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AGC Comments Addendum (Copies of Studies) -- Vol. 35

Report on Critical Per- and Polyfluoroalkyl Substance Uses

Pursuant to Section 347 of the James M. Inhofe National Defense Authorization Act for
Fiscal Year 2023 (Public Law 117-263)



August 2023

Office of the Assistant Secretary of Defense for Energy,
Installations, and Environment

Office of the Assistant Secretary of Defense for Industrial
Base Policy

The estimated cost of this report or study for the Department of Defense is approximately \$83,000 in Fiscal Year 2023. This includes \$47,900 in expenses and \$45,100 in DoD labor.
Generated on 20230718 RefID: 1-22557AD

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Acronyms

AFFF	Aqueous film forming foam
AIM Act	American Innovation and Manufacturing Act of 2020
CMRMP	Chemical and Material Risk Management Program
DoD	Department of Defense
ECTFE	Ethylenechlorotrifluoroethylene
EPA	U.S. Environmental Protection Agency
EU	European Union
F3	Fluorine-free foam
FY	Fiscal Year
HFCs	Hydrofluorocarbons
HFOs	Hydrofluoroolefins
Li-ion	Lithium-ion
MCMEU	Mission-critical military end use
MilDep	Military Department
NDAA	National Defense Authorization Act
NDT	Non-destructive testing
OASD(IBP)	Office of the Assistant Secretary of Defense for Industrial Base Policy
ODASD(E&ER)	Office of the Deputy Assistant Secretary of Defense for Environment and Energy Resilience
OECD	Organisation for Economic Co-operation and Development
PA&T	Policy, Analysis, & Transition
PFA	Perfluoroalkoxy alkanes
PFAA	Perfluoroalkyl acid
PFAS	Per- and polyfluoroalkyl substances
polyFAA	Polyfluoroalkyl acid
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
SOTA	State-of-the-Art
SOTP	State-of-the-Practice
U.S.	United States
USS	United States Ship
UV	Ultraviolet

I. Introduction

Section 347(a) of the James M. Inhofe National Defense Authorization Act (NDAA) for Fiscal Year (FY) 2023 (Public Law 117-263) directs the Secretary of Defense, in consultation with the Defense Critical Supply Chain Task Force (i.e., the Office of the Assistant Secretary of Defense for Industrial Base Policy (OASD(IBP))) and the Chemical and Material Risk Management Program (CMRMP) of the Office of the Assistant Secretary of Defense for Energy, Installations, and Environment (OASD(EI&E)), to submit to the Committees on Armed Services of the House of Representatives and the Senate a report outlining the uses of per- and polyfluoroalkyl substances (PFAS) that are critical to the national security of the United States. This report focuses on critical uses in the sectors outlined in the February 2022 Department of Defense (DoD) report titled *Securing Defense-Critical Supply Chains* and sectors of strategic importance for domestic production and investment to build supply chain resilience.

PFAS are common chemicals used across DoD. Most weapons platforms incorporate PFAS, and PFAS are found throughout the defense industrial base in roles supporting mission critical component production and supply. PFAS uses may be direct, where a PFAS is a constituent in a consumable item or is incorporated into an article (e.g., end item), or indirect, where a PFAS is used to formulate another chemical or is part of a manufacturing process. These uses and processes are necessary to the production of key components of the defense industrial base, such as microelectronic chips and lithium-ion (Li-ion) batteries.

PFAS are chemically quite stable, and many are water and oil repellent, heat resistant, and/or stain resistant, often leading to non-stick surfaces on various materials. Examples of applications of PFAS are in plastics, o-rings, gaskets, lubricants, coolants, and fabrics. DoD is reliant on the critically important chemical and physical properties of PFAS to provide required performance for the technologies and consumable items and articles which enable military readiness and sustainment. Losing access to PFAS due to overly broad regulations or severe market contractions would greatly impact national security and DoD's ability to fulfill its mission, and impact domestic defense industrial base manufacturing and supply.

This report provides details on what is currently known about direct and indirect mission critical PFAS uses that could impact mission readiness if the substances are no longer available. It also highlights the challenges and costs related to finding and qualifying equal or improved performing alternatives to existing PFAS materials in sectors of strategic importance to DoD. It is important to note that the information contained in this report is limited to what was available at the time of its drafting. As such, the information presented represents a fraction of the mission critical PFAS uses due to a lack of knowledge of the complete chemical composition in

consumables and articles (e.g., end items)¹. In addition, there is significant uncertainty regarding the presence of PFAS in products that make up a complex value chain. A more complete understanding of PFAS essential uses would require an extensive and complex evaluation of the market, a gap analysis of current requirements for manufacturer-provided product information, and illumination of the value chain of products.

II. Definitions

For purposes of this report, the terms used within section 347(a) of the NDAA for FY 2023 are defined in the following sub-sections.

II.1 Per- and Polyfluoroalkyl Substances

There is currently no consensus definition of PFAS as a chemical class.² Congress did not define PFAS within section 347(a) of the NDAA for FY 2023 for purposes of this report.³ While there is no consensus definition, regulators in the European Union (EU) and the United States have proposed, but not yet adopted, different chemical-structure-based (rather than hazard- or risk-based) definitions. In anticipation of the most stringent future regulatory actions, DoD used the definition put forward by the Organisation for Economic Co-operation and Development (OECD) in its 2021 report, *Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance*,⁴ for collecting data and developing this report. OECD states “The term ‘PFASs’ is a broad, general, non-specific term, which does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene carbon moiety.” OECD cautions that this definition should not be used in deciding how to group and manage PFAS in regulatory actions; however, future PFAS legal and

¹ A consumable is defined as “an item of supply or an individual item (except explosive ordnance and major end items of equipment) that is normally expended or used up beyond recovery in the use for which it is designed or intended. An end item is the “final combination of end products, component parts, or materials that is ready for its intended use, e.g., ship, tank, mobile machine shop, or aircraft.” *DoD Supply Chain Terms and Definitions* (February 21, 2023). https://www.acq.osd.mil/log/LOG_SD/policy_vault.html/DoD_Supply_Chain_Terms_and_Definitions.pdf.

² *Per- and Polyfluoroalkyl Substances (PFAS) Report: A Report by the Joint Subcommittee on Environment, Innovation, and Public Health*, Per- and Polyfluoroalkyl Substances Strategy Team of the National Science and Technology Council, March 2023.

³ Congress previously defined PFAS in the NDAA for FY 2021 for purposes of establishing the interagency working group to coordinate federal activities related to PFAS research and development. Section 332(g)(1) defines PFAS broadly as (A) man-made chemicals of which all of the carbon atoms are fully fluorinated carbon atoms; and (B) man-made chemicals containing a mix of fully fluorinated carbon atoms, partially fluorinated carbon atoms, and nonfluorinated carbon atoms. William M. (Mac) Thornberry National Defense Authorization Act for Fiscal Year 2021, Pub. L. 116-283 (2021).

⁴ “PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF₃) or a perfluorinated methylene group (–CF₂–) is a PFAS.” OECD, *Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance* (Series on Risk Management No. 61), July 9, 2021. [https://one.oecd.org/document/ENV/CBC/MONO\(2021\)25/En/pdf](https://one.oecd.org/document/ENV/CBC/MONO(2021)25/En/pdf).

regulatory frameworks may disregard the OECD caution and seek to restrict the use of PFAS based on chemical structure.

The figure below provides an overview of the PFAS groups based on the OECD definition. This very broad definition encompasses more than 38,000 individual PFAS chemicals.⁵ DoD uses are represented in each major category of PFAS (i.e., perfluoroalkyl acids (PFAAs) and polyfluoroalkyl acids (polyFAAs)), PFAA precursors, and other PFAS (e.g., fluoropolymers, fluoroelastomers).

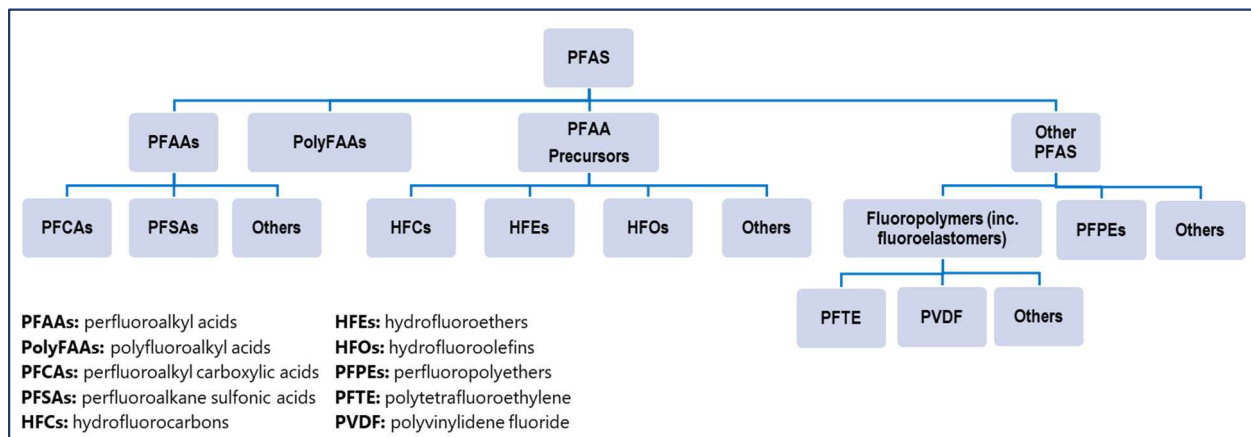


Figure: Overview of PFAS Groups (refined from OECD 2021)

II.2 Critical to the National Security

Congress did not define “critical to the national security of the United States” within section 347(a) of the NDAA for FY 2023. The term “mission-critical military end use (MCMEU),” however, is defined in regulations promulgated by the U.S. Environmental Protection Agency (EPA) under the American Innovation and Manufacturing Act of 2020 (AIM Act).⁶ The AIM Act addresses the phasedown of production and consumption of hydrofluorocarbons (HFCs) (e.g., regulated substances). MCMEUs are “[t]hose uses of regulated substances by an agency of the Federal Government responsible for national defense that have a direct impact on mission capability, as determined by the U.S. Department of Defense, including, but not limited to uses necessary for development, testing, production, training, operation, and maintenance of Armed Forces vessels, aircraft, space systems, ground vehicles, amphibious vehicles, deployable/expeditionary support equipment, munitions, and command and control systems.”⁷

The MCMEU definition focuses on *regulated substances*. As with HFCs, PFAS are undergoing increased regulation. But in addition to regulation, market forces can directly impact

⁵ Williams, et al. 2022. Assembly and Curation of Lists of Per- and Polyfluoroalkyl Substances (PFAS) to Support Environmental Science Research. *Front. Environ. Sci.* 10:850019. doi:10.3389/fenvs.2022.850019.

⁶ 42 U.S. Code 7675.

⁷ See 40 Code of Federal Regulations 84.3, “Phasedown of Hydrofluorocarbons” (October 5, 2021).

mission capability by limiting DoD’s ability to source and use PFAS and PFAS-containing products. The most recent example is 3M’s decision to phase out production of PFAS and PFAS-containing products by 2025.⁸

For purposes of data collection and report development, DoD used the MCMEU definition with the recognition that both market forces and increased regulation can have a direct impact on mission capability.

II.3 Sectors Considered

Section 347(a) of the NDAA for FY 2023 directs DoD to focus this report on critical PFAS uses in the four focus areas identified in DoD’s February 2022 report *Securing Defense-Critical Supply Chains*.⁹ The four focus areas—kinetic capabilities, energy storage and batteries, microelectronics, and castings and forgings—have critical supply chain vulnerabilities posing the most pressing threats to national security. In addition, this report focuses on semiconductors—a sector of strategic importance for domestic production and investment to build supply chain resilience—and strategic and critical minerals. These areas are described as:

- **Kinetic capabilities:** Current missiles systems and advanced and developing missile capabilities, including hypersonic weapons technology, as well as directed energy weapons.
- **Energy storage and batteries:** High-capacity batteries, with a particular focus on lithium batteries.
- **Microelectronics and semiconductors:** State-of-the-Practice (SOTP) and legacy microelectronics, State-of-the-Art (SOTA) microelectronics, and semiconductors.
- **Castings and forgings:** Metals or composites developed into key parts and manufacturing tools through high-intensity processes.
- **Strategic and critical minerals:** Minerals to supply U.S. military, industrial, and essential civilian national emergency needs, with emphasis on those that are not produced in sufficient quantities in the United States.

III. Data Collection Methodology

Data collection efforts for this report were led by the CMRMP of the ODASD(E&ER) and the OASD(IBP) and included engagement with the DoD Components and Military Departments (MilDeps), industry, and industry associations.

⁸ “3M to Exit PFAS Manufacturing by the End of 2025” (December 20, 2022). <https://news.3m.com/2022-12-20-3M-to-Exit-PFAS-Manufacturing-by-the-End-of-2025>.

⁹ Securing Defense-Critical Supply Chains: An Action Plan Developed in Response to President Biden’s Executive Order 14017 (February 2022). <https://media.defense.gov/2022/Feb/24/2002944158/-1/-1/1/DOD-EO-14017-REPORT-SECURING-DEFENSE-CRITICAL-SUPPLY-CHAINS.PDF>.

III.1 CMRMP Data Call

In March 2023, the CMRMP asked the DoD Components and MilDeps to provide information about its critical uses of PFAS, to include use of neat PFAS, use of PFAS-containing products, the functionality provided by the PFAS, specific uses and applications, and availability of alternatives (if known).

III.2 Additional Industry Engagement

The CMRMP held engagement sessions with various industries and industry associations to obtain information about the PFAS and PFAS-enabled products that they (or their member industries) manufacture and how DoD uses those products. The CMRMP shared this information with the DoD Components and MilDeps to inform their data collection efforts.

