Review

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Review

Recent Advancements in Per- and Polyfluoroalkyl Substances (PFAS) Detection by Sensors and Surface-Enhanced Raman Scattering (SERS) Method: A Review

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ABSTRACT: Per- and polyfluoroalkyl substances (PFAS), a large group of developing contaminants, have recently become the subject of increased concern due to their potentially hazardous effects. They are classified as poisonous substances that can be found in a variety of aquatic situations. The widespread usage of PFAS across numerous industries has resulted in a high environmental and biological accumulation of the substance. Identification and elimination of PFAS from the environment is crucial since they are tenacious and have the potential to cause cancer. Traditional methods of PFAS content assessment, while useful in some cases, are often inadequate for continuing environmental control and monitoring. Within academia, there is a noticeable desire for rapid, cost-effective, durable, and readily transportable techniques targeted at detecting PFAS compounds in field settings. As a result, environmental labs and other governmental and non-governmental bodies may start testing more often as mandated by legislation. PFAS-detecting sensors, which offer an innovative solution that can be applied in situ and is affordable and simple to use, have emerged as a promising method for assessment based on the existing research. In addition, it may give administrators and users of water worldwide useful information they can use. This article provides a thorough summary of recent developments, limitations, and performance considerations in PFAS detection sensors. The Surface-enhanced Raman scattering (SERS) method has also been covered because of its excellent sensitivity and specificity for detecting pollutants, making it a potential solution for sensing PFAS. Intelligent sensing systems for PFAS detection should benefit from this research.

Keywords: Per- and polyfluoroalkyl substances; PFAS detection sensors; surface-enhanced raman scattering; emerging contaminants

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1. INTRODUCTION

Perfluorocarbons, affectionately known as the elusive perfluorinated compounds (PFCs), dance within the realm of molecules, donning a mysterious allure akin to their counterparts, the PFASs. These molecular maestros, with shared traits and clandestine chemistry, weave a tale of intrigue in the scientific symphony [1,2]. Despite these similarities, PFCs exhibit fundamental differences from PFASs. Unlike PFAS compounds, PFCs consist solely of carbon and fluorine atoms, with the absence of oxygen, hydrogen, sulfur, and nitrogen atoms [3,4]. The inception of PFASs dates back to 1950, and they are entirely synthetic in nature [1,5–7]. These compounds consist of at least one perfluoroalkyl group (C_nF_{2n+1}) linked to a hydrophilic head group [8–10]. Approximately 4,700 distinct PFAS have already been registered in the global market, with nearly 4,000 of them identified in diverse matrices [11]. The significant chemical structures of PFAS are illustrated in Figure 1.

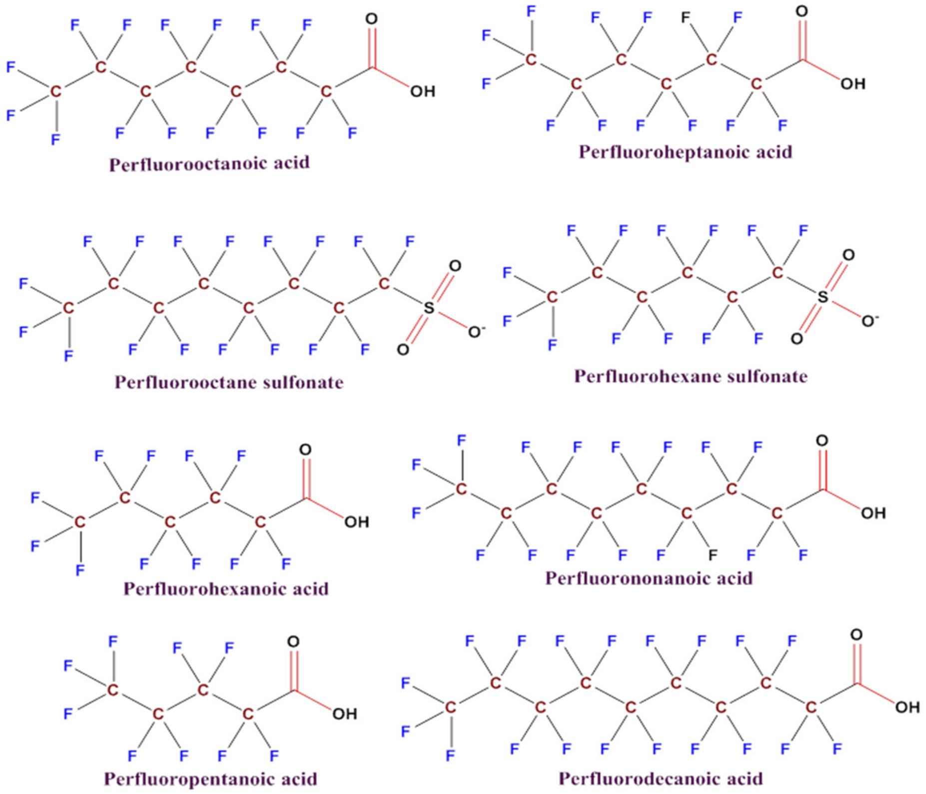

Figure 1. Chemical composition of perfluorinated [12].

