PFAS and fluorocarbons into shorter-chain variants.[14,15,18-20]

5. Line 60 and below: TFA is not a typical PFAS and some regulators even exclude it from the definition. This is due that a major source of TFA is cooling agent atmospheric loss and transformation into TFA which is contained than in rain water. Maybe this should be added here.

Response: We included a discussion about the sources of TFA, its limited regulations, and how its unique properties differ from those of short- and long-chain PFAS.
Response (pg. 2-3): For instance, trifluoroacetic acid (TFA, C2) is a major degradation product of various fluorinated gases used as cooling agents, such as in refrigeration, which then accumulates in the water cycle.[21-23] Consequently, trifluoroacetic acid (TFA, C2) was found in river water (up to 140 ppb, 1.23 μM)24 and in wastewater treatment plant effluent (206 ppb, 1.81 μM).[25] Despite the lesser regulatory emphasis on ultra-short-chain PFAS, considering that the drinking water regulation for long-chain PFAS is below 4 ppt,[26] these concentrations exceed that limit by up to ten thousand times. Moreover, their smaller sizes, higher mobility, and relatively lower hydrophobicity make them challenging to remove using conventional separation technologies.[2,15]

6. Line 78: There are indeed literature studies on TFA removal by adsorption and even adsorption with electro-stimulated desorption which should be mentioned here. See e.g. https://doi.org/10.1016/j.jhazmat.2022.129051

Response: We have included recent literature that illustrates the removal of ultra-short-chain PFAS, including the reference suggested by the reviewer.
Revision (pg. 3): Recent studies have demonstrated the removal of ultra-short-PFAS via adsorption,[35] electrosorption,[23] or direct defluorination using photocatalysis techniques.[36-38]

7. Lines 153-155: Please improve language. ‘more redox reactions’ is not scientific language.

Response: We revised the sentence as follows:
Revision (pg. 7): Furthermore, TMA and TMPMA are less hydrophobic than ferrocene,[39,52,53] allowing for higher molar ratios of redox-active moieties within the polymer. Consequently, this higher molar ratio of TMA promotes a greater extent of redox reactions at equivalent polymer concentrations compared to other water-soluble polymers.

8. Line 162: Why this high TFA concentration in the mg/L range while µg/L is mentioned as relevant range above. The ratio of TFA to chloride in such cases would be even worse.

Response: Initially (Fig. 2), we investigated a high concentration of TFA (1 mM, 114 mg/L) to evaluate the maximum performance of the redox-polymer ED platform for removing ultra-short-chain PFAS. However, in the following figures (Fig. 4-6), we conducted PFAS removal experiments at concentrations relevant to real-world scenarios (µg/L range, down to 1 µM). This allowed us to investigate PFAS removal in relation to chloride ratios, energy consumption, wastewater treatment, and upconcentration. Particularly, in Fig. 2, we compared the performance of NF-enabled redox-ED and AEM-based redox-ED systems by analyzing the TFA concentration profiles across the feed, accumulation, and redox channels. To minimize measurement errors in mass balance calculations, concentrations higher than the relevant range were utilized, as elaborated in the subsequent section titled "*Removal of ultra-short-chain PFAS in tandem with desalination.*"

9. Figure 2 caption contains errors.

Response: We corrected the grammatical errors in the caption of **Figure 2**.

10. In the section on membrane fouling for anion exchange membranes, the authors should refer to the extensive literature on PFAS anion removal by ion exchange resins. Based on this knowledge it is not surprising that PFAS anions adsorb on AEMs.

Response: We have included a discussion on the utilization of quaternary ammonium groups in ion exchange resins for PFAS removal, supported by relevant citations.
Revision (pg. 11): The irreversible adsorption observed on the AEM is attributed to the presence of the quaternary ammonium functional group, recognized for its strong affinity towards PFAS.[56,57] In fact, this quaternary ammonium group has been demonstrated to be an effective candidate for ion-exchange resin materials for removing PFAS of various chain lengths, including PFBS, PFHxA, and PFOA.[11,57-59] Due to its irreversible PFAS adsorption, AEM suffers performance deterioration, encountering 1.9-fold and 1.3-fold increases in charge-transfer (R_{ct}) and system resistances (R_s), respectively (**Fig. 3e**).

11. Line 269: Please improve language kJ/mmol_PFAS is not describing PFAS removal but energy consumption related to PFAS removal.

Response: We have revised the sentence to enhance its clarity.
Revision (pg. 13): Consequently, our system is more suitable for calculating the overall energy consumption required for both PFAS removal and desalination (kJ/mmol$_{NaCl+PFAS}$) rather than calculating energy consumption for PFAS removal (kJ/mmol$_{PFAS}$).

12. Fig. S3.2 Important information on experimental conditions should be added in figure captions. If loss is reported than the adsorbent concentration as well as PFAS concentration added should be provided.

Response: In response to the reviewer, we have incorporated key experimental conditions into the figure captions. In addition to Fig. S3.2., we have extensively revised captions in the supporting information to include details about experimental conditions (e.g., S3.1, S3.3, and S3.4). The revised version of the caption for Fig. S3.2 is provided below:
Revision (Fig. S3.5 caption): The irreversible loss (%) of PFAS contents after 24-hour immersion of (a) AEM, (b) CEM, and (c) NF (2.0 × 2.0 cm^2) in 1 mM TFA, PFPrA, PFBA, PFHxA, and PFOA. FTIR spectra of pristine and after membrane fouling test for (d) AEM, (e) CEM, and (f) NF, showing the notable C=O and C-F peak formations on AEM.

13. Lines 300 to 308: The concentration of sorption-active material needs to be mentioned here as well. Otherwise, reporting reduction values is not meaningful.

Response: In response to the reviewer's feedback, we've incorporated key experimental information into the main text. We've still maintained comprehensive information about experimental details in the Method section titled "*PFAS electrosorption and defluorination experiments*" to ensure the main discussion section remains concise.
Revision (pg. 14-15): To probe the underlying removal mechanism, we first conducted electrosorption studies with an equimolar mixture of 1 mM TFA, PFPrA, PFBA, PFHxA, and PFOA in solution along with 10 mM NaCl. The electrosorption experiment was performed in an H-cell using 3.0 × 3.0 cm^2 ACC (with an average weight of 200-250 mg) on both anode and cathode electrodes. The system was operated at a voltage of 1.0 V (two-electrode system) for 1 hour to achieve equilibrium electrosorption values. Detailed experimental information can be found in the Methods section titled "*PFAS electrosorption and defluorination experiment*."

14. Line 323-324: The reader cannot evaluate the performance of the system from removal percentages alone. Operation parameters are needed here. Neither the text nor the figure caption does contain such information.

Response: We've incorporated key experimental information into the main text. We've still maintained comprehensive information about experimental details in the Method section titled "*Investigation of desalination performance and tandem PFAS removal*" to ensure the main discussion section remains concise.
Revision (pg. 16-17): We introduced 10 μM of TFA or PFPrA to 20 mL of the real wastewater matrix as representative PFAS contaminants (see wastewater matrix in Supplementary **Table S6**). We performed a real wastewater treatment test at 1.0 V for 24 hours, using 30 mM of TMA in P(TMA$_{33}$-*co*-TMPMA$_{17}$-*co*-

$METAC_{50}$) as the electrolyte and ACC (3.0 × 3.0 cm^2) on both anode and cathode electrodes. For more detailed experimental procedures, refer to the "*Investigation of desalination performance and tandem PFAS removal*" section in the Methods.

15. Line 337-339: Obviously, the polymers have a considerable sorption affinity towards PFAS. This needs to be quantified, e.g. by sorption isotherms or at least a sorption coefficient. What are the consequences of this sorption effect for reusing the system? It is impossible to use solvent to clean the polymer in real applications.

