Research on Chemical Intermediates (2022) 48:3633–3683
https://doi.org/10.1007/s11164-022-04778-7

Occurrence, analysis and removal of pesticides, hormones, pharmaceuticals, and other contaminants in soil and water streams for the past two decades: a review

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Abstract

Chemical waste constitutes a group of environmental pollutants including pesticides, heavy metals, hormones, pharmaceuticals, and healthcare products that are widely distributed in our environment due to their wide use in various human activities. The presence of these compounds within local communities and ecosystems has drawn significant interest in improving the detection and bioremediation efforts of these compounds. Since these pollutants are highly mobile and stable under ambient conditions, there is a need to detect such pollutants in water and soil samples as an initial step that helps to eliminate their effect through adsorption or photocatalytic degradation processes. This review aims to highlight the origin of these pollutants and recent advancements in available analytical tools to detect such pollutants in environmental samples with a focus on pesticides, hormones, and pharmaceutical products. The environmental ecosystems of focus in this review involve soil, groundwater, and freshwater ecosystems. Various extraction and other pretreatment processes were also highlighted with a major focus on methods reported to decontaminate and help the environment through photocatalytic degradation of these pollutants under various conditions.

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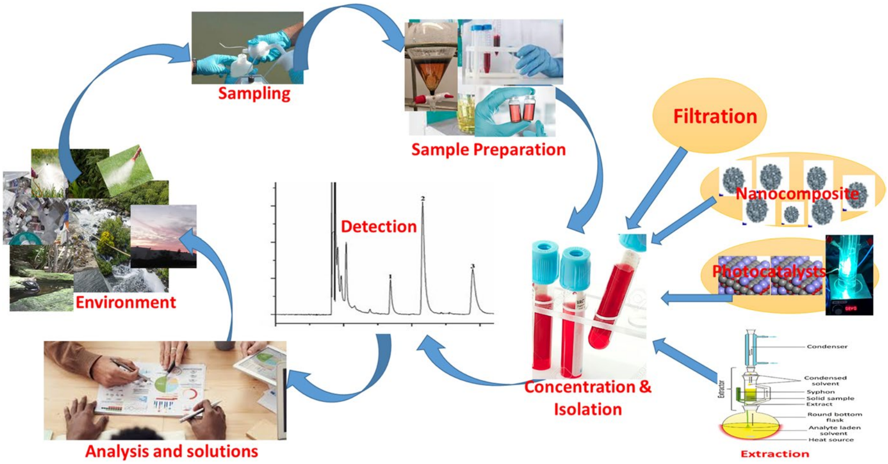
Graphical abstract



Keywords Pharmaceutical waste · Hormones · Pesticides · Organic pollutants · Phorodegradation · Mass spectrometry

Introduction

Recent advances in industrial chemical research and development have resulted in a substantial rise in pollutant production throughout arable land worldwide. From 1990 to 2000, the global pesticide production annual total was upwards of 20 million tons until widespread legislation discontinued commercial uses of various pesticides beginning in 2004 [1, 2]. As a result of these advancements, thousands of chemical pesticides and pollutants are still continually deposited in residential areas on an annual basis subsequently leading to exposure in wildlife and human communities [3]. This exposure to human and animal communities has seen substantial increases in recent years due to a myriad of factors that promote pollutant contact and environmental dispersion [4]. Commercial cultivation of valuable crops has resulted in a substantial demand for chemical compounds with either specific or ubiquitous modes of action within target systems that negate agricultural losses [5]. As demands within the U.S. economic output increased, industrial sectors involving potentially polluting compounds expanded significantly.

Beginning in the 1950s, a steady increase in the demand for agricultural and chemical infrastructure addressed commercial needs that led to increased chemical pesticide synthesis and applications [5–10]. The additional accumulation of pharmaceutical and carbon-based medical therapeutics has been reported extensively by Kolpin et al. and has indicated residual levels of these compounds are increasing annually [8, 9]. Chemical pesticides such as carbaryl and dieldrin have been synthesized in large quantities and applied ubiquitously in various areas to assist in

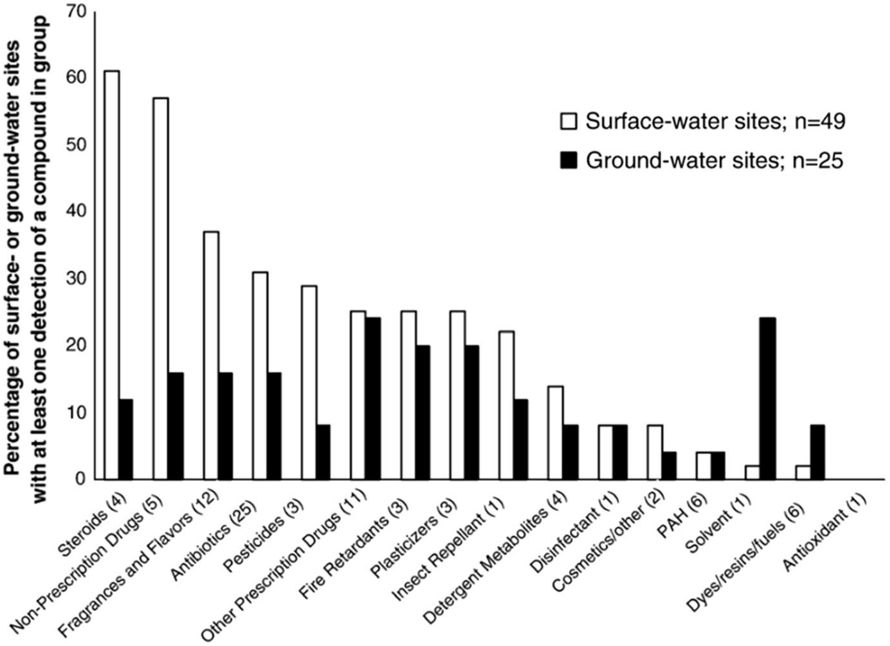


Fig. 1 Percent abundance of chemical pollutants detected in surface and groundwater sampling; Retrieved with permission from reference [9]

widespread pest management practices. As pesticide technology has advanced, the demand for chemical applications has reduced considerably due to the development of sustainable alternatives, yet deposits from past applications are a common source for these pollutants to disperse or accumulate [7, 8, 11]. As these chemical supplies increase, the accessibility and distribution of these compounds for commercial and residential uses increase exponentially [10]. Throughout the United States and other developed nations, the primary uses for these compounds are to enhance the protection of valuable crops from pest insects and to deter arthropod disease vectors from infecting hosts such as wildlife or humans [11]. Figure 1 summarizes the quantified chemical pollutants detected in surface and groundwater samples given that not all organic waste compounds were detected due to their potential to decompose or their presence in low concentrations as shown for the antixidant (1) sample [9]. Only until recently have developing nations begun to address the impact of continual applications in and around community settings [12]. Accumulation of these constituents in the natural environment arises from a variety of conduits with primary sources being runoff from aqueous systems or dispersion from contaminated soils [13].

Within the northeastern United States, evidence of pollutant accumulation through commercial applications and industrial waste has raised concerns regarding long-term effects on wildlife and human populations [13–15]. In addition to excess organic pesticide deposition, the accumulation of trace pollutants from industrial runoff has also become an area of increasing concern to the long-term health of human and animal communities. These compounds can either be of organic or

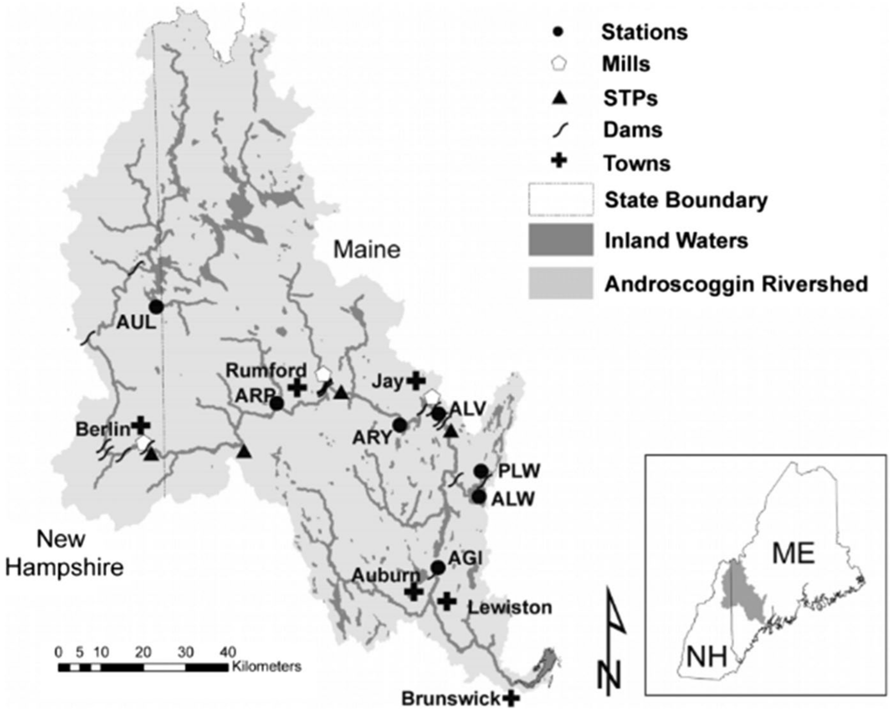


Fig. 2 Location of Pulp Mill processing and pollutant discharge areas within the northeastern United States; Retrieved with permission from reference [19]

inorganic nature which further complicates monitoring and remediation efforts due to different chemical properties between phases. Within industries such as pulp and paper processing, the wastewater generated as a byproduct of wood bleaching and digestion presents a substantial source of persistent pollutants such as dioxins or aryl chloride compounds [16, 17]. Recycling of generated wastewater has been studied to consistently follow the concentrations of chemical byproducts that are flushed downstream through natural waterways such as rivers and streams [18]. Figure 2 shows a sample map location of pulp mill processing and pollutant discharge areas within the northeastern United States [19].

The intrinsic chemical properties of these carbon-based compounds make degradation through natural removal pathways such as microbial or photodegradation difficult [19]. The combination of unnatural degradation and mass industrial production has led to the distribution of these compounds within residential and wildlife areas. The application of these compounds to sites is achieved in the form of aerosol or granular dispersions methods which influence the solubility of these chemical pesticides when applied to host environments [20]. The routes of exposure in food webs often come in the form of primary food sources, such as algal species, that have been routinely exposed to these recalcitrant compounds [21, 22]. Increases in bioaccumulation in higher-order wildlife species such as deer or avian species are mostly caused by the accumulation in the metabolic systems of plants or prey animals [22, 23].

This review highlights the trends in pollutant origination, current methods associated with pollutant detection, and removal conducted within the past two decades in the United States. The ecological dynamics that can result from these pollutant exposures differ depending on the exposure environment. The impact of persistent pollutants within human and wildlife communities is not necessarily limited to organic compounds but also inorganic chemical species that originate from industries essential to regional economies. Analyses of chemical transformations and concentrations involving techniques such as Raman spectroscopy or mass spectrometry, both of which are primary monitoring methods that determine the fate of these compounds before community exposures to high concentrations. Applications of these methods can vary in detection and operating costs, which can impede future uses in environmental health monitoring. The primary topics discussed follow changes in trends regarding pollutant spread and remediation involving improvements made to current methods such as photocatalysis or luminescence measurement. Trends involving this remediation strategy include surface enhancement, pollutant transformation products, and the role these compounds have within environmental settings.

Persistent organic pollutants in soil and groundwater systems

Community contact with chemical pollutants typically arises from the increased presence of contaminated soils and products that are sourced from these areas. Along with sediment deposits, accumulations of chemical pollutants within soil layers are one of the leading contributors to chemical transfer through waterways within an affected environment [24, 25]. Carbon-based organic pollutants are the common species detected in pesticide monitoring, yet historic industrial reports also suggest the use of inorganic elements as chemical cofactors [24, 25]. The impact of inorganic pollutants has been documented extensively yet their roles in the decline of community health have only recently been discussed in public health literature [14, 26]. Focus on inorganic contributions to pollutant transport can assist investigators in elucidating the interference pathways inorganic ions present in organic pollutant monitoring efforts. Analyses by Hope et al. [18] provided evidence of inorganic chemical transport through wastewater discharges that enable chemical hydrolysis, chelation, and subsequent element speciation [18]. Pollutants involving metallic chemical species primarily originate from industrial wastewater discharges and pesticide formulations that contain metallic species for preservation and degradation-resistant purposes [27–31]. Upon exposure to soil layers, the permeation into lower sublayers and groundwater layers permit further pollutant settlement and downstream transport. Although these additives in industrial mixtures are present in minute concentrations, studies on the cytotoxicity of these formulations suggest acute toxicity and biomagnification in host tissue [32]. The inherent toxicity present in metallic species arises from changes in outer shell valence states which contribute to the formation of distinct elemental species with different chemical properties and the formation of organometallic analogs.

Speciation of metallic pollutant compounds in soil systems involves valent state transformation and systems transport, which permits chelation of organic compounds and organometallic compound speciation [33–35]. Transition metal elements such as Hg, Cu, Cd, Co, As, Pb and Ni are found naturally in trace amounts yet increasing residue levels within saturated and unsaturated soil zones have been recorded [29–32]. Solubility of these metallic elements into mono- or divalent species is influenced by chemical reactions within the environment and contributes to the enhanced transport from the soil into groundwater systems [33, 34]. Interactions with dissolved organic content (DOC) and other organic constituents in soil facilitate the speciation of transition elements into organometallic compounds, which decrease solubility and enhance the probability of bioaccumulation [36, 37]. Soils of wildlife areas adjacent to treated agricultural plots are vulnerable to organometallic exposure since microbial and arthropod communities may not bear-resistant attributes [38]. Organic pollutants that are present in various concentrations can also chemically interact with these compounds and contribute to downstream transformations [33–42]. Due to the lack of inherent metabolic qualities, microbes within these communities are not likely to metabolize recalcitrant inorganic compounds present, allowing them to permeate into soil and groundwater matrices [40].

Both inorganic and organic physical transfer processes involved in soil pollutant accumulation, such as leaching and site runoff, allow the expansion of pollutant drift and adjacent wildlife contamination [41, 42]. Investigations by Kanan et al. determined natural degradative processes such as photodegradation enable the formation of transformed organic and organometallic chemical species that can present increased toxicity than parent molecules in biological systems [43, 44]. Chemical processes such as adsorption contribute to pollutant persistence in affected soils by inhibiting transport and subsequent degradation by microbial or photophysical pathways [44, 45]. Humic analogs within topsoil layers have been reported to allow for the formation of covalent bonds within functional groups which can promote inorganic pollutant chelation and persistence [45]. Investigations on pollutant transport suggest pollutant transport through subsoil horizons and permeable bedrock layers, which can subsequently contaminate aquifer systems [45–48]. Pollutant transport through soil layers is an extensive environmental hazard that can be difficult to monitor using current detection techniques. Limitations in detecting soil pollutants can arise from interference by soil components such as humic acids or metallic ions.

Persistent organic pollutants in freshwater systems

Pollution within waterway systems is a primary conduit for contamination deposits and runoff accumulation within inland and coastal regions [48, 49]. The geophysical nature of aquatic systems such as rivers and lakes are desirable areas for soluble pollutants to accumulate over time. Predisposition to changes in geochemical cycling has been hypothesized to lead to an increase in susceptibility to chemical pollution within these aquatic systems [50, 51]. The work of Amirbahman et al. has indicated chemical speciation and byproduct transformation can have significant effects on the pollutant distribution and biological interactions during transport in water [52, 53]. The deposition of chemical species in commercial water systems typically arises from runoff within industrial facilities such as paper and textile mills. In industrial processes such as commercial paper production, wastewater is constantly generated and deposited elsewhere as digestion and finishing of paper products continue [53]. Chemicals such as chlorophenols and chlorinated alkyl chains are known to be by-products of pulp digestion and contribute substantially to pollution caused by effluent runoff [54, 55]. Continual dispersion of pollutants into waterways facilitates dispersion across sedentary aquatic systems such as lakes or vernal pools [55–57]. Throughout the twentieth century, pollution stemming from these chemical deposits was the primary cause of significant pollution in the northeastern United States and continental North America.

In the U.S. state of Maine, pollution of major waterways such as the Androscoggin and Penobscot river watersheds was widespread enough to spur legislative efforts from local and federal government policy [58]. Before the Clean Water Act of 1972, pollution within affected river systems was apparent to the point of physical observations such as solution immiscibility and odor accumulation from community bystanders [58]. The work of Walter Lawrence indicated that chemical pollutions such as sulfites and other analogs were significant contributors to pollution discharge and byproduct odor [59]. These byproducts form as a result of the Kraft chemical process which is an industry-standard digestion process in commercial paper-producing facilities [59–62]. Digestion of cellulose fibers has been reported to produce a significant amount of contaminated liquid waste which is abundant in soluble chemical products and chemical additives that were discharged into Maine waterways [60]. Structurally, these pollutants resemble other organic pollutants such as pharmaceuticals or hormones.

Due to the aqueous phases of these compounds, removal of this contaminated wastewater is usually diluted in treatment facilities before dispersion into natural waterways [63]. Legislative action has worked to limit the amount of wastewater generated from industrial production and implement remediation protocols that better optimize common chemical detection methods discussed [64, 65]. Aeration of wastewater has been used to increase the degradation of parent chemical effluents and regulate the formation of organic and inorganic pollutant byproducts [66]. Efficient monitoring of certain inorganic compounds such as organophosphorus and organosulfur have sparked recent investigative interests due to the acute toxicological threat posed to humans and wildlife [67]. The primary mode of action within these compounds is to arrest essential metabolic signaling cycles that trigger tissue damage and pest population reduction [68]. These toxicological properties can occur in a variety of concentrations which also poses a significant problem for aquatic monitoring and remediation community services [69]. Despite landmark policies, trace pollutant concentrations continue to be a problem throughout global communities and the demand for efficient monitoring and remediation efforts increases annually. In order to enhance current pollutant monitoring frameworks, detection methods used by agencies require mechanistic classifications of parent compounds and associated byproducts.

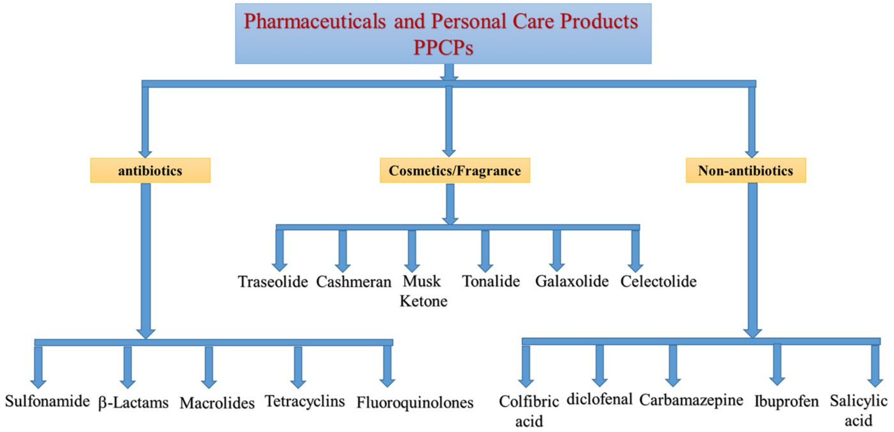


Fig. 3 Classification of the PPCPs based on their mode of action

Classification of the organic target pollutants

Pharmaceutical and personal care products

Pharmaceutical and personal care beauty products (PPCPs) are one of the major categories that impose concerns on the environment. Besides their release from manufacturing sites, hospitals, and nursing homes [70–73], PPCPs are generally transformed, or even unchanged within the wastewater treatment plants and then are moved to the aquatic environment due to their high stability [70]. The removal of these products from wastewater is challenging due to their diverse structures and physical properties. They include all chemicals and drugs like antibiotics, hormones, anti-inflammatory drugs, lipid regulators, steroids, and antiepileptics. In literature, these products can be classified into three major categories based on their mode of action as presented in Fig. 3. These hazardous substances discharged from manufacturing industries and hospitals can not be removed from water bodies via traditional methods such as photolysis. Instead, it is very important to apply physical, chemical, and biological methods to ensure complete removal and pollutant mineralization.

