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Organochlorine pesticides remediation techniques: Technological perspective and opportunities

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ABSTRACT

Organochlorine pesticides have been widely used in agriculture to control agricultural pests. Although effective in controlling pests, organochlorine pesticides present numerous hazards to ecosystems and human health due to their persistence in the environment, bioaccumulation, and toxicity. Scientific studies have shown that organochlorines may be associated with endocrine and neurological problems. Several strategies have been developed to apply treatment techniques to remove pesticides from various ecosystems, both aquatic and terrestrial. Physicochemical and biological methods have revealed other potentialities for remediation of aqueous environments contaminated with organochlorine pesticides. In addition, combined processes using different approaches have been highlighted as efficient alternatives to mitigate the impacts of agrochemicals on the environment, e.g., physical technique followed by a biological process. However, there are still numerous gaps that need to be explored and elucidated. Therefore, this review addressed the impacts of organochlorine pesticides on ecosystems and some treatment techniques used to remove agrochemicals from water. Furthermore, new findings, technological perspectives, and opportunities on this subject were presented and discussed.

Introduction

Numerous uncertainties that afflict society have been repeatedly addressed in the literature and have worried specialists yearly, mainly about rapid population growth, soil degradation, the emergence of new super-resistant pathogens (Xie et al., 2023), the imbalance of biogeochemical cycles, and the exaggerated use of agrochemicals in farming (Silva and Baltrusaitis, 2021). Challenges related to the current agricultural system have raised questions in the scientific community about the potential long-term impacts on society. Pollution of water and soil by a variety of substances, such as pesticides, has led to ecosystem degradation and new diseases. Pesticides are chemical substances commonly used in agriculture to control pests, diseases, and weeds that affect agriculture. Pesticides are essential for successful agricultural productivity and ensuring food security. However, pesticides pose significant risks to the environment and human health (de Oliveira et al., 2021).

Excessive use of pesticides can lead to soil, water, and air contamination, causing an imbalance in natural ecosystems (Yang et al., 2022). Fig. 1 illustrates the possible pathways of ecosystem contamination by pesticides. Contamination of water bodies can harm aquatic life, resulting in ecological imbalances and risks to human health. According to the World Health Organization (WHO), many people are affected by acute poisoning caused by exposure to agrochemicals (da Silva Júnior et al., 2022). Direct or indirect exposure to pesticides can trigger numerous health problems in the body, for example, in the endocrine and nervous systems (Kumar et al., 2023; Rohani, 2023; Scorza et al., 2023). Populations that are widely exposed to pesticides, such as

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farmers, are even more vulnerable to pesticide hazards.

Organochlorine pesticides (OP) are agrochemicals widely used in agriculture (Kida et al., 2018). They have raised concern among specialists due to their persistence in the environment and their ability to accumulate in organisms along the food chain (Jayaraj et al., 2016). There are numerous types of organochlorine pesticides, for example, methoxychlor and dicofol. However, some organochlorine pesticides have been banned in recent years due to adverse effects on the environment and human health (Chehade et al., 2022). Recent publications have increasingly reported progress in the ecological remediation of pesticides (Muñoz-Palazon et al., 2023; Pillay et al., 2022; Saleh et al., 2020). The application of physical, chemical, and biological techniques, such as adsorption and bioremediation, has been shown as a solution to mitigate the environmental impacts caused by pesticides (Dutta et al., 2022).

Pesticides play an important role in agriculture. On the other hand, their inappropriate application can have adverse effects on both nature and human health. As uncertainties surrounding the use of agrochemicals continue to rise, it is imperative to consider the preservation of important and scarce resources such as water for future generations. Therefore, it is critical to address questions regarding the use of pesticides to produce a long-term solution to their impact on the environment and human health. Hence, this review aims to examine the effects of organochlorine pesticides on ecosystems and evaluate various treatment techniques used to remove agrochemicals from water. Moreover, new findings, technological perspectives, and opportunities on this topic are presented and discussed.