Response: To investigate the binding constants (K_a) of our terpolymer, P(TMA-*co*-TMPMA-*co*-METAC), with PFAS, we conducted ^{19}F-NMR spectroscopic titration experiments (**Figs. S2.7-2.11**). Since TMA does not participate in the electrosorption of PFAS, our focus was on the TMPMA and METAC moieties, which contain potential binding sites for PFAS (amine groups). Then we used TFA and PFHxA to represent ultra-short and relatively longer chain lengths, respectively. The results showed that our binding constants are 1,000 to 10,000 times weaker than the strong interactions (K_a > 10,000) reported in the literature. This indicates that the TMPMA and METAC moieties in P(TMA-*co*-TMPMA-*co*-METAC), along with TMA, are unlikely to participate significantly in PFAS adsorption, particularly in the presence of a strong binding agent like activated carbon cloths. Consequently, we believe that the polymer interaction with PFAS will have minimal impact on the overall system performance.

Recycling polymers in real-world applications is more complex than in lab-scale settings and thus requires further investigation into techno-economic and environmental feasibility. To address the reviewer's concern, we have revised our manuscript to reduce the emphasis on the polymer recycling discussion and acknowledge the differences in the practicability of polymer recycling between industrial and lab scales. Additionally, we have included further lines in our discussion for future studies, highlighting the importance of conducting a techno-economic analysis to assess the economic and environmental impacts of polymer synthesis.

Revision (pg. 7): In this regard, the redox-active moiety, TMA, facilitates redox reaction without direct interactions with PFAS,[8-10] enhancing the up-concentration of ultra-short- to short-chain PFAS and promoting the electrosorption of long-chain PFAS on the electrodes. To further investigate the sorption affinity between redox polymer and PFAS, we calculated the binding constant (K_a) between the TMPMA and METAC moieties and PFAS (TFA and PFHxA) using ^{19}F-NMR spectroscopic titrations (detailed methodology available in the methods section titled "*Polymer binding affinity towards PFAS*"). The calculated K_a values for TMPMA towards TFA and PFHxA are 9.74 M^{-1} and 40.2 M^{-1}, respectively, and for METAC, they are 8.9 M^{-1} and 38.1 M^{-1}, respectively (**Fig. S2.11**). Since K_a values for strong binding typically exceed 10^4 M^{-1},[50,51] these results confirm that the TMPMA and METAC moieties in P(TMA-*co*-TMPMA-*co*-METAC), along with TMA, are unlikely to participate significantly in PFAS adsorption.

AND

Revision (pg. 18): This up-concentration experiment provides insights into a single process for PFAS treatment using the redox-polymer ED, which includes desalination and PFAS removal from the feed solution and its up-concentration. Additionally, stable long-term operation highlights the reusability and stability of redox copolymers. However, the polymer recycling process in real-world applications is more complex than in lab-scale settings. Therefore, it is crucial to conduct techno-economic analyses and life-cycle assessments in the near future to thoroughly evaluate the feasibility of polymer recycling, considering both economic and environmental implications.

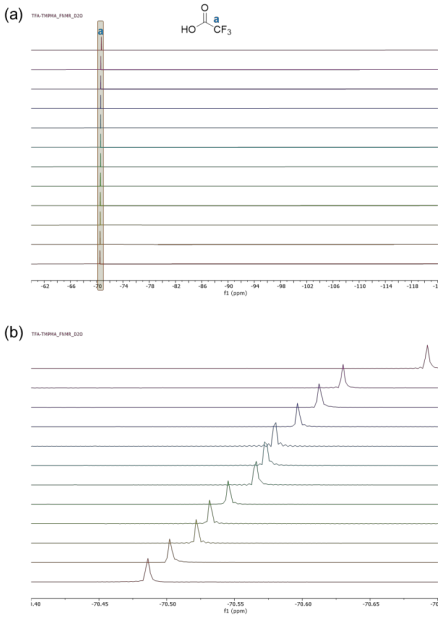

Fig. S2.7: ^{19}F-NMR spectra (600 MHz, D_2O) of TMPMA titration in 20 mM TFA solution: (a) full spectrum range (-60 to -122 ppm) and (b) fluoride peak shift at Ca with 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, and 2.0 equivalents (from the bottom to top plots) of TMPMA (-70.4 to -70.7 ppm).

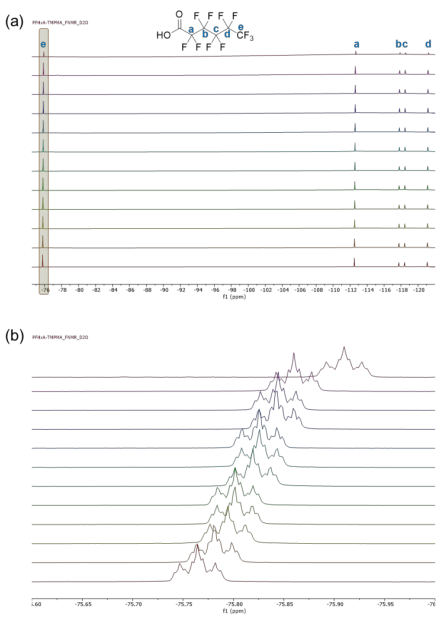

Fig. S2.8: ^{19}F-NMR spectra (600 MHz, D_2O) of TMPMA titration in 20 mM PFHxA solution: (a) full spectrum range (-74.5 to -122 ppm) and (b) fluoride peak shift at Ce with 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 0.8, 0.9, 1.0, and 2.0 equivalents (from the bottom to top plots) of TMPMA (-75.6 to -76 ppm).

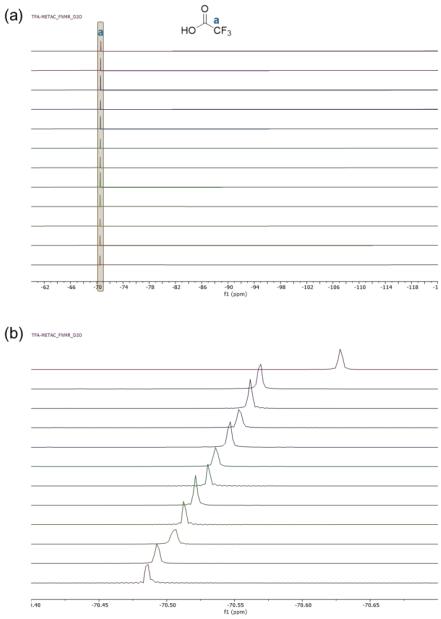

Fig. S2.9: ^{19}F-NMR spectra (600 MHz, D_2O) of METAC titration in 20 mM TFA solution: (a) full spectrum range (-60 to -122 ppm) and (b) fluoride peak shift at Ca with 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, and 2.0 equivalents (from the bottom to top plots) of METAC (-70.4 to -70.7 ppm).

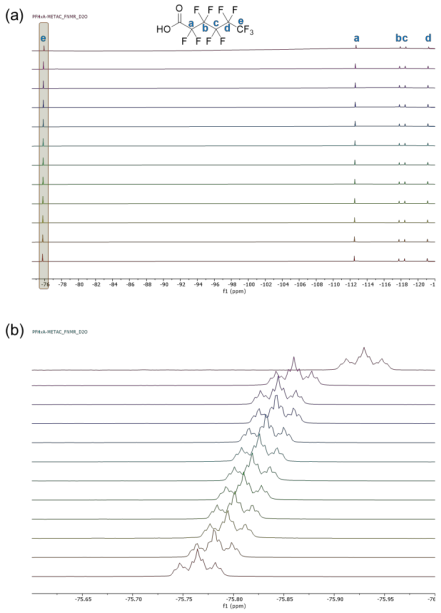

Fig. S2.10: ^{19}F-NMR spectra (600 MHz, D_2O) of METAC titration in 20 mM PFHxA solution: (a) full spectrum range (-74.5 to -122 ppm) and (b) fluoride peak shift at Ce with 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 0.8, 0.9, 1.0, and 2.0 equivalents (from the bottom to top plots) of METAC (-75.6 to -76 ppm).