Across a historical expanse exceeding six and a half decades, the intricate craft of producing PFASs for commercial purposes has unfolded through the adept utilization of two principal methodologies: the rigorous Electrochemical Fluorination and the meticulous artistry of Telomerization. These stalwart methods have stood the test of time, contributing to the nuanced legacy of PFAS manufacturing [1,13,14]. Electrochemical fluorination was stopped in 2002 due to the large amount of branched-chain PFAS it produced. Within the scholarly realm, the venerable electrochemical telomerization, an alchemical symphony orchestrating the generation of fluorotelomer alcohols, emerges as the preeminent method in the illustrious craft of PFAS production. Its widespread adoption attests to its prominence, casting an academic spotlight on the nuanced processes underlying the intricate world of per- and polyfluoroalkyl substances. Linear fluorinated molecules with an even number of fluorine atoms are often the result of telomerization [15]. Coated with PFAS, nonstick cookware and fast-food packaging (including pizza boxes and popcorn bags) can withstand both water and oil [16]. Pharmaceuticals, personal care items, cosmetics, and medical equipment are just a few of the many industries that use PFAS [17,18]. Fluorotelomer alcohol molecules in commercial items, poor treatment of industrial wastewater, or precursor degradation discharge PFAS into the environment [19]. In daily life, water, air, food, and everyday items intertwine to introduce individuals to the enigmatic compounds of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) [20].

Reducing pollution from sources like PFAS necessitates effective waste management and recycling programs [21–24]. The release of substances containing PFAS into the environment can be avoided through the implementation of effective waste management practices [24]. Realizing that PFAS could be in recycling streams highlights the need to implement responsible waste recycling strategies to reduce environmental contamination [22,25–30]. Efficient wastewater cotreatment of Dissolved Organic Nitrogen (DON) and PFAS becomes a linchpin in preventing environmental contamination [31–33]. Responsible waste recycling strategies act as guardians, averting the inadvertent release of PFAS into recycling streams and reinforcing the commitment to effective waste management practices [33]. Comprehensive PFAS management strategies are necessary because effective sanitation and hygiene practices are critical for minimizing the spread of contaminants [34–37]. Artificial intelligence (AI) can also optimize sorting processes and identify possible sources of PFAS contamination, which can improve the efficiency of PFAS management systems [38–42]. AI-powered waste treatment and environmental monitoring systems help take preventative actions against PFAS exposure [38].

Research on the toxicological consequences of PFASs has shown that these chemicals can have a wide variety of negative effects, such as on the immune system, reproductive system (both during embryonic and postnatal development), liver health, developmental processes, and the endocrine system [43]. In a global regulation, Germany, the US, and Canada harmonize efforts to restrict PFOA and PFOS in drinking water. Their shared pursuit transcends limitations, aiming to diminish both the production and consumption of these compounds [44]. In the potable water systems, the United States Environmental Protection Agency (EPA) has issued a sovereign decree, limiting PFOA and PFOS to a mere 0.07 ng/L [45]. This regulatory vigilance ensures the sanctity of our life-sustaining elixirs. Consequently, health departments and regulatory organizations monitor PFAS traces [46]. The health concerns posed by PFOA and PFOS can be felt even at nanomolar amounts [47]. Therefore, sensitive detection techniques or equipment are required for these PFAS. Various precise and sensitive analytical procedures are available. Some of the problems with analytical procedures are the time and effort needed to prepare samples, the high expenses of operations, the necessity for trained individuals to evaluate and interpret the results, and the fact that they aren't applicable in real-world scenarios[48]. Therefore, it is essential to create unique sample preparation and quick detection techniques.

