

Nanotechnology in Environmental Pharmaceutical Analysis

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ABSTRACT

Lately, monitoring pharmaceutical contaminants in the environment has gained increasing recognition due to the consistent detection of abandoned pharmaceuticals in various environment component, such as water and soil, from continual discharges of wastewater treatment plants, pharmaceutical companies, hospitals, and farms. It mentioned contaminants involves the development of methodologies that are capable of identifying significant concentrations and measuring them in different environmental systems. This review aims to present the role of nanotechnology in environmental pharmaceutical analysis, as reported in recent studies. The diversity of the mentioned studies has enabled the characterization of a plethora of nanomaterials such as carbon-based nanomaterials, magnetic and metal nanoparticles, and metal-organic frameworks that have improved various aspects of sample preparation and detection. Recent studies in the field of chromatography and sensors have indicated that, in comparison to traditional methods, nano-assisted methodologies are characterized by lower detection thresholds and by greater extraction efficiencies and the Nano-sensor (NS) has the potential for on-site monitoring and for real time monitoring. The performance of NS has the potential to be characterized by high sensitivity and rapid response time. On the other hand, the absence of established guidelines, high cost, poor stability, and detrimental performance of certain nanomaterials remain significant obstacles. Prospective studies effort needs to focus on the characterization and development of nanomaterials that are safe for the environment and towards the establishment of guidelines that are aimed at validation in order to improve the effectiveness and apply studies that utilize nanotechnology for the analysis of pharmaceuticals in the environment.

Keywords: : Nanotechnology, Environmental analysis, Pharmaceutical residues, Nano-based sensors, Water pollution monitoring

1. Introduction

1.1 Background

The growing availability and consumption of pharmaceutical products have led to drug residues being released into the environment via numerous pathways, such as municipal wastewater, hospital wastewater, discharges from pharmaceutical factories, and runoff from the use of veterinary drugs in agriculture. Standard wastewater treatment facilities do not target pharmaceutical products for removal, resulting in these compounds being removed from wastewater and distributed into surface waters, groundwater, and soils. [1, 2]. Pharmaceutical pollution has been detected in a wide variety of water bodies all over the world, including rivers, lakes, oceans, and even drinking water, and at concentrations of nanograms to micrograms/liter [3]. While the concentrations may seem low, the biologically active nature of the compounds that characterize pharmaceuticals, which can have an effect at low doses, raises concerns for the safety and the ecosystem of the pharmaceuticals in the water. Even at very low concentrations, the presence of such compounds in the environment can lead to chronic toxicity, bioaccumulation, and other effects to organisms, that can be subtle and alter their functioning[4]. Environmental pollution by pharmaceuticals is especially concerning due to the various chemical make-ups, persistence, and by-products that result during breakdown processes. Numerous drugs remain only partially metabolized during the human or animal processes and considerable amounts remain unchanged or are excreted as active metabolites that can enter the drainage system[5]. In addition, some medicines are very chemically stable and resistant to biodegradation and therefore, can remain for long durations in water and soil ecosystems [6]. Sensitive and selective analytical techniques able to identify and quantify various contaminants in intricate environments are crucial in the analysis of pharmaceutical pollutants. Environmental samples include various organic matter, salts, microorganisms, and additional pollutants that may obstruct the analytical process. Therefore, the accurate analysis of pharmaceuticals usually relies on detection instruments of high complexity and the advanced techniques of sample preparation. However, traditional analytical techniques may provide an analysis that lacks the needed sensitivity or efficiency for large scale routine monitoring, especially for ultra-trace detection [7, 8].

