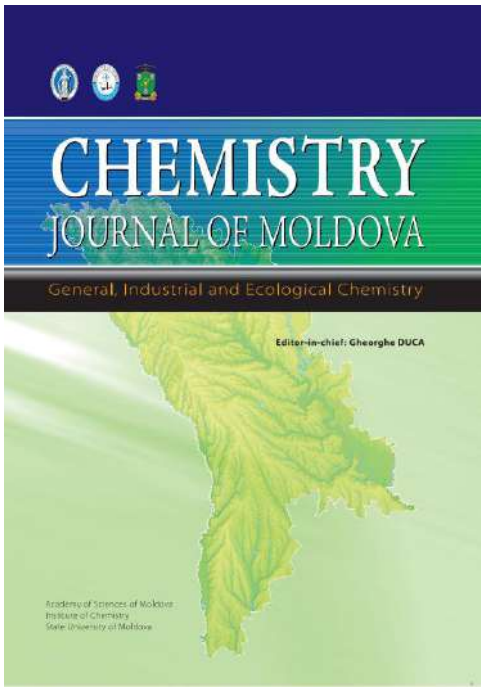


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NATURAL DEEP EUTECTIC SOLVENTS FOR REMEDIATION OF PER- AND POLYFLUOROALKYL SUBSTANCES, TIRE WEAR, AND OTHER PERSISTENT ORGANIC POLLUTANTS IN AQUATIC ENVIRONMENTS

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Abstract. The pervasive contamination of aquatic ecosystems by per- and polyfluoroalkyl substances (PFAS), micro- and nanoplastics (MNPs), tire wear particles (TWP), and other persistent organic pollutants (POPs) constitutes one of the major environmental challenges of the 21st century. These synthetic compounds, characterized by exceptional chemical stability and resistance to degradation, are now distributed worldwide and present significant risks to the integrity of our ecosystem and human and animal health. Conventional remediation technologies, including activated carbon adsorption and membrane filtration, are limited in terms of efficiency, cost, energy consumption, and hazardous waste generation. This comprehensive review examines the evolving use of Natural Deep Eutectic Solvents (NADES), a novel class of green solvents derived from naturally occurring, biodegradable compounds, as a sustainable, highly effective alternative for removing these persistent pollutants from water. NADES operate *via* powerful liquid-liquid extraction and adsorption mechanisms, leveraging extensive hydrogen-bonding networks to achieve removal efficiencies of approximately 99% for target contaminants. The review analyses current knowledge on NADES fundamentals, contaminant characteristics, extraction mechanisms, comparative advantages over conventional methods, and technical challenges related to their viscosity, scalability, and economic viability. As part of our ongoing DEEP-CLEAN project, we analyse experimental evidence at the laboratory scale, discuss regeneration strategies essential to implementing the circular economy, and evaluate the regulatory landscape that is likely to drive innovation in this field. NADES represents a novel concept for sustainable water treatment, offering a technically viable, economically competitive, and environmentally friendly solution to address the global crisis of persistent contamination in aquatic environments. The review proposes future research directions that integrate computational design, artificial intelligence (AI), and process optimization to facilitate its transition from laboratory experiments to industrial-scale deployment.

Keywords: NADES, PFAS, TWP, green chemistry, liquid-liquid extraction.

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List of Abbreviations

AFFF	Aqueous film-forming foams
AI	Artificial intelligence
ANSI	American National Standards Institute
AOP	Advanced oxidation processes
ATSDR	Agency for toxic substances and disease registry
BMED	Bipolar membrane electrodialysis
BPA	Bisphenol A
ChCl	Choline chloride
COSMO-RS	Conductor-like screening model for real solvent
DFT	Density functional theory
EBCT	Empty bed contact time
EDC	Endocrine-disrupting chemicals
EPA	Environmental protection agency
FTOH	Fluorotelomer alcohol
GAC	Granular activated carbon
HBA	Hydrogen bonding acceptor
HBD	Hydrogen bonding donor
HF	Hydrofluoric Acid
HM	Heavy metals
LCA	Life cycle analysis
LLE	Liquid-liquid extraction
MCDA	Multi-criteria decision analysis
MCL	Maximum contaminant levels
MD	Molecular dynamics
MGD	Million gallons per day

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MNP	Micro- and nanoplastics
NADES	Natural Deep Eutectic Solvents
NF	Nanofiltration
NOM	Natural organic matter
NSF	National Sanitation Foundation
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyls
PCP	Personal Care Products
PET	Polyethylene terephthalate
PFAA	Perfluoroalkyl acid
PFAS	Per- and polyfluoroalkyl substances
PFCA	Perfluoroalkyl carboxylic acid
PFHxS	Perfluorohexane sulfonic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PLA	Polylactic acid
POP	Persistent organic pollutants
PPD	Phenyl phenylenediamine
PS	Polystyrene
RO	Reverse osmosis
SPE	Solid-phase extraction
TOPO	Trioctylphosphine oxide
TRL	Technology readiness level
TRWP	Tire and road wear particles
TWOP	Tire wear organic particles
TWP	Tire wear particles
UF	Ultra filtration
VOC	Volatile organic compounds
WWTP	Wastewater treatment plants

Introduction

Water contamination crisis

The integrity of freshwater and marine ecosystems supports both ecological diversity and human civilization, yet they face unprecedented challenges from synthetic pollutants with extraordinary environmental persistence. Among the most environmentally concerning of these contaminants are PFAS, perfluorooctanoic acid (PFOA), and perfluorooctanesulfonic acid (PFOS)-commonly known as “forever chemicals”, named for their virtual indestructibility in natural systems - and similar POPs [1-5]. These compounds, engineered for their remarkable stability, hydrophobicity, and chemical resistance, have become integral to modern industrial processes and consumer products, ranging from non-stick cookware and waterproof textiles to firefighting foams, including tire manufacturing [6]. However, the very molecular characteristics that render them commercially valuable- that is, the strong Carbon-Fluorine bond in PFAS, responsible for forming the recalcitrant compounds- ensure their long persistence once released into the environment [7,8]. The global presence and distribution of these contaminants is indeed overwhelming. PFAS have been detected in every part of the environment on Earth, from Arctic ice cores and Antarctic snow to tropical rainwater, groundwater aquifers, and even the blood serum of the general human population [9,10]. Recent meta-analyses reveal that a substantial fraction of both surface and groundwater worldwide contain PFAS at concentrations exceeding current health advisory levels, with contamination often occurring in regions with no identifiable nearby point source [11]. Additionally, TWPs, generated by the mechanical abrasion of an estimated 1.5 billion vehicle tires globally, account for 5–10% of total oceanic microplastics and potentially 45% of all environmental microplastic pollution [12,13], as shown in Figure 1.

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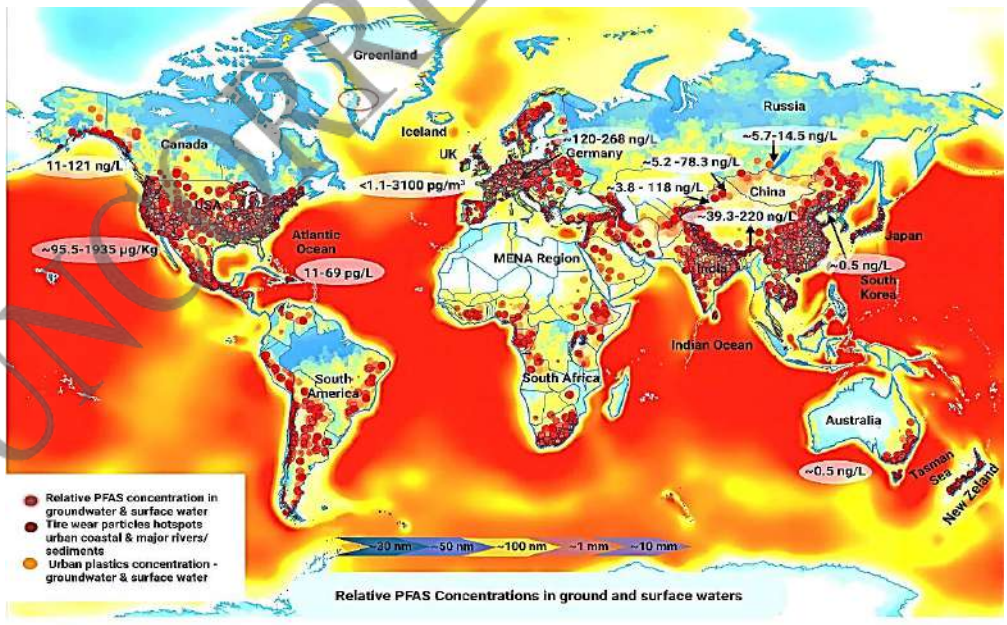


Figure 1. PFAS concentrations in ground and surface waters at representative hotspots worldwide.
(Schematic drawn using Biorender software. Data are extracted using various databases, including Kaggle. Please note that data from some regions were not available, which does not indicate non-existent contaminants.)

These particles, commonly also termed TWP and organic TWP (TWOP), are laden with complex mixtures of rubber polymers, carbon black, heavy metals, and toxic additives, including the harmful 6-PPD-quinone, which infiltrate aquatic systems primarily through stormwater runoff, leading to acute toxicity among species, causing chronic ecosystem disruption [14,15]. Physicochemical degradation and composition are influenced by environmental factors and by various anthropogenic pollutants, including MNPs, PFAS, 6-PPD, TWP, and heavy metals (HM). These contaminants are transported globally *via* air and water and bioaccumulate, causing adverse environmental impacts and subsequent damage to organisms. The human health implications of chronic exposure to PFAS, MNPs, TWP, and HMs are increasingly evident in recent literature [4,16,17]. Recent epidemiological studies have demonstrated links between PFAS exposure and elevated risks of kidney and testicular cancers, reproductive dysfunction, developmental delays in children, immunosuppression, thyroid disease, and metabolic disorders, including elevated cholesterol and obesity [18-20]. The mechanisms of toxicity include endocrine disruption, oxidative stress induction, and interference with lipid homeostasis at certain pollutant concentrations, even at parts-per-trillion levels [21]. For TWP and MNPs, the leaching of additives, particularly 6-PPD-quinone, has been directly linked to mass mortality events in Pacific salmon populations and is acutely toxic to diverse aquatic biota [14,22].

Concerns arising from scientific evidence and public concerns have led to rapid evolution in regulatory frameworks. The United States Environmental Protection Agency (EPA) established the first-ever National Primary Drinking Water Regulations for PFAS in 2024, setting maximum contaminant levels (MCLs) of 4.0 parts per trillion (ppt) for PFOA (termed C8, from its chemical formula $C_8HF_{15}O_2$) and PFOS, among the lowest regulatory thresholds for any chemical contaminant [23]. Drinking Water Directive (EU) 2020/2184 is a key EU regulation for PFAS, establishing limits for their presence in drinking water (the directive applies to all water intended for human consumption, including tap water, bottled water, and water used in the food industry), including a PFAS total limit at 0.5 µg/L. The limit applies to the sum of 20 specific PFAS compounds [24]. Furthermore, the Stockholm Convention lists PFOS, PFOA, and perfluorohexane sulfonic acid (PFHxS) as POPs subject to global elimination [25]. This regulatory intensity creates an urgent demand for remediation technologies capable of achieving removal at the few ppt level at economically viable costs. Current water treatment approaches for PFAS and MNPs predominantly rely on physical separation methods, using primarily granular activated carbon (GAC) adsorption and high-pressure membrane filtration (reverse osmosis (RO) and nanofiltration) [26,27]. While these technologies can achieve significant contaminant removal under optimal conditions, they are subject to fundamental limitations. GAC demonstrates reduced efficacy against certain short-chain PFAS compounds (C4-C6), and its performance is severely compromised by natural organic matter, necessitating frequent and costly replacements [28,29]. High-pressure membrane systems, though highly effective, are prohibitively energy-intensive and generate a concentrated brine waste stream containing mobilized contaminants, thus posing a disposal challenge with limited remediation options [27,30].

Breaking Carbon-Fluorine (C-F) bonds are one of the most challenging reactions for chemists, both in chemical synthesis and in environmental remediation of recalcitrant fluorinated hydrocarbons. A catalyst capable of breaking this bond could also be used to disintegrate PFAS. Advanced oxidation processes (AOPs), including electrochemical oxidation and photocatalysis, are other techniques used for destructive removal through cleavage of the C-F bonds; however, some techniques present limitations due to extremely high energy consumption, incomplete mineralization with formation of toxic transformation products, and impractically slow kinetics for treating large water volumes even at trace concentrations [31,32]. Bioremediation, while environmentally attractive in principle, has the fundamental problem that the C-F bond is among the strongest in organic chemistry, rendering PFAS essentially resistant to microbial degradation [26]. For PFAS, TWP, and POPs, conventional filtration is ineffective and economically unrealistic as particle sizes are reduced to the nanoscale, particularly where toxicological concerns are most acute [33]. Due to these technological inefficiencies, NADES have emerged as a promising, fundamentally unique approach to the remediation of PFAS, TWP, and POPs. Furthermore, NADES are a distinct class of green solvents, typically formed by combining naturally occurring compounds in specific molar ratios, yielding a eutectic mixture with a markedly lower melting point than the pure components [34,35]. This mechanism creates a liquid solvent at or near room temperature, stabilized by an extensive network of intermolecular hydrogen bonds rather than by ionic or covalent interactions [36,37]. The fundamental advantages of NADES for environmental applications are manifold. For example, their composition arises from primary metabolites, ensuring inherent biodegradability, negligible toxicity, and compatibility with biological systems, in contrast to conventional organic solvents and many ionic liquids [38,39]. NADES exhibit exceptional, tunable solvation capacity, capable of

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dissolving a remarkably diverse range of compounds, from highly polar to hydrophobic, enabling selective extraction of target contaminants. Additionally, their negligible volatility reduces concerns about atmospheric emissions and supports complete solvent recovery and recycling, aligning with principles of the circular economy [38,40]. Lastly, the physicochemical properties of NADES, including polarity, viscosity, hydrophobicity, and extraction selectivity, can be designed through the selection of specific Hydrogen bonding acceptor-Hydrogen bonding donor (HBA-HBD) combinations and molar ratios, providing an unprecedented range for optimization [41,42].

Despite the considerable promise shown in recent laboratory studies, comprehensive assessment of NADES for persistent contaminant remediation remains limited, and its use in industrial-scale applications has not yet been fully realized. In this review, which was conducted for projects such as DEEP CLEAN and TWP remediation at certain sites, and a book on Micro and Nanoplastics in Aquatic Environments [4], the aim is to provide an integrated, critical analysis of the current state of NADES-based remediation methodologies. The fundamental physicochemical properties and formation mechanisms of NADES that enable their applications in environmental remediation are further addressed to provide comprehensive information on the nature, sources, distribution, and toxicological profiles of PFAS, TWP, and related POPs in aquatic environments. Additionally, the molecular mechanisms by which NADES achieve extraction is analysed, supported by experimental evidence and computational modelling, and evaluate their efficacy, selectivity, and comparative advantages relative to conventional treatment technologies. A critical assessment of technical challenges, including viscosity, mass transfer limitations, solvent leaching, and scalability issues, is provided, along with an examination of regeneration strategies and economic viability for valorisation, including the regulatory landscape and infrastructure integration requirements. Finally, critical research gaps and future directions are delineated to advance NADES research from the laboratory to mainstream water treatment technology. A systematic literature search was conducted for each project listed above, and the most relevant articles were selected for this review and organized using reference management software.

Background

Natural deep eutectic solvents

Definition, chemical composition, and formation mechanisms

NADES represent an innovative class of green solvents whose formation is predicated on a simple yet effective molecular phenomenon [43]. When a liquid mixture of two or more naturally occurring compounds is combined in a specific stoichiometric ratio, it exhibits a melting point significantly lower than any of its individual solid components. This reduction in melting point results from complex physical interactions, primarily from the formation of an extensive three-dimensional (3D) network of hydrogen bonds among the constituent molecules [41]. The formation mechanism centres on the interaction between two functional classes of molecules. The HBA is typically a quaternary ammonium salt, with choline chloride (ChCl) being the most commonly used due to its natural abundance, exceptionally low cost, and low toxicity, making it an essential nutrient [44,45]. The quaternary ammonium cation and its associated anion provide electron-rich sites that can accept hydrogen bonds. The HBD component encompasses a far more diverse array of naturally occurring metabolites, including carboxylic acids, polyols, sugars, amino acids, and even urea or thiourea, as shown in Figure 2, though the latter are less strictly "natural [35]. When these components are thoroughly mixed at a precise molar ratio, commonly 1:1, 1:2, or 1:3, with mild heating (~50–80°C) and continuous stirring, the hydrogen bonds that stabilize the crystal lattice structures of the individual solid compounds are thus disrupted [36,45].