Organochlorine pesticides and adverse impacts

Literature shows that numerous pesticides are applied in agriculture, and approximately 40% of them are organochlorines (Jayaraj et al., 2016). In addition, OP have been widely used in emerging countries due to their economic viability. OP have numerous properties and therefore have been applied not only in farming for the elimination of insects. Also, OP have been used indiscriminately for pest control in households and industries. Organochlorines are considered highly hazardous and have high solubility. The overuse of agrochemicals in crops has resulted in numerous adverse on public health impacts. Some reports have linked organochlorines to various adverse outcomes, for example, Parkinson's disease (Pouchieu et al., 2018). Prolonged exposure to organochlorines can cause the compounds to accumulate in the body and affect organs and reproduction (Jayaraj et al., 2016; Witczak et al., 2021). The main organochlorines used in agriculture are dichlorodiphenyltrichloroethane (DDT), lindane (γ-HCH), and chlordane (Kida et al., 2018).

DDT is an organochlorine pesticide commonly used for insect control (Yang et al., 2022). This pesticide is soluble in organic solvents and insoluble in water, allowing it to accumulate in the tissues of living organisms (Wang et al., 2023). Considering its impact on the environment and human health, many countries have restricted the use of DDT

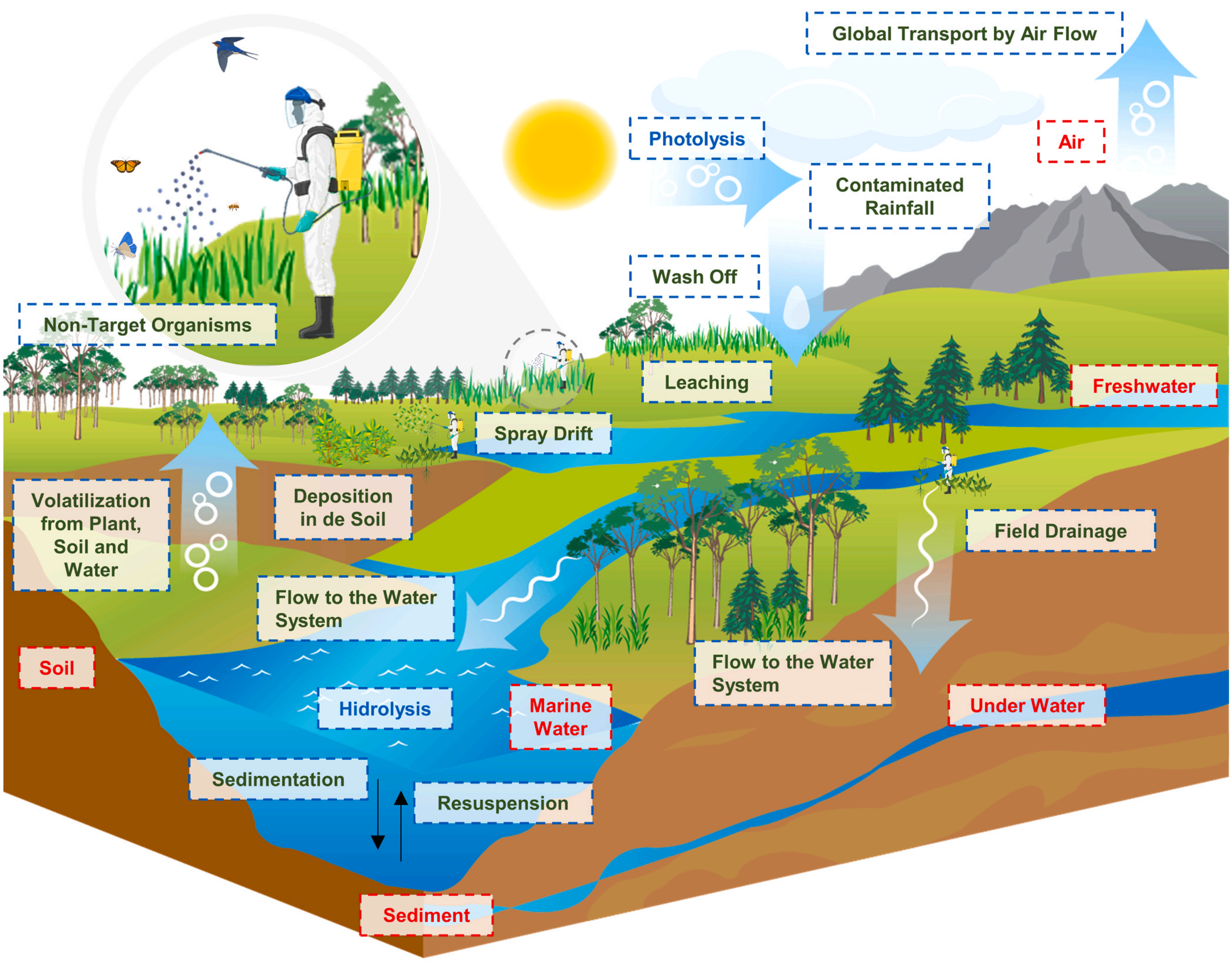

Fig. 1. Possible pathways of contamination by organochlorine pesticides used in agriculture.

in agriculture. However, India still allows the production of DDT, and other countries, such as Colombia and Brazil, use it for malaria control (van den Berg et al., 2017). Given its high persistence in the environment (Jayaraj et al., 2016), regular monitoring of water and soil at DDT is essential. Bioaccumulation of organochlorine compounds in living organisms can disrupt the food chain and lead to several adverse effects, including reduced biodiversity and imbalanced aquatic ecosystems (da Silva Júnior et al., 2022). Moreover, studies suggest that DDT and similar substances may interfere with estrogen receptors and cause estrogenic effects (Wang et al., 2023). In fact, a pilot study has shown that in vivo exposure of rats to DDT specifically alters mitochondrial function in skeletal muscle (Chehade et al., 2022).