Limitations in sensitivity and the need for labor-intensive processes are some of the problems with current technologies for PFAS detection. The improved sensitivity, selectivity, stability, adaptability, and non-destructive properties of SERS make it an attractive method for PFAS detection. By overcoming the drawbacks of current PFAS detection techniques, SERS has the potential to transform PFAS detection and make a substantial contribution to our knowledge of these persistent environmental pollutants. Future directions for research include creating new SERS substrates with improved PFAS sensitivity and selectivity, incorporating SERS sensors into field-based portable devices, increasing the range of PFAS compounds that can be detected with SERS, and using SERS for environmental monitoring and analysis in the real world [49].

2. CURRENT PFAS DETECTION METHODS

2.1. PFAS Sample Preparation and Extraction

Preparing, cleaning, and concentrating samples for PFAS detection can be somewhat challenging because to their complicated matrices and limited environmental presence. Figure 2 shows the whole procedure for PFAS extraction from solid and liquid sources using well-established methods such as ion pair extraction, dispersive liquid-liquid microextraction, liquid-liquid extraction (LLE), and alkaline digestion [50].

These methods are sometimes inefficient, lengthy, and necessitate the co-extraction of lipids, which makes chromatographic analysis more difficult. Additionally, they often require analysis to be performed off-site. Non-polar solvents are capable of extracting non-ionic chemicals from their solution matrices. It is commonly recommended to employ weak anion exchange (WAX) cartridges when dealing with shorter chain PFCs in the range of C4 to C6. Conversely, for longer-chain PFAS exhibiting substantial recoveries in water and soil samples, the use of C18 and hydrophilic-lipophilic-balanced (HLB) cartridges is advised. A study conducted by L. Wang et al. in 2010 found that PFAS levels in bivalves' soft tissues may be evaluated using methyl-tert-butyl ether (MTBE) extraction followed by SPE purification on a WAX phase, despite the fact that this approach contains critical steps that might lead to analyte loss [51]. In an unconventional approach, acetonitrile, coupled with shaking or sonication, proves adept at extracting PFCs from diverse biological matrices—ranging from insect larvae to forage fish, crustaceans, and bivalves. The efficacy of oasis WAX cartridges in purging environmental contaminants, including short chain perfluorinated carboxylic acids (PFCAs), is underscored in two enlightening studies [52,53]. In 2017, a study was conducted on 12 perfluorinated compounds in the coastal area of the Shandong peninsula [54]. The adept researchers employed Oasis HLB (0.2 g, 6 mL) to discern the presence of PFAS [54]. In a pioneering stride beyond conventional SPE, two researchers in 2018, birthed a magnetic SPE method tailored for the extraction ballet of PFCs [12]. This innovation gracefully sidesteps the customary filtering interlude, ushering in a streamlined era where the separation process unfurls with newfound ease and celerity. In 2019, another research suggested an electrochemical preconcentration approach [55]. In a mere 10-minute cadence, this methodology deftly extracted 10 distinct PFAS variants from ambient samples, showcasing concentrations that spanned the spectrum from 0.5 ng/L to 500 ng/L [55]. In a collaborative efforts of S. X. L. Goh and H. K. Lee in 2018 unfolded a tale where PFCs were meticulously extracted from industrial effluent [56]. The method of choice, akin to a delicate brushstroke, involved the sophisticated artistry of hollow fiber microextraction techniques. A honeycomb-like cylindrical core, embraced by four intricately sealed hollow fibers, manifested as the elegant embodiment of experimental design [56]. In a quest to maximize the volumetric extraction potential nestled within the wall pores, a pioneering method emerged—hollow fiber-based liquid-pressured microextraction. This innovative approach delved into the intricate art of saturating the hollow fiber wall pores without deliberately infiltrating the lumen with solvent. The composition involved submerging the assembly of hollow fiber extraction instruments into the solvent extractant, revealing the efficacy of ultrasonic solid-liquid extraction in this scientific symphony [57]. The results showed that this process is a safe, quick, easy, and inexpensive way to extract PFAS from food matrices and popcorn bags, with recovery rates near to 100%. In 2021, a research suggested that ultrasonic solid-liquid extraction has proven to be a simple and rapid extraction process with high PFAS recoveries from paper packaging materials [58]. The advent of this novel method unfolds as a tapestry woven with threads of heightened sensitivity, abbreviated analytical timelines, and the graceful streamlining of extraction procedures. However, amid the triumphs of this approach, the traditional SPE methods cast shadows with potential drawbacks—whispers of sample contamination and the subtle departure of surface-active PFAA to the very vessels cradling the samples. In addition, SPE is complicated enough without having to deal with column obstruction.

