

UNDERSTANDING AND TACKLING PFAS IN DRINKING WATER

Executive Summary

Per-and polyfluoroalkyl substances (PFAS) are "Man-made chemicals that have been used in industry and consumer products worldwide since the 1940s. They have been used to make nonstick cookware, water-repellent clothing, stain resistant fabrics and carpets, some cosmetics, some firefighting foams, and products that resist grease, water, and oil." ¹Also known as "forever chemicals," PFAS do not break down and are found in our air, water, soil, and even in our blood nearly everywhere on the planet.

Once thought to be innocuous and harmless, PFAS have gone unregulated for almost three quarters of a century. They are only now being understood as a probable long-term danger to human life and health. The PFAS situation is the United States is dire. Definitive studies show that exposure to PFAS leads to "adverse health outcomes" including decreased fertility, developmental delays in children, increased risk of cancers, reduced immunology, inability to properly regulate hormones, increased levels of obesity, and more.

The threat is ubiquitous. 83% of American waterways sampled have PFAS. 133 million people are exposed to PFAS through their water supplies and over 57,000 PFAS contaminated sites exist in the United States alone (nearly 50,000 industrial facilities, 4,200 wastewater treatment plants, nearly 4,000 military sites, and over 500 airports).

The economic cost of this problem is massive. 6,400 PFAS related lawsuits have been filed since 2005. More than one billion dollars in settlements have been awarded for monitoring, cleanup, and supply of PFAS free water paid by 3M, Dupont, Johnson Controls, Wolverine Worldwide, et al. Major producers of PFAS are now on notice. Communities are actively testing their water and proceeding aggressively with litigation to cover costs of remediation and alternative water sources.

Significant regulation is emerging. On March 14, 2023, the Environmental Protection Agency (EPA) announced the proposed National Primary Drinking Water Regulation (NPDWR) for six types of PFAS, to create legally enforceable Maximum Contaminant Levels (MCLs) in drinking water. This will require public water systems to monitor and notify consumers of PFAS levels in their water, and, most importantly, require the reduction of PFAS levels in drinking water if more than the MCLs of 4 parts per trillion.

Until now, commercially viable platforms to capture and destroy PFAS to this legally required level have not been available. There are existing technologies that can clean PFAS in water, but each has its own drawbacks. Activated Carbon can capture PFAS, but then the carbon must be periodically replaced. Reverse Osmosis and Nanofiltration can clean some of the water, but there is still a waste stream, now with a much higher concentration of PFAS that must be dealt with. Waste chemical streams from Ion Exchange Resin regeneration are also an issue. While each technology can work, one cross-cutting problem with each of them is cost. These systems have large up-front capital and annual operating expenses. BNNano's solutions, making use of patented Boron Nitride NanoBarbsTM, radically changes the economics of PFAS removal and destruction.

¹<u>https://www.atsdr.cdc.gov/pfas/health-effects/overview.html</u>

Boron Nitride NanoBarbsTM are the more economical way to provide clean, safe water. For single use systems, NanoBarbs can be incorporated into existing point of use technologies. For larger systems – industrial, municipal, and environmental cleanup – NanoBarbs, along with ultraviolet (UV) light systems, will provide a more economical solution for removing PFAS in contaminated water, eliminating the negative health impacts.

BNNano's solutions use state-of-the-art materials science technology combined with UV energy to remediate PFAS. Boron Nitride materials first capture PFAS molecules and then, in conjunction with UV energy, catalytically destroy the PFAS. Because the PFAS molecules are destroyed in place, there is no need for filter media replacement and removal. This results in significantly smaller size systems with virtually no waste stream. BNNano's solutions eliminate harmful PFAS chemicals with much lower up-front capital and annual operating expenses.

BNNano's solutions are scalable across consumer, municipal, industrial, and mobile remediation.

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What is PFAS?

Recent headlines² often mention "PFAS" or "forever chemicals," including the routine:

- "Why you can't always trust claims on nontoxic cookware"
- "Locally caught fish are full of dangerous chemicals called PFAS, study finds⁴" and
- "PFAS pollute 83% of U.S. waterways⁵"

And the outlandish:

- "PFAS Forever Chemicals Are Turning Up in Menstrual Products⁶"
- "Firefighters Union Pushes to Rid Protective Gear of Forever Chemicals7" and
- "It's raining PFAS: Even in Antarctica and on the Tibetan Plateau, rainwater is unsafe to drink.⁸"

The Center for Disease Control defines per- and polyfluoroalkyl substances (PFAS) as "Man-made chemicals that have been used in industry and consumer products worldwide since the 1940s. They have been used to make nonstick cookware, water-repellent clothing, stain resistant fabrics and carpets, some cosmetics, some firefighting foams, and products that resist grease, water, and oil."⁹ Known as "forever chemicals," PFAS do not break down and can be found in our air, water, soil, and blood nearly everywhere on the planet.

Studies show that exposure to PFAS leads to "adverse health outcomes," including decreased fertility, developmental delays in children, increased risk of cancers, reduce immunology, inability to properly regulate hormones, increased levels of obesity, and more.¹⁰ There are over 9,000 types of PFAS in existence today, with new compounds discovered all the time.¹¹ Given the ubiquity, quantity, and variability of these compounds, researchers face challenges in isolating and studying their specific impact on public health¹², which is often a precursor to regulatory action. However, as identified by the National Institute of Environmental Health Sciences (a division of the National Institutes of Health), countless studies across multiple¹³ disciplines showing the harmful impacts of PFAS are beginning to mount. Results of this ongoing research include updated laws, rules, and regulations at federal, state, and local levels of government, not just in the United States, but globally¹⁴ as well.