Hormones

A variety of natural and man-made chemicals provide endocrine activity in vertebrates. These chemicals are identified as endocrine-disrupting chemicals (EDCs) and were found to be present in water resources due to their vast use. EDCs including natural steroidal hormones [74], pharmaceuticals, and personal care products (PPCPs) were detected in environmental and aquatic wildlife samples [75]. Several studies have reported the effect of these substances in water bodies, highlighting their negative effects on humans and animals [76].

For instance, estrogens are an important group of compounds in menstrual and estrous reproductive cycles (a few examples are presented in Table 1) with Estrone

Table 1 Summary of the most common hormones detected, uses and chemical structures

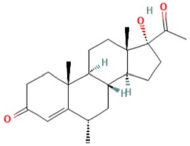
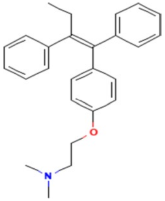
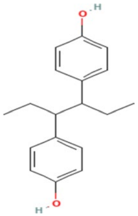
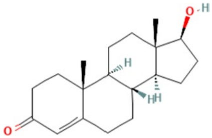
Hormone/estrogens	Structure	Uses/comment	References
Medroxyprogesterone		Female hormone (progestin) to reduce menopause symptoms is also added to estrogen replacement therapy to reduce the risk of cancer of the uterus	[85–91]
Tamoxifen		Used for women and men diagnosed with hormone-receptor-positive, early-stage breast cancer after surgery and to reduce breast cancer risk in women	[92–100]
Hexoestrolum		Used as a hormonal antineoplastic agent	[101–105]
Testosterone		A sex hormone and anabolic steroid in males which plays a key role in the development of male reproductive tissues	[106–111]

Table 1 (continued)

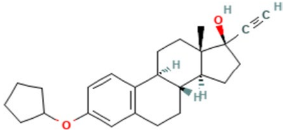
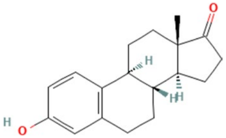
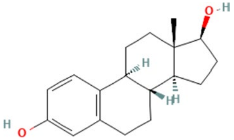
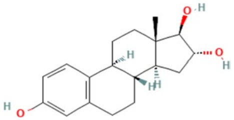
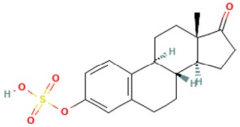
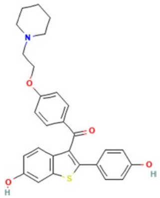
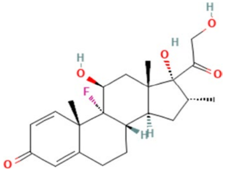
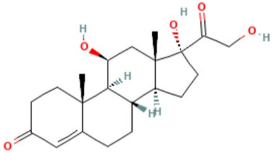
Hormone/estrogens	Structure	Uses/comment	References
Quinestrol		Used in menopausal hormone therapy, hormonal birth control, and to treat breast cancer and prostate cancer	[112–117]
Estrone (E1)		A minor female sex hormone	[118–121]
17B-Estradiol (E2)		It is involved in the regulation of the estrous and menstrual female reproductive cycles	[122–127]
Estriol (E3)		A dominant estrogen during pregnancy	[128–132]
Estrone sulfate		Used as hormone replacement therapy, treatment some types of infertility and breast and prostate cancer	[133–137]

Table 1 (continued)

Hormone/estrogens	Structure	Uses/comment	References
Raloxifene		Used to prevent and treat osteoporosis	[138–146]
Dexamethasone		Used to treat rheumatic problems, skin diseases, severe allergies, asthma, chronic obstructive lung disease	[147–155]
Hydrocortisone		Used to treat adrenocortical insufficiency, adrenogenital syndrome, high blood calcium, thyroiditis, rheumatoid arthritis, dermatitis, and asthma	[156–163]

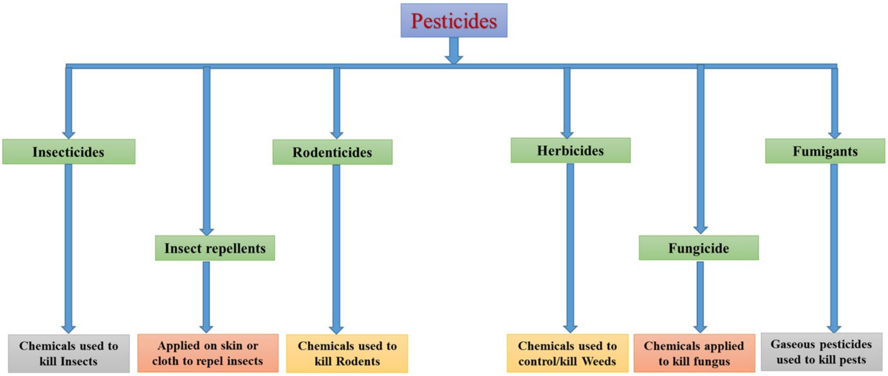


Fig. 4 Classification of pesticides based on their mode of action

(E1), estradiol (E2), and estriol (E3) are among the most commonly used estrogens [77]. These natural compounds (E1, E2, and E3) are with a similar structure except for variations at the 16 and 17 sites as presented in Table 1. Such compounds were found to play major roles in regulating the physiological functions of various organs including the brain, heart, and bone [78–80]. These steroid estrogens are the most widely investigated as female hormones because of their high estrogenicity at low concentrations and their availability in various matrixes including drinking, ground, and surface water [81].

Glucocorticoids Dexamethasone (DEX) and hydrocortisone (HDS) are steroid hormones with hydroxyl moiety as an active group with HDS has three hydroxyls identified at different positions. Their mode of action stems from binding to their intracellular receptor, which is a ligand-inducible transcription factor belonging to the nuclear receptor family [82]. Upon ligand binding, the glucocorticoid receptor (GR) complex changes its conformation and travels to the nucleus so it will interact with coregulators that assist GR transcriptional actions [83]. Dexamethasone is used to treat various skin diseases, severe allergies, asthma, and chronic obstructive lung disease [84].

Pesticides

Due to the vast increase in the world's population, the demand for food production enhanced significantly during the past few decades to protect crops and thus food supplies. Pesticides can be classified based on their difference in application or based on their major chemical groups as summarized in Figs. 4 and 5, respectively.

Since many pesticides are toxic to humans, understanding the ultimate fate and transport of these chemicals in the environment becomes a necessity. Photochemical reactions are important as they occur in both the natural environment and in the context of wastewater treatment [164–185]. Besides the toxic effect they impose, most pesticides are of concern due to their potential for bioaccumulation. Since some of these pollutants are stored rather than metabolized, significant accumulation elevates the concentration levels as identified and magnified in the food chain. Given the risk

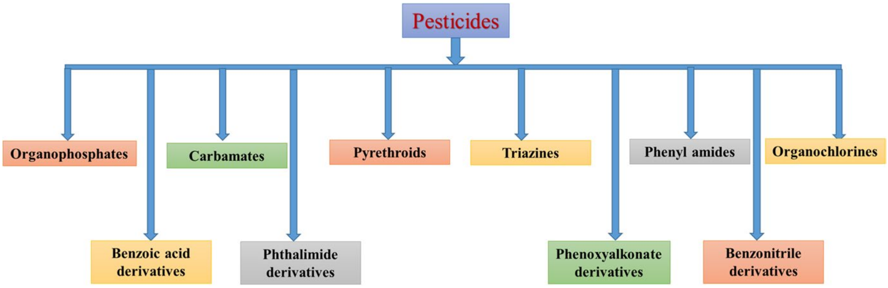


Fig. 5 Classification scheme for pesticides based on their functionality

associated with the extensive use of pesticides, it is important to study their stability under ambient conditions and provide ways to decompose and decontaminate them from the environment. Several studies and data were gathered to understand the fate and transport of these pollutants in the environment as well as their behavior in aquatic and soil environments. For example, in anoxic environments, pesticide biodegradation may involve different mechanisms relative to oxic environments [186]. Pesticides may also be subjected to transient anoxia that will result in the potential for anaerobic microbial activity that may affect the transformation of the chemical structure of the pesticide by different means. The duration of anoxic conditions influences the redox regime and consequently the composition of the microbial community [186]. Recently, major concerns by scientists and governmental agencies researching speciation and assessment of the pesticides contamination level in the water, soil, and sediment samples [187], provide adsorbing material that reduce the contamination level [43, 164–175], as well as to fabricate various catalysts to reduce their potential to accumulate and enhance their photodegradation rate [164–185].

Detection and analysis methods

Pharmaceutical monitoring data in marine waters are necessary for water quality assessment to allow enhancing future regulations and management decisions. The use of integrated monitoring through long-term ecotoxicological tests on sensitive marine species at environmental levels facilitates a better understanding to assess the ecological risk of these compounds for the marine and environmental ecosystems. Below, we provide a comprehensive review of various detection procedures and techniques that tactile the current challenges in monitoring strategies of pharmaceuticals and industrial organic pollutants in marine matrices through the analysis of the available recent scientific literature.

Advanced chromatography and mass spectrometry

Chromatography is one of the most common techniques used to assess the chemical purity of drug substances and the pharmaceutical industry from drug development to quality control (QC) applications [188–195]. In particular, reversed-phase liquid chromatography (RPLC) is a universal process to analyze mild to polar substances [188, 196, 197]. Given the hydrophilicity and the ionic features of most, the pharmaceutical products, various modifications in pharmaceutical research and development are implemented including the use of method development software, fast-LC, 2D-LC, SFC, HILIC, LC–MS, GC and GC/MS, stationary phase deactivation, ultra-high performance/pressure liquid chromatography, and variety of modified columns dedicated to biopharmaceutical analysis [188, 190–192, 198–208].

For example, Radjenovic et al. have reported the fate and the behavior of pharmaceutical residues during conventional wastewater treatment using membrane bioreactor for activated sludge treatment [190]. Time-of-flight (TOF) gas chromatography–mass spectrometry and liquid chromatography-mass spectrometry are used in the environmental monitoring of pharmaceutical residues and their known degradation products [190]. The TOF detector provides accurate-mass measurements and full-scan spectra that help to identify the degradation products [190, 199]. LC/ TOF-mass spectrometers can utilize both for target analytes and other non-target analytes [199].

Lipid-rich matrices including pesticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) are identified and quantified in a whale earplug. The analytes were selectively extracted using high-pressure liquid extraction and analyzed using gas chromatography–mass spectrometry with electron capture negative ionization and electron impact ionization [201]. The average percent recoveries for the persistent organic pollutants (POPs) were 91% with limits of detection ranging from 0.00057 to 0.96 ng/g. Pesticides, PCBs, and PBDEs were also detected in a single blue whale (Balaenoptera musculus) cerumen lamina at very low concentrations from 0.11 to 150 ng/g [201]. Liquid chromatography (LC) coupled with high-resolution mass spectrometry (Exactive-Orbitrap) was used to quantify hundreds of toxic substances, found in ginkgo Biloba nutraceutical products, including pesticides and mycotoxins [209]. Recoveries between 70 and 120% with relative standard deviation (RSD) values lower than 20% were obtained for 260 of the compounds with 5 and 10 μg/kg limits of detection and quantification, respectively [209]. Lopez et al. used liquid chromatography with both diode array and mass spectrometric detection (LC–DAD–MS) toward the determination of six estrogens (17b-estradiol, estriol, estrone, ethynylestradiol, mestranol, and diethylstilbestrol) and four progestogens (progesterone, levonorgestrel, norethindrone, and ethynodiol diacetate) in several types of water bodies. For most compounds 85% recoveries with detection limits as low as 1 ng/L were achieved [202].

Solid-phase microextraction modified silanols along with gas chromatography-mass spectrometry (GC–MS) was developed for simultaneous detection of exogenous endocrine-disrupting chemicals (EDCs) and endogenous steroid hormones in environmental aqueous and biological samples [202, 210]. The limit of detection (LOD) and limit of quantitation (LOQ) values of target compounds in river water were in the range of 2–3.78 ng/L and 8–126.1 ng/L, respectively [202]. Further, both gas chromatography and liquid chromatography-tandem mass spectrometry were used for the analysis of 58 potential Endocrine disrupting compounds (EDCs) in various water matrices using a single solid-phase extraction (SPE) of a 1 L sample.

Instrument detection limits ranged between 0.12 and 7.5 pg with corresponding method reporting limits of 1–10 ng/L in water with % recoveries between 50 and 112% for all compounds [206]. Further, combined high-sensitive MS instrumentation is used for protein labeling workflows that provide wide-ranging labeling reagents [191].

Six types of endocrine-disrupting chemicals including bisphenol A, triclosan, two alkylphenols, two phenylphenols, eleven organophosphorus pesticides, and seven parabens were identified in Seafood samples and detected using ultrasound-assisted extraction, continuous solid-phase extraction, followed by GC–MS analysis [211]. The method is very accurate with a 0.5–20.0 ng/kg detection limit and up to 84–105% recoveries [211]. Further, Huang et al. detected eight pharmaceuticals in aqueous samples using automated derivatization solid-phase microextraction coupled with gas chromatography-mass spectrometry [212]. The modified method was directly applied to surface water where flurbiprofen, naproxen, and tolfenamic acid are detected with a detection limit at ng/L levels [212]. Solid-phase extraction applied for a simultaneous determination of nine pharmaceuticals and three hormones in water samples was reported [213]. The method showed good analytical results including recoveries of 85–103%, low limits of detection (0.01–0.06 ng L^{-1} for 100 mL of water), and good linearity throughout the studied concentration ranges [213]. In addition, dispersive solid-phase extraction using acetonitrile, magnesium sulfate, and sodium chloride to a small number of blood samples was an efficient method to separate a variety of pharmaceuticals belonging to various therapeutic categories of drugs and poisons with the typical limit of detection below 20 ng/mL [214].

Sequential superheated liquid extraction of pesticides, pharmaceutical, and personal care products with different polarity from marine sediments followed by gas chromatography–mass spectrometry detection have been extensively studied. For example, a superheated liquid extraction method was efficient to isolate various pesticides, pharmaceuticals, and personal care products including triclosan, estrone, 17(3-estradiol, diethylstilbestrol, 4-octylphenol, procymidone, permethrin, oxyfluorfen, bisphenol A and 2,8-dibenzodichloro-p-dioxin from sediments was reported [215]. The extracted samples were accurately detected by gas chromatography-mass spectrometry [216]. Soliman et al. reported a rapid gas chromatography–mass spectrometry screening method for human pharmaceuticals, hormones, antioxidants, and plasticizers in water [217]. Nineteen compounds were detected with recoveries from 57 to 120% were reached with detection levels varied between ng/L and μg/L levels [217].

Recently, Ultrasound-assisted extraction followed by gas chromatography–mass spectrometry was successfully used to detect twenty pharmaceutical contaminants in soil samples [218]. Detection limits from 0.3 to 1.7 ng/g were reached with above 80% absolute recoveries obtained for most of the target compounds [218]. In another study, soil samples were extracted by different solvents using ultrasonic treatment at 42 kHz, followed by solid-phase extraction and N-methyl-N-(tert- butyldimethylsilyl) trifluoroacetamide derivatization before GC–MSD detection [219]. The method was useful in the selective and accurate detection of six different pharmaceuticals and personal care products namely; clofibric acid, ibuprofen, naproxen, ketoprofen, diclofenac, and triclosan as well as three endocrine-disrupting compounds namely; 4-*tert*-octylphenol, 4-*n*-nonylphenol, and bisphenol A [219]. Recoveries of all the analyzed compounds were from 63.8 to 110.7% for the spiking level of 100 ng/g of dry soil [219].

Time of flight mass spectrometry

Time of flight mass spectroscopy is one of the most accurate methods for pharmaceuticals, pesticides, hormones, and health care products [220–225]. Comprehensive two-dimensional liquid chromatography coupled to a high-resolution time of flight mass spectrometry was applied for accurate chemical characterization of sewage treatment plant effluents [220]. Twenty compounds were found in an extract of a wastewater effluent, based on their accurate mass identified from the ChemSpider database [220]. He et al. detected fifty pesticides in wine using liquid chromatography/quadrupole time-of-flight mass spectrometry combined with liquid chromatography/quadrupole linear ion trap mass spectrometry [221]. Further, 136 pharmaceuticals and hormones were detected in sludge using a simple extraction method followed by analysis with liquid chromatography–time-of-flight-mass Spectrometry [222]. Most of the target compounds were identified at detection limits from 1 to 2500 ng/g, depending on the nature of the substance [222].

Liquid chromatography triple quadrupole mass Spectrometry LC–QqQ-MS/MS and liquid chromatography quadrupole time-of-flight mass spectrometry (LC–QTOF-MS) are used in the screening of pesticides and other contaminants in water samples [223]. All the analyzed pesticide samples including buprofezin, chlorfenvinphos, chlorpyriphos, atrazine-desethyl, diazinon, dimethoate, diuron, hexythiazox, imazalil, prochloraz, and pyriproxyfen were found at concentrations higher than 0.5 μg/L [223]. As an example, Fig. 6 shows the UHPLC–TOF MS chromatograms and accurate mass spectra for several pharmaceuticals and pesticide contaminants detected in influent wastewater samples [223]. The extracts were screened for 43 pesticides along with their degradation products at limits of detection (LOD) ranging from 0.04 to 2 ng/L [223]. In addition, ultra-high-performance liquid chromatography coupled to quadrupole-orbitrap high-resolution mass spectrometry was used for multi-residue screening of pesticides, drugs, and mycotoxins in edible insects [225]. With a single screening methodology, the method provides a broad range of physicochemical diverging residues in insect tissue with good recoveries between 70 and 120% [225].

