



Stereoselective analysis of chiral pesticides: a review

Vinod Kumar Vashistha · Sonika Sethi · Ankit Mittal · Dipak Kumar Das ·
Rajasekhar V. S. R. Pullabhotla · Renu Bala · Suman Yadav

Received: 27 December 2022 / Accepted: 4 January 2024 / Published online: 16 January 2024
© The Author(s), under exclusive licence to Springer Nature Switzerland AG 2024

Abstract Chiral organic pollutants, including pesticides, herbicides, medicines, flame retardants, and polycyclic musk, represent a significant threat to both the environment and human health. The presence of asymmetric centers in the structure of chiral pesticides introduces stereoisomers with distinct distributions, fates, biomagnification capacities, and cytotoxicities. In aquatic environments, pesticides, as persistent/pseudo-persistent compounds, have

been detected in substantial quantities, posing severe risks to non-target species and, ultimately, public health through water supply and food exposures. In response to this environmental challenge, stereoselective analytical methods have gained prominence for the identification of pesticide/drug enantiomers in recent years. This review examines the environmental impact of chiral pesticides, emphasizing the distinct biological activities and distribution patterns of their stereoisomers. By highlighting the advancements in liquid chromatography for enantiomeric analysis, the review aims to underscore the urgent need for a comprehensive understanding of these pollutants to facilitate informed remediation strategies and ensure the safer dispersal of chiral organic pollutants in the environment, thereby addressing the potential risks they pose to ecosystems and human health. Future research should focus on developing sustainable and efficient methodologies for the precise analysis of stereoisomers in complex matrices, particularly in sewage water, emphasizing the importance of sewage processing plants in ensuring water quality.

V. K. Vashistha (✉) · D. K. Das
Department of Chemistry, GLA University,
Mathura 281406, India
e-mail: vkviitr@gmail.com; vkv.uol@gmail.com

S. Sethi
Department of Chemistry, GD Goenka University,
Gurugram, Haryana, India

A. Mittal
Department of Chemistry, Shyamlal College, University
of Delhi, Delhi, India

R. V. S. R. Pullabhotla
Department of Chemistry, Faculty of Science, Agriculture
and Engineering, University of Zululand, P/Bag X1001,
KwaDlangezwa 3886, South Africa

R. Bala
Department of Chemistry, Kalindi College, University
of Delhi, Delhi, India

S. Yadav
Department of Chemistry, Swami Shraddhanand College,
University of Delhi, Delhi, India

Keywords Chiral organic pollutants · Remediation ·
Detection · Liquid chromatography · Chiral pesticides

Introduction

The importance of water in modern technological civilization, from a health, economic, and, most

importantly, a contemporary standpoint, cannot be overstated. Water for human consumption, agricultural, technical, commercial, or household purposes, must meet specific standards that are closely related to both water quality and delivery. Growing industrialization, poor water quality, purposeful or inadvertent intrusion of hazardous components and/or contaminants, and unequal allocation of freshwater resources are all factors that limit water availability (Leal Filho et al., 2022). Although treated wastewater might well be contaminated with bacteria and trace amounts of hazardous compounds, especially those integrated by manmade activities via direct point contamination or indirect routes such as effluent discharge and surface drainage, it is challenging. Moreover, freshwater rivers and streams for potable water processing plants can be located inside the waterway network that serves as a wastewater treatment plant discharge location simultaneously.

Anthropogenic activities have resulted in widespread pollution of the native surroundings associated with rapid socioeconomic growth. Caused by human activities, organic pollutants have now diffused across the environment and could be particularly resistant to breakdown operations in microbial populations (Akhtar et al., 2021). Several persistent organic pollutants (POPs) are no longer manufactured or used in many countries across the world due to their detrimental effects on wildlife and humans.

There has been a significant amount of attention and extensive research on new organic contaminants across the world, and there is a rising need to control such compounds to fully understand the hazards that pose threats to human health and the environment (Yadav et al., 2021). The detection or characterization of organic pollutants might be used to indicate human activity in a certain environment. Although there is a priority on traditional pollutants, especially those that are tenacious, such as synthetic chemicals, agrochemicals, and disinfection by-products, emerging organic pollutants, such as medical products and basic commodities, hormone levels, illicit narcotics, degradation products, and algal microbes or other biochemically derived organisms, have started to acquire significant attention (Khan et al., 2022). Pesticides and other agrochemicals, for example, could imply commercial agriculture or hygienic facilities (Dhananjayan et al., 2020), while organometallic chemicals, polychlorinated biphenyls, and polycyclic

aromatic hydrocarbons could be markers of metropolitan pollution, or run-off from manufacturing plants (Singh et al., 2022). When such compounds enter the aquatic ecosystem, they may have negative effects on humans, animals, and aquatic species. Moreover, plenty of the synthetic organic pollutants disposed into waterways by individuals, industry, and wildlife are considered to be dangerous compounds, and many others may not degrade fast, but rather accumulate in the environment or food supply (Unuofin, 2020; Rathi et al., 2021).

Novelty statement This comprehensive review distinguishes itself by providing a focused exploration of the environmental impact of chiral pesticides, emphasizing the distinctive biological activities and distribution patterns of their stereoisomers. In a novel approach, the review integrates the urgent need for a comprehensive understanding of chiral organic pollutants (COPs) with the advancements in liquid chromatography for enantiomeric analysis, thereby offering a unique perspective on the identification and characterization of pesticide/drug enantiomers. By intertwining environmental risks, stereoselective analytical methods, and potential remediation strategies, this review contributes a nuanced and timely synthesis that advances our comprehension of the complexities surrounding chiral organic pollutants, promoting informed decision-making for safeguarding ecosystems and human health.

Stereochemical features of chiral pesticides

Chiral pesticides have been of great interest in the growth of environmental science and comprise chemicals like insecticides, fertilizers, medicines, fire repellents, and synthesized PCBs muscle, offering a wide range of physicochemical characteristics and uses (Hassaan & El Nemr, 2020). Agrochemicals are typically sold as a racemic mixture, even though their biocompatibility is primarily tied to a single stereoisomer (Musarurwa & Tavengwa, 2020). Approximately one-third of available pesticides exhibit chirality, with many being utilized as racemates despite the fact that optimal activity often resides in a specific enantiomer (Tudi et al., 2021). This practice may lead to adverse effects on non-target organisms, as evidenced by studies on environmental fate, field experiments, toxicology, and biodegradation related

to some widely used pesticides (Meng et al., 2022). Therefore, if stereoselective binding takes place, standard ecological risk estimates of chiral pesticides are inappropriate. Consequently, it is crucial to establish sensitive and trustworthy methodologies for quantifying chiral pesticides to comprehend their behavior, distribution, and fate as well as to properly estimate the risks they pose to humans and the environment. The presence and enantiomeric compositions of chiral pesticides in aqueous systems (like a river or industrial effluent and outflow wastewater), soils, cereals, plants, and fruits have received a lot of interest (Lucci et al., 2022).

Several pesticides with one or more asymmetric centers were commonly found in water resources, including surface water, groundwater, seawater, and numerous reservoirs, as a result of extensive use (Yao et al., 2015a). Nevertheless, a few examples of agrochemicals that are available as pure enantiomers include various pyrethroid insecticides, aryloxypropanoate herbicides, and triazole fungicides (Maia et al., 2017; Sharma et al., 2021). Around one-third of the pesticides on the marketplace are chiral, and the majority of them are sold as a racemic mixture even though the desired activities depend on one single enantiomer and the others can create toxic or adversative effects on non-targeting species. There has been little awareness paid to pesticide chirality, particularly in terms of toxicological effects and potential ecological risks (Ji et al.,

2023). The potential adverse effects due to the use of chiral pesticides are shown in Fig. 1.

The environmental hazards of pesticides have customarily been assessed mainly due to their specific structural features. Research findings started in the 1990s showed that microbes are inclined to deteriorate hexachlorocyclohexane enantiomers selectively (Hühnerfuss et al., 1995), and the variations in distribution patterns and promising bioaccumulation among enantiomers in the ecosystem could occur (Garrison, 2006). Six primary classifications of worldwide employed chiral pesticides were investigated since 2002. In a report utilizing LC50, one of the stereoisomers showed at least ten times more hepatotoxicity than their counter stereoisomers to freshwater resources invertebrates *C. dubia* and *D. magna*, in the case of some synthetic pyrethroid (SP) and organophosphates (OPs).

Classification of chiral pesticides

There are six main classes of chiral pesticides.

(i) Synthetic pyrethroids (SPs)

SPs are synthetic counterparts of natively occurring pyrethrins derived from dried blooms of *C. cineraria folium* (Matsuo, 2019). Typically, the pyrethroid possesses two or more chiral centers, with an acidic group, an alcoholic group, or both groups.

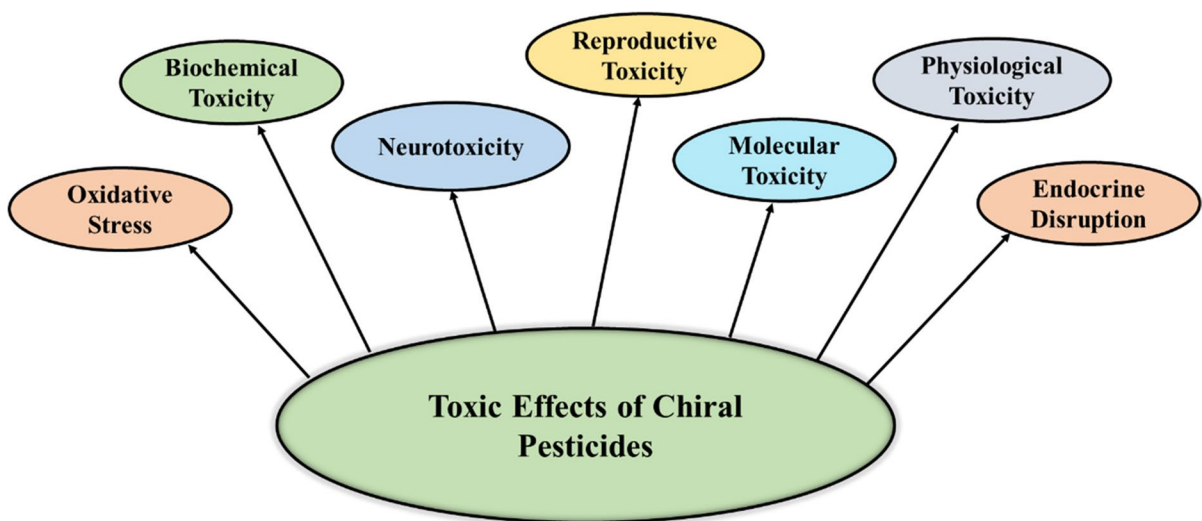


Fig. 1 Adverse effects of chiral pesticides

Consequently, the majority of pyrethroids occur as two or four enantiomer or diastereomer pairs, rendering them the pesticide class having a large number of asymmetric centers in their framework. At the beginning of the 1980s, SPs were established in numerous species of insects and are extensively utilized in farming and the household (Chen & Wang, 1996). Nonetheless, in the ecological investigation, the fate and/or cytotoxicity variations between the individual SP diastereomers have been rarely examined, mainly because of the lack of single-enantiomer standards (Kaziem et al., 2020) and the difficulty in detection and separation of the stereoisomers. The structural framework of various pesticides is presented in Fig. 2.