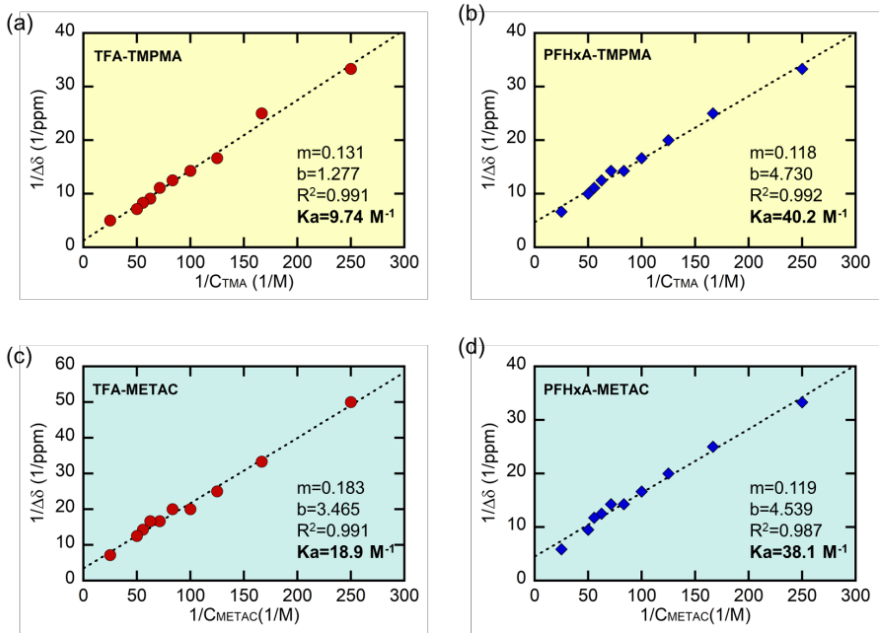

Fig. S2.11: Benesi-Hildebrand plots and calculated binding constants (Ka) for (a) TFA and (b) PFHxA at different TMA concentrations, and for (a) TFA and (b) PFHxA at different METAC concentrations, calculated using the ^{19}F-NMR titration method.

16. Lines 384-386: "We successfully treated ultra-short-chain PFAS simultaneously with desalination down to potable water standards." This statement is ambiguous. Desalination to potable water was for sure achieved but the challenge is to remove PFAS to finally reach ng/L concentrations. This was not shown in this study.

Response: We modified the sentence to accurately convey our findings.
Revision (pg. 20): We successfully remediated ultra-short-chain PFAS, even when the salts were present at 10-10,000 times higher concentration than the target PFAS. Simultaneously, the system enabled desalination to potable water salinity levels.

17. The authors should discuss the advantages and disadvantages of the suggested one-step desalination and PFAS removal process compared to sequential treatment. Please note that the aspect of sequential desalination and PFAS electrosorption was discussed in a recent review on electrosorption for removal of micropollutants: https://doi.org/10.1016/j.cej.2023.144354

Response: Considering the reviewer's input, we have added discussions on the potential advantages of our redox-polymer ED compared to conventional PFAS removal processes, specifically for removing PFAS in high-concentration ranges or mixed PFAS. Additionally, we have discussed the limitations that need to be addressed for future real-world deployment and scenarios where our system is less advantageous compared to state-of-the-art PFAS removal methods, referencing the literature suggested by the reviewer. However, cross-comparison of performance values across various PFAS removal technologies is challenging due to the lack of standardized performance metrics. Regarding overall removal percentage, the redox-polymer ED system is comparable to adsorption, ion exchange, and membrane technologies for long-chain PFAS,

while it presents advantages tothese conventional technologies for short-chain PFAS.[8] Finally, we recognize that a rigorous comparison will require a systematic study and TEA, which can be the topic of future studies. These points have been incorporated into the main text.

Revision (pg. 16): Overall, by leveraging both ion migration and electrosorption, our redox-polymer ED system is capable of addressing a wide variety of PFAS compounds in a single operation, effectively overcoming the conventional sequential PFAS treatment process. We believe that the redox-ED platform can intensify the water remediation process, especially advantageous for mixed chain-length PFAS at high concentration levels, as its capacity is not limited by active materials,[31] nor does it require high energy inputs such as pressure.[17] The overall PFAS removal percentage of our redox-polymer ED system is comparable to adsorption (≥ 80%), ion exchange (50-90%), and membrane technologies (≥ 90%) for long-chain PFAS, while it outperforms adsorption (≤ 40%) and ion exchange (≤ 55%) for short-chain PFAS.[11,60] However, to make the system more practical for water treatment and eventual industrial deployment, we need to improve the overall water treatment rate (currently 1.79 L/h/m^2). This can be achieved by increasing the concentration of redox species with stacked electrodes and arranging additional channels (FC and AC) in series, as demonstrated in previous electrodialysis studies.[61,62] Nonetheless, comprehensive evaluations of diverse real-world scenarios—including initial concentrations, specific target PFAS types, and desired target concentrations—are essential. Additionally, rigorous techno-economic analyses must be conducted prior to real-world deployment to ensure the feasibility and effectiveness of our system compared to state-of-the-art PFAS removal methods.

AND

Revision (pg. 20): Further optimization of the molar ratio of P(TMA-*co*-TMPMA-*co*-METAC), exploration into the physicochemical attributes of NF concerning PFAS removal efficiency, and judicious systematic engineering for the up-concentration process are necessary for improving both the molecular-level electrochemical properties and the overall system performance. Nonetheless, our study signifies the first stride towards process-intensified electrochemical PFAS removal from ultra-short-chain all the way to long-chain PFAS.

18. Electrooxidation using BDD electrodes is known to mineralize PFAS but it is also known to oxidize chloride to hazardous chlorate species. Please discuss this issue in relation to the simultaneous up-concentration of chloride and PFAS.

Response: Taking into account the reviewer's feedback, we evaluated perchlorate production and changes in chloride concentrations over 8 hours of the defluorination test and incorporated relevant details regarding perchlorate generation as a byproduct.

Revision (pg. 18): Due to high oxidation power, BDD oxidized chloride into perchlorate as a disinfection by-product.[68-70] Over 80% of chloride (20 mM) present in the defluorination test was converted into perchlorate (Supplementary **Fig. S6.2**). Considering the health risks associated with ClO_4^-,[68,69] reducing chlorine oxidation is essential to improve defluorination efficiency and address a pressing topic in U.S. drinking water safety. With further optimization of defluorination conditions and advancements in anode materials, our proof-of-concept defluorination results inspire us to envision a sustainable and energy-efficient PFAS treatment process alongside desalination.