III.3 OASD(IBP) Industry Sector Data Collection Process

The Kinetic Capabilities Team at Policy, Analysis, & Transition (PA&T), OASD(IBP), engaged with PA&T Industry Sector leads and their industry partners to identify PFAS uses that are critical to U.S. national security. These sectors include Kinetic Capabilities, Energy Storage and Batteries, Microelectronics and Semiconductors, Castings and Forgings, and Strategic and Critical Materials. The Sector leads identified PFAS uses in industry, operation, manufacturing, processes, components, parts, and materials. They also discussed how and where losing access to PFAS could have significant mission readiness impacts and what they could do or are doing to mitigate those impacts.

IV. Results

DoD's known critical uses of PFAS are summarized in the following sub-sections, organized by focus area, and in the Appendix. The complexities in dissecting the defense industrial base value chain and supply chain dependencies, in addition to the lack of transparency in chemical and material content data, prevented the CMRMP from gathering comprehensive data on all critical PFAS uses.

Critical PFAS uses were identified in almost every major weapon system category including but not limited to fixed wing aircraft (trainers, fighters, bombers, transports, refuelers, ground support, unmanned, and associated support equipment); rotary wing aircraft (attack, transports, heavy lifts, search-and-rescue, and associated support equipment); surface ships (combat, destroyers, aircraft carriers, cutters, landing crafts); submarines; missiles (air-to-air, ground-to-air, air-to-ground, ballistic); torpedo systems; radar systems; and battle tanks, assault vehicles, and infantry carriers.

IV.1 Kinetic Capabilities

Kinetic capabilities represent a direct use of PFAS, as PFAS are found in a variety of applications across the DoD munitions portfolio. About a dozen fluoropolymers, including fluoroelastomers, are ingredients in polymer bonded explosives, pyrotechnics, and propellant components used in munitions, decoy flares, and chaff. They serve as high temperature resistant binders and resins. These uses, which represent some of the few purely military PFAS applications, include:

- Unique binder materials specifically developed for use in the energetic portion of conventional and strategic weapons platforms.
- Fluoroelastomers, such as Viton™, used as a binder in explosive and booster charge formulations integrated into many DoD munitions.
- Fluoropolymers, such as Teflon™, used in pyrotechnics and as a material used in the manufacture of munitions for a variety of missile systems.

PFAS are used in a variety of applications during energetics processing and testing. Currently, non-PFAS alternatives do not exist for most of these applications, and the likelihood of developing alternatives for these uses is estimated to range from moderate to almost impossible. If available, alternatives require multi-year processes and cost program offices millions of dollars to requalify every missile system that used the material, even if products are similar.

IV.2 Energy Storage and Batteries

Impacts to national security from PFAS applications in energy storage and battery applications are indirect. Manufacturers use fluoropolymers (e.g., polytetrafluoroethylene (PTFE)) and polyFAAs in multiple subcomponents in modern Li-ion batteries. They serve as heat transfer materials or insulation and provide weather resistance and ultraviolet (UV) light resistant functionalities to final components. Military applications rely on Li-ion battery technologies that are largely innovated in the civilian sector. Manufacturers use PFAS in the electrolyte solutions, cathode binders, and separator coatings; and, to a lesser extent, PFAS are found in casing materials and gaskets due to their deterioration resistance properties.

PFAS materials also play an important role in battery manufacturing. Filters and other components of manufacturing equipment are essential to battery production. The battery industry's ability to make products for a broad range of commercial and military applications would be greatly impacted if PFAS were no longer available for use in these components. The significant time and money needed to identify and qualify alternatives as replacements would cause ripple effects throughout the economy as consumers and users absorb the additional cost.

Fully eliminating PFAS from energy storage in the U.S. economy would likely take more than 10 years. Energy storage is a broad issue for U.S. industrial competitiveness as well as an important part of Federal initiatives around combating climate change. DoD is not the primary

consumer of batteries in the United States, but battery supply chain issues would impact the ability to produce missiles and field military vehicles that increasingly rely on batteries.

IV.3 Microelectronics and Semiconductors

The semiconductor industry produces the chips that drive modern electronic devices. The microelectronics packaging and assembly industry integrates these chips into the electronic products used every day across the defense enterprise. In the semiconductor industry, fluoropolymers, fluoroelastomers, polyFAAs, and other fluorochemicals are used in a number of applications and at every stage of semiconductor fabrication. These uses include etching materials (photoresists), etching coolants, masks in photolithography processes, packaging materials that provide heat dissipation for the chip, and cleaning gases at various stages in the microchip production process. Examples of specific PFAS in the semiconductor industry include polyvinylidene fluoride (PVDF; a fluoropolymer), ethylenechlorotrifluoroethylene (ECTFE; a fluoropolymer), FKM/FFKM (fluoroelastomers), and perfluoroalkoxy alkanes (PFAs).

One significant use of PFAS in semiconductor manufacturing is during the photolithography process, where the patterns that define the microchip circuitry are developed onto bare silicon surfaces. Manufacturers use photolithography specialty formulations containing fluorinated compounds in various steps of this process to ensure final chip quality and reduce the probability of defects. PFAS are ideal for these purposes due to their low surface tension and compatibility with other chemicals. The PFAS materials used in these processes are typically no longer present in the finished product, except in some specific applications, such as imaging chips used in cameras, displays, and some medical devices.

Similar to the energy storage industry, PFAS are essential for semiconductor manufacturing equipment and factory infrastructure. The exceptional combination of heat and chemical resistance and chemical inertness allows fluoropolymers to be used both in equipment components (e.g., tubing, gaskets, containers, filters) and lubrication (e.g., various oils and greases). These same properties are also needed to ensure the functioning of the surrounding infrastructure.

In wider microelectronics applications, PFAS remain key industrial materials in applications that integrate microchips into electronic products, such as printed circuit boards. PTFE and PFA base laminate materials are currently used in many radio frequency (RF) and microwave circuits, as they provide unique properties related to isolating RF and microwave signals. Identifying and qualifying potential replacement materials will require significant time, particularly for use in fielded systems. There currently are no available drop-in replacement materials for a PTFE designed printed board. Lack of access to PTFE laminate will necessitate the redesign and requalification of the printed board, the assembly, and potentially the system.

Several PFAS-containing vapor phase soldering and flux removal products are used in the manufacture of printed circuit boards. Vapor phase soldering is used primarily for printed

board assembly when there is a high thermal mass, in combination with advanced technologies such as fine-pitch features, or when there are temperature sensitive components used. Alternative materials are not currently identified and would need to be evaluated for performance and safety. New equipment may be required to implement new vapor phase soldering liquids. PTFE cable jackets are used in printed circuit board and other electronic systems in connectors and wire. PTFE has unique properties as a wire insulator including fire, smoke, and chemical resistance to mitigate the risk of wire exposure in harsh environments. PTFE can withstand 450°C and is used widely in products that have been developed to meet MilSpec applications. Manufacturers also use fluoropolymers as electronics sealants and encapsulants to protect microelectronic components from degradation due to environmental, chemical, or UV-light exposure. Vapor degreasing solvents, used in a variety of cleaning processes during microelectronics production, contain hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs), which, in many cases and in the broadest sense, are defined as PFAS. These materials impart fire suppression properties to the degreasing solvent, creating safer manufacturing environments for workers.

Currently, no alternatives to PFAS have been identified that can provide the functional properties required for photolithography or some applications in semiconductor manufacturing equipment. Even if alternative chemicals and technologies were discovered today, due to the extremely complex qualification process throughout the value chain, it would take another 15 years to deploy them in high-volume manufacturing. Therefore, continued access to PFAS is a prerequisite for high-volume and advanced semiconductors. Lack of continued access to PFAS could lead to an inability to produce and supply semiconductor manufacturing technology.

Replacing most PFAS uses in semiconductor fabrication would require industry-wide re-tooling and other process innovations, at a minimum. Some might be achievable within 10 years, but many would not. As stated above, there are some PFAS uses for which no alternatives are known. For these uses, it may be necessary to invent novel chemistries and processes. Replacing PFAS in semiconductor fabrication could be a 25-year effort and may not succeed in all respects if alternatives cannot be identified or qualified at the microchip level.

Consideration must also be given to the resultant impact on DoD programs. It is highly probable that manufacturers would need to change semiconductor manufacturing processes to accommodate PFAS replacements. This change has the potential to result in the costly requalification of specific components. For example, radiation hardened microelectronics applications typically mandate requalification if a manufacturer substantively alters the fabrication process, which can easily exceed \$10 million; many programs lack intrinsic funding for requalification.

IV.4 Castings and Forgings and Strategic and Critical Minerals

Specialty fluorochemical gases and fluids are used for advanced metalworking, casting, and fabrication due to the temperature and wear resistance functionalities they provide. These

gases and fluids are used in the production of advanced metal parts throughout U.S. industry, including military-specific parts. Requiring a move to PFAS-free alternatives in under 10 years may make construction using certain alloys impossible and require returning to previous methods of construction leading to lower performance, shorter life, and higher weight of constructed parts.

In both the casting and forging and strategic and critical minerals industries, loss of access to PFAS is an indirect threat to national security and a potential source of significant disruption to supply chains vital to the DoD mission. These industries depend on PFAS in products used during normal business operations. A product used as a liquid cold spray in castings and forgings or coolant in drilling operations for critical minerals may contain PFAS, but the product user would not know that PFAS are present until the product is discontinued. Both industries are at risk of losing critical capabilities with little warning, as there are limited requirements for companies to provide composition information for the materials used to create the products they sell to DoD or on the commercial market. The risk for these industries is particularly high, even if the probability is low, because there may be no warning for critical product obsolescence and no ability to develop and qualify alternatives in a timely fashion.

PFAS are also contained in mold release chemicals and release films typically used in composite manufacturing processes. Loss of access of PFAS would impact the commercial composites manufacturing industry and, indirectly, the DoD who is reliant on the commercial industry for applications.

Mold release chemicals are applied to mold hardware to prevent the composites from strongly adhering to the mold hardware during cure. The mold release chemicals typically contain PFAS chemicals or a PTFE polymer spray. Peel plies are used to prevent attachment of vacuum bag materials and other disposable molding materials to the composite part and to impart a textured surface to the molded component to improve adhesion in secondary bonding or painting. Peel plies are typically made of non-PFAS polymers, such as polyamides and polyesters; however, to prevent adhesion of the composite to the peel ply, PFAS modification (most commonly) or silicone modification is done to the fabric. Additionally, if high cure temperatures are required, PTFE and PVDF peel plies are typically used. Polymer release films are similar to peel plies but are generally used with composite resins that need to release gasses during cure. Many of these release films are polyethylene, polypropylene, or other polyolefins and work well for many applications; however, certain applications (typically higher temperature curing systems) require use of fluoropolymers, such as PTFE, PVDF, and others. Pre-preg release film is used to keep individual layers of pre-pregs (e.g., fabrics that are pre-impregnated with a fully curable, mixed resin system during manufacture) separated from each other within the rolls of materials that are prepared and transported for use in composites manufacturing facilities. Fluoropolymer release films are generally used to ensure the releasability of the release film during composite layup. Silicones are also useable for this application but are generally not used because of the low rigidity of silicone films.

IV.5 Additional Mission Critical PFAS Uses

Mission critical PFAS uses extend beyond the five industries discussed to this point. DoD identified a range of additional critical uses for which the potential risk of supply chain disruption would undercut not only mission readiness but the U.S. economy. These uses are discussed in more detail in the following sub-sections.

IV.5.1 Refrigeration and Air Conditioning, Cooling, and Electronics Thermal Control

Most refrigerants used in civil and military cooling and refrigeration applications can be classified as PFAS. Many next-generation refrigerant alternatives adopted by U.S. industry (and U.S. households) between now and the end of 2025 are also PFAS. Under the AIM Act and EPA technology transition regulations, the U.S. economy is in the process of switching from one set of PFAS-classified refrigerants (e.g., HFCs) to a new generation of refrigerants (e.g., HFOs), which are also, in the broadest definitions, considered to be PFAS. Known non-PFAS alternatives (e.g., hydrocarbon or ammonia alternatives) pose flammability, toxicity, or high-pressure concerns. The same PFAS that are used in quantities of several hundred million pounds per year throughout the U.S. economy for cooling applications are used in much smaller quantities (i.e., a fraction of one percent) for military cooling and military thermal control of all kinds.

IV.5.2 Fire Suppression in Naval Vessels, Aircraft and Ground Combat Vehicles

Fluorochemical specialty gases are used in “clean agent” fire suppression in naval vessels, aircraft, and ground combat vehicles. Most known clean agent, low-corrosion, low-weight, low-toxicity alternatives will likely be classified as PFAS, broadly defined.

Since the advent of regulations against halogenated agents, Naval vessels commonly utilize an HFC clean agent in compartments subject to flammable/combustible liquid fuel fires such as engine modules and hazardous material storage spaces. For new U.S. Naval ship designs, the Navy continues to move to alternate fire suppression technologies (e.g., water mist) where suitable, however limited use of HFC remains for those spaces where the alternatives are not appropriate. For existing ship HFC uses, there is no “drop-in” replacement for these HFC agents.