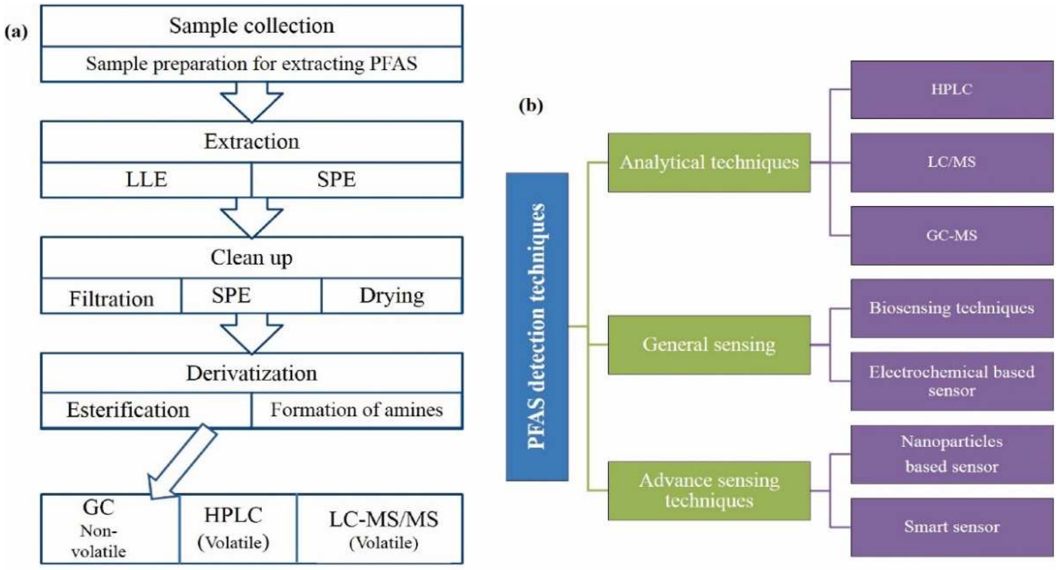

Figure 2. a) An overview of the PFAS extraction process from solid or liquid samples. b) A range of detection techniques for finding PFAS in environmental samples (S. Ganesan et al., 2022). Notes: LLE = Liquid-liquid extraction, SPE = Solid phase extraction, GC = Gac chromatography, HPLC = High-

performance liquid chromatography, LC-MS/MS = Liquid chromatography with tandem mass spectrometry.

2.2. *Analysis of PFAS via Chromatography*

Table 1 shows a panorama of diverse techniques employed for the extraction and detection of PFAS levels in environmental samples. The virtuosity of High-Performance Liquid Chromatography (HPLC) adorned with conductivity or fluorimetric detectors, alongside the prowess of LC-MS/MS, graces the scientific stage as commonplace methodologies. Gas Chromatography (GC) lends its precision to the measurement of volatile PFAS, while Ion Chromatography (IC), Nuclear Magnetic Resonance (NMR), and the symphony of Fourier Transform Infrared Spectroscopy (FTIR) emerge as less frequented methods [59,60]. Delving into the depths of radiochemical techniques unveils an ability to discern branched-chain PFAS [1]. Among these, LC-MS stands as a luminary, offering a promising pathway for evaluating PFAS in a spectrum of environmental matrices, showcasing detection limits that venture into the nanogram realm. The scientific community's gaze has progressively shifted towards LC-MS, leveraging its capabilities for the identification of PFAS in sludge, water, and serum [61–63].

Table 1. Several methods are currently accessible for extracting and detecting PFAS levels in environmental samples.

Techniques	Samples Type	Limit of Detection (LOD)	Extraction Methods	Detected PFASs	References
LC-MS/MS	Water	0.6 – 8.7 ng/L	Liquid-liquid extraction	PFOA, PFOS, PFHxA, PFODA, PFHpS, PFDS	[64]
HPLC-MS/MS	Water	0.01-1.15 ng/L	Solid phase extraction	PFOS, PFOA, PFNA, PFHpA, PFDA, PFHxS,	[65]
LC-MS/MS	Milk	0.057 ng/L (PFOA), 0.021 ng/L (PFOS)	Liquid-liquid extraction	PFNA, PFDA, PFOA, PFHpA, PFBS, PFHxS, PFOS, PFUnA	[66]
LC-MS/MS	Liquid Sample	0.29 - 6.6 ng/L	Solid phase extraction	PFOS, PFOA, PFNA, PFDA, PFBA, PFUnA,	[67]
LC-MS/MS	Fruits and Vegetables	0.07 ng/g (PFOS)	Solid phase extraction	PFOS, PFOA	[68]
HPLC-MS/MS	Sediment	1.5 – 10.9 ng/L	Liquid-liquid extraction	PFOS, PFDA, PFOA, PFDoA, PFHxS, PFNA	[69]
HPLC-MS/MS	Cabbage, lettuce, mustard leaf,	0.017-0.180 ng/g	Ultrasonic extraction	PFOS, PFHxS	[70]
LC-MS/MS	Vegetables	0.002 – 3.73 ng/g	Liquid-liquid extraction	PFOS, PFOA, PFDA, PFBA, PFBS	[71]
HPLC-MS/MS	Surface water	50 – 1790 ng/L	Solid phase extraction	FOSA, MeFOSA, EtFOSA, MeFOSE	[72]
HPLC-MS/MS	Different Water Samples	0.05–0.22 ng/L	Solid phase extraction	PFOS and PFOA	[73]