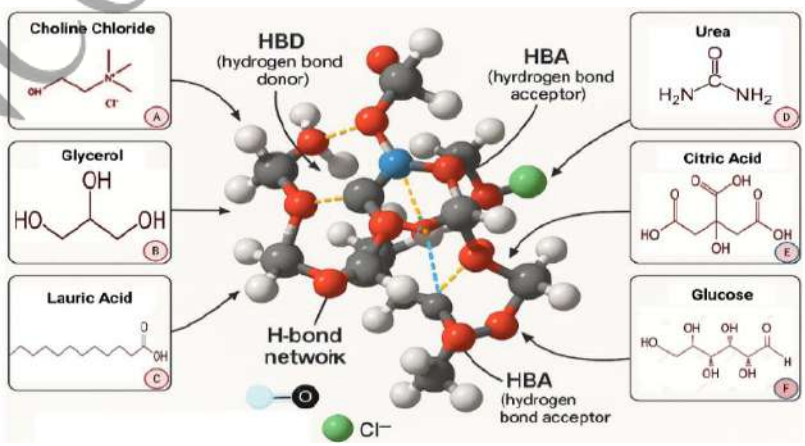


Figure 2. Hydrogen-bonded supramolecular NADES network.
(Schematic drawn using BioRender**)**

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Simultaneously, new intermolecular hydrogen bonds form between HBA and HBD species, creating a supramolecular network that prevents crystallization and maintains the mixture in a liquid state even upon cooling to room temperature or below [44]. This process can be described as charge delocalization; that is, hydrogen-bonding interactions distribute electron density across a larger molecular network, thereby effectively lowering the energy barrier to maintaining the liquid phase [45]. Advanced spectroscopic techniques provide direct evidence for these molecular interactions. Fourier-transform infrared (FTIR) spectroscopy reveals characteristic shifts in the vibrational frequencies of hydroxyl (O-H) and carbonyl (C=O) groups upon NADES formation, confirming their participation in new hydrogen bonds. Nuclear magnetic resonance (NMR) spectroscopy demonstrates changes in the chemical environments of protons and carbons involved in hydrogen bonding, further validating the supramolecular structure [34]. Computational methods, such as density functional theory (DFT) and molecular dynamics (MD) simulations, have been instrumental in clarifying the 3D architecture of these hydrogen-bonded networks and predicting the thermodynamic stability of different HBA-HBD combinations [41].

Classification of NADES formulations

The selection of HBA and HBD components, along with their molar ratios, enables the design of NADES with a wide variety of physicochemical properties, creating a large library of designer solvents. Based on their primary composition, NADES are broadly classified into several major categories, each with distinct characteristics and specific applications.

Choline-based NADES constitute the most widely investigated class, leveraging choline chloride as the HBA paired with diverse HBDs [35,44]. Representative examples include ChCl:urea (1:2), which was among the first DES synthesized and exhibits high polarity suitable for extracting polar analytes; ChCl:glycerol (1:2), characterized by moderate polarity and high viscosity; ChCl:citric acid (1:1) introduces acidity and additional hydrogen bonding sites; and ChCl:glucose (1:1 or 2:1) combines biocompatibility with moderate hydrophilicity [36,45]. The versatility of choline-based systems arises from the ability to systematically modulate solvent properties by varying the HBD link.

Sugar-based NADES utilize monosaccharides or disaccharides as primary components, often in combination with organic acids or polyols [34,39]. Examples of sugar-based NADES include glucose:fructose:water (1:1:1), which creates a highly biocompatible, low-toxicity medium ideal for food and pharmaceutical applications. These NADES are particularly useful for their complete safety and exceptional biodegradability [39]. Table 1 lists representative NADES formulations and their physicochemical properties.

Table 1

Representative NADES formulations and their physicochemical properties.

NADES Type	*HBA*	*HBD*	*Molar Ratio (HBA:HBD)*	*Melting Point (°C)*	*Viscosity (mPa·s) at 25°C*	*Density (g/cm³) at 25°C*	*pH (at 25°C)*	*Polarity*	*Water Content (% w/w)*	*Ref.*
ChCl:Urea	Choline Chloride	Urea	1:2	12	750	1.25	6.5-7.5	High	0	[35]
ChCl:Glycerol	Choline Chloride	Glycerol	1:2	<25	259-376	1.18-1.20	6.0-7.0	High	0	[38]
ChCl:Glucose	Choline Chloride	Glucose	5:2	<25	8500-12000	1.24-1.28	5.5-6.5	Very High	0	[38]
ChCl:Fructose	Choline Chloride	Fructose	5:2	<25	7000-9500	1.23-1.27	4.4-6.1	Very High	0	[44]
ChCl:Citric Acid	Choline Chloride	Citric Acid	1:1	<25	850-1200	1.22-1.25	2.5-3.5	Very High	0	[36]
ChCl:Malic Acid	Choline Chloride	Malic Acid	1:1	<25	950-1350	1.20-1.23	2.8-3.8	Very High	0	[36]
ChCl:Lactic Acid	Choline Chloride	Lactic Acid	1:2	<25	650-900	1.14-1.17	2.0-3.0	High	0	[36]
Betaine:Glycerol	Betaine	Glycerol	1:2	<25	300-450	1.15-1.18	6.5-7.5	High	0	[46]
Betaine:Lactic Acid	Betaine	Lactic Acid	1:2	<25	550-750	1.16-1.19	2.5-3.5	High	0	[47]
Betaine:Citric Acid	Betaine	Citric Acid	1:1	<25	900-1100	1.21-1.24	2.8-3.8	Very High	20	[47]
Proline:Malic Acid	Proline	Malic Acid	1:1	<25	1200-1600	1.18-1.22	3.0-4.0	High	0	[35]
Glucose:Fructose:Water	Glucose	Fructose + Water	1:1:1	<25	5000-7000	1.30-1.35	5.0-6.0	Very High	33	[48]
Menthol:Thymol	Menthol	Thymol	1:1	~0	15-25	0.92-0.95	6.0-7.0	Low	0	[49]
Camphor:Menthol	Camphor	Menthol	1:1	~5	20-30	0.90-0.93	6.0-7.0	Low	0	[49]
ChCl:Ethylene Glycol	Choline Chloride	Ethylene Glycol	1:2	<25	36-42	1.12-1.14	6.5-7.5	High	0	[50]
ChCl:Levulinic Acid	Choline Chloride	Levulinic Acid	1:2	<25	800-1100	1.15-1.18	2.5-3.5	High	0	[50]
Fructose:ChCl	Fructose	Choline Chloride	1:1	<25	6000-8000	1.25-1.28	4.5-5.5	Very High	0	[48]
K_2CO_3:Glycerol	K_2CO_3	Glycerol	1:6	<25	150-250	1.35-1.40	11.5-13.5	Very High	0	[51]

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Amino acid-based NADES leverage the zwitterionic character of amino acids, which possess both carboxyl (acidic) and amino (basic) functional groups, enabling unique pH buffering and interaction capabilities. Proline-based systems, such as proline:malic acid (1:1) or proline:glycerol (1:3), have demonstrated special applications due to proline's inherent stability and its role as a natural osmolyte in stress-adapted organisms [34,52]. These NADES exhibit tunable polarity, high solvation capacity for polar and zwitterionic biomolecules, intrinsic biocompatibility, and adjustable acidity/basicity, making them attractive for green catalysis, bioprocessing, and biomolecular stabilization.

Hydrophobic NADES represent a functionally critical subclass designed specifically for liquid-liquid extraction applications in which immiscibility with water is essential [53,54]. These formulations typically employ terpenes or long-chain fatty acids as HBDs, paired with suitable HBAs. Examples include menthol:decanoic acid (1:1), which has been used for extracting hydrophobic organic pollutants, and the highly effective trioctylphosphine oxide (TOPO):lauric acid (1:1) system, which achieved >99% removal of PFOA in aquatic remediation applications [52,54]. The hydrophobicity arises from the predominance of nonpolar hydrocarbon chains, while sufficient hydrogen bonding capacity is retained to maintain the eutectic state.

Physicochemical properties

The unique physicochemical properties of NADES are directly related to their supramolecular hydrogen-bonded architecture, which is a major contributor to their performance in remediating environmental pollutants. The defining structural feature of NADES is the extensive 3D network of hydrogen bonds that permeates the liquid matrix. This network creates a highly structured environment for solvents with multiple interaction sites that can attract diverse chemical functionalities in solute molecules. The result is an exceptionally high and broadly tunable solvation capacity. NADES can effectively dissolve compounds across a wide range of polarities, from highly polar molecules, such as amino acids and nucleotides, to moderately polar flavonoids and phenolics, to relatively nonpolar terpenoids, and even some lipids [39,45]. This versatility far exceeds that of conventional single-component solvents, which generally excel at dissolving either polar or nonpolar compounds but not both. For pollutant remediation, this broad solvation potential enables the simultaneous extraction of chemically diverse contaminants from complex matrices [55]. A few other characteristics are noteworthy and listed below.

Viscosity and rheological behaviour: A common characteristic of most NADES is elevated viscosity, ~2–3 orders of magnitude higher than that of water or conventional organic solvents [44,45]. At room temperature, viscosities typically range from 50 to >10,000 centipoise (cP), compared to 1 cP for water. This high viscosity is a direct consequence of the strong intermolecular hydrogen bonding, which restricts molecular mobility and increases internal friction. While high viscosity can pose challenges for mass transfer and handling, it is highly responsive to external modulation. Addition of water, ~10–30% (v/v), can reduce viscosity by an order of magnitude or more by intercalating NADES components and partially disrupting the hydrogen bond network. Similarly, increasing temperature predictably decreases viscosity, following Arrhenius-type temperature dependence. Addition of water is a key strategy in remediation applications to balance extraction efficiency and process kinetics.

Polarity and hydrophobicity tunability. The polarity of a NADES, typically characterized by solvatochromic dye methods or the dielectric constant, can be systematically tuned over a broad range through careful selection of its components. Choline chloride-based NADES with highly polar HBDs, such as urea or glycerol, exhibit polarities approaching that of water (dielectric constant, $\varepsilon \approx 80$). In contrast, those incorporating less polar polyols or organic acids demonstrate intermediate polarity ($\varepsilon \approx$ 20-40). Hydrophobic NADES formulated with terpenes or long-chain fatty acids can achieve polarities comparable to alcohols or even approaching alkanes ($\varepsilon < 10$) [53,54]. For aqueous remediation *via* liquid-liquid extraction (LLE), hydrophobicity is key, requiring formulations that are immiscible with water to enable efficient phase separation after extraction.

Thermal stability and low volatility. NADES exhibit exceptional thermal stability, with decomposition temperatures typically exceeding 150–200°C and in some cases even higher than 250°C [44,45]. This thermal robustness permits their use in elevated-temperature extraction protocols, such as microwave-assisted or ultrasound-assisted extraction, without risk of degradation. Equally importantly, NADES possess essentially zero vapor pressure at ambient and moderately elevated temperatures due to the strength of their intermolecular interactions [35,38]. The low volatility eliminates the problem of atmospheric emissions, a significant environmental and occupational hazard associated with volatile organic compounds (VOCs). It facilitates complete solvent recovery without evaporation losses.

*Biodegradability and toxicity profile***:** NADES's environmental and safety credentials stem from its natural composition. Components such as choline chloride, sugars, amino acids, and organic acids are primary metabolites integral to biological systems, ensuring their ready biodegradation by microbial communities upon environmental release.

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Toxicological assessments primarily conducted using standard model organisms (*e.g.*, *Vibrio fischeri* bioluminescence inhibition, algae growth inhibition, zebrafish embryo toxicity) consistently demonstrate that NADES composed entirely of natural metabolites exhibit low to negligible toxicity, particularly relative to conventional organic solvents and many ionic liquids [56,57]. However, it is crucial to recognize that biodegradability and toxicity are formulation-specific, and the inclusion of certain components or the use of high concentrations of acidic HBDs can increase toxicity, necessitating case-by-case evaluation.

Green chemistry synthesis methods

The preparation of NADES is intrinsically aligned with the 12 Principles of Green Chemistry, representing a paradigm of sustainable chemical practice [58]. The synthesis process is remarkably straightforward and typically requires no complex purification, organic solvents, or hazardous reagents. The most common preparation method is thermal mixing, also known as the heating-and-stirring method. In this approach, the HBA and HBD components are weighed according to the desired molar ratio, combined in a glass vessel, and heated with continuous magnetic stirring at temperatures typically 50–100°C until a clear, homogeneous liquid forms, usually within 30 minutes to 2 hours. Upon cooling to room temperature, the liquid state persists. This method is consistent with high atom economy, as 100% of the starting materials are incorporated into the final product, with no side reactions or byproducts. Alternative methods include freeze-drying, where components are first dissolved in water, frozen, and subjected to lyophilization to sublime the water and yield pure NADES [35]; vacuum evaporation, which uses resistive-heating evaporation under reduced pressure to remove water from an aqueous solution of the components; microwave-assisted synthesis, which uses dielectric heating to dramatically accelerate NADES formation, often achieving complete homogenization in under 5 minutes with lower energy consumption [45]; and ultrasound-assisted synthesis, where acoustic cavitation promotes rapid mixing and eutectic formation. The green-chemistry aspects of NADES synthesis are quite realistic. The process satisfies the principles of waste prevention, high atom economy (100% conversion), use of non-toxic, natural components, design for energy efficiency (low-temperature, solvent-free), use of renewable biomass-derived components, reduced derivative synthesis, non-flammable, non-volatile chemistry, and design for biodegradable products [38,58]. This comprehensively aligns NADES as a model sustainable solvent system.

NADES vs. conventional solvents, ionic liquids, and environmental concerns

To fully appreciate the green chemistry advantages of NADES, it is necessary to present a comparative analysis with established solvent systems. Conventional organic solvents (*e.g.*, methanol, acetonitrile, dichloromethane, hexane) have been the pillars of industrial chemistry for over a century, valued for their low cost and well-characterized properties. However, these solvents are predominantly petroleum-based, highly volatile, often toxic, and frequently flammable, posing risks of acute poisoning, carcinogenicity, and neurotoxicity, as well as an explosion hazard [59,60]. Their environmental persistence varies, as chlorinated solvents are recalcitrant and bioaccumulative. The use of large volumes of VOCs in industrial processes represents a significant source of hazardous emissions and generates substantial quantities of toxic waste that require energy-intensive incineration for disposal [59].

While Ionic liquids (ILs) share some properties with NADES, significant differences exist. ILs are liquid salts at or near room temperature and generally viewed as potential "green solvents" in the 1990s, primarily due to their negligible vapor pressure and thermal stability [61,62]. The synthesis of ILs typically involves multi-step reactions with alkylating agents (often toxic and carcinogenic, such as with methyl iodide), requires extensive purification to remove halide impurities and unreacted starting materials, and generates substantial chemical waste. High-purity ILs can be prohibitively expensive, often costing more than $500/kg. More importantly, while initially promoted as non-toxic, systematic toxicological investigations have revealed that many common ILs, particularly those with long alkyl chains or certain anions, are highly toxic to aquatic organisms and mammalian cells, and some exhibit poor biodegradability and potential for environmental accumulation [63]. On the contrary, NADES offer significant advantages in this comparative landscape. Their synthesis is more straightforward, cheaper, generates zero waste, and uses safe starting materials. The cost of NADES components is typically 1–2 orders of magnitude lower than ILs, often under $10/kg for bulk materials [38]. The biodegradability and low toxicity of NADES derived from primary metabolites are inherent and predictable, whereas IL properties vary widely and unpredictably with molecular structure [39,56]. While ILs may exhibit superior thermal stability in some applications, the overall sustainability profile of NADES-throughout its life cycle-is clearly a "greener" option than modern designer solvents.

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PFAS, Tire Plastics, and POPs in Aquatic Environments

PFAS: Chemistry and Classification

Per- and polyfluoroalkyl substances constitute a large, structurally diverse family of synthetic organofluorine compounds, numbering between 8K and 14K individual chemicals, that have been manufactured since the 1940s for numerous industrial and consumer applications [64,65]. The unifying structural motif is a carbon backbone to which multiple fluorine atoms are covalently bonded. In perfluoroalkyl compounds, every carbon atom (excluding the terminal functional group) is bonded exclusively to fluorine, while in polyfluoroalkyl compounds, at least one carbon is bonded to hydrogen. This distinction is critical, as polyfluorinated precursors can undergo environmental transformation to yield highly stable perfluoroalkyl end-products. The C-F bond, with a dissociation energy of approximately 485–544 kJ/mol, is one of the strongest single bonds in organic chemistry [66,67]. This exceptional bond strength, combined with fluorine's high electronegativity, creates a dense electron cloud that shields the carbon backbone from nucleophilic, electrophilic, and radical attack, rendering PFAS extraordinarily resistant to thermal, photolytic, chemical, and biological degradation [7,26]. This molecular architecture is attributed to several unique properties, such as exceptional thermal stability, chemical inertness to strong acids and bases, and amphipathic character, where a hydrophobic fluorinated “tail” is paired with a hydrophilic functional “head” group (typically carboxylate or sulfonate), resulting in powerful surfactant properties [64,66]. Classification of PFAS are based on its structural features. Perfluoroalkyl carboxylic acids (PFCAs), such as perfluorooctanoic acid (PFOA, C8) and perfluorononanoic acid (PFNA, C9), contain a carboxylate functional group (-COOH). Perfluoroalkane sulfonic acids (PFSAs), including “forever chemical” perfluorooctanesulfonic acid (PFOS, C8) and perfluorohexanesulfonic acid (PFHxS, C6), possess a sulfonate group (-SO_3H) [21,64]. These perfluoroalkyl acids (PFAAs) form terminal degradation products and are among the most environmentally persistent and bioaccumulative PFAS. Chain length is another critical classification parameter; long-chain PFAS (≥C8 for PFCAs, ≥C6 for PFSAs) generally exhibit greater bioaccumulation potential, while short-chain PFAS (C4-C7 PFCAs, C4-C5 PFSAs) are more mobile in groundwater and more resistant to conventional adsorbent removal [21,68]. Other categories include fluorotelomer alcohols (FTOHs) and perfluoroalkyl ether acids (PFEAs), such as GenX chemicals, which were introduced as “safer” alternatives to PFOA but are now considered persistent and potentially harmful [6,69].