Tandem mass spectrometry

Tandem mass spectrometry was extensively used for the accurate detection and analysis of pharmaceutical drugs, pesticides, and hormones from various environmental samples [224, 226–234]. For example, online solid-phase extraction (SPE)–liquid chromatography-electrospray–tandem mass spectrometry (LC–MS-MS) was successfully used in detecting 74 pharmaceuticals in environmental and sewage waters with high selectivity and sensitivity in ng/L detection

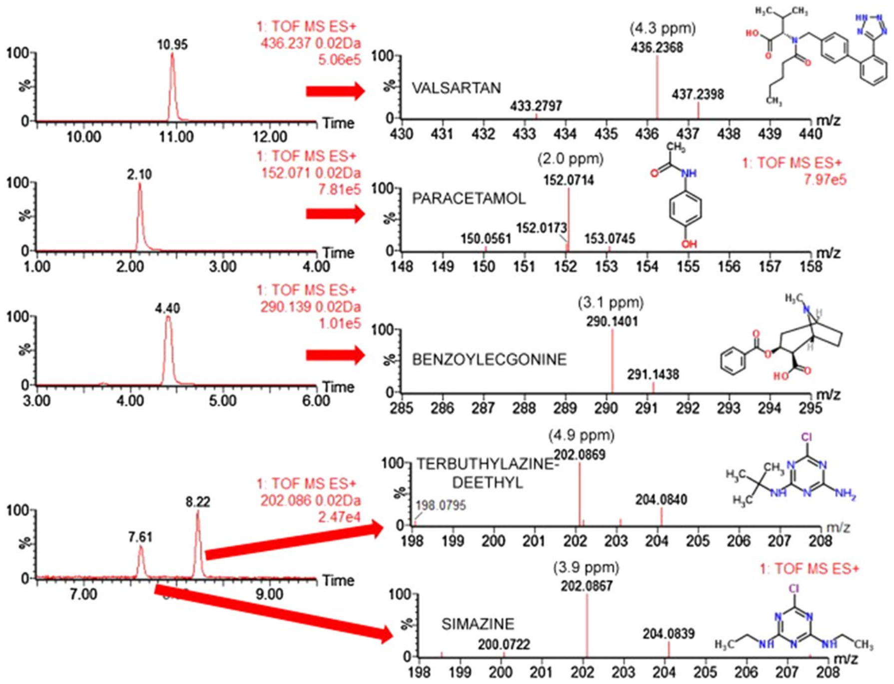


Fig. 6 UHPLC–QTOF MS extracted-ion chromatograms at different m/z (mass window 20 mDa) for pharmaceuticals valsartan and paracetamol, the main metabolite of cocaine (benzoylecgonine), pesticide simazine, and a transformation product (terbuthylazine-diethyl); Retrieved with permission from reference [223]

limit scale [226]. The same method was developed for the analysis of six pharmaceuticals by isotope dilution. These selected pharmaceuticals were chosen as representative indicator compounds and were used to evaluate the performance of the online SPE method in four distinct water matrices. Detection limit ranged from 10 to 25 ng/L, based on a 1 mL extraction volume was reached with a matrix spike recoveries ranging from 88 to 118% for all matrices investigated, including finished drinking water, surface water, wastewater effluent, and septic tank influent [229]. In addition, a simultaneously developed process based on off-line solid-phase extraction and ultra-high performance liquid chromatography coupled to tandem mass spectrometry (SPE–UHPLC–MS/MS) for the detection of seven pharmaceuticals and two metabolites belonging to the non-steroidal anti-inflammatory drugs and analgesics therapeutic groups [227]. The obtained detection limits range from 0.02 to 8.18 ng/L [227].

Single-hole hollow molecularly imprinted microspheres were applied to extract six triazine pesticides from cereal, rice and wheat samples, followed by HPLC–MS/MS detection [228]. The method reached detection limits of triazines in the range of 0.08–0.16 ng/g with triazine recoveries for spiked samples of 5 ng/L reaching from 81 ± 4 to 96 ± 4% [228]. Aparicio et al. used a dispersive solid-phase extraction followed by liquid chromatography-tandem mass spectrometry in detecting household and industrial chemicals, personal care products, and hormones in leafy and root vegetables [230]. The method showed low detection limit ranges in 0.025 and 12.5 ng/g with 81–126% recoveries obtained for all detected samples [230]. Steroid hormones were detected by cyclic-organophosphate derivatization followed by UPLC-MS/MS detection [234]. The sensitivity and % recoveries of the method depend on the hormone tested. The obtained limit of detection ranges from 130 pg/mL for β-estradiol to 240 pg/mL for estriol. The method's recovery rate for the lowest concentration tested (800 pg/mL) is 88.1–96.3% [234].

A matrix-solid phase dispersion (MSPD) followed by a HILIC-MS/MS detection method aimed at the use of active solid supports and less toxic solvents was developed for the simultaneous determination of nineteen pharmaceuticals, four personal care products (PPCPs), and four degradation products in sewage sludge samples [231]. The prepared calibration curves in methanol and the matrix extract showed an excellent correlation coefficient ranging from 0.98 to 0.99 with detection limits from 1.25 to 1250 ng/g is obtained [231]. Liquid chromatography coupled with tandem mass spectrometry was used for the analysis of 44 of the foremost pharmaceuticals consumed by the elderly. The extraction cartridge, pH, and volume, as well as the liquid chromatography-tandem mass spectrometry conditions, were optimized to minimize matrix effects and obtain high yields. Excellent and selective detection was obtained, with recoveries between 27 and 116% [232].

Luminescence-based detection

Luminescence is the process of natural emission of light induced by absorbed energy. Upon irradiation, a photon of certain energy is absorbed by an organic molecule, various photophysical changes occur including vibrational relaxation, fluorescence, phosphorescence, or intersystem crossing. The luminescence properties of a target molecule (luminophore) could be modulated by introducing energy and electron-transfer processes, the presence of heavy-atom effects, and changes in concentration and electronic density. The concept of the diverse fluorescence-based chemosensors is initiated by the photo-induced electron transfer process (PET), which is the most common approach to building suitable luminescent sensors. These sensors require three major components that must be carefully selected: fluorophore spacer-receptor model where an ionic or molecular input at the receptor site can modulate the emission, causing the luminescent emission to be switched either "off–on" or "on–off" upon sensing.

Luminescence-based sensing and detecting assays are also reported for the detection of various organic pollutants including pesticides, hormones, and pharmaceutical products [126, 235–245]. Several reviews described various modified luminescence assays for sensitive and selective detection of organic pollutants in environmental samples [235, 240, 241, 245, 246]. For example, electrogenerated chemiluminescence (ECL) is a widely used analytical technique in clinical testing, biowarfare agent detection, and pharmaceutical analysis [247]. The ECL method biosensors include immunoassays, immunosensors, aptamer-based and enzyme-based biosensors all are designed for the pharmaceutical quantification with most studies reviewed [247]. Nano-based materials including quantum dots and carbon dots were adapted as novel ECL emission materials and enhancers in typical ECL systems [247]. Sigroi et al. investigated the adsorption of dissolved organic matter on activated carbon by filtration from different water samples like wastewater, surface water, and synthetic water. It was determined that fluorescing components with maxima intensity at higher excitation wavelengths, correspond to humic-like fluorescence substances, highly adsorbed than other components in all waters [236]. Correlation models were developed to monitor breakthroughs of emerging organic contaminants during activated carbon filtration using fluorescence indexes and UV_{254} where fluorescence indexes resulted in more sensitive surrogates than UV_{254} to predict emerging organic contaminants breakthrough during the adsorption of the activated carbon granules [236]. Also, the same group has reported the use of different fluorescence excitation and emission probes and relevant data interpretation and analysis to monitor the removal of emerging contaminants in full-scale wastewater treatment plants [243].

The use of fluorescence and UV absorption for the detection of low levels of the biogenic succinic acid (SA), an antioxidant pharmaceutical is illustrated [237]. It is shown that the fluorescence spectra of SA systems are capable of detecting SA at concentrations ranging from 10^{-7} to 10^{-5} M [237]. The study confirmed the potential use of fluorescence as a marker of bio-effects of diluted aqueous biologically active compound systems [237]. A competitive fluorescence-linked immunosorbent assay based on monoclonal antibodies conjugated with quantum dots was used for rapid and sensitive analysis of DT-13 and its metabolite levels in biological samples with recovery rates ranging from 85.28 to 101.40% [239].

Fluorescence-based biosensing probe using the thermophilic esterase 2 from A.acidocaldarious, was developed for the continuous monitoring of organophosphate compounds [242]. The addition of aliquots of the paraoxon pesticide was detected and quantified in real-time by measuring the fluorescence quenching of the probe-enzyme complex [242]. Steady-state luminescence was used to examine the emission properties of aromatic luminescent compounds and their inclusion complexes with 13-cyclodextrin (J3CD) and hydroxypropyl-13-cyclodextrin (HPCD). Various pesticides and indoles were examined, where 3CD and HPCD can be employed instead of organic solvents in the spectrofluorimetric determination of several compounds with different aromatic nuclei and different polarities [248]. Tb-based metal–organic framework (Tb-MOF) nanozyme has dual functions of a catalyst and luminescent sensor specifically for the determination and degradation of hormone 17β-estradiol (E2) and its derivatives (E1, E3, and EE2), a class of disruptors with strong effect on the human endocrine system. fluorescence probe for the detection and degradation of Estrogen Endocrine Disruptors (E2) [126].

Raman spectroscopy

When electromagnetic radiation falls on atomic or molecular samples it may be absorbed, transmitted, or scattered. The scattered radiation may be at a similar, lower, or higher wavenumber of the incident electromagnetic radiation, which results in Rayleigh, stokes, or anti-stokes Raman scattering, respectively. Given that, the intensity of the scattered light is proportional to its wavelength and the Raman scattering is very weak and hard to observe, it is essential for the incident radiation to be monochromatic. Recent advances in electronics, lasers, optics, and nanotechnology have made Raman spectroscopy suitable in many various applications including for environmental and pharmaceutical sectors. In specific, surface-enhanced Raman spectroscopy (SERS) is an ultrasensitive analytical technique that provides selective molecular fingerprint information in a short response time with minimal sample pretreatment conditions. The Raman scattering is enhanced through enhanced adsorption of the molecules on rough nanostructure surfaces such as gold or silver nanoparticles.

Several studies highlight the use of Raman spectroscopy in the food industry and environmental monitoring and analysis [198, 249–254]. For example, Surface Enhanced Raman Spectroscopy (SERS) is a sensitive technique that enhances Raman scattering when molecules are adsorbed on rough and active nanostructure surfaces like gold or silver nanoparticles. The method gives selective spectral enhancement that led to an increase in the sensitivity of the method [249]. The lowest limit of detections obtained was 0.45 µg/L for Mercury; for pharmaceuticals, 2.4 µg/L for propranolol; for endocrine disruptors, 0.35 µg/L for 17β-estradiol; for perfluorinated compounds, 500 µg/L for perfluorooctanoic acid [249].

The silver nanoparticle-based platform was modified as a SERS to detect methomyl, acetamiprid-(AC) and 2,4-dichlorophenoxyacetic acid-(2,4-D) residue levels in green tea via solid-phase extraction [250]. The method provides a linear correlation between the SERS and concentration with a very low detection limit range of 1.88–5.6 ng/ml [250]. Chemical imaging using confocal Raman has the potential to spatially image pharmaceutical active ingredients and relate their distribution to product performance [252]. In specific, UV Raman microscopy with 266 nm laser irradiation of four pharmaceutical compositions of interest, including two types of tablets containing low doses of active ingredients (in the 0.2% w/w range), an amorphous dispersion containing 1% w/w of a small molecule drug, and an enteric-coated layered peptide formulation. Resonance Raman enhancements are observed for four of the active ingredients studied in these formulations [252]. Further, coated Au nanoparticles (NPs) with Prussian blue (PB) shell (Au@PB NPs) were developed and used for quantitative detection of dopamine (DA) concentrations in blood serum and crystal violet (CV) contaminants in lake water using Raman spectroscopy [198]. Similarly, surface-enhanced Raman scattering using gold nanoparticles provide an accurate fingerprint to determine a low-concentration and selective detection of indole-like plant hormones [253].

Surface plasmon resonance sensors

Surface plasmon resonance (SPR) has an affinity for biomolecular interaction analysis [255–264]. Depending on the detection features, SPR devices are classified as angular, intensity, wavelength, and polarization modulations. By immobilizing one of the partners of the pair on an active metal surface and allowing, the other partner to flow in excess over that surface will generate a change in the refractive index at the metal surface upon the interaction between both partners when the equilibrium is reached at that surface.

Due to their high sensitivity and chemical stability, and ease to functionalize the surface with multiple biological ligands, gold nanoparticles (Au-NPs) provide an excellent SPR platform for chemical and biological species using plasmonic Au-NPs as a sensitive signal transducer. This affinity received great attention in the field of environmental sciences and medicine [260, 261, 263, 265]. Similarly modified gold surfaces with alkane thiolates and carboxylic groups are well documented for covalent attachment of proteins, peptides, and DNA molecules [265–270].

Recently, several colorimetric sensors were developed for the detection of a variety of hormones, proteins, DNA (deoxyribonucleic acid) [265–286]. For example, DNA-mediated Au-NPs have been widely used to develop sensors for the detection of the genetic mutation of DNA for cancer diagnosis [287]. A direct SERS detection was demonstrated with glucose at physiologically relevant concentrations [288]. In addition, it provides biomarkers for tumors based on breath analysis of patients introducing an early diagnosis for gastric cancer patients from healthy persons [289]. For example, the interaction of citrate-coated gold NPs (AuNPs) with human plasma proteins was selected as a case study to evaluate the applicability of the localized surface plasmon resonance (LSPR) as evaluated against fluorescence spectroscopy [257]. Results obtained from the interaction of AuNPs with bovine serum albumin, glycosylated human transferrin, and non-glycosylated recombinant human transferrin are well-correlated with the Stern–Volmer constants obtained from fluorescence spectroscopy. This introduces LSPR as a new method for the investigation of a nano-bio interface [257].

Lechuga et al. developed binding inhibition immunoassays on an SPR from Sensia SL, where hormones immobilized by amino-coupling on the sensor surface under certain conditions that enable the detection of growth hormone [259], follicle-stimulating (hFSH) and luteinizing hormones (hLH) [262] in human serum samples with high sensitivity. All biosensors were reusable from 50 to 100 consecutive assay cycles and specific for each analyte [259, 262]. SPR immunosensor was developed for the detection of cortisol and cortisone levels in urine and saliva samples [277]. The free cortisol levels in these matrices were used as an indicator for adrenal or gland disorder, and in doping analysis a marker of glucocorticoid illicit use. Specific antibodies immobilized on polycarboxylate-hydrogel-based coatings resulted in sensitive detection (~ 2.8 nM) with a linear detection range from 5 to 154 µg/L for cortisol and 30–174 µg/L for cortisone. The data correlated well with the reference LC/MS–MS commonly used method in pharmacological and anti-doping applications [277].

Electrochemical biosensors

Electrochemistry has been a major technique in detecting the change in the oxidation number of metals and non-metal species. The technique involves a simple setup such as cyclic voltammetry which contains a reference, counter, and working electrodes. Electrochemistry has been involved in environmental remediation in the cycling of metals, remediation of water, and detection of pollutants. Electrochemistry techniques are portable, fast response time, cost-effective, and can be coupled with other techniques to detect heavy metals and organic pollutants [290–296].

Endocrine disruptive compounds including bisphenols (BPs), phthalates, and pesticides are widely used in various industries. Electrochemistry is a powerful technique for detecting such materials due to its simplicity, high sensitivity, and low detection limit [291]. Further, nanostructural materials integrated into electrochemical analytical tools were also used for quantification of endocrine-disrupting chemicals (EDCs) in environmental and biological samples. For example, seven EDCs including; alkylphenols/phenols, bisphenol A, parabens, triclosan, phthalates, pesticides, and natural/ synthetic sex hormones were fully detected and analyzed via electroanalytical techniques integrated with functional nanomaterials such as ((1) metal nanoparticles: Au, Ag, and Pt; (2) nanomaterials: MoS_2, TiO_2, GQDs, rGO, MWCNTs, SWCNTs, rGO, ZnO, Fe_3O_4, and SiO_2 [292]. The performance of nanomaterial-based electrochemical sensors was also reviewed and evaluated in comparison to results obtained from common techniques like GC–MS and LC–MS [292].

Wearable electrochemical sensors are a rapidly emerging class of drug-sensing devices that addresses the growing need for personalized medicine [293]. They serve as powerful screening tools in the hands of law enforcement agents supporting on-site forensic investigations and monitoring of important therapeutic drugs and the detection of major drugs of abuse [293]. Three pollutants including triclosan, ibuprofen, and diclofenac were detected in surveillance of seawater and several fish species using the UPLC-QqQ/MS technique [294]. All three pharmaceuticals in different sampling sites were detected and total concentrations ranged from 0.10 to 1.54 μg/L in surface water but not found in fish muscle with seasonal variations were observed [294]. The removal was found the best in the dry season, due to efficient irradiation and higher activity of microorganisms [294, 295] (Table 2).

Biosensors provide an efficient method in allowing environmental monitoring of pollutants like antibiotics, hormones, endocrine-disrupting chemicals, and pesticides in real water samples [296]. The detection is based on providing a sensitive antibody immunoassay that was a proven sensitive tool for estrone which resulted in a detection limit below 0.20 ng L^{-1} with a 1.40 ng L^{-1} quantification limit with recovery rates between 70 and 120% [296]. Table 3 summarizes the above-mentioned detection methods along with major advantages and disadvantages associated with each method.

