Pesticides: Environmental fate, human health impacts, and analytical techniques from extraction to removal

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Abstract: Pesticides are a catchall term. It includes a wide range of chemicals used to destroy several types of harmful pests (weeds, insects, etc.). They are used in large quantities due to their effectiveness. Although it is intended to eliminate the target pest, it bypasses that and reaches the environment via various sources, thus causing soil and water contamination. Also, pesticide exposure increases the possibility of human infection with poisoning and serious illness. It is impossible to know all of the pesticides' detrimental effects on their users, but many of these concerns are well-known, have manifested in the past, and have been documented in different researches, such as poisoning occurrences, malignancies, etc. This review manuscript highlights the sources and fate of pesticides in different environmental compartments, their health impacts, and the analytical techniques deployed for their analysis. In addition, the review considered different remediation techniques employed in reducing their footprint within the various environmental compartments.

Keywords: Environmental fate; Human health effects; Advanced detection techniques; Decontamination water techniques; Removal percentage

1. Introduction

Pesticides are a mixture of substances used to prevent, control, or destroy organisms that are considered unwanted (plants, insects, fungi), regardless of how they are used (agriculture, industries, urban areas (eg: gardens, roadways, etc.). A total of 80% of pesticides are used to eradicate insects, 15% is herbicides, 1.46% is for fungal plant diseases, and 3% for the rest of the types of pesticides (Rajmohan et al., 2020). Fungi and weeds pose a major threat to a variety of agricultural crops (Khammassi et al., 2023; Bazzi et al. 2013). Most arable crop production procedures include the use of pesticides. Pests and diseases are estimated to be responsible for one-third of crop losses. When conducting intensive agriculture in order to produce food and resources for a growing global population, the use of pesticides is the primary means of reducing crop losses and increasing agricultural yields (Carvalho, 2006; Rowell, 2014). Their widespread application in modern agriculture contributes significantly to environmental pollution (Adeniyi et al., 2021). Pesticides are large gamuts
of chemical components divided into classes (herbicides, insecticides, fungicides) according to their function, chemical compositions, origin, mode of action, toxicity, type of active ingredients, etc. World consumption of herbicides is about 47.5%, insecticides are about 29.5%, and fungicides are 17.5% (Aktar et al., 2009), (Rajmohan et al., 2020). They are one of the most common xenobiotics emitted by anthropogenic sources, with over 4 million tons applied worldwide each year (Maggi et al., 2019). The correct use of pesticides assisted in boosting agricultural output as well as maintaining human health. However, their indiscriminate use endangers the ecosystem, biodiversity, and human health (Bouterfas et al., 2020).

It is difficult to pinpoint all of the sources of pollution caused by pesticides. They are able to migrate into different compartments of the environment and cause its pollution, due to their physicochemical properties and their diversity of fields in which they are used. Spraying pesticides is the most popular technique of application. However, it can pollute the atmosphere, water, soil, and agricultural runoff. Environmental pollution by pesticides is attributable to a variety of factors, including runoff from farmland and previously polluted land, intensification of volatile pesticides, improper pesticide transportation and storage, improper pesticide spraying, and inadequately disposal of treated and/or untreated wastewater from the pesticide industry (Agrawal et al., 2010), (Eqani et al., 2013), (Hageman et al., 2006), (Huizhen et al., 2014). These chemicals are causing an increase in water contamination, although, at low concentrations, they pose a major environmental concern (Agrawal et al., 2010).

Pesticides in high concentrations target several environmental sections, but they also lead to the establishment of diseases and symptoms that are hazardous harming human health. There is a potential for acute or chronic toxicity even when exposed to low doses (Abhilash and Singh, 2009), (Maggi et al., 2019). Pesticides can affect humans through three different pathways of exposure. The most common way to be exposed to pesticides is through ingestion or nutrition, it can also be acquired by skin contact, particularly as a result of pesticide usage in the house, and finally, it can be acquired through inhalation of contaminated air, especially for individuals residing near to farmlands (Yusà et al., 2014). Pesticide exposure and human health data during the last 2 decades have demonstrated that numerous pesticides induce neurodegenerative disorders, that some affect prenatal growth and create congenital malformations, and that others are carcinogens (Asghar and Malik, 2016).

The presence of significant amounts of pesticide leftovers in complex matrices has become a significant issue, raising considerable environmental and human health implications that can't be overlooked (Shamsipur et al., 2016). Abandoning pesticides completely in the future is absolutely not possible for the good of human development and the economy. Therefore, it requires the development of special and effective remedial measures to mitigate the negative effects of pesticides, whether on the ecosystem or human health (Nie et al., 2020). For this reason, it is vital to understand and be aware of the features and components of the pollutant to be eliminated in order to select an appropriate treatment strategy (Rodriguez-Narvaez et al., 2017). Given the large variety of chemical classes, pesticide analysis is a critical step and accurate procedure that necessitates the selection and application of the best appropriate techniques with the lowest possible threshold values among the many different available techniques.

The objective of this review is to highlight the sources and fate of environmental pollution by pesticides as well as their various and severe symptoms for human health, and also to discuss a set of conventional and advanced analytical methods (from extraction to removal) valid for determining the presence of pesticides in the environment. Moreover, this work summarizes several types of techniques and their pesticide removal capacity (in %). Table 1 summarizes previous review studies on pesticides.
Table 1. Review articles on pesticides

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<th>Year</th>
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<tr>
<td>1</td>
<td>2021</td>
<td>Pesticides</td>
<td>Drinking Water</td>
<td>This article discuss the: -Types of pesticides identified in the water bodies, -Origins of pesticide contamination, -Dispersal and occurrence of pesticides in soil and water, -Toxicity effects on human health, -Methods for treating pesticide-contaminated water.</td>
<td>(Syafrudin et al., 2021)</td>
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<td>2</td>
<td>2021</td>
<td>Pesticides</td>
<td>Wastewater</td>
<td>This review looks at opportunities for dealing with pesticide-infested water and anticipates a comparative assessment that may accompany upcoming technical research on pesticide removal from wastewater. Also, it highlights and reviews the effects of pesticides on human health and the environment, adulteration of pesticides in water, pesticide-infested water treatment techniques, available processes, technical challenges, economics, and prospects.</td>
<td>(Jatoi et al., 2021)</td>
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<td>3</td>
<td>2021</td>
<td>Pesticide residues</td>
<td>Environment</td>
<td>This review presents the new developments in analytical methods for the detection of pesticide residues. Also highlighting the practical application of newer technologies in pesticide detection, the current challenges, limitations and future perspectives for developing green analytical techniques for easy-to-use and on-site applications.</td>
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<td>Contaminated Water</td>
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<td>5</td>
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<td>Pesticides</td>
<td>Environment (Water and soil) Human health</td>
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2. Sources of pesticides in the aquatic environment and soil

Pesticide contamination poses a significant environmental concern. Pesticide evolution and diversity have aided in the elimination of many types of unwanted pests and improved especially
agricultural performance. However, the use of pesticides of all kinds and classes in multiple activities has contributed to the emergence of several point and diffuse (non-point) sources of contamination. Also, the intensive use of a variety of pesticides leads to the presence of residues in a variety of unexpected areas and the attack of nontarget species (Ortiz-Hernández et al., 2013). Where there are different variables that promote the flow of pesticides from the site of application to the various environmental compartments where they can build up to high levels (Maggi et al., 2019, Quaglia et al., 2019), and through the mechanisms of uptake and uptake by soil granules, the transport and biological availability of pesticides can be determined (Rajmohan et al., 2020). Thus, controlling pesticides remains imperative to monitor their levels in the environment and their direct or indirect impact on human health. In addition to the necessity of not exceeding the maximum authorized consumption limits (Samsidar et al., 2018).