Presence of PFAS in aquatic systems

The routes by which PFAS enter aquatic environments vary on local, regional, and global scales, reflecting the pervasive spreading of these chemicals through modern industrial society. Point sources include direct industrial discharges from PFAS manufacturing facilities, metal plating operations, textile and leather treatment plants, and semiconductor devices foundries [70,71]. The use of aqueous film-forming foams (AFFF) for firefighting, particularly at military airbases, civilian airports, several military installations, such as aircraft carriers and forward operation bases (FOBs, and firefighter training facilities, has resulted in severe localized contamination, with groundwater plumes extending over several kilometres and PFAS concentrations reaching milligram/litre levels in source zones [72,73]. The diffused sources include a wide array of consumer products containing PFAS, such as non-stick cookware coatings, stain-resistant fabrics and carpets, grease-resistant food packaging, waterproof outdoor gear, cosmetics and personal care products, and several pesticide formulations [6,74]. The use, washing, and disposal of these products result in continuous release to municipal wastewater. Conventional wastewater treatment plants (WWTPs) are generally ineffective at removing PFAS; however, some biological and oxidative treatment processes may bio-transform polyfluorinated precursors into more stable PFAAs, resulting in net increases in PFAS concentrations in treated effluent [75,76]. Effluent discharge from WWTPs thus represents a chronic, high-volume pathway for PFAS entry into rivers and coastal waters.

Atmospheric transport is a crucial pathway for the global dissemination of PFAS [71,77,78]. Volatile polyfluorinated precursors, including FTOHs, can split into the gas phase and undergo long-range atmospheric transport. Once airborne, they are subject to photochemical oxidation, transforming into PFCAs, which are then deposited *via* precipitation [77-79]. This atmospheric cycling explains the detection of PFAS in Arctic and Antarctic snow caps, remote alpine lakes, and global rainfall at concentrations often exceeding health-related drinking water values, demonstrating that no location on Earth now remains uncontaminated [9,80]. The consequence is globally pervasive contamination. A recent comprehensive analysis of over 45,000 groundwater samples worldwide revealed that >31% exceeded the EPA’s 2024 MCL of 4 ng/L for individual PFAS, with contamination present on every inhabited continent [11]. Surface water monitoring in Europe shows that PFOS concentrations exceed environmental quality standards in the majority of monitored rivers and lakes [81]. Marine environments are not spared; PFAS have been detected in seawater, sediments, and biota across the Atlantic, Pacific, and Arctic Oceans,

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with concentrations in marine mammals and seabirds exceeding toxicological concern levels [82,83].

Tire wear microplastics

Tire-wear (micro)Plastics, or, when mixed with road debris, known as Tire and Road Wear Particles (TRWPs), represent one of the single most significant sources of pollution globally [12,13]. These particles are generated by unavoidable mechanical friction between vehicle tires during normal driving-accelerating, braking, and cornering-at a rate estimated at 5–10 grams of tire material per vehicle per 100 kilometres driven [13,15]. With over 1.5 billion motor vehicles operating globally, this translates to an estimated annual release of 1.3 to 6.9 million metric tons of TWPs into the environment, with 5–10% ultimately reaching marine systems and potentially 45% of all environmental microplastics originating from tire wear [12,13]. The chemical composition of TWPs is exceptionally complex, reflecting the highly engineered nature of modern tire formulations. Tires contain numerous materials and chemicals, many of which are proprietary, and these matrices consist of natural rubber (polyisoprene from *Hevea brasiliensis*) and synthetic elastomers, predominantly styrene-butadiene rubber (SBR) and polybutadiene, which together comprise 40–60% of tire mass [15,84]. Vulcanization, the process of crosslinking rubber chains to create elasticity and durability, employs sulphur (1–2%) and zinc oxide (1–3%) as catalysts, thereby contributing significant levels of heavy metals [15,85]. Reinforcing fillers, primarily carbon black and amorphous silica, constitute 25–40% of tire mass and provide structural strength and UV resistance [86]. In general, tires contain 200-400 distinct, mostly proprietary chemical additives that serve diverse functions [87]. These include antioxidants and antiozonants to prevent degradation (notably *N*-(1,3-dimethylbutyl)-*N′*-phenyl-*p*-phenylenediamine, or 6-PPD, at 1–2% by weight, DTXSID9025114), plasticizers and processing oils, accelerators, and flame retardants. When a tire is worn, the resulting particles carry this entire chemical cocktail into the environment, where a critical transformation also occurs: 6-PPD reacts rapidly with atmospheric ozone to form 6-PPD-quinone (6-PPDQ), a highly toxic transformation product. This compound has been unequivocally identified as the causative agent of acute mortality in coho salmon (*Oncorhynchus kisutch*) in urban streams of the Pacific Northwest, with LC_{50} values <1 μg/L and effects observable at concentrations routinely measured in stormwater [88].

Limited studies have examined TWPs specifically from landing airstrip surfaces, which are directly relevant to aviation operations, such as research on Tire Wear Airstrip Particles (TWAP) at civilian airports, which analysed particle morphology, size distribution, and composition, noting a wide range of particle sizes and a significant mineral component from pavement and brake wear. While TWPs are a globally recognized source of microplastic and particulate pollution across roads, airports, and urban air, however there is a significant gap in publicly known data on quantitative measurements of TWP concentrations or their chemical characterization in naval environments, such as aircraft carrier flight decks, hangar bays, or forward operating bases (FOBs); necessitating occupational exposure assessments for military deck crews related to TWPs; and risk assessments specific to enclosed hangar bay air quality and particle pathways from aircraft carrier operations.

The physical properties govern the fate and transport of TWPs in aquatic systems. Tire rubber possesses a specific gravity of approximately 1.15–1.18, higher than water, causing particles to sink rather than float [15,86]. The primary transport vector is urban stormwater runoff; during precipitation events, accumulated tire wear is mobilized from road surfaces and channelled directly into receiving waters through storm drains without treatment [78,89]. In flowing systems, particles are subject to advection and dispersion but tend to settle preferentially in low-velocity zones. In lakes and coastal environments, TWPs accumulate in benthic sediments, which act as long-term sinks [90]. Sediment concentrations of TWPs have been measured at levels ranging from hundreds to tens of thousands of mg/kg in urban lake sediments and highway stormwater retention ponds, orders of magnitude higher than those of other microplastic types [89,91]. Extrapolating from available data on an estimated 3 billion tires produced annually may yield ~729 million kg of particulate matter, 570,000 kg of NH^{4+}, and over 2 million kg of suspended solids, requiring approximately 104 billion MJ of energy and over 70 billion litres of water to process the waste [92].

Pollution persistence and bioaccumulation

The “forever chemicals” terminology has gained prominence in public discourse and scientific literature to describe synthetic organic compounds characterized by extreme environmental persistence, essentially permanent on human timescales, and resistance to all known natural degradation processes. Most commonly associated with PFAS, the concept applies to any chemical whose molecular structure exhibits resistance to biodegradation, photolysis, hydrolysis, and thermal decomposition under environmental conditions. No naturally occurring enzymes are known to possess the catalytic capacity to dissociate the C-F bond under ambient conditions [93]. While some advanced oxidation processes (AOPs) under extreme conditions (*e.g.*, incineration above 1000°C with specific catalysts) can achieve defluorination, they are energetically prohibitive for

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environmental-scale applications. Perfluoroalkyl acids, such as PFOA and PFOS, are terminal degradation products and, once formed, undergo no further abiotic or biotic transformation in natural systems [7]. Bioaccumulation and biomagnification processes in aquatic food webs compound the impacts of persistence [94,95]. Bioaccumulation refers to the uptake and retention of a chemical by an organism from both water and diet at rates that exceed excretion and metabolism, resulting in elevated tissue concentrations [96]. For PFAS, this process is particularly pronounced for long-chain compounds. Unlike most persistent organic pollutants, which accumulate in lipid tissues, PFAS bind preferentially to proteins in blood, liver, and kidney due to their amphipathic character, resulting in unique bioaccumulation patterns [94,97]. Biomagnification refers to the increase in contaminant concentration with each successive trophic level in a food chain [98]. Primary producers (phytoplankton) absorb dissolved PFAS from water; herbivorous zooplankton that consume contaminated phytoplankton accumulate higher concentrations; planktivorous fish accumulate still higher concentrations from their diet; and apex predators (piscivorous fish, marine mammals, seabirds) exhibit the highest body burdens, sometimes 10,000X greater than ambient water concentrations [83,95]. Biomagnification factors (BMFs) exceeding 1.0, indicating increasing concentration with trophic levels, have been documented for PFOS in marine food webs, with BMFs ranging from 2 to 10 between successive trophic levels [95,99]. This trophic amplification presents severe risks to top predators, including impacts on wildlife populations and human health through seafood consumption.

Toxicological impacts on aquatic ecosystems and human health

The ecotoxicological consequences of PFAS and tire-derived plastics (TWP, TWOP) on aquatic organisms are extensive, operating through multiple mechanisms of toxicity across diverse taxa. For PFAS, chronic exposure to environmentally relevant concentrations (ranging from low µg/L to ng/L) induces a cascade of adverse biological effects. Studies on fish species have demonstrated hepatotoxicity, with altered liver enzymes and lipid metabolism; reproductive impairment, including reduced fecundity and delayed sexual maturation; developmental abnormalities in embryos and larvae; and neurotoxicity, with anomalous swimming behaviour and neurotransmitter levels [100,101]. Invertebrates, including commercially important species such as mussels and oysters, exhibit oxidative stress responses, DNA damage (genotoxicity), immune suppression, and reduced growth rates in response to PFAS exposure [102,103]. Mechanistically, PFAS exerts toxicity through multiple pathways. Being endocrine-disrupting chemicals (EDCs), PFAS interfere with steroid hormone synthesis and signalling, disrupting thyroid function, estrogen and androgen pathways, and corticosteroid regulation [100,104]. Activation of peroxisome proliferator-activated receptors (PPARs) modifies lipid metabolism and energy homeostasis [105]. PFAS also induces mitochondrial dysfunction and oxidative stress, generating reactive oxygen species that damage cellular macromolecules [106]. These individual-level effects translate into reduced reproductive success, altered community structure, and potentially the decline of populations in sensitive species [100]. For TWPs and TWOPs, toxicity manifests through dual mechanisms, such as physical effects from particle ingestion and chemical toxicity from leached additives. While physical impacts, such as gut blockage, reduced feeding, and internal abrasion, are observable, mounting evidence indicates that chemical leaching is the primary driver of toxicity [78]. The transformation product 6-PPD-quinone is acutely toxic to coho salmon at concentrations below 1 µg/L, causing pre-spawn mortality through cardiovascular collapse [14,88]. Sub-lethal effects in diverse fish species include developmental abnormalities, neurobehavioral changes, and reproductive impairment [22,87]. Leachates from TWPs and TWOPs induce oxidative stress, DNA damage, and altered gene expression in zebrafish and other model organisms [15,107]. Human health risks from PFAS exposure are well-documented through extensive epidemiological and toxicological research. The U.S. Agency for Toxic Substances and Disease Registry (ATSDR) and EPA have established that PFAS exposure is associated with multiple adverse health outcomes. These include increased risk of kidney and testicular cancers, thyroid disease and disrupted thyroid hormone levels, elevated serum cholesterol and increased cardiovascular disease risk, pregnancy-induced hypertension and preeclampsia, reduced antibody response to vaccination in children, decreased fertility and reproductive disorders, liver damage with elevated liver enzymes, and developmental effects including low birth weight and delayed developmental milestones [18–20,23]. The biological half-lives of PFOA and PFOS in humans are approximately 2–4 years and 5–8 years, respectively, enabling chronic accumulation from low-level exposures. Biomonitoring data reveal that PFAS are detectable in the blood serum of >98% of the U.S. population, underscoring the universal nature of exposure [108]. Table S1 (supplementary Table 1) lists the sources, concentrations, and toxicity thresholds for PFAS, TWP, and TWOP, as provided by various sources.

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NADES-based remediation: mechanisms and methods

Molecular mechanisms of contaminant extraction using NADES

The efficacy of NADES in removing persistent contaminants from aqueous systems stems from their molecular-level interactions with target pollutants. The primary remediation mechanism is liquid-liquid extraction (LLE), in which a water-immiscible NADES phase is brought into contact with contaminated water, and contaminants are extracted from the aqueous phase into the NADES phase, driven by thermodynamically favourable interactions [54,109]. This extraction is governed by the principle that solvation preferentially dissolves in phases where they experience the strongest solvation forces. At the molecular level, the extraction mechanism is dominated by hydrogen-bonding interactions between the functional groups of NADES components and those of contaminant molecules. For PFAS compounds, which possess either carboxylate (-COO^-) or sulfonate (-SO_3^-) functional head groups, the acidic protons in organic acid HBDs (*e.g.*, lauric acid, decanoic acid) can form strong hydrogen bonds with these anionic centres. Simultaneously, the HBA component (*e.g.*, trioctylphosphine oxide - TOPO) provides additional interaction sites through its phosphoryl oxygen (P=O), which can engage in hydrogen bonding with any remaining protic sites on the PFAS molecule. The cumulative strength of these multiple interaction points creates a high affinity of PFAS for the NADES phase. Beyond hydrogen bonding, hydrophobic interactions between the long fluorocarbon chain of PFAS and the nonpolar regions of hydrophobic NADES components provide additional driving force for extraction. The van der Waals forces, albeit individually weaker than hydrogen bonds, are strong along the PFAS chain and significantly contribute to overall solvation. For longer-chain PFAS, this hydrophobic contribution is crucially important. The outcome is a synergistic combination of polar and nonpolar interactions that enables NADES to effectively "recognize" and "sequester" PFAS molecules from water.

Computational chemistry has been instrumental in explaining these mechanisms at the atomic level. Density Functional Theory (DFT) calculations quantify the interaction energies between NADES components and PFAS molecules, revealing binding energies typically around –30 to –80 kJ/mol for hydrogen-bonded complexes, which are much stronger than the –20 to –30 kJ/mol characteristically involved in PFAS hydration [52,53]. The Conductor-like Screening Model for Real Solvents (COSMO-RS) predicts partition and activity coefficients, thereby enabling in silico screening of large libraries of potential NADES formulations prior to experimental validation [110]. Additionally, molecular dynamics (MD) simulations provide dynamic insights into how NADES molecules surround and disrupt the hydration shell of PFAS, effectively "extracting" PFAS from the aqueous phase. Visualization of MD trajectories reveals that PFAS molecules become embedded within the 3D hydrogen-bonded network of the NADES, with multiple simultaneous interactions preventing their return to the aqueous phase. A schematic of the extraction process for PFAS and other contaminants, including TWP, HMs, and MNPs, is shown in Figure 3.

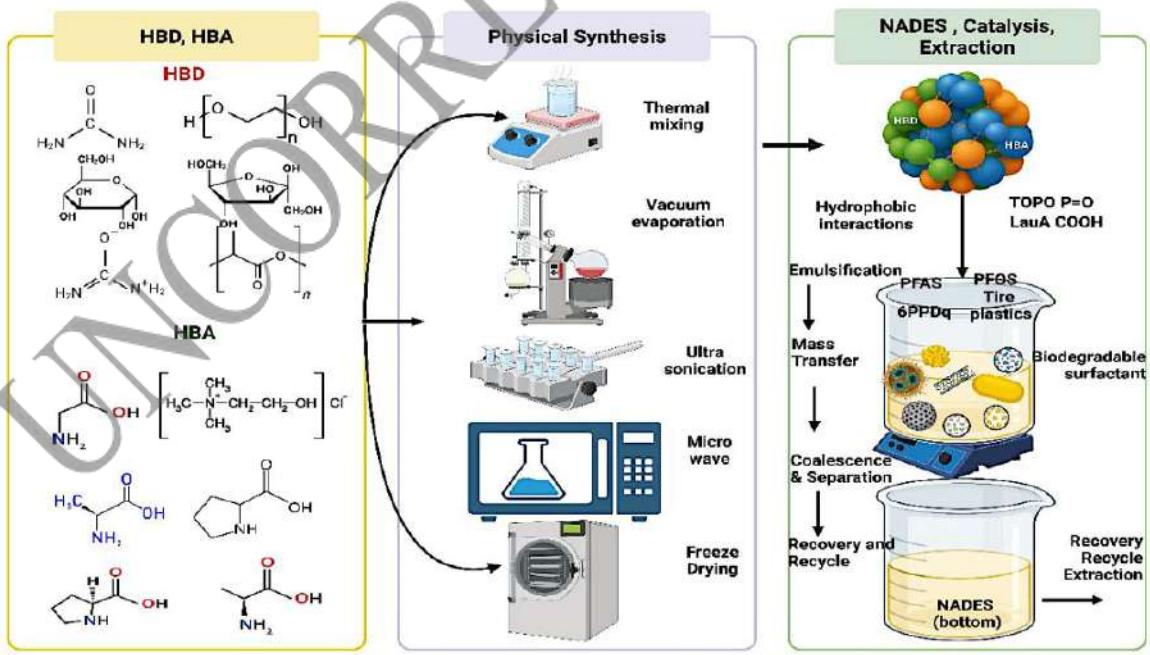


Figure 3. Extraction process for PFAS and other contaminants, using NADES (produced using BioRender).