Well over 10 million pounds of PFAS fire suppressants are installed in civil aircraft engine, cargo compartment, and lavatory fire suppression systems, and in hand-held aircraft fire extinguishers, worldwide. This includes halons (which meet PFAS definitions but are frequently excluded from draft PFAS regulations because they are separately covered by ozone depleting substance regulations) and all currently implemented aviation replacements for halons. In 2022, Working Paper 96 presented at the 41st Assembly of the International Civil Aviation

Organization recommended considering PFAS use in aircraft fire suppression an essential use in prospective PFAS regulations to maintain progress in replacing halons.¹⁰

IV.5.3 Aqueous Film Forming Foam

Mission critical ocean-going vessels employed by DoD and the Military Services continue to use aqueous film forming foam (AFFF) containing PFAS for combating Class B (flammable/combustible liquid) fuel spill fires. U.S. Navy ships are required to use AFFF qualified to MIL-PRF-24385. MIL-PRF-24385 qualified AFFF provides the capability to rapidly control and extinguish shipboard fires. AFFF is critical for fire emergencies on flight decks where aircraft movement, fueling, launch/recovery, and weapons loading occur, and substantial risk exists for loss of aircraft, ship, and life if a fire is not rapidly controlled and extinguished.

Past flight deck fires, such as those that occurred on the United States Ship (USS) FORRESTAL, USS ENTERPRISE, and USS NIMITZ, all demonstrate the potential for such catastrophic events to occur. The risk of devastating loss of life and warfighting capability in incidents such as these, and the more recent fire emergency which resulted in the loss of the USS BONHOMME RICHARD, necessitates the use of the most effective firefighting agents available.

Beyond the potential for the immediate loss of life and impacts to operational capability that can result from an uncontrolled fire on a warship, the defense industrial base has limitations with respect to repairing or delivering replacement national security assets, including ordnance, aircraft, and ships. It could take a decade or longer to replace large amphibious assault ships and aircraft carriers.

Currently available fluorine-free foams (F3s) have significant limitations compared to AFFF that preclude their use on DoD ocean-going vessels, including the U.S. Navy fleet. Those limitations include reduced firefighting performance; chemical and physical properties that make them unsuitable for use with existing ship firefighting foam storage and delivery systems; and cross-agent compatibility issues. There are currently no equivalent, fully performing firefighting alternatives to AFFF for shipboard use.

DoD continues to sponsor research and development for F3 technologies to address these limitations, with the goal that continued technology improvements will support efforts toward a future path for use on ships. To date, DoD has invested approximately \$45.8M since 2017 toward the development and qualification of F3 technologies.

Until such time that a capable F3 alternative is found, the safety and survivability of naval ships and crew from shipboard fires depends on the continued availability of MilSpec

¹⁰ International Civil Aviation Organization (ICAO), Working Paper 96: Aircraft Halon Replacement, A41-WP/96, 28 July 2022. https://www.icao.int/Meetings/a41/Documents/WP/wp_096_en.pdf.

AFFF products and their PFAS-containing constituents, which were formulated, tested, qualified, and implemented in order to save lives and military assets.

IV.5.4 Lines, Hoses, O-Rings, Seals and Gaskets, Tapes, and Cables and Connectors

Dozens of different fluoropolymers (e.g., PVDF, ECTFE, PTFE) and fluoroelastomers (e.g., FKM/FFKM) are critical to modern UV-resistant, ozone-resistant, weather-resistant, temperature-resistant, high pressure-resistant, chemical-resistant “rubberized” fuel lines. They are also key materials in hoses, tubing, hydraulic system lines, O-rings, seals and gaskets, tapes, and cables and connectors widely used in civil and military aircraft, space systems, vehicles, weapon systems, utility systems, and other applications. Alternatives are not as resistant to embrittlement and break-down and have a much shorter useful life, leading to more frequent part replacement, which is not feasible for space or satellite uses.

IV.5.5 Electronic/Dielectric Fluids

Fluorochemicals are found in electronic and dielectric fluids that are used in civil and military radars and high-power electronics and electrical system/utility system components because of their dielectric and heat transfer properties. Industry and DoD have repeatedly investigated alternatives for these applications. Known alternatives have high global warming potential (e.g., sulfur hexafluoride) or may pose health/environmental risks (e.g., the polychlorinated biphenyls banned by the U.S. Toxic Substances Control Act and the Stockholm Convention on Persistent Organic Pollutants). Examples of PFAS-containing electronic/dielectric fluids used by DoD include 3M™ Fluorinert™ Electronic Liquids FC-40, FC-72, FC-770, and FC-3283.

IV.5.6 Advanced Oils, Greases, Fluids, and Lubricants

PFAS are used in many advanced turbine engine oils, greases, fluids, and lubricants due to their wear- and heat-resistant properties. These uses are common throughout the most demanding applications in the U.S. civil transportation, industrial, and space sectors. Analogous PFAS-containing oils, lubricants, and fluids are used in military critical ground, sea, air, and space applications. Previous generations of oils, fluids, and lubricants approached, but did not equal, the performance of PFAS additives that have become more prevalent in high performance oils, greases, fluids, and lubricants over the past 20 years.

Castrol Braycote 640AC is an example of a PFAS-containing grease, designed to be oxidizer and propellant compatible for use in aerospace vehicles, spacecraft, rocket and aircraft engines, and associated ground support equipment, oxygen equipment, and transport equipment. Braycote 640AC is typically used to lubricate threaded fasteners, connectors, valves, gaskets, elastomers, and bearings. Perfluorinated greases, in general, exhibit excellent shelf lives due to their intrinsic inertness.

Two additional examples of PFAS-containing greases used by DoD (and original equipment manufacturers and the maintenance, repair, and overhaul industry) are NYCO GREASE GN25013 and NYCO GREASE GN617. PTFE is used as a thickener in both products and perfluoropolyether is used as the base stock for GN617.

IV.5.7 Precision Cleaning Fluids

Fluorochemicals are used in precision cleaning applications, including the cleaning of sensitive oxygen systems in civil and military aerospace.

IV.5.8 Degreasing/Cleaning Fluids

The MilDeps reported the use of PFAS-containing degreasing/cleaning products and contact cleaners (e.g., 3M™ Novec™ Engineering Fluids, 3M™ Novec™ Contact Cleaners, 3M™ Novec™ Contact Cleaner/Lubricant) in vapor degreasing and flux removal.

The Army reported the use of FCC2 Enhanced Fiber Connector Cleaner and Preparation Fluid, which contains butane, 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy, for cleaning fiber optic connectors in secure link manager assemblies and primary modem assemblies.

The MilDeps reported the use of fluorinated non-destructive testing (NDT) solvent cleaner/remover for precleaning before NDT and for removing excess surface penetrant from an inspection area before applying developer during liquid penetrant testing.

The MilDeps also reported that PFAS-containing degreasers are used to effectively remove grease, oil, tar, and other substances from military equipment to increase its operating efficiency. These degreasers leave no residue, have no flash or fire point, and serve as an alternative to legacy solvents (e.g., n-propyl bromide, trichloroethylene, tetrachloroethylene).

IV.5.9 Adhesives

The MilDeps reported the use of the following adhesives, which contain PFAS: 3M™ Super Foam Fast Spray Adhesive 74-Orange, 3M™ Hi-Strength Spray Adhesive 90 (aerosol), and 3M Scotch-Weld Epoxy Adhesive DP420 Off-White, Part A.

IV.5.10 Insulation and Foam Blowing

Fluorochemicals are components of insulation and foam blowing products used in civil and military aircraft and space vehicles/rocket motors.

IV.5.11 Resins for Specialty Materials

Fluoropolymers are used in resins for specialty high-temperature or weather-/UV-resistant composites due to their temperature-, pressure-, wear-, and chemical-resistance properties. Fluoropolymers are also used in high cleanable, high weathering and chemical

resistant coatings for military assets. Many aircraft topcoats contain fluoropolymer resins due to their UV and chemical resistance properties. PFAS are not actually in the coatings themselves but are used in fluoropolymer resin manufacturing.

Moving to alternatives in under 10 years may require a return to previous methods of parts construction which produced shorter life and higher weight composites with lower performance characteristics.

IV.5.12 Specialty Filters and Membranes

Fluoropolymers are used in specialty filters and membranes (e.g., aviation filters) due to their temperature-, pressure-, and wear-resistance properties. PFAS are also found in several air filtering masks and air filtering respirators used by DoD.

IV.5.13 Fabrics, Fabric Liners, and Fabric Barriers

A variety of textiles used in uniform clothing and footwear items, tents, and duffle bags are treated with PFAS to repel water and oils while providing durability to laundering, UV light exposure, and temperature cycling. The main PFAS used on textiles are fluoropolymers, such as PTFE and short chain PFAS, known as C6 or C4 chemistries. PFAS can be incorporated as an additive mixed into individual fibers or sprayed as a coating onto finished fabrics during manufacturing or after sale and are present in/on textiles in two forms: a non-polymerized compound that can be washed out or evaporated or as a molecule integrated into a fluorine free polymer network via covalent bonds. The MilDeps reported the use of PFAS in chemical, biological, radiological, and nuclear protective equipment (the Uniform Integrated Protection Ensemble Family of Systems) and in a number of uses within health care communities.

Coretech, the biological protective fabric lining used on the Joint Biological Agent Decontamination System, includes a barrier layer for biological protection during the decontamination of aircraft. The barrier layer contains PFAS.

IV.5.14 Customized Applications

Customized applications like gyroscope suspension fluids and analytic gases and fluids for thermometric and other sensors use specialty fluorochemicals because of their pressure-resistant, wear-resistant, and temperature control properties. These applications require very small quantities of specialty PFAS and are particularly susceptible to disruptions in PFAS supply chains due to challenges in attracting manufacturers to develop low-volume commodities.

V. Conclusions

This report summarizes known direct and indirect uses of PFAS that are critical to the national security of the United States, but it is not comprehensive. Also highlighted are the challenges and costs related to finding and qualifying alternatives to existing PFAS materials in

sectors of strategic importance to DoD. The information contained in this report is limited to what was available at the time of its drafting. As such, the information presented represents a fraction of the mission critical PFAS uses due to a lack of transparency in the chemical composition in consumables and articles. In addition, there is significant uncertainty regarding the presence of PFAS in products that make up a complex value chain. A more complete understanding of PFAS essential uses would require an extensive and complex evaluation of the market, a gap analysis of current requirements for manufacturer-provided product information, and illumination of the value chain of products.

PFAS are critical to DoD mission success and readiness and to many national sectors of critical infrastructure, including information technology, critical manufacturing, health care, renewable energy, and transportation. DoD relies on an innovative, diverse U.S. industrial economy. Most of the structurally defined PFAS are *critical to the national security of the United States*, not because they are used exclusively in military applications (although a few are) but because of the civil-military commonality and the potentially broad civilian impact. This report provides details on what is currently known about direct and indirect mission critical PFAS uses that could impact mission readiness if the substances are no longer available.

Emerging environmental regulations focused on PFAS are broad, unpredictable, lack the specificity of individual PFAS risk relative to their use, and in certain cases will have unintended impacts on market dynamics and the supply chain, resulting in the loss of access to mission critical uses of PFAS. These market responses will impact many sectors of U.S. critical infrastructure, including but not limited to the defense industrial base. Collectively, international and U.S. regulatory actions to manage PFAS' environmental impacts and identify and eliminate PFAS from the market, and the resulting market changes, pose risks to DoD operations and the defense industrial base supply chain. In addition, impacts to the global PFAS supply chain will present risks to the DoD Foreign Military Sales program and to North Atlantic Treaty Organization interoperability.

The Department will continue to oversee coordinated lines of effort to expeditiously identify essential uses of PFAS, prioritize actions according to vulnerabilities to national security, and address mission readiness associated with the potential loss of access to PFAS. Actions include:

- Implementing DoD PFAS policy directing the DoD Components and MilDepts to determine the PFAS content in DoD weapon systems, to the extent feasible, and enabling continued access to mission critical uses, while encouraging safe use by DoD personnel and adoption of PFAS-free alternatives.
- Engaging with industry to identify PFAS content in other materials commonly used within the DoD to assess potential obsolescence risks and potential PFAS alternatives.
- Engaging with industry and federal agencies during routine meetings to assess obsolescence risks, mission criticality, and potential PFAS alternatives.

- Investing in research, development, and qualification efforts required to demonstrate conformance with Military Standards or Specifications.
- Collaborating across the Federal Government to develop a long-term research plan for the most challenging applications where it will take a decade or more to find viable replacements.
- Investing in research to support advanced manufacturing approaches by improving purification, deconstruction technologies, scale-up of sustainable materials design and manufacturing, and circularity for the most critical and irreplaceable PFAS.

Concurrent with efforts to identify essential uses of PFAS, the Department is phasing out non-essential and non-critical PFAS uses in accordance with NDAA requirements where there is no mission impact (e.g., in food packaging, cookware, furniture, personal protective firefighting equipment). Additionally, per the 2023 U.S. Government Accountability Office (GAO) recommendations,¹¹ the Department is developing an approach to implement the April 2023 prohibition for military exchange resale procurements. The Department is also updating DoD Instruction 4105.72, *Procurement of Sustainable Goods and Services*, to include procedures specifically targeted to implementing the provisions of Executive Order 14057, *Catalyzing Clean Energy Industries and Jobs Through Federal Sustainability*, with respect to limiting the procurement of items containing PFAS.

Eliminating PFAS from non-essential uses is an important step toward addressing public concerns and protecting human health and the environment. Mission critical PFAS uses provide significant benefits to the framework of U.S. critical infrastructure, and national and economic security. DoD will consider future policy actions to manage non-essential and essential PFAS uses and will implement these actions with the intent of protecting human health and the environment while ensuring no adverse impacts to U.S. critical infrastructure and national security.

If future PFAS legal and regulatory frameworks ignore the OECD caution on the use of its PFAS definition and seek to broadly restrict the use of PFAS based on chemical structure, there could be extensive economic, industrial competitiveness, and quality-of-life impacts to U.S. society. The PFAS universe is structurally and physiochemically diverse and subgroups of PFAS may be more or less stable, persistent, and/or bioaccumulative compared to well-studied PFAS such as perfluorooctane sulfonate and perfluorooctanoic acid.¹² Congress and the Federal regulatory agencies should avoid taking a broad, purely “structural” approach to restricting or banning PFAS. It is critical that future laws and regulations consider and balance the range of

¹¹ U.S. Government Accountability Office (GAO). Persistent Chemicals: Actions Needed to Improve DoD’s Ability to Prevent the Procurement of Items Containing PFAS. GAO-23-105982. April 2023.

