Review

Persistence of pesticides-based contaminants in the environment and their effective degradation using laccase-assisted biocatalytic systems

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ABSTRACT

Inevitable use of pesticides due to modern agricultural practices and the associated worldwide environmental pollution has called the special attention of the researchers to overcome the persistence, recalcitrance, and multi-faceted toxicity of pesticides-based emerging contaminants. Some restricted use pesticides (RUPs) are highly toxic and carcinogenic chemicals that can be easily accumulated into non-target organisms, including humans, aquatic invertebrates, algae, and microbes. With regard to physicochemical strategies, enzymes-mediated bioremediation is a compelling and meaningful strategy for biodegradation and biotransformation of pesticides into harmless chemical species. Oxidoreductases hydrolases and transferases are among the most representative classes of enzymes pursued and engineered for this purpose. Ligninolytic enzymes, particularly laccases, are of exceptional interest due to high efficiency, specificity, eco-sustainability, and wide-ranging substrates. However, the use of native enzymes is often hindered in industrial processes for the effective removal of refractory compounds by their high cost and susceptibility. Many of these drawbacks can be addressed by enzyme immobilization on some suitable support materials. Increase in stability, reusability, reduction of product inhibition, enhanced activity, specificity, and easier product separation are amid the desirable characteristics of immobilization to construct biocatalysts for continuous systems. This review summarizes recent and up-to-date literature on the use of enzymes, explicitly, free as well as immobilized laccases in the degradation of different pesticides. In the first part, source and occurrence of pesticides in the environment, their types, and associated detrimental effects on the ecosystem/human health are comprehensively described. Afterward, we highlighted the use of different enzymes with a particular emphasis on laccase for the degradation and detoxification of an array of pesticides. Finally, the review is closed with concluding remarks, and possible future direction is proposed in this very important research arena. In conclusion, it is envisioned that effective deployment of laccase-assisted biocatalytic systems for the degradation or removal of diverse pesticides and related contaminants will help to better understand the persistence and removal fate of these hazardous pollutants. Moreover, the current research thrust presented in this review will additionally evoke researcher to engineer robust and sustainable processes to remediate pesticides-contaminated environmental matrices effectively.

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1. Introduction

During the last century, pesticides and other agrochemicals have become an important component of modern global agricultural systems, leading to a substantial improvement in crop yields by controlling insects and disease (Carvalho, 2017; Ali et al., 2019). The exponential increase in the human population further stresses the necessity for augmenting food production. Nevertheless, the extensive applica-

tion of these pesticides possesses several negative influences ranging from ecological pollution to damage of biodiversity (Pico et al., 2018; Barbieri et al., 2019; Köck-Schulmeyer et al., 2019). Dispersion of agrochemical residues in the environment and agriculture land cause disastrous contamination of ecosystems (i.e., dust, soils, air, sediments, and water) and adulterating human foods, around the world (Aamir et al., 2018; Kumar et al., 2018; Li, 2018). Besides, pollution of aquatic systems by pesticide residues also compromised marine food resources, fisheries, and aquaculture. Recently, reports have confirmed the neurotoxic effect of pesticides (Pereira et al., 2015); therefore, widespread exposure to pesticides results in serious health hazards, even directly or indirectly lead to death (Simonelli et al., 2007).

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Fig. 1. The EPA categorized toxicity classes of pesticides. The outer boxes represent overall toxicity ratings along with their representative labels.

The US Environmental Protection Agency (EPA) regulates both active ingredients and pesticide formulations under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). The EPA regulations ensure that pesticide usage does not have unreasonable adverse effects on humans and the environment. Based on the legalization and registration process, the EPA has differentiated general use pesticides (GUPs) and restricted use pesticides (RUPs). This differentiation between GUPs and RUPs is primarily based on the toxicity class.

The EPA differentiated toxicity classes of pesticides are shown in Fig. 1. Given the well-documented toxicity and adverse effects of pesticides on different living being systems (Fig. 2), researchers have rekindled their interest in eliminating pesticides from the environment by a range of chemical, physical, and biological approaches (Maqbool et al., 2016; Mir-Tutusa et al., 2018). However, degradation of pesticides-based pollutants by these methods may not be favorable due to the high cost of treatment, inefficiency, and time-inadequacy (Zeng et al., 2017). The quest for newer, efficient, and environmentally responsive processes has increased importance to tackle the persistence of pesticides and to overcome the issues mentioned above. Many recent studies demonstrated that enzymatic catalysis as “green bioremediation” has drawn substantial attention as attractive alternative and environmentally friendly solution compared to physicochemical methods for the degradation and detoxification of pesticides from diverse environments including soil and aqueous media (Ahmed et al., 2017; Asgher et al., 2014; Bilal et al., 2017). Use of enzyme offers several advantages, including high degradation efficiencies against different pollutants, and stability against varying pH, temperature, and salinity conditions. Moreover, enzyme-mediated treatments are easy to control as no protection and/or de-protection steps involved and essentially have no adverse influence on the environment (Bilal et al., 2018a; Kupski et al., 2019).

Application of the ligninolytic enzymes, particularly laccases are of exceptional interest due to its wide-ranging substrates, and great capability for environmental applications (Jin et al., 2016; Bilal et al., 2017; Chauhan and Jha, 2018; Bilal et al., 2019). Laccases are extracellular glycoproteins with a ubiquitous distribution in nature, ranging from various fungi to higher plants. Laccase enzyme is recog-

Fig. 2. Human-health related adverse effects of pesticides on different living being systems.

Table 1

Literature search results obtained from the Scopus database.

Search terms	Document types	# of articles from all years		# of articles from top journals		# of articles based on territory		Total articles
Environmental impact of pesticides	Article, review, book chapter, conference paper, book	2020	1	Science of The Total Environment	467	United States	2507	8462
		2019	332	Environmental Toxicology and Chemistry	283	United Kingdom	649	
		2018	575	Chemosphere	245	China	619	
		2017	559	Environmental Science and Technology	201	France	618	
		2016	498	Environmental Pollution	192	Canada	504	
		Others	6, 497	Others	7074	Others	3565	
Occurrence of pesticides in the environment	Article, review, book chapter, conference paper	2019	48	Science of The Total Environment	72	United States	153	786
		2018	68	Environmental Science and Pollution Research	35	China	98	
		2017	65	Chemosphere	34	Germany	70	
		2016	72	Environmental Science and Technology	23	France	62	
		2015	50	Environmental Pollution	20	Italy	55	
		Others	483	Others	602	Others	348	
Biocatalytic degradation of pesticides	Article, review, conference paper	2019	2	Journal of Hazardous Materials	2	United States	3	8
		2018	2	Biochemical Engineering Journal	1	Australia	1	
		2015	1	Bioresource Technology	1	Belgium	1	
		2007	1	Biotechnology and Bioengineering	1	Germany	1	
		2000	1	Biotechnology Progress	1	Italy	1	
		Others	1	Others	2	Others	1	
Degradation of pesticides by laccase	Article, review, book chapter, conference paper, note	2019	4	International Biodeterioration and Biodegradation	4	China	11	70
		2018	8	Applied Microbiology and Biotechnology	3	India	11	
		2017	8	Biodegradation	3	Sweden	6	
		2016	10	Chemosphere	3	Mexico	5	
		2015	2	Environmental Science and Pollution Research	3	United States	5	
		Others	38	Others	54	Others	32	
Degradation of pesticides using immobilized laccase	Article, conference paper, review	2019	3	Chemosphere	2	China	3	13
		2018	2	Advances in Colloid and Interface Science	1	India	2	
		2017	2	Bioconjugate Chemistry	1	Italy	2	
		2016	3	Environmental Division 2018 Core Programming Area at the 2018 Aiche Annual Meeting	1	Austria	1	
		2002	1	Environmental Technology United Kingdom	1	Chile	1	
		Others	2	Others	7	Others	4	