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For the removal of MNPs, the mechanisms differ in scale but fundamentally operate on similar principles. NADES molecules adsorb onto the surface of plastic particles by forming non-covalent associations with the polymer chains through hydrogen bonding to any polar functional groups, dipole-dipole interactions, and van der Waals forces [111,112]. This surface coating aggregates particles, altering their wettability and effectively making them more "compatible" with the NADES phase, thereby facilitating their separation from water. MD simulations correlate extraction efficiency with the calculated binding energy between NADES molecules and polymer surfaces, thereby providing predictive capability for design and formulation optimization.

PFAS removal efficiency and selectivity

Remediation of PFAS using DES has been validated by several experimental studies that demonstrate exceptional removal efficiency, operational robustness, and high selectivity. The most comprehensive and systematically designed investigation reported the development of a hydrophobic DES composed of TOPO and lauric acid (1:1 molar ratio) for extracting PFOA from water [52]. This study employed a multi-criteria decision analysis (MCDA) framework integrating computational screening (COSMO-RS), physicochemical property measurements, environmental impact assessment, and experimental validation [110]. In terms of performance metrics, the TOPO:LauA system achieved a single-stage extraction efficiency of 99.74% for PFOA from deionized water at an initial concentration of 1.0 mg/L, with a solvent-to-water volume ratio of 1:10 [52]. By comparison, toluene, the conventional benchmark solvent, achieved only ~82% under identical conditions. The extraction equilibrium was reached within 1 minute, indicating rapid mass transfer despite the solvent's viscosity. This demonstrates the system's robustness across variable environmental conditions. Extraction efficiency remained >98% over a pH range of 3 to 9, within a temperature range of 15 to 100°C, and PFOA concentrations spanning four orders of magnitude from 0.1 mg/L to 1000 mg/L. This pH independence is particularly significant, as many conventional methods are highly pH-sensitive. Selectivity was evaluated using synthetic municipal wastewater containing a complex mixture of organic and inorganic constituents. The TOPO:LauA DES maintained extraction efficiency >95% for PFOA in this complex matrix, demonstrating minimal interference from competing species. When tested with a mixture of six PFAS compounds (PFOA, PFOS, PFHxA, PFBA, PFHxS, PFBS), the system extracted all target analytes with efficiencies ranging from 91% to 99%, indicating broad-spectrum capability.

Spectroscopic analysis (^{1}H NMR, FTIR) confirmed that the DES components remained chemically stable throughout the extraction process, with no detectable degradation products [52]. A complementary study investigated a menthol: acetic acid (1:1) hydrophobic NADES for the extraction of perfluoroheptanoic acid (PFHpA), a short-chain PFAS [53]. This system achieved extraction efficiencies ranging from 80.2% to 90.7% depending on process conditions. The extraction was insensitive to initial PFHpA concentration (tested from 0.23 to 350 mg/L) and water pH (tested from 2 to 11). Using our DEEP-CLEAN project, a predictive database correlating key molecular descriptor-Kamlet-Taft parameters (α, β, π^*), polarity index, viscosity, and dielectric constant-with PFAS and TWOP affinity was developed. However, this investigation also revealed a critical challenge: post-extraction analysis showed significant leaching of acetic acid from the NADES into the treated water, reducing the pH to about 2.2. While this did not compromise PFAS removal efficiency, it represents a secondary contamination that must be addressed either by reformulating the solvent with more hydrophobic HBDs that are less water-soluble or by implementing post-treatment neutralization steps.

Broader computational methods have identified additional promising DES formulations. TOPO-based systems with various carboxylic acids consistently exhibit high affinity for PFAS. Terpene-based DESs (camphor, thymol, cineole combined with fatty acids) show strong performance, as predicted, for both long-chain (PFOA, PFOS) and short-chain PFAS. L-arginine-based DESs have been computationally predicted to exhibit selectivity for short-chain PFAS, potentially addressing a key weakness of conventional adsorbents. Using MD simulation, a novel DES composed of cineole and linoleic acid (1:1) demonstrated strong affinity for both PFOA and PFOS, with binding energies indicating thermodynamically favourable extraction.

Microplastics removal: mechanisms and efficiency

The application of NADES for MNPs remediation represents a conceptually and mechanistically somewhat similar yet different approach, targeting plastic particles rather than dissolved molecules. Laboratory studies have demonstrated that specific NADES formulations can effectively capture and remove MNPs from water through what researchers have termed an "eco-friendly magnetic" effect [113,114]. This representation describes the chemical-affinity-driven aggregation and phase-separation process. Experimental studies utilized NADES derived from natural and coconut-based materials to extract common plastics, including PET, PS, and PLA, from aqueous suspensions. Removal efficiency ranged from 50% to 93%, depending on the specific NADES formulation, plastic type, particle size, and process

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conditions [114]. Higher efficiencies were generally observed for larger particles (5–100 μm) than nanoplastics (<1 μm), and for plastics with more polar functional groups compared to purely hydrocarbon polymers such as polyethylene.

Molecular dynamics simulations validate experimental observations by calculating binding energies between NADES components and plastic polymer surfaces. In a study, a strong positive correlation was established between calculated binding energy and experimentally measured extraction efficiency, confirming that the process is driven by thermodynamically favourable NADES-plastic interactions rather than simple physical capture. The simulations further showed that NADES molecules form ordered layers on plastic surfaces, with HBD groups oriented toward any polar sites on the polymer and hydrophobic regions engaging in van der Waals interactions with the polymer backbone. The advantages of NADES-based MNP removal are particularly interesting, as conventional filtration and centrifugation become ineffective due to the size limitations of filter membranes and the long settling times required for low-density, small particles. NADES offer a chemical rather than purely physical approach and can target particles as small as 0.1 μm. Additionally, because the process does not rely on filtration, it avoids membrane fouling issues that plague conventional technologies. The complete biodegradability of NADES components ensures that the remediation process does not introduce new persistent synthetic pollutants, given that many emerging technologies for microplastic removal carry their own environmental risks.

Process parameters and optimization

The efficiency of NADES-based extraction is influenced by several operational parameters that are optimized for performance and economic viability. Among other factors, the solvent-to-water volume ratio is a primary determinant of contaminant removal and process cost. Higher ratios improve extraction efficiency; however, they increase solvent consumption and, hence, the cost. The TOPO:LauA system has achieved >95% PFOA removal at a 1:10 DES:water ratio, representing an excellent balance. Lower ratios (1:20, 1:50) slightly reduce efficiency but may be economically favourable for large-scale applications, particularly when coupled with multi-stage extraction. Contact time and mixing intensity govern mass transfer kinetics. The rapid equilibrium (~1 min) observed for TOPO:LauA suggests minimal mass-transfer resistance, likely due to the strong thermodynamic driving force. However, higher viscous NADES formulations may require longer contact times or enhanced mixing *via* ultrasonication or vortexing to achieve equivalent performance. Temperature influences both NADES viscosity and partition coefficients. The broad temperature robustness (15–100°C) of PFAS extraction indicates that ambient-temperature operation is viable, thus minimizing energy consumption. Water pH is generally not a critical parameter for properly formulated hydrophobic NADES, as demonstrated by the pH-independence of TOPO:LauA over pH 3–9. However, pH can influence the protonation state of ionizable PFAS, potentially affecting their hydrophobicity and extractability. For basic or neutral PFAS precursors, acidic conditions may enhance extraction by protonation. Water composition, including salinity, natural organic matter (NOM) content, and competing ions, can influence extraction efficiency. High salinity may enhance PFAS extraction through salting-out effects, reducing their aqueous solubility [53]. NOM can compete for interaction sites on NADES or form complexes with PFAS, potentially reducing extraction; however, the selectivity shown in synthetic wastewater suggests this effect is quite manageable.

NADES *vs.* conventional technologies

Activated carbon adsorption: capabilities and constraints

Granular activated carbon (GAC) and powdered activated carbon (PAC) are two of the most widely used techniques for PFAS removal from drinking water and wastewater [26,28]. Activated carbon operates *via* physisorption, in which contaminants adsorb onto the extensive internal pore network of the carbon matrix through van der Waals, hydrophobic, and/or electrostatic interactions. For long-chain PFAS, GAC can achieve ~90–99% removal under optimal conditions, *e.g.*, low initial concentrations, absence of competing organics, and long empty bed contact times (EBCT). However, activated carbon faces significant limitations. Short-chain PFAS are increasingly prevalent and poorly adsorbable, with removal efficiencies often <50% [28,29]. The shorter hydrophobic tail reduces affinity for the carbon surface. Competitive adsorption from NOM is a critical problem in real-world applications. NOM can occupy adsorption sites, reduce capacity, and accelerate innovation by shortening GAC service life by 50–70% compared to clean water [115]. High NOM waters may require pre-treatment or more frequent carbon replacement, substantially increasing costs. Regeneration and disposal pose significant challenges. Spent GAC contains concentrated PFAS and must be managed as hazardous waste. Thermal regeneration, *i.e.*, heating to 800–900°C in a controlled atmosphere to volatilize and combust adsorbed organics, is energy-intensive, expensive, and often ineffective for PFAS due to their thermal stability. Incineration at >1000°C with alkaline additives is required for PFAS destruction, but is not universally available and generates its own emissions concerns. Consequently, spent carbon is often landfilled, creating long-term environmental liability

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and failing to achieve actual remediation. Finally, from an economic viewpoint, GAC capital costs are moderate ($5-15 per kg for standard media), but operational costs accumulate rapidly due to short service life (3-12 months typical for PFAS-contaminated water) and disposal fees ($1-5 per kg for hazardous waste incineration). For a small municipal system (1 MGD capacity), annual GAC costs can range from $100K to $500K, depending on contamination levels. By contrast, NADES-based extraction offers several advantages, such as higher efficiency for short-chain PFAS due to specific chemical interactions rather than nonspecific adsorption, minimal impact from NOM due to high selectivity, complete regenerability through separation and recycling, and potential for pollutant recovery or concentration for subsequent treatment, creating a pathway for closed-loop remediation.

Membrane filtration

Nanofiltration (NF) and reverse osmosis (RO) achieve PFAS removal through size exclusion and electrostatic repulsion, with removal efficiencies typically exceeding 90–99% for most PFAS compounds [27,30]. These systems are highly effective across the full spectrum of PFAS chain lengths, including short-chain compounds that evade GAC, making them the "gold standard" for drinking water treatment when high removal is critical [30]. However, membrane technologies are largely constrained by high energy consumption. Operating pressures for NF range from 5–20 bar, and for RO from 15–80 bar, requiring substantial pumping energy, typically 0.5–2.0 kWh/m³ for NF and 2–5 kWh/m³ for RO. For a 10 MGD (38,000 m³/d) facility, this translates to annual energy costs of $50K–$200K at the prevailing electricity rate. Membrane fouling from suspended solids, colloidal matter, biological growth, and scaling from dissolved minerals seriously degrades performance, requiring extensive pre-treatment and frequent cleaning with harsh chemicals, thereby shortening membrane lifespan (~5–7 years) and adding operational complexity. The most problematic aspect is brine waste management. RO systems typically operate at 75–85% recovery, meaning 15–25% of the feed water becomes a concentrated brine reject stream containing all removed contaminants at 4–7 times the feed concentration. For PFAS-contaminated water, this creates highly problematic waste, since it is too contaminated for discharge in surface water or sewers and yet lacks inexpensive treatment options. Current practices include deep-well injections, evaporation ponds, or expensive advanced treatment, none of which is universally applicable or sustainable. NADES-based LLE basically avoids the brine problem. The extracted contaminants are concentrated in the recyclable NADES phase rather than in a dilute brine, and the treated water is discharged directly without generating a secondary waste stream that requires further management. Energy consumption is limited to mixing and pumping, potentially orders of magnitude lower than high-pressure membranes. While membranes excel at treating large volumes to very high purity, NADES may be more economically attractive for moderate-volume, high-concentration applications.

Advanced oxidation processes

Advanced oxidation processes include electrochemical oxidation, sonolysis, photocatalytic oxidation, and sulphate radical-based systems, to achieve complete mineralization, *i.e*., the breakdown of PFAS into fluoride ions, CO_2, and water, by generating highly reactive species capable of C-F bond cleavage [31,32,116,117]. Electrochemical oxidation using boron-doped diamond (BDD) anodes has demonstrated the most promising results, achieving >90% defluorination of PFOA and PFOS under optimized conditions [118,119]. However, AOPs face several challenges, which include large energy requirements, often exceeding 100–1000 kWh/m³ for appreciable degradation of PFAS at environmental concentrations, making treatment of drinking water or large wastewater volumes cost-prohibitive. Reaction kinetics are generally slow, with degradation half-lives ranging from hours to days, requiring impractical residence times for flow-through applications. Incomplete mineralization can yield shorter-chain PFAS or other fluorinated byproducts, some of which may be more mobile or toxic than parent compounds, requiring extensive monitoring to verify treatment efficacy. Matrix effects are severe, such as the presence of chloride, carbonate, and NOM, which consume oxidants, thereby reducing efficiency and increasing costs significantly [32]. Consequently, AOPs may be viable only for concentrated waste streams or for specific niche applications rather than for bulk water treatment.

Thermal treatments (incineration at >1000°C with alkaline additives) achieve complete PFAS destruction but apply only to solid/sludge matrices, not to dilute aqueous solutions [26]. Supercritical water oxidation at temperatures >374°C and pressures >221 bar can mineralize PFAS, but requires extreme conditions and specialized equipment, limiting practical deployment [31]. The strategic role of NADES in this technology space is as a concentration and separation technology, leveraging its high extraction efficiency and regenerability to produce a small volume of concentrated PFAS solution that can then be subjected to destructive treatment with economically feasible energy inputs. This "extract, concentrate, and destroy" paradigm represents a more holistic and economically rational approach than directly attempting to destroy diluted, contaminated water. Table 2 below provides a comparative overview of mitigation technologies and their technology readiness levels (TRLs).

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Table 2

Comparative overview of mitigation technologies and their TRLs.

Technology	*Removal Efficiency (% for PFOA/ PFOS)*	*Removal Efficiency (% for TWPs)*	*Energy Consumption (kWh/m³)*	*Capital Cost ($/m³/day capacity)*	*Operational Cost ($/m³ treated)*	*Waste Stream Generated*	*Regeneration Feasibility*	*Technology Readiness Level (TRL)*
GAC	85-99	30-70 (mainly small MPs / additives)	0.05–0.2	Medium	Low-Medium	Spent GAC (solid; PFAS and possibly sorbed microplastics/additives)	Yes - thermal/ chemical; PFAS destruction challenging; MNPs mostly destroyed during high-temperature regeneration	7-9
Ion Exchange (IX)	90-99+	<10 (limited; MPs too large for resin pores)	0.05–0.3	Medium-High	Medium	Spent resin + regenerant brine with concentrated PFAS (liquid + solid)	Yes - resin regenerable; PFAS-rich brine requires further treatment; not suitable as primary MNP control	6-8
RO/NF	95-99+	90-99+ (microplastics retained by membranes)	0.5–2.5	High	High	Concentrated brine containing PFAS, dissolved organics, and retained MNPs.	Membrane cleaning is possible; brine and cleaning waste still contain PFAS and MNPs	6-8
AOP (electrochemical)	60-95	10-40 (partial oxidation/fragmentation)	1–5+	Medium-High	Medium-High	Degradation byproducts include short-chain PFAS, organics, electrode sludge, and fragment MPs	Electrodes are reusable; no regeneration of sorbent; PFAS and polymer by-products may require post-treatment	4-6
NADES-LLE	80-99	30-70 (can extract additives / smaller particles)	0.2–1.0	Medium (lab/pilot scale)	Medium	PFAS- and organic-rich NADES phase; may contain fine MNPs or dissolved TWOPs.	Potentially yes - NADES can be regenerated by back-extraction or distillation; routes still being optimized	3-5
Solid-supported NADES	85-99	40-80 (sorption/entrapment of small MPs & additives)	0.1–0.5	Medium-High (novel materials)	Medium	Spent solid (support + NADES-PFAS-MNPs complex)	Conceptually regenerable *via* solvent washing or thermal treatment; protocols under development	2-4

Notes: TWP, TWOP, ~1-500 μm, Capital and Operational Costs are relative categories (Low/Medium/High); actual values vary by region, scale, and level of integration.
TRL: 1-3 (lab/early concept), 4-6 (pilot/demo), 7-9 (full-scale/commercial).
RO/NF: high removal for both PFAS and TWP; GAC and IX (Ion Exchange) are excellent for PFAS but weak as sole MNP controls.

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Challenges of NADES-based remediation

Viscosity, mass transfer, and phase separation

Despite their considerable benefits, NADES face fundamental technical challenges that must be addressed to allow commercial-scale development. The most prevalent issue is high viscosity, typically 50–10,000 cP at room temperature, compared to <5 cP for conventional solvents and 1 cP for water. High viscosity impedes mass transfer by creating friction during laminar flow, slowing the transport of contaminants from the bulk aqueous phase to the NADES interface and into the NADES bulk. This results in longer equilibration times, reduced extraction kinetics, and potentially incomplete contaminant removal under fixed-contact-time conditions. Viscosity also creates engineering challenges for practical operations. Pumping viscous fluids requires higher energy inputs and specialized pump designs, such as gear and progressive cavity pumps, which increase capital and operational costs [96]. Mixing viscous NADES with water to achieve close contact for extraction may require mechanical agitation, sonication, or other energy-intensive methods, rather than simple stirring. Heat exchangers and flow-through contactors have experienced decreased performance due to inadequate heat and mass transfer in viscous media [36].