Major methods used to decontaminate water bodies from organic pollutants

Diverse sources and potential health risks associated with organic pollutants such as pesticides, hormones, and pharmaceutically active entities along with their transformation into our water supplies makes it important to decontaminate and remove such contaminant from water resources. The transportation fate of these pollutants

Table 2 Major reported detection techniques for various organic pollutants

Analyte/sampling	Solvent/medium	Major detection methods	Detection limit/%recovery	References
Lipid-rich extraction matrices	High-pressure liquid extraction	Gas chromatography- time-of-flight (ToF) mass spectrometry	Limits of detection ranges from 0.00057 to 0.96 ng/g	[201]
Toxic substances, found in ginkgo biloba nutraceutical products	Aqueous medium	Liquid chromatography (LC) coupled to high-resolution ToF mass spectrometry	Recovery between 70 and 120%	[209]
Estrogen and progestogens detecton	Water bodies	Liquid chromatography with both diode array and ToF mass spectrometric detection	85% recoveries with detection limits as low as 1 ng/L	[202]
Detection of exogenous endocrine-disrupting chemicals (EDCs) and endogenous steroid hormones	Aqueous biological samples	Solid-phase microextraction modified silanols and gas chromatography-ToF mass spectrometry	LOD and LOQ values in river water were in the range of 2–3.78 ng/L and 8–126.1 ng/L	[204]
58 potential Endocrine disrupting compounds	Water matrices	Gas chromatography and liquid chromatography-tandem mass spectrometry	Recoveries between 50 and 112% for all detected compounds	[206]
Six types of endocrine-disrupting chemicals	Seafood samples	Ultrasound-assisted extraction, continuous solid-phase extraction, followed by ToF GC–MS analysis	Up to 84 to 105% recoveries	[211]
Eight pharmaceuticals	Aqueous samples	Solid-phase microextraction coupled with gas chromatography-ToF mass spectrometry	Detection limit at ng/L levels	[212]
Simultaneous determination of 9 pharmaceuticals and 3 hormones	Aqueous samples	Solid-phase extraction and gas chromatography	Recovery rate of 85–103%, low limits of detection	[213]
Various pharmaceuticals	Water samples	Dispersive solid-phase extraction and gas chromatography	Detection below 20 ng/ mL	[214]
Pesticides, pharmaceutical, and personal care products	Sediments	Superheated liquid extraction method and gas chromatography-ToF mass spectrometry	Samples were accurately detected with low detection limit	[215]
Human pharmaceuticals, hormones, antioxidants, and plasticizers	Water samples	Rapid gas chromatography- ToF mass spectrometry	57–120% recoveires	[217]

Table 2 (continued)

Analyte/sampling	Solvent/medium	Major detection methods	Detection limit/%recovery	References
Twenty pharmaceutical contaminants	Soil sample	Ultrasound-assisted extraction followed by gas chromatography- ToF mass spectrometry detection	More than 80% of absolute recoveries	[218]
Six different pharmaceuticals and personal care products	Soil sample	Ultrasound-assisted extraction and gas chromatography- ToF mass spectrometry	Recovers from 63.8 to 110.7% with spiking level of 100 ng/g in dry soil	[219]
Twenty different compounds	Wastewater effluent	Liquid chromatography and ToF mass spectrometry	ChemSpider database accurately analyze the mass of the major compounds	[220]
Fifty differentpesticides	Wine	Liquid chromatography/quadrupole ToF mass spectrometry	Detection limits from 1 to 2500 ng/g	[222]
Pesticides and other contaminants	Water sample	LC–QqQ-MS/MS and LC–QToF-MS	LOD ranged from 0.04 to 2 ng/L	[223]
Pesticides, drugs, and mycotoxins	Edible insects	Ultra-high-performance liquid chromatography and quadrupole-orbitrap high-resolution mass spectrometry	Recovery rate between 70 and 120%	[225]
74 different pharmaceuticals	Environmental and sewerage water	solid-phase extraction and LC– tandem MS–MS	Detection limit in ng/L scale	[226]
Six pharmaceuticals by isotope dilution	Water matrics	solid-phase extraction and LC–tandem MS–MS	Recovery ranged from 88 to 118%	[226]
Seven pharmaceuticals and two metabolites	Water matrics	solid-phase extraction–UHPLC–tandem MS/MS	Detection limits ranges from 0.02 to 8.18 ng/L	[227]
Extract six triazine pesticides	Cereal, rice, and wheat samples	HPLC- tandem MS/MS	Recovery range rises from 81 ± 4% to 96 ± 4%	[228]
Detecting household, industrial chemicals and personal care products	Leafy and root vegetables	Dispersive solid-phase extraction and liquid chromatography-tandem mass spectrometry	Recovery rate of 81–126%	[230]

Table 2 (continued)

Analyte/sampling	Solvent/medium	Major detection methods	Detection limit/%recovery	References
Steroid hormones	Aqueous	Cyclic-organophosphate derivatization and UPLC- tandem MS/MS	Recovery rate of 88.1–96.3%	[234]
19 pharmaceuticals, 4 (PPCPs) and 4 degradation products	Sewerage sludge samples	MSDP and HILIC- tandem MS/MS	Detection limits from 1.25 to 1250 ng/g	[231]
Analysis of 44 of the foremost pharmaceuticals	Consumed by elderly	Liquid chromatography coupled to tandem mass spectrometry	Recovery between 27 and 116%	[232]
Dissolved organic matter on activated carbon	Water samples	Fluorescence indexes and UV_{254}	Sensitive surrogate than UV_{254}	[236]
Removal of emerging contaminants	Wastewater treatment plant	Fluorescence excitation and emission probes	Proof for the feasibility of use of fluorescence spectrometry as a monitoring tool to quantify the removal of ETOrCs by a representative range of conventional wastewater treatments	[243]
Low levels of the biogenic succinic acid and antioxidant pharmaceutical	Aqueous	Fluorescence and UV absorption	Detecting in concentrations ranging from 10^{-7} to 10^{-5} M	[237]
DT-13 and its metabolite levels	Biological samples	Fluorescence-linked immunosorbent assay	Recovery rate ranged from 85.28 to 101.40%	[239]
Organophosphate Compounds	Aqueous	Fluorescence-based biosensing probe	Addition of aliquots of the paraoxon pesticide is detected	[242]
Emission properties of aromatic luminescent compounds	Solvent: water	Steady-state luminescence	Analysis of several compounds with different aromatic nuclei and different polarity	[248]
Estrogen Endocrine Disruptors (E2)	Tb-based metal organic framework (Tb-MOF) nanozyme	Fluorescence probe	Degrade E2 like natural horseradish peroxidase (HRP) and sense E2 as low as 50 pM by its luminescence	[126]
Molecules adsorbed on rough and active nanostructure	Gold and silver nano-particles	Surface-enhanced Raman spectroscopy	Detection ranges various between-materials	[249]

Table 2 (continued)

Analyte/sampling	Solvent/medium	Major detection methods	Detection limit/%recovery	References
Methomyl, acetamiprid-(AC) and 2,4-dichlorophenoxyacetic acid-(2,4-D) residue levels	Green tea	Silver nanoparticle-based platform modified as a SERS	Low detection limit ranges 1.88–5.6 ng/ml	[250]
Four pharmaceutical compositions	Hydrated solutions	UV Raman microscopy	Resonance Raman enhancements were observed for four of the active ingredients	[252]
Dopamine (DA) concentrations	Blood serum and crystal violet (CV) contaminants in lake water	Coated Au nanoparticles (NPs) with Prussian blue (PB) shell (Au@PB NPs) and Raman microscopy	Recoveries in the range of 90.9–107.5% and an acceptable accuracy with RSDs below 7.0%	[198]
Indole-like plant hormones	Methanol/HCl	Surface-enhanced Raman scattering using gold nanoparticles	Raman scattering with a sensitive limit of 2.0 nM of indole-3-butyric acid (IBA)	[253]
Quantification of endocrine disrupting chemicals	Environmental and biological samples	Nanostructural materials integrated into electrochemical analytical tools	Comprehensive and thorough review	[292]
Pollutants including triclosan, ibuprofen, diclofenac	Seawater and fish species	UPLC-QqQ/MS technique	Concentrations ranged from 0.10 to 1.54 µg/L in surface water. No detection in fish species	[294]
Environmental monitoring of pollutants	Real water samples	Sensitive antibody immunoassay (Bio-sensor)	Recovery rates between 70 and 120%	[296]

Table 3 Advantages and disadvantages of the main detection methods discussed in this review

Detection method	Advantages	Disadvantages
Time of flight Mass Spectrometry	Simplicity, ruggedness, ease of accessibility to the ion source Provides fast acquisition rates, spectral continuity Powerful for qualitative and quantitative analyses across a wide dynamic range in the presence of complex matrices Provides unlimited mass range with rapid data acquisition rate	High cost with limited resolution and sensitivity Require fast electronics since ions reach at the transducer in ms-scale Not portable Less widely used compared to other techniques like quadrupole mass detectors
Quadrupole mass spectrometer	Most common type of mass spectrometers More compact, less expensive and more rugged than other mass detectors Has ability to perform for both qualitative and quantitative analyses Provide high scan rates where the entire mass can be seen in less than 100 ms	High cost and maintenance The scanning nature limits the acquisition rate and leads to spectral bias Low resolution with poor mass accuracy Not portable unit The analytical chain can vary in function to the molecule under investigation like GC or LC–MS, type of ionization, low or normal pressure
Tandem (Ms/Ms)	Having two independent mass analyzers in two different regions in space, it gives both mass spectra of samples and fragments Provides large scale analysis with capacity to study complex mixtures regardless to their entity along with metabolites Can generate characteristic fragment ions from molecular ions, and improve the selectivity of quantitative measurements' Wide range of analysis that covers organic chemistry, biochemistry, genetics, pharmaceutical, and medicine	Expensive Not portable Require specialized technician to operate
Surface enhanced Raman Spectroscopy	No pre-sampling treatment Laser source can be easily focused on small samples Very useful to study samples in aqueous solutions since water is very weak in Raman Powerful detection method for biological and environmental samples	Not developed as a routine analytical technique Poor reproducibility in practical applications, mainly due to the high heterogeneity of the emission enhancement Require frequent optical alignment

Table 3 (continued)

Detection method	Advantages	Disadvantages
Luminescence based detection	Very sensitive technique used for various applications in vivo Can provide great deal of data in both quantitative and qualitative analysis Contactless and nondestructive method of probing the electronic structure of materials	Does not work for high concentrations of the analyte In most photoluminescent systems chromophore aggregation generally quenches light emission so it is necessary to use and study fluorophores in dilute solutions or as isolated molecules The technique is limited to luminescent/conjugated analytes
Electrochemical biosensors	Can be designed for specific gas or vapor in ppm detection limit Easy to operate with good resolution and linear range Provide reliable, repeatable detection with low cost	Highly dependent on temperature EC sensors normally has short shelf life (6–12 months, providing calibration) Factors including, humidity, high temperatures, exposure to target gas may dry out and deplete the electrolyte Despite its recent use in monitoring, EC do not meet all environmental monitoring requirements

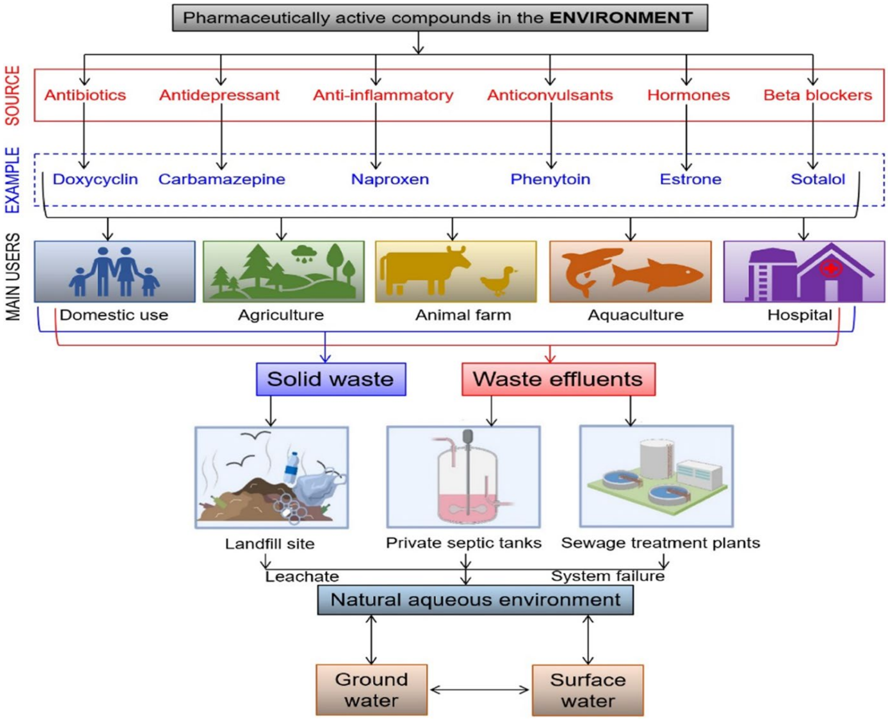


Fig. 7 Pharmaceutically active entities and their transformation routes to our water supplies; Retrieved with permission from reference [297]

fluctuates considerably depending on the treatment methodologies, such as ozonation, chlorination, biodegradation, photooxidation, filtration, sedimentation, and coagulation. Figure 7 shows major sources of pharmaceutical pollutants and their fate and transportation in soil and water bodies as described by Rasheed et al. [297].

Filtration process

The nanofiltration of chemical pollutants has been applied in different real drinking water sources and is commonly coupled with simultaneous ultrafiltration initially to remove particulate and large colloidal organic whereasnanofiltration allows for enhanced purity through the removal of molecular constituents [298]. 67.4–99.9% rejections were obtained for the pesticides and hormones regardless of the water composition. This high percentage of rejection is related to the size exclusion and hydrophobic interactions of either parent molecules or subsequent by-products formed during natural degradative processes [298]. Further, the overall nanofiltration efficiency to remove the selected compounds were not found to be highly affected by the pre-adsorption of most of the studied compounds [298]. In contrast, several factors are deemed important to be optimized such as the membrane molecular weight and size, salt rejection, porosity, morphology, charge, and hydrophobicity along with the molecular weight, charge, and hydrophobicity of the pharmaceutical pollutants [299]. Moreover, nanofiltration uses modified cellulose acetate membranes; one with reactive diisocyanate along with dihydroxy naphthalene disulfonate, and the second is tailored with a hydrophilic membrane that incorporates poly(ethylene glycol) was conducted to remove pharmaceuticals and personal care products [300]. The long-term nanofiltration showed a significant effect using the significant effect of CSMM blending on the separation performance of ibuprofen for long hours of operation was observed using charged surface modifying macromolecule (CSMM) additive [300].

The application of an aqueous two-phase system (ATPS) for selective extraction and clean-up of emerging contaminants like pesticides, pharmaceuticals, personal care products, and hormones from aqueous matrices was reported in the literature [301]. The ATPS is an alternative to the conventional liquid–liquid extraction technique but is based on the principles of green chemistry since does not use organic solvents. The two-phase extraction process can extract neutral, anionic, cationic, polar, and nonpolar compounds, even when present simultaneously in the same sample [301].

To improve the performance and robustness of membrane technology, it is important to combine membranes with other systems, such as activated carbon, nanomaterials, and enzymatic degradation. Membranes modified with nanomaterials receive significant attention in the removal and decontamination of pharmaceutical and other organic pollutants from water and environmental samples [302]. For example, fabricated ZnO nanoparticle-coated ceramic was used as an ultrafiltration membrane for remediation of pharmaceutical components [302]. The membrane was employed for the removal of atenolol and ibuprofen drugs from synthetic solution where 96% and 99% removal of atenolol and ibuprofen were obtained, respectively [302]. Membrane bioreactors (MBRs) show unreliable results for the removal of pharmaceutically active compounds due to their structural complexity and effects on the different species of microorganisms. For example, reports showed that MBRs remove acetaminophen, ibuprofen, ketoprofen, gemfibrozil, bezafibrate, and naproxen efficiently (N 90%) while the removal rates of carbamazepine and diclofenac are very low (b 40%) with a wider range of variation for other compounds [299].

Khanzada et al. provide an overview of the state-of-the-art membrane-based technologies and their use of micropollutants in the removal of MPs [303]. The review provides a detailed summary of the available advanced membrane-based treatment methods including nanofiltration, ultrafiltration, forward osmosis, and membrane distillation [303]. Endocrine-disrupting compounds and pharmaceuticals are among the most harmful and abundant emerging organic compounds present in natural waters and are not effectively removed by conventional treatments. Nanofiltration has proven to be a promising technology in removing such contaminants when membrane materials and operational conditions are appropriately applied [303, 304].

Sand/anthracite biofilter coupled with a biologically active granular activated carbon (SA-GAC) is used as a pretreatment after coagulation in a drinking water treatment plant. SA-GAC biofiltration showed effective membrane to the removal of pharmaceuticals and personal care products (PPCPs), reducing approximately 53.4% of mass concentration and 79% of adverse health risk, where the activated carbon played the key role [305]. Due to the diverse molecular structures of PPCPs, the removability of individual PPCPs was quite different and independent of their influent concentrations where prechlorination showed limited enhancement for the removal of PPCPs [305].

A combined membrane photocatalysis reactor (MPR) showed excellent activity for the removal of pharmaceuticals and endocrine-disrupting chemicals [216]. In specific, Aeroxide® P25 TiO_2 was used in the photodegradation of 33 trace organics contaminants, including drugs, analgesics, antibiotics, surfactants, or herbicides [216]. Interestingly all studied compounds were eliminated by photocatalysis at different rates where Eighteen compounds were completely degraded after 1 h, and a group of fourteen compounds degraded between 50 and 88% with tris(2-chloroethyl) phosphate was found to be the only undegradable pollutant under the same conditions [216]. A polar organic chemical integrative sampler with nylon membranes was modified to monitor emerging organophosphate ester contaminants in urban surface water [306]. The low sorption capacity of the nylon membrane to moderately hydrophobic compounds makes it possible for monitoring organophosphate esters in surface water in the long term [306]. The average concentration of organophosphate pesticides was 4.97 ± 1.35 ng/L (range 2.64 ± 1.28–6.54 ± 0.18 ng/L) and the average concentration of organophosphate flame retardants was found to be 400 ± 88 ng/L (range 316 ± 24–615 ± 36 ng/L) across nine sampling sites [306].

Diverse charged commercial nanofiltration membranes result in adsorption and rejection of trace levels of organic pollutants [307]. It is found that under neutral pH, the opposing impact of adsorption on rejection was $< 6\%$ when the tight ESPA1 and NF90 membranes were used and 7–36% when the loose NF270 and HL were used [307]. In addition, while electrostatic attraction caused the rejection by the tight membranes to decrease by 0.8–4.3%, using loose membranes resulted in a decrease by 13.4–28.3% with lower rejection observed for tight and loose neutral membranes [307].

Adsorption on activated surfaces

Recently published work presents different adsorbents for emerging contaminants (EC's) removal from water and wastewater including activated carbons, modified biochars, nano adsorbents carbon nanotubes, and composite adsorbents [297, 308–320]. Pharmaceuticals and personal care products (PPCPs), are increasingly being introduced into water systems due to current lifestyles [297, 309, 310]. These products are not eliminated during current wastewater treatment processes. MOF-derived nanocomposite showed a selective potential to adsorb PPCPs from water bodies especially using diverse solvents, such as acetone, acetonitrile, ethanol, methanol, HCl, and NaOH [308]. MOF-derived materials are found to be highly selective removal of various pollutants including active residues from pharmaceuticals, pesticides, surfactants, hormones, and personal care products with high efficiency. This is expected due to their large surface area, size, dispersibility, tunable structure, and repeated use capability [308].

While MOFs are known as sorbents, it is necessary to modify and optimize their adsorption potential given that some MOF families are moisture and base sensitive. This hinders their potential use in real-life applications such as wastewater, and body fluid treatment [309]. Computational tools are becoming a powerful technique to facilitate the discovery of new material to accelerate scientific advancement in the MOF screening including; materials molecular dynamics simulation in adsorption kinetics, optimizing the density functional parameters in alternating and optimizing the host–guest interactions [309]. The magnetic covalent organic framework (COF) showed an interesting adsorbent feature for the extraction of endocrine-disrupting pesticides from water samples [310]. Significant adsorption efficiencies for lipophilic chlorpyrifos and atrazine pollutants were observed with a reported capacity of 270 mg/g and 54 mg/g, respectively [310]. Theoretical calculations showed that the binding between COF and the pesticides occurs via van der Waals interactions. The study also reveals that the two pesticides can be recovered in acetonitrile with 90% efficiency [310].

In one study, six integrated fixed films activated sludge (IFAS) were used to quantify and evaluate TrOC and estrogenic activity removal over 24 h [311]. The analysis covers total suspended solids (TSS), chemical oxygen demand (COD), ammonia, total nitrogen (TN), total phosphorus (TP), estrogenic activity, and 98 TrOCs [311]. The total solids per liter of wetted reactor volume ranged from 2.5 to 7.6 g. Qualitative comparison with carbon-activated sludge shows potentially higher IFAS removal efficiencies for some compounds including atenolol, diclofenac, gemfibrozil, N, N-diethyl-meta-toluamide (DEET), 4-nonylphenol, and 4-tert-octylphenol, as well as the chlorinated flame retardants tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) and tris(chloropropyl) phosphate (TCIPP) with TN removal, was varied since it is associated to nitrate removal [311].

The adsorption behavior of 30 chemicals with microalgae such as Chlorella Vulgaris where adsorption isotherms conducted for neutral and ionic forms of contaminants [312]. Based on the obtained results, the adsorption affinities were theoretically predicted following the concept of the linear free energy relationship [312]. It was found that dispersive force, H-bond basicity, molecular volume, and electrostatic interaction of anion may contribute to the model developed based on the entire dataset where the adsorption property of the surface of C. Vulgaris differs from those of Gram-negative bacteria Escherichia coli and dissolved organic matters in an aquatic environment [312]. Similarly, an integrative and multi-biomarker approach using marine clam Ruditapes philippinarum exposed to 15 µg/L concentration of carbamazepine (CBZ), diclofenac (DCF), and ibuprofen (IBU), three pharmaceuticals for two weeks and was evaluated throughout the exposure and depuration process [313]. It was found that the exposure reduces changes in the biochemical responses to the harmful role of the pharmaceuticals that become negative after short-term exposure [313].