¹² EPA Framework for Estimating Noncancer Health Risks Associated with Mixtures of Per- and Polyfluoroalkyl Substances (PFAS) (Public Review Draft), EPA-822-P-23-003 (March 2023).

environmental and health risks associated with different individual PFAS, their essentiality to the U.S. economy and society, and the availability of viable alternatives.

Appendix: Summary of Known Mission Critical PFAS Uses

PFAS	Application	Functionality	Availability of Alternatives	Time Frame / Cost to Develop and Qualify Alternatives*
Kinetic Capabilities				
Fluoropolymers (e.g., Teflon™)	Ingredients in binders and resins used in PBX, pyrotechnics, and propellant components that are used in a variety of applications across the DoD munitions portfolio.	High temperature resistance	NA*	NA
Fluoroelastomers (e.g., Viton™)				
PFAS	Used in energetic slurry processing.	Enables high levels of mixing between key energetic components.	NA	NA
Fluorinated performance fluids (e.g., 3M™ Fluorinert™ fluids)	Enable energetics laboratory research. Are critical for developing and transitioning new energetic materials.	NA	NA	NA
Energy Storage and Batteries				
Fluoropolymers (e.g., polytetrafluoroethylene (PTFE))	Multiple subcomponents in modern Li-ion batteries: electrolyte solutions, cathode binders, separator coatings, casing materials, and gaskets.	Serve as heat transfer material or insulation. Provide weather-resistance, UV light-resistance, and deterioration-resistance properties.	NA	Fully eliminating PFAS from energy storage in the U.S. economy would likely take 10+ years.
Polyfluoroalkyl acids (PolyFAAs)				
PFAS	Battery manufacturing: filters and other components essential to production.	NA	Possibly available	Time and cost to identify and qualify alternatives would be significant and have ripple effects throughout the economy.
Microelectronics and Semiconductors				
Fluoropolymers	Semiconductor fabrication: etching materials and masks in photolithography processes; cleaning gases.	Dielectric, heat transfer, and insulation functionalities.	Currently no alternatives to PFAS for photolithography.	NA
Fluoroelastomers				
PolyFAAs				
Other PFAS				

Appendix: Summary of Known Mission Critical PFAS Uses

PFAS	Application	Functionality	Availability of Alternatives	Time Frame / Cost to Develop and Qualify Alternatives*
Fluoropolymers	Semiconductor manufacturing equipment and factory infrastructure: equipment components (e.g., tubing, gaskets, containers, filters) and lubrication (various oils and greases).	Heat and chemical resistance, and chemical inertness.	Currently no alternatives for some applications in semiconductor manufacturing equipment. Replacing most PFAS uses in semiconductor fabrication would require industry-wide re-tooling and other process innovations. Some might be achievable within 10 years, but many would not.	Development of alternatives for some uses may require the invention of novel chemistries and processes. Due to the extremely complex qualification process, it would take another 15 years to deploy alternatives, once developed, in high-volume manufacturing. Replacing PFAS in semiconductor fabrication could be a 25-year effort and may not succeed in all respects if alternatives cannot be identified or qualified at the microchip level. Replacing PFAS has the potential to initiate costly requalification of specific components. Example: radiation hardened microelectronics applications typically mandate requalification if a manufacturer substantively alters the fabrication process, which can easily exceed \$10 million.

Appendix: Summary of Known Mission Critical PFAS Uses

PFAS	Application	Functionality	Availability of Alternatives	Time Frame / Cost to Develop and Qualify Alternatives*
PTFE	Microelectronics applications: base laminate materials used in many RF and microwave circuits.	Provide unique properties related to isolating RF and microwave signals. Used in radar, antenna, guidance systems, 5&6 G infrastructure, and other network/transmission applications.	There is no drop in alternative material. Any material replacement for fielded systems would require redesign of the printed board and potentially the electronic system to account for material property differences. Fielded systems that have been redesigned may require requalification.	Developing and or identifying suitable alternative materials and qualifying them could be a forward-looking action for all future DoD systems. This however does not address sustainment of existing systems. There will continue to be a need to have PTFE laminate materials available for system sustainment until all systems currently designed with PTFE are retired.
PFA				
PFAS	Manufacture of printed circuit boards (PCBs): vapor phase solder and flux remover products.	Vapor phase soldering process is used for PCB assemblies with high thermal mass, fine-pitch structures, and temperature-sensitive components to minimize risk to materials, structures and components. The material stability and flame retardant qualities are well suited for the enclosed high temperature operation of the process.	It is unknown if there are suitable materials that can be used, however it is likely that current equipment may need to be replaced or modified to accommodate the replacement materials.	Developing and evaluating new materials could take 5 years or more. Equipment replacement would add time and have a cost impact.
PTFE	PCBs: cable jackets used in PCB connectors.	Used because it has excellent fire, smoke, and chemical resistance. Wide temperature range -200 to 260C constant use and up to 450C for peak exposure.	It is unknown if there are suitable replacement materials for all of the applications for PTFE wire jacket material. PTFE is higher cost than some other wire jacket materials. When it is selected for use there are typically no other suitable replacement materials.	Qualification of alternatives will be both costly and time consuming. Many materials will require new UL or other certification body approval before they can be implemented. Many current products are MilSpec certified.

Appendix: Summary of Known Mission Critical PFAS Uses

PFAS	Application	Functionality	Availability of Alternatives	Time Frame / Cost to Develop and Qualify Alternatives*
Castings and Forgings and Strategic and Critical Minerals				
Specialty fluorochemical gases and fluids	Advanced metalworking, casting, and fabrication processes used in the production of advanced metal parts throughout U.S. industry, including military-specific parts.	Temperature and wear resistance.	NA	Moving to alternatives in under 10 years may require returning to previous construction methods and may make construction using certain alloys impossible.
PTFE, PVDF, other PFAS	Mold release chemicals and release films typically used in composite manufacturing processes.	Prevent composites from strongly adhering to mold hardware.	NA	NA
Refrigeration and Air Conditioning, Cooling, Electronics Thermal Control				
HFOs	Next-generation refrigerant alternatives (to HFCs) used in civil and military cooling and thermal control applications.	NA	Known non-PFAS alternatives (e.g., hydrocarbon or ammonia alternatives) pose flammability, toxicity, or high-pressure concerns.	NA
Fire Suppression in Aircraft and Ground Combat Vehicles				
Fluorochemical specialty gases	“Clean agent” fire suppression in aircraft and ground combat vehicles.	NA	Most known clean agent, low-corrosion, low-weight, low-toxicity alternatives will likely be classified as PFAS, broadly defined.	NA
Aqueous Film Forming Foam (AFFF)				
PFAS	AFFF use to combat Class B (flammable/combustible liquid) fuel spill fires on mission critical ocean-going vessels employed by DoD and the Military Services.	MIL-PRF-24385 qualified AFFF provides the capability to rapidly control and extinguish shipboard fires.	Current F3s have significant limitations compared to AFFF that preclude their use on DoD ocean-going vessels, including the U.S. Navy fleet.	NA

Appendix: Summary of Known Mission Critical PFAS Uses

PFAS	Application	Functionality	Availability of Alternatives	Time Frame / Cost to Develop and Qualify Alternatives*
Lines, Hoses, O-Rings, Seals and Gaskets, Tapes, and Cables and Connectors				
Fluoropolymers (e.g., PVDF, ECTFE, PTFE)	Critical to modern “rubberized” fuel lines. Key materials in hoses, tubing, hydraulic system lines, O-rings, seals and gaskets, tapes, and cables and connectors widely used in civil and military aircraft, space systems, vehicles, weapon systems, utility systems, and other applications.	Functionalities include UV-resistance, ozone-resistance, weather-resistance, high temperature-resistance, high pressure-resistance, and chemical resistance.	Alternatives are not as resistant to embrittlement and break-down and have a much shorter useful life, leading to more frequent part replacement, which is not feasible for space or satellite uses.	NA
Fluoroelastomers (e.g., FKM/FFKM)				
Electronic/Dielectric Fluids				
Fluorochemicals	Used in electronic and dielectric fluids used in civil and military radars, high-power electronics, and electrical system/utility system components.	Provide dielectric and heat transfer properties.	Industry and DoD have repeatedly investigated alternatives in these applications. Known alternatives have high global warming potential (e.g., sulfur hexafluoride) or may pose health/environmental risks (e.g., the polychlorinated biphenyls).	NA
Advanced Oils, Greases, Fluids, and Lubricants				
PFAS	Used in many advanced turbine engine oils, greases, fluids, and lubricants common throughout the U.S. civil transportation, industrial, and space sectors. Analogous oils, lubricants, and fluids are used in military critical ground, sea, air, and space applications.	Wear- and heat-resistant properties. Perfluorinated greases exhibit excellent shelf lives due to their intrinsic inertness.	Previous generations of oils, fluids, and lubricants approached, but did not equal, the performance of PFAS additives that have become more prevalent in high performance oils, greases, fluids, and lubricants over the past 20 years.	NA

Appendix: Summary of Known Mission Critical PFAS Uses

PFAS	Application	Functionality	Availability of Alternatives	Time Frame / Cost to Develop and Qualify Alternatives*
Precision Cleaning Fluids				
Fluorochemicals	Precision cleaning applications such as cleaning of sensitive oxygen systems in civil and military aerospace.	NA	NA	NA
Degreasing / Cleaning Fluids				
PFAS	Degreasing/ cleaning products and contact cleaners used in vapor degreasing and flux removal.	NA	NA	NA
	Non-destructive testing solvent cleaner/remover used for precleaning and for removing excess surface penetrant before applying developer during liquid penetrant testing.	NA	NA	NA
	Degreasers used to effectively remove grease, oil, tar, and other substances from military equipment to increase its operating efficiency.	Leaves no residue, has no flash or fire point, and serves as an alternative to chlorinated solvent-based cleaners (e.g., 1,1,1-trichloroethane).	NA	NA
	Connector cleaner and preparation fluid used for cleaning fiber optic connectors in secure link manager assemblies and primary modem assemblies.	NA	NA	NA
Insulation and Foam Blowing				
Butane, 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy	Components of insulation and foam blowing products used in civil and military aircraft and space vehicles/rocket motors.	NA	NA	NA

Appendix: Summary of Known Mission Critical PFAS Uses

PFAS	Application	Functionality	Availability of Alternatives	Time Frame / Cost to Develop and Qualify Alternatives*
Resins for Specialty Composites				
Fluoropolymers	Resins for specialty high-temperature or weather-/UV-resistant composites.	Temperature-, pressure-, wear-, and chemical-resistance properties.	NA	Moving to alternatives in under 10 years may require a return to previous methods of parts construction and an acceptance of lower performance, shorter life, and higher weight composites.
Specialty Filters and Membranes				
Fluoropolymers	Used in specialty filters and membranes (e.g., aviation filters); and in air filtering masks and air filtering respirators used by DoD.	Temperature-, pressure-, and wear-resistance properties.	NA	NA
PFAS				
Fabrics, Fabric Liners, Fabric Barriers				
PFAS	- Fabrics used in a variety of uniform clothing and footwear items, tents, and duffle bags. - Reported use in chemical, biological, radiological, and nuclear protective equipment. - Used in the biological protective fabric lining used in the Joint Biological Agent Decontamination System.	Water and oil repellency.	NA	NA
Customized Applications				
Specialty fluorochemicals	Used in customized applications like gyroscope suspension fluids and analytic gases and fluids for thermometric and other sensors.	Pressure-resistant, wear-resistant, and temperature control properties.	NA	NA

* NA = no information provided through data collection efforts.



Performances of PTFE and PVDF membranes in achieving the discharge limit of mixed anodic oxidation coating wastewaters treated by membrane distillation

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Received: 2 February 2024 / Accepted: 22 May 2024 / Published online: 3 June 2024
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Abstract

The mixed wastewater generated by anodic oxidation coating facilities contains high levels of various contaminants, including iron, aluminum, conductivity, chemical oxygen demand (COD), and sulfate. In this study, the effectiveness of the membrane distillation (MD) process using polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) membranes was investigated to treat mixed wastewater from an anodized coating factory. The results indicate that both hydrophobic membranes effectively removed targeted contaminants. However, the PTFE membrane achieved higher removal efficiencies, with over 99% removal of sulfate, conductivity, iron, and aluminum, 85.7% of COD, and 86% of total organic carbon (TOC). In contrast, the PVDF membrane exhibited a significant decline in removal efficiency as the temperature increased and performed well only at lower feed temperatures. The PTFE membranes outperformed the PVDF membranes in treating chemically intensive anodic oxidation wastewaters. This superiority can be attributed to the PTFE membrane's morphology and structure, which are less influenced by feed water temperature and chemicals. Additionally, its slippery surface imparts anti-adhesion properties, effectively preventing membrane fouling, and maintaining the treated water quality and flux for longer operation time.