(ii) Organophosphates (OPs)

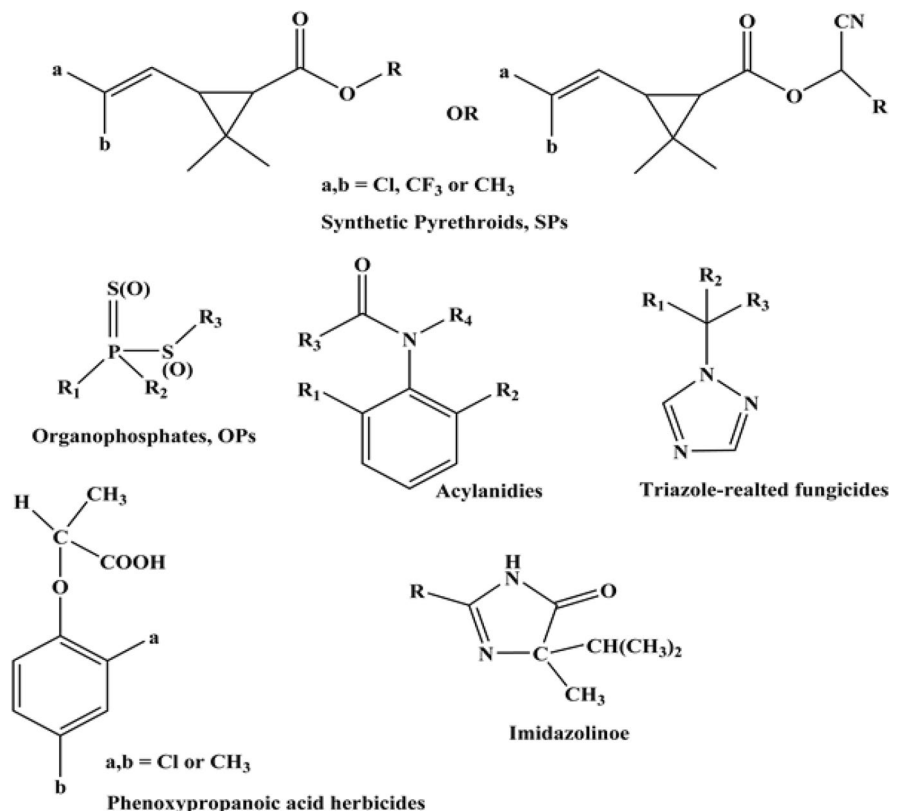
OPs are usually synthetic esters, phosphoric acid, phosphonothioate, phosphonothioic acid, amides, or thiol derivatives. Chiral OPs can be classified into three basic classifications: chiral compounds containing P, C, and C and P chiral centers (Mukherjee & Gupta, 2020). To date, most chiral OPs are available

as racemates in the marketplace. Though, pesticide activity is typically based on the superior activity of one stereoisomer, whereas the other may display toxicity on non-targeted species (Carrão et al., 2020). For instance, the severe aquatic toxicity to *C. dubia* and *D. magna* indicated that (–)-trichloronate (Fig. 3b) was 8–11-folds more noxious than its (+)-enantiomer, and (+)-methamidophos (Fig. 3c) was 7-folds more noxious than its (–)-counterpart (Kaziem et al., 2020). Furthermore, the stereoselective toxicities of numerous OPs and their separations were described (Badr, 2020). The (+) stereoisomer of O, O-dimethyl-1-(4-chlorophenoxyacetoxy) ethyl phosphonate was 8.08-fold higher noxious than its (–)-stereoisomer in serious toxic effects on *D. magna*. The structures of several important OPs are presented in Fig. 3.

(iii) Acylanilides

Acylanilide (Fig. 2) herbicides are broadly employed and are of particular interest to the fate of these synthetic organic molecules. Metolachlor (Fig. 3d) is a representative member of the

Fig. 2 Structures of different types of pesticides



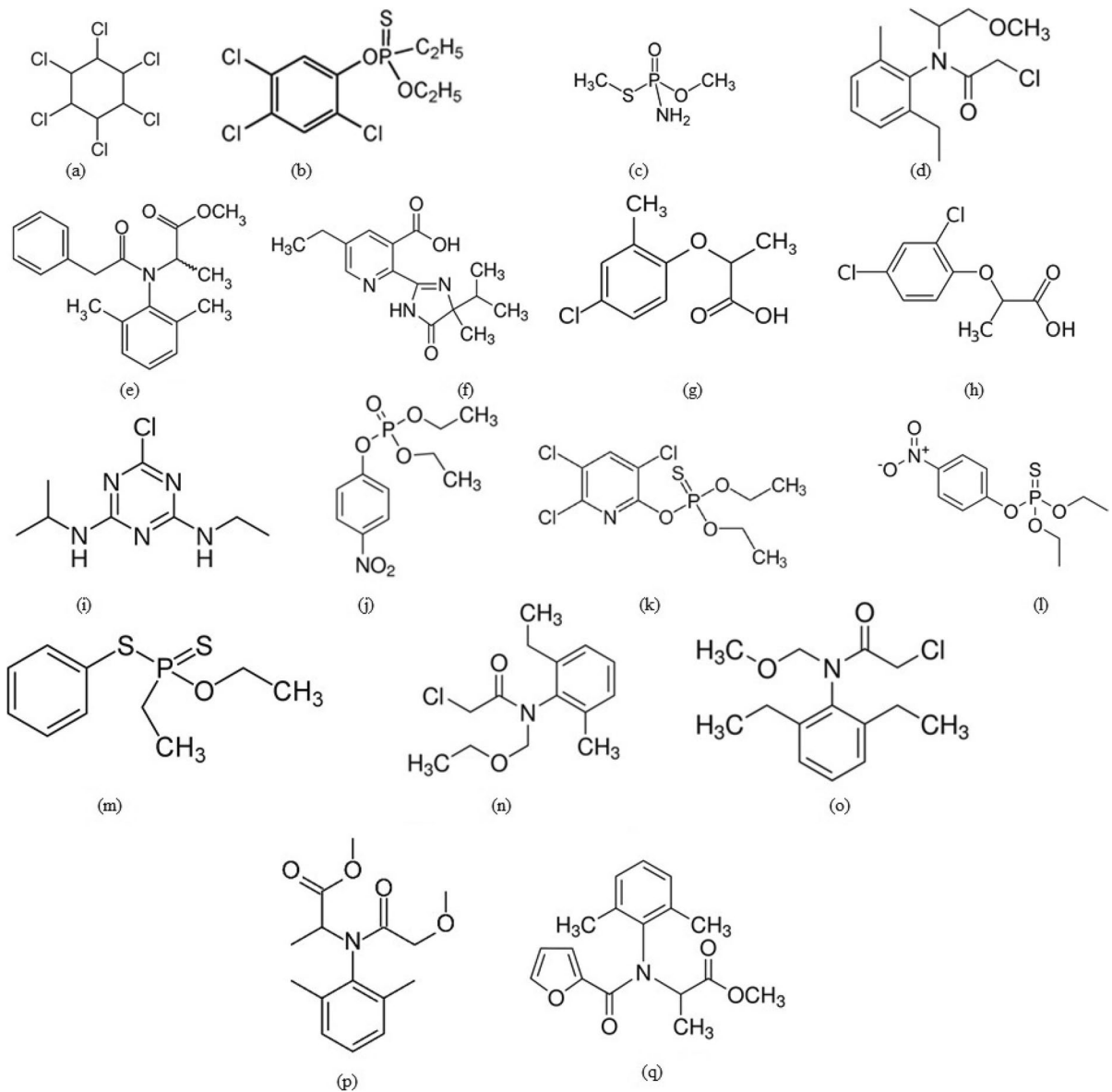


Fig. 3 Structures of chiral pesticides: (a) hexachlorocyclohexane, (b) trichloronate, (c) methamidophos, (d) metolachlor, (e) benalaxyl, (f) imazethapyr, (g) mecoprop, (h) dichlorprop,

(i) atrazine, (j) paraoxon, (k) chlorpyrifos, (l) parathion, (m) Fonofos, (n) acetachlor, (o) alachlor, (p) metalaxyl, and (q) furalaxyl

acylanilide class of pesticides. It possesses two chiral centers and is thus available in the form of four isomers. It is a popular and selective acylanilide herbicide for regulating widespread broad-leaved weeds in maize and other plants. The herbicidal potency of metolachlor lies principally in only two stereoisomers (aSS) and (aRS) (Moser et al., 1982).

Benalaxyl (BEN, Fig. 3e) is another significant member of acylanilide. Primarily, it was developed in 1981 and was employed for control of oomycetes, predominantly fungi of the class *Peronosporaceae*, *Phytophthora plasmopara*, and *Pythium spp.* BEN encompasses a pair of stereoisomers with a chiral center in the alkyl group.

(iv) Imidazolinones

Imidazolinones were introduced at the beginning of the 1980s by the American Cyanamid Company and were extensively used as herbicides for a variety of agro products. Imidazolinones contain a chiral center in their structural framework (Fig. 2). Investigations of stereoselectivity in herbicidal potency suggested that the (*R*)-imazethapyr (Fig. 3f) displayed ten times more inhibition to acetolactate synthase than the (*S*)-form (Huang, 2012).

(v) Phenoxypropanoic-acid herbicides

Phenoxypropanoic acid (PA) pesticides (Fig. 2) were developed as systemic and post-emergence pesticides between the 1940s and 1950s. Mecoprop (Fig. 3g) and dichlorprop (Fig. 3h) are typical chiral PA pesticides. They are used in farming, gardens, grasslands, and industrial enterprises to control wide-leaf weeds. Mecoprop and dichlorprop both have a chiral center. Their (*R*)-form is recognized to possess a higher herbicide potency compared to the (*S*)-form (Tsuda et al., 1985). The racemic combinations are still mainly employed, discharging significant quantities of stereoisomer sediment into the area with uncertain ecotoxicology for non-targeting vegetation.