Mitigation strategies include water addition, but this must be carefully controlled to avoid excessive dilution that disrupts the eutectic structure and reduces extraction efficiency [120]. Elevated temperature (40–60°C) reduces viscosity substantially by increasing molecular mobility, but it also incurs energy costs [36]. The most sustainable solution is logical solvent design, *i.e.*, by selecting HBA-HBD combinations that inherently yield lower viscosity while maintaining high extraction efficiency. This is an active area of research leveraging computational screening to predict viscosity from molecular structure. Phase separation following extraction can be straightforward for NADES with a significantly large density differential from water (*e.g.*, ρ=1.2–1.4 g/cm³), where gravitational settling achieves clean separation within minutes [52,54]. However, for formulations with densities close to water, separation may require centrifugation, coalescence, or membrane-based phase separation, adding more complexity and cost. Solvent leaching or component partitioning into the treated-water phase, as observed in the menthol:acetic acid system, represents a critical failure mode. It constitutes secondary contamination, potentially compromising water quality and leading to a progressive loss of solvent. This issue is addressed by designing NADES with hydrophobic components, such as long-chain fatty acids, terpenes, and TOPO, that exhibit minimal water solubility. A thorough post-extraction water-quality analysis is vital to verify the absence of leaching before any NADES formulation is considered suitable for real-world application.

Laboratory to commercial transition

The impressive performance metrics reported in laboratory studies, while scientifically convincing, do not inevitably translate to commercial viability. Scalability challenges typically encompass reproducibility, process engineering, and economic competitiveness at the production scale. Batch-to-batch variability in NADES preparation can arise from variations in raw material purity, incomplete mixing in large reactors, or imperfect temperature control during synthesis. Establishing quality-control protocols, standardized synthesis procedures, and supply-chain management for large-scale NADES production is critical. Process intensification is required to translate batch laboratory extractions (now at ~10–100 mL scale) for continuous industrial operations (flow rates of 1000–10,000 m³/day). Continuous counter-current LLE using mixer-settler units or packed/tray columns is common in chemical engineering but must be adapted to the unique properties of NADES. The high viscosity and potential for emulsion formation complicate the design of traditional contactors. Solid-supported NADES immobilized on porous supports offer a promising alternative, enabling packed-bed or fixed-bed reactor configurations that simplify operation and eliminate the need for phase separation [121]. However, mechanical stability, capacity, and regeneration of solid-supported systems require further development. Capital costs for NADES-based systems at industrial scale remain uncertain due to a lack of pilot-scale demonstrations and economic analyses. While raw material costs are low, the requirements for specialized mixing equipment, temperature-control systems, and regeneration infrastructure increase total capital investment. Operational costs depend critically on regeneration efficiency and cycle life. If NADES can be recycled for 50–100 extraction cycles with minimal degradation-as suggested by limited laboratory studies-operational costs will be dominated by energy for mixing/pumping, and periodic solvent makeup, likely making it competitive with GAC. If cycle life is limited to <10 cycles, costs escalate rapidly. Additionally, regulatory approval and technology acceptance by water utilities and environmental regulators constitute a critical, non-technical scalability barrier. NADES are novel materials with limited operational track records. Demonstrating long-term reliability, safety, and compliance with drinking water standards will require extensive pilot testing, third-party validation, and development of regulatory frameworks for DES-based water treatment.

Economic viability and life cycle assessment

The ultimate determinant of technology adoption is economic competitiveness compared to

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incumbent technologies. Preliminary economic assessments of this technology suggest favourable cost comparisons under certain conditions, but comprehensive comparisons are lacking. Raw material costs for NADES components are generally low, e.g., choline chloride (~$2–5/kg bulk), glycerol (~$1–3/kg), sugars (~$1–2/kg), organic acids (~$2–10/kg depending on purity), terpenes (~$10–50/kg), and fatty acids (~$2–15/kg) [38,44]. By contrast, high-purity ionic liquids can cost $100–$1,000/kg. For a formulation like TOPO:LauA, material cost is estimated at ~$15-25/kg, with TOPO being the primary cost driver. Solvent inventory costs for a 1 MGD (3785 m^3/d) treatment facility operating with a 1:10 DES:water ratio would require ~400 m^3 (~500,000 kg at ρ~1.2 g/cm^3) of NADES in circulation, representing an initial capital investment of ~$7.5–12.5 million in solvent alone. However, if this solvent is used for 50 cycles, the per-volume cost is estimated at $0.02-0.03/$m^3$ of water treated, which is highly competitive with GAC ($0.05–0.15/$m^3$) and membrane systems ($0.10–0.30/m^3) [26,30]. This calculation underscores the critical importance of demonstrating high-fidelity regeneration and extended solvent lifespan. Life cycle assessment (LCA) provides a holistic evaluation of environmental impacts beyond simple economic metrics, accounting for energy consumption, raw material extraction impacts, manufacturing emissions, operational-phase emissions, and end-of-life disposal across various impact categories (climate change potential, eutrophication, ecotoxicity, *etc*.) [122]. Limited LCAs on DES-based biomass processing suggest a lower environmental impact than conventional organic solvent systems, primarily due to renewable feedstock sourcing and the elimination of VOC emissions. However, LCAs specific to NADES-based water treatment are largely absent from the literature. A comprehensive LCA must account for upstream impacts of component production, energy consumption during synthesis, extraction, and regeneration, infrastructure requirements, and downstream impacts of solvent disposal at end-of-life, including biodegradation products and potential for any lingering toxicity [123]. It is critical to have such an analysis for NADES to be considered green; otherwise, the analysis remains primarily qualitative.

Regulatory and policy considerations

The regulatory environment for PFAS and emerging contaminants is evolving rapidly, creating both drivers and constraints for new remediation technologies. The U.S. EPA's 2024 Final PFAS National Primary Drinking Water (NPDW) Regulation establishes MCL of 4.0 ng/L (ppt) for PFOA and PFOS individually, 10 ng/L for PFHxS, PFNA, and HFPO-DA (GenX), and a Hazard Index (HI) for mixtures [23]. Public water systems must comply by 2029, a requirement that will require significant investments in treatment infrastructure, estimated at $1.5 billion annually nationwide. This regulatory mandate creates immediate market demand for effective, economically viable PFAS removal technologies. Concurrently, EPA has proposed designating PFOA and PFOS as hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund, enabling enforcement actions at contaminated sites and establishing liability for responsible parties [124]. The EU's Registration, Evaluation, Authorization and Restriction of Chemicals restriction proposal would ban the manufacture and use of all PFAS as a class by 2030, with limited exemptions, fundamentally reshaping the regulatory landscape [24]. Internationally, the Stockholm Convention's listing of PFOS, PFOA, and PFHxS as POPs mandates global phase-out, though implementation timelines vary by jurisdiction [25]. For NADES-based remediation to gain regulatory acceptance, several requirements must be met, such as, (a): Demonstrated efficacy through EPA-validated methods and third-party testing to verify achievement of MCL compliance; (b) Safety verification ensuring that NADES components and any degradation products do not introduce new contaminants exceeding drinking water standards; (c) Process reliability with proven performance across variable water quality conditions and long-term operational stability; and (d) Waste management protocols for regeneration residuals and spent solvent. Currently, no NADES-based water treatment systems have received regulatory approval or NSF/ANSI certification for drinking water applications, indicating a series of critical tasks that require significant investment over many years.

Regeneration, reusability, and circular economy integration

Regeneration technologies

The economic and environmental sustainability of NADES-based remediation centres on the ability to regenerate and reuse the solvent over several cycles. Regeneration involves separating the extracted contaminants from the NADES matrix and restoring its extraction capacity. Multiple regeneration strategies have been investigated, each with distinct advantages, limitations, and applicability depending on contaminant type and NADES composition. Membrane-based separation represents the most thoroughly developed and promising approach. A hybrid technique combining ultrafiltration (UF) followed by bipolar membrane electrodialysis (BMED) achieved NADES recovery ratios of 97.7% in biomass pretreatment applications [125]. In this two-stage process, UF (molecular weight cut-off 1–10 kDa) first removes any high-molecular-weight impurities or co-extracted macromolecules. Subsequently, BMED, which

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employs ion-exchange membranes and a specialized bipolar membrane that electrolyzes water to generate H^+ and OH^- ions, enables the separation of the ionic or ionizable NADES components from neutral contaminants based on charge and size [126]. Under an applied electric field, cations migrate through the cation-exchange membrane and anions through the anion-exchange membrane, effectively compartmentalizing NADES components in one compartment and contaminants in the other, and is well-suited for NADES and charged contaminants. Another regeneration technique, known as anti-solvent precipitation, exploits differential solubility. Adding a miscible antisolvent to the loaded NADES-contaminant mixture can selectively precipitate contaminants while keeping NADES components in solution, or vice versa. Subsequent filtration or centrifugation separates the precipitated phase. This method is simple and requires minimal equipment, but may not achieve complete separation, particularly if contaminants and NADES matrix have similar solubility profiles. Recovery yields of ~85–95% have been reported [38]. Yet another technique, called Distillation (or vacuum evaporation), can regenerate NADES when contaminants have boiling points that are significantly different from those of NADES components. For VOCs, heating the loaded NADES under vacuum can selectively evaporate contaminants, leaving behind purified NADES. However, PFAS and other persistent pollutants are non-volatile, making this approach inapplicable to such targets. Conversely, some HBD components can be distilled off, leaving contaminants in the HBA and thereby disrupting NADES structure and reorganization. Solid-phase extraction (SPE) or adsorption can be employed post-extraction to sequester contaminants from the NADES. Passing the loaded NADES through an adsorbent column can selectively capture contaminants while allowing NADES to flow through [45]. The adsorbent is then discarded or regenerated separately. This approach adds a unit operation but may be economically favourable for high-value or difficult-to-separate contaminants. Chemical or oxidative destruction in situ within the NADES phase is an emerging concept. Since PFAS are resistant to chemical attack, AOP could potentially mineralize PFAS while leaving NADES matrix intact, given their greater reactivity or rapid biodegradability of degradation products. However, this has yet to be verified experimentally. While a more detailed discussion is outside the scope of this article, Table 3 provides an overview of regeneration methods, their advantages and disadvantages, and their applicability.

Reusability cycle life

Demonstrating that NADES exhibit high extraction efficiency across multiple regeneration cycles is critical for validating their circular-economy potential. The TOPO:LauA system for PFOA removal underwent seven consecutive extraction-regeneration cycles using a simple back-extraction procedure. After each extraction cycle, the loaded DES was treated with a small volume of an organic solvent, such as methanol, to extract PFOA, followed by evaporation of the methanol to regenerate the pure DES. Extraction efficiency remained >98% across all seven cycles, with no statistically significant degradation [52].

^{1}H NMR and FTIR spectroscopy confirmed that the chemical structure of the DES components remained unchanged, demonstrating molecular-level stability. In biomass fractionation applications, a choline chloride:lactic acid NADES was successfully reused for 5 cycles, with recovery rates of 95-98%/cycle using the UF-BMED method, and the extraction performance, called delignification efficiency, remained essentially constant [126]. Another study on phenolic compound extraction from olive pomace using a betaine:glycerol NADES achieved four reuse cycles with 92–95% solvent recovery *via* water dilution and evaporation, with only a 5-8% decrease in extraction yield by the fourth cycle [46]. These results are highly encouraging, suggesting that properly formulated NADES are chemically robust and can achieve lifetimes of 20–100+ cycles with high regeneration fidelity. However, several limitations exist, including the fact that most reusability studies have been conducted under controlled laboratory conditions using synthetic contamination solutions. Real-world water matrices containing diverse co-contaminants, suspended solids, and microbial activity may introduce degradation pathways not observed in simplified systems. Long-term studies are absent from the literature. Furthermore, mechanical losses during handling, phase separation, and regeneration can cumulatively deplete solvent inventory even if chemical degradation is minimal, necessitating periodic replenishment. Economic considerations require quantifying the trade-off using the regeneration cost/cycle and the number of cycles before performance degradation mandates solvent replacement.

Integration with circular economy principles

In the grand scheme of sustainable NADES-based remediation, contaminant removal must adopt several circular-economy principles, including resource recovery, closed-loop material flows, waste minimization, and value creation from waste streams [127]. In this paradigm, water contaminated with PFAS or MNPs is not just viewed as waste requiring treatment, but also as a potential resource from which these materials can be recovered for further processing. For PFAS, the high purity and concentration achieved *via* NADES extraction enable subsequent fluorine recovery.

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Table 3

Overview of regeneration methods, advantages and disadvantages, with applications.

Regeneration Method	*Mechanism*	*NADES Recovery Efficiency (%)*	*Energy Input (kWh/kg NADES)*	*Applicability (Contaminant Type)*	*Advantages*	*Limitations*
Membrane-based (UF–BMED)	Size/charge-based separation *via* ultrafiltration coupled with bipolar membrane electrodialysis to remove ions/charged solutes and recover the NADES phase	80–95	0.5–2.0	Ionic species, salts, metal ions, and charged organic contaminants	Mild conditions, no phase change, relatively low thermal stress, scalability, and continuous operation	Membrane fouling, capital cost, limited effectiveness for non-ionic organics, and pretreatment are often needed
Anti-solvent precipitation	Addition of a miscible anti-solvent to decrease the solubility of solutes, inducing precipitation and allowing separation from NADES	70–95	0.3–1.0	High–molecular-weight organics, polyphenols, pigments, proteins	Simple operation, good for thermolabile compounds, relatively low thermal load	Requires anti-solvent handling/recovery, dilution of NADES, and possible loss of volatile components
Distillation/evaporation	Thermal removal of volatile components (typically water or low-boiling co-solvents) to concentrate and regenerate the NADES phase	60–90	2.0–5.0	Volatile co-solvents, low-boiling impurities	Well-established technology, high degree of purification from volatile species	High energy demand, thermal degradation of NADES or target compounds, not suitable for non-volatile contaminants
Solid-phase extraction (SPE)	Adsorptive removal of contaminants on solid sorbents (*e.g.*, polymeric resins, activated carbon, ion-exchange resins), followed by elution/regeneration	70–98	0.2–1.0	Aromatic organics, dyes, phenolics, metal ions (with functionalized sorbents)	High selectivity, low energy input, can be tailored *via* sorbent chemistry, and minimal NADES loss.	Sorbent cost and regeneration/disposal, capacity limits, potential co-adsorption of NADES components
In situ oxidation	Chemical or electrochemical oxidation of dissolved contaminants within the NADES phase (*e.g.*, H_2O_2, persulfate, electro-Fenton) to degrade into smaller/benign species	50–85	1.0–4.0	Organic pollutants (dyes, pharmaceutical residues, phenolics)	No phase separation step needed, effective for refractory organics, can restore NADES functionality	Risk of partial NADES degradation, requires oxidant or power input, formation of by-products, and careful control of conditions needed

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Fluorine is a strategic element with high economic value, used in pharmaceuticals, agrochemicals, and advanced materials [66]. While current technology for recovering elemental fluorine or fluorine-bearing chemicals from PFAS is in the early stages of research, electrochemical or thermochemical processes could defluorinate concentrated PFAS solutions and capture fluoride as recoverable HF or CaF_2. This transforms PFAS from a waste-disposal challenge into a secondary source of fluorine, thereby offsetting remediation costs. For MNPs, NADES extraction produces a concentrated plastic-solvent mixture. Simple solvent evaporation or anti-solvent precipitation can recover relatively pure plastic material, which could be reprocessed into new polymer products through mechanical or chemical recycling. While recycling contaminated environmental microplastics is more challenging than recycling clean post-consumer plastics due to degradation and contamination, niche applications for low-grade recycled polymer could be viable, particularly for higher-value plastics like PET. The regenerated NADES itself represents resource conservation. By avoiding single-use solvents and achieving >95% recovery over multiple cycles, material consumption is reduced by 95–99% compared to a linear model. The synthesis of NADES from renewable biomass feedstocks further enhances circularity, as these components can be continuously produced from agricultural resources without depleting finite fossil reserves. Energy optimization is integral to circular design. Regeneration methods should minimize energy inputs; membrane-based separation is generally more energy-efficient

(0.5–2 kWh/kg) than thermal methods such as distillation (5–20 kWh/kg). Integrating renewable energy sources to power NADES synthesis and regeneration operations would further reduce the carbon footprint and enhance sustainability metrics. Realizing this circular economic vision requires system-level thinking and the integration of extraction, regeneration, contaminant valorisation or processing, and solvent recycling into a strategically optimized process. It requires collaboration across value chains, since water utilities, chemical manufacturers, recycling industries, and policymakers must develop the infrastructure, markets, and regulations to support circular NADES-based remediation.