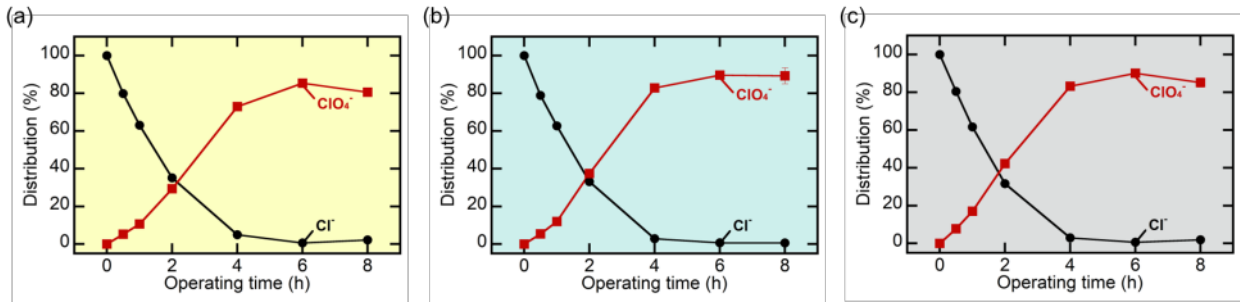

Figure S6.2. Chloride oxidation kinetics during defluorination of (a) TFA, (b) PFPrA, and (c) PFHxA for 8 hours of the oxidation process. The findings indicate that, on average, 98.4% of Cl^- disappeared, with 85.0% of the initial chloride being converted to ClO_4^-. The remaining chloride (%) and perchlorate production (%) were calculated based on the starting NaCl concentrations (20 mM).

19. Line 438-439: Please explain in detail how the fluoride release during electrooxidation of the PFAS using the activated carbon electrode was determined. For which purpose was the combustion method described in lines 438-439 applied? Electrooxidation of PFAS by carbon electrodes would be a real breakthrough. IF you want to claim this, you need to provide much stronger evidence than what is described so far in the manuscript. This needs a mass balance of fluorine, as starting compound, all shorter-chain products and fluoride. In the best case all fluorine is released as fluoride into the solution phase (alkaline washing of solids to release fluoride is usually done).

Response: We employed ion chromatography (IC) to determine fluoride release during electrooxidation in solution. The combustion method was exclusively utilized for the analysis of activated carbon cloth (ACC) materials to measure the contents of C, H, N, and F. The electrooxidation of PFAS stems from the oxidation reaction of BDD, which generates hydroxyl radicals. In our defluorination study, ACC served as the cathodic electrode (counter electrode) to release the long-chain PFAS that were electrosorbed during PFAS removal in the redox-polymer ED platform (**Fig. S6.3**), while BDD (working electrode) produced hydroxyl radicals for the mineralization of released PFAS. The determination of defluorination was based on the mass balance of fluorine measured by IC. To provide further clarity on our methodology, we expanded the discussion on measurement techniques and calculations within the titled "*PFAS electrosorption and defluorination experiments*" section of the Method. Additionally, elaborated on the anticipated defluorination process and provided an illustrative schematic in Supplementary **Fig. S6.3**.

Revision (pg. 19): With boron-doped diamond (BDD) as an anode, TFA and PFPrA showed complete PFAS degradation and defluorination in 6 hours, while PFHxA exhibited complete degradation, as well as 76% defluorination in 8 hours (**Fig. 6f** and Supplementary **Fig. S6.1**). Electrosorbed PFHxA undergoes two steps of the defluorination process: desorption from the ACC and subsequent defluorination in the solution using hydroxyl radicals generated by the BDD (Supplementary **Fig. S6.3**). Consequently, the mineralization of PFHxA requires a longer defluorination period compared to TFA and PFPrA, which are more volatile and do not require a desorption step.

AND

Revision (pg. 24-25): Fluoride, chloride, and perchlorate concentrations were measured by the IC (refer to the "liquid-phase analytics" section for specific IC operational parameters). Defluorination (%) was

subsequently determined by assessing the mass balance of initial PFAS concentrations in solution (for TFA and PFPrA) or electrosorbed (for PFHxA), whereas the remaining chloride (%) and perchlorate production (%) were calculated based on the starting NaCl concentrations (20 mM).

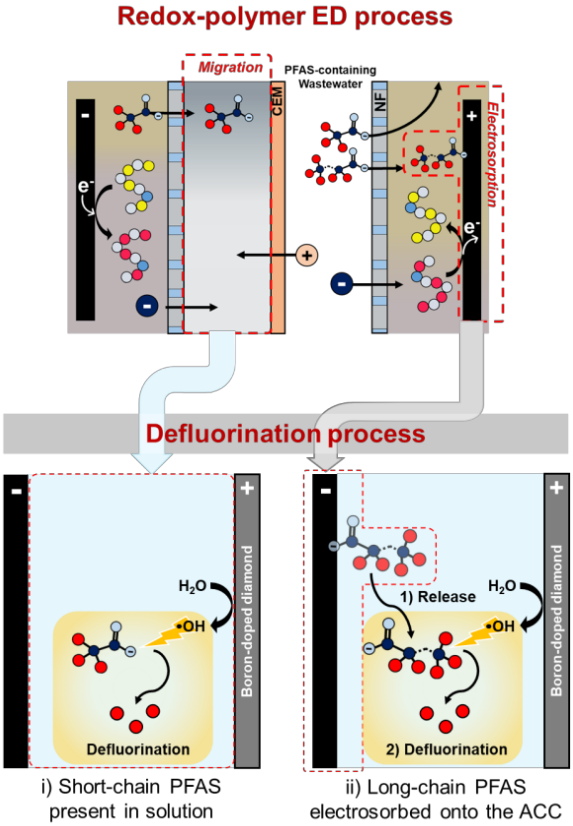

Fig. S6.3. Anticipated defluorination process via hydroxyl radical generated by the boron-dopped diamond: i) Defluorination process of short-chain PFAS up-concentrated in solution and ii) long-chain PFAS electrosorbed onto the activated-carbon clothes during the redox-polymer ED process.

20. Overall, the required residence/treatment time appears to be rather high. What is the ratio of treated water flow (m^3/h) per active area of the electrodialysis unit (m^2) for achieving a certain removal degree and how does this compare to the state-of-the art? It is not sufficient to just discuss removal degrees without using parameters to quantify the effort spent.

Response: The current lab-scale system achieves a water treatment rate of 1.79 $L/h/m^2$ with over 85% removal of Cl-, PFPrA, PFBA, PFHxA, and PFOA. Our performance can be improved by increasing the concentration of redox species with stacked electrodes, as well as by arranging additional channels (FC and AC) in series.[15,16] Increasing the concentration of redox species will facilitate more redox reactions for ion removal, while stacking the FC and AC in series allows for simultaneous treatment of multiple feed channels, thereby enhancing the overall treatment rate in our redox-polymer ED system.

In numerous studies on various PFAS removal technologies, cross-comparison of performance values is difficult due to the lack of standardized performance metrics. For instance, ion-exchange resins and electrosorption systems typically express their performance in mol/g and mg/g, whereas membrane

technologies (e.g., reverse osmosis) report performance in terms of removal and rejection percentage.[7-14] Regarding overall removal percentage, the redox-polymer ED system is comparable to adsorption, ion exchange, and membrane technologies for long-chain PFAS, while it outperforms these conventional technologies for short-chain PFAS.[8] To incorporate the reviewer's suggestions, we have discussed potential strategies for scaling up and improving the water production rate as future work, as well as a comparison of PFAS removal with state-of-the-art technologies.

Revision (pg. 16): We believe that the redox-ED platform can intensify the water remediation process, especially advantageous for mixed chain-length PFAS at high concentration levels, as its capacity is not limited by active materials,[31] nor does it require high energy inputs such as pressure.[17] The overall PFAS removal percentage of our redox-polymer ED system is comparable to adsorption (≥ 80%), ion exchange (50-90%), and membrane technologies (≥ 90%) for long-chain PFAS, while it outperforms adsorption (≤ 40%) and ion exchange (≤ 55%) for short-chain PFAS.[11,60] However, to make the system more practical for water treatment and eventual industrial deployment, we need to improve the overall water treatment rate (currently 1.79 L/h/m²). This can be achieved by increasing the concentration of redox species with stacked electrodes and arranging additional channels (FC and AC) in series, as demonstrated in previous electrodialysis studies.[61,62]

Reviewer #4 (Remarks to the Author):

This manuscript reports on an NF-enabled redox polymer electrodialysis system to remove both ultra-short-chain and regular perfluorocarboxylates. This study is comprehensive and the characterizations are of high quality. The system design followed general mechanisms but showed effective removal of ultra-short-chain PFCAs. With the help of redox-responsive polymer, the PFCA removal by the new ED system is better than the conventional system. The removal section is OK to go.