² <u>https://pfascentral.org/news?page=2</u>

³ https://6abc.com/consumer-reports-nonstick-pans-cookware-chemicals/12580170/

⁴ https://www.cnn.com/2023/01/17/health/freshwater-fish-pfas-contamination-wellness/index.html

⁵ <u>https://www.eenews.net/articles/pfas-pollute-83-of-u-s-waterways/</u>

⁶ https://time.com/6254060/pfas-period-chemicals-underwear-tampons/

⁷ https://www.wsj.com/articles/firefighters-union-pushes-to-rid-protective-gear-of-forever-chemicals-11674760345

⁸ <u>https://phys.org/news/2022-08-pfas-antarctica-tibetan-plateau-rainwater.html</u>

⁹ https://www.atsdr.cdc.gov/pfas/health-effects/overview.html

¹⁰ https://www.epa.gov/pfas/our-current-understanding-human-health-and-environmental-risks-pfas

¹¹ https://www.cdc.gov/niosh/topics/pfas/default.html

¹² https://www.niehs.nih.gov/health/topics/agents/pfc/index.cfm

¹³ https://www.niehs.nih.gov/health/topics/agents/pfc/index.cfm

¹⁴ <u>https://news.bloomberglaw.com/environment-and-energy/ban-on-most-pfas-use-and-production-proposed-in-european-union</u>

Where is PFAS in the United States?

The number of sites identified¹⁵ as containing PFAS continue to grow in the United States. One analysis¹⁶ identified as many as 57,142 sites with PFAS in the United States alone, including nearly 50,000 industrial facilities, 4,200 wastewater treatment plants, nearly 4,000 military sites, and over 500 airports. Given the lack of comprehensive testing and data available to date, this is likely an underestimate.¹⁷ The tracking of PFAS¹⁸ continues to evolve, and government involvement will likely increase in the months and years ahead.

As the health effects become more widely known and the number of sites with identified PFAS contamination have increased, federal, state, and local governments are calling to ban, destroy, filter, clean, and remove these chemicals from military bases, clothing, cosmetics, drinking water systems, and many other areas.

Federal Action on PFAS

Environmental Protection Agency

The regulatory environment for PFAS at the federal level is robust, but in its infancy. Launched under the Biden Administration, the Environmental Protection Agency has developed a PFAS Strategic Roadmap¹⁹, including key commitments over the next few years. Broadly, those goals include researching, restricting, and remediating PFAS through a "whole-of-agency" approach.

On March 14, 2023, the Environmental Protection Agency (EPA) announced the proposed National Primary Drinking Water Regulation (NPDWR) for six types of PFAS, to create legally enforceable Maximum Contaminant Levels (MCLs) in drinking water. This will require public water systems to monitor and notify consumers of PFAS levels in their water, and, most importantly, require the reduction of PFAS levels in drinking water if more than the MCLs of 4 parts per trillion.

While the Superfund program is the most recent action taken by the EPA, several additional actions have been initiated or completed in the past year at the Agency:

- January 2023 proposed rule to prevent significant new use of estimated 300 PFAS sites that have been inactive²⁰
- Dec 2022 permitting memo on industrial wastewater and permitting rules to reduce PFAS discharge into waterways²¹
- Dec 2022 proposed rule to ensure PFAS users disclose on the Toxics Release Inventory²²

¹⁵ <u>https://www.ewg.org/interactive-maps/pfas_contamination/</u>

¹⁶ https://pubs.acs.org/doi/10.1021/acs.estlett.2c00502

¹⁷ <u>https://thehill.com/policy/equilibrium-sustainability/3684169-scientists-say-forever-chemicals-may-be-contaminating-57000-us-sites/</u>

¹⁸ <u>https://pfasproject.com/</u>

¹⁹ https://www.epa.gov/pfas/pfas-strategic-roadmap-epas-commitments-action-2021-2024

²⁰ <u>https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfas</u>

²¹ https://www.epa.gov/system/files/documents/2022-12/NPDES_PFAS_State%20Memo_December_2022.pdf

²² https://www.epa.gov/toxics-release-inventory-tri-program/changes-tri-reporting-requirements-and-polyfluoroalkyl

- Aug 2022 proposal to designate specific types of PFAS, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) as hazard substances under the Superfund law requiring cleanup (as previously mentioned)²³
- Dec 2021 rule expanding PFAS monitoring in drinking water²⁴
- Many other additional actions²⁵
- Tracking tool launched to find PFAS in communities across the nation²⁶

As the Agency undertakes regulatory action, through both the Inflation Reduction Act and Infrastructure Investment and Jobs Act, funding for existing and new programs has greatly increased, ranging from \$2 billion to address emerging contaminants in small or disadvantaged communities²⁷, to ongoing research²⁸, to \$750,000 in recent awards to improve the understanding of PFAS exposure. The largest source of funding, through the IIJA, includes \$50 billion to strengthen the nation's drinking water and wastewater systems, "the single largest investment in clean water that the federal government has ever made."²⁹ This funding is distributed through states, with flexibility to meet local needs.

Department of Defense

Given the large impact and quantities of PFAS on military bases, coupled with the reliable funding made available through the National Defense Authorization Act, the Department of Defense has a large role to play in identifying, removing, and cleaning PFAS contamination at its approximately 3,500 current or former sites.