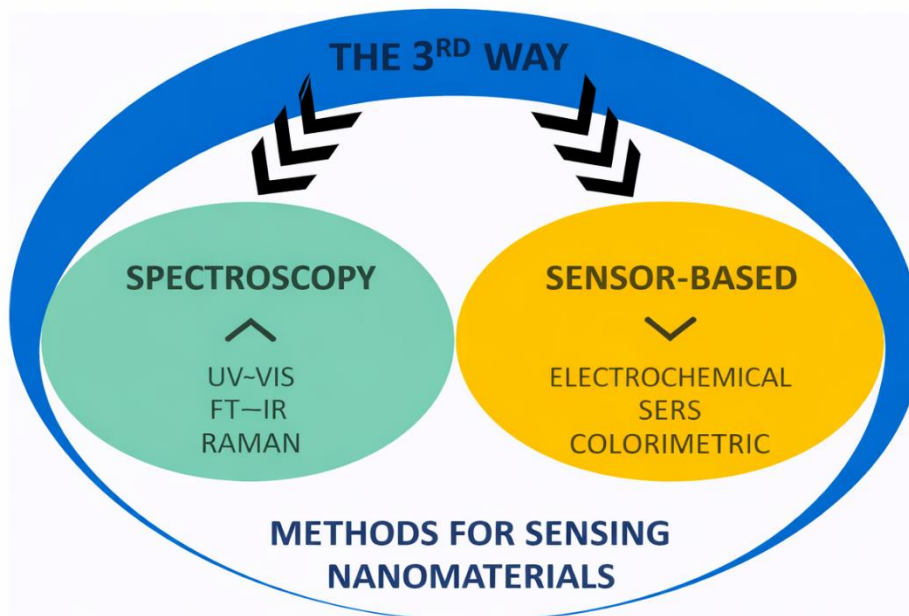


Figure 1. Schematic representation of the main analytical approaches used for nanomaterial detection, including spectroscopic techniques and sensor-based methods, and their integration as a combined analytical strategy for environmental analysis.

1.2 Significance of the Study

Research on the effects of toxins in the ecosystem has shown that exposure to pharmaceuticals can cause endocrine disruption, reproductive issues, behavioral changes, and stunted growth in aquatic life [9]. From an analyst's viewpoint, the prompt identification of pollutants in pharmaceuticals is crucial for the efficient assessment of environmental risks, compliance with regulations, and assessment of the efficacy of wastewater treatment systems. However, surveillance of the environment is complicated by the ongoing release of novel pharmaceutical substances and derivatives of transformation. Consequently, there is a need for new methods of analysis to enhance the sensitivity, selectivity, and operational effectiveness of detection[10, 11] . Nanotechnology is beginning to address some of these analytical challenges. Unique physico-chemical properties of some nanomaterials, such as increased surface area, and the ability to tune surface chemistry and strong adsorption to improve extraction and detection

performance are considered. Furthermore, the ability to create innovative nano-enabled analytical devices to aid in the monitoring of pharmaceuticals in environmental samples is considered [12, 13].

The main objective of this review is to evaluate the role of nanotechnology in enhancing environmental pharmaceutical analysis. Specifically, this study aims to:

1. Review the major sources and types of pharmaceutical contaminants in the environment.
2. Examine conventional analytical methods used for pharmaceutical detection and their limitations.
3. Discuss the application of nanomaterials in sample preparation and detection processes.
4. Compare the performance of nano-analytical methods with traditional approaches.
5. Highlight current challenges and future perspectives for nano-enabled environmental monitoring.

By synthesizing recent scientific literature, this review seeks to provide a comprehensive overview of how nanotechnology contributes to improving environmental pharmaceutical analysis and supports more effective environmental monitoring strategies.

2. Pharmaceutical Residues in the Environment

2.1 Sources of Pharmaceutical Contamination

Various man-made processes related to human healthcare, industrial manufacturing, and farming practices lead to the introduction of pharmaceutical compounds in the ecosystem. One of the major contributors is the municipal wastewater sewers, which contain the remnants of the drugs patients have been prescribed and uses therapeutically. Many of these drugs have not been fully broken down in the human body, so the wastewater from urination carries these parent compounds along with their active metabolites to the municipal wastewater treatment facilities (WWTPs). Conventional WWTPs are not built to fully remove wastewater pollutants, and that includes pharmaceutical compounds, so they release them into the surface waters [14]. Another significant contributor to pharmaceutical pollution includes hospital effluents, specifically antibiotics, cytostatic drugs, contrast agents, and anesthetics. Hospital wastewater may contain higher quantities of certain drugs than municipal sewage, and, therefore, may disproportionately contribute to the pharmaceutical burden of the urban wastewater systems [15, 16]. Furthermore, pharmaceutical production plants, if their industrial effluents and wastewater treatment systems

are inadequate and/or poorly managed, may discharge drug residues to the adjacent water bodies[17]. The use of veterinary medicines in livestock production and aquaculture also significantly leads to environmental contamination of pharmaceuticals through agricultural practices. Agriculture and Environment [18] explains that animals are given antibiotics, antiparasitic agents, and growth promoters, and these substances are frequently excreted without changes and enter soil and surface water through manure application, runoff, and leaching. In aquaculture, systems, the direct introduction of pharmaceuticals to aquatic environments occurs, where these substances can persist and affect non-target organisms.