Notes: PFOA = Perfluorooctanoic acid, PFOS = Perfluorooctane sulfonic acid, PFHxA = Perfluorohexanoic acid, PFODA = Perfluorooctadecanoic acid, PFHpS = Perfluoroheptane sulfonate, PFDS = Perfluorodecane sulfonate, PFNA = Perfluorononanoic acid, PFHpA = perfluoroheptanoic acid, PFDA = Perfluorodecanoic acid, PFHxS = Perfluorohexane sulfonate, PFBS = Perfluorobutane sulfonate, PFUnA = Perfluoroundecanoic acid, PFBA = Perfluorobutyrate, PFDoA = Perfluorododecanoic acid, FOSA = Perfluoroctano sulfonamid, MeFOSA = N-methyl perfluorooctane sulfonamide, EtFOSA = N-ethyl perfluorooctane sulfonamide, MeFOSE = N-Methyl perfluorooctane sulfonamido ethanol.

2.3. *PFAS Detection by Sensors*

Within the biosensing, a singular entity arises—an amalgamation of vital components meticulously choreographed to collect, with precision, both quantitative and analytical data. This architectural marvel features a biological receptor seamlessly interfacing with a transduction device, encapsulating the essence of a biosensor. Comprising fundamental elements, this symphony harmonizes a biological recognition entity, a transducer, and an intricately designed signal processing system, as elucidated in a scholarly exploration [74]. The discerning and specific nature of biosensors relies on both a biorecognition system and a transducer. Sensitive biosensors are crafted using phages, whole-cell organisms, antibodies, and aptamers [75]. In molecular mimicry, Molecularly Imprinted Polymers (MIPs) emerge as virtuosos, replicating interactions reminiscent of substrate-enzyme and antigen-antibody engagements. The evolution of intricate sensing apparatus owes its prowess to the synergy of biomimetic materials and electrochemical technologies, transcending the limitations of unmodified or catalyst-modified sensors and unfurling novel realms of application potential. Within this molecular ballet, MIPs engage with target molecules, orchestrating a transformative symphony that alters their mass, absorbance, and refractive index—a nuanced performance dictated by the intricate tapestry of structure and surface charge [76]. Additionally, MIPs provide a polymeric matrix with voids or recognition sites that complement the form, size, and functional groups of the target analyte on the electrode surface (refer to Figure 3) [77]. The utilization of MIPs enhances both the sensitivity and selectivity of sensors due to their expansive surface area. Table 2 unfolds as a curated panorama, offering a succinct overview of the myriad sensor systems meticulously crafted for the discernment of PFAS.