Keywords Electroplating · Membrane distillation · Wastewater · Anodic oxidation · Sulfate · Chemical oxygen demand

Abbreviations/Symbols

PTFE	polytetrafluoroethylene	SM	standard methods
PVDF	polyvinylidene fluoride	APHA	American Public Health Association
MD	membrane distillation	Eq	equation
TOC	total organic carbon	SEM	scanning electron microscopy
COD	chemical oxygen demand	FTIR	Fourier transform infrared spectroscopy
EC	European Council	n.d.	no date
pH	potential of hydrogen	PET	polyethylene terephthalate
MCr	membrane crystallization	NaOH	sodium hydroxide
PP	polypropylene	Ca(OH) ₂	calcium hydroxide
DCMD	direct contact membrane distillation	•OH	hydroxyl radical
et al.	et alia	%	percentage
USA	United States Of America	/	per
MN	Minnesota	μS	microSiemens
LEP	liquid entry pressure	cm	centimeter
		m	meter
		°	degree
		mg	milligram
		L	liter
		m ²	square meter
		°C	Celsius degree
		μm	micrometer
		min	minute
		cm ²	square centimeter

Responsible Editor: Angeles Blanco

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mL	milliliter
R	membrane rejection
J	membrane permeate flux
C_f	feed solution contaminant concentration
C_p	permeate solution contaminant concentration
Q_p	permeate flow rate
A	membrane surface area
CF_2	difluorocarbene
CH_2	methylene
C	carbon
H	hydrogen

Introduction

Distillation, a separation technology with a centuries-old history, has been widely employed in various industries and has found applications in water treatment and desalination. In response to the performance limitations and high energy consumption inherent in the distillation process, industries have been exploring higher-performance, cheaper, and environmentally friendly separation technologies to replace the traditional distillation method (Kiss and Kattan Read 2018). In recent years, membrane processes, an advanced water treatment method, have experienced increasing applications in various areas, including domestic and industrial wastewater treatment, drinking water treatment, and desalination applications (Bera et al. 2022; Kamali et al. 2019; Kesari et al. 2021; Mojiri and Bashir 2022). With the significant ongoing advancements in material science and membrane technology, the membrane distillation process has evolved, integrating a distillation process and membrane separation (Ahmed et al. 2020; Alkhudhiri et al. 2012; Basile et al. 2015; Biniiaz et al. 2019; Deshmukh et al. 2018; Drioli et al. 2015; Ghaffour et al. 2019).

Membrane distillation (MD) is an advanced membrane technology with main applications in seawater and brackish water desalination (Ahmed et al. 2020; Basile et al. 2015; Susanto 2011). On the other hand, the MD process has been widely applied for the purification of wastewater generated by a variety of industries, but also for the recovery of valuable materials (metals) and the reduction of harmful pollutants in wastewater prior to discharge (Aijaz et al. 2022; Biniiaz et al. 2019; Bramsiepe et al. 2012; Foureaux et al. 2020; Kamali et al. 2019; Kiss and Kattan Read 2018; de Sousa Silva et al. 2021; Zheng et al. 2015). The MD technique uses specially designed hydrophobic membranes that allow water vapor to pass through due to a thermally driven mechanism, all while maintaining their structural integrity (Souhaimi and Matsuura 2011; Tibi et al. 2020; P. Wang and Chung 2015). This method operates at lower temperature and pressure compared to traditional distillation and pressure-based membrane processes, while still providing

excellent purification performance by effectively removing all non-volatile compounds, including organics and various ions such as sulfate, aluminum, and iron (Boubakri et al. 2015; Cath 2010; Hou et al. 2014; Kezia et al. 2015; Souhaimi and Matsuura 2011; Tomaszewska 2001; Van der Bruggen and Vandecasteele 2002; Zoungrana et al. 2017; Zoungrana et al. 2016). MD has been reported to be particularly effective for treating industrial wastewater, including mixed anodic oxidation wastewater, which often contains similar pollutants to those found in various industries such as electroplating, mining, clothing, battery manufacturing, and mineral processing (Helen Kalavathy and Miranda 2010; Molinari et al. 2008). Several patents and studies in the literature demonstrate the applicability of MD systems, either alone or in combination with other processes, for desulfurization and heavy metal removal (Attia et al. 2017; Haiyang et al. 2019; Hubadillah et al. 2017; Lou et al. 2020; Zhumei et al. 2016; Zoungrana et al. 2016; Zoungrana et al. 2016). While research specifically on treating wastewater from anodic oxidation coating facilities is limited, existing studies suggest membrane separation techniques, including MD, hold promise for effectively treating these wastewaters.

Aluminum is a widely used metal worldwide, and anodized coating, a unique electrochemical process, imparts diverse properties to aluminum. While various chemicals can be employed to achieve different properties during the coating process, sulfuric acid stands out as the most commonly used electrolyte in this particular coating method (Kaufman 2019; Runge and Pomis 2000; Sulka 2020). The anodic oxidation process generates two separate streams, acidic and alkaline. The wastewater intended for treatment is collected by mixing these streams, resulting in a neutral pH range. However, the mixed wastewater still contains pollutants such as iron, aluminum, high conductivity, COD, and sulfates at high concentrations (Vargel 2004). Conventional treatment of anodic oxidation wastewater often relies on chemicals like sodium hydroxide (NaOH) and calcium hydroxide ($Ca(OH)_2$). These chemicals can be expensive and generate sludge, which is costly to manage. According to Mymrin et al., the annual global production of anodized aluminum amounts to 450,000 tons, with an equivalent amount of aluminum anodized sludge generated for each 1 kg of anodized aluminum manufactured. This production is distributed among various countries, with Japan accounting for 39%, the USA for 22%, the European Union for 22%, and the remaining 17% being produced by other nations. This contributes to approximately 100,000 tons per year of aluminum anodized sludge generation in the European Union (Mymrin et al. 2021). Advanced oxidation processes and biological degradation methods have been investigated and proven to be inappropriate for anodizing industry wastewater treatment. In fact, oxidative degradation is hindered by heavy metal non-biodegradability and the scavenging of $\bullet OH$ radicals by anions like phosphates, sulphates, and

nitrites present in the anodic oxidation wastewaters. Biological degradation is also unsuitable due to the solution pH and high heavy metal concentrations, which are inhospitable for most microorganisms (Ighalo et al. 2022). Separation processes such as nanofiltration, reverse osmosis, and adsorption techniques have demonstrated effective pollutant removal when dealing with various pollutant species in anodic oxidation wastewaters (Ali et al. 2020), however, the nature and constitution of anodizing industry wastewater require membranes with unique properties to successfully achieve an acceptable discharge limit. The application of advanced treatment methods is crucial to achieving better discharge standards for these wastewaters and reducing their damage to the environment.

Membrane distillation is an advanced treatment technology that has been demonstrated to be a viable alternative technique for treating non-vapourable compound-polluted water. A previous study demonstrated that such a process can be effective in the treatment of acidic anodic oxidation wastewaters (Türk et al. 2022). Ali et al. achieved 99.4% conductivity removal and extracted high-purity sodium sulfate crystals from anodic oxidation wastewater using combined MD/Membrane Crystallization (MD/MCr) with polypropylene (PP) hollow fiber membranes (Ali et al. 2019). It is worth noting that various parameters control the performance of MD processes, among which the hydrophobic membrane properties, the characteristics of the water to be treated and the operation parameters are the most important. As hydrophobicity is a fundamental requirement in the membrane distillation process, the membrane material should possess intrinsic hydrophobic properties, or its surface must undergo modification to acquire hydrophobicity. Commonly used membrane materials for MD include PP, polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) (Khayet 2011). Despite the critical role of hydrophobic membranes in MD, limited research has investigated the suitability of commercially available membranes for treating chemically intensive wastewater, especially those containing challenging pollutants like anodic oxidation wastewater. Existing studies lack investigation into the specific chemicals and their threshold concentrations that membranes can resist. Additionally, the influence of membrane structure on resistance is not fully understood, as some membranes show resistance to certain pollutants while others do not. Recognizing that the polymers used in membrane fabrication significantly impact their properties, this study aims to evaluate the influence of the structural properties of commercially available PTFE and PVDF hydrophobic

membranes on their performance and integrity when treating anodic oxidation wastewater in an MD process. All Abbreviations and symbols used in this paper will be defined and reported in the “Abbreviations/symbols” section.

Materials and methods

Characterization of wastewater from an anodization plant

To conduct the present study, wastewater samples were collected from an anodization plant located in Istanbul, Turkey, which produces both acidic and alkaline wastewater streams. A mixed wastewater sample, resulting in a neutral pH, was collected for the study. An overview of the wastewater characteristics is provided in Table 1. According to the Turkish Water Pollution Control Regulation, the maximum allowable levels for the discharge of treated wastewater effluent into the environment 3 mg/L Al, 100 mg/L COD, and pH in the range of 6 to 9. Discharge regulations of sulfate limit its content to 1700 mg/L to protect infrastructure systems (SKKY 2004).

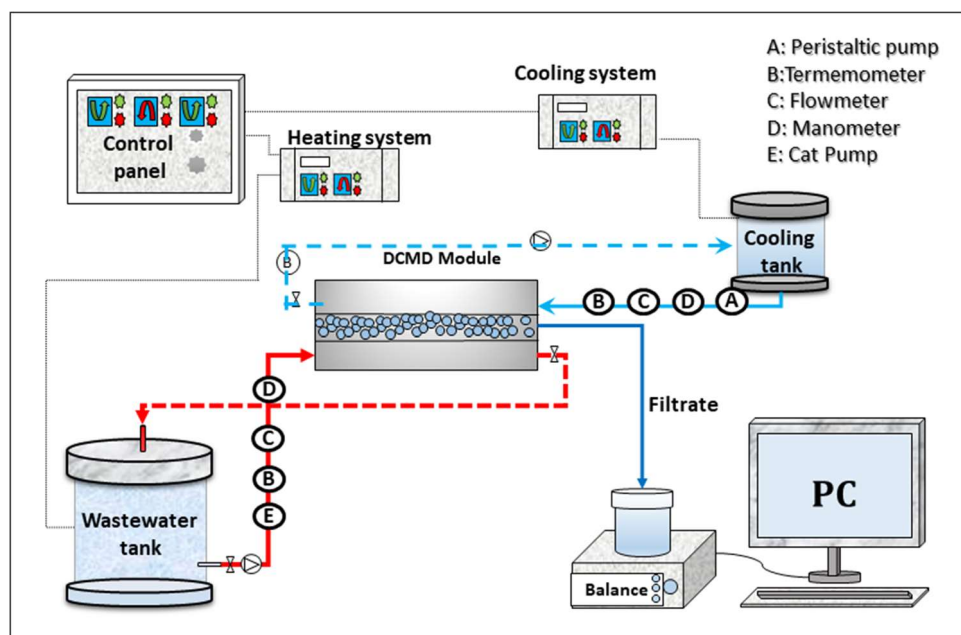
Membrane distillation system and operation

A modified lab-scale flat-sheet direct contact membrane distillation (DCMD) system was used in the present study. The modification intended to reduce the temperature polarization and the heat loss by conduction suffered by the DCMD process (Zoungrana et al. 2016). An MD module with an effective membrane surface area of 0.015 m² was used. The flow rate, temperatures, and operating pressures were continuously monitored using a flow meter, digital temperature probes, and manometers, respectively. Additionally, a digital balance linked to a personal computer was employed to measure the permeate mass and compute the flux. The temperature of the cooling water was kept constant at 10 °C, using a heat-exchanger. The wastewater was pumped into the MD module at a flowrate of 4.5 L.min^{−1}, using a CAT pump 2SF35SEEL-stainless steel direct-drive plunger pump (Minneapolis, MN, USA) and operated for 2 h at four different heating temperatures: 50, 60, 70, and 80 °C. The schematic representation of the current MD process is given in Fig. 1.

Table 1 Characteristics of anodization plant wastewater

Parameters	pH	COD mg/L	TOC mg/L	Sulfate mg/L	Conductivity μS/cm	Aluminum mg/L	Iron mg/L
Wastewater	6.91	322	81.3	17238	17110	625.5	10.35

Fig. 1 Schematic representation of the DCMD setup used in the study



Hydrophobic membranes used

The MD system was operated using two distinct hydrophobic membranes produced from PTFE and PVDF polymers, respectively, with varying pore sizes, 0.45 μm of and 0.22 μm . All the membranes were manufactured by Membrane-Solution-LLC (Shanghai, China) and their physical properties are presented in Table 2. The membranes were conditioned at room temperature around 24 ± 1 $^{\circ}\text{C}$ before being used in the MD process.

Analysis and methods

The treatment performance of the MD process depends on two key factors: membrane rejection and permeate flux. Membrane rejection (R) represents the fraction of contaminants separated from the permeate stream and is typically expressed as a removal efficiency percentage (as shown in Eq. 1). Membrane permeate flux (J) quantifies the amount of water passing through a unit area of the membrane within a specified unit of time (as indicated in Eq 2).

$$R = \frac{C_f - C_p}{C_f} * 100\% \quad (1)$$

where R is the foulants removal efficiency (%), C_f and C_p are the concentration of the contaminant in the feed solution and in the permeate solution, respectively.

$$J = \frac{Q_p}{A} \quad (2)$$

J is the membrane flux (L/h/m^2), Q_p represents the permeate flow rate (L/h), and A stands for the surface area of the membrane (m^2).