Lindane ((1r,2 R,3 S,4r,5 R,6 S)-hexachlorocyclohexane, also called γ-HCH) is another organochlorine pesticide widely used for agricultural pest control and seed treatment (Xu et al., 2020). Such as DDT, γ-HCH is also persistent and can accumulate in the tissues of living organisms. The presence of γ-HCH in soils, waters, and organisms can lead to irreversible impacts. Prolonged exposure to γ-HCH has been reported to have adverse effects on human health, such as on the neurological and endocrine systems. γ-HCH is well documented to exhibit neurotoxicity, and one of the most concerning toxic targets of lindane is the γ-aminobutyric acid (GABA) receptors. The use of γ-HCH has been banned in many countries (Johri et al., 2000). However, residues can still be detected in aqueous environments. Exposure of earthworms to aged lindane has been reported (Xu et al., 2020). Exposure to aged lindane caused GABA-independent inhibitory toxicity of acetylcholine and induced changes in earthworm locomotion, suggesting that the pesticide, whether in a free or bound state, could exert significant effects when present in the organism.

Chlordane, a broad-spectrum pesticide used to treat various crop pests, can be synthesized by the Diels-Alder reaction followed by a chlorination process that yields a mixture of isomers (Wu et al., 2021). In recognition of its harmful effects on the environment and human health, the U.S. Environmental Protection Agency (EPA) has implemented a complete ban on the use of chlordane (de Oliveira et al., 2023). Notably, chlordane has a high resistance to chemical and biological degradation, which minimizes the likelihood of environmental degradation and mobility. However, in regions with high concentrations of organic solvents, chlordane can dissolve in rainwater and leach into the soil, where it eventually reaches groundwater. A recent study focused on chlordane exposure in *Drosophila* larvae revealed remarkable results (Wu et al., 2021). Exposure to elevated concentrations of chlordane resulted in decreased larval survival. Conversely, exposure to lower pesticide concentrations resulted in impaired glucose and lipid metabolism, increased insulin secretion, and disruption of insulin signaling pathways, highlighting the negative effects of even low levels of chlordane exposure on various physiological processes.