Each year, massive amounts of pesticide active ingredients are used all over the world, where their use is linked to agricultural growth (Elfikrie et al., 2020) and is required to protect and boost productivity. Furthermore, an astonishing fraction of stable chemical compounds are employed by different industries, and the widespread use of pesticides in urban gardening is also regarded as a major origin of pollution by pesticides in urban areas (Syafrudin et al., 2021). Not to mention the leakage that occurs during manufacturing, transportation, and uncontrolled random storage (Relyea, 2005). But even though pesticides have a significant effect, their utilization has severely affected biodiversity in the aquatic environment (Vörösmarty et al., 2010, Pimm et al., 2014, Song et al., 2017, Zhang et al., 2019, Song et al., 2019, Yi et al., 2019).

Sum it up, pesticide water pollution results from the continuous emission of long-lasting chemicals used in urban areas, farming activities, and manufacturing plants (Syafrudin et al., 2021). Through which, as already aforementioned, various points and diffuse sources of contamination were formed. The underlying distinction among both kinds of pollution sources is that punctual pollution (often in an unintentional manner) stems from a single, identifiable, geographically well-defined source, and that source results from miscellaneous ways such as chemical runoff or pesticide misuse (Aydinalp and Porca, 2004). It is most damaging to the environment, where the environment is polluted with high concentrations of chemical pollutants and then slowly melts (Fogg et al., 2003). Thus, the severity of this type of contamination can range from mild to drastic. Whilst diffuse pollution occurs as a result of the accumulation of pesticides over a wide space, and that source results from the release of industrial pollutants into the atmosphere and their subsequent deposition in the sea and soil, or leakage of pesticides and fertilizers used for agricultural lands (Aydinalp and Porca, 2004). This type of pollution is not localized and is challenging to control because it spreads from various sources and destinations around the world, explaining the presence of notable concentrations of certain pollutants in water, soil, and even the atmosphere.

Aside from the steadily growing use and consumption of pesticides in recurring human activities, there are other contributory factors to pesticide entry and spread into the aquatic environment and their reach the soil, for instance: climatic changes, different properties of pesticides (mode of action, stability, solubility, etc.), as well as the amount and application technique used, allowing their mobilization from the site of action and transmission to the environment (Quaglia et al., 2019). Regardless of the source of contamination, there is a proportion of pollutants that are not absorbed, causing them to seep into the ground and deteriorate into residues, which are usually less toxic than the initial pesticide. Certain pesticides, depending on their solubility in water, are transported by surface runoff during rainfall, thereby contaminating surface water like lakes and rivers, and they can also accumulate or infiltrate through the soil to attain subterranean waters (Syafrudin et al., 2021),
where soil type and texture (soil permeability) have the greatest impact on the speed and ease of transition of water and pollutants to groundwater.

3. Pesticides' behavior in the environment

Pesticides have the potential to enter the environment when used on a target plant or during disposal. After being released into the environment, pesticides may go through processes including transfer (or mobility) and degradation that lead to the production of new compounds in the environment (Liu et al., 2015, Marie et al., 2017, Scholtz and Bidleman, 2007, Singh, 2012). Pesticides are transferred from the target site to other environmental media or non-target plants, through several processes such as adsorption, leaching, volatilization, spray drift, and runoff. Figure 1 illustrates pesticide mobility mechanisms in the environment. Environmental behavior varies with different kinds of chemicals. For instance, organophosphate pesticides exhibit noticeable acute toxicity in mammals despite having low persistence, whereas organochlorine chemicals like dichlorodiphenyltrichloroethane (DDT) have minimal acute toxicity, but exhibit a substantial capacity to accumulate in tissues and continue to harm organisms over the long term. Most nations have outlawed their sale, due to their nature, their residues linger in the environment for a very long time (Damalas and Eleftherohorinos, 2011, Kim et al., 2017).

Figure 1. Simplified diagram of pesticide mobility mechanisms in the environment

3.1. Degradation of pesticides

Pesticides can be degraded by light, microbes, or chemical reactions (Bouya et al., 2012; Abian et al., 1993). The degradation process might take hours to years, relying on the pesticides' chemical characteristics and environmental conditions (Tcaciuc et al., 2018, Wu et al., 2018). The processes of pesticide degradation govern pesticide persistence in soils and produce a variety of metabolites (Tariq and Nisar, 2018). Moreover, it introduces the concept of pesticide half-life in the environment (Marie
Pesticide degradation by sunlight is known as photodegradation (Wei et al., 2018). This type of pesticide degradation has attracted enormous research interest due to a simpler and greener approach (Rani et al., 2023). Niclosamide, as an example, under the influence of light, could hydrolyze to produce 5-chlorosalicylic acid and 2-chloro-4-nitroaniline (Liu et al., 2015). To some degree, all insecticides are photodegradable, and the rate of degradation is dependent on the insecticide's characteristics, the light intensity, and the exposure time (Singh, 2012). Microbial degradation refers to pesticide degradation by microorganisms like fungi and bacteria (Han et al., 2013). This type of degradation is affected by several factors, such as soil moisture and pH, soil porosity structure, oxygen, and temperature (Qian et al., 2017, Singh, 2012, Su et al., 2017, Yue et al., 2017). The enantioselective degradation of benalaxyl, for example, is mostly controlled by pH, with increased degradation occurring in soils with greater pH values (Qian et al., 2014). Chemical degradation means that pesticides may be degraded in the soil via chemical processes (Bansal, 2011). Furthermore, being always active, the chemical reaction of sunlight radiation plays a crucial role in molecule degradation on the surfaces of soil (Quan et al., 2015). The temperature of the soil, the levels of pH, moisture, and pesticide binding to the soil all influence the rate and kind of degradation of the chemical (Singh, 2012).