The recent Defense Authorization Act requires the Department of Defense to identify critical uses of PFAS and report on efforts to buy items without PFOA and PFOS.³⁰ Additionally, the bill provides \$1.2 billion for cleaning up contaminated military sites and \$11 million for PFAS-related research.³¹

Congress

The Bipartisan Congressional PFAS Task Force brings together colleagues from both sides of the aisle and a broad geographic background.³² The Task Force was active in the previous session of Congress and is likely to reform for the 118th session of Congress. One accomplishment in the

 $^{^{23}\ \}underline{https://www.epa.gov/superfund/proposed-designation-perfluorooctanoic-acid-pfoa-and-perfluorooctanesulfonic-acid-pfos}$

²⁴ https://www.epa.gov/dwucmr/fifth-unregulated-contaminant-monitoring-rule

²⁵ <u>https://www.epa.gov/pfas/key-epa-actions-address-pfas</u>

²⁶ <u>https://echo.epa.gov/trends/pfas-tools</u>

²⁷ https://www.epa.gov/dwcapacity/emerging-contaminants-ec-small-or-disadvantaged-communities-grant-sdc#Imp

²⁸ <u>https://www.epa.gov/newsreleases/epa-awards-nearly-750000-funding-research-pfas-exposure-pathways</u>

²⁹ https://www.epa.gov/newsreleases/epa-releases-new-memo-outlining-strategy-equitably-deliver-clean-waterthrough

³⁰ https://debbiedingell.house.gov/news/documentsingle.aspx?DocumentID=3796

³¹ https://www.ewg.org/news-insights/news-release/2022/12/ewg-applauds-congress-tackling-forever-chemicalsnational

³² <u>https://www.legistorm.com/organization/summary/156486/Bipartisan_Congressional_PFAS_Task_Force.html</u>

previous session included passage of the PFAS Action Act in the U.S. House of Representatives, which was supported³³ by the Biden Administration but never passed the U.S. Senate. Additionally, Congress secured funding in the 2022 omnibus totaling \$2.76 billion for state revolving fund water programs, including 700 communities that bypassed the state revolving fund and were appropriated directly.³⁴ Calls for continued³⁵ and increased funding are bipartisan and consistent, providing a level of long-term certainty and durability to regulators and programmatic requests.

State Action on PFAS

While federal action and regulations are often laborious and time intensive processes which set a floor or threshold for PFAS levels and cleanup, many states have leapt ahead in regulating, suing, and funding PFAS related policies or companies. This analysis is not exhaustive but does illustrate the broad depth and direction of the action taken by state policymakers to address PFAS in their own jurisdictions.

New York passed an unprecedented \$2.5 billion Clean Water Infrastructure Act of 2017 to help communities upgrade aging drinking water and wastewater systems with modern filtration systems and support for the state Superfund program. Additionally, it requires the state to "determine any potential impacts from PFAS and/or other contaminants of concern on drinking water sources...and to provide recommendations for remediation and mitigation measures."³⁶ Recently, New York has moved to ban PFAS from clothing³⁷ and has some of the strictest rules of any state in the nation on safe levels of PFAS in drinking water.³⁸

Not to be outdone, California has banned PFAS in textiles and cosmetics.³⁹

In North Carolina, home of EPA Administrator Michael Regan, lawsuits have been filed against PFAS manufacturers.⁴⁰ The Administrator recently visited the state to suggest stronger water pollution limits should be updated in federal law.⁴¹

Michigan has a PFAS Action Response Team⁴², and is especially mindful of the harm pollutants can cause in drinking water, as happened with lead in Flint.

³³ https://www.whitehouse.gov/wp-content/uploads/2021/07/HR2467.SAP-Final.docx.pdf

³⁴ https://subscriber.politicopro.com/article/2022/12/earmarks-turn-water-infrastructure-funding-a-game-of-politicalpower-00075207?source=email ³⁵ <u>https://dankildee.house.gov/media/press-releases/reps-kildee-fitzpatrick-lead-new-bipartisan-push-funding-</u>

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³⁶ https://www.dec.ny.gov/chemical/108831.html

³⁷ https://spectrumlocalnews.com/nys/hudson-valley/ny-state-of-politics/2023/01/03/new-york-moves-to-ban-pfas-<u>chemicals-from-clothes</u> ³⁸ <u>https://www.health.ny.gov/environmental/water/drinking/docs/water_supplier_fact_sheet_new_mcls.pdf</u>

³⁹ https://www.morganlewis.com/pubs/2022/10/california-bans-pfas-in-textiles-cosmetics-but-governor-vetoesreporting-requirement

⁴⁰ https://www.northcarolinahealthnews.org/2022/11/01/pfas-evidence-is-piling-up-and-putting-polluters-onnotice/ ⁴¹ https://www.charlotteobserver.com/news/politics-

government/article272471721.html?taid=63eacf0fbe05cf000178ae01&utm campaign=trueanthem&utm medium=t rueanthem&utm source=twitter

⁴² https://www.michigan.gov/pfasresponse

Colorado has a PFAS grant funding program to sample, assist, and build infrastructure for communities impacted by PFAS.43

Several other states have advanced, adopted, or initiated their own PFAS actions, especially in drinking water regulation and safety. Additionally, municipal drinking water utilities are collecting and sharing PFAS levels in their systems.⁴⁴

Nonprofit & Private Entities

Nonprofits tracking PFAS use in products are considering "PFAS-free" labels to combat misinformation and false advertising campaigns.⁴⁵

Regulations and funding programs in both the public and private sectors will result in continuing emphasis on PFAS reduction, removal, and destruction at the federal, state, and local levels. The PFAS market alone is estimated to total over \$6 billion in the next decade, just in the United States.⁴⁶ The broader environmental remediation market is expected to be nearly \$110 billion in 2022.⁴⁷ Investors with over \$8 trillion in assets are urging the phase out of forever chemicals in new products by manufacturers. Lawsuits targeting these chemical producers are surging and are expected to cost over \$30 billion. The Toxic Substances Control Act and other regulations will likely require manufacturers to disclose their use of PFAS in manufactured goods⁴⁸, creating even more transparency and pressure to regulate and limit the use of forever chemicals.

Municipal water providers, manufactures, military sites, and other industries will need technology solutions that are able to meaningfully remove PFAS at a low-cost, scalable, low-energy process, and with minimal leftover waste.