An appropriate management and sustainable agricultural practices are essential to minimize the risks associated with organochlorine pesticides. In general, the presence of OP can cause several negative consequences on the planet due to their chemical properties and persistence in nature. Organochlorine pesticides can be toxic to many aquatic organisms, for example, fish and amphibians. The imbalance of marine ecosystems caused by OP can lead to a decline in biodiversity and indiscriminate food chain contamination. In addition, OP are recognized for their high persistence in the environment, i.e., degradation occurs slowly in nature. The risks of OP exposure to humans are numerous, for example, carcinogenic risks and impacts on the immune system. Prolonged exposure to OP can increase the likelihood of developing some cancers and make organisms more susceptible to infections. Experts also express concern that pesticides could cause genetic mutations in pests that result in their ability to resist their effects (Gardner et al., 1998; Hassan and Nemat Alla, 2005). Genetic mutations are changes in the genetic material of an organism that can be caused by external factors, such as chemical exposure (Gressel, 2011). When pests with mutations that make them resistant reproduce, these genetic traits are transferred to their offspring (ffrench-Constant, 2013). Over time, the pest population may acquire increasing resistance to the pesticide, leading to increased pesticide doses or resort to more effective pesticides. This worrisome cycle may lead to the need for more pesticides to control pests, increasing risks to human health and the environment. One study investigated the genetic basis of resistance in DDT by examining chromosomes in a population of *Drosophila melanogaster* (Dapkus and Merrell, 1977). The study concluded that DDT resistance in a given lineage was associated with three major chromosomes, and the significant differences in chromosome effects and mean dominance suggested that only a limited number of resistance genes were involved. Recently, a model was developed to assess how pesticide doses contribute to the development of resistance (Muniz-Junior et al., 2023). Results suggest that pesticide resistance can increase even at low doses and that reducing the levels of agricultural chemicals in combination with other strategies can reduce resistance over time (Kos et al., 2009). Fig. 2 illustrates some harmful effects caused to ecosystems and living organisms. Thus, it is essential to take effective precautionary and regulatory measures to minimize exposure to agrochemicals and implement safe and sustainable alternatives in the control of agricultural pests.

Treatment techniques

The fate of organochlorine pesticides is not limited to the site of application. Thus, OP can contaminate several ecosystems, both terrestrial and aquatic. Due to the complexity of the contaminant, the removal of agrochemicals from water and soil is still challenging for specialists. Various techniques have been used to remove OP. Conventional water treatment processes, such as adsorption and filtration, can be effective alternatives in the remediation of contaminated systems (Pellenz et al., 2023). Adsorption is a promising strategy for the removal of pesticides from water bodies. The mechanisms controlling adsorption of agrochemicals can be classified into distinct types, including electrostatic, hydrophobic, pore-filling, hydrogen bonding, and π-π interactions (Qiu et al., 2022). These mechanisms are shown in Fig. 3 and illustrate how adsorbents facilitate pesticide removal. The efficiency of the pore-filling process in an adsorbent depends on the molecular size of the compounds and the properties of the pores with which they interact (Jiang et al., 2018). In particular, materials with high porosity exhibit increased surface adsorption capacity. Electrostatic interactions contribute to the formation of ionic bonds and include both attraction and repulsion. This interaction results in pollutants being attracted to opposite charges (Solanki and Boyer, 2017). Hydrogen bonds represent a specific inter- or intramolecular connection (Fang et al., 2021). In certain adsorbents such as biochar, hydrogen bonding is found to be the most important mechanism for adsorption of polar organic compounds (Kamali et al., 2021). Hydrophobic interaction is a multi-layered process involving partitioning and attraction and is influenced by the solubility of the contaminants (Zhang et al., 2018). The formation of π-π interactions involves conjugation between C-C bonds in the adsorbent and benzene rings of the pollutant. The extent of pollutant adsorption on the material is influenced by the presence of oxygen-containing functional groups (Tan et al., 2016). Also, chemical treatments have been reported as attractive alternatives for removing OP from water. The application of oxidizing or reducing chemical agents, such as hydrogen peroxide, which reacts with pesticides and converts them to fewer toxic products, has been used recurrently. Besides, biological treatments using microorganisms to degrade pollutants have achieved promising results in removing pollutants from aqueous systems contaminated with organochlorine pesticides.