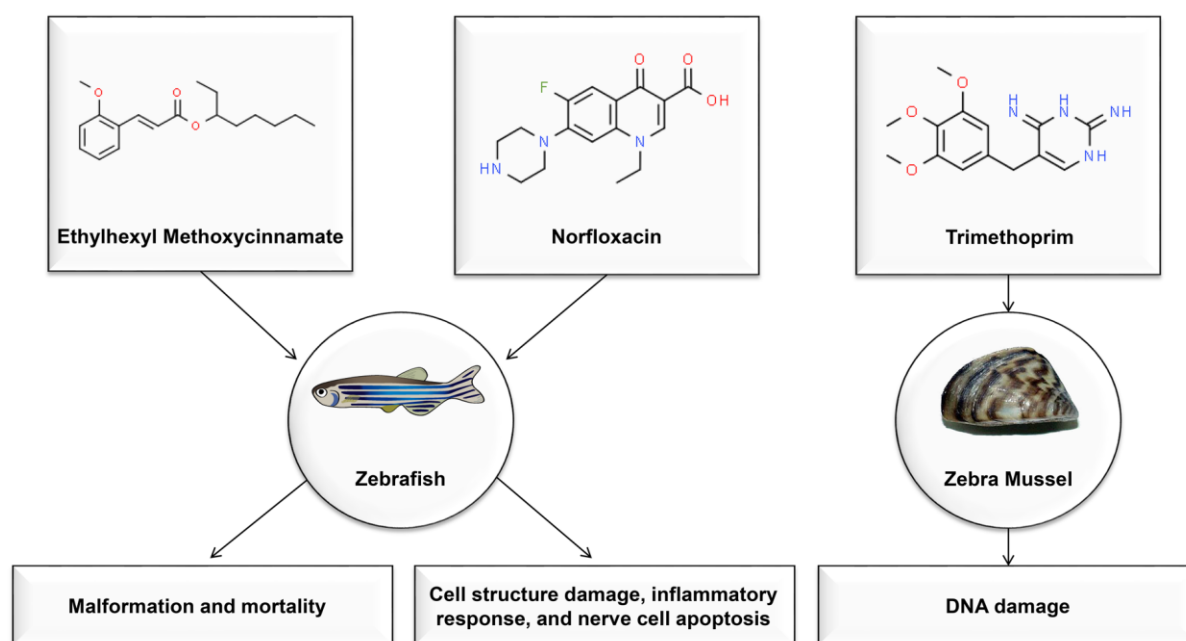


Figure 2 .Toxic effects of PhAC in aquatic organisms.

Environmental contamination is made worse by throwing away older or unused medications inappropriately. Expired medication can be considered household waste which contributes to the flushing of waste and introduces unsafe pharmaceuticals to waste and leachate systems. Groundwater can be contaminated by unsafe pharmaceuticals. Many areas, especially in developing countries, do not have adequate awareness concerning the disposal of unsafe drugs which makes environmental exposure increasingly unsafe [19].