nized to be a proficient, specific, and eco-sustainable biocatalyst, and has been widely applied in various fields, such as dye and wastewater degradation, food-processing industry, paper and pulp industry, and bioremediation of an array of aromatic, xenobiotics, phenolics, and many other recalcitrant pollutants (Zeng et al., 2017; Antecka et al., 2018; Vera et al., 2019; Zdarta et al., 2018a). It can also oxidize non-phenolic compounds in the presence of a suitable natural or synthetic redox mediator. Laccase-mediator systems (LMS), have been observed to bio-transform a variety of toxic pollutants present in dyes, personal care products, and herbicides (Barrios-Estrada et al., 2018; Jankowska et al., 2019).

Despite the numerous advantages as high efficiency, selectivity, low energy necessities, and marginal environmental impact, the employment of native enzyme in industrial processes for the effective removal of refractory compounds is hindered by their high cost and susceptibility (Bilal et al., 2018b, 2018c; Bilal and Iqbal, 2019a). Promisingly, many of the associated drawbacks can be addressed by enzyme immobilization on suitable carrier supports. Increase in stability, reusability, reduction of product inhibition, enhanced activity, specificity, and easier product separation are among the most desirable advantages of immobilization (Zdarta et al., 2018b; Bilal

and Iqbal, 2019b; Feng et al., 2019). So far, numerous reports have documented the ameliorated ability of the immobilized form of the laccases in biodegradation and biotransformation of organic pollutants. Nano-porous silica beads-conjugated laccase exhibited about 90% degradation of 2,4-dinitrophenol within 12 h and remained stable presenting over 80% of its original activity even after 30 days of treatment (Dehghanifard et al., 2013). Wang et al. (2012) recorded 2-fold increased phenol removal with magnetic mesoporous silica nanoparticles insolubilized laccase, and the biocatalyst preserved 71.3% bio-degradation efficiency after ten continuous treatment batches in a fluidized bed. After 8 h of incubation, 50%, 97%, and 71% degradation of diclofenac, naphthol, and 2,4 dichlorophenol were achieved by the laccase cocktail (Rodríguez-Delgado et al., 2016).

This review summarizes recent and up-to-date literature information on the use of enzymes in the degradation of different pesticides/herbicides/insecticides. After a comprehensive description of the source, occurrence and types of pesticides, and associated detrimental effects on the ecosystem/human health, the use of different enzymes with a special emphasis on free and immobilized laccases for the degradation and detoxification of an array of pesticides is highlighted.

Table 2

Literature search results obtained from the PubMed database.

Search terms	Total articles	# of articles published in the last five years filtered with best match term "pesticides."					
		2019	2018	2017	2016	2015	Others
Environmental impact of pesticides	10,694	963	2050	1976	1963	1791	1951
Occurrence of pesticides in the environment	1039	92	215	254	213	178	87
Biocatalytic degradation of pesticides	21	4	4	6	1	5	1
Degradation of pesticides by laccase	60	5	16	11	14	7	7
Degradation of pesticides using immobilized laccase	14	2	5	2	4	1	–

2. Literature methodology – inclusion/exclusion criteria

In order to cover the reviewed contents to justify the scientific theme, literature was surveyed from the authentic databases, such as Scopus and PubMed, and discussed following inclusion/exclusion criteria. For initial screening, relevant data was collected based on the existence of all or any of the following terms, i.e., the environmental impact of pesticides; occurrence of pesticides in the environment, biocatalytic degradation of pesticides, degradation of pesticides by laccase, and degradation of pesticides using immobilized laccase, in the article title, abstract and keywords. Table 1 summarizes the search results obtained from the Scopus. The literature search queries were performed on July 9, 2019, at "https://www.scopus.com". In PubMed, the literature was searched for the last five years with the best match term "pesticide". The search results obtained from the PubMed database are summarized in Table 2. Based on inclusion/exclusion criteria, any type of article related to contaminants apart from pesticides and their treatments using strategies other than laccase (free and immobilized) were considered irrelevant to the scope of this review and thus excluded accordingly. The further exclusion was taken into account if none of the searched term was dealt with and discussed in the results section for articles. Following that based on the term "pesticide", a comprehensive literature analysis was performed to overview the detailed classification along with other characteristics features of organophosphorus pesticides, as summarized in Table 3. Based on the literature data obtained, the following sections and subsections were conceptualized and discussed with suitable examples as a core of this review.

3. Pesticides in the environment – source and occurrence

The rate of environmental pollution is increasing day-by-day due to anthropogenic activities. The food demand at a rapid pace promotes the use of pesticides (crop protection products) in contemporary agricultural/farming practices at an increasing rate (Morillo and Villaverde, 2017). Over the past decade, a massive amount of pesticides and other pollutants were released in the atmosphere because

of agricultural and industrial development (Morillo and Villaverde, 2017; Varjani et al., 2018). The excessive use of pesticides/chemical fertilizers in modern agriculture practices have led to contamination of different environmental matrices, including air, land, and water. Consequently, the contaminated environmental matrices adversely affect human health and non-targeted animals in several ways (Fig. 3) (Liu et al., 2019). The term 'pesticide' comprehends an array of organic compounds intended to prevent, destroy, or control weeds (herbicide), insects (insecticide), pests (pesticide), and fungi and molds (fungicide) (Andleeb et al., 2016). Traces of these toxic compounds may enter rivers, surface water, and groundwater through soil leaching, surface run-off, underground run-off, and accidental leakage (Liao et al., 2017; Liu et al., 2019). Reports have revealed the occurrence of OCPs in environmental samples at an elevated level than OPPs in areas, where OCPs are continuously applied for pest management. Higher concentrations of OCPs have also been detected in various body fluids such as breast milk, serum, and urine (Idowu, 2013).