Diatomaceous earth functionalized with graphene-magnetite was applied to remove dichlorodiphenyldichloroethylene, dichlorodiphenyldichloroethane, DDT, and methoxychlor (Sanad et al., 2023). The removal efficiency for the organochlorine pesticides tested was 97%. Zerovalent iron supported on biochar produced from *Nephelium lappaceum* bark residues was used to remove six organochlorine

Fig. 2. Some harmful effects caused to ecosystems and living organisms by pesticides.

pesticides from water (Batool et al., 2022). The nanocomposite showed the advantage of adsorption and dechlorination of pesticides in aqueous medium, removing 96–99% (120 min; pH 4). The application of chitosan beads and porous crab shell powder to remove numerous organochlorine pesticides in an aqueous solution was reported (Lu et al., 2011). Adsorption of pesticides by chitosan beads and crab shell powder showed efficient removal of pollutants at concentrations ranging from 2.0 ng•mL^{-1} to 2.8 ng•mL^{-1} (> 99%).

Recently, the application of oxidation with hydrogen peroxide, the use of ultrasonic waves, and a combined approach involving both techniques for organochlorine pesticides removal was reported (Kida et al., 2018). Ultrasonic waves were found to be the most effective method for removing organochlorine pesticides from water compared to other treatments. The combined process was also proved to be more efficient than hydrogen peroxide alone. Photocatalytic degradation of organochlorine pesticides using a biologically produced bismuth vanadate catalyst has been reported (Chawla et al., 2022). Bio-fabricated bismuth vanadate nanoflowers showed promising photocatalytic fragmentation in the degradation of 2,4-dichloro phenoxy acetic acid and 2-(2,4-dichloro phenoxy)propionic acid of 90.2% and 70.52%, respectively. Immobilized titanium dioxide was applied to remove several pesticides via solar still (Gandhi et al., 2021). Promising removals were achieved with α-hexachlorocyclohexane and fenvalerate of 82.9% and 94.4%, respectively.

Microbial degradation of 2,4-dichlorophenoxyacetic acid by axenic and mixed consortium has been recently reported (Vanitha et al., 2023). The efficiency of pesticide degradation by axenic culture and mixed intercropping showed virtually complete removal and 85–90%, respectively. Another study that applied a lindane-degrading bacteria isolated from an agricultural field removed 90% of the pesticide (Sahoo et al., 2019). The strain produced a biofilm, in which the addition of substrate increased biofilm formation. In addition, the strain demonstrated the ability to promote plant growth, a promising property for bioremediation of soils contaminated with organochlorine pesticides. Multi-stage constructed wetlands with subsurface flow were used for landfill leachate treatment and remove organochlorine pesticides (Yang et al., 2022). Substrate adsorption (50.55 - 72.74%) and microbial degradation (20.38 - 27.89%) were the main ways of removing pesticides.

There are several ways to treat organochlorine pesticides. The choice of the appropriate treatment technique may depend on numerous variables, such as the chemical properties of the pesticide, the contaminated area, and the economic viability. Furthermore, hybrid techniques that utilize different approaches are a promising alternative for remediation of systems contaminated with organochlorine pesticides. Pesticide remediation using combined methods offers numerous advantages, such as lower energy costs and simultaneous application to multiple contaminants. The remediation of systems contaminated with organochlorine pesticides has been of great interest to specialists. Thus, continuous efforts to develop new technologies that efficiently remove or degrade pesticides have become a trend.

Advances and limitations

Pesticides play an important role in agriculture, as they may control agricultural pests, prevent crop losses, increase productivity, and ensure food quality. However, the excessive use of agrochemicals in agriculture, application without professional supervision, non-use of safety equipment, ineffective monitoring of environmental ecosystems, lack of environmental regulation, and inefficiency of some treatment techniques pose some challenges (da Silva Júnior et al., 2022). Organochlorine pesticides are widely used worldwide, with a significant proportion of these substances entering the environment due to uncontrolled spraying, leaching, volatilization, and sedimentation. Consequently, only a fraction of the pesticides applied actually reaches the target organisms. This loss of pesticides poses a major challenge to ecosystems by creating imbalances in biogeochemical cycles and endangering non-target organisms. In addition, the long shelf-life of organochlorine compounds exacerbates the difficulty of effectively treating these contaminants. Given the persistence of organochlorine