(vi) Triazole-related fungicides

The triazole-based fungicides possess one or two chiral centers in their structures and were primarily established in the mid-1970s. Triazole-based pesticides are employed on fruit trees, smaller fruits, veggies, and grasses. The structure of this type of pesticide contains asymmetric centers of triazole fungicides at the adjacent position of the 1,2,4-triazole ring (Fig. 2).

Objective and focus of the review

This review highlights and analyzes the recent advances in environmental monitoring and environmental decontamination. The present state and origins of pesticide chemicals, possible health hazards, superiority, disadvantages, and prospects of existing advanced cleanup procedures are also discussed. We highlighted the research and the application of these environmental management practices monitoring and

chiral pesticide analysis, notably liquid chromatography. The stereoselective detection and assessment of chiral pesticides in ecological samples utilizing liquid chromatography are presented in this review.

Detection and remediation of chiral pesticides

Environmental monitoring of pesticides has been thoroughly studied recently (Huang et al., 2017; Lozowicka et al., 2016). Unfortunately, there has been a relatively limited study done on the stereoselective assessment of chiral pesticides in environmental matrixes. Previously, the majority of enantio-separation methods for the analysis of chiral pesticides were mostly based on liquid chromatography (Cheng et al., 2017; Gao et al., 2016). The variety of enantioselective separation technologies is quickly increasing due to the emergence of new chiral stationary phases and their capacity to work in multifunctional modes (normal, reverse, or polar organic modes) (Linhart et al., 2019). There are several approaches developed for detecting pesticides in sediment samples in both liquid and solid phases. Identification of chiral pesticides from aquatic specimens has also been done using a variety of approaches. It is indeed possible that this is due to their strong adsorption specificity for soil particles. As pollutants in the groundwater are so little, their analytical processes should incorporate both treatment and pre-concentration to achieve the projected detection sensitivity.

Pharmaceutical analysis in drug development is primarily concerned with techniques for identifying and quantifying potential drug candidates, determining purity, identifying by-products and degradation products in suitability and stability testing, and determining the fate of the active substance in the organism. Different chromatographic and capillary electrophoresis approaches are the most common analytical methods used to identify and quantify chiral pesticides. Vashistha's research group has been studying the chirality of pharmacologically significant chemicals since the discovery of enantioselective chromatographic techniques several years previously (Vashistha et al., 2022a; Vashistha, 2022b; Vashistha et al., 2022b; Gupta et al., 2022; Bhardwaj & Vashistha, 2022; Vashistha et al., 2017; Vashistha & Bhushan, 2019; Vashistha & Bhushan, 2020; Kumar Vashistha, 2022a, 2022b; Vashistha & Kumar, 2020; Kumar Vashistha, 2022). Enantiospecific synthesis, characterization, and testing are problematic with asymmetric substances. When

certain compounds are intentionally introduced into the environment, much more complicated challenges arise in terms of detecting, monitoring, and predicting their fate and hazards. In respect of expense, bio-remediation outperforms physical remediation procedures by achieving complete biological pollutant decomposition avoiding indiscriminately waste of locally available resources and indigenous fauna and flora. Nonetheless, in natural biological evolution, particularly spontaneous mutation, the bioremediation ability of native bacteria is commonly reduced in contaminated locations, particularly when multiple bioremediation characteristics are required, like co-contaminated regions with more than one organic substance.

Enantioselective degradation of chiral pesticides has been observed in soils, sediments, waterways, and plants (Buerge et al., 2016; Yao et al., 2015b), which could result in enantiomer concentration of more or less harmful stereoisomers. The method could be biologically (through microbes) or chemically driven (by chemical reaction). Various methods of bioremediation of pesticides are discussed below in sub-sections.

Acclimation

Monitoring for indigenous pathogens is thought to be an effective option because such varieties may be able to endure excessive wastewater conditions (Xiong et al., 2017). Various target strains necessitate distinct functioning processes; nevertheless, such processes can be broadly categorized. During this methodology, the deformation is enriched in the existence of variable concentrations of precursors based on the objectives. A combination of genetic manipulation and non-genetic recruitment can be used to cultivate facultative cultivars (Zhou et al., 2017).

When the environmental conditions are altered, organisms often undergo an acclimatization phase to maintain balance in internal systems, which affects gene expression (Corcoran et al., 2019). According to one study, *S. intermedius* may be trained to tolerate lindane contamination in the range of 5 to 120 mg/L while still removing the substance with an efficiency of 99% (Borowitzka, 2018).

Bacterial immobilization

In the domain of phytoremediation, immobilization relates to a technique for putting free microorganisms

in a specified geographical area by chemical or physical methods to maintain them functional and reusable (Patel et al., 2018). Because of the aforementioned key characteristics, the immobilization technique may be a viable substitute for traditional remediation techniques: (i) highly maintained cell catalytic performance and cell density, (ii) easy separation and robust reusability, and (iii) enhanced preservation attributable to safeguard from harsh conditions (Mohamad et al., 2015; Derakhshan Nejad et al., 2018). There have been reports of using immobilized algae to remove pollutants.

The various kinds of regularly utilized immobilization techniques include surface adsorption, covalent bonding, cross-linking, and embedding (Sun et al., 2017; Vasilieva et al., 2018). Because of its simplicity of use and non-toxicity, surface adsorption is the most used technique among these. The key to the immobilization technique is the choice of carrier, which can include plant fibers, sugarcane bagasse, sawdust, corncobs, and expanded perlite (Dzionic et al., 2016). Diatomaceous earth, alginate, ion exchange resin, chitosan, and cellulose are examples of popular immobilization carriers. Both organic and inorganic materials may be exploited as immobilization carriers (Górecka & Jastrzębska, 2019).

Nonetheless, the acquisition of bioremediation competence by native bacteria in polluted environments via natural biological development, such as random mutagenesis, commonly happens at an irrationally sluggish rate, particularly when numerous bio-degradation properties are taken into consideration necessary, as in the particular instance of locations co-contaminated with numerous organic substances. Biodegradation refers to the process by which organic contaminants are broken away via bacteria. In contrast to physical and chemical approaches, phytoremediation does have the benefit of becoming less expensive, and the total breakdown of COPs may be accomplished without causing any harm to the natural surroundings. Strategies for microbial decontamination must be designed in a consistent manner, which involves the following steps:

- (i) the development of unified microbes in which desirable enzymes or phytoremediation methods from diverse species are integrated for specific cell responses; or
- (ii) the development of enzymatic reactions with desirable distinctive features through location-specific mutagenesis (protein level).

Because enzymes comprise folded structures, even little changes in amino acid sequencing can modify their enzymatic performance, and the extent of the effect on other biological characteristics is practically hard to anticipate. Biomedical engineering (BME) might be used advantageously in bioremediation procedures to boost the capability of enzymes or bacteria. To meet the demand for microbes and enzymes for the bio-degradation of POPs, two major BME techniques involving genetically engineered pathogens and performance-enhancing have been established. Nonetheless, BME has several downsides, such as the difficulty of creating enzymes with unique functionalities. Furthermore, before this research, the whole structural, mechanical, and dynamic properties of the enzyme are required, and X-ray crystallographic and bioinformatics are the methodologies of choice for such examinations.

The phytoremediation of chiral pesticides is a fast-expanding area of interest. The primary goal of the study is to alter enzymes that can react to the intended outcome. As a result, using BME for the phytoremediation of novel pollutants could be difficult. Researchers estimate that breakthroughs in the knowledge of enzyme structure, activity, folding, routes, and dynamics would enable the functionalization of these enzymes (Derakhshan et al., 2019). The applications of these BME approaches for enhancing microorganisms' capacity to bioremediate insecticides and prescription medicines in the surroundings are explored here.

Chiral pesticides enter the soil habitat by a variety of routes, including transformation or decomposition, sorption-desorption, evaporation, absorption by floras, overflow to surface waters, and transit to subterranean water. Transformation or decomposition is a distinct and important technique that governs the ecological availability and movement of chiral pesticides, comprising a variety of actions such as abiotic and biotic degradation (Fig. 4). Chiral pesticides can be metabolized to byproducts or completely mineralized into individual elements during these operations.

Giri and co-workers highlighted various bioremediation technologies for pesticide degradation. The review was focused on the impact of various environmental factors on the biodegradation of pesticides (Shekher Giri et al., 2020). These factors include pesticide structure, concentration, pH, temperature,

and moisture of soils. The review also discusses the bioremediation methods for the degradation of organophosphate, organochlorine, carbamates, and pyrethroid pesticides in soil and aquatic systems. A comparison in terms of the benefits and disadvantages of current bioremediation techniques and conventional physicochemical methods for the bioremediation of pesticides has been analyzed.

Atrazine (ATZ, Fig. 3i) herbicide featured a family of *s*-triazine herbicides that was developed in the 1950s. *Pseudomonas* sp. *ADP*, among several studies of microorganisms, has been found accountable for atrazine metabolic routes (de Souza et al., 1995; Sadowsky et al., 1998). During the biological degradation of atrazine with *Pseudomonas* sp. *ADP*, ATZ is degraded to cyanuric acid utilizing the ATZ A, B, and C enzymes, which are consequently mineralized to CO₂ and NH₃ by enzymes that frequently originated in earthy microorganisms.

OPs are substantially lethal neurotoxins utilized in pesticides and warfare chemicals. Pesticides like paraoxon, chlorpyrifos, and parathion (Fig. 3j-l) are listed in the OP family. According to a recent study, toxic effects and the biodegradation of the enantiomers of chiral pesticides show different enantioselectivity. For instance, the (-)-fonofos (Fig. 3m), an OP insecticide, was fifteen times more noxious to *C. dubia* and *C. magna* than (+)-fonofos. The rate of biodegradation of the fonofos stereoisomers has not been described. The (+)-enantiomer of *cis*-bifenthrin was ~20-fold more lethal than the (-) form to both *C. magna* and *C. dubia* and was also more insistent since the (-)-form was predominantly decayed by microorganisms (Liu et al., 2005).