4. Pesticides and their types

Pesticides have been classified into different categories based on usage, formulation type, source of origin, mode of action/entry, toxicity, function, and pest organism they kill (Fig. 4). Broadly speaking, pesticides are categorized as either organic or inorganic based on their structure. Along with carbon in the structure, organic pesticides also contain oxygen, fluorine, phosphorus, and chloride sulfur. On the other hand, inorganic pesticides are composed of compounds like copper, sulfur, and other elements. Depending on the functional groups and presence in the same chemical class or family, pesticides have been categorized into four classes/families, i.e., (1) organophosphates, e.g., malathion, (2) carbamates, e.g., carbofuran, (3) triazines, e.g., atrazine, and (4) phenoxys, e.g., 2,4-Dichlorophenoxyacetic acid (2,4-D). Almost all pesticides in the same class/family have similar chemical structure along with a similar mode of action, poisoning symptoms, persistence, first aid, clean-up, and safety guidelines. However, each pesticide has an explicit target site based on the mode of action (Wang et al., 2017).

Organochlorine pesticides (OCPs), composed of carbon, hydrogen, and chlorine, are a large group of chemicals used to repel and destroy weeds, insects, bacterial and fungal impacts (Jayaraj et al., 2016). Fig. 5 illustrates the molecular structures of some selected OCPs. Most of the organochlorines are insecticides such as benzene hexachloride (BHC), dichlorodiphenyltrichloroethane (DDT) and its analogs including aldrin, chlordane, dieldrin, endrin, endosulfan, and heptachlor (Katayama and Matsumura, 1993; Jayaraj et al., 2016). These groups of pesticides are white, crystalline, semi-volatile and soluble in organic solvents and fats, and tend to aggregate in the environment and food crops (Barragan-Huerta et al., 2007; Rani et al., 2017). Among the OCPs, DDTs and hexachlorocyclohexanes (HCHs) are the most widely applied OCPs in public health, agriculture, and eradicating tsetse fly, termite, and mosquitoes (Kafilzadeh, 2015; Yahaya et al., 2017). In the past, the large-scale production and use of these pesticides was prohibited and swapped gradually with other pesticides because of their high ecological toxicity, high persistence, health impacts and robust affinity to bioaccumulation cause environmental pollution (Ahmed et al., 2015; Rani et al., 2017; Gopalan and Chenicherry, 2018). For instance, use of Aldrin and dieldrin were banned in Kenya in 1992, and DDT was banned in 1985 (Wandiga, 2001). Similarly, the manufacturing, use, and import of aldrin and dieldrin have been banned in India since 2013, whereas DDT was banned since 1989 (Gopalan and Chenicherry, 2018). OCPs origi-

Table 3
Classification overview of organophosphorus pesticides^{a,b,c}.

Name	Classification	Identification (CAS) number	Molecular weight	Chemical structure
Fenitrothion	Insecticide	122-14-5	277.24	
Parathion	Insecticide, acaricide	56-38-2	291.26	
Anilofos	Herbicide	64249-01-0	367.8	
Ditalimfos	Fungicide	5131-24-8	299.3	
Chlorpyrifos	Insecticide	2921-88-2	350.59	
Fenamiphos	Nematicide	22224-92-6	303.4	
Malathion	Insecticide, acaricide	121-75-5	330.36	
Bensulide	Herbicide	741-58-2	397.52	
Edifenphos	Fungicide	17109-49-8	310.38	
Phosphamidon	Nematicide	13171-21-6	299.69	
Phosphamidon	Insecticide, acaricide	13171-21-6	299.69	
Bromophos	Insecticide	2104-96-3	—	
Butamifos	Herbicide	36335-67-8	—	
Crufomate	Insecticide, anthelmintic	299-86-5	291.71	
Cyanophos	Insecticide	2636-26-2	243.21	
Pyrazophos	Fungicide	13457-18-6	—	
Fosamine Ammonium	Herbicide	25954-13-6	170.13	
Dichlorvos	Insecticide, acaricide	62-73-7	220.98	
Omethoate	Insecticide, acaricide	1113-02-6	213.2	
Etrifos	Insecticide	38260-54-7	292.29	

Table 3 (Continued)

Name	Classification	Identification (CAS) number	Molecular weight	Chemical structure
Glyphosate	Herbicide	38641-94-0	228.22	
Fenitrothion	Insecticide	122-14-5	277.24	
Phoxim	Insecticide	14816-18-3	298.32	
Sulprofos	Insecticide	35400-43-2	322.45	
Piperophos	Herbicide	24151-93-7	—	
Sulfotep	Insecticide, acaricide	3689-24-5	—	
Terbufos	Insecticide, nematocide	13071-79-9	288.4	
Thiometon	Insecticide, acaricide	640-15-3	246.35	
Vamidothion	Insecticide, acaricide	2275-23-2	287.35	
Triazophos	Insecticide, acaricide	24017-47-8	313.3	
Naled	Insecticide, acaricide	300-76-5	380.79	

^a Living beings are prone to organophosphorus pesticides via three major exposure routes, i.e., (1) inhalation, (2) ingestion, and (3) dermal absorption.

^b Potential adverse health effects of organophosphorus pesticides includes the inhibition of acetylcholinesterase in the nervous system, respiratory, myocardial and neuromuscular transmission impairment, Intermediate Syndrome, delayed neuropathy, cholinergic syndrome, carcinogenic, mutagenic, teratogenic, nicotinic effects, etc.

^c Environment is prone to the organophosphorus pesticides via three major routes of entry, i.e., (1) industrial waste or effluent discharged directly into the environment (water), (2) seepage from buried toxic wastes into the surrounding environment (soil or water), and (3) contamination of running water directly or from run-off during spraying operations can occur.

nated from domestic wastes, industrial effluents, agricultural activities, and other point/nonpoint sources incorporate into environmental components through the air, runoff, and other agents (Ahmed et al., 2015). DDTs and HCHs are often regarded as characteristic compounds to evaluate the ecological status of OCPs, due to their numerous applications, human health, and environmental impact (Gereslassie et al., 2019). Owing to the increasing persistence and adverse effects of DDT on the environment and living beings, the use of DDT as a pesticide was banned worldwide under the Stockholm Convention in 2001.

Organophosphorus pesticides (OPPs) are phosphoric acid esters that can improve both the quality and quantity of crop yields in agricultural practices (Cederlund et al., 2016; Schenk et al., 2016), and used as warfare nerve agents such as sarin, soman, tabun, and others. Their use has been substantially increased in the past decade due to potential efficacy for improving crop productivity. Nevertheless, the widespread use of these pesticides can lead to environmental pollution and posturing a menace to human health and aquatic life. Fenitrothion, parathion, chlorpyrifos, Malathion, and phosphamidon are some examples of OPPs applied in the agricultural fields (Ghanem et al., 2007; Schenk et al., 2016). A detailed classification overview along with other characteristics features of organophosphorus pesticides are summarized in Table 3. These pesticides can cause acute toxicity to humans when exposed to their elevated levels through irreversible inactivation/inhibition of the acetylcholinesterase en-

zyme. This enzyme is indispensable for nerve function in humans, insects, and numerous other animals (Jayaraj et al., 2016; Schenk et al., 2016). It is of profound significance to transform toxic OPPs into harmless compounds to mitigate environmental contamination. Reports have shown that OPPs can be readily hydrolyzed by exposure to air, light, and soil, but traces of these pesticides have been identified in food and drinking water (Jokanović, 2018). Carbamates are pre-emergent herbicides obtained from carbamic acid (Tatarková et al., 2013), such as aldicarb, carbofuran, ethienocarb, oxamyl, and methomyl. Generally, they are employed in the form of baits or sprays in the field to alleviate pests (Zhang et al., 2013). Carbaryl was the first insecticide to be used in the field. It exhibits great potential to control a broad range of insects and is associated with less toxicity to humans. The carbamates possess a similar mode of action to that of OPPs (Hayatsu et al., 2001; Schenk et al., 2016). Plant roots and leaves easily absorb carbamates due to their high-water solubility (Zhang et al., 2013).

