




Review

The Socio-Environmental and Human Health Problems Related to the Use of Pesticides and the Use of Advanced Oxidative Processes for Their Degradation: Brazil

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Abstract: The present study reviews the quantitative data on the use of pesticides and their relationship to environmental and human health problems in Brazil. The detection of residual concentrations of pesticides in food and water consumed by humans has raised questions regarding the overuse of pesticides and their consequences. This global concern was registered as the second goal of sustainable development by the United Nations, which refers to sustainable agriculture and alternatives to pesticides. However, besides recognizing the harmful effects of these contaminants on the environment and human health, there is also a need to understand treatment techniques that can remedy the existing conditions and thus alleviate the problems that affect water treatment plants. In this context, this study compiles information pertinent to the use of pesticides and highlights the prospects for the degradation of these persistent pollutants with emphasis on Brazilian data, one of the countries that had the greatest increase in the consumption of pesticides in the world.

Keywords: pesticides; AOP; persistent organic pollutants



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1. Introduction

There are countless purposes for the use of pesticides; however, the main objective is to intensify agricultural production, whether for the control of pests, pathogens, or diseases, for hormonal and growth control, as well as changes in plant metabolism [1]. However, resistance to pesticides and adaptation of target pests has resulted in large production losses and increased dosages applied to crops. In the 1940s, U.S. farmers lost 7% of their crops to pests, and since the 1980s, the percentage loss has increased to 13%, even though more pesticides are being used. This is attributed to the fact that more than 500 pest species have developed resistance to pesticides, which is often caused by the continued use of pesticides of the same classes [2].

For several years, the use of pesticides produced high yields in the agricultural sector; however, the misuse or overuse of these compounds can cause substantial harm to human health and the environment. In the 1960s, researchers demonstrated that organochlorine pesticides (OCPs) cause physiological and environmental disturbances; however, they are still used in agriculture and remain a source of poisoning in humans [3].

The disposal of effluents from pesticide manufacturing industries and the extensive use of pesticides in agricultural fields lead to the contamination of surface and underground watercourses. In 2019, the Oswaldo Cruz Foundation warned about data from the Ministry of Health's Water Quality Surveillance Information System for Human Consumption (SISAGUA) regarding the presence of pesticides in drinking water and classified it as a systemic contamination in water; more than 27 pesticides were detected in 25% of Brazilian municipalities. Furthermore, it is evident that conventional water treatment methods are not sufficient for removing these contaminants.

As most pesticides are toxic and hazardous in nature, it is essential to develop effective methods for the degradation of these pesticides [4]. Water treatment technologies have emerged for the degradation of a wide class of persistent contaminants. Among these technologies, advanced oxidative processes (AOPs) have shown promising results because they are based on the generation of highly oxidizing radicals capable of degrading these pollutants [5–7].

The present study aimed to review the socioenvironmental and human health issues of pesticides related. The study also identified recent studies that refer to the use of AOPs for the degradation of chemical pesticides.

2. Development

2.1. *The Socio-Environmental and Human Health Issues Related to the Use of Agrochemicals in Brazil*

The total number of inhabitants on the planet should exceed the current 7.7 billion to 9.7 billion in 2050, which is why high-scale food production is a factor of great importance for all sectors of society [8]. For this, food production uses several tools to increase its productivity, with pesticides being one of the most used for this purpose, offering consumers good-looking products. The quality of food with regard to chemical residues is something of concern for human health as it has the potential for the development of pathologies, such as cancer [9].

According to the FAO report [10], in 2020, the Americas were responsible for the largest import of pesticides and the highest levels of application, reaching 1.17 kg per person per year, with the US, followed by Brazil, being the largest consumers. Carneiro et al. (2022) [11] warned about the biased change in Brazilian legislation that aimed to prioritize the productive sector without complying with environmental integrity; as an example, he cited the authorization of the Brazilian government for the use of 562 new pesticides in 2021, many of which were banned in other countries.

Currently, 399 active ingredients of pesticides registered in Brazil for agricultural use were identified, excluding microbiological and biological control agents, making Brazil a leader both in the use, purchase, and sale of pesticides [8,9].

In November 2017, the North American Space Agency (NASA) and the United States Geological Survey (USGS) carried out a mapping and calculations based on the Landsat 8 satellite of the cultivated area of the planet, aiming to subsidize food security. According to the study, there are about 1.87 billion hectares of crops in the world, while the world population reached 7.6 billion in 2017; that is, an average of four people can be fed per hectare [12].

According to the National Health Surveillance Agency (Anvisa), the world pesticide market grew 93% in the last decade, while the Brazilian market grew 190%. In the 2011 Brazilian harvest, 71 million hectares of temporary crops (soybeans, corn, sugarcane, and cotton) and permanent crops (coffee, citrus fruits, and eucalyptus) were planted, which is equivalent to spraying around 853 million liters (formulated products, i.e., pesticides) on these crops, mainly herbicides, fungicides, and insecticides, with an average of 12 L per hectare and an average of 4.5 L of pesticides per resident in environmental exposure/occupation/food [13].

According to calculations by Embrapa Territorial (2017) [14], Brazil occupies fifth place in the ranking of a cultivated area with about 65,913,738 hectares planted, which

corroborates studies published by NASA, with values of 63,994,479 hectares planted in the country. However, the productivity of crops can vary greatly, depending on soils, climate, the technology used, and the type and quality of crops produced, as well as the management used. This results in large differences between the agricultural performances of different cultivars [15].

The large planted area in Brazil has made the country the world's largest consumer of pesticides, with an alert status considering the high level of pesticide residues in food consumed by individuals. The implementation of policies such as the Green Revolution, genetically modified crops, the increase in "pests" in crops, agricultural credit subsidies, and tax exemptions are factors that have contributed to the increase in pesticide consumption. In addition to these factors, there is weak state supervision of their use, as well as the lack of policies to reduce the use of pesticides and encourage agroecological production. In large areas of monoculture, these toxic solutions are sprayed onto crops by tractors and planes, affecting not only plant "pests" but also nontarget organisms and environmental substrates such as soil, water, and air [16].

The Water Map was a study compiled from the Ministry of Health database, using data from analyzes of water treated by companies and agencies responsible for supply. The study detected chemical and radioactive substances that may pose a health risk. In some cases, the concentrations exceeded the established maximum limit, and a total of 65 substances were detected, the majority being derived from pesticides. They were divided into two groups: those most at risk of developing chronic illnesses such as cancer; substances that pose health risks, which include all other substances that also pose risks, according to the international literature and the Ministry of Health [17].

These substances can be decisive in relation to their effects on human health, depending on the form and duration of exposure and the type of specific toxicity of the product. The effect can be acute due to short-term exposure (i.e., hours or days), with quick and noticeable signs and symptoms typical of product intoxication or other adverse reactions such as skin lesions, skin irritation, mucous membranes of the eyes, nose and throat, stomach pain (epigastric pain), nausea, vomiting, diarrhea, dehydration or chronic, with prolonged exposure over the years, with generally irreversible adverse effects such as various tumors (hepatic, brain, and lung tumors) genetic malformations (teratogenicity) and allergies among others [18].

From 2007 to 2011, according to the Notifiable Diseases Information System (SINAN), the number of new accidents at work with pesticides increased by 67.4%, and the coefficient of intoxication increased by 126.8%, with this increase being greater among women (178%) [9]. Therefore, this process led to social, environmental, and public health problems.