Studies revealed that selective degradation by microbes resulted in the enhancement of one enantiomer against another enantiomer. Such alterations in the stereoisomeric content can be generated by physiologically mediated chiral inversion. Determination of stereo-configuration of trace COPs is a challenge, and therefore, a methodical strategy is required for reducing risk evaluation uncertainty that includes incidence, fate, and transportation in diverse environment variables of these contaminants (Sanganyado et al., 2017). For quantification of enantiomers, GC-MS was the process of selection, followed by the use of LC-MS using CSP (Bose et al., 2021) and using a modified β -CD column and methyl-derivatized β -CD columns (Abad-Gil & Marina,

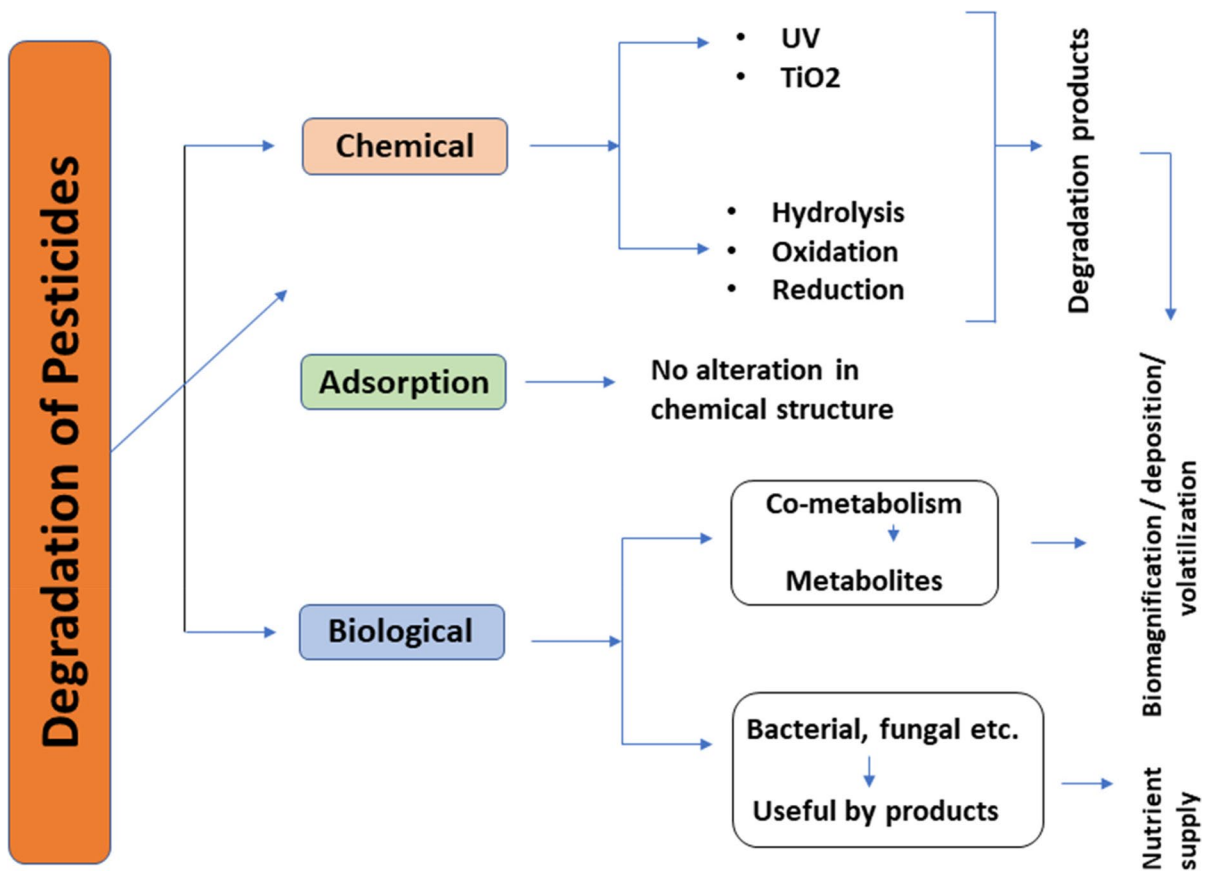


Fig. 4 Different degradation processes for pesticides

2023). Decomposition of chloroacetanilide herbicides metolachlor (MET), acetochlor, and alachlor (Fig. 3n-o) and related microbial cultures was assessed in vertical up-flow wetland columns employing a blend of hydro-chemical and DNA-based methods. The mass decomposition of chloroacetanilides, which were consistently procured at 1.8–1.9 M for 112 days, appeared primarily in the rhizobial region under nitrate and sulfate-reducing environments and averaged nearly $61 \pm 14\%$, $52 \pm 12\%$, and $29 \pm 19\%$ for acetochlor, alachlor, and rac-metolachlor, respectively.

MET enantiomeric fraction of 0.494 ± 0.009 in the oxic region and 0.480 ± 0.005 in the rhizobial region demonstrated that the (S)-MET was preferentially biodegraded. Chloroacetanilide ethane sulfonic acid and oxanilic acid were only observed in small quantities (0.5 nM), implying comprehensive deterioration and the procedure of previously unidentified chloroacetanilide decay routes. Hydrochemical

factors and levels of oxygen were important predictors of microbial populations, while chloroacetanilide sensitivity had no discernible effect. Collectively, the outcomes emphasize the significance of chloroacetanilide anaerobic decay in wetlands and underline the possibility of supplementary chemical and biological methods for the characterization of processes involved in the environmental evaporation of chloroacetanilide (Elsayed et al., 2015).

Stereoselectivity in ecological toxicity and bioremediation of enantiomeric pesticide benalaxyl (BEN) (Fig. 3e) to aquaculture algae *S. obliquus* has been investigated. The h-EC(50) values were 2.893 mg L⁻¹, 3.867 mg L⁻¹, and 8441 mg L⁻¹, respectively, for racemic (R)-(-) and (S)-(+)-BEN. Consequently, BEN stereoisomers were stereoselective in their severe toxic effects. Furthermore, various health risks have been ascertained using dyes like chlorophyll a and chlorophyll b, antioxidant enzyme activity, and

superoxide dismutase (SOD). Chlorophyll a was instigated by (*S*)-(+)-BEN and hindered by (*R*)-(-)-form at a level of 1 mg L^{-1} . Chlorophyll b was both instigated at 1 mg L^{-1} , but (*S*)-(+)-enantiomer was four times greater than (*R*)-(-)-enantiomer. (*S*)-(+)-BEN hindered more catalase action at 3 mg L^{-1} and 5 mg L^{-1} , instigated less SOD action and malondialdehyde (MDA) composition at 5 mg L^{-1} than (*R*)-(-)-BEN. Evaluation of data observed on stereoselectivity during anti-oxidative stress when *S. obliquus* responds to BEN. In the bioremediation investigation, the half-lives of (*S*)-(+)-BEN and (*R*)-(-)-BEN were 4.07 days and 5.04 days, respectively, resulting in comparative enhancement of (*R*)-(-)-enantiomer. These findings exhibited that adverse impacts and bioremediation of BEN in *S. obliquus* were stereoselective, and that kind of distinctions in the pesticide danger should be properly considered (Huang et al., 2012).

An HPLC technique with a chiral column to resolve the enantiomers of metalaxyl (MTX) (Fig. 3p) and furalaxyl (FUR) (Fig. 3q), and successive detection by triple quadrupole MS, was used. A *Brevibacillus breves* strain demonstrated a stereoselective trend of deterioration in the culture broth and ideally the corresponding (*R*)-(-)-forms. Furthermore, crops augmented with both insecticides at the same composition (*R*)-(-)-FUR deteriorated quicker. The determination of enantiomers of FUR and MTX were obtained using isocratic elution and mobile phase containing $\text{CH}_3\text{CN} + 0.1\% \text{ CH}_3\text{COOH} + 0.1\% \text{ HCOOH}$ and $10 \text{ mM CH}_3\text{COONH}_4$, 2-propanol (59:40:1, v/v/v) at a flow rate of 0.8 mL min^{-1} . The chiral column functioned in a column oven at $26 \text{ }^\circ\text{C}$. The recovery for all analytes ($n=6$) in liquid media was 97.5%. Quantitative estimation of enantiomers was carried out by employing the peak areas ratio of the test analytes and ^{13}C -MTX as internal standard. It was needed as LC-MS quantification matrices could lead to an increase in the signal or signal deletion. All calibration graphs from LOQ to 5 mg L^{-1} levels were linear ($R^2 > 0.99$) (Sulimma et al., 2013). Table 1 provides an overview of chiral pesticide detection and phytoremediation.

Bauer and colleagues worked on developing an effective approach for identifying pesticide metabolites (Bauer et al., 2018). In a prototype strategy, the bioactive components thiacloprid (pesticidal neonicotinoid), azoxystrobin (a fungicidal

strobilurinemethoxyacrylate), and difenoconazole were applied to two Brassica species, pakchoi (*B. Rapa ssp. Chinensis*) and broccoli (*B. oleracea var. Italica*), which differ in morphological features (a triazole fungicide). Pesticide dispersion in various plant tissues and also their disintegration and bioremediation rates were investigated. In research using the Brassica plants *pakchoi* and *broccoli*, the HR-MS approach permitted the identification of pesticide metabolites. Following the kinetic investigation, the metabolite screening technique showed separate metabolite synthesis and disintegration routes of the pesticides in addition to the deterioration of the parental chemicals. During the experimentation, thiacloprid and azoxystrobin were converted to a wide range of metabolites. Furthermore, virtually all of the pesticides produced a wide range of phase I and II metabolites that may be identified using HR-MS approaches. The findings acquired from this investigation of the kind and quantity of toxic metabolites in the three pesticides give useful and fresh insights into the existence and dispersion of their leftovers and associated substances in *pakchoi* and *broccoli* from pre-harvest periods to harvest which is especially essential since it allows for an assessment of the possible danger connected with the intake of agricultural goods.

The test procedure reported in this work offers a suspected assessment methodology for assessing the true influence of pesticides sprayed on plant and food specimens. These metabolites are typically not discovered in the routine analysis since the focused techniques used contain only designated lawfully pesticide metabolites in addition to active chemicals. The metabolite suspicious screening method may provide a powerful tool for revealing unauthorized pesticide utilization, particularly in organic produce, because favorable pesticide metabolite findings could be utilized as observational proof for the usage of agrochemicals even though the active ingredient is no longer observable. Additionally, using standard reference chemicals, the suspicious screening technique will allow the deployment of a focused strategy for formerly tested constituents.