5. Pesticide and human health

Pesticides are deliberated as an efficient and cost-effective tool for pest management. However, owing to their mechanism of action, they not only destroy the target creature but also damage non-target organism, including humans. The World Health Organization reports approximately 3 million annual cases of pesticide poisoning and up

Fig. 3. Pesticide drift and adverse consequences of excessive use of pesticides/chemical fertilizers in modern agriculture practices that can lead to contamination of different media including (1) air, (2) land, and (3) water. Reprinted from Liu et al. (2019), with permission from Elsevier. Copyright (2019) Elsevier B.V.

Fig. 4. Broader classification routes of pesticides: (A) general classification, (B) based on the mode of action/entry, (C) based on usage types, and (D) based on the formulation type.

to 220,000 deaths, predominantly in emerging countries. Non-specific use of pesticides and unintentional acquaintances occur to other organisms, particularly, young and developing organisms are

highly vulnerable to their detrimental effects. The amount of pesticide as well as the persistence time mainly determined the toxic effect of pesticide exposure. Some pesticides are extremely toxic to hu-

Fig. 5. Molecular structures of some organochlorine-based pesticides. (A) Chlordane, (B) Dichlorodiphenyltrichloroethane, (C) Heptachlor, (D) Lindane, (E) Dieldrin, (F) Pentachlorophenol, (G) Endrin, (H) Pentachloronitrobenzene, (I) Clofentezine, (J) Hexachlorophene, (K) Hexachlorobenzene, (L) Endosulfan sulfate, (M) β -Endosulfan.

mans resulting in undesirable effects with only a few drops in the mouth or on the skin. Other less toxic pesticides can also cause harmful effects by their continuous and long-term exposure (Singh et al., 2018). Close association of pesticides is associated with diverse health disorders and malignancies such as leukemia, Parkinson's disease, Hodgkin's disease, non-Hodgkin lymphoma, Burkitt lymphoma, respiratory, reproductive, and endocrine disorders (Wang et al., 2014; Luo et al., 2016; Brouwer et al., 2017; Sabarwal et al., 2018). According to the WHO, (2002) many pesticides have been documented as endocrine disruptor compounds (EDCs), which interfere with endocrine systems, leading to devastating consequences on physiological processes, i.e. growth, development, and reproduction in organisms or their offspring.

Some pesticides including maneb, paraquat, and rotenone result in Reactive Oxygen Species (ROS)-mediated oxidative stress and thus several cause neurodegenerative disorders in the body (Fig. 6) (Sabarwal et al., 2018). Parkinson's disease, at the cellular level, is meticulously related to excessive ROS generation from mitochondrial electron transport complexes, which consequently, causes serious damages to mitochondrial DNA and other bio-macromolecules (Nandipati and Litvan, 2016). Likewise, Alzheimer's disease is clinically characterized by the accumulation of an abnormal amyloid protein and is tightly related to oxidative stress. Continuous exposure to dieldrin, paraquat, organophosphates, and organochlorine has observed to produce ROS-driven neurotoxicity, which in turn is cou-

pled with Alzheimer's disease (Yan et al., 2016). Various epidemiological and clinical reports have demonstrated a close relationship between pesticide contact and asthma and bronchial hyper-reactivity symptoms. Exposure of agrochemicals or pesticide/herbicides may cause a severe asthma exacerbation by inflammation, irritation, endocrine disruption, or immunosuppression (Kim et al., 2017). In another study, Sylvie Azandjeme et al. (2013) revealed that exposure to OCPs and metabolites is thought to cause a high risk of type 2 diabetes and associated comorbidities. Similarly, OPPs-based pollutants exposure are a potential risk affecting the reproductive system of the male by mechanisms such as a decrease in sperm counts, density, viability, and motility, inhibiting sperm formation, abnormal sperm morphology, and reduction of testis weights (Mehrpour et al., 2014).

6. Degradation of pesticide—conventional vs. enzyme-mediated bioremediation techniques

Different physical and chemical strategies have been attempted to confront the persistence of organochlorine pesticides and to reduce their detrimental effects in the ecosystems. For example, He et al. (2011) utilized UV irradiation and ozonation (UV/O_3) amalgamated approach to degrade chlorophane (CP) and dichlorophen (2,2'-methylene bis(4-chlorophenol) (DCP) pesticides in the aqueous environment and recorded an increase in the oxidation rate of both pesticides by 1 order of magnitude. Nevertheless, the existence of high or-

Fig. 6. Pesticide modulates various cellular and sub-cellular activities leading to genetic and epigenetic changes and causes various diseases or cell death. Reprinted from Sabarwal et al. (2018), with permission from Elsevier. Copyright (2018) Elsevier B.V.

Table 4

Degradation studies of various pesticides by free laccases in the presence of different redox mediators.

Source of enzyme	Amount of enzyme	Redox mediator	Pesticide	Degradation (%)	Time	Reference
<i>Pseudomonas</i> sp.	210 nkat/mL	No/sinapic acid	Chlorpyrifos	80.56/83.25%	6 h	Chauhan and Jha (2018)
<i>Pseudomonas</i> sp.	210 nkat/mL	No/sinapic acid	Dichlorophos	45.99/45.82%	6 h	Chauhan and Jha (2018)
<i>Pseudomonas</i> sp.	210 nkat/mL	No/sinapic acid	Monocrotophos	75.45/78.82%	6 h	Chauhan and Jha (2018)
<i>Pseudomonas</i> sp.	210 nkat/mL	No/sinapic acid	Profenovos	81.84/82.15%	6 h	Chauhan and Jha (2018)
<i>Trametes versicolor</i>	0.30 U/mL	HBT	Isoproturon	100%	24 h	Zeng et al. (2017)
<i>Trametes versicolor</i>	0.30 U/mL	HBT	Isoproturon	68.2%	24 h	Zeng et al. (2017)
<i>Trametes versicolor</i>	0.05 U/mL	Violuric acid	Pyrimethanil	100%	24 h	Jin et al. (2016)
<i>Trametes versicolor</i>	0.05 U/mL	Violuric acid	Isoproturon	100%	24 h	Jin et al. (2016)
<i>Trametes versicolor</i>	0.05 U/mL	1-Hydroxybenzotriazole	Atrazine	90%	8 d	Jin et al. (2016)
<i>Trametes versicolor</i>	0.05 U/mL	Acetosyringone	Chlorothalonil	90%	8 d	Jin et al. (2016)
<i>Trametes versicolor</i>	0.05 U/mL	Vanillin	Chlorpyrifos	90%	8 d	Jin et al. (2016)
<i>Trametes versicolor</i>	0.15 U/mL	ABTS	Glyphosate	40.9%	24 h	Pizzul et al. (2009)
<i>Trametes versicolor</i>	0.15 U/mL	Mn ²⁺ +Tween 80	Glyphosate	62.8%	24 h	Pizzul et al. (2009)
<i>Trametes versicolor</i>	0.15 U/mL	ABTS+Mn ²⁺ +Tween 80	Glyphosate	90.1%	24 h	Pizzul et al. (2009)