3.2. Migration of pesticides

3.2.1. Sorption

Pesticide use has skyrocketed, posing a major hazard to the soil. Once pesticides are employed, only a small quantity of the pesticides utilized has a protective role in fighting plant diseases. Pesticides, on the other hand, penetrate the soil in massive quantities, resulting in severe soil pollution (Qin et al., 2014, Xue et al., 2006). The sorption process is a process that attaches pesticides to soil particles owing to the attraction between them (Bošković et al., 2020, Liu et al., 2010, Obregón Alvarez et al., 2021). Pesticide adsorption is influenced by soil variables such as pH, organic matter, and soil amendment (Dong et al., 2013; Liu et al., 2010; Ren et al., 2011; Si et al., 2006; Yue et al., 2017). Additionally, organic or clay-rich soils are far more adsorptive to pesticides than coarse, sandy soils since these soil types have a larger particle surface area or more locations where insecticides can bind (Bošković et al., 2020, Han et al., 2013, Wu et al., 2018, Yuan et al., 2014). Pesticide degradation in the soil is also impacted by humidity (Singh, 2012). Dry soils usually have a higher potential for pesticide sorption than moist soils, due to the fact that water molecules compete with pesticides for binding sites in wet soils (Tudi et al., 2021). The adsorption of DDT into sediments is affected by the humic acid colloid (Gao et al., 2014, Si et al., 2006). Some pesticides can linger for a long time in the soil (Gao et al., 2008, Si et al., 2006), which allows plants to absorb them as they grow. Crops may be harmed by these pesticides or may retain their residues (Duan et al., 2008, Lozowicka et al., 2015). Clay particles with a negative charge are drawn to and readily bind positively charged pesticide molecules (Đurišić-Mladenović et al., 2010).

3.2.2. Leaching

There are several pesticides that are registered and utilized on a global scale, with some of them having a high likelihood of polluting groundwater due to their leaching (Fontana et al., 2010, Singh, 2012). A number of factors have an impact on leaching (Connell, 2005, Han et al., 2013, Singh, 2012). Pesticides that are dissolved in water can migrate with the water in the soil, making solubility a significant component for leaching. A further important element influencing pesticide leaching is soil permeability (Fontana et al., 2010). The likelihood of pesticides leaching into the soil is also increased by soil permeability. The half-life in aerobic soil and the adsorption coefficient (Koc) both have an
Impact on insecticide leaching (Connell, 2005). In addition, the residence time of pesticides in the environment affects the amount of leaching. A low-persistence pesticide may only last a short while in the soil, which makes it less likely to leak (Geng et al., 2017). For instance, imidacloprid has high environmental destiny features because it is persistent (DT50 in soil = 187 days). A significant element affecting the downward leaching of pesticide solutes into groundwater is precipitation (Labite et al., 2013). Furthermore, the key variables affecting the leaching characteristic of pesticides are meteorological circumstances, such as annual rainfall and annual average temperature (Singh, 2012). Temperature also affects soil evapotranspiration, which affects how pesticides leach into the soil. Both water infiltration and the transfer of pesticides to groundwater are affected by soil properties such as soil organic content and texture (Connell, 2005, Geng et al., 2017, Sijm et al., 2007). Among these soil properties, soil texture is the factor that has the greatest influence on how water and pesticides move through the soil (Ou et al., 2020). Additionally, pH levels, the amount of organic matter in the soil, and anaerobic soil microorganisms are all mentioned as significant regulators of phenazines’ ability to degrade (Geng et al., 2017). The effect of soil characteristics on pesticide absorption was covered by Bošković et al., 2020. Their findings showed that the pesticide adsorption was strongly correlated with pH, and less so with the soil organo-mineral complex, as well as C and N in soil organic matter. Although component analysis revealed an association in multidimensional space, particle sizes or cation exchange capacity did not correlate with adsorption. For the impact of crop residues on soil water and temperature regimes, it is also necessary to consider the possible evaporation rate.

3.2.3. Spray Drift

Spray drift is the atmospheric migration of spray droplets that have been applied to a treatment site during the application of pesticides, resulting in environmental degradation and tainted food (Connell, 2005, Ghaste et al., 2020, Grella et al., 2020, Ou et al., 2020, Pourreza et al., 2020, Singh, 2012, Van Steenwyk et al., 2021, Vieira et al., 2020, Wang et al., 2020, Zhang et al., 2020). Aquatic ecosystems are the receivers of numerous residues of pesticides, chlorpyrifos as an example, because of agricultural runoff and leaching spray drift causing toxicity to aquatic organisms, thereby the enzymes of oxidative stress and histological changes in the vital organs of tilapia due to exposure to chlorpyrifos; The result of the study shows that sub-lethal concentrations of chlorpyrifos can cause oxidative stress and histological changes in tilapia tissues (Farhan et al., 2021).

3.2.4. Volatilization

The process of a solid or liquid becoming a gas is known as volatilization. After being volatilized, pesticides can be removed from the treated surface by air currents (Singh, 2012). The vapor pressure, temperature, humidity, air movement, and soil characteristics like texture, organic matter content, and wetness are some significant elements that affect the pesticide's rate of volatilization (Alamdar et al., 2014, Connell, 2005, Zhu et al., 2017). The volatility of the pesticide will increase with the vapor pressure (Tudi et al., 2021). Also tending to increase volatilization include high temperatures, low relative humidity, and air movement (Connell, 2005). Organochlorine pesticides, for instance, are more likely to be dispersed in the atmosphere in tropical regions than do temperate regions (Chakraborty et al., 2015; Lamhadi et al. 2014; Garoiz et al., 2011). Moreover, the likelihood of a pesticide volatilization is decreased when it is strongly adsorbed to soil particles (Wong et al., 2008). According to Lisouza et al., 2020, the primary method through which humans are exposed to organochlorine pesticides by volatilization is via contaminated surface waters.
3.2.5. Surface runoff

Pesticide runoff means pesticide migration in water along an inclined surface (Das et al., 2020). Pesticides may be bonded to soil particles in eroding soil or may migrate as chemicals dissolved in water. This is closely related to numerous variables, including an area’s slope or grade, soil texture and moisture content, rainfall quantity, and timing, irrigation, and edibility (Connell, 2005). Runoff occurs when water poured into a field moves too quickly for the soil to absorb it (Singh, 2012). Pesticide runoff is brought on by over-irrigation, which causes a buildup of extra surface water. Pesticide contamination of the aquatic environment (wells, lakes, ponds, and streams) comes from pesticide runoff, which can have a detrimental effect on humans, animals, and plants (Aktar et al., 2009, Qin et al., 2014).

4. Impacts of pesticide contamination on water and soil

4.1. On water

Water pollution is a global problem (Bougarrani et al., 2017). Numerous pollutant substances have been found in the aquatic medium, such as pesticides (Connell, 2005; Singh, 2012). Pesticide pollution of water resources is caused by pesticide mobility in water (Mazlan et al., 2017, Singh, 2012). The prevalence of pesticide types in aquatic environments varies, with herbicides and their metabolites being the most common types of pesticides (Mohaupt et al., 2020; Paris et al., 2018; Schreiner et al., 2016). Their constant application in large doses and their great water solubility can be credited for their ubiquitous occurrence in water. In contrast, insecticides are less frequently discovered in water, due to their short and occasional applications. In addition, the majority of pesticides are lipophilic and bond to sediment, which makes them hard to be found in the grab water samples. However, for fungicides, they are found only in trace amounts in water. This is because they are applied in a way that results in fairly low but constant concentrations (Schreiner et al., 2016).