We appreciate the reviewer's positive feedback on our findings. In response to the reviewer's feedback on electrooxidation, we have extensively revised our manuscript. Specifically, we have addressed the generation of perchlorate as a by-product during BDD oxidation and presented the kinetics of perchlorate formation during defluorination (Supplementary **Fig. S6.2**). Additionally, we have provided a more detailed discussion on the anticipated defluorination process for both short-chain PFAS (TFA and PFPrA) and relatively long-chain PFAS (PFHxA), which were electrosorbed, along with illustrative mechanisms (Supplementary **Fig. S6.3**). Below are our specific responses:

1. However, I do not find an effective connection to the PFAS destruction with BDD in the last paragraph (Line353-369). First, the BDD treatment configuration is different from the proposed ED system. It is a separate topic but the authors tried to mix it to oversell the ED system.

Response: We agree with the reviewer's point. Although electrooxidation was not the main focus of our study, it provided valuable insights into the complete treatment (defluorination) following our redox-polymer ED operations. In response to the reviewer's feedback, we have shifted our emphasis more toward the redox-ED system and placed less emphasis on BDD oxidation.

2. Second, it is not clear how the electrosorbed PFHxA was defluorinated. I do not find any information on whether the PFHxA was desorbed from the polymer/membrane by some solvent washing before the BDD oxidation.

Response: To provide further clarity on our methodology, we elaborated on the anticipated two-step defluorination processes for PFHxA and provided an illustrative schematic in Supplementary **Fig. S6.3**.

Revision (pg. 19): With boron-doped diamond (BDD) as an anode, TFA and PFPrA showed complete PFAS degradation and defluorination in 6 hours, while PFHxA exhibited complete degradation, as well as 76% defluorination in 8 hours (**Fig. 6f** and Supplementary **Fig. S6.1**). Electrosorbed PFHxA undergoes two steps of the defluorination process: desorption from the ACC and subsequent defluorination in the solution using hydroxyl radicals generated by the BDD (Supplementary **Fig. S6.3**). Consequently, the mineralization of PFHxA requires a longer defluorination period compared to TFA and PFPrA, which are more volatile and do not require a desorption step.

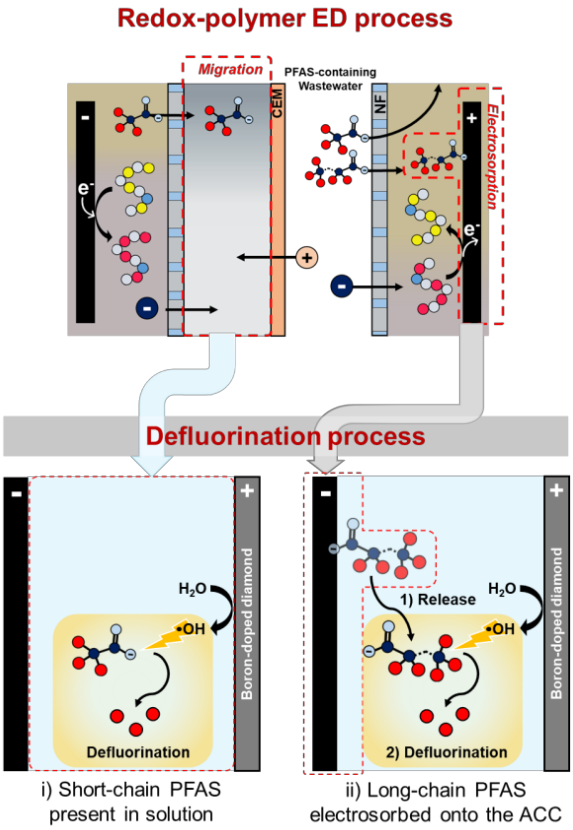

Fig. S6.3. Anticipated defluorination process via hydroxyl radical generated by the boron-dopped diamond: i) Defluorination process of short-chain PFAS up-concentrated in solution and ii) long-chain PFAS electrosorbed onto the activated-carbon clothes during the redox-polymer ED process.

3. Third, the solution contained chloride, and BDD oxidation is known for converting chloride into other harmful species such as chlorate and perchlorate.

Response: We acknowledged the production of perchlorate during BDD oxidation and experimentally evaluated its generation over an 8-hour defluorination test (Supplementary **Fig.6.2**). This information has been incorporated into the main text along with future research directions for mitigation.

Revision (pg. 19): Due to high oxidation power, BDD oxidized chloride into perchlorate as a disinfection by-product.[68-70] Over 80% of chloride (20 mM) present in the defluorination test was converted into perchlorate (Supplementary **Fig. S6.2**). Considering the health risks associated with ClO_4^-,[68,69] reducing chlorine oxidation is essential to improve defluorination efficiency and address a pressing topic in U.S. drinking water safety. With further optimization of defluorination conditions and advancements in anode materials, our proof-of-concept defluorination results inspire us to envision a sustainable and energy-efficient PFAS treatment process alongside desalination.

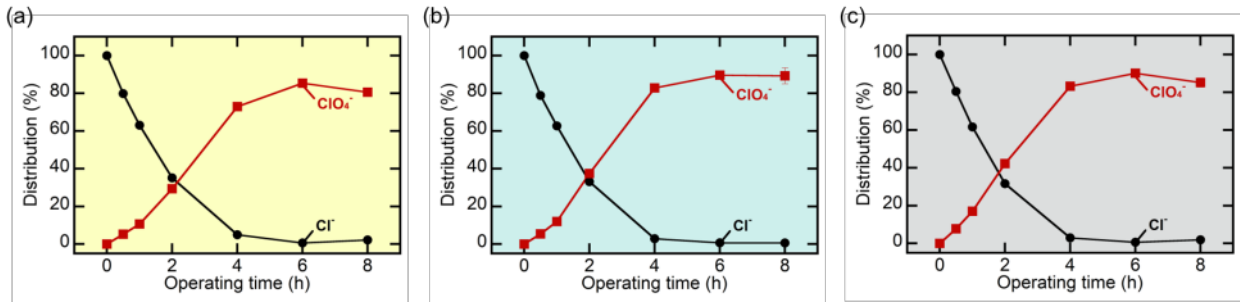

Figure S6.2. Chloride oxidation kinetics during defluorination of (a) TFA, (b) PFPrA, and (c) PFHxA for 8 hours of the oxidation process. The findings indicate that, on average, 98.4% of Cl^- disappeared, with 85.0% of the initial chloride being converted to ClO_4^-. The remaining chloride (%) and perchlorate production (%) were calculated based on the starting NaCl concentrations (20 mM).

Although the authors could argue that this problem is not in the scope of this study, I would then point out that the entire defluorination section is also out of the scope of the study because BDD is not an integrated component in the ED system. So I would suggest the authors remove the defluorination section because it is oversold. However, if the authors choose to keep the BDD oxidation step in this study as an important treatment for PFAS destruction, a comprehensive profile of chlorine oxidation products must be provided. So, either no report or a comprehensive information profile is recommended. Partially reporting the favorable aspect will not help solve the PFAS issue.