Nanofiltration process applied on a mixture containing nine estrogens and progestogens sex hormones using two membranes which differed polymer. A retention coefficient of 74.1–100% was obtained for asymmetric membrane prepared from cellulose acetate (NF-SF10) under high desalting degree (NaCl and $MgSO_4$). Whereas, filtration of deionized water with the mixture of sex hormones

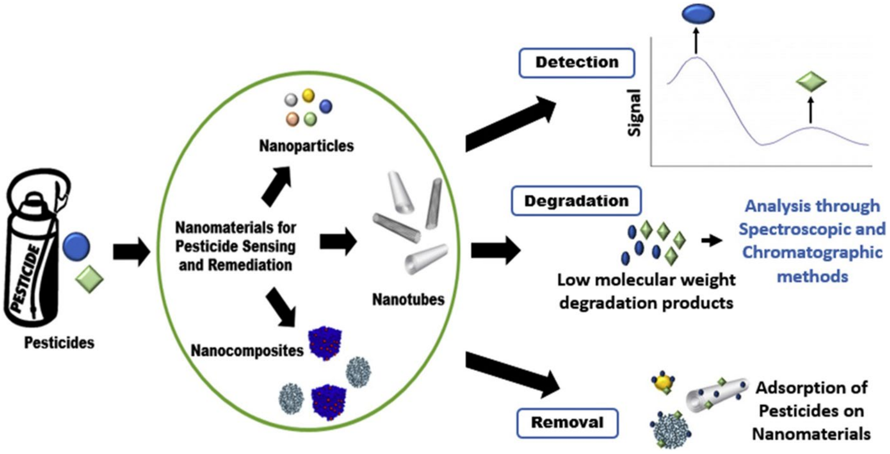


Fig. 8 Schematic representation of pesticide detection, degradation, and removal using nanomaterials; Retrieved with permission from reference [318]

shows lower adsorption of the hormones on the membrane by approx. 21% (NF-SF10) and 30% (NF-DS5DK) [315]. Moreover, adsorption of pharmaceuticals onto isolated polyamide active layer of nanofiltration (NF) and reverse osmosis (RO) membranes showed that apparent differences existed between the polyamide (PA) active layer from the polysulfone [317]. The PA layer was found to exhibit higher adsorption capacities for the positively charged PhACs and similar adsorption capacities for the neutral PhACs due to its higher capacity for forming hydrogen bonds with PhACs [317].

Recently, Rawtani et al. reported on different types of nanomaterials (AuNPs, AgNPs, and SiO_2 NPs as well as CNTs and HNTs) utilized for the removal of pesticides from several samples including water, fruits, and vegetables [318]. Various surface modifications enhance the adsorption potential of these nanomaterials for pesticide sensing [318]. Several types of nanomaterials including nanoparticles, nanocomposites, and nanotubes were used in recent times for pesticide sensing, adsorption, and degradation as illustrated in Fig. 8. For instance, graphene oxide and AgNPs along with other nanoparticles such as FeNPs, Fe/Ni NPs, TiO_2 NPs, ZnO NPs, and nanotubes (HNTs) all shown rapid high potential to decompose the studied pesticides with 90% efficiency [318]. Similarly, $MoS_2/BiFeO_3$ doped silver orthophosphate catalyst tends to degrade organic pollutants upon irradiation with visible light [319]. Further, thirteen carbon materials comprising commercial activated carbons and lab-made materials are used to decontaminate water samples from polar and nonpolar pharmaceuticals including sulfamethoxazole, triclosan, carbamazepine, diclofenac, mefenamic acid, 17-α-ethinylestradiol, 17-β-estradiol, estrone, gemfibrozil, and clofibric acid [320]. The combination of a micro and mesopore network with rich oxygen-based surface chemistry gave an acidic nature so the activated hydrochars at lower temperatures present the best overall recoveries ranging from 20.9 to 82.4% for the simultaneous determination of the PhCs with discrete chemical properties using high-performance liquid chromatography diode array detection [320].

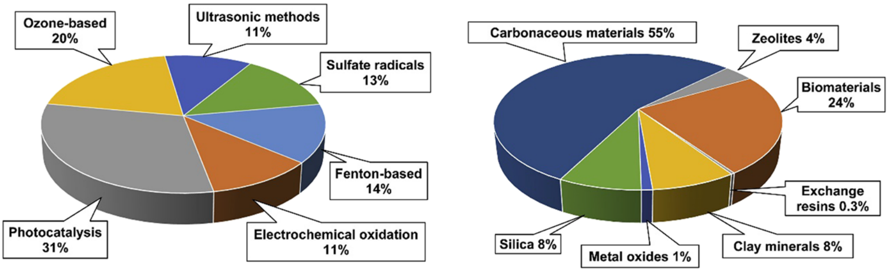
Modified adsorbing catalytic and photocatalytic materials

Micropollutants such as pharmaceuticals, hormones, pesticides, and phenolic utility chemicals in sewage water are major evolving problems because of increased use and observed hostile effects on the environment. In this section, we will highlight major advances that lead to decontaminating water resources from such pollutants.

Water treatment facilities using activated-sludge processes are more efficient hormone removals than the one that uses biofilm-treatment techniques [321]. The removal stems from the adsorption affinity to sludge surfaces wherein turbid samples the removal of Caffeine, Ibuprofen, Estrone, Naproxen, and Estradiol tend to decline [321]. Combining and coupling biological oxidation, semiconductor photocatalysis with the Fenton process were found to have high-performance pharmaceutical pollutants degradation and removal from water in pilot-scale experiments where the adsorption of pollutants and H_2O_2 or oxygen onto catalysts increases the rate of reaction by increasing the lifetime for hydroxyl radicals [322, 323]. Such advanced oxidation processes (AOPs) utilize the high reactivity of hydroxyl radicals to progressively oxidize organic compounds to innocuous products.

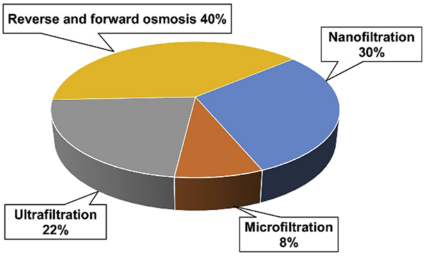
A comprehensive review study reported detailed AOPs on various pharmaceuticals including the use of TiO_2-mediated photocatalytic treatment and its effectiveness in degrading pharmaceutical residues. This review furthermore highlights the success in the removal of pharmaceuticals from different water matrices [323]. In another published work, it was found that the compounds bisphenol A (BPA), diethyltoluamide (DEET), 17α-ethinyl estradiol (EE2), perfluorobutanoic acid (PFBA), carbamazepine, caffeine, and atrazine were the most frequently detected in water sources, with significant concentration levels [324]. The use of a photoactive semiconductor-based material such as TiO_2, ZnO, WO_3, and CuO can accelerate the photodecomposition of such pollutants (see Fig. 9) [325]. Metal-based photocatalysts may absorb radiation at an energy equal to or higher than that of their bandgaps thus exciting the valence electrons so they can jump to the conduction band making electron–hole pairs that trigger oxygen reactive species in the oxidation of the pollutants [325]. Electrochemical Advanced Oxidation Processes (EAOPs) showed promising processes for the removal of such persistent and recalcitrant organic contaminants from water bodies [326].

The performance of the AOPs has been evaluated based on percentage removal, time, and electrical energy consumed to degrade different classes of pharmaceutical activated carbons (PhACs) [327]. In specific, ozone-based AOPs were found to be favored due to their low treatment time, low cost, and high efficiency, but complete degradation cannot be achieved by these processes, and various transformation products are formed [327]. This partial oxidation may result in forming more toxic products than the parent compounds. The presence of organic compounds, nitrate, and phosphate are found to hinder the degradation process, while chlorine and sulfate showed a positive and efficient oxidation effect [327]. Eight pharmaceuticals



(A) Most used AOP

(B) Most used adsorbent materials



(C) Membrane technologies

Fig. 9 New technologic approaches for the treatment of EC. Different AOP (**a**), Most used adsorbent materials (**b**), Membrane technologies (**c**); Retrieved with permission from reference [325]

including gemfibrozil, nimesulide, furosemide, paracetamol, propranolol, dipyrone, fluoxetine, and diazepam were treated from three different water matrixes using the Fenton AOPs. Optimized conditions at pH of 5.0 along with 12.5 and 533 ppm of iron and hydrogen peroxide concentrations, respectively provide mineralization rates and pharmaceutical degradation in which twelve transformation products (TPs) were tentatively identified and classified of high toxicity as identified by UHPLC-QTOF MS [328].

Several metal-based photocatalysts were used to enhance the degradation of various organic pollutants from water samples [122, 329–351]. For example, TiO_2 made and used as heterogeneous photocatalyzed the degradation of 3-chloro-4-methoxyaniline pesticide derivative [331]. Modified TiO_2 as photocatalyst for degradation of malathion and imidacloprid in water [335, 336]. Graphitic-C_3N_4/TiO_2 nanocomposite prepared as an active photocatalyst for efficient decomposition of hazardous organic industrial pollutants in an aqueous medium such as phenol [208]. Nitrogen-doped carbon enhanced mesoporous TiO_2 was made via the sol–gel method and found to be an active photocatalyst for the photodegradation of methyl orange with up to 97% total removal efficiency. The nanocomposite is also an effectively active catalyst for the degradation of methylene blue and phenol [329]. Moreover, several $FeTiO_3$/TiO_2 catalysts prepared with the sol–gel method exhibited significant absorption in the ultraviolet (UV) region for degradation of Orange G and 4-chlorophenol under illumination from a visible light [341]. Facile synthesis of TiO_2–PC composites has superior degradation performance over that with bare TiO_2 treatment [349]. In addition, Mn-doped TiO_2 showed strong photocatalytic. mineralization/

intermediate activities of organic pollutants like ketoprofen and chlorothalonil [340]. Finally, AgX/TiO_2 loaded on mordenite was found to be active in the photodegradation of Acid Blue [347].

Three-dimensional graphene aerogel was found to have excellent adsorption capacity to organic solvents [330]. This fabricated adsorbent has a good mechanical property and low density suitable for adsorption of chlorinated solvents with high selectivity [330]. $(Cu, Fe)_2O_3$ was found to be a good photocatalyst to decompose ibuprofen with 88% conversion obtained within 240 min under visible illumination [339]. Further, MCM-41@Cu–Fe–LDH magnetic nanoparticles were modified with cationic surfactant for the removal of Alizarin Yellow from water samples as monitored with HPLC [343]. Adsorption data fit the Langmuir model, showing a maximum adsorption capacity of 121.95 mg g^{-1} [343]. Similarly, BiOBr/BiOCl composites were found to have optimal visible light absorption with excellent photocatalytic activity in the degradation of rhodamine B and salicylic acid under xenon radiation [344]. Cobalt doped-ZrO_2 multi-walled carbon nanotubes were found to be efficient for photodecolorization of trypan blue dye in an aqueous solution in 3 h [346]. NaY/$Mn_{0.5}Zn_{0.5}Fe_2O_4$ nanocomposite to adsorb and degrade methyl parathion pesticide [334]. Ferrous ions with air-bubble cavitation assist the degradation of organic dyes like Congo Red, Rhodamine B, Methyl Orange, and Methyl Violet monitored with TOC, and HPLC techniques [348]. The method is found to be feasible and promising for the treatment of organic wastewater [348]. Enhanced photocatalytic degradation for organic pollutants by a novel m-Bi_2O_4/$Bi_2O_2CO_3$ photocatalyst under visible light [351].

A broad spectrum of trace organic contaminants (TrOCs) by membrane distillation (MD)-enzymatic membrane bioreactor (EMBR) using the Laccase-catalyzed process was investigated [352]. The degradation level of TrOC was highly influenced by the molecular properties of the organic contaminants where degradation s above 90% was observed for TrOCs containing strong electron-donating functional groups like amine and hydroxyl functionalities [352]. Photolytic and photocatalytic removals of 17a-ethinylestradiol (EE2) and levonorgestrel (LNG) from water samples were investigated under UVC radiation [353]. The results showed that 92% of EE2 and 97% of the LNG contaminants were removed upon direct exposure to UVC for 30 min with hydroxyl radicals significantly contributed to the removal efficiency of both compounds in water [353]. The photochemical fates of the histamine H-receptor antagonists cimetidine and ranitidine were studied under oxygen and hydroxyl radicals [354]. The bimolecular rate constant for cimetidine reaction with $^{\cdot}OH$ in water was 6.5×10^9 M^{-1} s^{-1}over the pH range 4–10 while the reaction of ranitidine hydrochloride with $^{\cdot}OH$ proceeds with a rate constant of 1.5×10^{10} M^{-1} s^{-1} [354]. Finally, compared to pure ZnO, the photocatalytic of ZnO incorporated with 1% Ce-doped exhibits the highest photocatalytic activity for the degradation of pharmaceuticals such as nizatidine, levofloxacin, and acetaminophen under irradiation with UV-B light [355].

Further, adsorption and biodegradation/transformation for the removal of a set of 29 TrOCs that represent pharmaceuticals, steroid hormones, phytoestrogens, UV-filters, and pesticides that occur ubiquitously in municipal wastewater were analyzed [356]. Various phenolic TrOCs are effectively removed through biosorption and biodegradation processes [357]. It was also determined that adding 1-hydroxy benzotriazole (HBT) as a mediator to the crude enzyme extract led to improvement of some phenolic as well as non-phenolic TrOC degradation [357]. The oxidation of pharmaceuticals, endocrine disrupting compounds, and pesticides during the ozonolysis indicates Ozonation that over 80% of caffeine, pharmaceuticals, and endocrine disruptors within the CT value of about 2 mg min L^{-1} were reached [358]. In another study, micropollutants were removed on average over 80% compared with raw wastewater, with an average ozone dose of 5.7 mg O_3 L^{-1} [359]. Further, detoxification and degradation of sulfamethoxazole by soybean peroxidase and UV + H_2O_2 remediation approaches were reported [360]. Optimized conditions for sulfamethoxazole degradation by the peroxidase enzyme showed an absolute requirement for a redox mediator (1-hydroxy benzotriazole) at low pH values. The degradation of the pollutant monitored with UV–Vis spectrophotometry and liquid chromatography-mass spectroscopy indicates the formation of diverse sets of intermediates indicating various degradation mechanistic protocols in which different levels of detoxification of the pollutants [360]. Table 4 summarizes the major methods reported to decontaminate water bodies from organic pollutants.

Conclusions

We provide a comprehensive review of various detection procedures and techniques that tactile the current challenges in monitoring strategies of pharmaceuticals and industrial organic pollutants in marine matrices through the analysis of the available recent scientific literature. Given the fact that both inorganic and organic physical transfer processes involved in soil pollutant accumulation, such as leaching and site runoff, allow the expansion of pollutant drift and adjacent wildlife contamination, analyses of chemical transformations and concentrations to determine the fate of these compounds before community exposures in high concentrations is significant. As a result of pollutant influxes, public health responses have resulted in major federal legislation that regulates effluent concentrations and industrial outputs.

Various detection procedures and techniques that tactile major challenges in monitoring strategies of pharmaceuticals and industrial organic pollutants in marine matrices through the analysis of the available recent scientific literature are presented and discussed in brief. As discussed in this review, in our opinion, we highlight major methods reported to identify and remove various organic pollutants from various samples under real environmental conditions.

i. Liquid chromatography (LC) coupled with high-resolution mass spectrometry was used to quantify hundreds of toxic substances, found in ginkgo Biloba nutraceutical products, including pesticides and mycotoxins. Recoveries between 70 and 120% with relative standard deviation (RSD) values lower than 20% were obtained for 260 of the compounds with 5 and 10 μg/kg limits of detection and quantification, respectively [209].
ii. Automated derivatization solid-phase microextraction coupled with gas chromatography–mass spectrometry was directly applied to surface water to identify

Table 4 Major methods used to decontaminate water bodies from organic pollutants

Decontamination method	Processing/sampling strategies	Comments	References
Filtration	Nano-filtration and ultra-filtration of hormones and pesticides from drinking water	67.4–99.9% rejections for the pesticides and hormones	[298]
	Nano-filtration using modified cellulose acetate membranes	Significant effect of charged surface modifying macromolecule on the separation performance of ibuprofen for long hours operation was observed	[300]
	Two-phase extraction process	Easily extract neutral, anionic, cationic, polar, and nonpolar compounds	[301]
	ZnO nanoparticle coated ceramic	Ultrafiltration membrane for remediation of pharmaceutical components	[302]
	Membrane bioreactors	Structural complexity resulting in unreliable results for the removal of pharmaceutically active compounds	[299]
	Sand active granular activated carbon biofiltration	Reducing 53.4% of mass concentration and 79% of adverse health risk	[305]
	Membrane photocatalysis reactor using Aeroxide® P25 TiO_2	Degradation of 18 components including drugs, analgesics, antibiotics, surfactants, or herbicide	[216]
	Polar organic chemical integrative sampler with nylon membranes	Average concentration of organophosphate pesticides: 4.97 ± 1.35 ng/L. Average concentration of organophosphate flame retardants: 400 ± 88 ng/L	[306]
	Diverse charged commercial nanofiltration membranes	Adsorption and rejection of trace levels of organic pollutants	[307]
	Nano-filtration process	Filtration of deionized water with the mixture of sex hormones shows lower adsorption of the hormones on the membrane by approx. 21% (NF-SF10) and 30% (NF-DS5DK)	[315]

Table 4 (continued)

Decontamination method	Processing/sampling strategies	Comments	References
Adsorption on activated surfaces	Metal organic framework nanocomposite	Adsorb PPCPs from water bodies	[308]
	Magnetic covalent organic framework	Extraction of endocrine-disrupting pesticides from water samples with 90% efficiency	[310]
	Integrated fixedfilm activated sludge	High removal efficiencies for compounds including atenolol, diclofenac, gemfibrozil, N,N-Diethyl-meta-toluamide (DEET), 4-nonylphenol, and 4-tert-octylphenol	[311]
	Integrative and multi-biomarker approach	Marine clam Ruditapes philippinarum exposed to 15 µg/L concentration of carbamazepine (CBZ), diclofenac (DCF), and ibuprofen (IBU), three pharmaceuticals for two weeks reduces the harmful effect of pharmaceuticals	[313]
	Nano-filtration and reverse osmosis membranes	PA layer exhibit higher adsorption capacities for positively charged PhACs and the neutral PhACs	[317]
	Nano-materials (AuNPs, AgNPs, and SiO_2 NPs as well as CNTs and HNTs)	Detection, degradation, and removal of pesticides from several samples including water, fruits, and vegetables	[318]
	$MoS_2/BiFeO_3$ doped silver orthophosphate catalyst	Organic pollutants upon irradiation with visible-light	[319]
	Micro and mesoporenetwork with a rich oxygen-based surface chemistry	Recoveries ranging from 20.9 and 82.4% for 13 carbon materials for commercial activated carbons and lab-made materials used to decontaminate water samples	[320]
Modified adsorbing and catalytic materials	Activated-sludge processes	Removal of Caffeine, Ibuprofen, Estrone, Naproxen, and Estradiol decline from sludge surfaces	[321]
	Semiconductor photo-catalysis with Fenton process	Pharmaceutical pollutants degradation and removal from water in pilot-scale experiments	[322, 323]
	TiO_2-mediated photo-catalytic treatment	Removal of pharmaceuticals from different water matrices	[323]
	TiO_2-mediated photo-catalytic treatment	Bisphenol A (BPA), diethyltoluamide (DEET), 17α-ethinyl estradiol (EE2), perfluorobutanoic acid (PFBA), carbamazepine, caffeine and atrazine detected in water sources	[324]