The legislation on pesticides and the like n° 7.802, of 11 July 1989, establishes that pesticides can only be used in Brazil if they have registrations in the competent federal agencies and in accordance with the guidelines and requirements of the agencies responsible for the areas of health, the environment, and agriculture. However, Brazilian legislation does not provide for periodic review of the registration of pesticides, and even today, products prohibited in other countries are used [8,19].

Furthermore, Decree No. 4074 of 4 January 2002, which regulates Law No. 7802/1989, establishes powers for the three bodies involved in registration: Anvisa, together to the Ministry of Health; Brazilian Institute of the Environment (IBAMA), together to the Ministry of the Environment; Ministry of Agriculture, Livestock and Supply [20].

Anvisa, in turn, toxicologically evaluates and classifies pesticides, and the results of toxicological analyzes are used to calculate the safety parameters, which consist of the acceptable daily intake (ADI) of each active ingredient. Ordinance 3 of 16 January 1992 establishes that the acceptable daily dose or acceptable daily intake (ADI) is the maximum amount that, ingested daily throughout life, does not seem to pose an appreciable risk to health, expressed in mg of pesticide per kg of body weight (mg/kg bw), based on these Anvisa results, predict the maximum residue limit (MRL) and the safety interval [21–23].

The MRL is regulated by Anvisa through the analysis of these results so that new products are registered or even postregistration, observing the residual concentrations in food products [22].

Ordinance 3 of 16 January 1992 regulates the safety interval or grace period, which is the time between the last application of the pesticide and the harvest or sale of the product. When the treatment is postharvest, it will be the time interval between the last application and the commercialization. In Brazil, there have been several policies regarding the production and use of pesticides, with the aim of increasing productivity and, in this sense, causing environmental, social, and public health damage, consolidating Brazil as one of the largest consumers of pesticides [24].

Notification of pesticide poisoning is mandatory and must be carried out by the health professional or person responsible for the care service, which provides the first care to the patient within 24 h of that care, using the fastest means available. In 2015, 11,863 cases of pesticide poisoning were reported across the country. In 2014, 12,695 notifications were registered. From 2007 to 2017, there have been more than 26 thousand cases of intoxication and more than 12 thousand cases of suicide attempts. In cases of poisoning, there are bodies that assist in emergency care, such as the management committee, representatives of the Brazilian Association of Toxicological Information Centers (ABRACIT), the Toxicological Information and Assistance Centers (CIATOX), toxicologists from university centers in the country and doctors of the work of the State Health Secretariats [25].

Thus, there is an increasingly evident need to predict the main effects on populations, communities, ecosystems, and other biological entities at a higher organizational level. The main routes of exposure to these products are ingestion, inhalation, and dermal absorption, making it necessary to survey the toxicity of these substances, as well as the importance of public policies for the reduction in these pesticides in food production, in the implementation of agroforestry, organic production, use of pesticides with more criteria for use and thus having a more conscious use of these products [26].

2.2. Main Classes of Agrochemicals and Their Effects on the Environment

In general, the active compounds of pesticides can be organic or inorganic and enter the water or soil by runoff or by leaching. The first generation of pesticides consisted of inorganic compounds based on arsenic, selenium, lead, copper, sulfur, and mercury and was used until the beginning of the 20th century due to their high toxicity [27]. According to the Abrasco Dossier (2012), organic vegetable and mineral pesticides are also classified as first-generation, and sulfur-based pesticides, boric acid, and arsenic are still used as ant killers [28].

Inorganic insecticides are classified into arsenicals such as white arsenic, aluminum arsenate, calcium, and lead; fluoride (cryolite and sodium fluoride) and miscellaneous composed of lime sulfur, sulfates, and carbonates, among others. Compounds containing arsenic were widely used as insecticides, herbicides, and defoliants [29,30].

Long exposure to inorganic arsenic compounds through drinking water can induce various diseases such as conjunctivitis, hyperkeratosis, hyperpigmentation, cardiovascular diseases, central nervous system and peripheral vascular disorders, skin cancer, and gangrene in the limbs [31].

The second generation of pesticides was characterized by the production of synthetic organic pesticides, resulting from the development of the chemical industry, especially after the Second World War, and are still the most used today [28]. The high range of new pesticides required the categorization of these compounds into classes characterized by their standards. The most common criteria for pesticide classifications are the following: mode of action and/or mode of entry in which the pesticide reaches the target pest or the approach by which a pesticide controls or kills the target pest; the chemical structure; the characteristics of pesticides and the characteristics of target pests [32].

As for its permanence in the environment, there are two main biological mechanisms that imply the decomposition of pesticides. The first is the microbiological interactions in

water and soil, while the second corresponds to the decomposition of the pesticide by the metabolism of living organisms that consume it as part of their food absorption [32].

Pesticides are more frequently classified according to their chemical structure. The most used classes of pesticides are organochlorines (OCPs), organophosphates (OPs), cabamates, pyrethroids, and neonitocinoids, which represent the most important class of synthetic insecticides in recent decades.

Table 1 lists some of the active ingredients and the most widely used pesticides in the world.

Table 1. Active ingredient and use of some agrochemicals.

| Active Ingredient | Use | Chemical Group | * µg/L |
|-------------------|--------------|-------------------|--------|
| Glyphosate | Herbicide | OP | 500 |
| Atrazine | Herbicide | Triazine | 2 |
| Parachat | Herbicide | Bipyridilium | 13 |
| DDT | Insecticidal | OCP | 1 |
| 2,4-D | Herbicide | OCP | 30 |
| Malation | Insecticidal | OP | 60 |
| Fipronil | Insecticidal | OCP | 1.2 |
| S-metolachlor | Herbicide | Chloroacetanilide | 10 |
| Lindane | Insecticidal | OCP | 2 |
| Thiamethoxam | Insecticidal | Neonicotinoid | 36 |
| Aldicarb | Insecticidal | Carbamate | 10 |

Notes: * Maximum value allowed for drinking water in Brazil (MS 888/2021) [33].

Many pesticides, mainly organochlorines, from both agricultural and industrial sources have high resistance to chemical and biological degradation and high solubility in lipids [34]. Both polychlorinated biphenyl residues and organochlorine pesticide residues are very persistent in the environment and, due to their liposolubility, end up in the fat of living beings, causing problems of contamination of food and human organisms [35].

The application of most OCPs was prohibited or restricted for a period in many countries, as their residues induce constant and significant impacts on the environment and ecosystems. They have been used mainly to control pests since the early 1980s; however, small amounts of DDT (dichlorodiphenyltrichloroethane) and HCH (hexachlorocyclohexane) are still produced as feedstocks for other chemicals or for export [36].

Insecticides from the cyclodiene group (endosulfan/Thiodan/lindane) and phenylpyrazoles (fipronil/Regent/etiprole) are also chlorinated. Lindane is a pesticide that is on the list of substances banned by Anvisa due to its high environmental persistence and neurotoxicity [37].

Fipronil has been proven to offer low-dose and highly effective insect control against a wide range of pests. Major agricultural uses include sugar cane, rice, and maize. In nonagricultural areas, control of cockroaches and ants stands out [38].

Ethiprole in mammals has low acute toxicity by oral, dermal, and inhalation routes, and the exact mechanism of toxicity in humans is not known. Toxicological studies suggest that the administration of ethiprole induces drug-metabolizing liver enzymes showing similarity to induction by phenobarbital [39].