Surface water generally has higher concentrations of pesticides than groundwater. Pesticides can contaminate groundwater when they leak from treated fields, mixing and washing facilities, or waste disposal sites (Salem et al., 2016). According to Fang et al., 2017, surface water systems, like lakes, streams, rivers, reservoirs, and estuaries, are particularly susceptible to the buildup of pesticides and other chemicals because they are relatively tiny captive sinks of human activity byproducts. The hydrologic cycle connects surface water systems to both atmospheric water and groundwater. In addition, seepage of the soil may allow pesticides in surface water to enter the groundwater. Evaporation and transpiration are other ways they get into the atmosphere (Adams et al., 2016). Surface waterways can be refilled by both groundwater and atmospheric water. Pesticide contamination of groundwater and surface water has been extensively reported in literature (Anderson et al., 2018, Aravinna et al., 2017, Brauns et al., 2018, Clemow et al., 2018, Guo and Wang, 2004, Otalvaro and Brigante, 2018). In the study by Mohaupt et al., 2020, herbicides surpassed the safe drinking water limit at 7% of the groundwater sites, compared to 5-15% for surface water. Similar to this, less than 1% of groundwater locations had pesticide levels above the safe drinking water limit, as opposed to 3-8% of surface water sites. In addition to having a direct effect on the local drinking water supply, pesticide contamination in water can also have an indirect effect by spreading to other species and affecting the soil and food chain (Donaldet al., 1999). Another example is glyphosate and its major metabolite, aminomethylphosphonic acid (AMPA), which are present 30 times more often in surface water than in groundwater (Horth and Blackmore, 2009). Another example, over 90% of the water and fish samples taken from United States streams contained multiple pesticides, according to the United States Geological Survey (Rose et al., 2018). As another example, 46 water samples from the Azagny
region of Côte d'Ivoire were analyzed by N’dohou et al., 2023, which showed that the environmental status of this water is bad and that its negative risks to aquatic organisms are very high.

4.2. On the soil

Pesticides can attach to soil particles, volatilize, disperse, degrade, wash away with water, or be absorbed by plants or other creatures in the soil. The primary pesticide targets on crops are typically flowers, leaves, or shoots. Nonetheless, the soil receives roughly 50% of the active substances used (Navarro et al., 2007). Furthermore, rainwater partially removes insecticides that have been applied to the leaves, allowing them to reach the soil. Additionally, decayed plant components, such as wilting flowers, will fall to the ground and could spread chemicals into the soil. The utilization of seeds treated by pesticides and directly treating soil for weeds, soilborne pathogens, or illnesses are also significant contamination pathways. For example, Goulson, 2013 reported in his work that neonicotinoids' active component, which is used for seeds, enters the soil at a rate of more than 90%.

Soil quality or function is its ability to leach, breakdown, and detoxify pesticides (Shakeri et al., 2015). Pesticides' mobility in soil is primarily regulated by their adsorption to particles of soil, which is influenced by the characteristics of soil like the content of organic matter, temperature, clay, pH of the soil, porosity, water content, microbial community as well as by agricultural practices and the physicochemical characteristics of the pesticide (Hilber et al., 2008, Vryzas, 2018). The amount of pesticides that can be absorbed increases with increasing organic matter content. Furthermore, for the pesticides atrazine, 2, 4-D, 2, 4, 5-T, and picloram adsorption rises with a fall in soil pH (Andreu and Picó, 2004). Certain pesticides may be quickly eliminated from the soil ecology in a matter of days, while others may remain for decades (Vryzas, 2018).

Pesticide degradation generates residues that contaminate the environment by lingering and transforming for years in aquatic ecosystems as well as terrestrial sites (Barron et al., 2017). In fact, pesticide contamination of soil and sediment has been a major issue in terrestrial areas, having a negative effect on food quality and the sustainability of agriculture. Furthermore, soil serves as the main repository for environmental pesticides in terrestrial areas, having a significant impact on the global distribution and fate of contamination due to its high capacity to retain pesticides in their structures through adsorption as well as its secondary source of re-emission of old organic pollutants into the atmosphere, groundwater, and living organisms (Al-Wabel et al., 2016). The features of pesticides, such as their water solubility, soil sorption constant (Koc), octanol/water partition coefficient (Kow), and half-life in soil, all have a strong bearing on how long pesticide residues remain in the soil (Zhang et al., 2013). High Kow and Koc values are characteristics of pesticides that are tightly attached to the soil, and both of these characteristics lead to strong sorption to the organic matter in the soil. As a result, it would be reasonable to anticipate hydrophobic, persistent, and bioaccumulative pesticides would persist in soil (Aktar et al., 2009; Wu et al., 2017). Certain pesticides, like endosulfan, organochlorine DDT, endrin, lindane, and heptachlor, are tightly bound to soil particles due to their persistent nature and have been banned in many countries, including China (Yadav et al., 2015; Zerouali et al., 2006).

5. Human health effects of pesticide exposure

Pesticides are mixtures of different ingredients that have been massively used ubiquitously for several years. Although it is intended to destroy pests, it goes beyond that to reach the environment as well as the human body and makes their contamination inevitable. Due to their bioaccumulation ability and their high persistence in human organisms, they are likely to cause defects in body functions.
(Syafrudin et al., 2021). According to the World Health Organization, developing countries suffer annually from very high numbers of poisoning cases (approximately three million) and deaths (22,000 cases) due to pesticides (Lah, 2011), furthermore, the peril of pesticide exposure threatens over 2,000,000 human beings (Hicks, 2013). These figures are likely to have risen as a result of the extensive use of pesticides (Blair et al., 2015). Neither part of the world's inhabitants is entirely safe from exposure to the severe foreseeable health consequences of pesticides (WHO and UNEP, 1990). Even outside of the work area, a large part of the population is susceptible to exposure. The sources and ways of exposure differ dramatically across various population groups (Colosio et al., 2017). The biggest risk of exposure occurs in the pesticide's manufacturing and formulation zones of operation. The potential for risk in manufacturing facilities is high since they handle a variety of dangerous chemicals like pesticides (Grewal et al., 2017). Workers' exposure levels are typically greater than those of the other population. Furthermore, occupational exposure to pesticides for industry workers is comparable to other occupational exposure conditions in the chemical industry in that it typically occurs in small, enclosed spaces, at levels that are typically constant over time, can be better controlled, and involves a limited number of identifiable compounds (Colosio et al., 2017).