Table 4 (continued)

Decontamination method	Processing/sampling strategies	Comments	References
	Electrochemical Advanced Oxidation Processes (EAOPs)	Removal of persistent and recalcitrant organic contaminants from water bodies	[326]
	Advanced oxidation processes	Degrade of different classes of pharmaceutical activated carbons	[327]
	Fenton AOPs	Gemfibrozil, nimesulide, furosemide, paracetamol, propranolol, dipyrone, fluoxetine, and diazepam treated from three different water matrixes	[328]
	(MD)-enzymatic membrane bioreactor (EMBR) using Laccase-catalyzed process	Degradation level of TrOC was high due to strong electron-donating functional groups	[352]
	UVC radiation	Photolytic and photocatalytic removals of 17a-ethinylestradiol (EE2) and levonorgestrel (LNG) from water samples	[353]
	Photo-catalytic of ZnO incorporated with 1% Ce-doped UVC radiation	Degradation of pharmaceuticals such as nizatidine, levofloxacin, and acetaminophen under irradiation with UV-B light	[355]
	Bio-sorption and biodegradation processes	Phenolic TrOC effectively removed from municipal waste	[357]
	Soybean peroxidase and UV + H_2O_2 remediation approaches	Detoxification and degradation of sulfamethoxazole mechanistic protocols in which different levels of detoxification of the pollutants have been achieved	[360]

eight pharmaceuticals in aqueous samples with detection limits at ng/L levels [212].

iii. An efficient sequential superheated liquid extraction method was used to isolate various pesticides, pharmaceuticals, and personal care products including triclosan, estrone, 17(3-estradiol, diethylstilbestrol, 4-octylphenol, procymidone, permethrin, oxyfluorfen, bisphenol A and 2,8-dibenzodichloro-p-dioxin from sediments. The method allows quantitative extraction of the majority of compounds at real environmental levels (low ppb) in a short time [215]

iv. Peysson and Vulliet detected 136 pharmaceuticals and hormones in sludge samples using a simple extraction method followed by analysis with liquid chromatography–time-of-flight-mass Spectrometry with varied detection limits from 1 to 2500 ng/g, depending on the nature of the pollutant substance [222].

v. Lopez-Serna et al. reported the use of solid-phase extraction (SPE)–liquid chromatography-electrospray–tandem mass spectrometry (LC–MS-MS) in detecting 74 pharmaceuticals in environmental and sewage waters within ng/L detection limit scale [226].

vi. Green chemistry process presented in an Aqueous two-phase system (ATPS) is an excellent alternative to the conventional liquid–liquid extraction technique that can extract neutral, anionic, cationic, polar, and nonpolar compounds, even when present simultaneously in the same sample without a need of organic solvents [301].

vii. Membranes modified with nanomaterials receive significant attention in the removal and decontamination of pharmaceutical and other organic pollutants from water and environmental samples. The membrane was employed for the removal of atenolol and ibuprofen drugs from synthetic solution where 96% and 99% removal of atenolol and ibuprofen were obtained, respectively [302]

viii. Sophia and Lima reviewed high surface area materials with efficient surfaces and porous tunnels for the removal of various pollutants including active residues from pharmaceuticals, pesticides, surfactants, hormones, and personal care products [308].

ix. A comprehensive review reported the success of the advanced oxidation processes in the removal of pharmaceuticals from different water matrices including the use of TiO_2-mediated photocatalytic treatment and its effectiveness in degrading pharmaceutical residues [323].

Funding Not applicable.

Availability of data and materials Not applicable.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

Ethical approval This work is submitted in Compliance with Ethical Standards. It is not being submitted nor published elsewhere in any form or language.

Consent to participate Not applicable, no human subjects are involved.

Consent to publish The participant has consented to the submission of this work to the journal.

References

1. M.A. La Merrill, C. Johnson, M. Smith, N. Kandula, A. Macherone, K. Pennell, A. Kanaya, Environ. Sci. Technol. **53**, 13906 (2019)
2. J.C. Hains, B. Taubman, A. Thompson, J. Stehr, L. Marufu, B. Doddridge, R. Dickerson, Atmos. Environ. **42**, 1727 (2008)
3. D.S. Grant, A.J. Bergesen, A.W. Jones, Am. Sociol. Rev. **1**, 389 (2002)
4. L. Charlestra, D.L. Courtemanch, A. Amirbahman, H. Patterson, Chemosphere **72**, 1171 (2008)
5. A.W. Chassé, T. Ohno, S.R. Higgins, A. Amirbahman, N. Yildirim, T.B. Parr, Environ. Sci. Technol. **49**, 9733 (2015)
6. L.E. Brown, C.Y. Chen, M.A. Voytek, A. Amirbahman, Mar. Chem. **177**, 731 (2015)
7. S.A. Norton, A. Amirbahman, L. Bacon, H. Ewing, M. Novak, A. Nurse, M. Retelle, J. Stager, M. Yates, Lake Reserv. Manag. **36**, 14 (2019)
8. D.W. Kolpin, E. Furlong, M. Meyer, E. Thurman, S. Zaugg, L. Barber, H. Buxton, Environ. Sci. Technol. **36**, 1202 (2002)
9. M.J. Focazio, D. Kolpin, K. Barnes, E. Furlong, M. Meyer, S. Zaugg, L. Barber, M. Thurman, Sci. Total Environ. **402**, 201 (2008)
10. M. Cai, S. Ma, R. Hu, J.K. Tomberlin, C. Yu, Y. Huang, S. Zhan, W. Li, L. Zheng, Z. Yu, J. Zhang, Environ. Pollut. **242**, 634 (2018)
11. A. Alyokhin, Y.H. Chen, Curr. Opin. Insect Sci. **21**, 33 (2017)
12. N. Defarge, J. Spiroux de Vendômois, G.E. Séralini, Toxicol. Rep. **5**, 156 (2018)
13. C.S. Cronan, Environ. Monit. Assess. **184**, 4279 (2012)
14. M.L. Bell, K. Ebisu, R.D. Peng, J.M. Samet, F. Dominici, Am. J. Respir. Crit. Care Med. **179**, 1115 (2009)
15. G.J. McDonald, S.A. Norton, I.J. Fernandez, K.M. Hoppe, J. Dennis, A. Amirbahman, Sci. Total Environ. **660**, 876 (2019)
16. M. Jordan, M.A. Sánchez, L. Padilla, R. Céspedes, M. Osses, B. González, J. Environ. Qual. **31**, 1004 (2002)
17. E.M. Sunderland, A. Amirbahman, N.M. Burgess, J. Dalziel, G. Harding, S.H. Jones, E. Kamai, M.R. Karagas, X. Shi, C.Y. Chen, Environ. Res. **119**, 27 (2012)
18. B.K. Hope, L. Pillsbury, B. Boling, Sci. Total Environ. **417–418**, 263 (2012)
19. B.F. Mower, K.R. Munkittrick, M.E. McMaster, R.J. Van Beneden, Environ. Toxicol. Chem. **30**, 142 (2011)
20. A.A. Basheer, Chirality **30**, 402 (2018)
21. R.G. Altman, R. Morello-Frosch, J.G. Brody, R.A. Rudel, P. Brown, M. Averick, Sci. Heal. Soc. Mov. **49**, 123 (2011)
22. W.A. Battaglin, P.M. Bradley, L. Iwanowicz, C.A. Journey, H.L. Walsh, V.S. Blazer, Sci. Total Environ. **643**, 651 (2018)
23. J.L.C. Shmool, L.D. Kubzansky, O.D. Newman, J. Spengler, P. Shepard, J.E. Clougherty, Environ. Health **13**, 91 pg 1–15 (2014)
24. M.L. Diamond, C. de Wit, S. Molander, M. Scheringer, T. Backhaus, R. Lohmann, R. Arvidsson, A. Bergman, M. Hauschild, I. Holoubek, L. Persson, N. Suzuki, M. Vighi, C. Zetzsch, Environ. Int. **78**, 8 (2015)
25. S. Irei, A. Takami, Y. Sadanaga, S. Nozoe, S. Yonemura, H. Bandow, Y. Yokouchi, Atmos. Chem. Phys. **16**, 4555 (2016)
26. I. Pantelaki, D. Voutsa, Sci. Total Environ. **613–614**, 389 (2018)
27. L. Filipović, V. Filipović, C.W. Walker, C. Williams, H.E. Preisdanz, J.E. Watson, J. Environ. Qual. **49**, 1011 (2020)
28. T. Navrátil, S.A. Norton, I.J. Fernandez, S.J. Nelson, Environ. Monit. Assess. **171**, 23 (2010)
29. D. Melzer, N.E. Rice, C. Lewis, W.E. Henley, T.S. Galloway, PLoS ONE **5**(1), e8673 (2010)
30. K.A. Merritt, A. Amirbahman, Earth-Sci. Rev. **96**, 54 (2009)

31. R.J. Van Meter, D.A. Glinski, W.M. Henderson, S.T. Purucker, Environ. Toxicol. Chem. **35**, 2734 (2016)
32. K.A. Merritt, A. Amirbahman, Limnol. Oceanogr. **53**, 1064 (2008)
33. K. Lyall, R.J. Schmidt, I. Hertz-Picciotto, Int. J. Epidemiol. **43**, 443 (2014)
34. A. Amirbahman, B.C. Holmes, I.J. Fernandez, S.A. Norton, Environ. Monit. Assess. **171**, 93 (2010)
35. G. Genchi, A. Carocci, G. Lauria, M.S. Sinicropi, A. Catalano, Int. J. Environ. Res. Public Health **17**, 679 (2020)
36. H.A. Doolittle, S.A. Norton, L.C. Bacon, H.A. Ewing, A. Amirbahman, Lake Reserv. Manag. **34**, 258 (2018)
37. M. Chiari, C. Cortinovis, C. Bertoletti, L. Alborali, M. Zanoni, E. Ferretti, F. Caloni, Food Addit. Contam. A Chem. Anal. Control. Expo. Risk Assess. **32**, 1867 (2015)
38. B. Zielinska, D. Campbell, D. Lawson, R. Ireson, C. Weaver, T. Hesterberg, T. Larson, M. Davey, L. Liu, Environ. Sci. Technol. **42**, 5661 (2008)
39. F. Crea, A. Pettignano, Molecules **25**, 10 (2020)
40. P. Porcal, A. Amirbahman, J. Kopáček, S.A. Norton, Environ. Monit. Assess. **171**, 71 (2010)
41. A.L. Al-Malki, S.S. Moselhy, Hum. Exp. Toxicol. **30**, 1666 (2011)
42. C.W. Hunt, T. Loder, C. Vörösmarty, Water. Air. Soil Pollut. **163**, 303 (2005)
43. S.M. Kanan, I.A.A. Yousef, N.M. Abdo, Appl. Catal. B Environ. **74**, 130 (2007)
44. M.C. Kanan, *A Study of the Photodegradation of Carbaryl: The Influence of Natural Organic Matter and the Use of Silver Zeolite Y as a Catalyst* (The University of Maine, Orono, 2002)
45. X. Sun, H. Liu, Y. Zhang, Y. Zhao, X. Quan, J. Environ. Sci. **23**, 773 (2011)
46. L.C. Backer, B. Bolton, J.A. Litz, J. Trevillian, S. Kieszak, J. Kucklick, Sci. Total Environ. **696**, 134041 (2019)
47. P.L. Miller, Y.P. Chin, J. Agric. Food Chem. **50**, 6758 (2002)
48. P.A. Gallagher, C.A. Schwegel, A. Parks, B.M. Gamble, L. Wymer, J.T. Creed, Environ. Sci. Technol. **38**, 2919 (2004)
49. S. Baken, F. Degryse, L. Verheyen, R. Merckx, E. Smolders, Environ. Sci. Technol. **45**, 2584 (2011)
50. L.E. Lesser, A. Mora, C. Moreau, J. Mahlknecht, A. Hernandez-Antonio, A. Ramirez, H. Barrios-Pina, Chemosphere **198**, 510 (2018)
51. T. Undabeytia, E. Morillo, C. Maqueda, J. Agric. Food Chem. **50**, 1918 (2002)
52. J.M. Peckenham, J.A. Nadeau, A. Amirbahman, R.S. Behr, Waste Manag. Res. **26**, 163 (2008)
53. A. Amirbahman, A.L. Reid, T.A. Haines, J.S. Kahl, C. Arnold, Environ. Sci. Technol. **36**, 690 (2002)
54. A.K. Singh, R. Chandra, Aquat. Toxicol. **211**, 202 (2019)
55. M.C. Mirabelli, S. Wing, Environ. Res. **102**, 96 (2006)
56. M. Kamali, Z. Khodaparast, Ecotoxicol. Environ. Saf. **114**, 326 (2015)
57. L.H. Kifner, A.J.K. Calhoun, S.A. Norton, K.E. Hoffmann, A. Amirbahman, Biogeochemistry **139**, 275 (2018)
58. J.P. Wise, J. Wise, C. Wise, S. Wise, C. Zhu, C. Browning, T. Zheng, C. Perkins, C. Gianios, H. Xie, J. Wise, Chemosphere **216**, 653 (2019)
59. J.M. Giddings, W.M. Williams, K.R. Solomon, J.P. Giesy, Rev. Environ. Contam. Toxicol. **231**, 119 (2014)
60. W.S. McFarlane, Environ. Hist. Durh. N. C. **17**, 307 (2012)
61. O. Ashrafi, L. Yerushalmi, F. Haghighat, J. Environ. Manag. **158**, 146 (2015)
62. I.D. Buchanan, Water Environ. Res. **89**, 1417 (2017)
63. E. Hoffman, J. Lyons, J. Boxall, C. Robertson, C.B. Lake, T.R. Walker, Environ. Monit. Assess. **189**, 257 (2017)
64. S.L. Shalat, K. Donnelly, N. Freeman, J. Calvin, S. Ramesh, M. Jimenez, K. Black, C. Coutinho, L. Needham, D. Barr, J. Ramirez, J. Expo. Anal. Environ. Epidemiol. **13**, 42 (2003)
65. L.J. Mills, C. Chichester, Sci. Total Environ. **343**, 1 (2005)
66. H. Selck, R.D. Handy, T.F. Fernandes, S.J. Klaine, E.J. Petersen, Environ. Toxicol. Chem. **35**, 1055 (2016)
67. V. Paul, M.S. Sankar, S. Vattikuti, P. Dash, Z. Arslan, Chemosphere **263**, 128243 (2021)
68. F. Liang, M. Lu, M.E. Birch, T.C. Keener, Z. Liu, J. Chromatogr. A **1114**, 145 (2006)
69. S. Stehle, A. Bline, S. Bub, L.L. Petschick, J. Wolfram, R. Schulz, Environ. Int. **133**, 105234 (2019)

70. A.B. Boxall, D.W. Kolpin, B. Halling-Sørensen, J. Tolls, Environ. Sci. Technol. **37**, 286A (2003)
71. D. Ashton, M. Hilton, K.V. Thomas, Sci. Total Environ. **333**, 167 (2004)
72. D. Bendz, N.A. Paxéus, T.R. Ginn, F.J. Loge, J. Hazard. Mater. **122**, 195 (2005)
73. L.H. Santos, A.N. Araújo, A. Fachini, A. Pena, C. Delerue-Matos, M.C.B. Montenegro, J. Hazard. Mater. **175**, 45 (2010)
74. R. Kase, B. Javurkova, E. Simon, K. Swart, S. Buchinger, S. Könemann, B.I. Escher, M. Carere, V. Dulio, S. Ait-Aissa et al., Trends Anal. Chem. **102**, 343 (2018)
75. A.D. Vethaak, J. Lahr, S.M. Schrap, A.C. Belfroid, G.P. Rijs, A. Gerritsen, J. De Boer, A. Bulder, G. Grinwis, R. Kuiper et al., Chemosphere **59**, 511 (2005)
76. B.E. Gillesby, T.R. Zacharewski, Environ. Toxicol. Chem. **17**, 3 (1998)
77. R. Kumar, N. Goyal, Life Sci. **269**, 11909 (2021)
78. Z. Liu, Y. Kanjo, S. Mizutani, Sci. Total Environ. **407**, 731 (2009)
79. G. Querio, S. Antoniotti, F. Geddo, F. Tullio, C. Penna, P. Pagliaro, M. Gallo, Vascul. Pharmacol. **141**, 106921 (2021)
80. H. Väänänen, P.L. Härkönen, Maturitas. S65 (1996)
81. H.P. Nguyen, L. Li, J.W. Gatson, D. Maass, J.G. Wigginton, J.W. Simpkins, K.A. Schug, J. Pharmaceut. Biomed. Anal. **54**, 830 (2011)
82. R. Sapolsky, L. Romero, A. Munck, Endocr. Rev. **21**, 55 (2000)
83. P.J. Barnes, Chem. Immunol. Allergy **100**, 311 (2014)
84. A. Mukhtar, A. Hassan, SN Compr. Clin. Med. **2**, 2637 (2020)
85. M. Berglin, D. Stram, A. Stenquist, S. Dessi, M.R. Weintraub, E. Zaritsky, Contraception **108**, 56 (2022)
86. M. Mittal, C. McEniery, P.R. Supramaniam, L. Cardozo, M. Savvas, N. Panay, H. Hamoda, Maturitas **161**, 18 (2022)
87. M. Eady, M. Payne, S. Sortijas, E. Bethea, D. Jenkins, Spectrochim Acta A Mol Biomol Spectrosc **259**, 119917 (2021)
88. R. Schickler, D. Crabtree-Sokol, J. Patel, N. Bender, A.L. Nelson, B.T. Nguyen, Contraception **3**, 100050 (2021)
89. Y. Lin, L.P. Bullock, C.W. Bardin, S.T. Jacob, Biochem. **31**, 4833 (1978)
90. K. Zhang, Y. Zhao, K. Fent, Environ. Sci. Technol. **51**, 6498 (2017)
91. L. Tsuruda, Y. Hou, T.M. Penning, Chem. Res. Toxicol. **14**, 856 (2001)
92. M. Blondon, A. Bodmer, L. Thouvenin, T. Lecompte, M. Righini, P. Fontana, A. Casini, Blood Adv. **6**, 2884 (2022)
93. Y. Unten, M. Murai, T. Koshitaka, K. Kitao, O. Shirai, T. Masuya, H. Miyoshi, Biochim. Biophys. Acta Bioenerg. **1863**, 148520 (2022)
94. S.A. Alomar, M. Găman, K. Prabahar, O.A. Arafah, F. Almarshood, S. Baradwan et al., Exp. Gerontol. **159**, 111680 (2022)
95. A. Amiruddin, M. Massi, A. Islam, I. Patellongi, M. Pratama, N. Sutandyo, R. Natzir, M. Hatta, N.H. Latar, S. Wahid, Ann. Med. Surg. **73**, 103092 (2022)
96. R. Addo, M. Haas, S. Goodall, Value Health Region. Issues **25**, 196 (2021)
97. M. Dehghan, M. Hedayati, S. Shivaee, H. Shakib, S. Rajabi, Gene Rep. **24**, 101266 (2021)
98. M. Borgatta, C. Hernandez, L.A. Decosterd, N. Chèvre, P. Waridel, J. Proteome Res. **14**, 279 (2015)
99. K. Sato, J. Kuriwaki, K. Takahashi, Y. Saito, J. Oka, Y. Otani, Y. Sha, K. Nakazawa, Y. Sekino, T. Ohwada, A.C.S. Chem, Neurosci. **3**, 105 (2012)
100. S.M. Hengel, E. Murray, S. Langdon, L. Hayward, J. O'Donoghue, A. Panchaud, T. Hupp, D.R. Goodlett, J. of Proteome Res. **10**, 4567 (2011)
101. S. Zhang, C. Ye, J. Li, X. Yu, M. Feng, Water Res. **206**, 117729 (2021)
102. P. Ordentlich, Y. Yan, S. Zhou, R.A. Heyman, J. Biol. Chem. **278**, 24791 (2003)
103. W.W. Ceglio, M.M. Rebeis, M. Santana, D. Miyashiro, J. Cury-Martins, J.A. Sanches, An. Bras. Dermatol. **97**, 14 (2022)
104. A. Yadav, E.R. Rene, M. Mandal, K. Dubey, Chemosphere **263**, 128285 (2021)
105. P. Wang, L. Xie, E.A. Joseph, J. Li, X. Su, H. Zhou, Chem. Rev. **119**, 10638 (2019)
106. D. Li, R. Liu, M. Wang, R. Peng, S. Fu, A. Fu, J. Le, Q. Yao et al., Cell Host Microbe **30**, 329 (2022)
107. M. Göttlich, M. Buades-Rotger, J. Wiechert, F. Beyer, U.M. Krämer, Neuropsychologia **165**, 108113 (2022)