ganic matter in sewage act as a quencher of oxidizing species produced by UV/O₃, and thus decreasing treatment efficacy by 38%. Biotechnological approaches, on the other hand, have also been developed to take advantage of whole organisms, a metabolic trait, or biocatalysts in transforming pesticides into innocuous compounds. In the case of whole microorganisms and metabolic pathways, pesticides are commonly utilized as co-substrates in reactions, where natural substrates are co-transformed along with the pesticide, thus eliminating them from the environment. A range of microbial communities including bacteria (*Pseudomonas* spp., *Rhodococcus* sp., *Bacillus* spp., etc.), as well as, fungi (*Aspergillus* spp., *Botrytis cinerea*, *Tricho-*

derma harzianum) have the ability to interact with different kinds of pesticides both physically and chemically, leading to structural alterations or complete degradation and transformation of the target molecule (Katayama and Matsumura, 1993; Ortiz-Hernández et al., 2013). Similarly, soluble or isolated enzymes have shown great potential as green catalysts to transform a diversity of natural or artificial substrates, thus circumventing the intricacy of cell culture (Karigar and Rao, 2011). Nonetheless, the explicit biochemistry of enzyme-based degradation necessitates an array of catalytic mechanisms owing to the complexity and chemical diversity of pesticides. Oxidoreductases hydrolases and transferases are among the most representative

Fig. 7. Degradation mechanism of isoproturon catalyzed by the laccase-HBT system, initial dimerization processes (A), and subsequent coupling processes (B). Reprinted from Zeng et al. (2017), an open-access article published under the CC-BY license (<http://creativecommons.org/licenses/by/4.0/>). Copyright (2016) The Author(s). Published by Elsevier B.V.

classes of enzymes that have demonstrated an active role in mitigating environmental pollution (Nigam and Shukla, 2015; Maqbool et al., 2016). Application of these enzymes in bioremediation has received substantial attention as a sustainable, selective, and environmentally-friendly alternative to conventional pesticides degradation strategies.

7. Enzyme-mediated degradation of pesticide

7.1. Degradation of pesticides by free laccases without mediators

In recent years, increasing numbers of studies have been intensively executed on the application of laccase to degrade and detoxify a wide variety of agrochemicals and pesticides with promising results. Zhao et al. (2010) reduced the dichlorodiphenyltrichloroethane (DDT) level in impacted soils using laccase from polypore white rot fungi. They have also been investigated as potent decomposers CP and DCP in an aqueous system. Shi et al. (2016) carried out the toxicity bio-assays in algae cultures incubated with laccase-catalyzed degraded chlorophen (oxCP) and dichlorophen (oxDCP) sub-prod-

ucts and found a significant toxicity reduction as evinced by the retrieval of cell growth in laccase-treated organochlorine samples. An extracellular thermo-alkali stabilized crude laccase was produced from the fermented extract of *Pseudomonas* sp. using potato peel as a bio-waste substrate. The extracted enzyme was purified with a specific activity of $1089.70 \pm 16.8 \text{ U mg}^{-1}$ and a molecular mass of 38 kDa. The pH and temperature optima were 9.0 and 80°C , respectively. The purified enzyme led to 80.56%, 45.99%, 75.45%, and $81.84 \pm 0.6\%$ degradation of chlorpyrifos, dichlorophos, monocrotophos, and profenovos pesticides, respectively without the incorporation of any redox mediator (Chauhan and Jha, 2018). Cypermethrin, a group of synthetic pyrethroid insecticides, are excessively applied in agriculture, Horticulture, forestry, households, and public health to manufacture textiles protection and control different pests (Lin et al., 2011; Sharma et al., 2016). Pyrethroid insecticides are also invariably used in vegetable crops and cotton as a substitute to OPPs (Lin et al., 2011), and to combat mosquito-borne and malarial diseases (Nkya et al., 2013). It is regarded as an environmental pollutant due to its prevalent usage, high persistence, and toxicity, which may

Table 5

Recent degradation studies of various pesticides by laccases immobilized on different support materials.

Source of enzyme	Enzyme support	Type of immobilization	Performance improvement	Application	Reference
<i>Trametes versicolor</i>	Acrylate-based microbeads	Covalent binding	Extended pH and temperature profiles accompanied by a substantial increase in shelf-life of the immobilized enzyme than free enzyme.	The laccase-acetosyringone system results in complete biodegradation of carbaryl pesticide and methylene blue. Insolubilized enzyme lost only 2% and 8% of the initial activity for CP and MB, biodegradation, respectively, in a fluidized bed reactor for 24 h.	Bayramoglu and Arica (2019)
Myceliophthora thermophile	Monodisperse microspheres of poly(glycidyl methacrylate)	Physical adsorption/ covalent binding	A large working pH and temperature range. Significant improvement in thermal, operational, and storage stability.	Complete degradation of AZPM after 1 h of reaction in the presence of 2,2-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) as a mediator	Vera et al. (2019)
Coriollopsis gallica	Mesoporous synthetic silica foam nanostructured silicon foam	Physical absorption	–	Efficient oxidation of dichlorophen pesticide, accompanied by a marked reduction in acute genotoxicity and apoptotic effects.	Vidal-Limon et al. (2018)
–	Activated bagasse/ cellulose nanofibers	Covalent binding	Catalytic activity over a pH range from 6 to 10 and up to 80 °C. Retained more than 60% of activity after 15 cycles. High stability preserving 75% of its relative activity after 45 days.	The biocatalyst achieved 78.71%, and 100% trifluralin degradation efficiency in 24 h in the presence of catechol, and humic monomers, guaiacol respectively, as mediators.	Bansal et al. (2018)
<i>Trametes versicolor</i>	Chitosan-coated and carbodiimide surface modified magnetic iron nanoparticles	Covalent binding	Significant increase in the stability against pH and temperature variations. Retained 95% of its activity after five consecutive cycles.	Under optimal conditions of pH 7.0 and 60 °C, the laccase-coupled MNPs showed excellent efficiency to degrade higher than 99% chlorpyrifos in 12 h.	Das et al. (2017)
<i>Aspergillus</i> sp.	Mesoporous silica	Cross-linking	Significantly improved repeatability of immobilized laccase as compared with the free enzyme	The immobilized biocatalyst achieved 42.28 and 15.93% removal ratio and the degradation ratio of 2,4-dichlorophenol pesticide, respectively.	Yang et al. (2016a)
<i>Trametes versicolor</i>	Tubular mesoporous silica containing ultrasmall superparamagnetic iron oxide nanoparticles	Cross-linking	Retained 20.8% of catalytic efficiency after seven continuous cycles.	45.6% degradation of methoxychlor pesticide in aqueous and reverse micelle environments by the immobilized enzyme.	Yang et al. (2016b)