Response: We acknowledge the reviewer's concerns. We believe that additional experimental data and acknowledgment of limitations on BDD oxidation provide a more comprehensive mineralization process. Despite our main focus in the current manuscript being on the development of a single-step PFAS removal via a redox-polymer ED platform, we still think that providing insights into the complete treatment of the PFAS after our removal step inspires us to envision a sustainable and energy-efficient PFAS treatment process. We acknowledge the reviewer's concerns. We believe that the additional experimental data and recognition of the limitations of BDD oxidation offer a more comprehensive view of the mineralization process. Although our primary focus in this manuscript is on the development of a single-step PFAS removal via a redox-polymer ED platform, we think that providing insights into the complete treatment of PFAS following our removal step inspires us to envision a sustainable and energy-efficient PFAS treatment process. In response to the reviewer's concern, we made an effort to highlight the PFAS removal and reduce the focus on the electrooxidation process.

References

1 Pérez-González, A. *et al.* Nanofiltration separation of polyvalent and monovalent anions in desalination brines. *Journal of membrane science* **473**, 16-27 (2015).

2 Nativ, P., Lahav, O. & Gendel, Y. Separation of divalent and monovalent ions using flow-electrode capacitive deionization with nanofiltration membranes. *Desalination* **425**, 123-129 (2018).

3 Van der Bruggen, B., Koninckx, A. & Vandecasteele, C. Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration. *Water research* **38**, 1347-1353 (2004).

4 Shirley, J., Mandale, S. & Kochkodan, V. Influence of solute concentration and dipole moment on the retention of uncharged molecules with nanofiltration. *Desalination* **344**, 116-122 (2014).

5 Brassolatti, P. *et al.* Bacterial cellulose membrane used as biological dressings on third-degree burns in rats. *Bio-medical materials and engineering* **29**, 29-42 (2018).

6 Gao, Z., Li, N., Chen, M. & Yi, W. Comparative study on the pyrolysis of cellulose and its model compounds. *Fuel processing technology* **193**, 131-140 (2019).

7 Kim, K. *et al.* Molecular tuning of redox-copolymers for selective electrochemical remediation. *Advanced Functional Materials* **30**, 2004635 (2020).

8 Yadav, S. *et al.* Updated review on emerging technologies for PFAS contaminated water treatment. *Chemical Engineering Research and Design* **182**, 667-700 (2022).

9 Saeidi, N., Harnisch, F., Presser, V., Kopinke, F.-D. & Georgi, A. Electrosorption of organic compounds: State of the art, challenges, performance, and perspectives. *Chemical Engineering Journal*, 144354 (2023).

10 Santiago, A. R., Medina, P. B. & Su, X. Electrochemical remediation of perfluoroalkyl substances from water. *Electrochimica Acta* **403**, 139635 (2022).

11 Román Santiago, A. *et al.* Imparting Selective Fluorophilic Interactions in Redox Copolymers for the Electrochemically Mediated Capture of Short-Chain Perfluoroalkyl Substances. *Journal of the American Chemical Society* **145**, 9508-9519 (2023).

12 Baldaguez Medina, P. *et al.* Investigating the Electrochemically Driven Capture and Release of Long-Chain PFAS by Redox Metallopolymer Sorbents. *ACS Applied Materials & Interfaces* **15**, 22112-22122 (2023).

13 Sun, H., Cannon, F. S. & He, X. Enhanced trifluoroacetate removal from groundwater by quaternary nitrogen-grafted granular activated carbon. *Science of the total environment* **660**, 577-585 (2019).

14 Zhou, J. *et al.* Efficient removal of trifluoroacetic acid from water using surface-modified activated carbon and electro-assisted desorption. *Journal of Hazardous Materials* **436**, 129051 (2022).

15 Kim, H., Kim, S., Kim, N., Su, X. & Kim, C. Multi-electrode scale-up strategy and parametric investigation of redox-flow desalination systems. *Desalination* **549**, 116350 (2023).

16 Kim, Y. & Logan, B. E. Series assembly of microbial desalination cells containing stacked electrodialysis cells for partial or complete seawater desalination. *Environmental science & technology* **45**, 5840-5845 (2011).

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The manuscript has been revised accordingly. The authors have address the comments well. It can be accepted for publication now.

Reviewer #2 (Remarks to the Author):

In the review round, the authors have carried out extensive supplementary tests. A comprehensive examination of membrane fouling through SEM, EDS, XPS, and EIS has been added in the section titled “Investigating membrane fouling by irreversible PFAS adsorption.” In response to my comments, the authors have rearranged the introduction, which significantly improved the clarity. More information on the experimental details and chlorine species has been provided. Overall, this reviewer is very satisfied with the revision. The manuscript is recommended for the next stage.

Reviewer #3 (Remarks to the Author):

The authors have significantly improved their manuscript and satisfactorily addressed most of my concerns. However, there are some issues remaining to be solved:
Fig. S6.3 is showing a scheme that is not in line with currently accepted knowledge, as neither long-chain nor short-chain perfluoralkyl acids (PFAAs) are degraded by OH-radicals at significant rates. The accepted mechanism for electrooxidation is direct electron transfer from the PFAA head groupt to the anode at the electrode surface.

Please revise: 'Consequently, the mineralization of
PFHxA requires a longer defluorination period compared to TFA and PFPrA, which are more volatile and
do not require a desorption step.' The term 'volatile' should be replaced by 'hydrophilic' as volatility of the protonated acid is not the relevant parameter for describing sorption tendency of the acid anion in water.

Page 16: 'The overall PFAS removal percentage of our redox-
polymer ED system is comparable to adsorption (≥ 80%), ion exchange (50-90%), and membrane technologies (≥ 90%) for long-chain PFAS, while it outperforms adsorption (≤ 40%) and ion exchange (≤ 55%) for short-chain PFAS.11,60' - I doubt that these numbers are appropriate for a comparison. Removal percentage is highly dependent on the type of adsorbent or resin and the

operation conditions (e.g. dosing of adsorbent powder or fixed-bed flow-through system at initial clean or extended partially loaded stage). Thus, providing a lumped removal percentage for 'adsorption' is simplistic.

Reviewer #4 (Remarks to the Author):

In R1, the authors responded to the questions regarding BDD oxidation byproduct from chloride and chose to keep BDD treatment in the manuscript as a complete removal-destruction scheme. This reviewer appreciates the solid experimental data that >80% of chloride was oxidized to perchlorate (the remaining 10+% chloride was converted into something else, such as chlorate, chlorite, etc.). This reviewer supports the publication of R1 as is.

In environmental engineering academia, BDD is heavily criticized for the complete oxidation of chloride into various toxic byproducts. This reviewer is interested in how other reviewers will comment on the new experimental result. If more questions/challenges come out from the perchlorate formation data, this reviewer suggests the authors propose/discuss other PFAS degradation technologies that do not oxidize chloride (for example: UV and hydrothermal treatment). A recent paper provides an interesting discussion on the perchlorate issue at the end (https://www.nature.com/articles/s44221-024-00232-7).

The perchlorate topic will only come out when EO using BDD is proposed. This work does not have to be necessarily bound to EO treatment for PFAS destruction.

Reviewer #1 (Remarks to the Author):

The manuscript has been revised accordingly. The authors have address the comments well. It can be accepted for publication now.

Response: We appreciate the reviewer's positive feedback on our revised manuscript.

Reviewer #2 (Remarks to the Author):

In the review round, the authors have carried out extensive supplementary tests. A comprehensive examination of membrane fouling through SEM, EDS, XPS, and EIS has been added in the section titled "Investigating membrane fouling by irreversible PFAS adsorption." In response to my comments, the authors have rearranged the introduction, which significantly improved the clarity. More information on the experimental details and chlorine species has been provided. Overall, this reviewer is very satisfied with the revision. The manuscript is recommended for the next stage.