The wastewater quality analysis in this study was conducted following the guidelines outlined in the Standard Methods (SM) for the Examination of Water and Wastewater published by the American Public Health Association (APHA). Table 3 provides an overview of the water quality analyses and corresponding methods utilized in this study. Additionally, the morphology and structure of both the neat and used membranes were analyzed using contact angle measurements (Attension, Theta Lite Optical Tensiometer), scanning electron microscopy (SEM), and Fourier

Table 2 Properties of PTFE and PVDF hydrophobic membranes used in the MD process

Membrane material	Pore size (μm)	Thickness (μm)	Flow rate (mL/min/cm^2 at 0.7 bar)	Bubble point (bar)	Liquid entry pressure (LEP) (bar)	Contact angles ($^{\circ}$)
PTFE	0.22	210 ± 30	12.75 ± 1.75	1.3 ± 0.2	4.75 ± 0.75	140.88
PTFE	0.45	195 ± 25	68.5 ± 5.5	0.75 ± 0.2	4.5 ± 50	140.49
PVDF	0.22	160 ± 20	5.4 ± 0.9	1.25 ± 0.15	3.75 ± 0.75	100.32
PVDF	0.45	150 ± 15	13.5 ± 3	1.1 ± 0.1	3.25 ± 0.25	98.51

Table 3 Water quality analyzes and methods

Parameter	Analysis
Conductivity	Thermo Scientific Orion 5-Star Multimeter
pH	Thermo Scientific Orion 5-Star Multimeter
Temperature	Thermo Scientific Orion 5-Star Multimeter
COD	SM-5220 D
TOC	SM-5310 B
Aluminum	SM-3120 B
Iron	SM-3120 B
Sulfate	SM-4500-SO ₄ ²⁻ E

Transform Infrared Spectroscopy (FTIR) (Agilent Technologies, Cary 630 FTIR Spectrometer).

Results and discussion

Performance optimization studies with MD

MD is a 3rd generation treatment technology used for the effective removal of ions, particles, and non-volatile materials in water and wastewater. In the present study, the MD was operated for 2 h at different feed temperatures using PVDF and PTFE membranes with both pore sizes of 0.45 µm and 0.22 µm, to study a comparative performance of each membrane for the treatment and purification of anodic oxidation wastewater. The treated wastewater quality, the

membrane flux, and the membrane resistance to wetting were the main parameters of the investigation.

The results displayed in Table 4 indicate that the contaminants' removal efficiencies are affected by the membrane pore size and increasing feedwater temperature. An increase in both the feed water temperature and the membrane pore induced a decrease in the contaminants removal efficiency. On the other hand, a particular increase in the organic matter concentration was observed in the MD filtrate, which is believed to result from the evaporation of some readily evaporable organic matters in the feed solution. Although increasing feed water temperature affected the foulant removal efficiencies of both PVDF and PTFE membranes, a significant decrease in the foulant removal efficiency of PVDF membranes was observed as the feed water temperature increased to 70 °C and above. It is plausible that the diminished retention ability observed in the study was partly attributed to the contact angles of the clean membranes. Specifically, the contact angles that are approximately 90 degrees may have led to membrane wetting upon exposure to higher feed water temperatures, consequently resulting in a weakened retention capacity. This phenomenon could potentially explain the observed outcomes, indicating the critical role of membrane properties and their interactions with the feed water in the performance of the MD system. Another reason is that as the temperature rises, evaporation becomes more efficient and as more vapor passes through the membrane, ion transport is thought to become more important. PTFE membrane filtration under various operating conditions and pore sizes demonstrated a significant reduction in

Table 4 Pollutant concentrations and removal efficiency in permeate after MD treatment

Membrane type and pore size	Feed temperature	Conductivity		Sulfate		COD		TOC		Aluminum		Iron	
		µS/cm	%	mg/L	%	mg/L	%	mg/L	%	µg/L	%	µg/L	%
PTFE 0.22 µm	°C												
	50	36.8	99.8	40.2	99.8	<20	>94	0.4	99.5	0.28	>99.9	0.23	>99.9
	60	78.4	99.8	48.7	99.8	<20	>94	2.7	96.7	0.31	>99.9	0.23	>99.9
	70	98.3	99.5	86.3	99.5	<20	>94	6.5	92	0.32	>99.9	0.25	>99.9
PTFE 0.45 µm	80	124.2	99.5	97.6	99.5	<20	>94	7.3	91	0.48	>99.9	0.41	>99.9
	50	41.2	99.8	40.6	99.8	<20	>94	5.4	93.4	0.35	>99.9	0.35	>99.9
	60	101.6	99.4	51.5	99.7	<20	>94	8.9	89.1	0.48	>99.9	0.48	>99.9
	70	150.3	99.2	92.4	99.5	22	93.2	8.6	89.4	0.58	>99.9	0.58	>99.9
PVDF 0.22 µm	80	178	99	110.2	99.4	36	85.7	11.3	86.1	0.63	>99.9	0.63	>99.9
	50	1740	89.9	1980	88.6	<20	>94	4.8	94.1	0.89	>99.9	0.31	>99.9
	60	2430	85.9	2440	85.9	39	87.9	11.4	86	0.83	>99.9	0.41	>99.9
	70	4860	71.6	3812	77.9	46	85.7	12.6	84.5	1.17	>99.9	0.67	>99.9
PVDF 0.45 µm	80	7890	53.9	4566	73.6	158	50.9	42.5	47.7	71.73	>99.9	1.17	>99.9
	50	1960	88.6	2110	87.8	42	87	12	85.2	1.57	>99.9	0.69	>99.9
	60	2520	85.3	2651	84.7	54	83.2	13.5	83.4	19.62	>99.9	0.91	>99.9
	70	5110	70.2	3910	77.4	216	32.9	57.6	29.2	26.07	>99.9	0.93	>99.9
	80	9230	46.1	4690	72.8	233	27.6	58.6	27.9	68.24	>99.9	1.42	>99.9

sulfate concentration in the permeate solution. The permeate's sulfate content was much lower than both the World Health Organization's (250 mg/L) and the Istanbul Water and Sewerage Administration's (1700 mg/L) discharge regulations. This demonstrates the potential of PTFE membrane filtration for sulfate removal from water sources, providing a promising solution for sulfate pollution in industrial and domestic wastewater treatment. On the other hand, PVDF membranes were not able to meet the limit values for sulfate concentration in the permeate solution at any of the utilized pore sizes and operating conditions. However, it maintained effective heavy metal removals from the wastewater. Prior MD studies involving various wastewaters have demonstrated a superior performance of PTFE over PVDF membranes, which is attributed to PTFE enhanced operability and higher mass transfer coefficient (J. Zhang et al. 2010).

Kesime et al. (2014) reported a successful use of PTFE membrane in DCMD to extract acid and water from an actual leach solution. They achieved an overall 80% water recovery, 99.9% sulfate and salt rejection (Kesime et al. 2014). A similar study with MD succeeded in removing 90.87% of sulfate, 99.58% chloride, 87.99% COD, and 95.51% conductivity (Zarasvand Asadi et al. 2012), and over 96% iron, aluminum, TOC, conductivity, COD, and sulfate (Noor et al. 2020). The contaminants removal trend in the present study exhibited in Table 4 is in conformity with the findings reported in previous studies. Furthermore, according to Xu et al. (2016), the removal efficiency of contaminants in the MD process demonstrated a relatively stable trend for all membrane pore sizes not exceeding 0.45 μm . However, a significant decline in removal efficiency was observed for pore sizes beyond 0.45 μm (Xu et al. 2016). The present study found that the PVDF membrane with a pore size of 0.22 μm exhibited higher contaminant removal compared to PVDF 0.45 μm . In contrast, no significant difference was observed between PTFE 0.22- μm and 0.45- μm membranes, suggesting a more advantageous application of the PTFE 0.45- μm membrane for the treatment of anodic oxidation wastewaters.

An important advantage of membranes with larger pore sizes, as opposed to those with smaller pores, is the higher mass transfer coefficient, leading to a substantial increase in membrane flux. The results of membrane fluxes depicted in Fig. 2 indicate that the flux values increased in proportion to the feed water temperature and membrane pore size. The flux remained relatively stable over the 2-h operation period for all membranes tested at each temperature. In most operational conditions, PTFE membranes consistently achieved higher flux compared to PVDF membranes, regardless of their pore size. Previous studies have reported that PTFE membranes yield higher flux than PVDF under identical operating conditions. The membrane support layer for PTFE and PVDF not only influences the flux but also affects the

energy efficiency of the process (Zhang et al. 2010). Li et al. (2018) reported that the PTFE membrane consistently exhibits improved flux and rejection capabilities for certain distinctive contaminants compared to PVDF membrane mainly due to their superior hydrophobic properties and lower wettability (Li et al. 2018).

At feed temperatures 50, 60, 70, and 80 $^{\circ}\text{C}$, the average flux for the 0.22 μm PTFE membrane were 11.90, 12.86, 14.29, and 16.79 $\text{L}/\text{m}^2 \text{ h}$ respectively. Comparatively, the 0.45 μm PTFE membrane achieved substantially higher flux, with average flux values of 12.90, 17.63, 20.79, and 27.44 $\text{L}/\text{m}^2 \text{ h}$ respectively, at the same temperatures. The increase of both feed temperature and the recirculation flow rate induces a decrease in membrane resistance considered as the primary contributor to the overall mass transfer resistance (Foureaux et al. 2021). The rise in flux with increasing feed temperatures had a mild impact on contaminants' removal efficiency in PTFE membranes, while in PVDF membranes, it significantly influenced the removal performance. The 0.22- μm PVDF membrane achieved mean flux values of 5.03, 6.93, 13.04, and 18.72 $\text{L}/\text{m}^2 \text{ h}$ at the same feed water temperatures. The PVDF membrane had higher flux with a larger pore diameter, similar to the PTFE membrane. The 0.45- μm PVDF membrane had an average flux of 9.17, 11.27, 13.75, and 20.08 $\text{L}/\text{m}^2 \text{ h}$ at the same temperatures. The size of the PTFE membrane's pores played a vital role in determining both the transmembrane flux and effluent quality, as illustrated in Fig. 2 and Table 4. The study findings suggest that at low feed water temperature, an increase in membrane pore size from 0.22 to 0.45 μm induces a comparable effect on flux as raising the feed temperature from 50 $^{\circ}\text{C}$ to 60 $^{\circ}\text{C}$. However, at higher temperatures, the influence of increasing the pore size becomes more pronounced than elevating the feed temperature from 70 to 80 $^{\circ}\text{C}$. Moreover, the relationship between feed temperature and flux varied depending on the membrane pore size, with an increase in feed temperature causing more water molecules to evaporate and, consequently, an increase in flux, particularly in membranes with 0.45- μm pore diameters. Although feed temperature was an essential factor affecting the flux, the pore size of the membrane also played a crucial role. In particular, the larger pore diameters in the 0.45- μm membranes facilitated more water vapor transmission at high feed solution temperatures, thereby leading to a more significant influence of feed temperature on the flux. Similar flux behaviors were observed in previous studies. Noor et al. achieved a flux of 14.8 $\text{L}/\text{m}^2 \cdot \text{h}$ using 0.20- μm PTFE membranes operated at a feed temperature of 70 $^{\circ}\text{C}$ (Noor et al. 2020). Zhang et al. reported that, under the same conditions, PTFE membranes with a higher contact angle and larger pore diameter achieved a greater flux compared to other membranes (Zhang et al. 2010). In a comparative study conducted by Kim et al., the results showed that both the contact angle

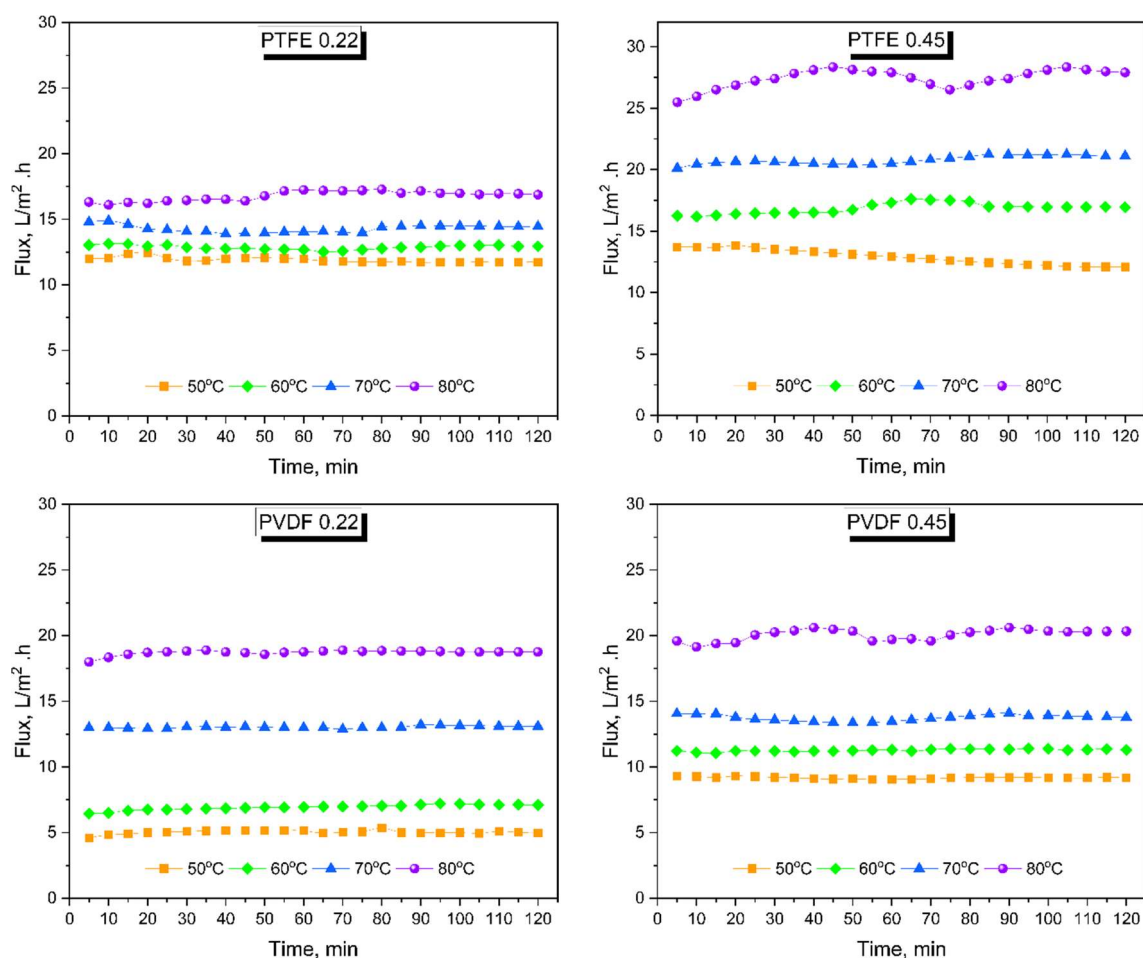


Fig. 2 Flux of PTFE and PVDF Membranes at various feed temperature

and the flux of the PTFE membrane were larger than those of the PVDF membrane (Kim et al. 2021).