108. Q. Xiao, X. Hou, C. Kang, L. Xu, L. Yuan, Z. Zhao, Q. Meng, J. Jiang, W. Hao, Toxicol. Lett. **356**, 161 (2022)
109. K. Xiao, J. Gao, S. Weng, Y. Fang, N. Gao, Q. Wen, H. Jin, H. Qiao, Mol. Pharm. **16**, 382 (2019)
110. I. León, E.R. Alonso, S. Mata, J.L. Alonso, J. Phys. Chem. Lett. **12**, 6983 (2021)
111. T. Asami, N. Nishizawa, H. Matsui, Y. Takatsu, A. Suzuki et al., J. Med. Chem. **57**, 6105 (2014)
112. A. Sidhu, N. Singla, M. Lonare, A. Mahal, Pestic. Biochem. Phys. **165**, 104544 (2020)
113. Q. Su, Y. Chen, J. Qin, T. Wang, D. Wang, Q. Liu, Pestic. Biochem. Phys. **143**, 122 (2017)
114. D. Wang, N. Li, M. Liu, B. Huang, Q. Liu, X. Liu, Physiol. Behav. **104**, 1024 (2011)
115. X. Lv, Y. Guo, D. Shi, Reprod. Biol. **12**, 285 (2012)
116. A. Talbot, R. Maltais, D. Poirier, ACS Combin. Sci. **14**, 347 (2012)
117. R.M. Kanojia, G.O. Allen, J.M. Killinger, J.L. McGuire, J. Med. Chem. **22**, 1538 (1979)
118. S. Saji, M. Takada, N. Honma, N. Masuda, Y. Yamamoto, K. Kuroi, H. Yamashita, S. Ohno, T. Ueno, M. Toi, Ann. Oncol. **23**, ix104 (2012)
119. G.T. Ankley, D. Feifarek, B. Blackwell, J.E. Cavallin, K.M. Jensen, M.D. Kahl, S. Poole, E. Randolph, T. Saari, D.L. Villeneuve, Environ. Sci. Technol. **51**, 4705 (2017)
120. M. Wetzel, S. Marchais-Oberwinkler, E. Perspicace, G. Möller, J. Adamski, R.W. Hartmann, J. Med. Chem. **54**, 7547 (2011)
121. A. Oster, S. Hinsberger, R. Werth, S. Marchais-Oberwinkler, M. Frotscher, R.W. Hartmann, J. Med. Chem. **53**, 8176 (2010)
122. Y. Long, D. Huang, L. Luo et al., Res. Chem. Intermed. **44**, 7117 (2018)
123. J. Blount, Y. Pan, M. Mauck, E. Datner, M. Kurz, P. Hendry, C. Lewandowski, C. Pearson, S. McLean, S. Linnstaedt, J. Pain **20**, S27 (2019)
124. P. Kumar, N. Baquer, Alzheimers Dement. **12**, 337 (2016)
125. K. Prokai-Tatrai, H. Xin, V. Nguyen, S. Szarka, B. Blazics, L. Prokai, P. Koulen, Mol. Pharm. **10**, 3253 (2013)
126. L. Wang, Y. Chen, ACS Appl. Mater. Interfaces. **12**, 8351 (2020)
127. Y. Hu, J. Li, X. Zhu, Y. Li, S. Zhang, X. Chen, Y. Gao, F. Li, ACS Appl. Mater. Interfaces. **7**, 15803 (2015)
128. P.L. Marca-Ghaemmaghami, R. Zimmermann, M. Haller, U. Ehlert, Psychoneuroendocrinology **125**, 105120 (2021)
129. I. Itoh, T. Hayashi, H. Endo, A. Iguchi, Jpn. J. Pharmacol. **75**, 19 (1997)
130. R. Lappano, C. Rosano, P. Marco, E.M. Francesco, V. Pezzi, M. Maggiolini, Mol. Cell. Endocrinol. **320**, 162 (2010)
131. C.S. Lee, E.E. Yost, D.D. Aday, S.W. Kullman, Environ. Sci. Technol. **50**, 8886 (2016)
132. O. Takenouchi, A. Kanno, H. Takakura, M. Hattori, T. Ozawa, Bioconj. Chem. **27**, 2689 (2016)
133. V. Frisée, G. Rigaux, P. Dufour, O. Barbato, F. Brutinel, S. Egyptien, P. Bossaert, S. Deleuze, E. Cavalier, J. Ponthier, Domest. Anim. Endocrinol. **78**, 106684 (2022)
134. X. Liu, T. Schwarz, M. Murawski, C. Tayade, R. Kridli, A.M. Prieto-Granados, C. Sharma, P.M. Bartlewski, Domest. Anim. Endocrinol. **71**, 106402 (2020)
135. H. Yamaguchi, M. Sugie, M. Okada, T. Mikkaichi, T. Toyohara, T. Abe, J. Goto, T. Hishinuma, M. Shimada, N. Mano, Drug Metab. Pharmacokinet. **25**, 314 (2010)
136. S. Kakusaka, M. Asayama, A. Kaihara, T. Sasano, T. Suzuki, J. Kurokawa, T. Furukawa, J. Pharmacol. Sci. **109**, 152 (2009)
137. J. Geisler, D. Ekse, H. Helle, N. Duong, P.E. Lønning, J. Steroid Biochem. Mol. Biol. **109**, 90 (2008)
138. F. Kang, Q. Zou, J. Huang, Exp. Gerontol. **159**, 111682 (2022)
139. Y. Sun, Y. Xiong, Y.L. Meng, H.O. Santos, F.L. Athayde, I.O. de Souza, L. Yang, Growth Horm. IGF Res. **60–61**, 101421 (2021)
140. G. Lambrinidis, C. Gouedard, S. Stasinopoulou, A. Angelopoulou, V. Ganou, A.K. Meligova, D.J. Mitsiou, P. Marakos, N. Pouli, E. Mikros, M.N. Alexis, Bioorg. Chem. **106**, 104482 (2021)
141. C.A. Tastad, R. Kohler, J.M. Wallace, Bone **146**, 115889 (2021)
142. S.M. Badr-Eldin, H. Aldawsari, O. Ahmed, N. Alhakamy, T. Neamatallah, S. Okbazghi, U.A. Fahmy, Int. J. Pharm. **600**, 120493 (2021)
143. M.N. Ebrahimi, M. Khaksari, G. Sepehri, G.A. Karam, A. Raji-amirhasani, H. Azizian, Life Sci. **263**, 118573 (2020)
144. C. Mota, A. Diniz, C. Coelho, T. Santos-Silva, M. Esmaeeli, S. Leimkühler, E.J. Cabrita, F. Marcelo, M.J. Romão, J. Med. Chem. **64**, 13025 (2021)
145. H. Li, H. Xiao, L. Lin, D. Jou, V. Kumari, J. Lin, C. Li, J. Med. Chem. **57**, 632 (2014)

146. Z. Liu, P. Wan, Z. Liu, M. Yang, S. Li, Y. Wang, Y. Gan, A.C.S. Biomater, Sci. Eng. **6**, 6186 (2020)
147. J. Villar, C. Ferrando, D. Martínez, A. Ambrós, T. Muñoz, J. Soler, G. Aguilar et al., Lancet Respir. Med. **8**, 267 (2020)
148. X. Wang, W. Jiang, Q. Huang, F. Pei, J. Arthroplasty **37**, 888 (2022)
149. R.M. Mohamed, E. Ahmad, B.H. Omran, A.T. Sakr, I. Ibrahim, M.F. Mahmoud, M.E. El-Naggar, Life Sci. **293**, 120304 (2022)
150. A. Pande, I. Sen, A. Gupta, A. Gupta, A. Sharma, Braz. J. Anesthesiol. (English Edition) (2021). https://doi.org/10.1016/j.bjane.2021.10.012
151. A. Oeyen, J. Kircher, M. Vogl, I. Ickert, N. Osada, R. Krauspe, B. Bittersohl, M. Herten, Arthroscopy Sports Med. Rehabil. **4**, e459 (2022)
152. Z. Wu, Y. Wen, H. Xiao, J. Zhu, B. Li, Y. Shangguan, H. He, H. Wang, L. Chen, Pharmacol. Res. **175**, 105990 (2022)
153. A. Buzatto, A. Malkawi, E.M. Sabi, A.H. Mujamammi, L. Li, A.M. Abdel Rahman, J. Proteome Res. **20**, 1558 (2021)
154. E.M. Robbins, A. Jaquins-Gerstl, D.F. Fine, C.L. Leong, C.E. Dixon, A.K. Wagner, M.G. Boutelle, A.C. Michael, A.C.S. Chem, Neurosci. **10**, 3521 (2019)
155. Z. Jia, X. Wang, X. Wei, G. Zhao, K.W. Foster, F. Qiu, Y. Gao, F. Yuan, F. Yu, G. Thiele, T. Bronich, J.R. O'Dell, D. Wang, ACS Nano **22**, 7663 (2018)
156. O.D. Kothgassner, M. Pellegrini, A. Goreis, V. Giordano, J. Edobor, S. Fischer, P.L. Plener, M.M. Huscsava, Psychoneuroendocrinology **126**, 105168 (2021)
157. S. Bonnin, J.J. Radosevich, Y.G. Lee, J.P. Feldman, J.F. Barletta, J. Crit. Care **62**, 111 (2021)
158. C. Renolleau, A. Toumazi, A. Bourmaud, J. Benoist, D. Chevenne, D. Mohamed, C. Alberti et al., J. Pediatr. **234**, 65 (2021)
159. C.L. Sprung, D. Annane, D. Keh, R. Moreno et al., N Engl. J. Med. **358**, 111 (2008)
160. R. Alqassieh, M. Odeh, M.Q. Al-Sabbagh, M. Alrabayah, Perioper. Care Oper. Room Manag. **23**, 100161 (2021)
161. M. Park, S. Park, J. Kim, J. Yu, E. Lee, S.R. Seo, S. Jo, Mol. Cell. Endocrinol. **494**, 110488 (2019)
162. K. Sridharan, B. Rathore, M. Yousuf, H.K. Reddy Rachamalla, S. Jinka, M.M. Jaggarapu, R. Banerjee, Mol. Pharm. **18**, 1208 (2021)
163. A. Karla, B. Rivera, A. Martínez-Richa, ACS Symp Ser. **1310**, 163 (2018)
164. F. Samara, F. Feghaly, S. Kanan, Catal. Today (2019). https://doi.org/10.1016/j.cattod.2019.12.024
165. C. Congdon, J. Gorham, S. Kanan, M. Kanan, R. Austin, H. Patterson, ACS Div. Environ. Chem. **43**, 840 (2003)
166. S. Kanan, M. Kanan, H. Patterson, Curr. Opin. Solid State Mater. Sci. **7**, 443 (2003)
167. M. Moyet, S. Kanan, H. Varney et al., Res. Chem. Intermed. **45**, 5919 (2019)
168. F. Samara, E. Jermani, S. Kanan, Arab. J. Chem. **12**, 1870 (2019)
169. S. Kanan, F. Samara, Trends Environ. Anal. Chem. **17**, 1 (2018)
170. S. Kanan, N. Abdo, M. Khalil, X. Li, I. Abu-Yousef, F. Barilrobert, H. Patterson, Appl. Catal. B **106**, 350 (2011)
171. S. Kanan, A. Malkawi, Desalin. Water Treat. **100**, 281 (2017)
172. J. Ahern, S. Kanan, Z. Sara, T. Job, R. Alnaizy, N. Abu Farha, H. Patterson, Environ. Sci. Pollut. Res. **22**, 3186 (2015)
173. S. Kanan, F. Samara, I. Abu-Yousef, N. Abdo, D. Tobias, Res. Chem. Intermed. **36**, 473 (2010)
174. S. Kanan, M. Kanan, H. Patterson, Res. Chem. Intermed. **32**, 871 (2006)
175. M. Kanan, S. Kanan, H. Patterson, Res. Chem. Intermed. **29**, 691 (2003)
176. M. Kanan, S. Kanan, R.N. Austin, H. Patterson, Environ. Sci. Technol. **37**, 2280 (2003)
177. J. Ahern, S. Kanan, H. Patterson, Comments Inorg. Chem. **35**, 59 (2015)
178. S. Kanan, S. Nusri, Adv. Mater. Res. **856**, 43 (2014)
179. S. Kanan, M. Moyet, Res. Chem. Intermed. **47**, 433 (2021)
180. F. Samara, M. Al Shamsi, S. Kanan, Res. Chem. Intermed. **46**, 1017 (2020)
181. S. Kanan, M. Moyet, R. Arthur, H. Patterson, Catal. Rev. **62**, 1 (2020)
182. S. Kanan, I. Abu-Yousef, N. Abdo, A. Abdel Hamid, Int. J. Environ. Eng. **6**, 370 (2014)
183. S. Kanan, M. Kanan, H. Patterson, J. Phys. Chem. B **105**, 7508 (2001)
184. S. Kanan, C. Tripp, R. Austin, H. Patterson, J. Phys. Chem. B **105**, 9441 (2001)
185. M. Hamada, A. Matar, A. Bashir, Braz. J. Microbiol. **46**, 1087 (2015)
186. G.K. Sims, R.G. Kanissery, *Microbial Metabolism of Xenobiotic Compounds* (Springer, Singapore, 2019), pp. 33–54

187. S. Sarker, M.A. Akbor, A. Nahar, M. Hasan, A.R. Islam, M.A. Siddique, Heliyon **7**, e07270 (2021)
188. V. D'Atri, S. Fekete, A. Clarke, J.-L. Veuthey, D. Guillarme, Anal. Chem. **91**, 210 (2019)
189. D. Shewiyo, D.E. Kaale, P.G. Risha, B. Dejaegher, J. Smeyers-Verbeke, Y. Heyden, J. Pharm. Biomed. Anal. **66**, 11 (2012)
190. J. Radjenovic, M. Petrovic, D. Barcelo, Trends Anal. Chem. **26**, 1132 (2007)
191. X.R. Liu, M.M. Zhang, M.L. Gross, Chem. Rev. **120**, 4355 (2020)
192. M. Petrovic, M. Farré, M. Lopez de Alda, S. Perez et al., J. Chromatogr. A **1217**, 4004 (2010)
193. J. Qiao, D. Xu, H. Lian et al., Res. Chem. Intermed. **41**, 691 (2015)
194. Z. Hu, H. Liao, Q. An et al., Res. Chem. Intermed. **42**, 2577 (2016)
195. Y. Wang, C. Chen, X. Cao et al., Res. Chem. Intermed. **41**, 2841 (2015)
196. M. Finšgar, A. Perva-Uzunalić, H. Behr, N. Ledinek, Ž Knez, Z. Novak, ACS Omega **5**, 7987 (2020)
197. J.Q. Qiao, N. Yuan, C.J. Tang et al., Res. Chem. Intermed. **38**, 549 (2012)
198. M. Li, J. Wang, Q. Chen, L. Lin et al., Anal. Chem. **91**, 15025 (2019)
199. S.D. Richardson, Anal. Chem. **84**, 747 (2012)
200. P. Yuan, D. Yang, R. Wang, N. Gong, L. Zhang, Y. Lu, G. Du, ACS Omega **5**, 25289 (2020)
201. E.M. Robinson, S.J. Trumble, B. Subedi, R. Sanders, S. Usenko, J. Chromatogr. A **1319**, 14 (2013)
202. M.J. López de Alda, D. Barceló, J. Chromatogr. A **892**, 391 (2000)
203. M.B.R. Cerqueira, J.R. Guilherme, S.S. Caldas, M.L. Martins, R. Zanella, E.G. Primel, Chemosphere **107**, 74 (2014)
204. L. Yang, T. Luan, C. Lan, J. Chromatogr. A **1104**, 23 (2006)
205. P. Wei, L. Hao, S. Thomas, A. Buchberger, L. Steinke et al., J. Am. Soc. Mass Spectrom. **31**, 1854 (2020)
206. R. Trenholm, B. Vanderford, J. Holady, D. Rexing, S. Snyder, Chemosphere **65**, 1990 (2006)
207. Z. Khiya, Y. Oualcadi, E.H. Mourid et al., Res. Chem. Intermed. **47**, 3131 (2021)
208. M.R. Islam, A. Chakraborty, M.A. Gafur et al., Res. Chem. Intermed. **45**, 1753 (2019)
209. G. Martínez-Domínguez, R. Romero-González, A. Frenich, Microchem. J. **118**, 124 (2015)
210. N. Tiwari, A. Asthana, K. Upadhyay, Res. Chem. Intermed. **39**, 2867 (2013)
211. A. Azzouz, L.P. Colón, B. Souhail, E. Ballesteros, Environ. Res. **178**, 108727 (2019)
212. S. Huang, F. Zhu, R. Jiang, S. Zhou, D. Zhu, H. Liu, G. Ouyang, Talanta **136**, 198 (2015)
213. A. Azzouz, B. Souhail, E. Ballesteros, J. Chromatogr. A **1217**, 2956 (2010)
214. F. Plössl, M. Giera, F. Bracher, J. Chromatogr. A **1135**, 19 (2006)
215. S. Morales-Muñoz, J.L. Luque-García, M.J. Ramos, A. Fernández-Alba, M.D. Luque de Castro, Anal. Chim. Acta **552**, 50 (2005)
216. R. Fernández, J. McDonald, S. Khan, P. Le-Clech, Sep. Purif. Technol. **127**, 131 (2014)
217. M.A. Soliman, J.A. Pedersen, I.M. Suffet, J. Chromatogr. A **1029**, 223 (2004)
218. J. Kumirska, P. Łukaszewicz, M. Caban, N. Migowska, A. Plenis, A. Białk-Bielińska, M. Czerwicka, F. Qi, S. Piotr, Chemosphere **232**, 232 (2019)
219. J. Xu, L. Wu, W. Chen, A. Chang, J. Chromatogr. A **1202**, 189 (2008)
220. X. Ouyang, P. Leonards, J. Legler, R. Oost, J. Boer, M. Lamoree, J. Chromatogr. A **1380**, 139 (2014)
221. Z. He, Y. Xu, L. Wang et al., Food Chem. **196**, 1248 (2016)
222. W. Peysson, E. Vulliet, J. Chromatogr. A **1290**, 46 (2013)
223. A. Masiá, M. Ibáñez, C. Blasco, J.V. Sancho, Y. Picó, F. Hernández, Anal. Chim. Acta **761**, 117 (2013)
224. D. Krakkó, V. Licul-Kucera, G. Záray, V.G. Mihucz, Microchem. J. **148**, 108 (2019)
225. E. De Paepe, J. Wauters, M. Borght, J. Claes, S. Huysman, S. Croubels, L. Vanhaecke, Food Chem. **239**, 187 (2019)
226. R. López-Serna, S. Pérez, A. Ginebreda, M. Petrović, D. Barceló, Talanta **83**, 410 (2010)
227. P. Paíga, A. Lolić, F. Hellebuyck, L.H.M.L.M. Santos, M. Correia, C. Delerue-Matos, J. Pharm. Biomed. Anal. **106**, 61 (2015)
228. Q. Zhao, L. Huiyu et al., J. Chromatogr. A **1376**, 26 (2015)
229. R.A. Trenholm, B.J. Vanderford, S.A. Snyder, Talanta **79**, 1425 (2009)
230. I. Aparicio, J. Martín, C. Abril, J.L. Santos, E. Alonso, J. Chromatogr. A **1533**, 49 (2018)
231. M.B.R. Cerqueira, K.L. Soares, S.S. Caldas, E.G. Primel, Chemosphere **211**, 875 (2018)
232. C. Gómez-Canela, T. Sala-Comorera, V. Pueyo, C. Barata, S. Lacorte, J. Pharm. Biomed. Anal. **168**, 55 (2019)
233. J. Nácher-Mestre et al., Chemosphere **154**, 231 (2016)
234. A. Szterk, J. Sitkowski, W. Bocian, Talanta **204**, 415 (2019)