Figure 1 shows some chemical structures of OCPs.

Organophosphates were discovered in the early 1930s in the Bayer division of the chemical conglomerate I.G. Farben. Although their use is decreasing due to regulatory action, organophosphates are still widely used for their broad spectrum of activity, flexibility of use, and good residual characteristics [38].

Organophosphates are commonly used in insecticides, herbicides, fungicides, agriculture, homes, and gardens. They have also been exploited as chemical weapons in the form of nerve agents. Among the OPs, the insecticide paraoxon and the herbicide dimethyl p-nitrophenylphosphate (DMNP) are the most studied substrates for OP decontamination.

Thus, rigorous efforts have been made to design molecules to remove or convert OPs into their nontoxic forms [40].

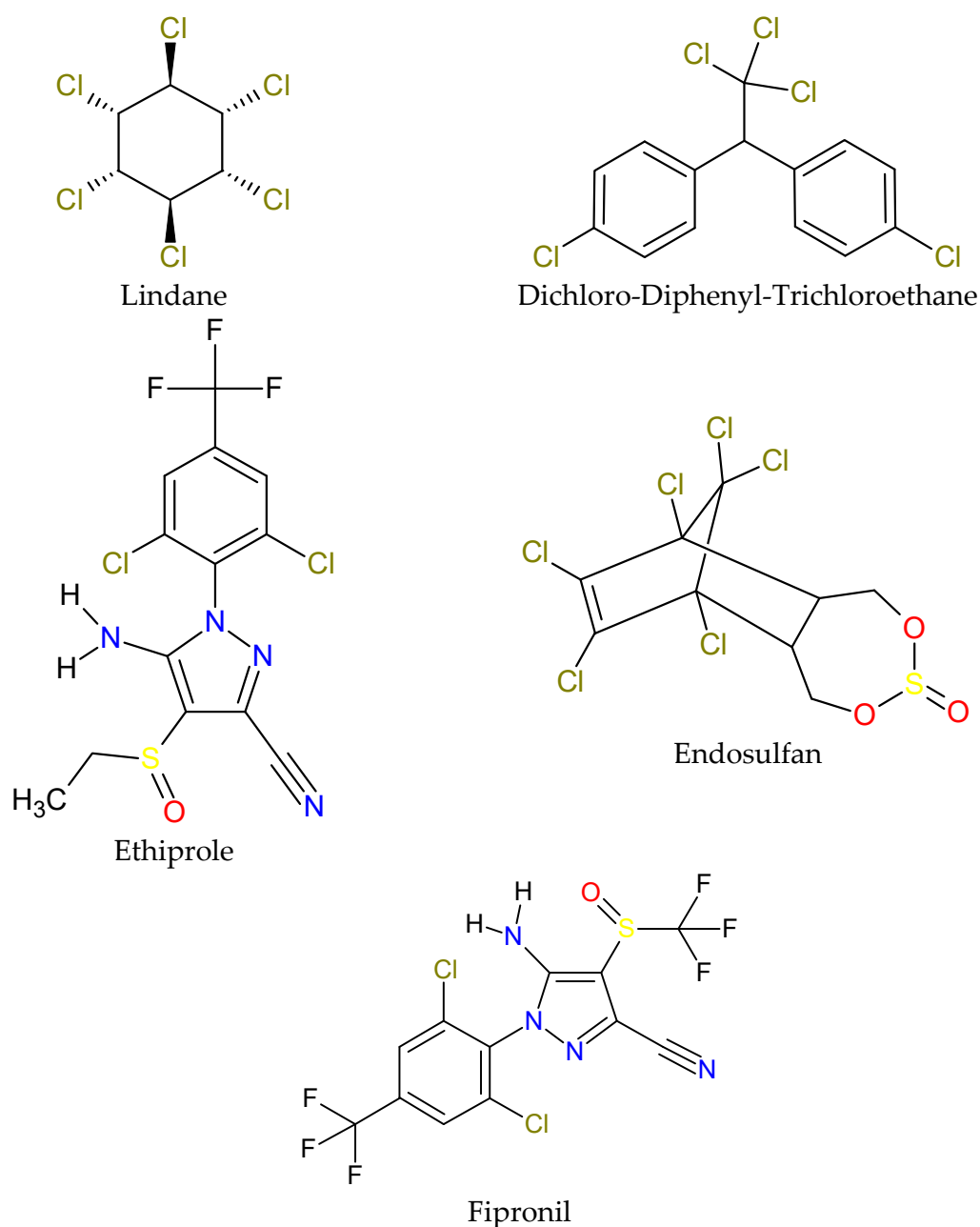


Figure 1. Structural formula of some of the major organochlorines (OCPs).

The excessive application of organophosphates in agriculture results in environmental impacts with devastating effects on pollinators and aquatic life, and this poses an immediate risk to health and sustainability [41]. The insecticide OP Dimethoate is used for the control of aphids and certain other pests on wheat, rye, triticale, sugar beet and other beet crops, seed crops, and ornamental plant production. When applied to standing water where mosquitoes breed, it acts as a larvicide, interrupting the life cycle of malarial protozoan parasites [38]. Terbufos is an OP insecticide and nematicide applied to the soil in cotton, peanuts, bananas, coffee, sugar cane, beans, and corn crops [42].

The structures of the main OPs are presented in Figure 2.