Zhang and colleagues studied the distribution features of stereoisomers in sedimentary rocks accumulated from an agricultural area river system near the mid and bottom stretches of the Yangtze River, which were evaluated at the catchment scale, and their

Table 1 Summary of chiral pesticides and the chiral analytical techniques used to quantify enantiomers in biodegradation studies

Chiral pesticide	Analytical method	Matrix	Quantitative results	Ref
Benalaxyl	HPLC-UV	Freshwater algae cultures	<ul style="list-style-type: none"> h-EC(50) values: 2.893 mg L⁻¹, 3.867 mg L⁻¹, and 8441 mg L⁻¹, respectively, for (RS)-BEN, (R)-(-), and (S)-(+)-BEN Half-lives of (S)-(+)-BEN and (R)-(-)-BEN was 4.07 days and 5.04 days 	Huang et al. (2012)
(RS)-metolachlor, acetochlor, and alachlor	hydro-chemical	Flow wetland columns	<ul style="list-style-type: none"> Mass decomposition of chloroacetanilides = 1.8–1.9 M for 112 days The rhizobial region under nitrate and sulfate-reducing environments and averaging nearly 61 ± 14%, 52 ± 12%, and 29 ± 19% for acetochlor, alachlor, and rac-metolachlor 	Elsayed et al. (2015)
Furalaxyl, metalaxyl	HPLC	Microbial liquid cultures	<ul style="list-style-type: none"> Recovery: 97.5% LOQ: 5 mg L⁻¹ 	Sulimma et al. (2013)
Cloquintocet-mexyl	HPLC-MS/MS	Plant tissues	<ul style="list-style-type: none"> LOD: 0.06–0.15 g kg⁻¹ LOQ: 0.2–0.5 g kg⁻¹ Mean recovery: 84.1–111.5% RSD: 1.2–9.8% 	Li et al. (2022)
Mefentrifluconazole	HPLC	Water samples	<ul style="list-style-type: none"> Linearity: 0.01 to 1 g mL⁻¹ LOQ: 0.01 g mL⁻¹ 	Jiang et al. (2022)
Prothioconazole-desthio	HPLC	Water samples	<ul style="list-style-type: none"> Linear range: 27.1 to 1000 g L⁻¹ LOD: 8.1–11.2 g L⁻¹ LOQ: 27.1–37.3 g L⁻¹ 	Jing et al. (2021)
Penthiopyrad	LC-MS	Water samples	<ul style="list-style-type: none"> LOD 0.003 g mL⁻¹ LOQ: 0.01 g mL⁻¹ 	Yang et al. (2021)
Myclobutanil, epoxiconazole, tebuconazole	HPLC-DAD	Water samples	<ul style="list-style-type: none"> LOD 0.0051–0.0090 g mL⁻¹ LOQ: 0.0169–0.0299 g mL⁻¹ RSD: 0.6 to 7.8% 	Jing et al. (2019)
Diniconazole, metalaxyl, paclobutrazol, epoxiconazole, myclobutanil, hexaconazole, napropamide Isocarbofos	LC-MS	River sediments	<ul style="list-style-type: none"> Linearity range: 2–500 ng g⁻¹ (epoxiconazole, paclobutrazol, and metalaxyl); 4–500 ng g⁻¹ (isocarbofos, hexaconazole, myclobutanil, diniconazole, and napropamide) Recovery: 87.0 to 104.1% RSD: < 10.1% LOD: 0.22 to 1.54 ng g⁻¹ LOQ: 0.91 to 4.00 ng g⁻¹ 	Zhao et al. (2018a)
Metalaxyl, epoxiconazole, myclobutanil, hexaconazole, napropamide, isocarbofos	LC MS	River water	<ul style="list-style-type: none"> Recovery: 83.0 to 103.2% RSD: < 11.5% LOD: 0.11 to 0.48 ng L⁻¹ LOQ: 0.46 to 1.49 ng L⁻¹ 	Zhao et al. (2018b)

Table 1 (continued)

Chiral pesticide	Analytical method	Matrix	Quantitative results	Ref
Triadimenol, hexaconazole, metalaxyl, napropamide, isocarboxiphos, epoxiconazole, paclobutrazol, dimiconazole, triazolone, fenamiphos, imazalil, fenbuconazole, profenofos, fipronil, tebuconazole, dimotefuran, propiconazole, difenoconazole	LC-MS/MS	River water, influent and effluent wastewater	<ul style="list-style-type: none"> • Recovery: 81.1 to 106.3% • Intra-day RSD: 2.1–11.9% • Inter-day RSD of 2.6–12.7%; • Correlation coefficients (r^2) > 0.9912 • LOQ: 2.04 ng L⁻¹ in liquid matrices and below 0.50 ng g⁻¹ in solid matrices 	Zhao et al. (2018c)

prospective correlation coefficients with the physico-chemical characteristics and associated microorganisms of the deposits were also investigated (Zhang et al., 2022). Sediment contamination was severe at some locations, with the cause of pollution probably being agricultural or industrial effluent. Furthermore, there were increased accumulated pesticide deposit concentrations at different locations. Cycloxyprid, dinotefuran, and diclofop-methyl were the most often discovered chiral pesticides in the research region. Furthermore, ethiprole and difenoconazole demonstrated high enantioselectivity in the research region. Stereoisomers of several chiral pesticides, including tebuconazole, have significantly varied distributions at various locations. Pearson correlation study revealed that soil catalase and microbial biomass carbon were major determinants in chiral pesticide enantioselectivity. By altering the organisms in the sediment, the influence of sediment physicochemical features on stereoselective dispersion was obtained. Interestingly, tebuconazole's stereoselective dispersion was shown to be strongly connected to the species *Arenimonas*. Most chiral pesticides' stereoselective dispersion was shown to be significantly associated with the prokaryotic bacterial communities. This work offers factual validation for agricultural non-point source contamination produced by chiral pesticides, as well as a scientific basis for investigating the elements that influence the destiny of chiral pesticide residues.

Li et al. used high-performance liquid chromatography-tandem mass spectrometry to conduct enantioselective isolation, analysis, and dissipation of the chiral insecticide cloquintocet-mexyl (CQM) (Li et al., 2022). Using a customized QuEChERS technique coupled with HPLC-MS/MS, an effective and novel enantioseparation method has been successfully developed and evaluated to measure the stereoisomers of CQM in soil, millet, enoki mushroom, oil-seed rape, and watermelon. In all five matrices, our approach consistently determined both CQM enantiomers. The detection and quantitation limits were in the range of 0.06–0.15 g kg⁻¹ and 0.2–0.5 g kg⁻¹, respectively. Using correlation coefficients of 0.9954, good linearities were found. At three spiking levels, the mean recoveries ranged from 84.1 to 111.5 percent, with RSD values varying from 1.2 to 9.8 percent. Furthermore, CQM stereoselective dissipation in soil revealed that (*R*)-cloquintocet-mexyl

was significantly decomposed. It is the first study to explain a chiral analytical approach and the stereoselective behavior of CQM, as well as to give fundamental data for CQM risk assessment in food and ecological sustainability.

For the examination of fipronil (a popular insecticidal nerve agent) and the associated transformation products, an HPLC–MS approach based on an amylose tris(3-chloro-5-methyl phenyl carbamate) column was designed (Paolini et al., 2022). The improved approach was able to separate several fiproles simultaneously and completely in a single run, along with the chiral differentiation of fipronil stereoisomers, fipronil metabolites, and photo products. The effectiveness of this procedure was proven by its use in assessing a sequence of fipronil samples subjected to sunshine. In conclusion, the research presented experimental methods and an effective tool for tracking the environmental fate of fipronil as well as its metabolites for its use in agricultural or other fields.

Dong and colleagues used HPLC–MS to determine phenthoate stereoisomers in plant-origin matrices. Phenthoate is a chiral organophosphate pesticide with two enantiomers that differ in toxicity, behavior, and insecticidal activity, and its acute toxicity on human health due to acetylcholinesterase inhibition emphasizes the importance of enantioselective detection of enantiomers (Dong et al., 2022). Therefore, this work attempted to design a simple, quick technique for the separation and identification of phenthoate stereoisomers in fruits, vegetables, and cereals. For the first time, the mixtures were separated using RP-HPLC–MS.

For the target identification of the chiral fungicide mefentrifluconazole (MEF), Jiang and co-workers introduced a liquid–liquid microextraction coupled with the HPLC method (Jiang et al., 2022). The method involves the use of 4-methoxyphenyl and 3-amino-1-propanol as green extraction solvents. A hydrophobic extraction solvent was then produced in situ by adjusting the pH to increase the efficiency of the extraction process. The method was shown to be linear in the range of 0.01 to 1 g mL⁻¹ with an LOQ value of 0.01 g mL⁻¹. The method is fast, simple, and environmentally friendly. Moreover, it was successfully used to enantioselectively determine the concentrations of MEF residues in water, fruit juice, and fermented liquor samples.

Jing and co-workers developed a straightforward, quick, and eco-friendly popping candy-assisted dispersive liquid–liquid microextraction method for the analysis of isomers of prothioconazole and its chiral metabolite prothioconazole-desthio in water, beer, baijiu, and vinegar samples, which could be determined concurrently using HPLC (Jing et al., 2021). To prevent the use of hazardous organic solvents, popping candy and a green medium-chain fatty acid (decanoic acid) were utilized as the extractant and solid dispersant, respectively. After extraction, decanoic acid was accumulated by crystallization at room temperature. This method had a linear range of 27.1 to 1000 g L⁻¹. The ranges for LOD and LOQ, respectively, were 8.1–11.2 g L⁻¹ and 27.1–37.3 g L⁻¹. The RSD value ranged from 1.1 to 7.1 percent, and the extraction recovery ranged from 80.8 to 102.5 percent.

Yang and co-workers introduced an LC–MS method for the stereoselective analysis of penthiopyrad (PEN) photolysation and hydrolyzation in various aquatic environments (Yang et al., 2021). The illumination intensity of 400 W was observed to be most suitable for photolyzing penthiopyrad. PEN photolysation was also affected by additional variables like pH, salinity, and flavonoids. Due to their chemical structures and physicochemical properties, the rate of photolytic degradation of penthiopyrad enantiomers gets reduced in an acidic medium. PEN photolysation was also affected by salinities; acceleration was observed in solutions with salinities of 0.5 percent or 3.0 percent because photosensitive chloride radical anions were effective in catalyzing the reaction, and when the salinity was 1.0 percent or 2.0 percent, the inhibitory effect of inorganic salt reduced the photolysation rate. It was observed that the addition of different flavonoids also affects the photolysation of penthiopyrad by reducing the degradation via the photo-quenching process. One important takeaway from this study is that the *S*-(+)-penthiopyrad was photolyzed faster than its (*R*)-enantiomer, thus representing the stereoselective photolysation of penthiopyrad.

PEN deteriorated more quickly in the acidic medium than in the other two aqueous systems with different pH levels throughout the hydrolyzation phase, which contributed to the hydrogen ion-induced catalyzed process. The hydrolyzation rate

of penthiopyrad stereoisomers in sterile/nonsterile natural water matrices was also affected by pH, with tap water (pH 7.1) degrading faster than rainwater (pH 7.3) and then slower than lake water (pH 8.8). Because of their mutually reinforcing effects, enantiomerically pure stereoisomers hydrolyzed more sluggishly than equimolar stereoisomers. The degradation process did not affect the penthiopyrad enantiomers' configuration stability. In some aqueous systems, comparable stereoselectivities of penthiopyrad hydrolysis and preferable deterioration of the *S*-(+)-form were seen. The outcomes might offer several pieces of information that could be used to more precisely illustrate the stereoselective environmental fate and threat of penthiopyrad in aquatic habitats. *R*-(-)- and *S*-(+)-penthiopyrad showed a good linear relationship ($R^2 > 0.99$) in various matrices, and their corresponding LOD and LOQ were 0.003 g mL^{-1} and 0.01 g mL^{-1} .