The risk of intoxication rises as pesticide concentrations and exposure duration rise. In addition to dose, concentration, duration, and so on, the route of pesticide entry into the body is an important factor in determining pesticide exposure-outcome. Pesticides can enter the human body via food, water (oral), respiratory (inhalation), and skin tracts by direct (pesticide industries, pesticide transportation, farmers, pesticide applicators, etc.) or indirect (food or water consumption) exposure to them (Sabarwal et al., 2018). The general population may be exposed by ingesting small quantities or large quantities (e.g. heavily contaminated food) of a complex mixture of pesticides present as residues in food. It is also possible that the main route of absorption is respiratory or dermal, and such exposure (environmental exposure) occurs near pesticide treatments, particularly in rural areas or where treatments are performed for public health purposes, or when indoor application and the presence of pesticides in materials such as Leather goods and wooden furniture. Inhalation is the primary pathway of exposure for workers in the chemical industry, while, for agricultural laborers, skin exposure is the primary pathway of exposure (Colosio et al., 2017). According to the WHO (WHO, 2004), the most common route of human exposure to pesticides is through oral exposure, where human death with pesticides through this tract is rapid and likely. It should be highlighted that many farmers have been exposed to drink poisoning, considered one of the oral exposure routes (Kim et al., 2017). Which requires knowing the level of food contamination and determining the maximum residue limits in order to ensure human being’s safety. In addition to oral exposure, the human body can also be exposed to pesticides contained in water via skin contact (Kumar et al., 2013, Zaidon et al., 2018). Also, the majority of farmers do not wear protective equipment when using pesticides, which greatly contributes to their entry into the body through inhalation and skin. The level of toxicity of each pesticide varies depending on its active ingredients. Once concentrations of pesticides in the body exceed those in the environment, their toxic effects begin to manifest (vander Werf, 1996), causing either acute or chronic poisoning.

Acute poisoning occurs forthwith or within a few hours of significant accidental or short-term exposure, where the period to the onset of exposure effects is relatively short. It's frequently misdiagnosed because its symptoms are extremely similar to those of other illnesses (Solomon et al., 2000). Pesticides account for less than 4% of all accidental poisoning deaths, as per provided poison control centers reports. According to a study conducted in Central America between 1992 and 2000, the prevalence of acute poisoning by pesticide cases increased from 6.3 to 19.5 per 100,000 people, and the mortality rate increased from 0.3 to 2.1 per 100,000 people (Henao and Arbelaez, 2002). The
An upsurge in cases could be attributed to both greater pesticides use and better data recording (PAHO, 2002). These recordings usually fail to distinguish between intentional, accidental, and occupational poisoning as well as to specify, at the very least qualitatively, how serious the poisoning is. However, the available data show that attempts at suicide are by far the most common cause of this type of poisoning, at least in developing nations, accounting for 44–91% and 26–60% of acute pesticide poisonings in South–East Asia and Central America, respectively (Besbelli, 2001, PAHO, 2002). Poisonings of this nature are a major issue that requires quick global attention (Blair et al., 2015). The bulk of unintentional acute poisoning by pesticides results from occupational sources (e.g. 5 to 32% cases in South-East Asia, 36% cases in Central American Countries (Besbelli, 2001, PAHO, 2002)), however, they can also be brought on by incorrect handling or storage of pesticides meant for home use or household pest control by members of the general public (Jeyaratnam, 1990). It is noteworthy that studies conducted over time show a remarkable decrease in acute poisoning, including suicides, as a result of regulations, such as restrictions on the use of the most toxic compounds and limiting general public access to agrochemicals, also because it has been well proven that easy availability to pesticides is one of the key factors influencing the frequency of acute suicide poisonings (Chang et al., 2012, Knipe et al., 2014).

Chronic poisoning occurs as a result of exposure to low-dose pesticides over long periods (days, months, or even years). It could also be the result of repeated acute poisoning. This type of poisoning occurs upon long-term exposure to pesticides either in farmers, professionals who use pesticides, farm or rural residents, relatives of pesticide users, and to a lesser extent, in the general population through residues in food and water, as well as owing to indoor and outdoor use for pest control. It is fairly simple to identify individuals who may have experienced chronic pesticide exposure, whether for work-related or non-work-related reasons; however, it is challenging to identify the compounds and the extent and source of exposure, especially in agriculture, and toxicological evidence and quantitative information about exposure are rarely available (Colosio et al., 2017). Because it is difficult to correlate health effects that are delayed (years before the onset of diseases or symptoms) and accurate assessments of exposures (during the relevant time period), studying these effects in humans is difficult due to the lack of clarity of evidence (Blair et al., 2015, Solomon et al., 2000). Since active compounds and application methods vary according to crops, geographic location, climate, and time, it is challenging to extrapolate from current data to assess prior exposures as well as the risk connected with a certain pesticide. This is particularly true for the general population when information on exposure and biological monitoring is sparse, if not nonexistent (Colosio et al., 2017). The following are some acute and chronic effects of pesticides shown in Figure 2.

Pesticides have been associated with a variety of malignancies, as well as a weaker immune system, congenital abnormalities, hematological morbidity, pulmonary dysfunction (UNEP, 1993), neurological disorders such as parkinsonism, neurobehavioral changes, diseases of the peripheral nervous system, also, contact dermatitis, whether allergic or irritating, which is the most prevalent clinical form of pesticide-related skin conditions, and erythema multifforme, ashy dermatosis, porphyria cutanea, and hair and nail abnormalities, acne are present the less prevalent diseases (Colosio et al., 2017, Spiewak, 2001), and others. Figure 3 summarizes the potential effects of pesticides on human health (a) and the health effects of some different types of pesticides (b). Even though many diseases and risks are known, determining all the effects of pesticides that are pernicious to human health remains complicated. Therefore, research on the use of biomarkers can be considered beneficial in assessing health risks to correlate the effects of pesticide exposure on human health (Zaidon et al., 2018).
Figure 2. Commonly cited health effects for each type of poisoning

6. Extraction, detection and removal techniques for pesticides

Pesticides are a broad range of chemical classes grouped and categorized according to the target crops. Its presence at ultrahigh concentrations is both environmentally devastating and hazardous to human health, making all stages of pesticide analysis a very challenging task.

A single experimental protocol cannot be used for all pesticide classes or even their degraded products. Also, the adoption of traditional techniques is no longer sufficient to track and analyze the widespread of pesticides, which become even more dangerous when its mixed, highlighting the importance of developing and innovating new analytical methods (more economical, fast, reliable, and effective) to treat all samples in a manner compatible with their nature, even at a low level of concentration, under opportune conditions and standards. Many different subtle, highly sensitive, and selective techniques are now used to achieve appropriate and effective monitoring of these chemicals, in order to ensure compliance, as far as possible, with the exposure pollution limit values, with the view of minimizing adverse consequences. In this part, we have compiled a set of conventional and advanced techniques cited in the literature.
Potential effects of pesticides on human health

- Respiratory problems
- Cognitive disorders
- Allergies and Irritations
- Immune system
- Liver damage
- Reproductive and fertility problems
- Cancers
- Heart failure
- Endocrine effects
- Neurological effects
- Hormonal imbalance

6.1. Extraction and detection techniques

Extraction is a selective process that is required before any sample analysis, and any defect at this stage can negatively impact all analysis processes (Campanale et al., 2021). It is an important step to reach a high concentration of analytes, depending on the solubility of the species to be extracted in a solvent, i.e. allows to increase the volume of analyte and to escape all other undesirables (Campanale...
et al., 2021). There are several extraction methods, the oldest of which is liquid-liquid extraction. Figure 4 below illustrates a series of pesticides extraction techniques for environmental samples. The studies of Hassaan and El Nemr, 2020 and Samsidar et al., 2018 summarized the advantages and disadvantages of each of these technologies separately.