cause harmful effects to non-target entities and several ecosystems. Laccase and esterase play a noteworthy role in the biodegradation and detoxification of these synthetic pyrethroid insecticides in the environment owing to their specific nature.

7.2. Degradation of pesticides by laccase-mediators system

Degradation studies of various pesticides by free laccases in the presence of different redox mediators are summarized in Table 4. Despite the obvious efficacy of laccase-mediator systems to decompose recalcitrant aromatic compounds, the use of mediator-based enzyme systems is generally hampered by the economic cost of synthetic mediators and the generation of toxic species (Cañas and Camarero, 2010). Mediators of natural origin, especially the lignin-related phenolic compounds are excellent and environmentally-friendly alternatives to overcome this issue (Grijalva-Bustamante et al., 2016). Kupski et al. (2019), for the first time, developed an optimized laccase-mediator system to remove different pesticides including bentazone, carbofuran, clomazone, diuron, pyraclostrobin, and tebuconazole in the aqueous samples. Among seven redox-mediating compounds screened, i.e., 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS), caffeic acid, chlorogenic acid, *p*-coumaric acid, ferulic acid, gallic acid, protocatechuic acid, and vanillin, the laccase-vanillin system showed the highest removal efficiency (77%) of pesticides. Ashe et al. (2016) evaluated the removal efficiency of four organic contaminants (oxybenzone, pentachlorophenol, atrazine, and naproxen) by laccase with different mediators i.e. ABTS, (1-hydroxybenzotriazole (HBT), *N*-hydroxyphthalimide (HPI), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), syringaldehyde (SA), violuric

acid (VA), and vanillin (VAN). Among these mediators, ABTS, HBT, and VA accomplished the highest removal of environmental pollutants. The herbicide isoproturon was effectively removed by Zeng et al. (2017) using six mediators such as acetosyringone, ABTS, HBT, SA, VA, and VAN. In contrast to natural mediators, the synthetic ones were found more effective in laccase-assisted catalytic degradation of isoproturon. According to literature reports, mediators follow three major mechanisms for substrate oxidation includes electron transfer, hydrogen atom transfer, and ionic mechanisms. ABTS follows electron transfer, whereas vanillin uses hydrogen atom transfer (Ashe et al., 2016). Trovaslet-Leroy et al. (2010) reported the effective degradation and detoxification of organophosphorus compounds and nerve agents O-ethyl S-[N,N-diisopropylaminoethyl] methylphosphonothiolate (VX), O-ethyl-S-[2-(diisopropylamino)ethyl] phenylphosphonothioate (PhX) and RVX by a laccase from *Trametes versicolor* in the presence of ABTS as a redox mediator. Among nine tested redox mediators, acetosyringone and syringaldehyde played a significant role in the destruction of halogenated pesticide by the ligninolytic enzymes. Under in vitro conditions, the laccase-mediator system containing ABTS, Tween 80, and Mn²⁺ as mediators result in the degradation of glyphosate pesticide by 40.9%, 90.1%, and 62.8%, respectively, after 24 h of incubation at 35 °C and 150 rpm (Pizzul et al., 2009).

Isoproturon is a kind of phenylurea herbicide with a wide spectrum of agricultural applications to limit the growth of weeds including silky bent-grass, ryegrass, and many broadleaf species in winter and spring wheat (Castillo et al., 2001). However, its use produces a potentially carcinogenic intermediate that adversely influences the environment, particularly marine invertebrates, microbes, and al-

Fig. 8. Reaction mechanism of methoxychlor degradation by magnetic host/guest-type immobilized laccase. Reprinted from Yang et al. (2016B), with permission from Springer Nature. Copyright (2016) Springer-Verlag Berlin Heidelberg.

gae. Around 3300t of this herbicide was applied to 3.0 million hectares of agronomic land in the UK in 1997. It has been detected as a contaminant in streams, rivers, marine, and ground waters because of its extensive and widespread practice in modern agriculture, around the globe (Sørensen et al., 2003). Considering its negative ecological impacts, it is highly desirable to eliminate this herbicide from wastewater. Zeng et al. (2017) examined the degradation of isoproturon using *T. versicolor* laccase using HBT as a redox mediator. Without a mediator, isoproturon was hardly disintegrated by laccase alone due to the presence of robust withdrawing electron group in its chemical organization. However, the LMS increased the degradation efficiency, leading to the complete degradation of isoproturon within 24 h in the presence of HBT. Optimal degradation occurred at an acidic pH and 50 °C, and incorporation of metal ions Cu^{2+} , Cd^{2+} , and Zn^{2+} promoted elimination rate by the laccase-HBT system. Addition of PEG can also enhance the herbicide degradation efficacy of the laccase-HBT system by improving the laccase stability. The possi-

ble mechanism of isoproturon degradation by the laccase-HBT system might be ascribed to oligomerization of oxidized isoproturon through the radical-radical coupling. Fig. 7 represents the speculated oligomerization processes for the degradation of isoproturon (Zeng et al., 2017). Under the optimum conditions, laccase produced from *Trametes versicolor* has shown a great ability for the degradation of five selected pesticides, i.e. atrazine, chlorothalonil, chlorpyrifos, isoproturon, and pyrimethanil in the presence of mediator acetosyringone, vanillin, violuric acid, and HBT. The enzyme was stable at pH and a temperature range from 5.0 to 7.0 and 25 to 30 °C, respectively. The degradation efficiencies of isoproturon and pyrimethanil were considerably faster as compared to atrazine, chlorothalonil, and chlorpyrifos. Results showed that isoproturon and pyrimethanil were completely decomposed within after 24 h, whereas the other three pesticides were 90% degrade even after 8 days of treatment (Jin et al., 2016). Finally, laccase-treated and transformed products showed significantly lower eco-toxicity to green algae as compared to the na-

Fig. 9. Schematic representation of bioremediation of pollutants in the reactor system. Reprinted from Bayramoglu and Arica (2019), with permission from Taylor & Francis. Copyright (2019) Taylor & Francis Group, LLC.