Jing performed a simple, fast, and efficient method for the determination of three triazole fungicides (myclobutanil, epoxiconazole, and tebuconazole) in water samples using HPLC–DAD (Jing et al., 2019). The method involves the consecutive addition of the extraction solvent 1-dodecanol (low density), volatile solvent dichloromethane (high density), and CaO to the aqueous sample (the latter reacting exothermically). Due to the bubbles created by the CaO reaction, dichloromethane can be more easily volatilized, which in turn causes 1-dodecanol to dissipate as tiny droplets in the aqueous system. As such, the use of a dispersive solvent is not necessary. The suspended 1-dodecanol is then quickly separated from the specimen by its solidification in an ice bath. The linear relationship varies under optimum conditions, which are $0.05\text{--}5 \text{ g mL}^{-1}$, with correlation coefficients greater than 0.99. The LOD and LOQ are $0.0051\text{--}0.0090 \text{ g mL}^{-1}$ and $0.0169\text{--}0.0299 \text{ g mL}^{-1}$, respectively. Myclobutanil, epoxiconazole, and tebuconazole recoveries in tap, reservoir, and river water range between 77.6 and 104.4 percent, with RSD values ranging from 0.6 to 7.8 percent. As a result, the strategy seemed to be trustworthy for detecting myclobutanil, epoxiconazole, and tebuconazole in water specimens.

Zhao et al. established a sensitive and selective LC–MS/MS method for the stereoselective resolution and estimation of six chiral pesticides in aquatic samples at enantiomeric levels (Zhao et al., 2018a).

To accurately estimate the threat to the ecosystem and comprehend completely how each enantiomer behaves, the composition of the six pesticide stereoisomers in ambient aqueous matrices was determined using this approach. For this, a series of cellulose- and amylose-based chiral columns was assessed. Under successful experimental conditions, RSD values were less than 11.5%, and the recovery values for pesticide enantiomers ranged between 83.0% and 103.2% at two spiking levels. Most enantioselective techniques described in the research concentrate on parental pesticides and exclude pesticide metabolites or degradation products, which are frequently chiral. Multi-residue approaches for ecological assessment are expected to develop into more dynamic, so they may concurrently conduct non-target or qualitative screening and tailored quantitative results.

Furthermore, Zhao and co-workers performed a simultaneous analysis of eighteen chiral pesticides from aquatic habitats like river water, influent and effluent wastewater, and soil matrices using an LC/MS–MS method (Zhao et al., 2018b, 2018c). For this purpose, magnetic amino-modified multi-walled carbon nanotubes were prepared and used to adsorb pesticides from complex matrices. To aid in multivariate optimization, response surface methodology was employed. The chiral insecticides were simultaneously enantioresolved on a Chiralpak IG column. The method showed good linearity, with correlation coefficients (r^2) better than 0.9912. The quantitation limits of the approach were less than 2.04 ng L^{-1} in liquid matrices and less than 0.50 ng g^{-1} in solid matrices. The devised technique has several advantages, including ease of use, speed, and a large concentration level. As a result, it is appropriate for assessing the enantiomeric ratios of chiral pesticides in various environmental samples.

Conclusion and future directions

The accurate identification of the proportion of stereoisomers is crucial for assessing asymmetric drug biodegradation. There are several methods available for assessing stereoisomers in complex matrices. The identification and characterization of asymmetric medicines and pesticides in sewage water is a difficult and time-consuming task. Furthermore, ecological and sustainable evaluation approaches for COPs must

be studied, with the ecological effect of this study into consideration. It should be possible to identify novel pesticides and their transformative intermediates and products in the ecosystem at the same time, as well as evaluate enantiospecific cytotoxicity to aquatic waterways.

The significance of sewage processing plants in terms of water supply could be emphasized. The most often recognized drugs are systematically evaluated in light of the climate, demographic features, and other main influencing elements. As the chiral assessment is typically performed with high dangerous solvent volumes, more focus should be placed on the proposed characteristics that recommend the usage of mobile phases sustainably and environmentally. The collection of on-site samples and clearance of the derived phase utilizing a direct test procedure is also considered to be environmentally friendly. The application of rapid, low-cost, and eco-friendly methods is highly desired and should have the potential to alter the level of living in developing countries.

Anthropogenic activities, such as industrialization, commercialization, and medicinal production, have all significantly damaged the ecosystem. The clearance of organic molecules that are resistant to decomposing, including polycyclic aromatic hydrocarbons, polychlorinated biphenyl, and pesticides, is considerably more challenging. The effectiveness of the phytoremediation strategy depends on factors such as the types of toxins present, environmental conditions, and the organisms within the global ecosystem. Evaluating the characteristics, advantages, and disadvantages of microorganisms, as a key component, could play a crucial role in determining their competence in phytoremediation. As a consequence, bioremediation strategies might be used to efficiently boost the capability of enzymes or microorganisms in ecological treatment operations. Despite several benefits, phytoremediation of novel pollutants has not been characterized as biodegradable. Future research should prioritize the development of innovative and sustainable techniques for wastewater treatment, emphasizing the integration of eco-friendly approaches like phytoremediation to mitigate the impact of anthropogenic pollutants on global ecosystems.

Abbreviations POP: Persistent organic pollutant; PCB: Polychlorinated biphenyl; PAH: Polycyclic aromatic hydrocarbons; SP: Synthetic pyrethroid; OP:

Organophosphate; BEN: Benalaxyl; PA: Phenoxypropanoic acid; BME: Biomedical engineering; ATZ: Atrazine; COP: Chiral organic pollutant; GC-MS: Gas chromatography tandem mass spectrometry; LC-MS: Liquid chromatography tandem mass spectrometry; CSP: Chiral stationary phases; β -CD: β -Cyclodextrin; MET: Metolachlor; DNA: Deoxyribonucleic acid; BEN: Benalaxyl; PA: Phenoxypropanoic acid; SOD: Superoxide dismutase; MDA: Malondialdehyde; MTX: Metalaxyl; FUR: Furalaxyl; HR-MS: High-resolution mass spectrometry; CQM: Cloquintocet-mexyl; HPLC: High-performance liquid chromatography; RP: Reversed phase; MEF: Mefentrifluconazole; PEN: Penthopyrad; LOD: Limit of detection; LOQ: Limit of quantitation; RSD: Relative standard deviation

Acknowledgements The authors are grateful to the Department of Chemistry, GLA University, Mathura, India, for all kinds of support in this study.

Author contribution Vinod Kumar Vashistha: study conception and design, writing original draft, review and editing; Renu Bala, Ankit Mittal: data collection, writing and review; Sonika Sethi: analysis and interpretation of results; Suman Yadav, Rajasekhar VSR Pullabhotla, Dipak Kumar Das: draft manuscript preparation, revision and final editing. All authors reviewed the results and approved the final version of the manuscript.

Funding No funding received.

Data availability Data sharing is not applicable as no new data is generated.

Competing interests The authors declare no competing interests.

Declarations All authors have read, understood, and complied as applicable with the statement on the “Ethical responsibilities of Authors” as found in the “Instructions for Authors” and are aware that with minor exceptions, no changes can be made to authorship once the paper is submitted.

Conflict of interest The authors declare no competing interests.

References

- Abad-Gil, L., & Marina, M. L. (2023). Enantioselective analysis of pesticides in food, biological, and environmental samples by chromatographic techniques and capillary electrophoresis. *Journal of Chromatography Open*, 4, 100099.
- Akhtar, N., SyakirIshak, M. I., Bhawani, S. A., & Umar, K. (2021). Various natural and anthropogenic factors responsible for water quality degradation: A review. *Water*, 13(19), 2660.