2.2 Types of Pharmaceuticals Detected in the Environment

Various environmental samples have identified numerous pharmaceutical classes, demonstrating the breadth of therapeutic uses and the extent of prescribing and consumption. Antibiotics, particularly sulfonamides, fluoroquinolones, tetracyclines, and macrolides, are among the most frequent contaminants reported in the literature and are commonly found in wastewater, rivers, and sediments[20]. Their environmental detection is especially alarming as they contribute to the development of antibiotic-resistant bacteria and resistance genes in the environment. Because of their easy accessibility and widespread use, analgesic and anti-inflammatory drugs like acetaminophen, ibuprofen, naproxen, and diclofenac are commonly found in our water supply and are poorly removed in water treatment. Diclofenac has recently been linked to fish kills and other negative impacts in fish and is increasingly being recommended to regulators in multiple countries for consideration in environmental watch lists[21]. Pharmaceutical pollutants impact the environment and the most deleterious of these pollutants include the most biologically active and hormonally active (including natural and synthetic) estrogens that can be identified at extremely low levels. Even at levels of ng/L, compounds like 17 α -ethinylestradiol and estradiol cause endocrine disruption and reproductive anomalies in aquatic organisms[9, 22]. Other classes of pharmaceuticals, including psychiatric medications, lipid regulators, and beta blockers have also been reported in the surface waters, which demonstrates the widespread and persistent environmental contamination of pharmaceuticals[23]. The presence of pharmaceutical mixtures instead of single compounds presents yet another challenge with respect to analysis and toxicological evaluation. Environmental organisms are often exposed to complex mixtures of pharmaceuticals that may have synergistic or antagonistic interactions. This makes risk assessment and management of the environment more difficult [22, 24].

2.3 Environmental and Health Impacts

The ongoing presence of drug residues in different parts of the environment is a serious threat to the ecosystem and to human beings. Unlike many classical pollutants, pharmaceuticals possess biological activity by design, and can influence biological processes, even at very low levels. Aquatic organisms are especially at risk, as frequently, both treated and untreated,

wastewater contains a wide variety of drug pollutants[12, 25]. Endocrine disruption is one of the many possible negative environmental effects caused by the presence of pharmaceuticals in the ecosystem. Man-made and natural substances that mimic hormones or that are structurally similar to hormones can disrupt the endocrine systems of various organisms such as fish and amphibians. Disruptive consequences can include feminization of males, shifted sex ratios, and reduced reproductive success [26, 27]. Contaminated ecosystems have collapsed fish populations as a result of long-term exposure to estrogenic compounds, which have been shown to negatively impact reproductive success on a population level[13]. Antibiotics also pose a significant environmental threat because of the promotion and dissemination of antimicrobial resistance (AMR). Bacteria in the surroundings that come into contact with small amounts of antibiotics can develop resistance and, through horizontal gene transfer, pass that resistance on to harmful microorganisms[28]. The environmental reservoir of resistance genes is a significant threat to existing antibiotics and, consequently, to public health[16]. Non-target organisms may also be impacted by pharmaceuticals by causing oxidative stress, behavioral changes, and immune system suppression. Research has documented changes in predator avoidance, decreased feeding, and stunted growth in aquatic organisms exposed to some antidepressants and beta-blockers [29]. While these effects may be sub-lethal and not cause immediate death, they can result in a shift in the stability and diversity of ecosystems over time. From a human health perspective, the presence of pharmaceuticals in drinking water, despite being usually found at very low levels, raises concerns due to the possible risks associated with long term exposure. Individual pharmaceuticals in drinking water are reported to be below the levels of therapeutic prescriptions, and evidence of the risk to health from such low exposure would be negligible, but the risk associated with being exposed to a multitude of chemicals in water and the possible harm from long term exposure remains unknown. Pregnant women, infants, and the immunocompromised may be particularly at risk from the low levels of pharmaceuticals in water[30]. The enduring presence of pharmaceutical compounds and their transformation products is yet another challenge to the assessment of environmental risks. The metabolites of pharmaceuticals are sometimes more toxic than the parent compounds and are formed during the chemical transformations that occur during waste water treatment and natural degradation

processes [31]. For accurate assessments of risks to the environment and public health, monitoring programs must focus on the degrading products alongside the target pharmaceuticals.