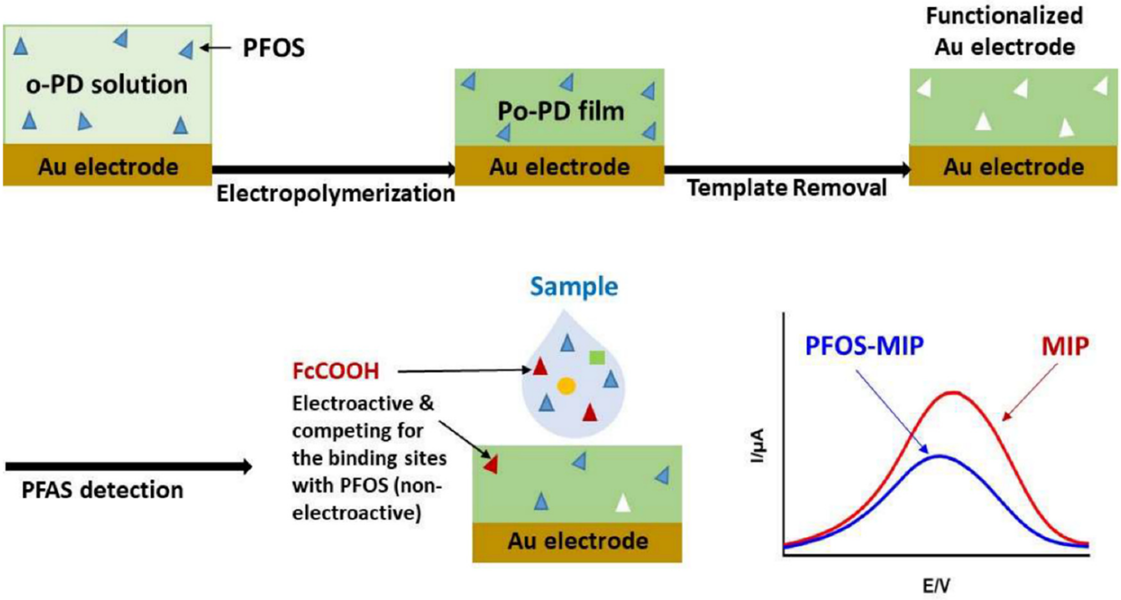

Figure 3. Integration of molecular imprinting and PFAS detection on a gold electrode: a schematic depiction. Po-PD = poly (o-phenylenediamine), MIP = molecularly imprinted polymer, o-PD = ortho-phenylenediamine (o-phenylenediamine) [77].

Table 2. Some of the PFAS detection sensor systems that are now available.

Detection System	Matrix	Limit of Detection (ng/L)	Detection Range (ng/L)	References
Spectrofluorometer	MPA-CdS QDs	124200	207000–16563000	[78]
Colorimetric detection	Gold nanoparticles	-	-	[79]
Electro chemiluminescence	Ultrathin nanosheets of carbon nitride	10	20–4000	[80]
Optical	Novel SPR	210	0 - 200000	[81]
Optical density	Bio-Gold Nanoparticles	2.5	2.5–75	[82]
Smartphone camera	Smart sensor	0.5	10000–1000000	[12]
Impedimetric	PFOS	0.0005	0.00005–50000	[83]

Note: MPA = 3-mercaptopropionic acid, CdS = Cadmium sulfide, QDs = Quantum Dots

2.4. Nanomaterial Based Sensor

Nanomaterials' strong electrical and magnetic conductivity, as well as their large surface area, make them useful for resolving lower detection limit problems in monitoring applications. The use of nanoparticles (NPs) offered a new strategy for creating inexpensive and portable PFAS detection devices [84]. Nanomaterials, including the luminescent brilliance of silver and gold nanoparticles, the metallic prowess of metal nanoparticles (MNPs), and the quantum wonders of quantum dots (QDs), assume a pivotal role in elevating the performance of biosensors to new heights. An uncomplicated sensor for detecting PFOA was developed. Early efforts to modify AuNPs involved utilizing thiol-terminated polystyrene. Upon introduction to the solution of AuNPs, the PFOA demonstrated a proclivity for aggregation, guided by the captivating dance of fluorine-fluorine interactions. The test performed admirably, with a noticeable shift in color from red to purple corresponding to increasing PFOA concentrations [84]. A study documented the assessment of PFCs using a probe based on Au-NPs [85]. This innovative approach employs a fusion of polyethylene glycol-terminated (PEG-thiols) and perfluoroalkyl-terminated (F-thiols) alkanethiol to intricately modify gold particles, sculpting them into a bespoke probeIn a mere half-hour temporal embrace, the ingeniously crafted probe unfurls its prowess, discerning the presence of PFCs within concentrations ranging from 0.1 to 1000 µg/L. This enhanced sensor manifests remarkable stability, boasting a detection limit finely tuned to 10 µg/L. Rigorous assessments conducted by the author within the realms of municipal and river water unveiled a sensor adorned with high selectivity specifically tailored for PFOA and PFOS [86]. In the eloquent narrative penned by a study, a groundbreaking chapter unfolded introducing upconversion nanoparticles (UCNPs) as the luminescent protagonists in the sensor saga, meticulously crafted for the detection of PFOS [87]. The genesis of these UCNPs took shape through the meticulous artistry of solvothermal synthesis. The synthesis and deposition of covalent organic framework (COF) on the surface of UCNPs occurred simultaneously. Increased selectivity and sensitivity for PFOS were noted in the synthesized UCNPs-COFs. In the unveiling of a sophisticated sensing platform, its application to scrutinize authentic water samples unfolds as a narrative of triumph, showcasing recoveries within the captivating range of 106% to 108% and an exquisite detection limit of 0.000075 ng/L for perfluorooctane sulfonate (PFOS). Embarking on a quest for a streamlined PFOS detection sensor, a research introduces a tale interwoven with titanium dioxide nanotubes (TiO_2-NTAs) [88]. Within this sensor realm, acrylamide, ethylene glycol dimethacrylate, and 2,2-azobis(2-methylpropionitrile) emerge as the protagonists, respectively donning the roles of functional monomers, cross-linker, and initiator agent in the polymerization imprinting process. The resulting sensor emerges as a testament to both selectivity and sensitivity towards PFOS, boasting a discerning limit of detection at 86 µg/L and a linear range spanning from 250 to 5001 µg/L. Results from using the technique on environmental samples were positive. In order to detect PFOA in environmental samples, another study created a QDs sensor [69]. Embarking on a scientific odyssey, CdTe@CdS-QDs materialized through the alchemical artistry of the sol-gel technique. The saga continued with the creation of silica films, meticulously imprinted at the molecular level onto CdTe@CdS-QDs. Aqueous ammonia, akin to a catalyst in this intricate ballet, presided over the proceedings. The narrative of creation unfolded with a polymerization technique, where 3-aminopropyltriethoxysilane donned the mantle of the functional monomer, and tetraethoxysilane stood as the cross-linker, weaving the intricate tapestry of molecular imprinting. The method demonstrated effectiveness, yielding a detection limit of 10.35 µg/L and a linear range spanning from 104 to 6211 µg/L [89]. Values of recoveries seen by the author varied between 91 and 107%, with a relative standard deviation of 5.6%. PFOA in water was detected using the designed sensor with high selectivity. Research by S. Chen and colleagues in 2015, a luminescent symphony unfolded as they meticulously crafted a luminophore imprinting polymer, adorning the ultrathin nanosheets of carbon nitride (utg-C_3N_4) through the ballet of an electropolymerization technique [80]. The resulting sensor, a testament to their precision, revealed a harmonious linearity extending across detection ranges from 20 to 40,000 ng/L. Finding a limit of detection of 10 ng/L was a significant achievement. Also, the sensor was used to the examination of water samples, with satisfactory recoveries (96%-103.8%) being attained. There was also significant concordance between HPLC-MS/MS and the findings.