Fig. 10. A) Schematic illustration for PCD as a sorptive and regenerative system with the ability to be functionalized by adsorption of enzyme onto its structure. B) Schematic illustration for OPH-PCD as a stable self-decontaminating bio-catalytic system for sorption and degradation of organophosphates. Reprinted from Moon et al. (2019), with permission from Elsevier. Copyright (2018) Elsevier B.V.

tive isotreturon indicating the usefulness of the LMS to remediate herbicide-containing industrial wastewater.

7.3. Degradation of pesticides by immobilized laccases

Some recent degradation studies of various pesticides by laccases immobilized on different support materials are summarized in Table 5. To achieve enhanced biodegradation of dichlorophen, Vidal-Limon et al. (2018) immobilized *Coriollopsis gallica* laccase on mesoporous synthetic silica foam nanostructured silicon foam (MSU-F) by physi-

cal absorption to develop a hybrid nanomaterial (laccase-MSU-F). High enzyme adsorption ($7 \mu\text{M}/\mu\text{g}$ MSU-F) on the nanocomposite suggest that enzyme stabilization into MSU-F internal pores could be interceded by noncovalent interactions (such as electrostatic interactions). The newly-synthesized laccase-MSU-F hybrid nanocomposite efficiently oxidized the dichlorophen pesticide, accompanied by a marked reduced in acute genotoxicity and apoptotic effects. Moreover, laccase-MSU-F nanomaterial diminished the onset of endocrine disruption by decreasing the dichlorophen affinity for steroid hormone nuclear receptors (NRs). The authors also found that silica-

based mesoporous MSU-F provides a potential “protecting effect” following laccase immobilization. Therefore, mesoporous nanocomposites can be scaled up to several grams due to its high loading capability. Recently, laccase from *Myceliophthora thermophila* (MtL) was immobilized onto monodisperse microspheres of poly(glycidyl methacrylate) (PGMA) and applied for azinphos-methyl (AZPM) biodegradation. The immobilized biocatalytic system demonstrated a wide-working pH and temperature range of optimal activity and significantly improved the thermal, operational, and storage stability. It achieved the complete degradation of AZPM after 1 h of reaction in the presence of ABTS as a mediator (Vera et al., 2019).

Trifluralin is a moderately persistent and toxic agricultural herbicide that is resilient to natural degradation technologies (Fragoieiro and Magan, 2005). Among the various pesticide treatment strategies, advanced oxidation processes (AOPs) have been largely attempted for trifluralin decomposition, which include photolysis in presence of UV and H_2O_2 (Chelme-Ayala et al., 2010a), hydroxyl radicals (Le Person et al., 2007), ozonation (Chelme-Ayala et al., 2010b), and photo-assisted degradation using SnO_2 -doped Cu_2O crystals (Du et al., 2010). However, some drawbacks such as the high operating cost and undesirable intermediates generation hinder the use of these processes. Bio-degradation of trifluralin pesticide using extracellular fungal laccase is a preferential option and has been assessed in previous studies (Lafi and Al-Qodah, 2006). Bansal et al. (2018) carried out the immobilization of laccase on activated bagasse/cellulose nanofibers (CNFs)-based carrier support with 85% immobilization yield. CNFs were extracted from a readily available agro-waste, bagasse using a cost-efficient and eco-friendly process. Polyethyleneimine (PEI) and glutaraldehyde (GLU) were used to introduce the amine group, and aldehyde through a Schiff base reaction during the immobilization process. The immobilized biocatalyst showed catalytic performance over a large pH range from 6 to 10 and investigated to be active up to 80 °C. The immobilized enzyme maintained more than 60% of the initial activity after 15 successive reaction cycles. It also exhibited high stability and retained 75% of its relative activity after 45 days. Finally, the practical efficacy of bagasse nano cellulose-grafted laccase was verified by investigating its capability to degrade trifluralin. Notably, the grafted biocatalyst achieved 78.71%, and 100% degradation efficiency in 24 h in the presence of catechol, and humic monomers, guaiacol respectively, as mediators.

Chlorpyrifos is an extensively used insecticide since 1965 for household and agricultural pest control. It can contaminate the site up to 24 km away from the point of applications, leading to undesirable environmental effects, and resultantly, necessitating its judicious remediation (Singh et al., 2004). The degradation of chlorpyrifos pesticide was investigated using laccase incorporated on chitosan coated, and carbodiimide surface modified magnetic iron nanoparticles (CENPs) with size ranged from 10 to 15 nm. The developed nanobiocatalyst was used for the degradation of chlorpyrifos in a batch reaction for 12 h under constant shaking. Under optimal conditions of pH 7.0 and 60 °C, the laccase-coupled MNPs showed excellent efficiency to degrade higher than 99% chlorpyrifos in 12 h. After immobilization, the overall activity of the enzyme was decreased than that to the free enzyme. Moreover, the nanobiocatalytic system possessed good recycling potential and demonstrated 95% of its original activity after five consecutive cycles. Based on gas chromatography–mass spectrometry (GC–MS) analysis, two main degradation products, i.e. 1,2 benzene dicarboxylic acid, bis(2-methyl propyl) ester and 2,4-bis(1,1 dimethylethyl) phenol were noticed in the treated extract (Das et al., 2017). Yang et al. (2016a) utilized glutaraldehyde-activated mesoporous silica having the large specific surface area for the immobilization of laccase by a cross-linking approach. After

ing the experiments, the optimal enzyme immobilization occurred under the processing conditions of pH 5.4, 25 °C, 4% GLU and 0.2 mg/mL laccase solution. The optimally immobilized biocatalyst was applied for the degradation and removal of a 2,4-dichlorophenol pesticide under different degradation environments. Results showed a removal and degradation ratio of 42.28 and 15.93%, respectively, by the cross-linked biocatalyst at pH 5.4, and 30 °C using 0.1 g of immobilized laccase. With reference to the soluble laccase, the recycling ability of the insolubilized enzymes was substantially increased. In another study, the same research group carried out the degradation of an organochlorine pesticide methoxychlor in aqueous media. Reports have demonstrated that methoxychlor can exert undesirable consequences by altering the secretion of pituitary follicle-stimulating hormone, and thus affect the reproductive system of both the male and female. In order to degrade methoxychlor, they constructed a nanobiocatalytic system by cross-linking laccase enzyme into superparamagnetic iron oxide nanoparticles, and the influences of various variables on pesticide removal were examined. The immobilized biocatalyst result in 45.6% bio-degradation of pesticide along with retention of 20.8% of its initial catalytic activity after seven repeated reaction cycles under the optimized conditions. Supplementation of ABTS to the system considerably increased the elimination efficiency. A plausible mechanism of methoxychlor degradation was speculated based on the intermediate metabolites detected by GC–MS and NMR analyses (Fig. 8) (Yang et al., 2016B).