3. Conventional Analytical Approaches

3.1 Chromatographic Techniques

Due to being easily integrated with more sensitive detectors and being able to separate samples with more efficiency, chromatographic methods have been consistently used to analyze samples from the environment for pharmaceutical contaminants. LC–MS/MS is the current gold-standard technique used for the detection and quantification of multiple pharmaceutical contaminants within complex matrices such as wastewater, water from rivers, and sediments [12, 32]. This method can identify and quantify several different pharmaceutical contaminants, even at ultra-trace levels, with a high degree of selectivity. More recent research looks to improve chromatographic efficiency using techniques that include miniaturization, fast chromatography, and green analytical chemistry. The application of ultra-high-performance liquid chromatography (UHPLC) has been utilized to save time while maintaining the requisite resolution and sensitivity[26, 33]. In addition, the use of less harmful solvents and the desire to reduce the environmental impact associated with chromatography has led to eco-friendly mobile phases and micro-scale extraction systems[34] . GC-MS continues to be used for volatile and semi-volatile pharmaceutical chemicals, particularly following derivatization procedures. However, the technique has serious limitations for polar and thermally unstable pharmaceuticals, indicating that LC-based methods are more flexible for use in environmental monitoring[35].

3.2 Spectroscopic Methods

Spectroscopic methods are rapid and non-destructive ways of identifying pharmaceuticals based on the detection of molecular vibrations and electronic transitions. Examples of these methods are Fourier transform infrared (FT-IR) spectroscopy and UV-visible spectroscopy which can both perform qualitative screenings and confirm chemical structures[36]. However, these methods are often not sensitive enough to detect pharmaceuticals at environmentally relevant concentrations. By detecting trace-level pharmaceuticals combined with nanostructured substrates, Raman spectroscopy, especially surface-enhanced Raman spectroscopy (SERS), has become popular. The most recent SERS detection limit for some pharmaceutical compounds in water samples is nanomolar and even picomolar, and was achieved using SERS-based platforms

with metal nanoparticles and hybrid nanocomposites. SERS-based platforms with metal nanoparticles and hybrid nanocomposites demonstrate detection limits of nanomolar and picomolar levels for several pharmaceutical compounds in water samples. These systems are ideal for field-based environmental monitoring because they provide rapid responses and require little sample preparation[37].

3.3 Limitations of Traditional Analytical Methods

Even though they possess analytical power, traditional chromatographic and spectroscopic methods have great impairments directed towards large environmental monitoring. Chromatographic methods take a long time and are expensive because they require a lot of sample preparation like extraction, purification, and concentration [38]. More sample preparation is needed because of accuracy detection loss because of matrix interferences. Rapid though, spectroscopic methods, to complex environmental matrices without prior enrichment, generally lack enough sensitivity and selectivity. Their application to trace-level pharmaceutical detection is limited because of overlapping spectral signals and a low signal-to-noise ratio[39]. These limitations have provided motivation for the pairing of nanotechnology with sample preparation. Enhanced analytical performance will be discussed in the following section.

4. Role of Nanotechnology in Pharmaceutical Analysis

4.1 Types of Nanomaterials Used in Environmental Analysis

Nanotechnology has introduced a wide range of nanomaterials that significantly enhance the performance of environmental pharmaceutical analysis through improved adsorption capacity, selectivity, and signal amplification. Carbon-based nanomaterials, including graphene, graphene oxide (GO), and carbon nanotubes (CNTs), are among the most widely used materials due to their large specific surface area, strong π - π interactions, and excellent chemical stability. These properties allow efficient adsorption of aromatic pharmaceutical compounds and facilitate their extraction from complex environmental matrices[29, 40]. The high interest in certain magnetic nanoparticles (particularly iron oxide (Fe_3O_4) nanoparticles) can be attributed to the ease in which they can be separated by external magnetic fields. Rapid and efficient preconcentration of pharmaceuticals from large sample volumes can be achieved with the aid of functionalized magnetic nanoparticles. This greatly streamline sample preparation and reduces the waste of solvents[41]. Selectivity toward certain classes of pharmaceuticals can be improved

with surface modification using different polymers, surfactants, or molecularly imprinted polymers. Due to the high strength of surface plasmon resonance, metal nanoparticles, particularly gold (Au) and silver (Ag) nanoparticles, are most often used in optical sensing. These materials are commonly employed in surface-enhanced Raman spectroscopy (SERS) and colorimetric sensors to detect pharmaceutical traces in water[42]. Also, Metal-organic frameworks (MOFs) and quantum dots have tunable optical and electrochemical properties making them attractive, new nanomaterials for use in electrochemical and fluorescent detection[43].