- Badr, A. M. (2020). Organophosphate toxicity: Updates of malathion potential toxic effects in mammals and potential treatments. *Environmental Science and Pollution Research*, 27(21), 26036–26057.
- Bauer, A., Luetjohann, J., Hanschen, F. S., Schreiner, M., Kuballa, J., Jantzen, E., & Rohn, S. (2018). Identification and characterization of pesticide metabolites in Brassica species by liquid chromatography travelling wave ion mobility quadrupole time-of-flight mass spectrometry (UPLC-TWIMS-QTOF-MS). *Food Chemistry*, 244, 292–303. <https://doi.org/10.1016/j.foodchem.2017.09.131>
- Bhardwaj, S., & Vashista, V. K. (2022). β -Cyclodextrin-based chiral nanocomposite for thin-layer chromatographic detection of enantiomers of fluoxetine. *JPC - Journal of Planar Chromatography - Modern TLC*, 35(1), 83–88. <https://doi.org/10.1007/s00764-022-00161-9>
- Borowitzka, M. A. (2018). The ‘stress’ concept in microalgal biology—homeostasis, acclimation and adaptation. *Journal of Applied Phycology*, 30(5), 2815–2825. <https://doi.org/10.1007/s10811-018-1399-0>
- Buerge, I. J., Krauss, J., López-Cabeza, R., Siegfried, W., Stüssi, M., Wettstein, F. E., & Poiger, T. (2016). Stereoselective metabolism of the sterol biosynthesis inhibitor fungicides fenpropidin, fenpropimorph, and spiroxamine in grapes, sugar beets, and wheat. *Journal of Agricultural and Food Chemistry*, 64(26), 5301–5309. <https://doi.org/10.1021/acs.jafc.6b00919>
- Carrão, D. B., Perovani, I. S., de Albuquerque, N. C. P., & de Oliveira, A. R. M. (2020). Enantioseparation of pesticides: A critical review. *TrAC Trends in Analytical Chemistry*, 122, 115719.
- Chen, Z.-M., & Wang, Y.-H. (1996). Chromatographic methods for the determination of pyrethrin and pyrethroid pesticide residues in crops, foods and environmental samples. *Journal of Chromatography A*, 754(1–2), 367–395. [https://doi.org/10.1016/s0021-9673\(96\)00490-6](https://doi.org/10.1016/s0021-9673(96)00490-6)
- Cheng, Y., Zheng, Y., Dong, F., Li, J., Zhang, Y., Sun, S., et al. (2017). Stereoselective analysis and dissipation of propiconazole in wheat, grapes, and soil by supercritical fluid chromatography-tandem mass spectrometry. *Journal of Agricultural and Food Chemistry*, 65(1), 234–243. <https://doi.org/10.1021/acs.jafc.6b04623>
- Corcoran, A. A., Seger, M., Niu, R., Nirmalakhandan, N., Lammers, P. J., Holguin, F. O., & Boeing, W. J. (2019). Evidence for induced allelopathy in an isolate of *Coelastrella* following co-culture with *Chlorella sorokiniana*. *Algal Research*, 41(101535), 101535. <https://doi.org/10.1016/j.algal.2019.101535>
- de Souza, M. L., Wackett, L. P., Boundy-Mills, K. L., Mandelbaum, R. T., & Sadowsky, M. J. (1995). Cloning, characterization, and expression of a gene region from *Pseudomonas* sp. strain ADP involved in the dechlorination of atrazine. *Applied and environmental microbiology*, 61(9), 3373–3378. <https://doi.org/10.1128/aem.61.9.3373-3378.1995>
- Derakhshan Nejad, Z., Jung, M. C., & Kim, K.-H. (2018). Remediation of soils contaminated with heavy metals with an emphasis on immobilization technology. *Environmental Geochemistry and Health*, 40(3), 927–953. <https://doi.org/10.1007/s10653-017-9964-z>
- Derakhshan, Z., Ehrampoush, M. H., Mahvi, A. H., Dehghani, M., Faramarzi, M., & Eslami, H. (2019). A comparative study of hybrid membrane photobioreactor and membrane photobioreactor for simultaneous biological removal of atrazine and CNP from wastewater: A performance analysis and modeling. *Chemical Engineering Journal (Lausanne, Switzerland: 1996)*, 355, 428–438. <https://doi.org/10.1016/j.cej.2018.08.155>
- Dhananjayan, V., Jayakumar, S., & Ravichandran, B. (2020). Conventional methods of pesticide application in agricultural field and fate of the pesticides in the environment and human health. In *Controlled Release of Pesticides for Sustainable Agriculture*. Springer International Publishing, Cham, pp 1–39. https://doi.org/10.1007/978-3-030-23396-9_1
- Dong, C., Zhou, J., Zuo, W., Li, Z., Li, J., & Jiao, B. (2022). Enantioselective determination of phenthoate enantiomers in plant-origin matrices using reversed-phase high-performance liquid chromatography-tandem mass spectrometry. *Biomedical Chromatography: BMC*, 36(1), e5229. <https://doi.org/10.1002/bmc.5229>
- Dzionek, A., Wojcieszynska, D., & Guzik, U. (2016). Natural carriers in bioremediation: A review. *Electronic Journal of Biotechnology: EJB*, 23, 28–36. <https://doi.org/10.1016/j.ejbt.2016.07.003>
- Elsayed, O. F., Maillard, E., Vuilleumier, S., Millet, M., & Imfeld, G. (2015). Degradation of chloroacetanilide herbicides and bacterial community composition in lab-scale wetlands. *The Science of the Total Environment*, 520, 222–231. <https://doi.org/10.1016/j.scitotenv.2015.03.061>
- Gao, B., Zhang, Q., Tian, M., Zhang, Z., & Wang, M. (2016). Enantioselective determination of the chiral pesticide isofenphos-methyl in vegetables, fruits, and soil and its enantioselective degradation in pak choi using HPLC with UV detection. *Analytical and Bioanalytical Chemistry*, 408(24), 6719–6727. <https://doi.org/10.1007/s00216-016-9790-7>
- Garrison, A. W. (2006). Probing the enantioselectivity of chiral pesticides. *Environmental Science & Technology*, 40(1), 16–23. <https://doi.org/10.1021/es063022f>
- Górecka, E., & Jastrzębska, M. (2019). Immobilization techniques and biopolymer carriers. *Biotechnology and food science.*, 75(1), 65–86. <https://doi.org/10.34658/BFS.2011.75.1>
- Hassaan, M. A., & El Nemr, A. (2020). Pesticides pollution: Classifications, human health impact, extraction and treatment techniques. *The Egyptian Journal of Aquatic Research*, 46(3), 207–220.
- Huang, C., Zhu, H., Yu, Y., Ding, Q., Jia, F., Zhao, B., et al. (2017). Simultaneous determination of pyrametostrobin and its two metabolites in cucumber and soil using a quick, easy, cheap, effective, rugged, and safe method with HPLC-MS/MS. *Journal of Separation Science*, 40(11), 2335–2343. <https://doi.org/10.1002/jssc.201700109>
- Huang, L., Lu, D., Diao, J., & Zhou, Z. (2012). Enantioselective toxic effects and biodegradation of benalaxyl in *Scenedesmus obliquus*. *Chemosphere*, 87(1), 7–11. <https://doi.org/10.1016/j.chemosphere.2011.11.029>
- Hühnerfuss, H., Pfaffenberger, B., Gehrcke, B., Karbe, L., König, W. A., & Landgraff, O. (1995). Stereochemical effects of PCBs in the marine environment: Seasonal variation of coplanar and atropisomeric PCBs in blue mussels (*Mytilus edulis* L.) of the German bight. *Marine pollution bulletin*, 30(5), 332–340. [https://doi.org/10.1016/0025-326x\(94\)00183-a](https://doi.org/10.1016/0025-326x(94)00183-a)

- Ji, C., Song, Z., Tian, Z., Feng, Z., Fan, L., Shou, C., & Zhao, M. (2023). Enantioselectivity in the toxicological effects of chiral pesticides: A review. *Science of the Total Environment*, 857, 159656.
- Jiang, H., Huang, X., Xue, H., Wang, M., Qi, Y., Jia, L., & Jing, X. (2022). Switchable deep eutectic solvent-based homogeneous liquid-liquid microextraction combined with high-performance liquid chromatography-diode-array detection for the determination of the chiral fungicide mefenflucanazole in water, fruit juice, and fermented liquor. *Chirality*, 34(7), 968–976. <https://doi.org/10.1002/chir.23445>
- Jing, X., Huang, X., Wang, H., Xue, H., Wu, B., Wang, X., & Jia, L. (2021). Popping candy-assisted dispersive liquid-liquid microextraction for enantioselective determination of prothioconazole and its chiral metabolite in water, beer, Baijiu, and vinegar samples by HPLC. *Food Chemistry*, 348(129147), 129147. <https://doi.org/10.1016/j.foodchem.2021.129147>
- Jing, X., Yang, L., Zhao, W., Wang, F., Chen, Z., Ma, L., et al. (2019). Evaporation-assisted dispersive liquid-liquid microextraction based on the solidification of floating organic droplets for the determination of triazole fungicides in water samples by high-performance liquid chromatography. *Journal of Chromatography A*, 1597, 46–53. <https://doi.org/10.1016/j.chroma.2019.03.040>
- Kaziem, A. E., Gao, B., Li, L., Zhang, Z., He, Z., Wen, Y., & Wang, M.-H. (2020). Enantioselective bioactivity, toxicity, and degradation in different environmental mediums of chiral fungicide epoxiconazole. *Journal of Hazardous Materials*, 386(121951), 121951. <https://doi.org/10.1016/j.jhazmat.2019.121951>
- Khan, S., Naushad, M., Govarathanan, M., Iqbal, J., & Alfadul, S. M. (2022). Emerging contaminants of high concern for the environment: Current trends and future research. *Environmental Research*, 207, 112609.
- Kumar Vashistha, V. (2022). Chiral analysis of pharmaceuticals using NMR spectroscopy: A review. *Asian journal of organic chemistry*, 11(12). <https://doi.org/10.1002/ajoc.202200544>.
- Leal Filho, W., Azul, A. M., Brandli, L., Lange Salvia, A., & Wall, T. (Eds.). (2022). *Clean water and sanitation*. Springer International Publishing.
- Li, M., Di, X., & Jiang, Z. (2022). Enantioselective separation, analysis and stereoselective dissipation of the chiral pesticide cloquintocet-mexyl using a modified QuEChERS method by high-performance liquid chromatography tandem mass spectrometry. *Chemosphere*, 291(Pt 3), 133084. <https://doi.org/10.1016/j.chemosphere.2021.133084>
- Linhart, C., Niedrist, G. H., Nagler, M., NAGRANI, R., Temml, V., Bardelli, T., et al. (2019). Pesticide contamination and associated risk factors at public playgrounds near intensively managed apple and wine orchards. *Environmental sciences Europe*, 31(1). <https://doi.org/10.1186/s12302-019-0206-0>.
- Liu, W., Gan, J., Schlenk, D., & Jury, W. A. (2005). Enantioselectivity in environmental safety of current chiral insecticides. *Proceedings of the National Academy of Sciences of the United States of America*, 102(3), 701–706. <https://doi.org/10.1073/pnas.0408847102>
- Lozowicka, B., Ilyasova, G., Kaczynski, P., Jankowska, M., Rutkowska, E., Hrynko, I., et al. (2016). Multi-residue methods for the determination of over four hundred pesticides in solid and liquid high sucrose content matrices by tandem mass spectrometry coupled with gas and liquid chromatograph. *Talanta*, 151, 51–61. <https://doi.org/10.1016/j.talanta.2016.01.020>
- Lucci, E., Dal Bosco, C., Antonelli, L., Fanali, C., Fanali, S., Gentili, A., & Chankvetadze, B. (2022). Enantioselective high-performance liquid chromatographic separations to study occurrence and fate of chiral pesticides in soil, water, and agricultural products. *Journal of Chromatography A*, 1685, 463595.
- Maia, A. S., Ribeiro, A. R., Castro, P. M. L., & Tiritan, M. E. (2017). Chiral analysis of pesticides and drugs of environmental concern: Biodegradation and enantiomeric fraction. *Symmetry*, 9(9), 196. <https://doi.org/10.3390/sym9090196>
- Matsuo, N. (2019). Discovery and development of pyrethroid insecticides. *Proceedings of the Japan Academy, Series B*, 95(7), 378–400.
- Meng, Z., Cui, J., Li, R., Sun, W., Bao, X., Wang, J., Zhou, Z., Zhu, W., & Chen, X. (2022). Systematic evaluation of chiral pesticides at the enantiomeric level: A new strategy for the development of highly effective and less harmful pesticides. *Science of the Total Environment*, 846, 157294.
- Mohamad, N. R., Marzuki, N. H. C., Buang, N. A., Huyop, F., & Wahab, R. A. (2015). An overview of technologies for immobilization of enzymes and surface analysis techniques for immobilized enzymes. *Biotechnology, Biotechnological Equipment*, 29(2), 205–220. <https://doi.org/10.1080/13102818.2015.1008192>
- Mukherjee, S., & Gupta, R. D. (2020). Organophosphorus nerve agents: Types, toxicity, and treatments. *Journal of Toxicology*, 2020, 1–16.
- Musarurwa, H., & Tavengwa, N. T. (2020). Green aspects during synthesis, application and chromatographic analysis of chiral pesticides. *Trends in Environmental Analytical Chemistry*, 27, e00093.
- Paolini, L., Hausser, N., & Zhang, T. (2022). Chiral resolution of the insecticide fipronil enantiomers and the simultaneous determination of its major transformation products by high-performance liquid chromatography interfaced with mass spectrometry. *Chirality*, 34(3), 473–483. <https://doi.org/10.1002/chir.23412>
- Patel, J. G., Kumar, N. J. I., Kumar, R. N., & Khan, S. R. (2018). Evaluation of nitrogen fixing enzyme activities in response to pyrene bioremediation efficacy by defined artificial microalgal-bacterial consortium of Gujarat India. *Polycyclic Aromatic Compounds*, 38(3), 282–293. <https://doi.org/10.1080/10406638.2016.1207684>
- Rathi, B. S., Kumar, P. S., & Vo, D. V. N. (2021). Critical review on hazardous pollutants in water environment: Occurrence, monitoring, fate, removal technologies and risk assessment. *Science of the Total Environment*, 797, 149134.
- Sadowsky, M. J., Tong, Z., de Souza, M., & Wackett, L. P. (1998). AtzC is a new member of the amidohydrolase protein superfamily and is homologous to other atrazine-metabolizing enzymes. *Journal of Bacteriology*, 180(1), 152–158. <https://doi.org/10.1128/JB.180.1.152-158.1998>
- Sanganyado, E., Lu, Z., Fu, Q., Schlenk, D., & Gan, J. (2017). Chiral pharmaceuticals: A review on their environmental occurrence and fate processes. *Water Research*, 124, 527–542. <https://doi.org/10.1016/j.watres.2017.08.003>
- Sharma, S. K., Paniraj, A. S. R., & Tambe, Y. B. (2021). Developments in the catalytic asymmetric synthesis of