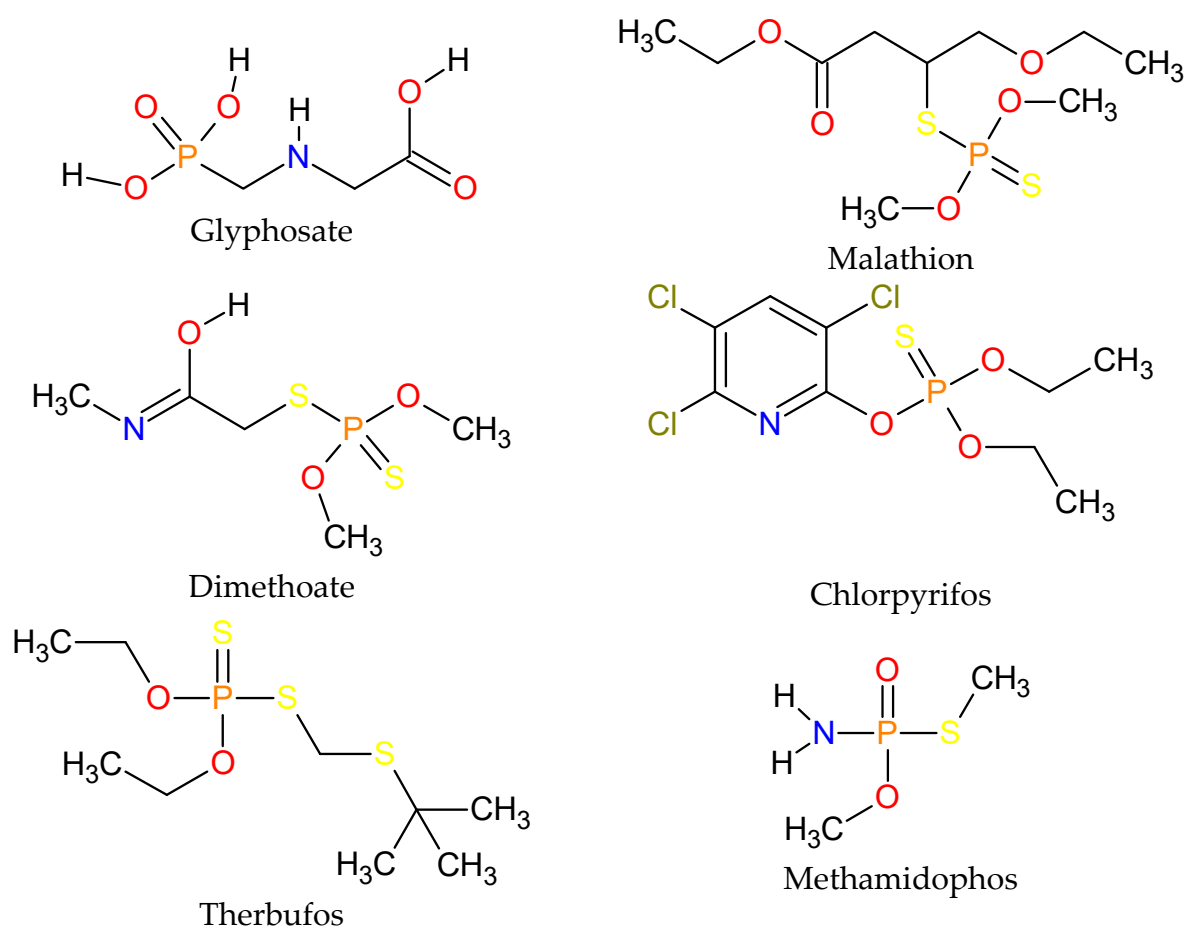


Figure 2. Structural formula of the main organophosphates (OPs).

Carbamates are organic pesticides derived from carbonic acid (Figure 3) and are structurally similar to organophosphates derived from phosphorus acid. Both classes of pesticides affect nerve signal transmission and can result in death from poisoning; they also act as stomach contact poisons, as well as fumigants (toxic vapors) [43].

Carbamate pesticides are widely used in agriculture and have broad biological activity, low bioaccumulation, toxicity to mammals, and short residual life. Although these pesticides can be degraded, their residues can still be found in some foods due to excessive use, which can enter the human body through the direct consumption of contaminated foods such as wine, juice, and milk. Carbamate pesticides are strong endocrine and central nervous system disruptors; at low doses, they can harm humans and animals [44].

The insecticidal activity of carbamates was first discovered in 1947 at the Geigy Company in Switzerland. However, it was only in 1956 that carbaryl, the first successful insecticidal carbamate, was introduced by Union Carbide [38].

Carbamates are primarily broad-spectrum insecticides used on cotton, fruit, vegetables, row crops, and forage. Carbaryl, which has a broad spectrum and low toxicity to mammals, is marketed under the trade name Sevin®. Some carbamates are systemic and can be applied in soil or seed treatment [38].

Systemic insecticides are those that, applied to leaves, branches, roots, soil, or similar, are absorbed and carried along with the sap to the various regions of the plant, acting on sucking insects or, sometimes, on chewing insects in the initial stages of development, different from the contact insecticides that act on the external part of the plant [45].

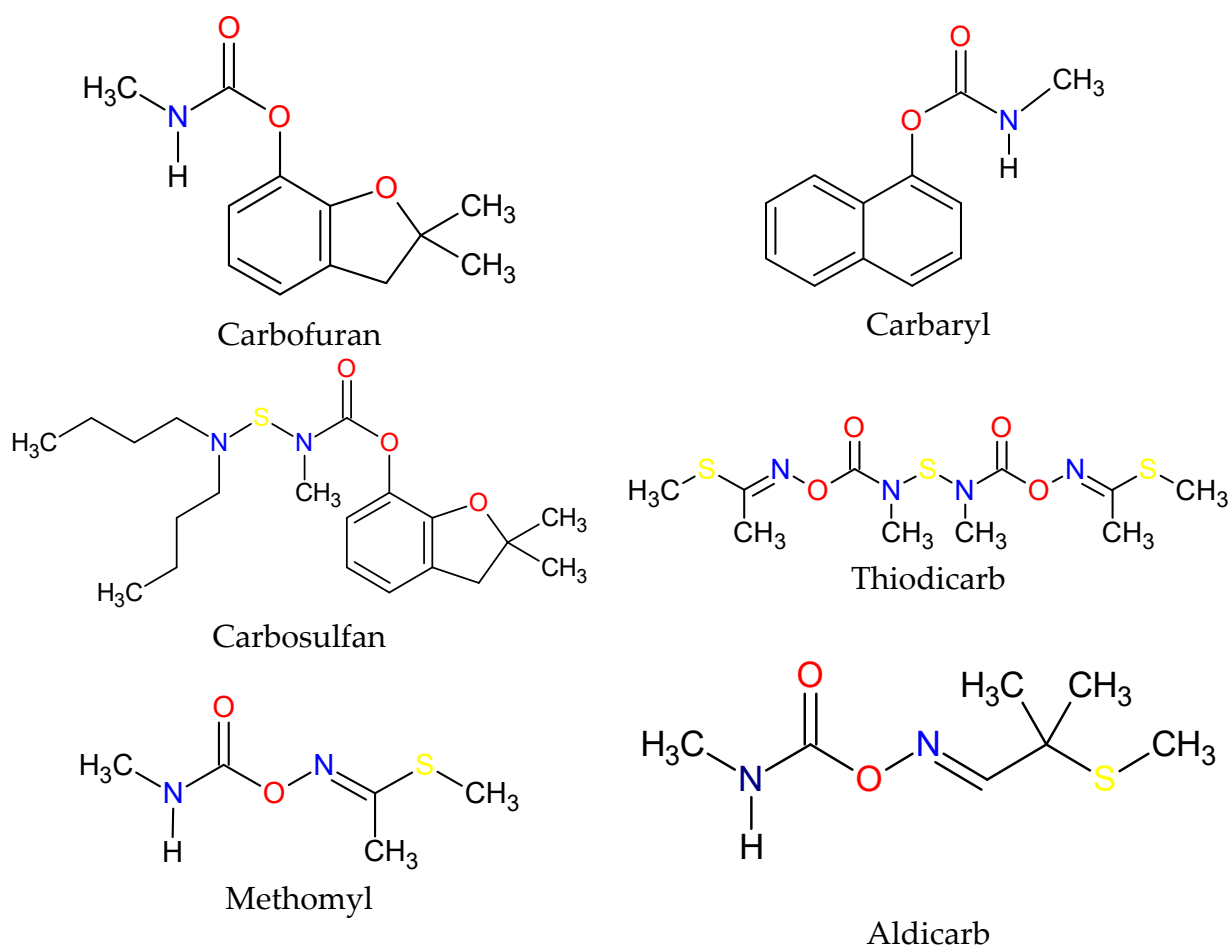


Figure 3. Structural formula of the main carbamates.

Thiodicarb belongs to the methylcarbamate oxime group. It is usually applied to the leaves of cotton, millet, corn, and soybean crops, cotton seeds, peanuts, rice, oats, rye, barley, beans, sunflower, castor beans, corn, soybeans, sorghum, and wheat, in sugarcane stalks and soybean seeds in the planting furrow, preplanting in soybean crops, and in the soil of coffee crops [42]. Figure 3 shows the chemical structure of the carbamates.