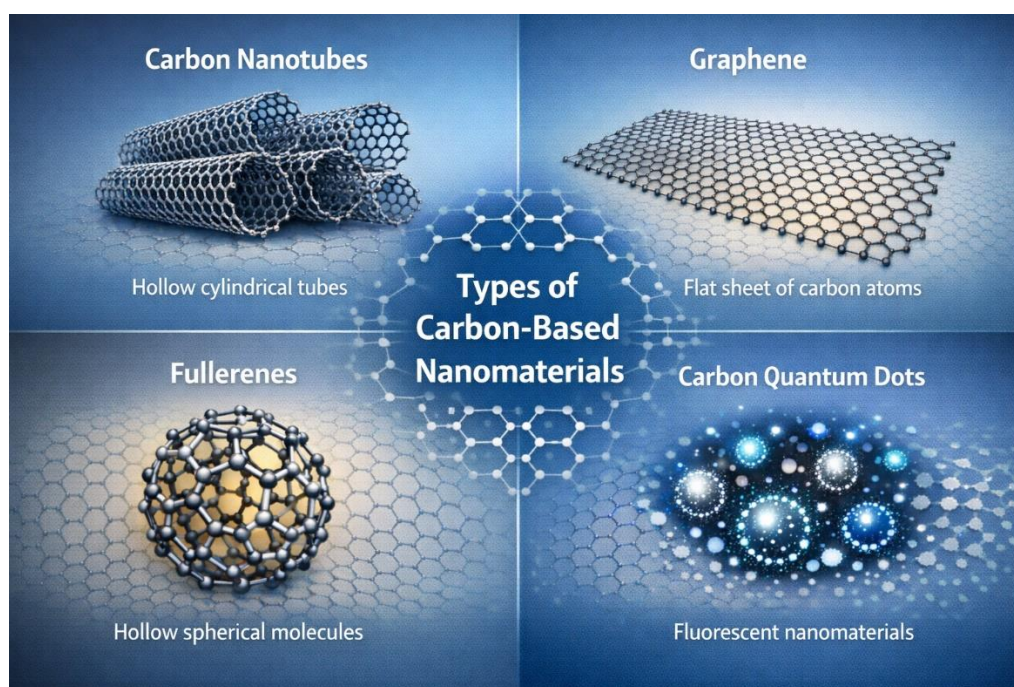


Figure 3. Types of carbon-based nanomaterials

4.2 Nano-Based Sample Preparation Techniques

Sample preparation is vital in the analysis of environmental pharmaceuticals, and the use of nanotechnology has provided significant advancements in the selectivity and efficiency of extraction. Nano-solid phase extraction (Nano-SPE) employs nano-sized sorbents, which leads to better surface contact with the target analytes, achieving better recovery, and higher rates, and lower detection limits than conventional SPE [38]. Magnetic solid-phase extraction (MSPE) is widely used because of the ease and speed of its separation. In MSPE, magnetic nanocomposites are directly introduced into the sample, and after adsorption of the pharmaceuticals, they are

removed with a magnet, so no filtration or centrifugation is needed[44]. This method has been used to extract antibiotics, anti-inflammatory drugs, and hormones from wastewater and surface water. Methods of microextraction using nanomaterials have been created to minimize the volume of solvents used and increase enrichment factors. Such methods allow effective preconcentration of pharmaceuticals before detection by chromatography and spectroscopy, and are therefore applicable for environmental analyses at trace levels[45].