In their scholarly endeavour to unveil the fingerprint of PFOS within biological samples, a study conceptualized a sensor ingeniously fashioned with the radiance of carbon quantum dots (CQD) [84]. The integration of CQD with a chitosan hydrogel was orchestrated through the methodical process of electrochemical polymerization, culminating in the formation of a durable covalent bond. The interaction between sulfonates from chitosan and QDS, and amino groups from PFOS through electrostatic repulsion, forms a compound. This novel approach demonstrates sensitivity in detecting various perfluorinated compounds, including PFOA, PFOS, PFBS, and perfluorooctanoic acid. The highest imprinting factor discovered by the author was 2.75. The concentrations that could be added up to 1 ng/L were only as low as 0.00002 ng/L. The designed sensor yielded satisfactory recoveries (81-98%). Using a water-soluble CdS-QDS, another study created a straightforward and quick fluorometric method for measuring PFOA [78]. The birth of radiant CdS-QDs, aglow with intense luminosity, unfolded through the transformative touch of 3-mercaptopropionic acid (MPA). In a dance of molecular interplay, the entrance of PFOA became the catalyst for an enchanting aggregation of MPA-CdS QDs, orchestrated by the alluring forces of fluorine-fluorine interaction. This mystical collaboration cast a spell, conjuring forth an augmented fluorescence emanating from the embrace of MPA-CdS QDs. The saga of detection unfolded with a determined linearity stretching from 207.03 μg/L to 16.56 mg/L, revealing its secrets with a calculated limit of detection at 124.2 μg/L.