Common Removal Techniques

There are several techniques commonly used to remove PFAS from water. These techniques can be used individually or in combination, depending on the type and concentration of PFAS compounds present in the water. The selection of a particular technique will depend on factors such as the cost, efficiency, and practicality of the method for a specific application.

Adsorption

Adsorption is a process in which molecules, ions, or particles adhere to the surface of a solid or liquid, forming a thin film or layer. This process occurs when the molecules or particles in a gas or liquid come into contact with a surface, and the attractive forces between the surface and the molecules cause them to adhere to the surface. The surface to which the molecules adhere is

⁴³ https://www.riograndecounty.org/news/county-announcements/item/484-pfas-grant-program-is-open-andaccepting-applications

⁴⁴ https://www.owasa.org/pfas-monitoring-program/

⁴⁵ https://www.ewg.org/withoutintentionallyaddedpfaspfc

⁴⁶ https://www.bluefieldresearch.com/ns/us6-15-billion-pfas-remediation-forecast-underpinned-by-changing-

regulatory-environment/ 47 https://www.prnewswire.com/news-releases/environmental-remediation-market-worth-163-4-billion-by-2027-exclusive-report-by-marketsandmarkets-301642595.html ⁴⁸ https://www.bakerlaw.com/alerts/pfas-reporting-obligations-2023-key-issues-considerations

typically a solid material, referred to as the adsorbent, which can be in the form of a powder, a granule, or a porous material.

Adsorption is different from absorption, which is the process of a substance being absorbed into another substance. In adsorption, the substance being adsorbed remains on the surface of the adsorbent material. The amount of adsorption depends on factors such as the surface area of the adsorbent material, the strength of the attractive forces between the adsorbent and the substance being adsorbed, and the concentration of the substance in the surrounding gas or liquid.

Adsorption has many applications in industry and technology, including the removal of pollutants from air and water, the purification of gases, and the separation of chemicals in chromatography. Adsorption is also used in consumer products, such as water filters, air purifiers, and odor eliminators, to remove impurities and improve the quality of the product.

Activated Carbon

Granular activated carbon (GAC) is a highly available and commonly used technology that is often considered for the attempted removal of PFAS.⁴⁹

Activated carbon is a widely used adsorbent that can be used to remove PFAS from water. The activated carbon is made from organic materials, such as coconut shells or wood, that have been treated with heat and oxygen to create a highly porous material with a large surface area. This porous structure allows the activated carbon to adsorb a wide range of contaminants, including PFAS.

In the case of PFAS removal, the activated carbon works by attracting and binding the PFAS molecules to its surface through adsorption. The PFAS molecules are attracted to the activated carbon's surface due to their hydrophobic (water repelling) nature and strong interactions with the carbon's surface. As the water passes through the activated carbon bed, the PFAS molecules are adsorbed onto the surface of the carbon, effectively removing them from the water.

Activated carbon is a popular choice for PFAS removal due to its low cost and ease of use. However, it has limitations, such as a limited capacity for PFAS adsorption, large volumes of material required, and the need for regular replacement or regeneration. Despite these limitations, activated carbon is used in various settings, including drinking water treatment, industrial wastewater treatment, and groundwater remediation.

Most studies characterizing PFAS absorption to GAC are performed in small laboratory scale experiments, which do not correlate well to larger scale, real world conditions.⁵⁰ A few pilot-scale studies have demonstrated that GAC is not likely an efficient or cost effective option for the removal of PFAS from drinking water. GAC solutions have a large amount of variation, and while virgin GAC beds work effectively at the onset, their performance can quickly degrade and often

⁴⁹ Liu, C. J., Werner, D., & Bellona, C. (2019). Removal of per-and polyfluoroalkyl substances (PFASs) from contaminated groundwater using granular activated carbon: a pilot-scale study with breakthrough modeling. *Environmental Science: Water Research & Technology*, *5*(11), 1844-1853.

⁵⁰ Rodowa, A. E., Knappe, D. R., Chiang, S. Y. D., Pohlmann, D., Varley, C., Bodour, A., & Field, J. A. (2020). Pilot scale removal of per-and polyfluoroalkyl substances and precursors from AFFF-impacted groundwater by granular activated carbon. *Environmental Science: Water Research & Technology*, 6(4), 1083-1094.

removes less than 10% of PFAS pollutants after a short period of time. Additionally, GAC materials do not work as well for shorter chained PFAS.⁵¹

GAC filter beds must be removed and replaced or regenerated when GAC capacity is exhausted. This creates additional waste collection/remediation challenges due to the large amount of GAC required for water treatment facilities. For example, a GAC solution for the Sweeny Water Treatment Facility in Wilmington North Carolina utilizes three million pounds of GAC that must be replaced every nine months.

Ion Exchange Treatment

Ion exchange is another method for PFAS removal. It is commonly used in industrial applications and water treatment facilities.⁵² In this process, contaminated water is passed through a bed of resins made of highly porous, polymeric material that is acid, base, and water insoluble. These tiny polystyrene beads are made from hydrocarbons, have been modified with functional groups (e.g., sulfonic, or carboxylic acid), and act like tiny powerful magnets to attract and trap contaminated materials.

There are two broad categories of ion exchange resins: cationic and anionic. The negatively charged cationic exchange resins (CER) are effective for removing positively charged contaminants while positively charged anion exchange resins (AER) are effective for removing negatively charged contaminants, like PFAS. The negatively charged PFAS molecules are attracted to the positively charged functional groups on the resin, bind to them, and are effectively removed from the water. Like GAC, AER can remove more than 90% of the PFAS when the materials are new but degrade over time. Their efficiency is also highly dependent on the choice of resin, bed depth, flow rate, and which PFAS compounds need to be removed.