Future directions

Computational design and high-throughput screening

The design of NADES with optimized properties for specific contaminants represents a strategic direction for computational chemistry and cheminformatics. The HBA-HBD potential combinations and molar ratios yield roughly 10^6 formulations when considering just 100 common natural compounds at variable ratios. Experimental synthesis and testing of this vast space could be prohibitively time-consuming and expensive. Hence, computational screening offers a viable solution. COSMO-RS has emerged as a powerful predictive tool, enabling calculation of activity coefficients, partition coefficients, and solvation energies from molecular structure alone [128]. By constructing a virtual library of NADES and calculating their predicted affinity for target contaminants, researchers can identify the most promising candidates for experimental validation, reducing the experimental burden by orders of magnitude. By training on existing datasets of NADES properties and molecular descriptors of components, ML models can predict the properties of novel NADES formulations without requiring quantum-chemical calculations, enabling even faster screening [129]. Quantitative structure-property relationship models correlate molecular structure features, such as molecular weight, number of hydrogen bond donors/acceptors, topological indices, with macroscopic properties, enabling inverse design, that is, by specifying desired properties, such as viscosity <100 cP, hydrophobicity >90%, PFOA partition coefficient >1000, it is possible to estimate which molecular components can achieve them [130]. MD simulations provide atomic-level insights into extraction mechanisms, diffusion kinetics, and interfacial phenomena that are inaccessible experimentally. High-performance computing enables MD simulations of increasingly complex systems at nanosecond to microsecond timescales, revealing how NADES molecules disrupt contaminant hydration shells, how contaminants diffuse through the NADES phase, and how interfaces stabilize or destabilize. Future research should prioritize the development of integrated computational-experimental workflows where high-throughput computational screening identifies candidates, automated synthesis platforms rapidly prepare small-scale batches, and high-throughput analytical methods assess performance. Iterative experimental feedback refines these models, creating a closed-loop optimization cycle to accelerate the discovery of next-generation NADES formulations.

Multi-Pollutant remediation

While current research has focused on PFAS and MNPs, NADES' versatile solvation properties make them potentially effective for a broader spectrum of aquatic contaminants, including pharmaceutical residues *via* human use and/or improper disposal practices, such as antibiotics, hormones, analgesics, pentachlorophenol, etc., and personal care products (PCPs), that are abundant in wastewater effluent and surface water, often at concentrations of ng/L to µg/L [131]. Many PCPs possess functional groups amenable to hydrogen bonding, suggesting that appropriately designed NADES could efficiently extract them. Preliminary studies on the extraction of flavonoids and alkaloids from plant matrices are due to NADES' affinity for structurally similar pharmaceutical compounds. Pesticides, herbicides, insecticides, and fungicides contaminate agricultural runoff and groundwater. Hydrophobic NADES could target nonpolar pesticides, whereas polar or ionic NADES could be tailored for polar or ionizable pesticides. EDCs such as bisphenol A (BPA), phthalates, and nonylphenol leach from plastics and industrial processes and have molecular structures compatible with NADES extraction mechanisms. Perhaps the most ambitious multi-contaminant remediation could be achieved through carefully engineered NADES matrices or sequential extraction stages using different NADES formulations. For example, a two-stage system could employ polar NADES to extract ionic contaminants (PFAS, glyphosate), followed by hydrophobic NADES to extract neutral organics (MNPs, PAHs, PCBs). This “one-solvent, multiple pollutants” approach would be transformative for treating complex industrial wastewaters or highly contaminated sites.

NADES-based extraction is perceived as an integrated treatment optimized for overall performance, cost, and sustainability. Pre-treatment, including pairing NADES extraction with upstream processes, can remove bulk contaminants and suspended solids that might interfere with extraction or contaminate the solvent, enhancing longevity and reducing regeneration frequency. Following NADES extraction, residual contaminants at ultra-low concentrations (<<1 ng/L) could be addressed through biological treatment, AOPs, or GAC, achieving compliance with the most

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stringent regulatory limits. Integrating NADES extraction upstream of membrane filtration could reduce membrane fouling and extend membrane life by removing hydrophobic organics and colloids that cause fouling, while also addressing PFAS and microplastics that membranes capture but concentrate into difficult-to-manage brine. The treated water from NADES extraction would reduce fouling potential, enabling higher membrane flux and recovery. Concentrating PFAS from diluted water into NADES (*e.g.*, 10 μg/L at a 1:1000 dilution) creates a manageable target for advanced oxidation. Electrochemical oxidation of the loaded NADES could achieve PFAS mineralization with dramatically lower energy input than treating the original dilute water, since reaction efficiency adjusts with concentration. The regenerated NADES are then recycled, and this "extract-concentrate-destroy-recycle" paradigm represents the most economically and energetically viable pathway for actually eliminating PFAS. Furthermore, the extraction of short-chain PFAS by DES remains a known challenge [132] and warrants investigation.

Solid-supported and immobilized NADES

Immobilization of NADES onto solid supports addresses several challenges by eliminating the need for phase separation, simplifying handling and pumping, and enabling continuous-flow-through operation compatible with standard water-treatment infrastructure. Synthesis methods for such configurations include impregnation of porous supports (silica, activated carbon, polymeric resins, cellulosic materials) with liquid NADES *via* vacuum infiltration or supercritical CO_2-assisted loading [121]. Solid-supported NADES retain the molecular-level extraction mechanisms of liquid NADES but may exhibit reduced capacity and slower kinetics due to additional diffusion barriers within the porous support. However, kinetic limitations are balanced by longer contact times in continuous columns. Studies on solid-supported NADES for organic pollutant extraction achieved removal efficiencies comparable to those of liquid-phase extraction while offering superior operational convenience. Regeneration of solid-supported systems can be accomplished in situ by passing a regeneration solution through the column, as with ion-exchange resins. Alternatively, spent solid-supported NADES can be removed from the column, subjected to the same regeneration methods as liquid NADES, and then re-impregnated onto fresh support. However, mechanical stability is a critical challenge; repeated wetting-drying or solvent-exposure cycles can cause NADES to leach from the support or physically degrade the support material. Chemical or covalent immobilization strategies, in which NADES components are bonded to the support *via* silane coupling agents or polymer grafting, could enhance stability but increase synthesis complexity. Pilot-scale demonstrations of packed-bed solid-supported NADES reactors are needed to validate scalability and robustness.

Regulatory pathways and commercialization

Transitioning NADES-based remediation from laboratory concept to deployed technology requires navigating complex regulatory approval processes, demonstrating real-world performance through pilot studies, and eventually attracting commercial investment. Pilot-scale studies at water utilities or contaminated sites are essential to validate performance under realistic conditions: variable flow rates, variable contaminant concentrations, presence of multiple contaminants and suspended solids, temperature variations, and operational stresses. A well-designed pilot study should operate continuously for 6–12 months, treating 10–100 m^3/day, with rigorous monitoring of influent and effluent quality, solvent stability, regeneration efficiency, and operational challenges. Technology certification demonstrating compliance with NSF/ANSI Standard 61 (Drinking Water System Components) and Standard 60 (Drinking Water Treatment Chemicals) – both for health effects - is required for drinking water applications in the U.S. and many other jurisdictions. This process involves toxicological testing of NADES components and potential degradation products, extraction studies to verify that no harmful substances leach into treated water, and independent third-party validation of performance claims. Intellectual property protection through patents on specific NADES formulations, synthesis methods, process designs, or regeneration techniques is crucial for attracting investment and enabling commercialization. Several patents have been filed on DES-based extraction methods, establishing the nascent IP landscape. Public-private partnerships among universities, research institutions, water utilities, and chemical/engineering companies can accelerate translation by pooling expertise, sharing costs and risks, and providing pathways to market. Market drivers are strong: the multi-billion-dollar global water treatment market is growing rapidly due to increasing contamination and tightening regulations. PFAS remediation alone represents a $2–5 billion/year addressable market in the U.S., with comparable or larger markets in Europe and Asia. The competitive advantages of NADES-high efficiency, broad contaminant spectrum, regenerability, green credentials-position them as attractive for market entry, particularly if pilot demonstrations validate technical and economic claims. Strategic investment in demonstration projects, regulatory engagement, and commercialization pathways over the next 5–10 years could establish NADES-based remediation as a mainstream technology by 2030-2035.

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Conclusion

The widespread presence of PFAS, TWP, and other POPs in aquatic environments demands remediation technologies that combine high performance, sustainability, and circular-economy principles. Conventional approaches are constrained by intrinsic limitations, including poor removal of short-chain PFAS; secondary waste generation from activated carbon; high energy use; brine disposal in membrane processes; byproduct risks in advanced oxidation; and chemical recalcitrance that limits bioremediation. NADES have emerged as a promising alternative. Derived from low-cost, biodegradable components *via* atom-economical synthesis, NADES exhibit tunable polarity, broad solvation capacity, negligible volatility, and high thermal stability. Their efficacy arises from dense hydrogen-bonding networks and complementary hydrophobic interactions that preferentially solvate target pollutants, thereby producing partition coefficients that exceed those of conventional solvents. Experimental studies demonstrate strong performance: hydrophobic NADES, such as TOPO–lauric acid systems, achieve >99% single-stage PFOA removal with rapid equilibration (~1 min) and stable operation across wide pH, temperature, and concentration ranges, while retaining selectivity in complex wastewaters. Reusability tests confirm sustained efficiency over multiple extraction–regeneration cycles, supporting circular operation. NADES also remove 50–93% of common microplastics (e.g., PET, PS, PLA), including nanoscale fractions poorly addressed by physical methods. Relative to incumbent technologies, NADES provide superior short-chain PFAS removal, eliminate brine waste, operate at substantially lower energy demand, minimize interference from natural organic matter, and are fully regenerable. Preliminary techno-economic assessments indicate competitive treatment costs (~\$0.02–0.03 m^{-3}), contingent on high-efficiency regeneration over extended cycle lifetimes. The use of NADES can be extended to TWP, which has become a major environmental challenge due to the large number of automobiles on roads. Key challenges remain, including high viscosity that limits mass transfer and complicates process design, requiring optimization of formulation, water content, or operating temperature, as well as treatment of short-chain PFAS. Scaling from laboratory experiments to commercial applications requires advances in process engineering, particularly solid-supported NADES for packed-bed operation. Solvent leaching must be avoided through careful component selection and rigorous effluent quality control. Economic viability depends on demonstrating long-term durability and energy-efficient regeneration, with membrane-assisted approaches such as UF–BMED showing promise. Regulatory acceptance will require pilot-scale validation, toxicological assessment, and the development of certification pathways. Future progress will be accelerated by computational design using COSMO-RS, ML, and MD, by expanding to broader classes of contaminants, and by integrating NADES into hybrid treatment trains. Overall, this article posits that the use of NADES to remediate MNPs, PFAS, pharmaceutical residues *via* human use and/or improper disposal practices, TWPs, and POPs is a viable, circular-economy-aligned platform for sustainable water treatment, bridging laboratory validation and commercial deployment.

Supplementary information

Supplementary data are available free of charge at http://cjm.ichem.md as PDF file.

References

1. Cousins, I.T.; DeWitt, J.C.; Glüge, J.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C.A.; Scheringer, M.; Wang, Z. The high persistence of PFAS is sufficient for their management as a chemical class. Environmental Science: Processes Impacts 2020, 22(12), pp. 2307–2312. DOI: https://doi.org/10.1039/D0EM00355G
2. Stabnikova, O.; Stabnikov, V.; Marinin, A.; Klavins, M.; Klavins, L.; Vaseashta, A. Microbial life on the surface of microplastics in natural waters. Applied Sciences 2021, 11(24), 11692 pp. 1–19. DOI: https://doi.org/10.3390/app112411692
3. Klavins, M.; Klavins, L.; Stabnikova, O.; Stabnikov, V.; Marynin, A.; Ansone-Bertina, L.; Mezulis, M.; Vaseashta, A. Interaction between microplastics and pharmaceuticals depending on the composition of aquatic environment. Microplastics 2022, 1(3), pp. 520–535. DOI: https://doi.org/10.3390/microplastics1030037
4. Vaseashta, A.; Klavins, M.; Stabnikova, O. Micro and nanoplastics in aquatic environment. CRC Press, 2025, pp. 1–358. DOI: https://doi.org/10.1201/9781003389460
5. Khachatryan, G.; Vaseashta, A.; Gevorgyan, G. Sources and impacts of microplastics in aquatic environment and remediation strategies. Micro and Nanoplastics in Aquatic Environment. CRC Press, 2025; pp. 174–201. DOI: https://doi.org/10.1201/9781003389460-6
6. Evich, M.G.; Davis, M.J.B.; MCCord, J.P.; Acrey, B.; Awkerman, J.A.; Knappe, D.R.U.; Lindstrom, A.B.; Speth, T.F.; Tebes-Stevens, C.; Strynar, M.J.; et al. Per- and polyfluoroalkyl substances in the environment. Science 2022, 375(6580), pp. 1–15. DOI: https://doi.org/10.1126/science.abg9065
7. Kurwadkar, S.; Dane, J.; Kanel, S.R.; Nadagouda, M.N.; Cawdrey, R.W.; Ambade, B.; Struckhoff, G.C.; Wilkin, R. Per- and polyfluoroalkyl substances in water and wastewater: a critical review of their global occurrence and distribution. Science of The Total Environment 2022, 809, 151003 pp. 1–19. DOI: https://doi.org/10.1016/j.scitotenv.2021.151003

UNCORRECTED PROOF

8. Améduri, B. Fluoropolymers as unique and irreplaceable materials: challenges and future trends in these specific per or poly-fluoroalkyl substances. Molecules 2023, 28(22), 7564 pp. 1–33. DOI: https://doi.org/10.3390/molecules28227564
9. Cousins, I.T.; Johansson, J.H.; Salter, M.E.; Sha, B.; Scheringer, M. Outside the safe operating space of a new planetary boundary for per- and polyfluoroalkyl substances (PFAS). Environmental Science & Technology, 2022, 56(16), pp. 11172–11179. DOI: https://doi.org/10.1021/acs.est.2c02765
10. Persson, L.; Carney Almroth, B.M.; Collins, C.D.; Cornell, S.; De Wit, C.A.; Diamond, M.L.; Fantke, P.; Hassellöv, M.; MacLeod, M.; Ryberg, M.W.; *et al*. Outside the safe operating space of the planetary boundary for novel entities. Environmental Science & Technology, 2022, 56(3), pp. 1510–1521. DOI: https://doi.org/10.1021/acs.est.1c04158
11. Podder, A.; Sadmani, A.H.M.A.; Reinhart, D.; Chang, N.-B.; Goel, R. Per and poly-fluoroalkyl substances (PFAS) as a contaminant of emerging concern in surface water: a transboundary review of their occurrences and toxicity effects. Journal of Hazardous Materials, 2021, 419, 126361 pp. 1–22. DOI: https://doi.org/10.1016/j.jhazmat.2021.126361
12. Baensch-Baltruschat, B.; Kocher, B.; Stock, F.; Reifferscheid, G. Tyre and road wear particles (TRWP) - a review of generation, properties, emissions, human health risk, ecotoxicity, and fate in the environment. Science of The Total Environment, 2020, 733, 137823 pp. 1–19. DOI: https://doi.org/10.1016/j.scitotenv.2020.137823
13. Kole, P.J.; Löhr, A.J.; Van Belleghem, F.G.A.J.; Ragas, A.M. Wear and tear of tyres: a stealthy source of microplastics in the environment. International Journal of Environmental Research and Public Health, 2017, 14(10), 1265 pp. 1–31. DOI: https://doi.org/10.3390/ijerph14101265
14. Tian, Z.; Zhao, H.; Peter, K.T.; Gonzalez, M.; Wetzel, J.; Wu, C.; Hu, X.; Prat, J.; Mudrock, E.; Kolodziej, E.P.; *et al*. A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon. Science, 2020, 371(6525), pp. 185–189. DOI: https://doi.org/10.1126/science.abd6951
15. Wagner, S.; Hüffer, T.; Klöckner, P.; Wehrhahn, M.; Hofmann, T.; Reemtsma, T. Tire wear particles in the aquatic environment - a review on generation, analysis, occurrence, fate and effects. Water Research, 2018, 139, pp. 83–100. DOI: https://doi.org/10.1016/j.watres.2018.03.051
16. Sidorenko, L.; Sidorenko, A.; Gutsul, T.; Rastimesina, I.; Vaseashta, A. Micro and nanoplastics–plastisphere, biotoxicity, impact on human health, and mitigation strategies. Nanomedicine & Nanotechnology Open Access, 2025, 10(2), pp. 1–17. DOI: https://doi.org/10.23880/nnoa-16000345
17. Vaseashta, A.; Stamatin, I.; Khudaverdyan, S. Micro/nano plastics in aquatic biota: concerns, risks, mitigation, and policies. Micro and Nanoplastics in Aquatic Environment, CRC Press, 2025, pp. 1–58. DOI: https://doi.org/10.1201/9781003389460-1
18. ATSDR, Toxicological Profile for Perfluoroalkyls. 2021, 993 p. https://www.atsdr.cdc.gov/toxprofiles/tp200.pdf
19. Fenton, S.E.; Ducatman, A.; Boobis, A.; DeWitt, J.C.; Lau, C.; Ng, C.; Smith, J.S.; Roberts, S.M. Per- and polyfluoroalkyl substance toxicity and human health review: current state of knowledge and strategies for informing future research. Environmental Toxicology and Chemistry, 2021, 40(3), pp. 606–630. DOI: https://doi.org/10.1002/etc.4890
20. Barry, V.; Winquist, A.; Steenland, K. Perfluorooctanoic acid (PFOA) exposures and incident cancers among adults living near a chemical plant. Environmental Health Perspectives, 2013, 121(11-12), pp. 1313–1318. DOI: https://doi.org/10.1289/ehp.1306615
21. Post, G.B.; Gleason, J.A.; Cooper, K.R. Key scientific issues in developing drinking water guidelines for perfluoroalkyl acids: contaminants of emerging concern. PLOS Biology, 2017, 15(12), e2002855, pp. 1–12. DOI: https://doi.org/10.1371/journal.pbio.2002855
22. Johannessen, C.; Liggio, J.; Zhang, X.; Saini, A.; Harner, T. Composition and transformation chemistry of tire-wear derived organic chemicals and implications for air pollution. Atmospheric Pollution Research, 2022, 13(9), 101533, pp. 1–18. DOI: https://doi.org/10.1016/j.apr.2022.101533
23. US EPA, Final PFAS National Primary Drinking Water Regulation. https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas
24. ECHA, Per- and polyfluoroalkyl substances (PFAS). https://echa.europa.eu/hot-topics/perfluoroalkyl-chemicals-pfas
25. Stockholm Convention on Persistent Organic Pollutants (POPs). http://www.pops.int/
26. Ross, I.; McDonough, J.; Miles, J.; Storch, P.; Thelakkat Kochunarayanan, P.; Kalve, E.; Hurst, J.; Dasgupta, S.S; Burdick, J. A review of emerging technologies for remediation of PFASs. Remediation, 2018, 28(2), pp. 101–126. DOI: https://doi.org/10.1002/rem.21553
27. Maimaiti, A.; Deng, S.; Meng, P.; Wang, W.; Wang, B.; Huang, J.; Wang, Y.; Yu, G. Competitive adsorption of perfluoroalkyl substances on anion exchange resins in simulated AFFF-impacted groundwater. Chemical Engineering Journal, 2018, 348, pp. 494–502. DOI: https://doi.org/10.1016/j.cej.2018.05.006
28. Zaggia, A.; Conte, L.; Falletti, L.; Fant, M.; Chiorboli, A. Use of strong anion exchange resins for the removal of perfluoroalkylated substances from contaminated drinking water in batch and continuous pilot plants. Water Research, 2016, 91, pp. 137–146. DOI: https://doi.org/10.1016/j.watres.2015.12.039
29. Kothawala, D.N.; Köhler, S.J.; Östlund, A.; Wiberg, K.; Ahrens, L. Influence of dissolved organic matter concentration and composition on the removal efficiency of perfluoroalkyl substances (PFASs) during drinking water treatment. Water Research, 2017, 121, pp. 320–328. DOI: https://doi.org/10.1016/j.watres.2017.05.047
30. Franke, V.; McCleaf, P.; Lindegren, K.; Ahrens, L. Efficient removal of per- and polyfluoroalkyl substances (PFASs) in drinking water treatment: nanofiltration combined with active carbon or anion