Figure 4. A set of valid pesticides extraction techniques for environmental samples

<table>
<thead>
<tr>
<th>Extraction Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersive liquid-liquid microextraction (DLLME)</td>
</tr>
<tr>
<td>Liquid-Liquid Extraction (LLE)</td>
</tr>
<tr>
<td>Solid-Phase Extraction (SPE)</td>
</tr>
<tr>
<td>Single Drop Microextraction (SDME)</td>
</tr>
<tr>
<td>Solid Phase microextraction (SPME)</td>
</tr>
<tr>
<td>Matrix Solid-Phase Dispersion (MSPD)</td>
</tr>
<tr>
<td>Hollow fiber-liquid phase microextraction (HF-LPME)</td>
</tr>
<tr>
<td>Combination SPE and DLLME</td>
</tr>
<tr>
<td>Stir bar sorptive extraction (SBSE)</td>
</tr>
<tr>
<td>Continuous Flow Microextraction (CFME)</td>
</tr>
<tr>
<td>Quick, Easy, Cheap, Effective, Rugged and Safe extraction (QuEChERS)</td>
</tr>
<tr>
<td>ICE Concentration Linked with Extractive Stirrer (ICECLES)</td>
</tr>
</tbody>
</table>

Following extraction, the analyte components are detected in environmental matrices at the lowest thresholds using conventional or advanced techniques. Conventional detection techniques include well-known techniques based on chromatography, which is a method of separating the various constituents present in a blend with the aim of purifying, identifying, and quantifying the substances in analysis specimens. It allows a solution of the substance being studied to percolate in a column of adsorbents where the existing components each progress at different speeds and are distributed in distinct zones, causing their fracture in order to be analyzed easily. The most types commonly used are gas chromatography (GC) and liquid chromatography (LC), which employ various detectors with varying degrees of specificity. Hassaan and El Nemr, 2020 reported in their study the different detection methods from the oldest to the most recent and tied them to the different forms of detectors used as well as the advantages and disadvantages of each technique. Many detectors showed good performance with various pesticides, but until now the mass spectrometry (MS) detector is considered the best (Jianget al., 2014). It exhibits large advantages (no derivatization, higher sensitivity, selectivity, and precision, good reproducibility, and a better anti-interference effect). It is also gaining distinguished importance in organic environmental analysis (Samsidar et al., 2018). The combination of these two techniques (MS-chromatography) achieves integration in the qualitative and quantitative performance of the individual techniques by combining high discrimination power and high separating power (Barceló and Hennion, 1997). For the vast majority of pesticides and for their dependability, sensitivity, and selectivity, LC-MS or GC-MS are widely used in laboratories; they are critical for the structurally sensitive and positive identification of particular types of pesticides as well as other environmental contaminants (Stan et al., 1995; Tran et al., 2012). GC-MS has been widely used in pesticide analysis. However, due to its success in the analysis of various pesticides, LC-MS has recently
become the most widely accepted and applied methodology (Liu et al., 2017; Martínez Vidal et al., 2009; Montory et al., 2017; Shamsipur et al., 2016), due to the lipophilic nature of pollutants being manufactured and frequently used.

6.2. Advanced techniques for detection of pesticides

Chromatography techniques have yielded positive results in pesticide analysis. Nevertheless, the majority of these techniques are labor-intensive, expensive, and insufficient for on-site monitoring. They also require skilled operators, are time-consuming, complex, and use a lot of organic solvents, making them unsuitable for examining large amounts of samples (Samsidar et al., 2018; Singh et al., 2020). Therefore, it has become necessary to adopt suitable new, dependable, rapid methods to detect pesticides in environmental samples using advanced detection devices as an alternative method to conventional techniques. Besides specificity and sensitivity, these techniques have demonstrated satisfactory results in pesticide detection, such as ease of use, affordable price, and efficiency for on-site monitoring (Samsidar et al., 2018).

6.2.1. Molecular Imprinted Polymer (MIP)

Molecularly imprinted polymers (MIPs) are custom-made substances with distinct recognition sites for a specific molecule. MIPs have found extensive use as selective sensing materials and are frequently employed to identify compounds from different molecular-weight ranges (Samsidar et al., 2018). They are an excellent component for sensing platforms due to their specificity, versatility in terms of materials, and physical shapes. MIPs have been praised for their affordability, ease of preparation, stability, and reproducibility, despite having excellent features, MIP-based sensors have hardly ever been used outside of laboratories (Kadhem et al., 2021; Samsidar et al., 2018). MIPs utilization are actively very common and developed for biological purposes. The use of MIPs in biological applications includes, for example, cancer diagnostics, sensors, in vivo applications, enzyme-linked assays, drug delivery (El-Schich et al., 2020). MIPs have essentially produced artificial materials that perform similarly to biological receptors, but with limited stability. The MIPs have been regarded as an advance in biosensing approach for overcoming the shortcomings displayed by normal antibodies, peptides, and enzymes which are frequently used as molecular recognition components (Samsidar et al., 2018). There are several protocols for the process of MIP synthesis (essential process). The imprinting process uses a variety of templates, ranging in size from bacteria or entire proteins down to the smallest glycosylated glycan structures or even amino acids.

A MIP sensor has been created by Tan et al., 2015 using reduced graphene oxide and gold nanoparticles embellished on glassy carbon electrodes. The carbofuran pesticide was properly detected by this fabricated MIP at a detection limit (LOD) of 2.0 x 10$^{-8}$ mol L$^{-1}$. Dichlorvos pesticide detection MIPs method-based lab-on-paper device with chemiluminescence (CL) (Liu et al., 2015). The MIP approach has demonstrated good dichlorvos selectivity for pesticide testing in vegetable samples. The obtained LOD value was 0.8 ng mL$^{-1}$.