AER has been shown to have a high capacity for many PFAS but is typically more expensive than GAC. Perhaps the most promising AER is a single use mode followed by incineration. Over time, AERs become saturated and must be replaced or regenerated. Regeneration uses a strong salt solution to displace the PFAS molecules from the resin, leaving the resulting water purified and free of PFAS, making it safe for human consumption and other uses. The AER materials create additional PFAS contaminated waste that must be collected and/or remediated. This often requires transportation from the treatment site to a qualified incinerator. This presents challenges due to the large mass of AER required for water treatment facilities.⁵³

Filtration

High-pressure membranes, such as nanofiltration or reverse osmosis, can remove PFAS. This procedure works by applying pressure to the water, forcing it through a membrane, and allowing only water molecules to pass through. The result is that a wide range of contaminants are removed,

⁵¹ Belkouteb, N., Franke, V., McCleaf, P., Köhler, S., & Ahrens, L. (2020). Removal of per-and polyfluoroalkyl substances (PFASs) in a full-scale drinking water treatment plant: Long-term performance of granular activated carbon (GAC) and influence of flow-rate. *Water Research*, *182*, 115913.

⁵² https://www.epa.gov/sciencematters/reducing-pfas-drinking-water-treatment-technologies

⁵³ https://www.epa.gov/sciencematters/reducing-pfas-drinking-water-treatment-technologies

including PFAS. This technology depends on membrane permeability, with tighter membranes in reverse osmosis than nanofiltration.

Reverse Osmosis

Reverse osmosis (RO) is a water treatment process that uses a semi-permeable membrane to remove impurities from water. In PFAS removal, the RO process traps the PFAS molecules, which are relatively large and cannot pass through the small pores, forming a layer of contaminants that can be removed periodically through a cleaning process.⁵⁴ The resulting water that passes through the membrane is purified and free of PFAS, making it safe for human consumption or other uses. Reverse osmosis has proven to be an effective method for removing PFAS from water and is increasingly used in water treatment facilities and other applications where water quality is critical.

Nanofiltration

Nanofiltration is a water treatment process that uses a semi-permeable membrane with a pore size of 1-10 nanometers to remove contaminants from water. During nanofiltration, contaminants are prevented from passing through based on their size and charge. Nanofiltration has been shown to be an effective method for removing PFAS from water, as it can remove PFAS compounds with molecular weights ranging from 500 to 1000 Dalton. It has also been shown to be more cost-effective than some other methods, such as reverse osmosis. However, nanofiltration has some limitations, such as the need for pre-treatment to remove suspended solids and the potential for membrane fouling. Additionally, some PFAS compounds, such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), may be more difficult to remove using nanofiltration due to their high stability and low molecular weight.

Research shows that both RO and nanofiltration are typically more than 90% effective at removing a wide range of PFAS, including shorter chain PFAS. In both types, approximately 80% of the feedwater (the water coming into the membrane) passes through the membrane to the effluent (treated water). Approximately 20% of the feedwater is retained as a highly concentrated waste. This can be difficult to treat or dispose, especially for PFAS.⁵⁵ Membrane separation processes require a large amount of energy and produce a large amount of highly concentrated waste and are likely not candidates for large scale PFAS removal.⁵⁶ This technology may best suited for home use, since the volume of water being treated is much smaller and the waste stream could be disposed of more easily with less cause for concern.⁵⁷

⁵⁴ Gude, V. G. (2011). Energy consumption and recovery in reverse osmosis. *Desalination and water treatment*, *36*(1-3), 239-260.

⁵⁵ Crone, B. C., Speth, T. F., Wahman, D. G., Smith, S. J., Abulikemu, G., Kleiner, E. J., & Pressman, J. G. (2019). Occurrence of per-and polyfluoroalkyl substances (PFAS) in source water and their treatment in drinking water. *Critical reviews in environmental science and technology*, *49*(24), 2359-2396.

⁵⁶ Robey, N. M., da Silva, B. F., Annable, M. D., Townsend, T. G., & Bowden, J. A. (2020). Concentrating per-and polyfluoroalkyl substances (PFAS) in municipal solid waste landfill leachate using foam separation. *Environmental Science & Technology*, 54(19), 12550-12559.

⁵⁷ Ross, I., McDonough, J., Miles, J., Storch, P., Thelakkat Kochunarayanan, P., Kalve, E., ... & Burdick, J. (2018). A review of emerging technologies for remediation of PFASs. *Remediation Journal*, 28(2), 101-126.

Emerging Technologies

Emerging technologies and materials offer new approaches for the removal of PFAS from water, with the potential to overcome the limitations of existing methods. However, further research is needed to optimize performance and scale for practical applications. One of the most promising new materials for the removal of PFAS is the family of boron nitride materials.

Boron Nitride Materials

Boron nitride (BN) based materials are a group of advanced materials composed of boron and nitrogen atoms. They exist in several crystal structures, including hexagonal boron nitride (h-BN) and cubic boron nitride (c-BN).

These materials and their composites have been tested in water purification methods given their unique structural and chemical properties (i.e., high surface area, structural defects, presence of functional groups) that enhance the interaction of pollutant molecules with the surface of BN materials. They have shown promise as an adsorbent for removing PFAS from water. In particular, hexagonal boron nitride (h-BN) has been studied for its high surface area and chemical stability, which make it an effective adsorbent for a range of contaminants.⁵⁸

Several studies have demonstrated that BN-based materials are preferable candidates for the adsorption of pollutants due to their porous structure, numerous structural defects, and the presence of ionic B-N bonds with "lop-sided" densities properties. BN-based materials with polar B-N bonds have more affinity for the adsorption of heavy metal ions, as compared to the carbon-based adsorbents. Furthermore, the coexisted basic sites (N atom) and Lewis acidic sites (B atom) play a vital role in the uptake of pollutants.⁵⁹

One approach for h-BN PFAS removal is to modify the material's surface with functional groups that have an affinity for PFAS compounds. For example, researchers have functionalized h-BN with carboxylic acid or amine groups, which can form hydrogen bonds with PFAS compounds and improve the adsorption capacity of the material.