UNCORRECTED PROOF

exchange. Environmental Science: Water Research & Technology, 2019, 5(11), pp. 1836–1843. DOI: https://doi.org/10.1039/C9EW00286C
31. Trojanowicz, M.; Bojanowska-Czajka, A.; Bartosiewicz, I.; Kulisa, K. Advanced oxidation/ reduction processes treatment for aqueous perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) - a review of recent advances. Chemical Engineering Journal, 2018, 336, pp. 170–199. DOI: https://doi.org/10.1016/j.cej.2017.10.153
32. Ateia, M.; Maroli, A.; Tharayil, N.; Karanfil, T. The Overlooked short- and ultrashort-chain poly- and perfluorinated substances: a review. Chemosphere, 2019, 220, pp. 866–882. DOI: https://doi.org/10.1016/j.chemosphere.2018.12.186
33. Enfrin, M.; Lee, J.; Gibert, Y.; Basheer, F.; Kong, L.; Dumée, L.F. Release of hazardous nanoplastic contaminants due to microplastics fragmentation under shear stress forces. Journal of Hazardous Materials, 2020, 384, 121393 pp. 1–31. DOI: https://doi.org/10.1016/j.jhazmat.2019.121393
34. Choi, Y.H.; van Spronsen, J.; Dai, Y.; Verberne, M.; Hollmann, F.; Arends, I.W.C.E.; Witkamp, G.-J.; Verpoorte, R. Are natural deep eutectic solvents the missing link in understanding cellular metabolism and physiology? Plant Physiology, 2011, 156(4), pp. 1701–1705. DOI: https://doi.org/10.1104/pp.111.178426
35. Dai, Y.; van Spronsen, J.; Witkamp, G.-J.; Verpoorte, R.; Choi, Y.H. Natural deep eutectic solvents as new potential media for green technology. Analytica Chimica Acta, 2013, 766, pp. 61–68. DOI: https://doi.org/10.1016/j.aca.2012.12.019
36. Tarikuzzaman, M.; Sagar, V.; Wong, M.J.; Lynam, J.G. Temperature effects on physiochemical characteristics of sugar-based natural deep eutectic solvents. Advances in Materials Science and Engineering, 2024, 6641317, pp. 1–13. DOI: https://doi.org/10.1155/2024/6641317
37. Albertini, B.; Bertoni, S.; Sangiorgi, S.; Nucci, G.; Passerini, N.; Mezzina, E. NaDES as a green technological approach for the solubility improvement of BCS class II APIs: an insight into the molecular interactions. International Journal of Pharmaceutics, 2023, 634, 122696, pp. 1–12. DOI: https://doi.org/10.1016/j.ijpharm.2023.122696
38. Abbott, A.P.; Harris, R.C.; Ryder, K.S.; D'Agostino, C.; Gladden, L.F.; Mantle, M.D. Glycerol eutectics as sustainable solvent systems. Green Chemistry, 2011, 13(1), pp. 82–90. DOI: https://doi.org/10.1039/C0GC00395F
39. Dai, Y.; Witkamp, G.-J.; Verpoorte, R.; Choi, Y.H. Tailoring properties of natural deep eutectic solvents with water to facilitate their applications. Food Chemistry, 2015, 187, pp. 14–19. DOI: https://doi.org/10.1016/j.foodchem.2015.03.123
40. Tang, B.; Zhang, H.; Row, K.H. Application of deep eutectic solvents in the extraction and separation of target compounds from various samples. Journal of Separation Science, 2015, 38, pp. 1053–1064. DOI: https://doi.org/10.1002/jssc.201401347
41. Kovács, A.; Neyts, E.C.; Cornet, I.; Wijnants, M.; Billen, P. Modeling the physicochemical properties of natural deep eutectic solvents. ChemSusChem, 2020, 13(15), pp. 3789–3804. DOI: https://doi.org/10.1002/cssc.202000286
42. Mbous, Y.P.; Hayyan, M.; Hayyan, A.; Wong, W.F.; Hashim, M.A.; Looi, C.Y. Applications of deep eutectic solvents in biotechnology and bioengineering-promises and challenges. Biotechnology Advances, 2017, 35(2), pp. 105–134. DOI: https://doi.org/10.1016/j.biotechadv.2016.11.006
43. Florindo, C.; Lima, F.; Ribeiro, B.D.; Marrucho, I.M. Deep eutectic solvents: overcoming 21st century challenges. Current Opinion in Green and Sustainable Chemistry, 2019, 18, pp. 31–36. DOI: https://doi.org/10.1016/j.cogsc.2018.12.003
44. Abbott, A.P.; Boothby, D.; Capper, G.; Davies, D.L.; Rasheed, R.K. Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. Journal American Chemical Society, 2004, 126(29), pp. 9142–9147. DOI: https://doi.org/10.1021/ja048266j
45. Liu, Y.; Friesen, J.B.; McAlpine, J.B.; Lankin, D.C.; Chen, S.-N.; Pauli, G.F. Natural deep eutectic solvents: properties, applications, and perspectives. Journal of Natural Products, 2018, 81(3), pp. 679–690. DOI: https://doi.org/10.1021/acs.jnatprod.7b00945
46. Fernández, M.D.L.Á.; Boiteux, J.; Espino, M.; Gomez, F.J.V.; Silva, M.F. Natural deep eutectic solvents-mediated extractions: the way forward for sustainable analytical developments. Analytica Chimica Acta, 2018, 1038, pp. 1–10. DOI: https://doi.org/10.1016/j.aca.2018.07.059
47. Mohd Fuad, F.; Mohd Nadzir, M. The formulation and physicochemical properties of betaine-based natural deep eutectic solvent. Journal of Molecular Liquids, 2022, 360, 119392. DOI: https://doi.org/10.1016/j.molliq.2022.119392
48. Koh, Q.Q.; Kua, Y.L.; Gan, S.; Tan, K.W.; Lee, T.Z.E.; Cheng, W.K.; Lau, H.L.N. Sugar-based natural deep eutectic solvent (NADES): physicochemical properties, antimicrobial activity, toxicity, biodegradability and potential use as green extraction media for phytonutrients. Sustainable Chemistry and Pharmacy, 2023, 35, 101218. DOI: https://doi.org/10.1016/j.scp.2023.101218
49. Maduka, T.O.; Wang, Q.; Suzuki, M.; Enyoh, C.E.; Wang, W.; Rana, Md.S. Hydrophobic natural deep eutectic solvents for extraction of bioactive compounds: multiscale characterization, quantum simulations, and molecular interaction studies with cry j 1 and amb a 1 Allergens. Separations, 2025, 12(8), 214 pp. 1–34. DOI: https://doi.org/10.3390/separations12080214
50. Huang, M.M.; Yiin, C.L.; Mun Lock, S.S.; Fui Chin, B.L.; Othman, I.; Binti Ahmad Zauzi, N.S.; Chan, Y.H. Natural deep eutectic solvents (NADES) for sustainable extraction of bioactive compounds from medicinal plants: recent advances, challenges, and future directions. Journal of Molecular Liquids, 2025, 425, 127202. DOI: https://doi.org/10.1016/j.molliq.2025.127202

UNCORRECTED PROOF

51. Komariah, L.N.; Arita, S.; Daffa Khairuddiin, M.; Ovindirani, S.A.; Erisna, D.; Paramasyifa, T.N. Multifunctional performance of deep eutectic solvent (DES) K2 CO3 –glycerol in biodiesel synthesis and purification. RSC Advances, 2026, 16(2), pp. 1789–1801. DOI: https://doi.org/10.1039/D5RA09382A
52. Eid, S.; Lemaoui, T.; Darwish, A.S.; Jaoude, M.A.; Banat, F.; Hasan, S.W.; AlNashef, I.M. Rapid and highly efficient removal of aqueous perfluorooctanoic acid using deep eutectic solvents for sustainable water remediation: an integrated experimental-modeling approach. Chemical Engineering Journal, 2024, 495, 153668, pp. 1–19. DOI: https://doi.org/10.1016/j.cej.2024.153668
53. Ribeiro, B.D.; Florindo, C.; Iff, L.C.; Coelho, M.A.Z.; Marrucho, I.M. Menthol-based eutectic mixtures: hydrophobic low viscosity solvents. ACS Sustainable Chemistry & Engineering, 2015, 3(10), pp. 2469–2477. DOI: https://doi.org/10.1021/acssuschemeng.5b00532
54. Van Osch, D.J.G.P.; Zubeir, L.F.; van den Bruinhorst, A.; Rocha, M.A.A.; Kroon, M.C. Hydrophobic deep eutectic solvents as water-immiscible extractants. Green Chemistry, 2015, 17(9), pp. 4518–4521. DOI: https://doi.org/10.1039/C5GC01451D
55. Smith, E.L.; Abbott, A.P.; Ryder, K.S. Deep eutectic solvents (DESs) and their applications. Chemical Reviews, 2014, 114(21), pp. 11060–11082. DOI: https://doi.org/10.1021/cr300162p
56. Hayyan, M.; Hashim, M.A.; Al-Saadi, M.A.; Hayyan, A.; AlNashef, I.M.; Mirghani, M.E.S. Assessment of cytotoxicity and toxicity for phosphonium-based deep eutectic solvents. Chemosphere, 2013, 93(2), pp. 455–459. DOI: https://doi.org/10.1016/j.chemosphere.2013.05.013
57. Wen, Q.; Chen, J.-X.; Tang, Y.-L.; Wang, J.; Yang, Z. Assessing the toxicity and biodegradability of deep eutectic solvents. Chemosphere, 2015, 132, pp. 63–69. DOI: https://doi.org/10.1016/j.chemosphere.2015.02.061
58. Anastas, P.T.; Zimmerman, J.B. Peer reviewed: design through the 12 principles of green engineering. Environmental Science & Technology, 2003, 37(5), pp. 94A–101A. DOI: https://doi.org/10.1021/es032373g
59. Capello, C.; Fischer, U.; Hungerbühler, K. What is a green solvent? A comprehensive framework for the environmental assessment of solvents. Green Chemistry, 2007, 9(9), pp. 927–934. DOI: https://doi.org/10.1039/b617536h
60. Jessop, P.G. Searching for green solvents. Green Chemistry, 2011, 13(6), pp. 1391–1398. DOI: https://doi.org/10.1039/c0gc00797h
61. Rogers, R.D.; Seddon, K.R. Ionic liquids--solvents of the future? Science, 2003, 302(5646), pp. 792–793. DOI: https://doi.org/10.1126/science.1090313
62. Plechkova, N.V.; Seddon, K.R. Applications of ionic liquids in the chemical industry. Chemical Society Reviews, 2008, 37(1), pp. 123–150. DOI: https://doi.org/10.1039/B006677J
63. Thuy Pham, T.P.; Cho, C.-W.; Yun, Y.-S. Environmental fate and toxicity of ionic liquids: a review. Water Research, 2010, 44(2), pp. 352–372. DOI: https://doi.org/10.1016/j.watres.2009.09.030
64. Buck, R.C.; Franklin, J.; Berger, U.; Conder, J.M.; Cousins, I.T.; de Voogt, P.; Jensen, A.A.; Kannan, K.; Mabury, S.A.; van Leeuwen, S.P. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integrated Environmental Assessment and Management, 2011, 7(4), pp. 513–541. DOI: https://doi.org/10.1002/ieam.258
65. OECD, Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance. OECD Series on Risk Management, Publishing: Paris, 2021, 61, 45 p. DOI: https://doi.org/10.1787/e458e796-en
66. Kissa, E. Fluorinated Surfactants and Repellents. Marcel Dekker: New York, 2001, 640 p.
67. Key, B.D.; Howell, R.D.; Criddle, C.S. Fluorinated organics in the biosphere. Environmental Science & Technology, 1997, 31(9), pp. 2445–2454. DOI: https://doi.org/10.1021/es961007c
68. Coggan, T.L.; Moodie, D.; Kolobaric, A.; Szabo, D.; Shimeta, J.; Crosbie, N.D.; Lee, E.; Fernandes, M.; Clarke, B.O. An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs). Heliyon, 2019, 5(8), e02316, pp. 1–11. DOI: https://doi.org/10.1016/j.heliyon.2019.e02316
69. Pan, Y.; Zhang, H.; Cui, Q.; Sheng, N.; Yeung, L.W.Y.; Guo, Y.; Sun, Y.; Dai, J. First report on the occurrence and bioaccumulation of hexafluoropropylene oxide trimer acid: an emerging concern. Environmental Science &Technology, 2017, 51(17), pp. 9553–9560. DOI: https://doi.org/10.1021/acs.est.7b02259
70. Eschauzier, C.; Beerendonk, E.; Scholte-Veenendaal, P.; De Voogt, P. Impact of treatment processes on the removal of perfluoroalkyl acids from the drinking water production chain. Environmental Science & Technology, 2012, 46(3), pp. 1708–1715. DOI: https://doi.org/10.1021/es201662b
71. Prevedouros, K.; Cousins, I.T.; Buck, R.C.; Korzeniowski, S.H. Sources, fate and transport of perfluorocarboxylates. Environmental Science & Technology, 2006, 40(1), pp. 32–44. DOI: https://doi.org/10.1021/es0512475
72. Houtz, E.F.; Higgins, C.P.; Field, J.A.; Sedlak, D.L. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. Environmental Science & Technology, 2013, 47(15), pp. 8187–8195. DOI: https://doi.org/10.1021/es4018877
73. Backe, W.J.; Day, T.C.; Field, J.A. Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from U.S. military bases by nonaqueous large-volume injection HPLC-MS/MS. Environmental Science & Technology, 2013, 47(10), pp. 5226–5234. DOI: https://doi.org/10.1021/es3034999
74. Bolan, N.; Sarkar, B.; Yan, Y.; Li, Q.; Wijesekara, H.; Kannan, K.; Tsang, D.C.W.; Schauerte, M.; Bosch, J.; Noll, H.; et al. Remediation of poly- and perfluoroalkyl substances (PFAS)

UNCORRECTED PROOF

contaminated soils – to mobilize or to immobilize or to degrade? Journal of Hazardous Materials, 2021, 401, 123892, pp. 1–22. DOI: https://doi.org/10.1016/j.jhazmat.2020.123892