- agrochemicals and their synthetic importance. *Journal of Agricultural and Food Chemistry*, 69(49), 14761–14780. <https://doi.org/10.1021/acs.jafc.1c05553>
- ShekherGiri, B., Geed, S., Vikrant, K., Lee, S. S., Kim, K.-H., Kumar Kailasa, S., et al. (2020). Progress in bioremediation of pesticide residues in the environment. *Environmental Engineering Research*, 26(6), 200446–200440. <https://doi.org/10.4491/eer.2020.446>
- Singh, N., Poonia, T., Siwal, S. S., Srivastav, A. L., Sharma, H. K., & Mittal, S. K. (2022). Challenges of water contamination in urban areas. In *Current directions in water Scarcity research*. Elsevier, pp. 173–202. <https://doi.org/10.1016/B978-0-323-91838-1.00008-7>
- Sulimma, L., Bullach, A., Kusari, S., Lamshöft, M., Zühlke, S., & Spitteller, M. (2013). Enantioselective degradation of the chiral fungicides metalaxyl and furalaxyl by *Brevibacillus brevis*: Biodegradation of chiral fungicides. *Chirality*, 25(6), 336–340. <https://doi.org/10.1002/chir.22158>
- Sun, Y., Lei, C., Khan, E., Chen, S. S., Tsang, D. C. W., Ok, Y. S., et al. (2017). Nanoscale zero-valent iron for metal/metalloid removal from model hydraulic fracturing wastewater. *Chemosphere*, 176, 315–323. <https://doi.org/10.1016/j.chemosphere.2017.02.119>
- Tsuda, Y., Kawai, K., & Nakajima, S. (1985). Microbial reduction of 2-phenylpropionic acid, 2-benzyloxypropionic acid and 2-(2-furfuryl)propionic acid. *Chemical & Pharmaceutical Bulletin*, 33(11), 4657–4661. <https://doi.org/10.1248/cpb.33.4657>
- Tudi, M., Daniel Ruan, H., Wang, L., Lyu, J., Sadler, R., Connell, D., Chu, C., & Phung, D. T. (2021). Agriculture development, pesticide application and its impact on the environment. *International Journal of Environmental Research and Public Health*, 18(3), 1112.
- Unuofin, J. O. (2020). Garbage in garbage out: The contribution of our industrial advancement to wastewater degeneration. *Environmental Science and Pollution Research*, 27(18), 22319–22335.
- Vashistha, V. K. (2022a). Detection and remediation of chiral pharmaceuticals from wastewater: A review. *Chirality*, 34(6), 833–847. <https://doi.org/10.1002/chir.23437>
- Vashistha, V. K. (2022b). Enantioselective analysis of mexiletine using chromatographic techniques: A review. *Current Analytical Chemistry*, 18(4), 440–455. <https://doi.org/10.2174/1573411016999201008125143>
- Vashistha, V. K., & Bhushan, R. (2019). Sensitive enantioseparation and determination of isoprenaline in human plasma and pharmaceutical formulations. *Biomedical Chromatography: BMC*, 33(8), e4550. <https://doi.org/10.1002/bmc.4550>
- Vashistha, V. K., & Bhushan, R. (2020). Thin-layer chromatographic enantioseparation of atenolol and propranolol using (S)-naproxen as chiral selector: Direct and indirect approaches. *JPC - Journal of Planar Chromatography - Modern TLC*, 33(2), 101–107. <https://doi.org/10.1007/s00764-020-00017-0>
- Vashistha, V. K., & Kumar, A. (2020). Development of a thin-layer chromatographic method for the enantioresolution of sotalol using levofloxacin as chiral selector. *JPC - Journal of Planar Chromatography - Modern TLC*, 33(6), 663–667. <https://doi.org/10.1007/s00764-020-00068-3>
- Vashistha, V. K., Martens, J., & Bhushan, R. (2017). Sensitive RP-HPLC enantioseparation of (RS)-ketamine via chiral Derivatization Based on (S)-Levofloxacin. *Chromatographia*, 80(10), 1501–1508. <https://doi.org/10.1007/s10337-017-3367-2>
- Vashistha, V. K., Sethi, S., Tyagi, I., & Das, D. K. (2022a). Chirality of antidepressive drugs: An overview of stereoselectivity. *Asian Biomedicine: Research, Reviews and News*, 16(2), 55–69. <https://doi.org/10.2478/abm-2022-0008>
- Vashistha, V. K., Verma, N., Kumar, R., Tyagi, I., Gaur, A., & Bala, R. (2022b). Enantioseparation of linezolid and tedizolid using validated high-performance liquid chromatographic method. *Chirality*, 34(8), 1044–1052. <https://doi.org/10.1002/chir.23472>
- Vasilieva, S., Shibzukhova, K., Morozov, A., Solovchenko, A., Bessonov, I., Kopitsyna, M., et al. (2018). Immobilization of microalgae on the surface of new cross-linked polyethylenimine-based sorbents. *Journal of Biotechnology*, 281, 31–38. <https://doi.org/10.1016/j.jbiotec.2018.03.011>
- Xiong, J.-Q., Kurade, M. B., & Jeon, B.-H. (2017). Biodegradation of levofloxacin by an acclimated freshwater microalga, *Chlorella vulgaris*. *Chemical engineering journal (Lausanne, Switzerland: 1996)*, 313, 1251–1257. <https://doi.org/10.1016/j.cej.2016.11.017>
- Yadav, D., Rangabhashiyam, S., Verma, P., Singh, P., Devi, P., Kumar, P., Hussain, C. M., Gaurav, G. K., & Kumar, K. S. (2021). Environmental and health impacts of contaminants of emerging concerns: Recent treatment challenges and approaches. *Chemosphere*, 272, 129492.
- Yang, G., Liu, Z., Lan, T., Dou, L., & Zhang, K. (2021). Potential enantioselectivity of the hydrolysis and photolysis of the chiral agrochemical penthiopyrad in aquatic environments. *Environmental Science: Water Research & Technology*. <https://doi.org/10.1039/d1ew00098e>
- Yao, G., Jing, X., Peng, W., Liu, X., Zhou, Z., & Liu, D. (2015a). Chiral insecticide α -cypermethrin and its metabolites: Stereoselective degradation behavior in soils and the toxicity to earthworm *Eisenia fetida*. *Journal of Agricultural and Food Chemistry*, 63(35), 7714–7720. <https://doi.org/10.1021/acs.jafc.5b03148>
- Yao, Z., Lin, M., Xu, M., Wang, T., Ping, X., Wu, S., et al. (2015b). Simultaneous enantioselective determination of isocarboxiphos and its main metabolite isocarboxiphos oxon in rice, soil, and water by chiral liquid chromatography and tandem mass spectrometry: Liquid chromatography. *Journal of Separation Science*, 38(10), 1663–1672. <https://doi.org/10.1002/jssc.201500155>
- Zhang, W., Li, T., Tang, J., Liu, X., Liu, Y., & Zhong, X. (2022). The profiles of chiral pesticides in peri-urban areas near Yangtze River: Enantioselective distribution characteristics and correlations with surface sediments. *Journal of Environmental Sciences (China)*, 121, 199–210. <https://doi.org/10.1016/j.jes.2022.02.001>
- Zhao, P., Lei, S., Xing, M., Xiong, S., & Guo, X. (2018a). Simultaneous enantioselective determination of six pesticides in aqueous environmental samples by chiral liquid chromatography with tandem mass spectrometry. *Journal of Separation Science*, 41(6), 1287–1297. <https://doi.org/10.1002/jssc.201701259>
- Zhao, P., Wang, Z., Li, K., Guo, X., & Zhao, L. (2018b). Multi-residue enantiomeric analysis of 18 chiral pesticides in water, soil and river sediment using magnetic solid-phase extraction based on amino modified multiwalled carbon

- nanotubes and chiral liquid chromatography coupled with tandem mass spectrometry. *Journal of Chromatography A*, 1568, 8–21. <https://doi.org/10.1016/j.chroma.2018.07.022>
- Zhao, P., Zhao, J., Lei, S., Guo, X., & Zhao, L. (2018c). Simultaneous enantiomeric analysis of eight pesticides in soils and river sediments by chiral liquid chromatography-tandem mass spectrometry. *Chemosphere*, 204, 210–219. <https://doi.org/10.1016/j.chemosphere.2018.03.204>
- Zhou, W., Wang, J., Chen, P., Ji, C., Kang, Q., Lu, B., et al. (2017). Bio-mitigation of carbon dioxide using microalgal systems: Advances and perspectives. *Renewable and Sustainable Energy Reviews*, 76, 1163–1175. <https://doi.org/10.1016/j.rser.2017.03.065>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.