2.5. PFAS Detection by Surface-Enhanced Raman Spectroscopy

In a recent scientific expedition, the canvas of detection unfolded with the mastery of SERS as the chosen medium for exploring the mysteries of PFAS [90]. The mesmerizing SERS effect, harnessed through the localized surface plasmon resonance (LSPR) of 40 nm silver nanoparticles (AgNPs), became the enchanting brushstroke in this artistic endeavour. In a temporal whisper of less than 30 seconds, the SERS technique exhibited its prowess, unveiling the ability to detect PFAS concentrations as ethereal as 20 femtograms per litre. The allure of the SERS technique lies in its potential to transcend the boundaries of PFAS contamination studies, offering a tableau of quicker, more sensitive, and less labour-intensive analyses, all within the realm of optical sensitivity. Within the intricate dance of Raman spectroscopy, where an excitation photon intertwines with a phonon in the analyte, losing energy along the way, wavelengths shift, and vibrational frequencies of phonons emerge as beacons for molecular identification. Amplification becomes a necessity for low analyte concentrations due to the rarity of spontaneous Raman scattering. In this narrative, 40 nm AgNPs assumed a pivotal role, entering a water symphony at a harmonious ratio of 2:3, casting their essence through the medium of drop-casting onto aluminium substrates to orchestrate the optimization of SERS enhancement. The spectral voyage unfolded within the cadence of 200 to 1800 cm^{-1}, with the rhythmic resonance of the asymmetric stretching mode of the difluoromethylene (CF_2) group, the essence of PFAS, revealing itself as a Raman feature peak around 1300 cm^{-1}. Concentration calibration curves, akin to musical scales, emerged, with the feature peak at 1300 cm^{-1} serving as the guiding melody to discern the concentration of water samples—each note unravelling the secrets of PFOA and PFOS.

In another research, SERS methods were used to find persistent flame retardants (PFAS), a major environmental problem, in firefighting foams [49]. With a 50 ppb PFOA detection limit, they were able to successfully identify PFOS, PFOA, and 6:2FTS. Graphene oxide (GO) membrane and nanosphere lithography were used to create two SERS substrates that showed GO's strong affinity for fluoro surfactants (FS). They created a loaded dye-FS precipitate ion pair on the substrates, dye-FS-Ag and dye-FS-GO, both of which successfully detected FS, using EV dye as a Raman probe. Dye-FS-Ag's Raman spectra showed a noticeable signal amplification on the Ag surface. Increased FS loading in the presence of a dye was demonstrated by controlled tests using the GO membrane [49].

Another study created a method for detecting PFOA, a contaminant belonging to the perfluoroalkyl substances (PFAS) class, utilizing SERS [91]. The inherent fluorescence of PFOA makes conventional SERS detection difficult because it masks the Raman signal. To address this issue, researchers applied a longer Raman excitation wavelength of 633 nm, effectively suppressing fluorescence while maintaining adequate Raman intensity. The researchers used crystal violet (CV) as a Raman label to improve the Raman signal and eliminate fluorescence. CV and PFOA interact to form ion pairs, resulting in a synergistic increase in Raman activity. This combination technique produced an amazing limit of detection (LOD) for PFOA of 10.52 ppb, confirming the method's exceptional sensitivity and promise for real-world environmental monitoring. This approach not only has high sensitivity but also allows for the detection of PFOA even in the presence of other chemicals. Achieving this specificity involves employing an indirect analysis approach, wherein the Raman signal of CV is heightened in the presence of PFOA, serving as an indicator for the existence of PFOA. The SERS technique's adaptability is further demonstrated by its ability to detect another common PFAS molecule, perfluorooctanesulfonic acid (PFOS). The method's broad applicability for PFAS detection is demonstrated by a LOD of 10-12 M [49].

3. CONCLUSIONS

In PFAS detection, post-sample preparation unveils a plethora of detection methods, each boasting advantages in terms of speed, simplicity, cost-effectiveness, and sensitivity when juxtaposed with traditional chromatography. The brisk pace of assays necessitates the evolution of innovative extraction procedures, heralding a paradigm shift in analytical methodologies. Analyzing PFAS in the intricate landscape of food encounters challenges rooted in the absence of standardized methods, beckoning the need for pioneering approaches. Continuous monitoring emerges as a beacon of efficacy, transcending the constraints of batch techniques and embracing the vast domains of both food and environmental samples. While the majority of approaches have concentrated on PFAS detection in water, their performance within complex matrices demands meticulous assessment and augmentation to enable direct detection. A harmonious convergence of disciplines becomes imperative to sculpt sensors of impeccable design, where nanoparticles play the role of virtuosos, orchestrating signal amplification to elevate sensitivity and selectivity. Despite the promising strides in sensor research, the crucible of real sample analysis and selectivity must occupy the forefront, sculpting flawless sensing systems attuned to the nuances of PFAS. Validation stands as the cornerstone in this odyssey, a pivotal step ensuring the accuracy of PFAS measurements and paving the way for widespread adoption. In the grand tapestry of innovation, these sensors and sensing systems emerge as catalysts, potentially revolutionizing the screening of real-world samples for PFAS by regulatory agencies and other entities. Their efficiency may outshine conventional analytical methods, ushering in a new era of precision and effectiveness in the quest for PFAS detection.

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