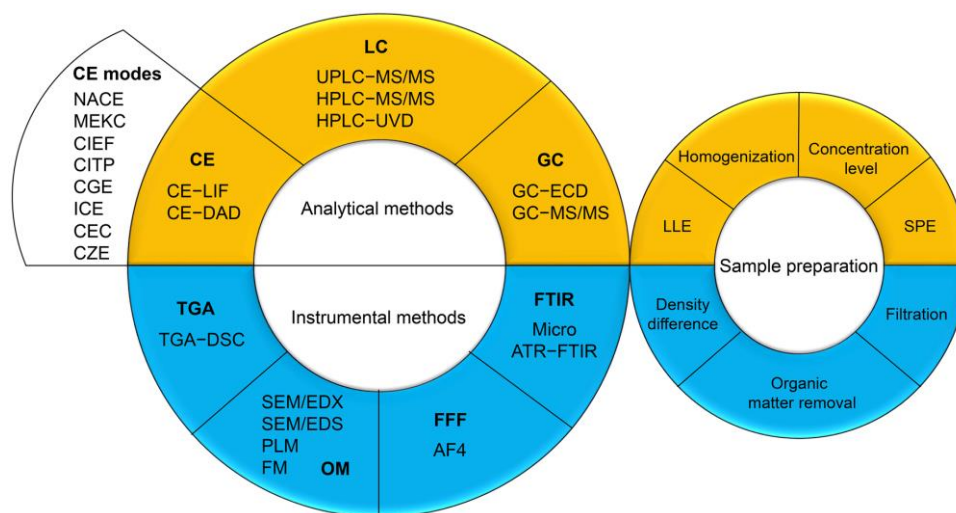


Figure 4. Techniques for analyzing of PhAC-NPs/MPs in aquatic organisms.

4.3 Nano-Sensors and Detection Platforms

The high sensitivity, portability, and fast response of nano-enabled sensors have changed pharmaceuticals detection for the better. An example is in the detection of pharmaceuticals at very low concentrations using modified nano-structural electrodes with enhanced electron transfer and greater surface area, which improves detection capabilities. Because of these unique features, these sensors are ideal for real time environmental monitoring and assessment. Signal amplification and recognition of nanomaterials are part and fluorescence and colorimetric optical nano-sensors. Antibiotics and analgesics in environmental water have been successfully targeted using laser-driven and luminous plasmonic nanoparticles. In addition, the ability to detect several pharmaceuticals in complicated systems is due to the enhancement of several pharmaceuticals through Raman signals with metallic nanostructures and is a feature of SERS platforms [38–40].

The combination of nano-sensors with microfluidic systems and wireless data transmission has provided innovative paths for ongoing monitoring of different environments. These types of smart analytical platforms are capable of having automated collecting and sampling of data streams, while also providing rapid detection and analyses. These capabilities are critical for early warning systems, and monitoring for regulatory compliance[46].

5. Performance Evaluation of Nano-Analytical Methods

5.1 Sensitivity and Detection Limits

Analytical techniques on the nano scale in the analysis of pharmaceuticals in the environment have multiple benefits, one of which is the ability to achieve the lowest possible detection limits (LOD) and quantification limits (LOQ). The phenomenon of sorption is the key to the improved sensitivity of nano materials over traditional sorbents and detectors[47]. Nano materials and/ or have been used in the extraction and detection processes exhibited LOD values that were one to two orders of magnitude less than traditional extraction processes. Nano solids phase extraction (Nano-SPE) and magnetic solid phase extraction (MSPE) systems are examples of this. Graphene-based sorbents and magnetic nanocomposites are examples of materials that paired with other techniques such as LC–MS/MS, have been used to detect antibiotics and anti-inflammatory medications in surface and wastewater samples at sub-ng/L concentrations[46]. The ability to measure such low concentrations of pharmaceuticals in the environment that have the potential to cause harm is significant.

Because of optimized electron transfer kinetics and improved optical signal amplification, nano-sensors exhibit sensitivity. In the case of electrochemical nano-sensors with carbon nanomaterials or metal nanoparticles, the detection limit has been reported to be in the picomolar range for various pharmaceutical compounds, such as diclofenac and ciprofloxacin[38]. Likewise, SERS-based nano-platforms with silver or gold nanostructures have ultra-trace detection and fast response times, making them ideal for real-time monitoring applications[44].