Another approach is to use h-BN as a component of a composite material for PFAS removal. For example, h-BN can be incorporated into a polymer matrix to create a composite membrane that can selectively adsorb PFAS compounds from water. This approach has the advantage of combining the high adsorption capacity of h-BN with the mechanical strength and durability of the polymer matrix.

Overall, boron nitride materials show promise as a new class of adsorbents for PFAS removal, with the potential to overcome some of the limitations of existing methods, such as high cost and low adsorption capacity. However, further research is needed to optimize the performance of these materials for practical applications.

Boron Nitride Nanomaterials

⁵⁸ Xiong, Jun, et al. "Hexagonal boron nitride adsorbent: Synthesis, performance tailoring and applications." *Journal of Energy Chemistry* 40 (2020): 99-111.

⁵⁹ Ihsanullah, I. (2021). Boron nitride-based materials for water purification: Progress and outlook. *Chemosphere*, 263, 127970.

Boron nitride nanomaterials can adsorb a wide range of contaminants such as heavy metals, dyes, antibiotics, and organic compounds from aqueous medium and PFAS. They offer several advantages over other materials for water purification applications:

- **High surface area**: Nanomaterials have a very high surface area to volume ratio, which allows them to interact more efficiently with pollutants in water. This means a smaller amount of nanomaterial is needed to achieve the same level of purification as larger particles or materials.
- Enhanced reactivity: Nanomaterials exhibit enhanced reactivity due to their high surface area, which allows for faster reaction rates and more efficient removal of pollutants. This can be particularly important for removing contaminants that are present at low concentrations in water.
- Selectivity: Nanomaterials can be engineered to have specific surface properties that allow them to selectively remove certain contaminants from water while leaving other important minerals and nutrients in the water.
- **Cost-effective**: While nanomaterials may be more expensive to produce than other materials, their high reactivity and selectivity can make them more cost-effective in the long run. This is because they can remove pollutants more efficiently, while requiring less material and energy to achieve the same purification level.

Recent advances suggest many of the issues involving water quality could be resolved or greatly ameliorated using nanoparticles, nanofiltration, or other products leveraging nanotechnology.⁶⁰ Various structural configurations of BN nanomaterials, such as boron nitride nanotubes, have been explored in water treatment applications.

Boron Nitride Nanotubes

Boron nitride nanotubes are a nanomaterial that are structurally similar to carbon nanotubes but are composed of boron and nitrogen atoms arranged in a tubular structure. They were first discovered in 1995 by researchers at the University of Oxford and have since gained attention for their unique physical and chemical properties.

Like carbon nanotubes, boron nitride nanotubes have a cylindrical structure, but their properties are different due to their different atomic composition. Boron nitride nanotubes are electrically insulating and have high thermal conductivity, making them an attractive material for applications where electrical insulation and heat dissipation are critical.

Boron nitride nanotubes also have exceptional mechanical properties, including high strength and flexibility, which make them an excellent material for reinforcement in composite materials. Additionally, they are biocompatible, which makes them a promising material for biomedical applications such as drug delivery and tissue engineering.

⁶⁰ Narayan, R. (2010). Use of nanomaterials in water purification. *Materials Today*, 13(6), 44-46.

Overall, boron nitride nanomaterials are promising given that their unique properties make them suitable for a wide range of applications in areas such as electronics, energy, and medicine. However, further research is needed to fully understand their properties and potential applications.

Boron Nitride NanoBarbsTM

Boron Nitride NanoBarbs[™] (BNNB) are a unique and patented morphology of a boron nitride nanotube. They are boron nitride nanotubes enhanced with hexagonal boron nitride (h-BN) crystals nucleated on the boron nitride nanotubes. The h-BN on the boron nitride nanotube creates an irregular surface serving to (1) limit agglomeration by maintaining sufficient distances between surfaces limiting van der Waals attraction between particles and (2) increase matrix interface interaction by acting as mechanical barbs while maintaining the B-N polarity.

Boron Nitride NanoBarbsTM are produced exclusively by BNNano and they have been proven more effective than boron nitride nanotubes at adsorbing PFAS.

BNNano - Proposed Solution Overview

BNNano uses state of the art materials science technology combined with UV energy to remediate PFAS. The two key steps to the full remediation of PFAS are to first capture and then destroy. Boron Nitride materials first capture PFAS molecules through adsorption, then catalytically assist the PFAS destruction in conjunction with UV energy. This photocatalytic process breaks the PFAS molecules down to fluoride, carbon dioxide, and hydrogen, eliminating the waste stream associated with other PFAS remediation technologies.

BNNano's initial work has been designed to mimic a holding tank for wastewater treatment. Holding tanks, also known as equalization tanks, are an essential component of wastewater treatment plants. They are designed to temporarily receive and store wastewater before it is treated to ensure a steady flow of wastewater to the treatment process. The process of treating wastewater in holding tanks is made up of a few steps.

- 1) **Receiving wastewater**: Wastewater from homes, businesses, and industries is collected and transported to the wastewater treatment plant via pipes. Once the wastewater arrives at the treatment plant, it is directed to the equalization tank. The equalization tank is a large tank designed to hold the incoming wastewater and equalize its flow over time. The tank provides a buffer for the wastewater treatment process, ensuring a consistent and steady flow of wastewater to the subsequent treatment process.
- 2) **Monitoring**: The wastewater in the equalization tank is continuously monitored for various parameters such as pH, temperature, and flow rate to ensure it meets the treatment plant's design criteria.
- 3) **Treatment process**: From the equalization tank, the wastewater flows to the subsequent treatment processes. The wastewater is first screened to remove large debris and then undergoes primary treatment, secondary treatment, and disinfection. During these processes, contaminants are removed from the wastewater to make it safe for discharge into the environment.