Pyrethroid insecticides are important alternatives for the chemical control of soybean pests when compared to phosphorus and carbamates insecticides, which are generally highly toxic to humans [46].

Pyrethroids were specifically designed to be more environmentally stable than pyrethrins, whose activity is measured in hours. They provide lasting control and improved mammalian safety over other products already developed. These compounds are generally effective against caterpillars, beetles, certain aphids and mites in crops and are used for mosquito, termite, and cockroach control in nonagricultural segments. Additionally, certain members of the class are used to control ectoparasites in pets and humans. Major applications include foliar sprays on vegetable crops, rapeseed, and cotton, as well as soil and foliar uses on maize [38].

Bifenthrin is an insecticide, formicide, and acaricide of the pyrethroid chemical group and has a specific toxicological classification for each product, according to art. 38 of the Resolution of the Collegiate Board of Directors (RDC N °294) on 29 July 2019. It is applied mainly on the leaves of many vegetables, located in banana crops, in the soil of potato crops, sugarcane, corn, and seeds of cotton, rice, beans, corn, soybeans, wheat, and stored products of rice, barley, beans, corn, and wheat [42].

In the late 1990s, pyrethroid insecticides accounted for a quarter of the global insecticide market and gained importance because of their low mammalian and high insect

toxicity, even at low doses [41]. These compounds are eventually degraded by microorganisms in soil and water and can also be degraded by sunlight on the surface of water, soil, or plants. Some pyrethroids can persist in the environment for a few months before being degraded [47].

Pyrethroid residues are often detected in different environmental compartments, including agricultural and nonagricultural sediments. Once they enter an aquatic system, pyrethroids rapidly dissipate from the dissolved aqueous phase, and organic carbon binds to the sediment particles. However, sediment-associated pyrethroids pose no risk to non-target organisms because of chemical decomposition that transforms primary agents into secondary agents [48]. Figure 4 shows the main pyrethroids.

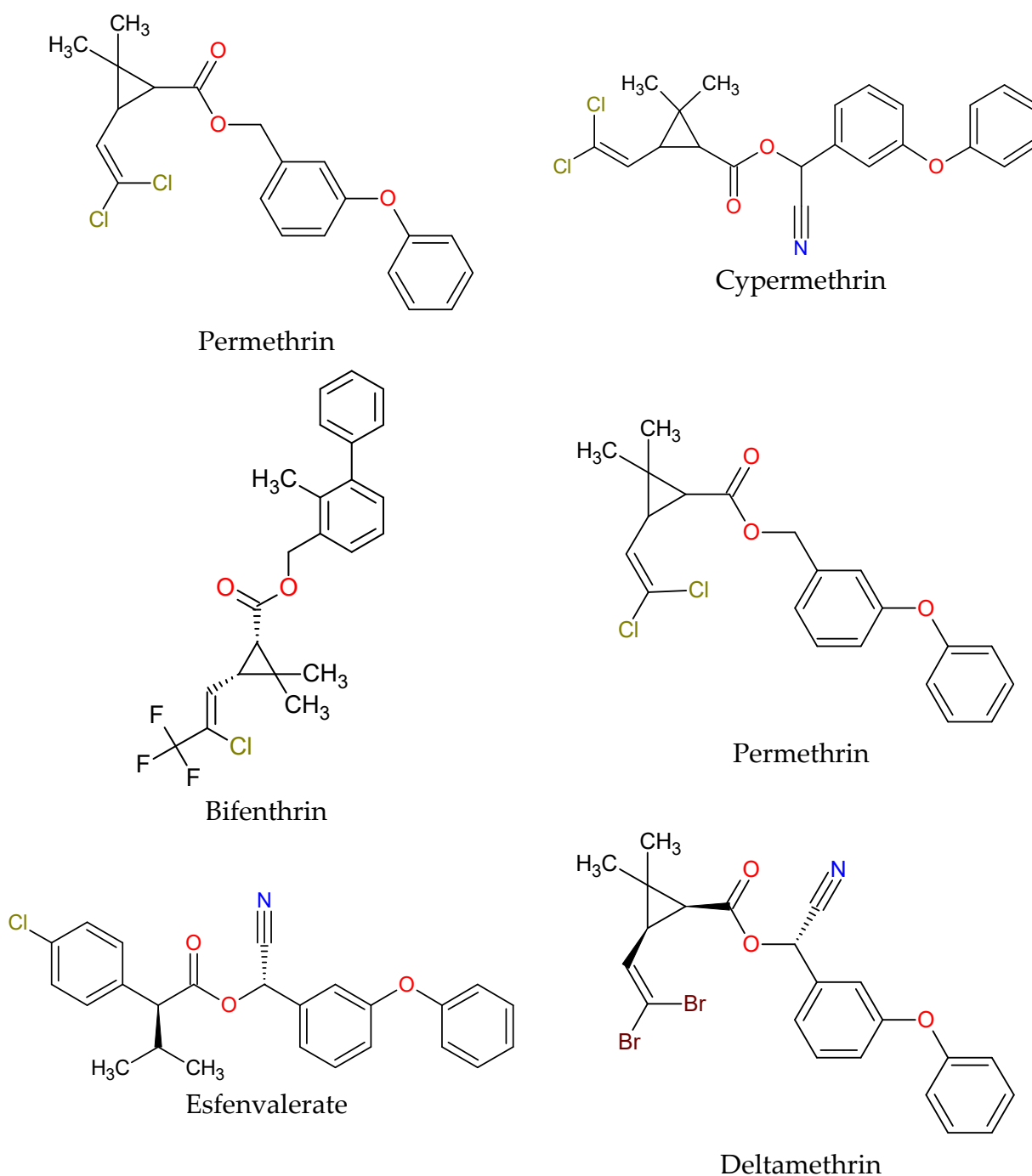


Figure 4. Structural formula of the main pyrethroids.

With the development of modern agriculture, neonicotinoid pesticides have been widely used and play an important role in promoting agricultural development [49]. Neonicotinoids have become the most widely used class of insecticides worldwide since their introduction in the 1990s and have been registered in 120 countries. In 2014, it accounted for over 25% of the global pesticide market, noting that in 2012, some pesticides, such as thiamethoxam and imidacloprid (Figure 5), accounted for approximately 85% of total neonicotinoid sales worldwide [50].