5.2 Selectivity and Matrix Effects

Given the complex nature of natural water and soil matrices, selectivity is an important consideration when evaluating the environment. Improvement of selective recognition of target pharmaceuticals can be achieved by functionalizing nanomaterials with certain chemical groups,

polymers, and molecularly imprinted polymers (MIPs)[12, 48]. Such functionalization can create conditions for the preferential adsorption of certain drug molecules, while the presence of other organic and inorganic materials is of less concern. Competing compounds and the suppression or enhancement of signals create what are known as matrix effects, and these continue to be among the most important analytical issues associated with the monitoring of pharmaceuticals. The problem of matrix effects is lessened through the use of nano-based extraction technologies that identify and isolate target analytes before measurement[45]. Particularly, the use of magnetic nanocomposites makes it easier to conduct certain separation and washing steps that lead to greater extract purity and improve analytical accuracy. In the context of nano-sensor applications, selectivity is typically acquired through the use of biological recognition elements, such as aptamers or enzymes, attached to nanostructured surfaces. These biosensor systems have high specificity, which has allowed them to achieve selective detection of certain antibiotics and hormones in environmental samples. However, the lasting stability and reproducibility of these bio-functionalized sensors remains a major concern for practical use[49]

5.3 Comparison with Conventional Methods

Nano-enabled methods demonstrate analytics performance that consistently outstrips conventional techniques in sensitivity, extraction efficiency, and analysis time, as shown in comparative studies. While traditional SPE and chromatographic methods can include extensive sample prep, methods based on nanotechnology often facilitate rapid extraction and preconcentration, substantially cutting analysis time[47]. Beyond performance advantages, nano-analytical systems can be miniaturized, a characteristic important for field-based environmental monitoring. Portable nanotechnology-based sensors that wirelessly transmit data are proposed for real-time monitoring of pharmaceuticals in rivers and in wastewater treatment[49]. Such systems can improve proactive environmental management by providing real-time detection and assessment of pollution. While promising, costs, nanomaterial instability, and issues related to the mass production of nanomaterials remain barriers for widespread use. The development of environmentally friendly, low-cost nanomaterials that exhibit superior analytical performance to current offerings should be the focus of future studies[50].

6. Conclusion

The review examines the potential of nanotechnology to tackle the specific challenges of analytical chemistry in the field of environmental pharmaceuticals. There is a need for sensitive, selective, and rapid analytical techniques to monitor and quantify residues of pharmaceuticals that are continuously discharged into the environment, and that may be present at trace levels in heterogeneous environmental media. While analytical techniques relying on classical approaches are available and widely used, they do not provide the needed sensitivity for global environmental assessments, and often are resource and time intensive in terms of the preparation of the samples. Detection of pharmaceuticals using analytical techniques grounded in nanotechnology is improving, due to the enhancements of selective recognition, signal amplification, and adsorption. In sample preparation detection, carbon-based nanomaterials, magnetic and metal nanoparticles, and hybrid nanocomposites outperformed others. In large-scale environmental monitoring programs, nano-solid phase extraction and magnetic extraction, because of their elevated recovery rates, less matrix interference, and shortened processing times, are better than traditional techniques[51]. Nano-sensors and biosensors further extend the analytical capabilities by enabling rapid, on-site detection with minimal sample handling. Electrochemical and optical nano-sensors exhibit ultra-low detection limits and real-time monitoring potential, which are critical for early warning systems and continuous environmental surveillance. The integration of nano-sensing platforms with microfluidic devices and wireless data transmission technologies supports the development of smart environmental monitoring networks that can provide continuous data streams for regulatory and research purposes[52]. Despite these advantages, several challenges remain that must be addressed before widespread implementation of nano-analytical technologies can be achieved. Concerns related to the environmental safety of nanomaterials, large-scale production costs, sensor stability, and standardization of analytical protocols continue to limit their routine application. Also, if the recyclable magnetic nanoparticles to mitigate high operational costs, 'Green Synthesis' protocols and surface functionalization with encapsulation to address nanomaterial instability would help monitoring strategies. In addition, regulatory frameworks for environmental monitoring have not yet fully incorporated nano-enabled analytical tools, creating barriers to their adoption in official monitoring programs[53, 54]. Future research should focus on developing environmentally

benign and cost-effective nanomaterials, improving long-term sensor stability, and establishing standardized validation procedures for nano-analytical methods. The integration of artificial intelligence and machine learning techniques with nano-sensor data is expected to further enhance analytical accuracy, automate data interpretation, and enable predictive environmental risk assessment. Such interdisciplinary approaches will play a crucial role in advancing sustainable environmental monitoring strategies and protecting ecosystems and public health from pharmaceutical pollution[53, 55, 56].

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