- 4) **NanoBarbTM treatment** would be incorporated after these primary contaminants are removed.
- 5) **Discharge**: After the wastewater is treated, it is discharged into the environment. In some cases, treated wastewater is reused for non-potable purposes such as irrigation, industrial processes, and toilet flushing.

Destruction of PFAS Pollutants via UV Energy (Photocatalytic Degradation)

Photocatalytic degradation of pollutants is a process that utilizes light energy to promote the chemical breakdown of pollutants in water or air. The process typically involves the use of a photocatalyst, which is a material that can absorb light and generate electron-hole pairs that react with pollutants to break them down into less harmful substances.

The photocatalytic degradation process is initiated when the photocatalyst absorbs light energy from a light source, such as the sun or a lamp. The energy is then transferred to the photocatalyst's electrons, which become excited and create electron-hole pairs. These electron-hole pairs can then interact with water or oxygen molecules in the environment to produce reactive oxygen species, such as hydroxyl radicals or superoxide ions, which can react with organic pollutants to break them down into simpler, less harmful compounds.

One common photocatalyst used for this process is titanium dioxide (TiO2), which is an inexpensive and widely available material that can be easily activated by UV light. Other photocatalysts used for photocatalytic degradation include zinc oxide (ZnO), iron oxide (Fe2O3), and tungsten trioxide (WO3).

Photocatalytic degradation of pollutants is a promising method for environmental remediation, as it offers a low-cost and environmentally friendly approach for the removal of pollutants from air and water. It has been successfully used for the treatment of a wide range of pollutants, including organic dyes, pesticides, and pharmaceuticals, and has potential for use in large-scale applications, such as wastewater treatment and air purification.

One study demonstrated the use of photocatalytic degradation to remove PFAS from water using a TiO2-based photocatalyst.⁶¹ The study found that under UV irradiation, the photocatalyst could effectively degrade PFAS compounds, breaking them down into simpler, less harmful compounds.

Other studies have also investigated the use of different photocatalysts, such as BiOBr and Bi2WO6, for the removal of PFAS from water.⁶² These photocatalysts have been shown to generate reactive oxygen species that can break down PFAS compounds into less harmful products.

BN-based materials have also demonstrated photocatalytic degradation of PFAS.

⁶¹ Lashuk, B., Pineda, M., AbuBakr, S., Boffito, D., & Yargeau, V. (2022). Application of photocatalytic ozonation with a WO3/TiO2 catalyst for PFAS removal under UVA/visible light. *Science of The Total Environment*, 843, 157006.

⁶² Liu, X., Duan, X., Bao, T., Hao, D., Chen, Z., Wei, W., ... & Ni, B. J. (2022). High-performance photocatalytic decomposition of PFOA by BiOX/TiO2 heterojunctions: Self-induced inner electric fields and band alignment. *Journal of Hazardous Materials*, 430, 128195.

Current Progress/Developments

To prove the efficacy of using Boron Nitride NanoBarbsTM to capture and destroy PFAS, a laboratory scale experiment was executed by mixing a known PFOA standard in deionized water. The water and PFOA mixture were formulated with contaminate concentration similar to what is found in drinking water in the United States.

Boron Nitride NanoBarbsTM were mixed into the contaminated water and analysis samples were taken at time intervals to measure the amount of PFOA that was removed (adsorbed) by the NanoBarbTM.

This laboratory scale experiment was designed to be a representative process that is similar to a standard holding tank water treatment system. In these experiments, the Boron Nitride NanoBarbsTM demonstrated that they remove 15% of the PFOA in 60 minutes and up to 25% removal in 120 minutes.



Graph 1 shows the amount of PFOA removed over time.

Graph1: PFOA Removed versus time, NO UV

To prove the efficacy of using Boron Nitride NanoBarbsTM combined with UV energy to capture and destroy PFAS, a laboratory scale experiment was executed by mixing a known PFOA standard in deionized water. The water and PFOA mixture was formulated with contaminate concentration similar to what is found in drinking water in the United States.

Boron Nitride NanoBarbsTM were mixed into the contaminated water while being exposed to UV energy. Samples were taken at time intervals to measure the amount of PFOA that were removed (adsorbed) and destroyed by the NanoBarbTM.

This laboratory scale experiment was designed to be a representative process that is similar to a standard holding tank water treatment system. In these experiments the Boron Nitride NanoBarbsTM demonstrated that they remove and destroy 90% of the PFOA in 60 minutes and up to 99.5% removal in 120 minutes.

Graph 2 shows the amount of PFOA removed over time.



Graph 2: PFOA Removed versus time, WITH UV

The simulated holding tank experiments demonstrated two important results:

- Boron Nitride NanoBarbs[™] are effective at removing PFAS by adsorption. The results prove that Boron Nitride NanoBarbs[™] can be used to develop filters and materials for the successful removal of PFAS from water supplies.
- 2) Boron Nitride NanoBarbsTM combined with UV energy is effective for the complete removal and destruction of PFAS contaminants. The results prove that Boron Nitride NanoBarbsTM can be used in combination with UV energy to develop systems that can be implemented in:
 - a. Industrial processes for the destruction of PFAS prior to the discharge of wastewater into public water supplies. Filters and materials can be used for the successful removal of PFAS from water supplies.
 - b. Municipality water systems for the removal and destruction of PFAS from public water supplies.
 - c. Remediation solutions for cleanup of spill and contaminated sites.

Next Steps

Material Development

The success of BNNano's initial laboratory experiments leads directly into the integration of Boron Nitride NanoBarbsTM into other materials, such as adsorption materials and composite materials (e.g., porous ceramic materials, thin film composite membranes, and polymer membranes).