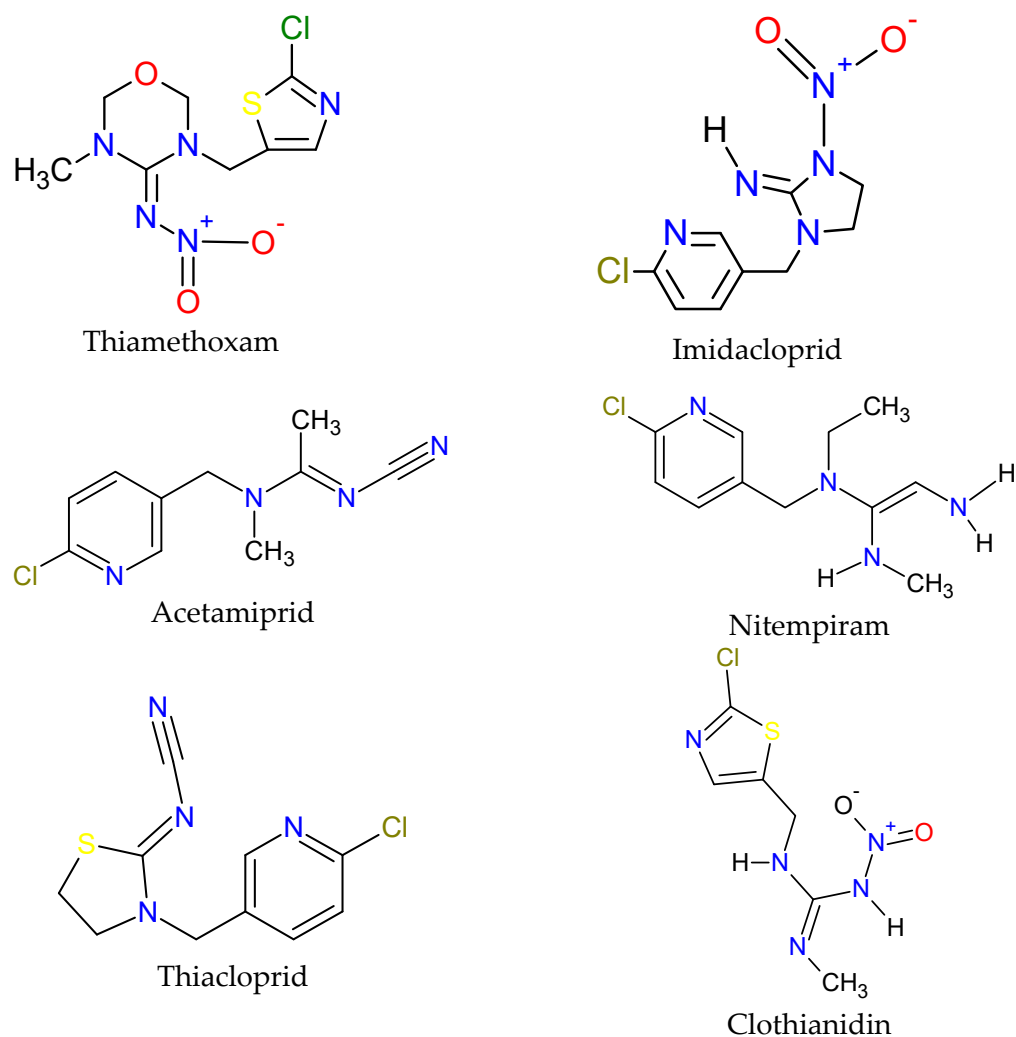


Figure 5. Structural formula of some neonicotinoids.

Neonicotinoids were initially considered to be the best substance for controlling a variety of insects, with minimal impact on wildlife and the environment. Its application represents a reduced risk compared with spray applications in seed coatings, with an excellent selective toxicological profile for insects [51].

Neonicotinoids are used in a variety of cultures; they act as nicotinic agonists of acetylcholine receptors, leading to the interruption of nervous stimuli in insects, and are associated with the global decline of bees [52].

Neonicotinoids provide excellent acute and residual control of sucking insects, including aphids, leafhoppers, and whiteflies, as well as certain chewing insects, including the Colorado potato beetle, rice water weevil, and moth. In addition, two neonicotinoids, thiacloprid and acetamiprid, have been shown to be effective in controlling many Lepidoptera pests. Imidacloprid, marketed in 1991, is the most widely used insecticide for crops worldwide and is also registered for many nonagricultural uses, particularly as a

flea-in-place treatment, turf treatment for white worms, and as a termiticide. Application rates for neonicotinoids are low compared to most insecticide groups [38].

2.3. The Advanced Oxidative Processes (AOPs) in the Treatment of Pesticides

In recent years, interest in AOPs applications for the removal of pesticides from aqueous media has increased. The pesticides that have been most studied include chlorpyrifos and diazinon, which are also the most commonly used pesticides on farms. In this context, AOPs demonstrate a 90% degradation efficiency for most OPs and can also achieve a minimum removal of 70% of target compounds below their respective quantification limits. Photocatalytic and Fenton processes are the most common technologies for the degradation of organophosphorus pesticides [53].

The removal efficiency of pesticides by conventional water treatment processes (coagulation/filtration/decantation/chlorination) is limited, whereas conventional combination with advanced treatment processes (ozonation + biological activated carbon and ultrafiltration) can effectively improve pesticide removal. Although the mineralization of organic matter by ozone is negligible, ozonation plays an important role in pesticide degradation [54].

AOPs may be able to degrade a variety of pesticide residues; however, each pesticide has its own specificity, resulting in different degradations due to differences in their chemical structures [55]. The main AOPs employed for pesticide degradation use combined processes with hydrogen peroxide, ozone, ultraviolet radiation, and Fenton-type processes; however, besides hydroxyl radicals (HO^\bullet), other radicals, such as carbonate and sulfate anion radicals, can also be used for this purpose. Table 2 presents some AOP efficiencies in pesticide degradation.

Table 2. Efficiencies of AOPs in pesticide degradation.

| AOPs | Pesticide | Efficiency | References |
|---------------------|-----------------------------------|----------------|------------|
| Fenton/Photo Fenton | OPS | >90% | [53] |
| | 2,4-D | TOC Remove 69% | [56] |
| Fenton | Malathion | 55% | [57] |
| Photo Fenton | | 70% | |
| Sono Fenton | | 98% | |
| Photo Fenton | Diazion | 100% | [58] |
| Fenton | | 85% | |
| Eletro Fenton | Lindane | 92% | [59] |
| Ozone | Parathion, diazinon, cypermethrin | 75% | [60,61] |
| Carbonate radical | Paration | 4–10% | [62] |
| | Chlorpyrifos | 15–45% | |

2.4. AOPs Using Hydrogen Peroxide

The use of H_2O_2 with UV offers several distinct advantages over other conventional UV-based advanced oxidation processes, such as UV/O_3 and UV/TiO_2 ; for example, H_2O_2 photolysis has a higher quantum yield of HO^\bullet production ($\Phi = 1.0$) than UV/O_3 ($\Phi \approx 0.1$). In addition, the $\text{UV}/\text{H}_2\text{O}_2$ process works effectively over a wide pH range, promoting an effective way to degrade organic pollutants with nonbiodegradable or slow biodegradation rates [63].

In Equation (1), the presence of H_2O_2 in an aqueous solution during irradiation increases the formation of hydroxyl radicals. However, any excess hydrogen peroxide is counterproductive because it reacts with hydroxyl radicals to form hydroperoxyl radicals (HOO^\bullet). In Equation (2), the concentration of H_2O_2 is optimized, and hence, the production of hydroxyl radicals is greater than the formation of H_2O and HOO^\bullet , which has a lower oxidation capacity than the HO^\bullet radical [64].



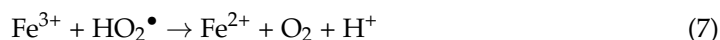
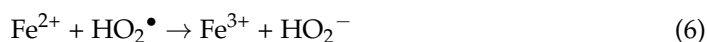


The generation of hydroxyl radicals in treatment systems without aeration reduces the removal efficiency and production of HO^\bullet because there is no oxygen available for electron transfer. Aeration plays a key role in the production of hydrogen peroxide by electron transfer from oxygen, which consequently increases the production of HO^\bullet [65].