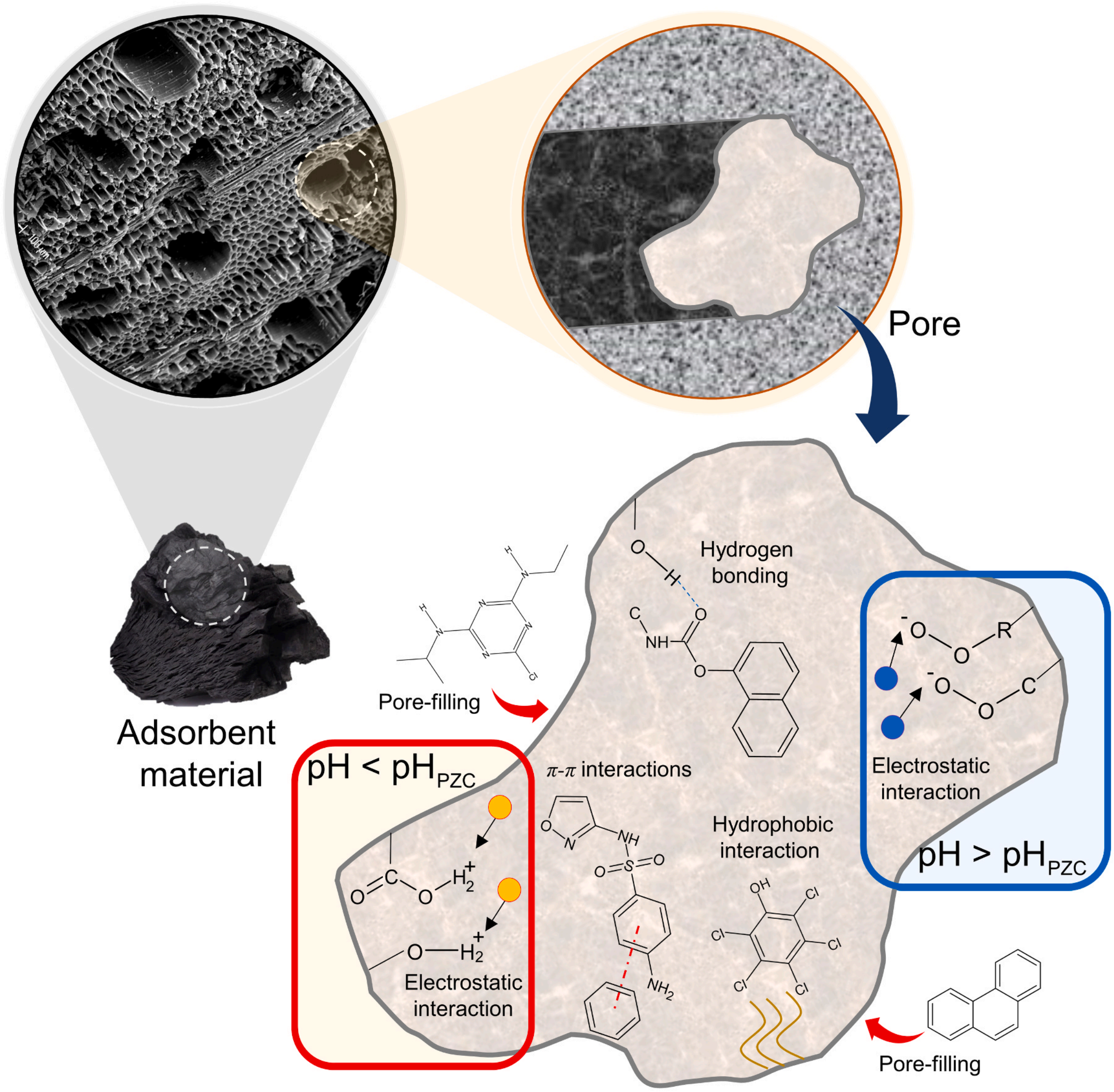

Fig. 3. Some reaction mechanisms in an adsorbent for pesticide removal.