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Boron Nitride NanoBarbTM Composite Materials

Nanocomposites are materials (ceramics, metals, polymers) in which discrete nanomaterials have been added. They enable the properties of the nanomaterial to be leveraged at micro and macro scales. In water purification, filters are commonly constructed from nonwoven fabric that consists of staple and long fibers bonded by chemical, heat, or solvent treatment. Examples include coffee filters, oil filters, and tea bags. Nonwoven water filters produced from nanocomposite NanoBarbsTM fibers would provide an effective form for drop in use to many existing filtration systems.

Combining Boron Nitride NanoBarbs[™] with materials commonly used for filtration applications will transform these common materials into composite materials that will become simple and cost-effective materials to remove PFAS from water.

Product Development

Consumer/Home Use

The marketplace for water filters for consumer use is growing rapidly, driven by increasing concerns over water quality and the potential health risks associated with contaminants in drinking water. Consumers are becoming more aware of the potential presence of harmful chemicals, bacteria, and other pollutants in their tap water, and are seeking ways to ensure that their drinking water is safe and healthy.

BNNano's product development for home use water filters includes filters that can be used in a simple pitchers, under-sink, appliance, and countertop filtration systems.



BNNano Consumer/Home Use Products

Municipality and Industrial Water Treatment

The US marketplace for municipal water treatment plants, essential for ensuring access to safe and clean drinking water, consists of small (25-500 population served) to very large (>100,000) community systems as seen in Table 1.⁶³

⁶³ https://www.epa.gov/ground-water-and-drinking-water/drinking-water-performance-and-results-report

System Size (population served)	Number of CWSs	Population Served (millions)	% of CWSs	% of US Pop Served by CWSs
Very Small (25-500)	26,897	4.6	54.1%	1.4%
Small (501-3,300)	13,321	19.2	26.8%	6.1%
Medium (3,301-10,000)	5,010	29.5	10.1%	9.3%
Large (10,001-100,000)	4,005	115.6	8.1%	36.5%
Very Large (>100,000)	447	147.6	0.9%	46.7%
Total	49,680	316.4	100%	100%

Table 1: US Community Water System Sizes

Industrial sites will now need to ensure effluent, and wastewater is monitored and treated for PFAS as well. The EPA has issued the memo "Addressing PFAS Discharges in NPDES Permits and Through the Pretreatment Programs." In the memo, the EPA recommends states address PFAS under the National Pollutant Discharge Elimination System (NPDES) permitting specifically for industry categories to include organic chemicals, plastics & synthetic fibers (OCPSF); metal finishing; electroplating; electric and electronic components; landfills; pulp, paper & paperboard; leather tanning & finishing; plastics molding & forming; textile mills; paint formulating, and airports. Also included is the recommendation for effluent and wastewater residuals monitoring for 40 PFAS compounds conducted on at least a quarterly basis.⁶⁴

BNNano's products and technology is readily scalable and modular, enabling the removal and destruction of PFAS in the wide-ranging water treatment plants currently in place in the United States and worldwide.

Expeditionary Remediation

The marketplace for water remediation to clean up chemical spills is a specialized industry that provides essential solutions for addressing environmental contamination caused by spills of hazardous chemicals and other pollutants. The market includes a wide range of products and services, from emergency response teams and specialized equipment to sophisticated treatment processes designed to remove pollutants from water sources.

One of the key drivers of the water remediation market is the increasing incidence of chemical spills and other forms of environmental contamination, particularly in industries such as oil and gas, transportation, and manufacturing. As public awareness of the risks associated with environmental contamination grows, the demand for effective water remediation solutions that can restore contaminated water sources and protect public health and the environment is becoming more critical.

In terms of technology, the market for water remediation is characterized by a wide range of treatment processes and technologies, including physical, chemical, and biological processes. Some of the most common technologies used in water remediation include activated carbon filtration, reverse osmosis, and advanced oxidation processes.

⁶⁴ https://www.epa.gov/newsreleases/epa-issues-guidance-states-reduce-harmful-pfas-pollution

Summary

PFAS or per- and polyfluoroalkyl substances are "Man-made chemicals that have been used in industry and consumer products worldwide since the 1940s." These chemicals have adverse health effects which have become more widely known including decreased fertility, developmental delays in children, increased risk of cancers, reduce immunology, inability to properly regulate hormones, increased levels of obesity, and more.⁶⁵ The number of sites with identified PFAS contamination have increased, federal, state, and local governments are calling to ban, destroy, filter, clean, and remove these chemicals from military bases, clothing, cosmetics, drinking water systems, and many other areas.

Multiple actions are being initiated to regulate and remove PFAS. Between the EPA, Department of Defense, Congress, individual State actions, nonprofit organizations, and private entities there is no organization untouched by the impact these forever chemicals have, specifically on water treatment. Numerous methods exist for removal of PFAS from the water supply from activated charcoal filtration ion-exchange adsorption to reverse osmosis filtration and nanofiltration. These current technologies provide the ability to remove PFAS from the water supply, however, they have limited ability to provide long-term removal with little to no ability to destroy PFAS.

Emerging technologies and new materials offer exciting alternatives that not only filter or remove PFAS, but also destroy in the process. Boron Nitride NanoBarbsTM, in combination with UV light, demonstrate great potential to remove and destroy PFAS in a low-cost and low-energy manner. Initial studies show significant PFAS reduction when utilizing the patented Boron Nitride NanoBarbsTM technology to filter contaminated water. With the combination of Boron Nitride NanoBarbsTM and UV energy, the data shows destruction of PFAS altogether, proving a powerful tool that will have significant impact to the lives of people and communities worldwide.

For additional information please contact BNNano at info@bnnano.com

⁶⁵ <u>https://www.epa.gov/pfas/our-current-understanding-human-health-and-environmental-risks-pfas</u>