Main properties of PTFE and PVDF membranes influencing their performance

While membrane pore size is considered an important property, the different membranes used exhibited variations in pore distribution, membrane thickness, membrane porosity, tortuosity, and LEP, all of which contributed to the performance of the membranes and their resistance to wetting during the treatment of anodic oxidation wastewater. As a fact in MD processes, larger membrane pore sizes are required for higher flux, but smaller pore sizes are necessary to prevent liquid penetration and membrane wetting. Therefore, the optimal pore size should be determined based on the feedwater and operating conditions. Additionally, pores on the membrane surface are generally not uniformly distributed, which can affect membrane flux. Conversely, as membrane thickness increases, mass transfer resistance also increases, leading to a reduction

in flow. Moreira et al. (2023) investigated the treatment of wastewater generated by gold mining operations with MD using PP, PTFE and PVDF membranes and reported that the PP membrane exhibited the highest flux owing to its reduced thickness in comparison to the other membranes. On the other hand, the PTFE membrane achieved an exceptional separation efficiency, over 99.2% of pollutants removal (Moreira et al. 2023). A thinner membrane promotes higher membrane permeability, while a thicker membrane reduces heat loss and might perform better in contaminants rejection. The right thickness will achieve good contaminant rejection and still maintain a reasonably high flux. PTFE 0.45- μ m membrane in the present study depicted such features. Membranes with high porosity offer more surface area for evaporation, resulting in increased transmembrane flux. However, high tortuosity can lead to reduced flux (Drioli et al. 2015; Essalhi and Khayet 2015). All such various properties should be taken into account while choosing the right membrane for a given water treatment in an MD process (Essalhi and Khayet 2015).

Comparing both PVDF and PTFE membranes used in the present study, the lower thickness of PVDF membranes provided an advantage in terms of membrane flux. However, such membranes may be less selective, resulting in lower effluent quality of treated anodic oxidation wastewater compared to PTFE membranes. Additionally, the lower thickness of PVDF membranes renders them more susceptible to fouling and wetting. PTFE membranes have the advantage of high porosity and excellent laminating strength. Both 0.22- and 0.45 PTFE- μm membranes exhibit good uniformity and pore distribution on the membrane surface, along with a low friction coefficient. They possess uniform pore distribution and high pore volume, with membrane porosity ranging between 85 and 93% (Omnexus [n.d.-a](#)). (An et al. [2016](#)) reported in a study that PTFE membranes exhibited greater porosity and hydrophobicity compared to the PVDF membranes leading to an increase in flux and served as a preventive measure against long-term fouling. These attributes along with polyethylene terephthalate (PET) used as a support material, contribute to a higher LEP of PTFE membranes (> 5 bars) compared to PVDF membranes (< 4 bars). PTFE membranes are, therefore, considered best suited for controlling membrane wetting, exhibiting consistent behavior, and achieving an overall better removal of contaminants (Xie et al. [2022](#)), and higher membrane flux with larger pore-size membranes.

Membrane distillation performance with 24-h experiment

The PVDF membranes used in the study exhibited lower performance in contaminant removal, failing to achieve satisfactory anodic oxidation wastewater treatment. On the other hand, all PTFE membranes achieved satisfactory removal of pollutants for anodic oxidation wastewater discharge. The PTFE 0.22- μm membrane exhibited the highest contaminant removal efficiency, while the PTFE 0.45- μm membrane was found to be the most suitable for achieving a high average flux while still meeting the target for contaminants removal in wastewater discharge. To assess the flux behavior over time, the MD process was carried out for 24 h at a feed solution temperature of 60°C using the PTFE 0.45- μm membrane. Over the 24-h operation, filtrate samples were continuously collected every 3 h to monitor flux dynamics and the membrane's performance in contaminant removal. This resulted in a total of eight samples. The membrane flux behavior is presented in Table 5.

The results in Table 5 reveal a continuous decline of the flux until the 15th hour, followed by a slower rate of decrease. Throughout the process, contaminants accumulate in the tank holding the feed due to the recycling of the concentrate flow. However, despite the gradual increase in pollutant concentration in the tank, the flux value remained

Table 5 Membrane flux values for 24-h membrane distillation treatment at 60°C

Membrane type and feed temperature	Time (h)	Average Flux (L/m ² h)
PTFE 0,45 μm - 60°C	0-3	17.65
	3-6	17.60
	6-9	17.49
	9-12	17.20
	12-15	17.09
	15-18	16.91
	18-21	16.90
	21-24	16.89

relatively stable and was not significantly affected. Over the course of more than 40 h of operation, (S. Zhang et al. [2014](#)) found only a negligible drop in flux during an MD process. Kim et al. reported that both the feed solution pH and operation time significantly affect the MD flux. However, they found that the flux reached a stable point between 61 and 65 h of operation (S. Kim et al. [2016](#)). Similar results were reported by Peng et al. when they conducted an MD process at 70°C for an extended period of time (Peng et al. [2005](#)). In the present study, a slight decline of the flux was observed during the initial hours of operation, with flux stability achieved after the 15th hour. The hydrophobic PTFE membrane has the ability to repel the feed solution from its surface, allowing only water vapor to come into contact and cross the membrane. As a result, membrane wetting and fouling are minimized. Furthermore, the membrane's structure endows it with resistance to variations in feed solution temperature and feed water pressure, ensuring the membrane maintains its integrity throughout the operation. Similar results were reported by (Foureaux et al. [2021](#)) with PTFE and PVDF membranes operated for 240 days in the treatment of wastewater from the mining industry. Both membranes exhibited consistent rejection efficiency and distillate flux even after being exposed to wastewater for over 8 months. Moreover, there were no notable alterations detected in the membranes' morphology or structure.

Table 6 indicates that there were minor fluctuations in the rejection efficiency during the 24-h MD operation at 60 °C. The removal efficiencies for iron, aluminum, COD, sulfate, TOC, and conductivity remained consistently high, above 99.9%, 99.9%, 94%, 99.7%, 89.1%, and, 99.4%, respectively. In another study conducted by Ali et al., the effectiveness of membrane distillation and membrane crystallization for treating wastewater from the anodizing industry was investigated. The MD/MCr unit was able to convert approximately 90% of the wastewater into useful products such as fresh water and salt crystals (Ali et al. [2019](#)). The PTFE membrane was able to maintain its integrity over the

Table 6 Fluctuations in rejection efficiency of 24-h PTFE 0.45- μm MD wastewater treatment at 60°C

Time	Conductivity		Sulfate		COD		TOC		Aluminum		Iron	
	$\mu\text{S/cm}$	%	mg/L	%	mg/L	%	mg/L	%	$\mu\text{g/L}$	%	$\mu\text{g/L}$	%
0–3	101.6	99.4	51.5	99.7	<20	>94	8.9	89.1	0.48	>99.9	0.45	>99.9
3–6	101.6	99.4	51.5	99.7	<20	>94	8.9	89.1	0.48	>99.9	0.45	>99.9
6–9	101.6	99.4	51.5	99.7	<20	>94	8.9	89.1	0.49	>99.9	0.45	>99.9
9–12	101.6	99.4	51.5	99.7	<20	>94	8.9	89.1	0.47	>99.9	0.45	>99.9
12–15	101.7	99.4	51.5	99.7	<20	>94	8.9	89.1	0.48	>99.9	0.46	>99.9
15–18	101.7	99.4	51.5	99.7	<20	>94	8.9	89.1	0.49	>99.9	0.46	>99.9
18–21	101.6	99.4	51.5	99.7	<20	>94	8.9	89.1	0.49	>99.9	0.46	>99.9
21–24	101.6	99.4	51.6	99.7	<20	>94	9.1	89.1	0.49	>99.9	0.46	>99.9

24-h operation, membrane wetting did not occur, and all contaminants in the feed solution were continuously removed with a stable and constant rejection efficiency.

Structure and surface morphology's influence on membrane performance

PTFE is a fluoropolymer with a chemical structure composed of polymerized $\text{CF}_2\text{-CF}_2$ units, forming a linear polymer. The fluorine atoms create a uniform and continuous sheath around the carbon-carbon bonds, providing excellent chemical resistance and stability to the molecule. This arrangement also grants the synthesized PTFE structure exceptional chemical resistance, heat tolerance, and good electrical insulating properties in hot and wet environments. The non-stick and slippery surfaces of PTFE membranes confer them with anti-adhesion properties, allowing them to resist fouling during MD processes (Omnexus [n.d.-a](#)). On the other hand, PVDF is a semi-crystalline thermoplastic fluoropolymer, consisting of a chain of alternating CH_2 and CF_2 groups. Its synthesis occurs through the polymerization of the PVDF monomer, 1,1-difluoroethylene ($\text{CH}_2=\text{CF}_2$). The polarity of CH_2 and CF_2 groups leads to the insolubility and electrical properties of PVDF membranes. From a structural point of view, fluorinated polymers of PVDF membranes show chemical inertness to a narrower range of chemicals compared to PTFE (Omnexus [n.d.-b](#)).

To gain a deeper understanding of membrane fouling and wetting in membrane processes, various characterization techniques are required, such as contact angle measurements, SEM, and FTIR. These techniques were employed to investigate the surface chemistry of both clean and neat membranes, with the aim of shedding light on the mechanisms underlying membrane fouling and wetting (Fortunato et al. [2016](#); Wu and Fane [2012](#)). The surface morphology of the membrane plays a crucial role in influencing its performance (Childress and Brant [2000](#)). The results revealed that an increase in feed water temperature led to a slight decrease in the contact angle of the PTFE membranes (as shown in Fig. [3](#)), suggesting a

minor loss in membrane hydrophobicity. Membranes that are hydrophobic in nature typically have contact angles that exceed 90° , with contact angle values increasing with greater hydrophobicity. When pore size and temperature increase, water can interact more easily with the membrane pores, leading to an increase in flux and a decrease in contact angle. The results of the short-term experiments conducted in the study revealed a surprising decrease in membrane hydrophobicity upon raising the feed water temperature. Consequently, the study highlights that membrane pore size, in addition to temperature, is a crucial factor that influences membrane performance. Larger pore diameters facilitate greater water vapor transmission, particularly evident in membranes with pore sizes of $0.45\ \mu\text{m}$, thereby underscoring the importance of pore size in determining the effectiveness of the membrane. Overall, these findings highlight the need for comprehensive characterization techniques to gain a better understanding of the behavior of membrane systems.

The findings reported in Fig. [3](#) show that the anodizing wastewater influences the membrane structure. As the feed water temperature increases, more steam is generated, and the impact of this temperature increase on the contact angles of the membranes becomes evident. Specifically, the contact angle of the membranes is a useful indicator of the changes in their hydrophobicity due to increasing feed water temperature. This effect is not only related to the characterization and temperature of the water, but also to the membrane structure. When PTFE membranes are examined, the initial high hydrophobicity value is still maintained at a very high level even though it decreases with increasing feed water temperature. This situation can also be explained by the fact that the permeate quality is affected by the increasing feed water temperature to a very small extent. The PVDF membranes had an initial contact angle of around 90° , and the increase in feed water temperature resulted in the decrease of the contact angle to 90° and below, significantly reducing the permeate quality. It is evident that the increase in the pore size of the membranes renders them more susceptible to wetting, as depicted in Fig. [3](#). Similar results about

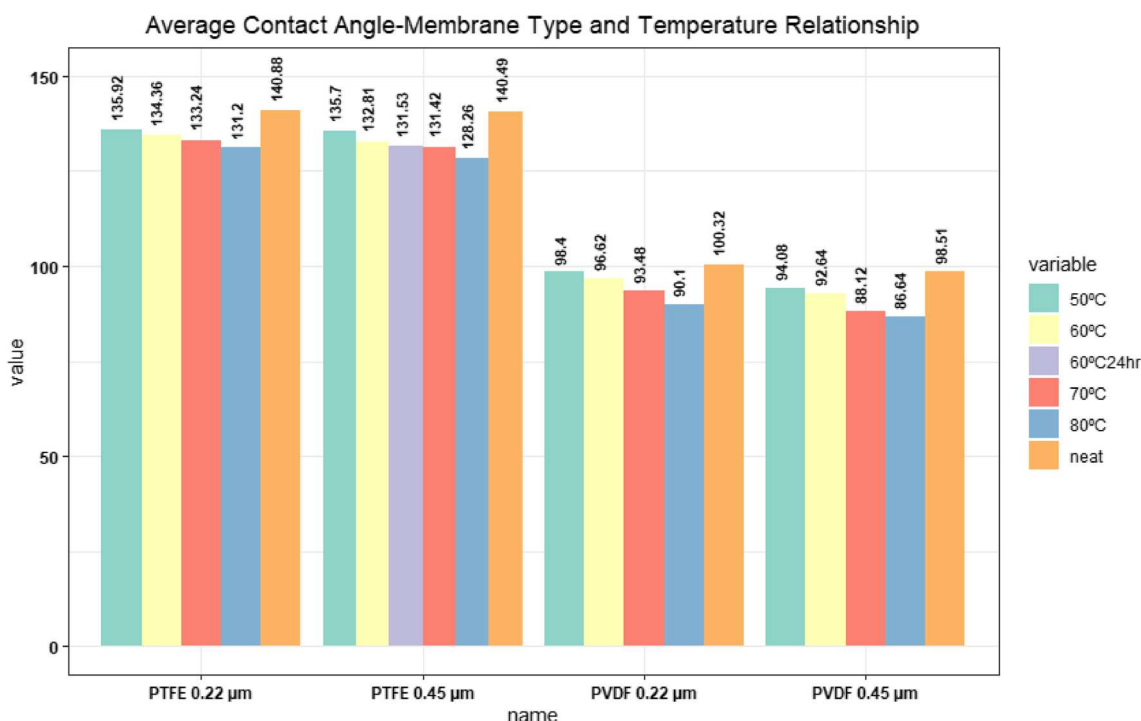


Fig. 3 Average contact angle-membrane type and temperature relationship

membrane wetting and fouling were reported by (Zougrana et al. 2016) and (Khaing et al. 2010).