Response: We sincerely thank the reviewer for their positive feedback on our revised manuscript.

Reviewer #3 (Remarks to the Author):

The authors have significantly improved their manuscript and satisfactorily addressed most of my concerns. However, there are some issues remaining to be solved:

Response: We thank the reviewer for the positive feedback on our revised manuscript. We have carefully revised our manuscript to address additional comments by re-illustrating the degradation scheme, as well as providing a table for state-of-the-art PFAS removal.

Fig. S6.3 is showing a scheme that is not in line with currently accepted knowledge, as neither long-chain nor short-chain perfluoralkyl acids (PFAAs) are degraded by OH-radicals at significant rates. The accepted mechanism for electrooxidation is direct electron transfer from the PFAA head group to the anode at the electrode surface.

Response: In response to the reviewer's comment, we re-illustrated the degradation mechanisms, to reflect direct electron transfer from the PFAS head group to the anode at the electrode surface.

Revision (pg. 19): Electrosorbed PFHxA undergoes two steps of the defluorination process: desorption from the ACC followed by defluorination. The defluorination involves multiple degradation processes, which involve direct electron transfers from PFAS to the BDD surface, and subsequent indirect oxidation of PFAS by hydroxyl radicals generated by the BDD (Supplementary **Fig. S28**).[69,70]

AND

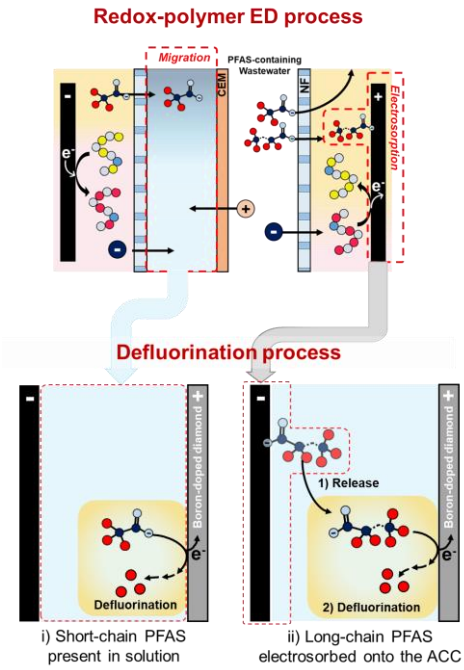

Fig. S28. Anticipated defluorination process: i) Defluorination process of short-chain PFAS up-concentrated in solution and ii) long-chain PFAS electrosorbed onto the activated-carbon clothes during the redox-polymer ED process.

Please revise: 'Consequently, the mineralization of PFHxA requires a longer defluorination period compared to TFA and PFPrA, which are more volatile and do not require a desorption step.' The term 'volatile' should be replaced by 'hydrophilic' as volatility of the protonated acid is not the relevant parameter for describing sorption tendency of the acid anion in water.

Response: In response to the reviewer's comment, changed the word from 'volatile' to hydrophilic.

Revision (pg. 19): Consequently, the mineralization of PFHxA requires a longer defluorination period compared to TFA and PFPrA, which are more hydrophilic and do not require a desorption step.

Page 16: 'The overall PFAS removal percentage of our redox-polymer ED system is comparable to adsorption (≥ 80%), ion exchange (50-90%), and membrane technologies (≥ 90%) for long-chain PFAS, while it outperforms adsorption (≤ 40%) and ion exchange (≤ 55%) for short-chain PFAS.11,60' - I doubt that these numbers are appropriate for a comparison. Removal percentage is highly dependent on the type of adsorbent or resin and the operation conditions (e.g. dosing of adsorbent powder or fixed-bed flow-through system at initial clean or extended partially loaded stage). Thus, providing a lumped removal percentage for 'adsorption' is simplistic.

Response: In response to the reviewer's comment, we have removed the comparison of state-of-the-art technologies based on percent removal. In numerous studies on various PFAS removal technologies, we agree that cross-comparison of performance values is challenging due to the lack of standardized performance metrics, especially between membrane-based technologies with adsorption and ion exchange. As the reviewer pointed out, the differences in the initial conditions make it even harder to make a fair

comparison. We addressed the limitations involved in cross-comparing different systems along with a survey table that outlines the initial conditions and operating parameters of state-of-the-art technologies, and have instead referred to a comprehensive table for comparison.

Revision (pg. 16): We summarized PFAS removal performance across various state-of-the-art technologies, in **Table S4**. Note that directly comparing PFAS removal performance across various state-of-the-art technologies can be challenging due to the lack of standardized performance metrics and different initial conditions. Our comparison, based on the removal performance summarized in **Table S4** and relevant review papers,[11,61] offers a preliminary indication that our system is comparable to adsorption, ion exchange, and membrane technologies for long-chain PFAS, while it outperforms adsorption and ion exchange for short-chain PFAS.

AND

Table S4. Summary of PFAS removal performance across various state-of-the-art technologies

Removal techniques	Materials	Target PFAS	Initial Concentration of PFAS (mM)	Removal performance	Ref
Adsorption	GAC, F400	PFOA	0.04-0.36	0.38 mmol/g	11
		PFBS	0.05-0.50	0.034 mmol/g	11
	GAC, Bamboo	PFOA	0.05-0.6	1.15 mmol/g	12
	Quaternary nitrogen-grafted carbon	TFA	0.09-0.88	0.289 mmol/g	13
Electro-sorption	Ferrocene-based polymer, PFPMAm	PFOA	0.10	0.169 mmol/g[a]	14
	Cobaltocenium-based polymer, PMAECoPF6	PFOA	0.10	0.217 mmol/g[a]	14
	Fluorinated redox polymer, P(A98F2)	PFHxA	0.10	2.74 mmol/g	15
	Fluorinated redox polymer, P(A39T53F8)	PFBA	0.10	0.922 mmol/g	15
	Surface defunctionalized activated carbon felt (DeACF)	TFA	1.75	0.263 mmol/g	16
Ion exchange	IRA 67	PFOA	0.29[a]	2.82 mmol/g	17
		PFHxA	0.1[a]	0.53 mmol/g	17
	IRA910	PFOA	0.50	3.47 mmol/g	18
		PFHxA	0.50	3.47 mmol/g	18
		PFBA	0.50	2.97 mmol/g	18
	Purolite A520E	PFOA	2.41	0.323 mmol/g	19
		PFBA	4.67	0.138 mmol/g	19
Membrane	NFG	PFOA	0.00024	55.6%	20
		PFHxA	0.00032	38.6%	20
		PFBA	0.00047	18.7%	20
	NF90	PFOA	0.00024	97.4%	20
		PFHxA	0.00032	99.6%	20
		PFBA	0.00047	86.0%	20
	NF270	PFOA	0.24	99%	21
		PFOA	0.24	92.2%	21
	BW30-2540	PFOA	0.02	99.9%[a]	22
	BW30-2540	PFBA	0.05	99.9%[a]	22
	NF90-2540	PFOA	0.02	99.8%[a]	22
	NF90-2540	PFBA	0.05	99.7%[a]	22
Current study (Figure 5)	**NF-enabled redox polymer ED**	**PFOA**	**0.01**	**94.4%**	
		PFHxA	**0.01**	**90.1%**	
		PFBA	**0.01**	**88.8%**	
		PFPrA	**0.01**	**90.3%**	
(Fig. 4)		**TFA**	**0.001-1**	**72.8-89.3%**	
		PFPrA	**0.001-1**	**57.6-86.1%**	

[a] Calculated or estimated from the provided data

Reviewer #4 (Remarks to the Author):

In R1, the authors responded to the questions regarding BDD oxidation byproduct from chloride and chose to keep BDD treatment in the manuscript as a complete removal-destruction scheme. This reviewer appreciates the solid experimental data that >80% of chloride was oxidized to perchlorate (the remaining 10+% chloride was converted into something else, such as chlorate, chlorite, etc.). This reviewer supports the publication of R1 as is.