6.2.2. Electrochemical biosensors

For the quick, accurate, and on-site detection of pesticides, electrochemical detection is one of the non-destructive, economically feasible, and efficient techniques most frequently used (Mazzei et al., 2004; Noori et al., 2020). Electrochemical biosensors primarily include a selective reaction between a target or analyte substance and recognition element. Electrochemical transducers are the most frequently employed, particularly those based on enzymes. Nevertheless, the lack of selectivity and
vulnerability to enzymatic inhibitors are two stability/storage constraints of enzyme-based electrochemical sensors (Bucur et al., 2018). For determining pesticide residues in diverse matrices, electrochemical enzymatic biosensors based on various nanomaterials dropped on the surface of electrodes have been created. In order to alleviate the stability problems of enzymatic sensors, nanomaterials are being employed to immobilize enzymes, which helps them get beyond these limitations. Because of the surface features that the nanomaterials’ surface afforded, the inclusion of nanomaterials to the enzyme-based sensors further enhanced their selectivity and electrochemical performance (Aragay et al., 2012; Periasamy et al., 2009). For the electrochemical detection of pesticides in solid samples, nanomaterials have recently been used to create paintable inks that can be used to manufacture on-site painted electrodes (Bakytkarim et al., 2019). Using silicon carbide and multiwalled carbon nanotubes (MWCNTs) as a nanomaterial ink and chitosan as a stabilizer, Bakytkarim et al., 2019 created an easy and environmentally benign approach to change electrodes. Low temperatures were used in the electrode modification method, and the modified electrode had a considerable increase in parathion residue sensitivity. The quick and nondestructive detection of pesticides on plant surfaces has also attracted interest in smart plant wearing biosensors (Giraldo et al., 2019). In addition, to track the presence of pesticide residues, various types of sensors have been used, such as voltammetric, amperometric and potentiometric biosensors.

6.2.3. Optical biosensors

The use of optical biosensors in numerous fields, such as food safety, security, life science, environmental monitoring, and medicine, has drawn a lot of attention. The optical transducers' optical characteristics, like absorption, reflectance, and fluorescence emission, will alter in response to the analyte. There have been numerous researches carried out on the use of optical biosensors, particularly enzyme-based biomolecules, to detect pesticides. A study using fluorescence sensing based on biomolecules was described by (Thakur et al., 2012). To determine the OPs, the pyranine dye (8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt) is conjugated with OP hydrolase (OPH). The OPs pesticides are modeled after malathion and methyl-parathion, respectively. The optimal temperature was 55–60°C, and the limits of detection were in the 2–5 g L⁻¹ range (Kankou et al., 2021). In order to determine OPs pesticides as well as gold nanoparticles (AuNPs) from agricultural samples, Yan et al., 2015 developed an optical biosensor using a combination of ratiometric fluorescence quantum dots (RF-QDs) and gold nanoparticles. Two quantum dots of different colors are hybridized to create RF-QDs, which improves the sensor's accuracy. The resultant biosensor was successfully used to detect OPs (parathion-methyl) pesticides, with detection limits of 0.018 ng mL⁻¹ being attained.

6.2.4. Colorimetric biosensors

One of the most straightforward, cost-effective, and quick techniques for pesticide analysis that does not require complicated equipment is colorimetric detection (Qian and Lin, 2015). In place of the traditional color-generating probes (dyes and enzymes), this technique has developed from straightforward paper-based assays to the use of colorimetric sensor arrays based on nanotechnology (Sulaiman et al., 2020, Martinez et al., 2007, Singh et al., 2020). A thorough analysis of paper-based sensors coupled with NPs demonstrated the benefits of functionalization and surface modification of NPs in terms of improved selectivity and sensitivity (Ge et al., 2014). Using graphene oxide-wrapped silver NPs, Minh et al., 2020 reported on the colorimetric detection of carbaryl insecticide with a remarkable detection range of 0.1e50 ppm. Since colorimetric detection of the same pesticide had previously been described by (Lee et al., 2018) via azo coupling reaction and chemical pretreatment
with a limit of detection of 15 ppm, these techniques have been proven to be superior. By creating a nanozyme (nanoceria) assisted technique for a dual-mode (smartphone-based colorimetric method and spectroscopic method) detection of organophosphorus pesticide, (Wei et al., 2019) have combined smartphone-assisted analytical technology. This method has been shown to be very effective at detecting pesticides on-site, but requires sample pre-treatment by hydrolyzing the pesticide into para-nitrophenol. In real environmental samples, and using (+) AuNPs, Qi et al., 2020 suggested an aptamer-based colorimetric approach for the detection of ultra-low concentrations of acetamiprid. The aptamer's conformational changes in the absence and presence of acetamiprid could be sensitively distinguished by (+) AuNPs, which turned from red to blue in the absence of acetamiprid. Figure 5 briefly shows the colorimetric detection mechanism, and Figure 6 provides a set of advanced detection techniques of pesticides.

![Figure 5](image)

**Figure 5.** Diagram of the colorimetric detection mechanism

### 6.3. Decontamination water techniques

Removing pesticides from water is currently among the top environmental preoccupations (Kankou et al., 2021). Physical, chemical, and biological techniques are used to decontaminate pesticide-polluted water and to limit one's spread in the environment. But although these remedial techniques exist, the best solution to reduce the pollution problem remains the adherence to the application of good practices by pesticide users.

![Figure 6](image)

**Figure 6.** A set of valid advanced detection techniques of pesticides

### 6.3.1. Chemical techniques

Chemical techniques are used to break down compounds that are toxic or have less biodegradability. Chemical treatments encompass the use of agents to improve the extraction of risky chemicals such as pesticides (Hamby, 1996, Miller and Spoolman, 2014). Chemotherapy and physical therapy are frequently used in tandem (Brooks et al., 2003, Dhal et al., 2013). Table 2 contains a combination used chemical techniques for decontaminate water polluted by pesticides with their percentage of pesticide removal efficiency. Figure 7 demonstrates the sono-Fenton process reaction mechanism.
**Table 2.** Chemical techniques used for decontaminate water polluted by pesticides and their percentage of pesticide removal efficiency