Of most recent, Bayramoglu and Arica, (2019) synthesized the cross-linked poly(glycidyl methacrylate-ethylene glycol dimethacrylate-glycidyl methacrylate), p(MMAEGMA-GMA) microbeads by suspension polymerization followed by the replacement of epoxy groups of the terpolymer with the cyclic carbonate groups under CO_2 atmosphere (i.e., p(MMA-EGMA-CCMA)). After characterization, the resulting both p(MMA-EGMA-GMA) and p(MMA-EGMA-CCMA) microbeads were subjected to laccase immobilization. p(MMA-EGMA-CCMA) microbeads-immobilized laccase can be executed at low temperature and showed expanded pH and temperature ranges accompanied by a substantial increase in shelf-life than free enzyme. The synthesized biocatalytic system was applied for the biodegradation and elimination of two kinds of micro-pollutants including carbaryl pesticide (CP) and methylene blue (MB) dye in the presence of various mediators. In contrast to 71% and 63% degradation of CP and MB, respectively, without the use of a mediator, the laccase-acetosyringone system caused complete biodegradation of both micro-pollutants. Furthermore, the insolubilized enzyme dropped only 2% and 8% of the initial activity for biodegradation of CP and MB, respectively, when operated in a fluidized bed reactor for 24 h. Fig. 9 presents the diagrammatic configuration of the fluidized bed reactor system employed for the degradation of micropollutants (Bayramoglu and Arica, 2019).

7.4. Degradation of pesticides by other immobilized enzymes

Microbial phosphotriesterases are very interesting enzymes for pesticides degradation and detoxification because of their higher biocatalytic efficacy and wider substrate specificity (Porzio et al., 2007). Vitola et al. (2019) developed a continuous biocatalytic membrane reactor for pesticide and organophosphate paraoxon decontamination using a triple mutant of the thermostable phosphotriesterase obtained from the *Sulfolobus solfataricus*. For this, various phosphotriesterases were covalently coupled to different polymeric membranes such as polyvinylidene fluoride, polyethersulfon. The enzymes displayed noteworthy stability at varying pH (5–9) and temperature ranges (10–100 °C) owing to their hyperthermophilic origin. High degradation

of paraoxon pesticide (about 90%) and durable stability of one year was observed by the hydrophilic membranes-based newly constructed biocatalytic system. This increased stability allows the biocatalyst remaining active over longer periods, improving storage, and overcoming the deactivation issues of the typical native enzyme. In contrast, the free enzyme completely lost its activity within a few months in a batch system. Halloysite nanotubes (HNT), a kind of kaolin clay, is regarded as promising support for biomolecules/enzymes immobilization owing to its larger specific surface area, low-cost, abundance, biocompatibility, and mechanical and chemical stability. In order to exploit its use as enzyme immobilization carrier, Fan et al. (2018) proposed two strategies for embedding and entrapping *C. fumago* chloroperoxidase (CPO) enzyme on outer as well as an inner wall of HNT. In comparison to the free enzyme, the thermal steadiness and resistance to organic solvents of the immobilized enzyme were substantially enhanced. The immobilized CPO retained 87.63% of its original activity after 1 h heating at 80 °C, whereas only 11.66% activity was recorded for the free CPO under identical conditions. Free dropped all its activity by incubation at 90 °C for 90 min, while the supported biocatalyst still exhibited 40.3% activity. Moreover, immobilized enzyme showed almost no activity loss in the presence of various organic solvents including acetonitrile, ethyl acetate, *N, N*-dimethyl formamide, and methanol, but free CPO displayed only 38.2%, 41.6%, and 23.5% of its original activity in acetonitrile, ethyl acetate, and methanol, respectively, and completely inactivated in *N, N*-dimethyl formamide in the same conditions. Finally, the immobilized biocatalytic system was found to be very efficient for degrading isoproturon in wastewater samples. It caused a complete degradation of isoproturon within 10 min that indicated its noteworthy practical implementation in remediating pesticide-harboring wastewater. Moon et al. (2019) developed a non-toxic novel bio-catalytic material by immobilizing organophosphorus hydrolase (OPH) onto poly- β -cyclodextrin (PCD) as a new sorptive reinforced self-decontaminating material for the intoxication of organophosphate (Fig. 10). The synthesized OPH-coated PCD not only provided support for encapsulating enzyme but also adsorbed methyl paraoxon (MPO) used as a simulant in a host-guest inclusion complex formation. Sorption profile for PCD demonstrated an inclination towards the more hydrophobic MPO against *para*-nitrophenol (pNP). Results revealed 1.7 times higher sorption capacity of MPO with PCD relative to pNP. As compared to the free enzyme, the reaction rate was 23% decreased by immobilized OPH-PCD. However, the bio-catalytic system presented complete hydrolysis (100%) of MPO into pNP for a period of 24 h in a continuous packed bed reactor with profound stability and reproducibility of the enzyme. The fast, reactive nature and durable stability render the resulting system as a promising approach for the detection and neutralization of hazardous chemical warfare agents/nerve agents and decontamination of the environment.

8. Concluding remarks and outlook

Pesticide contamination has become a global problem nowadays that affects not only the ecosystems (soil and water resources) but also the health of humans, animals, microorganisms, and plants. Therefore, it is of great significance to propose green, sustainable, and environmentally friendly strategies for complete remediation of pesticides from the polluted milieu. A comprehensive and up-to-date overview of the literature presented herein highlights the potential of enzymes in biodegradation and detoxification of a range of agrochemicals and pesticides. Among different kinds of pesticide-degrading enzymes, laccases are of exceptional interest due to high efficiency, specificity, eco-sustainability, and wide-ranging sub-

strates. Laccases catalyzed the oxidation of aromatic compounds containing a phenolic functional group. However, this degradation range can be expanded towards non-phenolic substrates by incorporating a suitable redox mediator. Furthermore, it is worthy of mentioning that the pesticide removal and degradation efficiency of biocatalysts can be significantly enhanced when they were applied in the immobilized forms. Several reports have documented the ameliorated ability of the immobilized form of the laccases to degrade and bio-transform a variety of toxic pollutants present in industrial dyes, personal care products, and pesticides/herbicides. Increase in stability, reusability, reduction of product inhibition, enhanced activity, specificity, and easier product separation are among the most desirable advantages of immobilization to develop biocatalysts for continuous systems in industrial bioprocessing. In addition to isolating and characterize new pesticide-degrading enzymes, there is also a need to scrutinize the environmental fates and toxicity of the metabolites generated as a result of pesticides mineralization. Moreover, large scale and in-depth assessment of enzyme-mediated degradation of pesticides are required, as observed in laboratories, under in situ field conditions to appraise the success of enzymatic bioremediation. Future studies should be carried out to characterize the genetic basis of the biodegradation of the pesticide by utilizing advanced omics-based strategies to identify the genes, and intermediate metabolites related to pesticides mineralization. A comprehensive understanding of the long-term ecological and economic impacts concerning enzyme applicability for the remediation of pesticides/herbicides is crucial to apprehend full potential and sustainability of immobilized enzyme technology.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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