FTIR spectroscopy is a widely used analytical technique across fundamental research, medicine, and engineering, particularly for identifying bonds within molecular structures. Analysis of FTIR spectra is a useful tool for understanding how membrane structure and major functional groups respond to various conditions (Alpatova et al. 2015; Hu et al. 2016; Vargo et al. 1991; Wang et al. 2015; Xue et al. 2015; Zhao et al. 2010). Figure 4 presents the primary peaks identified during the analysis of both used and unused

membranes. The results indicate that the clean PTFE membrane exhibits two distinct peaks at 1205 cm^{-1} and 1150 cm^{-1} . These peaks are associated with $-\text{CF}_2$ and $-\text{CF}_3$ group stretching vibrations (Wang et al. 2014; Wang et al. 2015). PTFE membranes showed no significant difference in peak patterns between wastewater treated for 2 h and 24 h at 60°C . However, peak stretching vibrations measured after 24 h were found to be less than those measured after 2 h. The used membranes showed a new peak development at 3390 cm^{-1} , which may be due to intermolecular O-H stretching of carboxyl, hydroxyl, and phenol groups, while the peaks

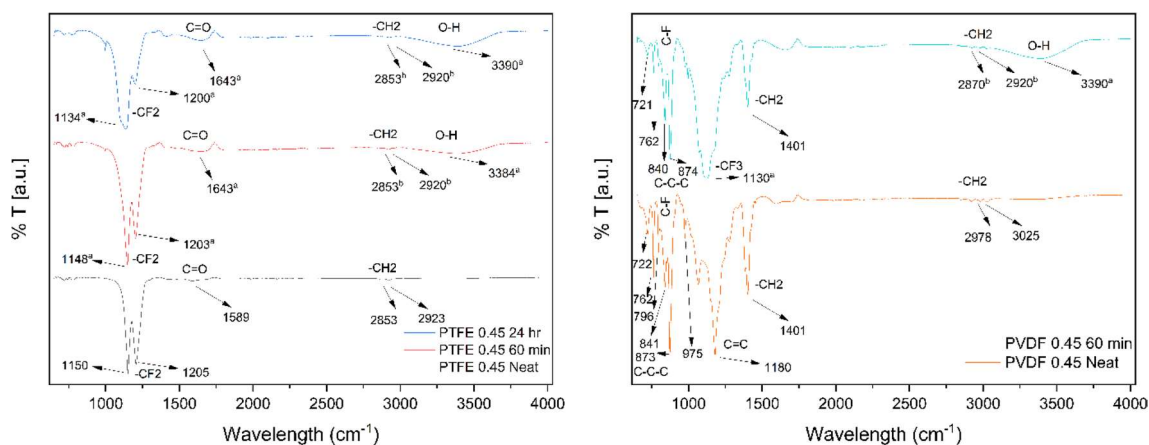


Fig. 4 FTIR spectra of the neat and dirty PTFE and PVDF membranes: **a** stretching, **b** anti-symmetric vibration

detected in the 2920–2853 cm^{-1} range are $-\text{CH}_2$ group (Hu et al. 2016; Xue et al. 2015). The 750–720 cm^{-1} peaks observed in used membranes are due to the $-\text{CH}_2$ group's shaking vibrations; the 1643 cm^{-1} peak, on the other hand, may be due to the $\text{C}=\text{C}$ stretching vibration. Compared to other used membranes, the peak of 1130 cm^{-1} occurring on the membranes after 24 h of operation may be related to the reduction in stretching vibration of the $-\text{CF}_3$ group or to sulfate ions (Coates 2006).

The peaks displayed by the clean PVDF membrane at 3025 and 2978 cm^{-1} are due to the vibrations of the asymmetric and symmetric CH_2 group. In the PVDF membrane, the peak at 1401 cm^{-1} is associated with the ripple vibration of the CH_2 group, while the peak at 1180 cm^{-1} is associated with the $\text{C}-\text{C}$ bonds (Bai et al. 2012). Furthermore, the peaks in the 981–750 cm^{-1} range correspond to the α and β phases of the PVDF membranes, while the peaks in the 878–839 cm^{-1} interval are associated with the asymmetric $\text{C}-\text{C}-\text{C}$ and $\text{C}-\text{F}$ stretch vibrations (Alpatova et al. 2015; Wang et al. 2014). After treating wastewater at 60 °C, a new peak formed at 3390 cm^{-1} on the PVDF membrane, which was observed in the used PTFE membranes and may be caused by intermolecular $\text{O}-\text{H}$ stretching of carboxyl, hydroxyl, and phenol groups. Another possible explanation for the peaks between 2920 and 2870 cm^{-1} is that the $-\text{CH}_2$ group is being stretched next to the $-\text{OH}$ group (Hu et al. 2016; Xue et al. 2015). Another peak detected on the used membrane has a wavelength of 1130 cm^{-1} and may relate to sulfate ions or a decrease in the stretching vibration of the $-\text{CF}_3$ group (Coates 2006).

SEM analysis provides valuable insights into both the topography and elemental composition of a material. Figure 5 showcases the topographic features of the membranes. Notably, micrographs of the clean membranes revealed a more uniform surface distribution on the PTFE membrane compared to the PVDF membrane. SEM analysis further revealed the deposition of organic materials on the membrane surfaces. PVDF membranes exhibited a higher degree of organic material deposition compared to PTFE membranes. This observation may explain the lower permeate flux and contaminant rejection performance observed in PVDF membranes. The micrographs of PTFE membranes revealed a superficial deposition of particles, potentially due to the presence of open holes on the membrane surface. The progressive accumulation of particles on the membrane surface might explain the decline of the permeate flux with time. The FTIR data, namely the $\text{O}-\text{H}$ tensions at the 3390 cm^{-1} peak and the probable sulfate ions at the 1130 cm^{-1} peak, may have their origins in the accumulations shown in the membrane micrographs. (Xie et al. 2022) achieved

similar findings of PTFE membranes exhibiting better fouling resistance compared to PVDF membranes. They argue that the surface scaling remained significant for the PVDF membrane due to its relatively low hydrophobicity, which failed to effectively impede the occurrence of heterogeneous nucleation on the membrane. As mentioned in previous sections, membrane pore sizes over 0.45 μm can induce lower performance, a point supported by their study, experiencing scaling with larger pores. They recommended a decrease in pore size and an increase in membrane hydrophobicity as a solution to enhance anti-scaling characteristics. This approach effectively mitigates the impact of both homogeneous and heterogeneous nucleation on the formation of gypsum scale.

Conclusion

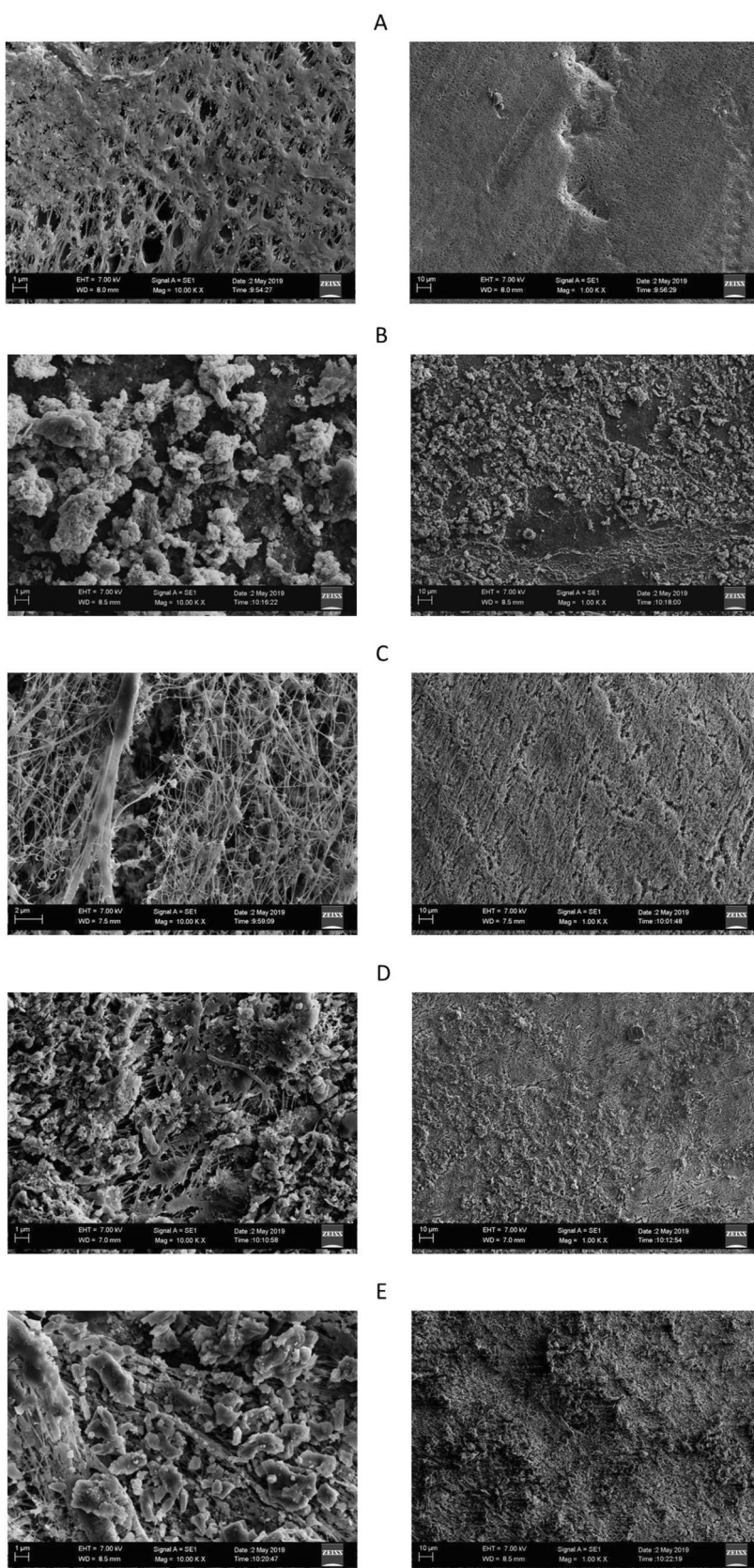
Wastewater from the anodized plating industries poses serious threats to aquatic ecosystems and must be treated before being discharged. Third-generation progressive treatment approaches, such as MD, are required to treat wastewaters with such high concentrations of contaminants since conventional treatment methods fail to do so. The performance of PTFE and PVDF membranes in removing contaminants from anodic oxidation wastewaters are mostly correlated to their structure, controlling both contaminants rejection efficiency and transmembrane flux.

Both 0.22- and 0.45- μm PTFE membranes effectively achieved the targeted water quality standards for anodic oxidation wastewater treatment across all tested feed temperatures, demonstrating excellent removal efficiencies exceeding 99% for conductivity, sulfate, aluminum, and iron and over 85.7% for organic matter removal. In contrast, PVDF membranes failed to meet the discharge requirements, especially at higher feed temperatures. A clear correlation between the pore size of the membranes, feed temperature, and removal efficiency was observed for both membrane materials. Smaller pore size membranes achieved better contaminant removal while maintaining lower fluxes throughout the MD treatment process.

While minor wetting was observed with PTFE membranes, fouling and wetting of PVDF membranes led to a decline in flux and significantly affected the permeate quality over time. The structure and morphology of PTFE membranes endowed them with slippery and anti-adhesion properties stronger than PVDF membranes, preventing fouling and wetting and maintaining their performance during MD operations for anodic oxidation wastewater treatment.

Author contribution Conceptualization: Mehmet Cakmakci; methodology: Oruc Kaan Turk, Ali Zoungrana; data collection: Ali Zoungrana,

Fig. 5 SEM: **A** Neat 0.4- μm PVDF membrane 1000 (right) and 10000 (left) magnification, **B** 60° C feed temperature after 2-hMD process 0.45- μm PVDF membrane 1000 (right) and 10000 (left) magnification, **C** neat 0.45- μm PTFE membrane 1000 (right) and 10000 (left) magnification, **D** 60° C feed temperature after 2 h-MD process 0.45- μm PTFE membrane 1000 (right) and 10000 (left) magnification, **E** 60° C feed temperature after 24-h MD process 0.45- μm PTFE membrane 1000 (right) and 10000 (left) magnification



Oruç Kaan Türk; formal analysis and investigation: all Authors; writing - original draft preparation: all authors; writing - review and editing: all authors; supervision: Ahmet Demir. The authors read and approved the final manuscript.

Funding Open access funding provided by the Scientific and Technological Research Council of Türkiye (TÜBİTAK).

Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval Not applicable (this study did not recruit any human/animal subjects).

Consent to participate Not applicable (this study did not recruit any human subjects).

Consent for publication Not applicable (this study is not published previously).

Competing interests The authors have no relevant financial or non-financial interests to disclose.

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