Hydrogen peroxide can also be used in combination with ultrasonic waves (H_2O_2 /sonication). This technique produces an oxidative environment via cavitation, which results in microbubbles located in supercritical regions in the aqueous phase [66]. However, pH values have a decisive effect on the oxidation potential of HO^\bullet radicals due to the reciprocal relationship with oxidation potential ($E_0 = 2.8$ V and 1.95 V for pH 3 and 11, respectively) [67]. The highest efficiency in the degradation of pesticide OCPs was observed at pH 3, and less effective removal of pesticides was observed both at pH 11 and under neutral conditions.

Electrogeneration of hydrogen peroxide from oxygen reduction is an efficient means of controlling organic pollutants in aqueous media. The maximum generation rate of hydrogen peroxide using oxygen reduction is -1.6 V compared to the saturated calomel electrode (SCE) for acidic and alkaline solutions. The apparent rate constants for the degradation of 2,4-D ranged from $0.9\text{--}6.3 \times 10^{-5} \text{ m s}^{-1}$ depending on the catalyst used (UV or UV + Fe (II)). The reduction in total organic carbon (TOC) was favored in an acidic medium, where a 69% decrease in concentration was observed in the H_2O_2 /UV/Fe (II) process. A similar performance was achieved by H_2O_2 /Fe (II), showing that UV radiation plays a secondary role in reagent regeneration [56].

The Fenton reaction involves the oxidation of ferrous ions to ferric ions to decompose H_2O_2 into hydroxyl radicals (Equation (3)). As shown in Equation (4), the ferric ions generated can be reduced by reacting with excess hydrogen peroxide to form ferrous ions and more radicals. Meanwhile, Equation (5) shows that the hydroxyl radicals can be scavenged by ferrous ions. Equations (6) and (7) represent the rate-limiting steps in the Fenton process, as the hydroperoxyl radicals are consumed, and ferrous ions are regenerated from ferric ions [68].



The Fenton process can be carried out homogeneously and heterogeneously and is also catalyzed by UV radiation (photo-Fenton) or ultrasonic waves (sono-Fenton). For example, additional HO^\bullet radicals are formed in photo-Fenton heterogeneous catalysis by hydrogen peroxide decomposition, rapid regeneration of Fe^{2+} under visible light, and formation of smaller amounts of iron sludge compared to the conventional Fenton process [69].

Heterogeneous Fenton and photo-Fenton processes can overcome the disadvantages of the conventional Fenton process, which is limited to a narrow pH range and produces a large amount of iron sludge. The electro-Fenton process also reduces the costs and risks associated with reagent handling, transportation, and storage [70].

Studies have examined the performance of Fenton (F), photo-Fenton (PF), and sono-photo Fenton (SPF) with respect to the oxidation of the organophosphorus pesticide malathion. The degradation efficiency decreased with increasing pH degradation of malathion followed by the order $\text{SPF} (98.79\%) > \text{PF} (70.92\%) > \text{F} (55.94\%)$. Of all the processes studied,

SPF is the most effective technique for the degradation and mineralization of malathion in an aqueous solution [57].

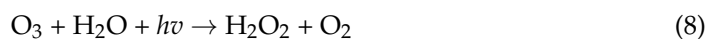
In the process of degradation of the pesticide diazinon (DZN) in water, two types of AOPs were applied; when compared, it can be observed that in the photo-Fenton process, the complete degradation of DZN and the byproducts obtained occurred after 5 min. The Fenton process achieved an 85% degradation yield after 60 min. Both experiments included an initial DZN concentration of $1 \text{ mg} \cdot \text{L}^{-1}$, which is a realistic concentration for wastewater [58].

The Fe^{3+} photo-Fenton system combined with ethylenediamin'-N, N'-disuccinic acid (EDDS) was satisfactory for the degradation of target pesticides up to pH 6 and showed better performance than the classical photo-Fenton system at pH 2.7. The higher efficiency was related to the increased photoactivity of the Fe^{3+} -EDDS complex, the higher solubility of iron in the presence of EDDS, and the limited complexation of iron with target pesticides. Moreover, pesticide degradation is strongly affected by operating parameters, thus emphasizing the importance of determining the optimal operating conditions to maximize degradation efficiency [71].

The oxidative degradation of the organochlorine pesticide lindane shows higher efficiency in the electro-Fenton process compared to the conventional Fenton process [59]. Treatment times longer than 60 min is required for the conventional Fenton process to achieve 92% lindane conversion when the contaminant is dissolved in water and 24 h in lindane-contaminated soil [59].

2.5. Ozone Process

The AOP techniques most commonly employ ozone, hydrogen peroxide, and ultraviolet (UV) radiation. Equations (8)–(10) describe the steps involved when ozone is used in the process. Ozone can initially react with water to form peroxide and O_2 , which can be broken down by radiation to form $\bullet\text{OH}$. Equation (10) shows that ozone molecules can also react with H_2O_2 to form more hydroxyl radicals. It is worth noting that O_3 gas is an unstable, reactive molecule that can be generated in situ [72].



Commercially available technologies for ozone generation are based on the corona discharge process, which involves the application of a high-voltage discharge into a cooled/dried gaseous phase containing oxygen (O_2 or air). However, ozone alone does not cause complete oxidation of some refractory organic compounds, as it exhibits a low reaction rate. Therefore, it must be combined with H_2O_2 , UV light, catalysts, photocatalysts, or ultrasound to enhance the production of hydroxyl radicals, thereby increasing the treatment efficiency [73].

Wu et al. (2007) [60,61] investigated two methodologies: first, a pesticide solution was mixed with an overdose of ozone, and second, pesticide-enriched vegetables were treated with ozonated water under different conditions. More than 75% of all the pesticides were degraded after treatment with ozone for 10 min. However, the pesticide removal percentages were comparatively low in vegetable samples as they were influenced by temperature, contact time, and ozone concentration [74].

Owing to the low reactivity of ozone with thiamethoxam, higher O_3 doses must be applied to groundwater and surface water for drinking water treatment. The ozone/ultraviolet (O_3/UV) process considerably reduced the O_3 dose and contact time for the degradation of thiamethoxam. These results suggest that ozonation may not be effective enough for

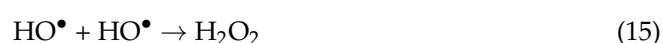
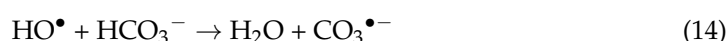
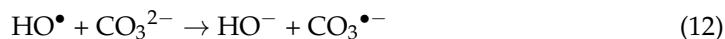
thiametoxam degradation, and other ozone-based AOPs may provide a viable way to improve thiametoxam removal in water treatment [75].

For water treatment by ozonation, the hollow fiber membrane contactor technology for ozone diffusion is a recent unit operation, where it is added uniformly to the water to be treated through many dosing points and with a large mass transfer surface area. In addition, membrane contactors offer other advantages, such as modularity, environmental friendliness, and independent flow adjustment for the gas and liquid phases. The gas can also be recycled to generate energy and save reagents. Many parameters influence mass transfer during ozonation using membrane contactors. When carefully chosen, the efficiency of the process can be significantly improved [76].

Ozone is a powerful oxidant with an electrochemical oxidation potential of 2.0 V (vs SHE), though it is lower than that of the hydroxyl radical (2.8 V vs. SHE). Ozone oxidation is an effective method for removing residual pollutants such as pesticides and other hazardous chemicals during the treatment of wastewater and water used for consumption [77].