pesticides in the environment, advanced technologies that can efficiently degrade these pollutants are necessary. Several strategies proposed by experts aim to mitigate the environmental and biological impacts of these pesticides. These strategies include reducing the application dose of agrochemicals and exploring new sustainable treatment methods for contaminated systems. Moreover, agricultural research has focused on the development and use of novel pesticides that have a different mode of action and lower resistance potential. These include innovations such as controlled-release agrochemicals and biopesticides (de Oliveira et al., 2020; Júnior et al., 2020; Sarwar, 2015). The controlled release technique involves the gradual release of pesticides in appropriate amounts based on the specific requirements of the crop. This method prevents excessive use of agrochemicals beyond what is necessary to control target pests (de Oliveira et al., 2020). Biopesticides, categorized as biochemical agents, control pests in a non-toxic manner. These agents consist of living organisms, their derivatives, or by-products and effectively control pests that are harmful to plant life (Sarwar, 2015). The integration of biopesticides with other strategies has gained prominence in agricultural science and offers a holistic approach to mitigate the impact of agrochemical use on crops (Hazra et al., 2017). However, there are still gaps that need to be addressed, such as: (a) addressing the operational consequences of large-scale extensive treatment caused by the simultaneous presence of pesticides and persistent pollutants such as microplastics and metallic nanoparticles in the natural environment (de Oliveira et al., 2023); (b) ensure the effectiveness of monitoring procedures to track the presence of pesticides in crops. This action aims to facilitate comprehensive management of environmental impacts and prevent irreversible consequences; (c) mitigate potential long-term risks to human and animal welfare from consumption of contaminated resources such as agricultural products and drinking water; (d) overcome the lack of comprehensive studies on the application of biological treatment techniques in contaminated areas.

Therefore, it is critical to emphasize the importance of continued research and further investigation to address the unanswered questions related to the use and effects of organochlorine pesticides. These ongoing efforts are essential to finding effective solutions and improving our understanding of the complex interactions between pesticides, the environment, and living organisms. Lastly, more studies aiming to enhance the understanding of the significant concerns regarding organochlorine pesticides should focus on the following: (a) deepen research on the interaction mechanisms with the soil, plants, microbiota, and pesticides for the new efficient formulations' sustainable development; (b) development of new efficient remediation strategies for numerous pesticides classes over a wide concentration range; (c) large-scale studies of pesticide degradation mediated by biological techniques, e.g., enzymatic bioremediation; and (d) mapping of organochlorine pesticide sources arising from anthropogenic activities.

Conclusions and future perspectives

Contamination of aquatic and terrestrial ecosystems by organochlorine pesticides has been recurrently reported. OP pollution has been a danger to the planet, mainly due to the appearance of diseases caused by pesticides. Understanding the fate, transport, transformation, toxicity, and impacts generated by organochlorine pesticides on the ecosystem must be systematically evaluated to elucidate the problems. New treatment techniques have been reported as efficient, for example, adsorption, ultrasonic waves, and bioremediation. OP treatment technologies must be viable and efficient in removing pollutants. However, developing treatment methods with advanced, accessible, and sustainable performance has been a significant challenge to make remediation widely applicable. In addition, environmentally sustainable treatment technologies that do not generate toxic by-products or waste to the environment have aroused the interest of specialists to deepen their knowledge in biological techniques, for example, phytoremediation. Ongoing research and development of innovative technologies are crucial to addressing the challenges of handling organochlorine pesticides. The research focus has been the study of new materials, advanced oxidation techniques, and efficient combined processes. Finally, collaboration among various entities should be encouraged to promote innovation and implement effective solutions to mitigate the environmental and human health impacts of organochlorine pesticides.

CRediT authorship contribution statement

Afonso Henrique da Silva Júnior: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. **Carlos Rafael Silva de Oliveira:** Investigation, Writing – review & editing. **Tarcísio Wolff Leal:** Investigation, Writing – review & editing. **António Benjamim Mapossa:** Investigation, Writing – review & editing. **Juliane Fiates:** Investigation, Writing – review & editing. **Antônio Augusto Ulson de Souza:** Supervision, Validation. **Selene Maria de Arruda Guelli Ulson de Souza:** Supervision, Validation. **Adriano da Silva:** Project administration, Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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