235. N. Siraj, B. El-Zahab, S. Hamdan, T.E. Karam et al., Anal. Chem. **88**, 170 (2016)
236. M. Sgroi, T. Anumol, P. Roccaro, F.G.A. Vagliasindi, S.A. Snyder, Water Res. **145**, 667 (2018)
237. I. Ryzhkina, L. Murtazina, S. Sergeeva et al., Environ. Technol. Innov. **21**, 101215 (2020)
238. H. Zhang, S. Yang, K. Ruyck et al., Trends Anal. Chem. **114**, 293 (2019)
239. R. Li, M. Shu, Y. Tian et al., J. Pharm. Biomed. Anal. **190**, 113508 (2020)
240. M.I. Gaviria-Arroyave, J.B. Cano, G.A. Peñuela, Talanta Open **2**, 100006 (2020)
241. S.M. Derayea, E. Samir, Microchem. J. **156**, 104835 (2020)
242. P. Carullo, M. Chino, G. Cetrangolo, S. Terreri et al., Sens. Actuators, B Chem. **255**, 3257 (2018)
243. M. Sgroi et al., J. Hazard. Mater. **323**, 367 (2017)
244. X. Luo, R. Wang, C. Lv, G. Chen, J. You, F. Yu, Anal. Chem. **92**, 1589 (2020)
245. T.L. Mako, J.M. Racicot, M. Levine, Chem. Rev. **119**, 322 (2019)
246. J. Lei, C. Hou, D. Huo et al., Res. Chem. Intermed. **42**, 7359 (2016)
247. Y. Zhang, R. Zhang, X. Yang, H. Qi, C. Zhang, J. Pharm. Anal. **9**, 9 (2019)
248. N.L. Pacioni, A.G. Bracamonte, A.V. Veglia, J. Photochem. Photobiol. A Chem. **198**, 179 (2008)
249. T.T.X. Ong, E.W. Blanch, O.A.H. Jones, Sci. Total Environ. **720**, 137601 (2020)
250. M.M. Hassan et al., Food Chem. **338**, 127796 (2021)
251. Y.-S. Li, J.S. Church, J. Food Drug Anal. **22**, 29 (2014)
252. F.G. Vogt, M. Strohmeier, Mol. Pharm. **10**, 4216 (2013)
253. F. Wang, X. Gu, C. Zheng, F. Dong, L. Zhang et al., Anal. Chem. **89**, 8836 (2017)
254. B.N. Ratha, R. Kar, Z. Bednarikova, Z. Gazova, S. Kotler et al., J. Phys. Chem. B **124**, 1125 (2020)
255. K. Lee, M. El-Sayed, J. Phys. Chem. B **110**, 19220 (2006)
256. V. Amendola, R. Pilot et al., J. phys. Condens. Matter **29**, 203002 (2017)
257. R. Barbir, B. Pem et al., Langmuir **37**, 1991 (2021)
258. M. Frasconi, C. Tortolini, F. Botre, F. Mazzei, Anal Chem **82**, 7335 (2010)
259. A. Calle, J. Rodríguez-frade, M. Mellado, L. Lechuga, Talanta **78**, 1011 (2009)
260. P. Howes, R. Chandrawati, M. Stevens, Science **346**, 1247390 (2014)
261. O. Tokel, F. Inci, U. Demirci, Chem. Rev. **114**, 5728 (2014)
262. A. Calle, J. Rodríguez-frade, M. Mellado, L. Lechuga, Anal. Chim. Acta **647**, 202 (2009)
263. W. Zhou, X. Gao, D. Liu, X. Chen, Chem. Rev. **115**, 10575 (2015)
264. Y. Chen, H. Ming, Photon. Sens. **2**, 37 (2012)
265. N. Al-Rawashdeh, W. Azzam, Res. Chem. Intermed. **37**, 759 (2011)
266. F. Ahmed, J. Wiley, D. Weidner et al., Cancer Genomics Proteomics **7**, 303 (2010)
267. J.-F. de Elena, C. Antonio, J. Pedrajas, L. Lechuga, Analyst **138**, 2023 (2013)
268. A. Ramanaviciene, N. German et al., Biosens. Bioelectron. **36**, 48 (2012)
269. E. Türkoğlu, M. Bakhshpour, A. Denizli, Biointerface Res. Appl. Chem. **9**, 4090 (2019)
270. Z. Yuan, C. Hu, H. Chang, C. Lu, Analyst **141**, 1611 (2016)
271. T. Yoshida, M. Sato, T. Ozawa, Y. Umezawa, Anal. Chem. **72**, 6 (2000)
272. D. Nurrohman, N. Chiu, Nanomaterials **11**, 216 (2021)
273. A. Thiel, A. Frutos, C. Jordan, R. Corn, L. Smith, Anal. Chem. **69**, 4948 (1997)
274. L. Guo, J. Jackman, H. Yang, P. Chen, N. Cho, D. Kim, Nano Today **10**, 213 (2015)
275. G. Tonga, K. Saha, V. Rotello, Adv. Mater. **26**, 359 (2014)
276. B. Parabowo, A. Purwidyantri, K. Liu, Biosensors **8**, 80 (2018)
277. M. Frasconi, M. Mazzarino, F. Botrè, F. Mazzei, Anal. Bioanal. Chem. **394**, 2151 (2009)
278. F. Torrini, P. Palladino, V. Baldoneschi, S. Scarano, M. Minunni, Anal. Chim. Acta **1161**, 338481 (2021)
279. A. Makaraviciute, A. Ramanavicius, Anal. Methods **7**, 9875 (2015)
280. S. Anna, A. Hermanowicz, A. Grycz, Z. Łukaszewski, Anal. Methods **13**, 642 (2021)
281. L. Chen, J. Li, L. Chen, A.C.S. Appl, Mater. Interfaces **6**, 15897 (2014)
282. A. Laromaine, L. Koh, M. Murugesan, R. Ulijn, M. Stevens, J. Am. Chem. Soc. **129**, 4156 (2007)
283. S. Thirugnanasambandan, R. Manogaran et al., Res Chem Intermed **46**, 3383 (2020)
284. H. Li, L. Rothberg, Proc. Natl Acad. Sci. USA **101**, 14036 (2004)
285. L. Guo, Y. Xu, A. Ferhan, G. Chen, D. Kim, J. Am. Chem. Soc. **135**, 12338 (2013)
286. X. Jiang, M. Waterland, A. Partridge, Anal Methods **3**, 368 (2010)
287. P. Cairns, Nat. Rev. Cancer **7**, 531 (2007)
288. B. Sharma, P. Bugga et al., J. Am. Chem. Soc. **138**, 13952 (2016)
289. Y. Chen, Y. Zhang et al., ACS Nano **10**, 8169 (2016)
290. E. Lacasa, S. Cotillas, C. Saez, J. Lobato, P. Cañizares, M.A. Rodrigo, Curr. Opin. Electrochem. **16**, 149 (2019)

291. S.I. Kaya, A. Cetinkaya, N.K. Bakirhan, S.A. Ozkan, Trends Environ. Anal. Chem. **28**, e00106 (2020)
292. A. Azzouz, S.K. Kailasa, P. Kumar, E. Ballesteros, K.-H. Kim, Trends Anal. Chem. **113**, 256 (2019)
293. H. Teymourian, M. Parrilla, J.R. Sempionatto, N. Montiel, A. Barfidokht et al., ACS Sensors **5**, 2679 (2020)
294. D. Pemberthy, M.Y. Padilla, A. Echeverri, G.A. Peñuela, Heliyon **6**, e04215 (2020)
295. M. Sedaghat, B. Vahid, S. Aber et al., Res. Chem. Intermed. **42**, 855 (2016)
296. J. Tschmelak, G. Proll, G. Gauglitz, Talanta **65**, 313 (2005)
297. T. Rasheed et al., Environ. Res. **185**, 109436 (2020)
298. S. Sanches, A. Penetra, A. Rodrigues, E. Ferreira et al., Sep. Purif. Technol. **94**, 44 (2012)
299. M. Taheran, S.K. Brar, M. Verma, R.Y. Surampalli, T.C. Zhang, J.R. Valero, Sci. Total Environ. **547**, 60 (2016)
300. D. Rana, B. Scheier, R.M. Narbaitz, T. Matsuura et al., J. Memb. Sci. **409–410**, 346 (2012)
301. R.C. Assis, A.B. Mageste, L.R. de Lemos, R.M. Orlando, G.D. Rodrigues, Talanta **223**, 121697 (2021)
302. P. Bhattacharya, D. Mukherjee, N. Deb, S. Swarnakar, S. Banerjee, J. Environ. Chem. Eng. **8**, 103803 (2020)
303. N.K. Khanzada, M. Farid et al., J. Memb. Sci. **598**, 117672 (2020)
304. S. Wang, L. Li, S. Yu, B. Dong, N. Gao, X. Wang, Chem. Eng. J. **406**, 126722 (2021)
305. J. Fu, W.-N. Lee, C. Coleman, K. Nowack, J. Carter, C.-H. Huang, Sci. Total Environ. **664**, 240 (2019)
306. J. Xiong, H. Li, X. Ma, B. Tan, J. You, Ecotoxicol. Environ. Saf. **202**, 110891 (2020)
307. Y.-L. Liu, X.-M. Wang, H.-W. Yang, Y.F. Xie, J. Memb. Sci. **551**, 37 (2018)
308. A.C. Sophia, E.C. Lima, Ecotoxicol. Environ. Saf. **150**, 1 (2018)
309. X. Li, W. Ma, H. Li, Y. Bai, H. Liu, Coord. Chem. Rev. **397**, 1 (2019)
310. A.-M. Aloizou, V. Siokas, C. Vogiatzi, E. Peristeri et al., Toxicol. Lett. **326**, 31 (2020)
311. M.J. Shreve, R.A. Brennan, Water Res. **151**, 318 (2019)
312. C.-W. Cho, Y. Zhao, Y.-S. Yun, Water Res. **151**, 288 (2019)
313. C. Trombini, M. Hampel, J. Blasco, Aquat. Toxicol. **208**, 146 (2019)
314. C. Jung, J. Park, K. Lim, S. Park et al., J. Hazard. Mater. **263**, 702 (2013)
315. M. Dudziak, M. Bodzek, Desalination **240**, 236 (2009)
316. A. Białk-Bielińska, J. Kumirska, M. Borecka et al., J. Pharm. Biomed. Anal. **121**, 271 (2016)
317. Y.-L. Liu, X.-M. Wang, H.-W. Yang, Y.F. Xie, Chemosphere **200**, 36 (2018)
318. D. Rawtani, N. Khatri, S. Tyagi, G. Pandey, J. Environ. Manag. **206**, 749 (2018)
319. T. Abraham, R.N. Priyanka, S. Joseph, N.J. Plathanam, M.G. Gigimol, B. Mathew, Appl. Mater. Today **21**, 100845 (2020)
320. S.M. Ahmad, A.S. Mestre, N.R. Neng, C.O. Ania, A.P. Carvalho, J.M.F. Nogueira, ACS Appl. Bio Mater. **3**, 2078 (2020)
321. H. Ejhed, J. Fang et al., Sci. Total Environ. **618**, 250 (2018)
322. A. Kumar, A. Rana, G. Sharma, M. Naushad et al., J. Mol. Liq. **290**, 111177 (2019)
323. D. Kanakaraju, B.D. Glass, M. Oelgemöller, J. Environ. Manag. **219**, 189 (2018)
324. A. Gogoi, P. Mazumder, V.K. Tyagi, G.G. Tushara Chaminda, A.K. An, M. Kumar, Groundw. Sustain. Dev. **6**, 169 (2018)
325. H. Ramírez-Malule, D.H. Quiñones-Murillo, D. Manotas-Duque, Emerg. Contam. **6**, 179 (2020)
326. D. Seibert et al., Sci. Total Environ. **748**, 141527 (2020)
327. A. Majumder, B. Gupta, A.K. Gupta, Environ. Res. **176**, 108542 (2019)
328. E. Cuervo Lumbaque et al., J. Environ. Chem. Eng. **6**, 3951 (2018)
329. D. Li, Y. Liu, H. Liu et al., Res. Chem. Intermed. **46**, 1065 (2020)
330. D. Lu, H. Liu, Res. Chem. Intermed. **46**, 253 (2020)
331. A. Khan, N.A. Mir, M.M. Haque et al., Res. Chem. Intermed. **38**, 1323 (2012)
332. S. Chatterjee, S. Kumari, S. Rath, S. Das, *Microbial Biodegradation and Bioremediation*, 2nd ed. (Elsevier, 2021), pp. 3–31
333. T. Singh, A.K. Bhatiya, P.K. Mishra, N. Srivastava, *Abatement of Environmental Pollutants* (2020), pp. 203–243
334. S. Yekta, M. Sadeghi, Res. Chem. Intermed. **44**, 1865 (2018)
335. B. Dhamaniya, A. Kumar, A. Srivastava et al., Res. Chem. Intermed. **43**, 387 (2017)
336. J. Sun, J. Dai, R. Liu et al., Res. Chem. Intermed. **46**, 149 (2020)

337. J.P. Escalada, A. Pajares, J. Gianotti, A. Biasutti, S. Criado, P. Molina, W. Massad, F. Amat-Guerri, N.A. García, J. Hazard. Mater. **186**, 466 (2011)
338. N.A. Anjum, K.F. Mendes, M.R. dos Reis, V. Tornisielo, A.C. Duarte, E. Pereira, *Soil Pollution* (2018), pp. 89–102
339. A. Kezzim, A. Boudjemaa, A. Belhadi et al., Res. Chem. Intermed. **43**, 3727 (2017)
340. K. Umar, M. Ibrahim, A. Ahmad et al., Res. Chem. Intermed. **45**, 2927 (2019)
341. M. Zarazúa-Morín, L.M. Torres-Martínez, E. Moctezuma et al., Res. Chem. Intermed. **42**, 1029 (2016)
342. Y. Kobayashi, Y. Tang, T. Kageyama, H. Yamashita, N. Masuda, S. Hosokawa, H. Kageyama, J. Am. Chem. Soc. **139**, 18240 (2017)
343. L. Adlnasab, M. Ezoddin, M.A. Karimi et al., Res. Chem. Intermed. **44**, 3249 (2018)
344. W. Maisang, S. Promnopas,S, Kaowphong, et al., Res. Chem. Intermed. **46**, 2117 (2020)
345. S. Rezaei, E. Dehghanifard, M. Noorisepehr, K. Ghadirinejad, B. Kakavandi, A. Esfahani, J. Environ. Manag. **250**, 109472 (2019)
346. W.W. Anku, S. Oppong, S. Shukla et al., Res. Chem. Intermed. **42**, 7231 (2016)
347. M. Padervand, H. Salari, S. Ahmadvand et al., Res. Chem. Intermed. **38**, 1975 (2012)
348. C. Ma, L. Zhang,J, Wang, et al., Res. Chem. Intermed. **41**, 6009 (2015)
349. P. Verma, S. Samanta, Res. Chem. Intermed. **44**, 1963 (2018)
350. M. Asadi, H. Sereshti, H. Rashidi Nodeh, Res. Chem. Intermed. **46**, 2789 (2020)
351. J. Wang, K. Chen, Y. Shen et al., Res. Chem. Intermed. **44**, 3061 (2018)
352. M.B. Asif, F. Hai, J. Kang et al., Bioresour. Technol. **247**, 528 (2018)
353. D. Nasuhoglu, D. Berk, V. Yargeau, Chem. Eng. J. **185–186**, 52 (2012)
354. D.E. Latch, B.L. Stender, J.L. Packer, W.A. Arnold, K. McNeill, Environ. Sci. Technol. **37**, 3342 (2003)
355. R. Al Abri, F. Al Marzouqi, A.T. Kuvarega et al., J. Photochem. Photobiol. A Chem. **384**, 112065 (2019)
356. K.C. Wijekoon et al., Bioresour. Technol. **144**, 247 (2013)
357. L.N. Nguyen et al., Int. Biodeterior. Biodegrad. **88**, 169 (2014)
358. R. Broséus, S. Vincent, K. Aboulfadl, A. Daneshvar et al., Water Res. **43**, 4707 (2009)
359. J. Margot et al., Sci. Total Environ. **461–462**, 480 (2013)
360. K.A. Al-Maqdi, S. Hisaindee, M.A. Rauf, S.S. Ashraf, Chem. Eng. J. **352**, 450 (2018)

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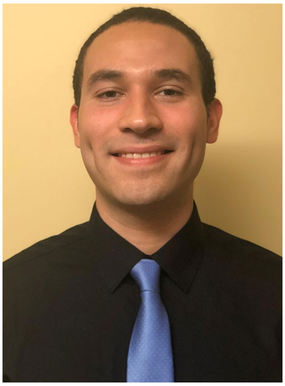

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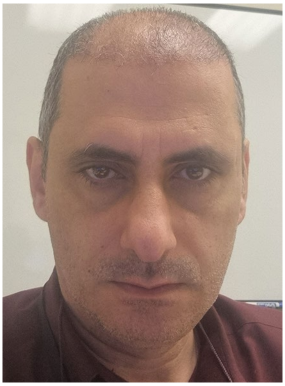

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