2.6. Carbonate Anion Radical

The carbonate anion radical ($\text{CO}_3^{\bullet-}$) can be generated by reactions between the carbonate ion and hydroxyl radicals, which occur via electron transfer. These radicals have the highest oxidizing potential at pH 7.0. The hydroxyl radicals can be produced by the photolysis of hydrogen peroxide by UV radiation, as shown in Equation (11). Equations (12) and (14) show the reaction of hydroxyl radicals with carbonate and bicarbonate anions, respectively, to generate the carbonate anion radical, whereas Equations (15) and (16) show the decay of both reactive radicals by recombination [78].



The $\text{CO}_3^{\bullet-}$ radical plays an important role as a mediator of biological processes, acting as an oxidant for a wide variety of biological targets. According to Wang et al. (2020) [75], the reduction potential of $\text{CO}_3^{\bullet-}/\text{CO}_3^{2-}$ is 1.59 V versus EPH. The experimental rate constants of the reactions of HO^\bullet with HCO_3^- and CO_3^{2-} are 8.5×10^6 and $4.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. The conjugate acid of the bicarbonate radical (HCO_3^\bullet) is a strong acid ($\text{pK}_a < 0$); therefore, HCO_3^\bullet is present in the anionic form ($\text{CO}_3^{\bullet-}$) under physiological conditions ($\text{pH} = 7.4$).

Moreover, HCO_3^- can stimulate hydrogen peroxide (H_2O_2) to generate $\text{O}_2^{\bullet-}$ and $\text{CO}_3^{\bullet-}$ [79]. The presence of $\text{O}_2^{\bullet-}$ radicals in HCO_3^- facilitates the production of $\text{CO}_3^{\bullet-}$, and both these radicals ($\text{O}_2^{\bullet-}$ and $\text{CO}_3^{\bullet-}$) jointly oxidize pollutants and ensure their degradation. Another mechanism of $\text{CO}_3^{\bullet-}$ formation occurs by the homolytic dissociation of the nitrosoperoxycarbonate anion (ONOOCO_2^-), which can be formed transiently in the cellular environment due to the reaction between peroxynitrite (ONOO^-) and CO_2 [80].

HO^\bullet , or $\text{CO}_3^{\bullet-}$ has high potential for the degradation of organic contaminants [81]. The carbonate anion radical can absorb radiation at a wavelength of 600 nm and has a long lifetime, with a velocity constant (k) ranging from 1×10^7 to $8 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is 100 times slower than most radicals [82].

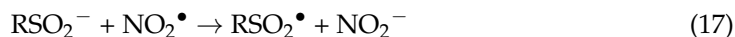
The carbonate anion radical is a more selective oxidant than OH^\bullet because it reacts with electron-rich compounds such as phenols, amines, and sulfur-containing species, many of which are present in pesticides [83]. Thus, the use of carbonate anion radicals represents a new alternative for wastewater treatment, making it important to study the mechanisms behind their formation and action.

Several methods can efficiently degrade refractory organic compounds in wastewater that contain carbonate by generating carbonate radicals. These methods are based on a system of titanium dioxide nanotubes (TNA) and modified carbon felt (MCF) photoelectrocatalytic arrays. In these methods, TiO_2 (TNA) is used as a photoanode to generate the valence hole (h_{vb}^+), whereas MCF is used as a cathode to produce H_2O_2 . HCO_3^- , which causes less pollution and is cost-effective, is used as the electrolyte to produce $\text{CO}_3^{\bullet-}$ [84].

The decrease in the number of carbonate radicals decreases the removal rate as well as reduces the electricity generation by the photoelectrocatalytic system (PEC) using HCO_3^- . This can produce holes and electrons in semiconductor materials using solar irradiation without an obvious change in pH during the degradation process [85].

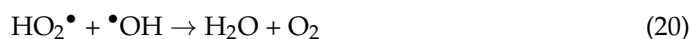
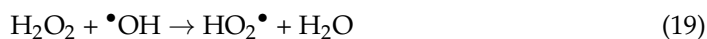
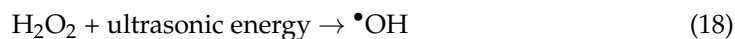
According to Shah et al. (2016) [86], the contribution of $\text{O}_2^{\bullet-}$ and $\text{CO}_3^{\bullet-}$ to the removal of the insecticide endosulfan implies a significant role for these radicals in the treatment of water contaminated with chlorinated organic compounds and sulfur. According to Wu and Linden (2010) [62], the carbonate radical accounts for approximately 4 and 10% of the degradation rate at 10 and 38 mM bicarbonate, respectively, for separation and is more efficient for chlorpyrifos, where the carbonate radical contributes approximately 15 and 45% of the overall reaction rate at 10 and 38 mM bicarbonate in hydrogen peroxide.

Nitrogen dioxide radicals (NO_2^\bullet) are a well-known reactive species capable of initiating oxidation and nitration reactions. In the interaction of $\text{CO}_3^{\bullet-}$ and NO_2^\bullet , radicals both react by a one-electron mechanism with sulfinates to form sulfonyl radicals as transient intermediates, as shown in Equation (17) [87].



The catalytic oxidation of sodium percarbonate is an alternative process in wastewater treatment for the removal of pesticides and other recalcitrant compounds from contaminated environments because it is nontoxic, safe to handle, and produces byproducts that inherently exist in the natural environment in the water matrix [88].

In ultrasound (US) irradiation, a high sonic beam energy is used to degrade organic pollutants by bubble cavitation, which occurs when liquid molecules are irradiated by high-intensity US waves. The cavitation effect generates hydroxyl radicals, and irradiation applications are coupled with powerful oxidizers such as H_2O_2 and persulfate (PS). The PS radical performed best when thermally activated with US irradiation, resulting in better organic removal due to free radical generation. The mechanism of free radical generation from H_2O_2 and PS after irradiation is shown in Equations (18)–(21) [89,90].



3. Conclusions

The consequences of the increasing pesticide use have noticeable impacts on aquatic and terrestrial ecosystems; hence, the use of pesticides must be reconsidered. Their persistence in the environment encourages the development of more sophisticated treatment

techniques, such as AOPs. However, using more chemicals for degradation may promote the formation of other byproducts in the environment, the toxicity of which should be evaluated.

Thus, even though pesticides can be treated, the reduction and conscious use of pesticides is essential to ensure the maintenance of human health and the biodiversity of the planet. This problem should be approached globally, including economic and fiscal discussions that can contribute to sustainable development with solid alternatives that aim to protect the environment and preserve life.

Meanwhile, even if environmental problems are growing regarding the use of pesticides, advances in relation to political issues seem to be receding; in 2022, UN specialists issued alerts for the increase in pesticide consumption in Latin American countries. Brazil was criticized for trying to weaken the regulatory framework for pesticides and Paraguay for not enforcing the laws that control the use of pesticides, both situations resulting in greater exposure of farmers, workers, and indigenous peoples to these contaminants.

Brazilian researchers are protected from the exaggerated consumption of pesticides resulting in health damage due to the exemptions and tax reductions allowed and practiced for this activity. Experts also warn of the damage to human health and the environment resulting from this indiscriminate use, which is immeasurable in view of the loss of biodiversity and commits billionaire resources to its recovery.

As a result of this imbalance, there will still be the challenge of developing a treatment technology to remove these contaminants that already reach the public water supply since the problem is accentuated considering that Brazil occupies the 112th position in the world ranking of sanitation in 2011, the which evaluated 200 countries.

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