75. Schultz, M.M.; Barofsky, D.F.; Field, J.A. Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/MS. Environmental Science & Technology, 2004, 38(6), pp. 1828–1835. DOI: https://doi.org/10.1021/es035031j
76. Sepulvado, J.G.; Blaine, A.C.; Hundal, L.S.; Higgins, C.P. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. Environmental Science & Technology, 2011, 45(19), pp. 8106–8112. DOI: https://doi.org/10.1021/es103903d
77. Armitage, J.M.; MacLeod, M.; Cousins, I.T. Comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources. Environmental Science & Technology, 2009, 43(15), pp. 5830–5836. DOI: https://doi.org/10.1021/es900753y
78. Olubusoye, B.S.; Cizdziel, J.V.; Bee, M.; Moore, M.T.; Pineda, M.; Yargeau, V.; Bennett, E.R. Toxic tire wear compounds (6PPD-Q and 4-ADPA) detected in airborne particulate matter along a highway in Mississippi, USA. Bulletin of Environmental Contamination and Toxicology, 2023, 111, 68, pp. 1–8. DOI: https://doi.org/10.1007/s00128-023-03820-7
79. Ellis, D.A.; Martin, J.W.; De Silva, A.O.; Mabury, S.A.; Hurley, M.D.; Sulbaek Andersen, M.P.; Wallington, T.J. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. Environmental Science & Technology, 2004, 38(12), pp. 3316–3321. DOI: https://doi.org/10.1021/es049860w
80. Wetherbee, G.A.; Baldwin, A.K.; Ranville, J.F. It Is Raining Plastic: U.S. Geological Survey Open-File Report 2019-1048, 2019, 1 p. DOI: https://doi.org/10.3133/ofr20191048
81. EEA, PFAS pollution in European waters. Briefing no. 19/2024, 2024. DOI: https://doi.org/10.2800/9324640. https://www.eea.europa.eu/en/analysis/publications/pfas-pollution-in-european-waters. Accessed: 11/20/2025.
82. Cai, M.; Zhao, Z.; Yin, Z.; Ahrens, L.; Huang, P.; Cai, M.; Yang, H.; He, J.; Sturm, R.; Ebinghaus, R.; et al. Occurrence of perfluoroalkyl compounds in surface waters from the North Pacific to the Arctic Ocean. Environmental Science & Technology, 2012, 46(2), pp. 661–668. DOI: https://doi.org/10.1021/es2026278
83. Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Gorzelany, J.F.; Hansen, K.J.; Jones, P.D.; Helle, E.; Nyman, M.; Giesy, J.P. Accumulation of perfluorooctane sulfonate in marine mammals. Environmental Science & Technology, 2001, 35(8), pp. 1593–1598. DOI: https://doi.org/10.1021/es001873w
84. Wik, A.; Dave, G. Occurrence and effects of tire wear particles in the environment – a critical review and an initial risk assessment. Environmental Pollution, 2009, 157(1), pp. 1–11. DOI: https://doi.org/10.1016/j.envpol.2008.09.028
85. Klöckner, P.; Reemtsma, T.; Eisentraut, P.; Braun, U.; Ruhl, A.S.; Wagner, S. Tire and road wear particles in road environment - quantification and assessment of particle dynamics by Zn determination after density separation. Chemosphere, 2019, 222, pp. 714–721. DOI: https://doi.org/10.1016/j.chemosphere.2019.01.176
86. Kreider, M.L.; Panko, J.M.; McAtee, B.L.; Sweet, L.I.; Finley, B.L. Physical and chemical characterization of tire-related particles: comparison of particles generated using different methodologies. Science of The Total Environment, 2010, 408(3), pp. 652–659. DOI: https://doi.org/10.1016/j.scitotenv.2009.10.016
87. Halle, L.L.; Palmqvist, A.; Kampmann, K.; Khan, F.R. Ecotoxicology of micronized tire rubber: past, present and future considerations. Science of The Total Environment, 2020, 706, 135694, pp. 1–13. DOI: https://doi.org/10.1016/j.scitotenv.2019.135694
88. McIntyre, J.K.; Prat, J.; Cameron, J.; Wetzel, J.; Mudrock, E.; Peter, K.T.; Tian, Z.; Mackenzie, C.; Lundin, J.; Stark, J.D.; et al. Treading water: tire wear particle leachate recreates an urban runoff mortality syndrome in coho but not chum salmon. Environmental Science & Technology, 2021, 55(17), pp. 11767–11774. DOI: https://doi.org/10.1021/acs.est.1c03569
89. Järlskog, I.; Strömvall, A.-M.; Magnusson, K.; Gustafsson, M.; Polukarova, M.; Galfi, H.; Aronsson, M.; Andersson-Sköld, Y. Occurrence of tire and bitumen wear microplastics on urban streets and in sweepsand and washwater. Science of The Total Environment, 2020, 729, 138950, pp. 1-13. DOI: https://doi.org/10.1016/j.scitotenv.2020.138950
90. Unice, K.M.; Kreider, M.L.; Panko, J.M. Comparison of tire and road wear particle concentrations in sediment for watersheds in France, Japan, and the United States by quantitative pyrolysis GC/MS analysis. Environmental Science & Technology, 2013, 47(15), pp. 8138–8147. DOI: https://doi.org/10.1021/es400871j
91. Werbowski, L.M.; Gilbreath, A.N.; Munno, K.; Zhu, X.; Grbic, J.; Wu, T.; Sutton, R.; Sedlak, M.D.; Deshpande, A.D.; Rochman, C.M. Urban stormwater runoff: a major pathway for anthropogenic particles, black rubbery fragments, and other types of microplastics to urban receiving waters. ACS ES&T Water, 2021, 1(6), pp. 1420–1428. DOI: https://doi.org/10.1021/acsestwater.1c00017
92. US EPA Where Rubber Meets the Road: EPA Researchers Study the Environmental and Health Impacts of Tires; US EPA: Washington, DC, USA, 2024. https://www.epa.gov/epcra/designation-pfoa-and-pfos-hazardous-substances-under-cercla-release-reporting-requirements. Accessed: 12/20/2025.
93. Yi, L.B.; Chai, L.Y.; Xie, Y.; Peng, Q.J.; Peng, Q.Z. Isolation, identification, and degradation

UNCORRECTED PROOF

performance of a PFOA-degrading strain. Genet Mol Res., 2016, 15(2), pp. 1–12. DOI: https://doi.org/10.4238/gmr.15028043
94. Conder, J.M.; Hoke, R.A.; Wolf, W.D.; Russell, M.H.; Buck, R.C. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. Environmental Science & Technology, 2008, 42(4), pp. 995–1003. DOI: https://doi.org/10.1021/es070895g
95. Houde, M.; De Silva, A.O.; Muir, D.C.G.; Letcher, R.J. Monitoring of perfluorinated compounds in aquatic biota: an updated review: PFCs in aquatic biota. Environmental Science & Technology, 2011, 45(19), pp. 7962–7973. DOI: https://doi.org/10.1021/es104326w
96. Arnot, J.A.; Gobas, F.A. A review of bioconcentration factor (BCF) and bioaccumulation factor (BAF) assessments for organic chemicals in aquatic organisms. Environmental Reviews, 2006, 14(4), pp. 257–297. DOI: https://doi.org/10.1139/a06-005
97. Ng, C.A.; Hungerbühler, K. Bioaccumulation of perfluorinated alkyl acids: observations and models. Environmental Science & Technology, 2014, 48(9), pp. 4637–4648. DOI: https://doi.org/10.1021/es404008g
98. Borgå, K.; Fisk, A.T.; Hoekstra, P.F.; Muir, D.C.G. Biological and chemical factors of importance in the bioaccumulation and trophic transfer of persistent organochlorine contaminants in arctic marine food webs. Environmental Toxicology and Chemistry, 2004, 23(10), pp. 2367–2385. DOI: https://doi.org/10.1897/03-518
99. Kelly, B.C.; Ikonomou, M.G.; Blair, J.D.; Surridge, B.; Hoover, D.; Grace, R.; Gobas, F.A.P.C. Perfluoroalkyl contaminants in an arctic marine food web: trophic magnification and wildlife exposure. Environmental Science & Technology, 2009, 43(11), pp. 4037–4043. DOI: https://doi.org/10.1021/es9003894
100. Ankley, G.T.; Cureton, P.; Hoke, R.A.; Houde, M.; Kumar, A.; Kurias, J.; Lanno, R.; McCarthy, C.; Newsted, J.; Salice, C.J.; *et al*. Assessing the ecological risks of per- and polyfluoroalkyl substances: current state-of-the science and a proposed path forward. Environmental Toxicology and Chemistry, 2021, 40(3), pp. 564–605. DOI: https://doi.org/10.1002/etc.4869
101. Gaballah, S.; Swank, A.; Sobus, J.R.; Howey, X.M.; Schmid, J.; Catron, T.; McCord, J.; Hines, E.; Strynar, M.; Tal, T. Evaluation of developmental toxicity, developmental neurotoxicity, and tissue dose in zebrafish exposed to genX and other PFAS. Environmental Health Perspectives, 2020, 128(4), 047005, pp. 1–22. DOI: https://doi.org/10.1289/EHP5843
102. Liu, P.; Zhan, X.; Wu, X.; Li, J.; Wang, H.; Gao, S. Effect of weathering on environmental behavior of microplastics: properties, sorption and potential risks. Chemosphere, 2020, 242, 125193, pp. 1–49. DOI: https://doi.org/10.1016/j.chemosphere.2019.125193
103. Zhang, Z.; Chen, W.; Chan, H.; Peng, J.; Zhu, P.; Li, J.; Jiang, X.; Zhang, Z.; Wang, Y.; Tan, Z.; *et al*. Polystyrene microplastics induce size-dependent multi-organ damage in mice: insights into gut microbiota and fecal metabolites. Journal of Hazardous Materials, 2024, 461, 132503, pp. 1–17. DOI: https://doi.org/10.1016/j.jhazmat.2023.132503
104. Costello, M.C.S.; Lee, L.S. Sources, fate, and plant uptake in agricultural systems of per- and polyfluoroalkyl substances. Current Pollution Reports, 2020, 10, pp. 799–819. DOI: https://doi.org/10.1007/s40726-020-00168-y
105. Rosen, M.B.; Das, K.P.; Wood, C.R.; Wolf, C.J.; Abbott, B.D.; Lau, C. Evaluation of perfluoroalkyl acid activity using primary mouse and human hepatocytes. Toxicology, 2013, 308, pp. 129–137. DOI: https://doi.org/10.1016/j.tox.2013.03.011
106. Liu, Z.; Huang, Y.; Jiao, Y.; Chen, Q.; Wu, D.; Yu, P.; Li, Y.; Cai, M.; Zhao, Y. Polystyrene nanoplastic induces ROS production and affects the MAPK-HIF-1/NFkB-mediated antioxidant system in daphnia pulex. Aquatic Toxicology, 2020, 220, 105420, pp. 1–8. DOI: https://doi.org/10.1016/j.aquatox.2020.105420
107. Gualtieri, M.; Rigamonti, L.; Galeotti, V.; Camatini, M. Toxicity of tire debris extracts on human lung cell line A549. Toxicology in Vitro, 2005, 19(7), pp. 1001–1008. DOI: https://doi.org/10.1016/j.tiv.2005.06.038
108. National Center for Health Statistics (U.S.), Fourth National Report on Human Exposure to Environmental Chemicals. NHANES 2005–2016, 2021, 3, 562 p. https://stacks.cdc.gov/view/cdc/105344
109. Bleus, D.; Jolivet, R.B.; Marchal, W.; Vandamme, D.; Dziubinska-Kuehn, K. The role of hydrogen bond formation in the extracting efficiency of NADES formulations. Journal of Molecular Liquids, 2025, 435, 128147, pp. 1–9. DOI: https://doi.org/10.1016/j.molliq.2025.128147
110. Mohan, M.; Keasling, J.D.; Simmons, B.A.; Singh, S. In silico COSMO-RS predictive screening of ionic liquids for the dissolution of plastic. Green Chemistry, 2022, 24(10), pp. 4140–4152. DOI: https://doi.org/10.1039/D1GC03464B
111. Mota-Morales, J.D.; Sánchez-Leija, R.J.; Carranza, A.; Pojman, J.A.; Del Monte, F.; Luna-Bárcenas, G. Free-radical polymerizations of and in deep eutectic solvents: green synthesis of functional materials. Progress in Polymer Science, 2018, 78, pp. 139–153. DOI: https://doi.org/10.1016/j.progpolymsci.2017.09.005
112. Benlebna, M.; Ruesgas-Ramón, M.; Bonafos, B.; Fouret, G.; Casas, F.; Coudray, C.; Durand, E.; Figueroa-Espinoza, M.C.; Feillet-Coudray, C. Toxicity of natural deep eutectic solvent betaine: glycerol in rats. Journal of Agricultural and Food Chemistry, 2018, 66(24), pp. 6205–6212. DOI: https://doi.org/10.1021/acs.jafc.8b01746
113. Shija, G. Sustainable NADES and ultrasound-assisted extraction of PFAS and microplastics in environmental matrices. Critical Reviews in Analytical Chemistry, 2026, pp. 1–21. DOI: https://doi.org/10.1080/10408347.2026.2644442
114. Hunter, J.R.; Qiao, Q.; Zhang, Y.; Shao, Q.; Crofcheck, C.; Shi, J. Green solvent mediated extraction of micro- and nano-plastic particles from water. Scientific Reports, 2023, 13, 10585,

UNCORRECTED PROOF

pp. 1–12. DOI: https://doi.org/10.1038/s41598-023-37490-6
115. Dickenson, E.R.; Higgins, C.P. Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances. Project #4322. The Water Research Foundation: Denver, 2016. https://www.advancesinwaterresearch.org/awr/20170103/MobilePagedArticle.action?articleId=1077332#articleId1077332
116. Duca, G.; Vaseashta, A. Environmental and Technological Aspects of Redox Processes. IGI Global, 2023, 435 p. DOI: https://doi.org/10.4018/979-8-3693-0512-6
117. Vaseashta, A.; Duca, G.; Travin, S.O. Molecular Oxygen Activation Mechanisms. Duca, G.; Vaseashta, A. Eds. Fundamental and Biomedical Aspects of Redox Processes. IGI Global, 2023, pp. 27–38. DOI: https://doi.org/10.4018/978-1-6684-7198-2.ch002
118. Zhuo, Q.; Deng, S.; Yang, B.; Huang, J.; Yu, G. Efficient electrochemical oxidation of perfluorooctanoate using a Ti/SnO2 -Sb-Bi anode. Environmental Science & Technology, 2011, 45(7), pp. 2973–2979. DOI: https://doi.org/10.1021/es1024542
119. Chaplin, B.P. Critical review of electrochemical advanced oxidation processes for water treatment applications. Environmental Science: Processes & Impacts, 2014, 16(6), pp. 1182–1203. DOI: https://doi.org/10.1039/C3EM00679D
120. Liu, G.; Zhu, Z.; Yang, Y.; Sun, Y.; Yu, F.; Ma, J. Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and seawater. Environmental Pollution, 2019, 246, pp. 26–33. DOI: https://doi.org/10.1016/j.envpol.2018.11.100
121. Dos Santos, V.B.; Garcia, C.D.; de Sousa, H.S.; Carvalho, V.A.; Oliveira, S.C.; Suarez, W.T. Deployment of solid-supported natural deep eutectic solvents via unmanned aerial vehicles to preconcentrate contaminants from environmental water samples. ACS Omega, 2025, 10(41), pp. 48808–48817. DOI: https://doi.org/10.1021/acsomega.5c06815
122. Life Cycle Analysis of Nanoparticles: Risk, Assessment, and Sustainability; Vaseashta, A. DEStech Publications, Incorporated in Lancaster, Pennsylvania, 2015, pp. 1-376. ISBN 978-1-60595-023-5.
123. Prabhune, A.; Dey, R. Green and sustainable solvents of the future: deep eutectic solvents. Journal of Molecular Liquids, 2023, 379, 121676. DOI: https://doi.org/10.1016/j.molliq.2023.121676
124. US EPA, Designation of Perfluorooctanoic Acid (PFOA) and Perfluorooctanesulfonic Acid (PFOS) as CERCLA Hazardous Substances. US EPA: Washington, 2024, 89(90), pp. 39124–39192. https://www.federalregister.gov/documents/2024/05/08/2024-08547/designation-of-perfluorooctanoic-acid-pfoa-and-perfluorooctanesulfonic-acid-pfos-as-cercla
125. Cheng, L.; Chen, X.; Gu, J.; Kobayashi, N.; Yuan, H.; Chen, Y. Chemical recycling of waste plastics: current challenges and perspectives. Fundamental Research, 2025, 5(3), pp. 919–922. DOI: https://doi.org/10.1016/j.fmre.2023.12.023
126. Liang, X.; Zhang, J.; Huang, Z.; Guo, Y. Sustainable recovery and recycling of natural deep eutectic solvent for biomass fractionation via industrial membrane-based technique. Industrial Crops and Products, 2023, 194, 116351. DOI: https://doi.org/10.1016/j.indcrop.2023.116351
127. Ellen MacArthur Foundation, Towards a Circular Economy: Business Rationale for an Accelerated Transition. 2015, 20 p. https://www.ellenmacarthurfoundation.org/towards-a-circular-economy-business-rationale-for-an-accelerated-transition
128. Klamt, A. COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design. Elsevier: Amsterdam, 2005, 246 p.
129. Verma, R.; Mohan, M.; Goud, V.V.; Banerjee, T. Operational strategies and comprehensive evaluation of menthol based deep eutectic solvent for the extraction of lower alcohols from aqueous media. ACS Sustainable Chemistry & Engineering, 2018, 6(12), pp. 16920–16932. DOI: https://doi.org/10.1021/acssuschemeng.8b04255
130. Verma, A.; Sharma, G.; Kumar, A.; Dhiman, P.; Mola, G.T.; Shan, A.; Si, C. Microplastic pollutants in water: a comprehensive review on their remediation by adsorption using various adsorbents. Chemosphere, 2024, 352, 141365. DOI: https://doi.org/10.1016/j.chemosphere.2024.141365
131. Petrie, B.; Barden, R.; Kasprzyk-Hordern, B. A review of emerging contaminants in wastewater and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Research, 2015, 72, pp. 3–27. DOI: https://doi.org/10.1016/j.watres.2014.08.053
132. Yu, H.; Zhang, P.; Song, D.; Chen, H.; Huang, P.; Rončević, S.D.; Sun, H. Rapid and efficient removal of ultrashort- and short-chain PFAS from contaminated water by pyrogenic carbons: a strategy via polypyrrole nanostructured coating. Environmental Science & Technology, 2025, 59(30), pp. 16034–16045. DOI: https://doi.org/10.1021/acs.est.5c06248

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