In environmental engineering academia, BDD is heavily criticized for the complete oxidation of chloride into various toxic byproducts. This reviewer is interested in how other reviewers will comment on the new experimental result. If more questions/challenges come out from the perchlorate formation data, this reviewer suggests the authors propose/discuss other PFAS degradation technologies that do not oxidize chloride (for example: UV and hydrothermal treatment). A recent paper provides an interesting discussion on the perchlorate issue at the end (https://www.nature.com/articles/s44221-024-00232-7). The perchlorate topic will only come out when EO using BDD is proposed. This work does not have to be necessarily bound to EO treatment for PFAS destruction.

Response: We appreciate the reviewer's positive feedback on our revised manuscript. As noted, our system can be integrated with various degradation systems to address the perchlorate issue. To further address the reviewer's concern about PFAS degradation, we have included an expanded discussion on potential technologies that could be combined with our redox-polymer ED platform, such as photoelectrochemical oxidation, as well as strategies to mitigate perchlorate generation with BDD electrodes. While the primary focus of this work is PFAS removal, we plan to expand our remediation process by incorporating different oxidation techniques in future studies.

Revision (pg. 20): In this regard, our system can be integrated with various PFAS degradation systems to address the perchlorate issue, including photoelectrochemical oxidation, plasma-based techniques, and ultrasonic irradiation.[17,76-78] Additionally, surface modification of anode and optimizing oxidation conditions (e.g., adding hydrogen peroxide) can help the electrochemical oxidation process suppress byproduct generation.[74,75,78] Therefore, further investigation into the defluorination process is crucial to envision a sustainable and energy-efficient PFAS treatment process that can be integrated with the redox-polymer ED system for comprehensive PFAS remediation alongside desalination.

REVIEWERS' COMMENTS

Reviewer #3 (Remarks to the Author):

Most comments have been satisfactorily addressed.
The new Table S4 is showing for adsorption processes two parameters named 'initial concentration of PFAS in mM' and 'removal performance' in mmol/g. If the data are extracted from batch experiments, these parameters are not giving any insight in performance as the concentration of adsorbent added would still be needed to get the picture.

If you only consider column/flow-through adsorber studies for Table S4 than 'initial' should be replaced by 'inflow', otherwise it is misleading.

If you also use batch experiment data in Table S4, I recommend to present 'equilibrium aqueous phase PFAS concentration in mM' instead of 'initial concentration of PFAS in mM' and 'equilibrium sorbent loading in mmol/g' instead of 'removal performance' in mmol/g. These two parameters reflect a sorption coefficient which is sufficient to describe a solute-adsorbent pair at least in a certain concentration range. Than, for a column experiment 'equilibrium aqueous phase PFAS concentration in mM' is the inflow concentration of PFAS if 'equilibrium sorbent loading in mmol/g' is the adsorbent loading at PFAS breakthrough.

Reviewer #3 (Remarks to the Author):

Most comments have been satisfactorily addressed.

The new Table S4 is showing for adsorption processes two parameters named 'initial concentration of PFAS in mM' and 'removal performance' in mmol/g. If the data are extracted from batch experiments, these parameters are not giving any insight in performance as the concentration of adsorbent added would still be needed to get the picture. If you only consider column/flow-through adsorber studies for Table S4 than 'initial' should be replaced by 'inflow', otherwise it is misleading.

If you also use batch experiment data in Table S4, I recommend to present 'equilibrium aqueous phase PFAS concentration in mM' instead of 'initial concentration of PFAS in mM' and 'equilibrium sorbent loading in mmol/g' instead of 'removal performance' in mmol/g. These two parameters reflect a sorption coefficient which is sufficient to describe a solute-adsorbent pair at least in a certain concentration range. Than, for a column experiment 'equilibrium aqueous phase PFAS concentration in mM' is the inflow concentration of PFAS if 'equilibrium sorbent loading in mmol/g' is the adsorbent loading at PFAS breakthrough.

Response: The adsorption data provided in the Table S4 is performed in batch experiments. As recommended by the reviewer, we have included additional values, such as equilibrium PFAS concentration and sorbent loading, to further detail the adsorption removal performance.

Revision (Supplementary Table 4):

Table 4. Summary of PFAS removal performance across various state-of-the-art technologies.

Removal techniques	Materials	Target PFAS	$C_{PFAS,i}$ (mM)	Removal performance	Ref
Adsorption	GAC, F400	PFOA	0.04-0.36	0.270 mmol/g, 0.193 mM, 0.1 g[a,b]	11
		PFBS	0.05-0.50	0.329 mmol/g, 0.233 mM, 0.1 g[a,b]	11
	GAC, Bamboo	PFOA	0.05-0.6	1.03 mmol/g, 0.34 mM, 10 mg[a,b]	12
	Quaternary nitrogen-grafted carbon (AWNQ)	TFA	0.09-0.88	34 μmol/g, 0.027 mM, 20 mg[a,b]	13
Electro-sorption	Ferrocene-based polymer, PFPMAm	PFOA	0.10	0.169 mmol/g[b]	14
	Cobaltocenium-based polymer, PMAECoPF6	PFOA	0.10	0.217 mmol/g[b]	14
	Fluorinated redox polymer, P(A98F2)	PFHxA	0.10	2.74 mmol/g	15
	Fluorinated redox polymer, P(A39T53F8)	PFBA	0.10	0.922 mmol/g	15
	Surface defunctionalized activated carbon felt (DeACF)	TFA	1.75	0.263 mmol/g	16
Ion exchange	IRA 67	PFOA	0.29[b]	2.82 mmol/g	17
		PFHxA	0.1[b]	0.53 mmol/g	17
	IRA910	PFOA	0.50	3.47 mmol/g	18
		PFHxA	0.50	3.47 mmol/g	18
		PFBA	0.50	2.97 mmol/g	18
	Purolite A520E	PFOA	2.41	0.323 mmol/g	19
		PFBA	4.67	0.138 mmol/g	19
Membrane	NFG	PFOA	0.00024	55.6%	20
		PFHxA	0.00032	38.6%	20
		PFBA	0.00047	18.7%	20
	NF90	PFOA	0.00024	97.4%	20
		PFHxA	0.00032	99.6%	20
		PFBA	0.00047	86.0%	20
	NF270	PFOA	0.24	99%	21
		PFOA	0.24	92.2%	21
	BW30-2540	PFOA	0.02	99.9%[a]	22
	BW30-2540	PFBA	0.05	99.9%[a]	22
	NF90-2540	PFOA	0.02	99.8%[a]	22
	NF90-2540	PFBA	0.05	99.7%[a]	22
NF-enabled redox polymer ED	**Cellulose-based NF (1 kDa), P(TMA-*co*-TMPMA-*co*-METAC)**	**PFOA**	**0.01**	**94.4%**	**Figure 5**
		PFHxA	**0.01**	**90.1%**	
		PFBA	**0.01**	**88.8%**	
		PFPrA	**0.01**	**90.3%**	
		TFA	**0.001-1**	**72.8-89.3%**	**Figure 4**
		PFPrA	**0.001-1**	**57.6-86.1%**	

[a] Equilibrium maximum adsorption capacity, equilibrium PFAS concentrations in aqueous phase, and sorbent loading.
[b] Calculated or estimated from the provided data.