<table>
<thead>
<tr>
<th>S.N°</th>
<th>Technique</th>
<th>Pesticides</th>
<th>% of pesticide removal efficiency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a- Adsorption</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>Chlorpyrifos (CP)</td>
<td>100%</td>
<td>(Maliyekkal et al., 2013)</td>
<td></td>
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<tr>
<td>2</td>
<td>Endosulfan (ES)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Malathion (ML)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>4</td>
<td>(2,4-D)</td>
<td>100%</td>
<td>(Tang et al., 2013)</td>
<td></td>
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<tr>
<td>5</td>
<td>Thiame-thoxam (TMX)</td>
<td>55%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Imidacloprid (ICL)</td>
<td>78%</td>
<td>(Wang et al., 2012)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Acetamiprid (ACT)</td>
<td>72%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Thiacloprid (TCL)</td>
<td>70%</td>
<td></td>
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</tr>
<tr>
<td>9</td>
<td>Atrazine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Promet</td>
<td>84%–96.4%</td>
<td>(Wu et al., 2012)</td>
<td></td>
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<tr>
<td>11</td>
<td>Ametryn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Prometryn</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>13</td>
<td>Phonamiphos</td>
<td>&lt;85%</td>
<td></td>
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<tr>
<td>14</td>
<td>Dimethoate</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>15</td>
<td>Parathion-methyl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Pirimiphos-methyl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Malathion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Fenthion</td>
<td>&gt;85%</td>
<td></td>
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<tr>
<td>19</td>
<td>Isocarbophos</td>
<td></td>
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<tr>
<td>20</td>
<td>Chlorfenvinphos</td>
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<tr>
<td>21</td>
<td>Profenofos</td>
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<tr>
<td>22</td>
<td>Methidathion</td>
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<tr>
<td>23</td>
<td></td>
<td>Phorate</td>
<td></td>
<td></td>
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<tr>
<td>24</td>
<td></td>
<td>Simeton</td>
<td>85%</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td>Simazine</td>
<td>82%</td>
<td></td>
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<tr>
<td>26</td>
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<td>Atrazine</td>
<td>98%</td>
<td></td>
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<tr>
<td>27</td>
<td></td>
<td>Ametryn</td>
<td>95%</td>
<td></td>
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<td>28</td>
<td></td>
<td>Prometryn</td>
<td>72%</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td></td>
<td>Cyprazine</td>
<td>90%</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>Cellulose/graphene composite</td>
<td>triazine pesticides 95% (Zhang et al., 2015)</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td></td>
<td>Ferrite manganese/graphene</td>
<td>Glyphosate &gt;89% (Yamaguchi et al., 2017)</td>
<td></td>
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<tr>
<td>32</td>
<td></td>
<td>Banana peel</td>
<td>Atrazine 98% (treated water) (Silva et al., 2013)</td>
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<tr>
<td>33</td>
<td></td>
<td></td>
<td>39–57% (river water)</td>
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<tr>
<td>34</td>
<td></td>
<td>AC-based adsorbent</td>
<td>Triazole 99% (Crini et al., 2017)</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>Biochar</td>
<td>carbamates 76.4% - 84.3% Metolachlor 70.2% (Ćwielag-Piasecka et al., 2018)</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td></td>
<td>Modified biochar</td>
<td>Triazine ~96% (Suo et al., 2019)</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td></td>
<td>Naturalclay</td>
<td>methomyl 30% sulfentrazone 99% (El-Geundi et al., 2012)</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td></td>
<td>Modified clay</td>
<td>sulfosulfuron 99% (Polubesova et al., 2005)</td>
<td></td>
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<tr>
<td>39</td>
<td></td>
<td></td>
<td>imazaquin 73%-93%</td>
<td></td>
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<tr>
<td>40</td>
<td></td>
<td></td>
<td>chlorotoluron 95%</td>
<td></td>
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<tr>
<td>41</td>
<td></td>
<td></td>
<td>acetochlor 90%</td>
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<td>42</td>
<td></td>
<td>Modified bentonite</td>
<td>deltamethrin 98% (Ahmad and Yasin, 2018)</td>
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<tr>
<td>43</td>
<td>b- AOPs</td>
<td>iron-catalyzed photo-activation of the persulfate system</td>
<td>atrazine 90% (Popova et al., 2019)</td>
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<tr>
<td>44</td>
<td></td>
<td>MnO2-HSO3</td>
<td>methyl parathion 72% (Wang et al., 2019)</td>
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<tr>
<td>45</td>
<td></td>
<td></td>
<td>methylparaoxon. 86%</td>
<td></td>
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</table>

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<table>
<thead>
<tr>
<th></th>
<th>Peroxymonosulfate (PMS)</th>
<th>2,4-D</th>
<th>92%</th>
<th>(Golshan et al., 2018)</th>
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<tr>
<td>49</td>
<td>nanocomposite photocatalyst containing MoS2/ZnS nanoparticles embedded in N/S doped graphite carbon</td>
<td>dicofol</td>
<td>85%</td>
<td>(Ahamad et al., 2020)</td>
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<td><strong>c- Ozonation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>isoproturon</td>
<td>70%</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>-</td>
<td>diuron</td>
<td>75%</td>
<td>(Ormad et al., 2008)</td>
</tr>
<tr>
<td>52</td>
<td>-</td>
<td>parathion methyl</td>
<td>75%</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>ozonation treatment was combined with activated carbon</td>
<td>atrazine</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>-</td>
<td>atrazine</td>
<td>90%</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>Ozonation using a pilot-scale reactor</td>
<td>alachlor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>treatment period between 30 min (for isoproturon) and 270 min (for alachlor)</td>
<td>atrazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>chlorfenvinphos</td>
<td>100%</td>
<td>(Maldonado et al., 2006)</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>diuron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>isoproturon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>nZnO-catalytic ozonation</td>
<td>atrazine</td>
<td>100% between 0.5 and 5 mg/L,</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td></td>
<td></td>
<td>90.2% increased to mg/L</td>
<td>(Pérez-Lucas et al., 2020)</td>
</tr>
<tr>
<td>62</td>
<td>ozonation combined with UV light</td>
<td>fluroxypyr</td>
<td>92%</td>
<td></td>
</tr>
<tr>
<td><strong>d- Fenton</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>-</td>
<td>fenitrothion</td>
<td>98.5% to 100%</td>
<td>(Barbusiński and Filipek, 2001)</td>
</tr>
<tr>
<td>64</td>
<td>-</td>
<td>chlorfenvinphos</td>
<td>97.1% to 100%</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>-</td>
<td>organochlorine pesticides</td>
<td>90%</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>Nitrogen-doped</td>
<td>MCPA</td>
<td>94%</td>
<td>(Ghanbarlou et al., 2020)</td>
</tr>
</tbody>
</table>
6.3.2. Biological techniques

Most biological purification systems relating to the disinfection of pesticide-contaminated wastewater rely on pesticide-digesting microorganisms, whose application to the restoration of contaminated soil is a new and evolving technique. Knowing that this process is considered difficult due to the toxicity of the pesticides to both different bacteria and fungi (Goodwin et al., 2018), nonetheless, once established, the biodegradation system is simple to maintain. The microorganisms serve as strong catalysts because they are extremely successful at converting organic pollutants and have the ability to change the structure and toxicity of pollutants on a large scale, as well as completely mineralize the organic molecules into somewhat less dangerous substances (Zawierucha and Malina, 2011). Bio-mixtures are typically composed of fertile humus materials to increase the possibility of pesticide, soil, and microorganism sequestration, whereas the bacteria present in the bio-mix could be of endogenous or exogenous origin (Jatoi et al., 2021; Saleh et al., 2020). The efficiency of decomposition during the treatment process is determined by the microorganisms used as well as the types of pollutants (Rajmohan et al., 2020). It is worth noting that bioremediation is classified as either aerobic or anaerobic (Jatoi et al., 2021; Saleh et al., 2020). Dichlorinated pesticides, for example, can be digested by either aerobic or anaerobic treatment (Javaid et al., 2016, Maltseva et al., 1996, Münze et al., 2017, Rawtani et al., 2018).

6.3.2.1. Soil treatment associated with Plants

Phytoremediation is an environmentally friendly technology, cutting-edge and cost-effective. Where both roots can be treated with microorganisms for the decomposition of pesticides and plant growth (Ahmad et al., 2012). In root processing, the soil volume is oriented around all the roots of the atmospheric roots and is highly dependent on the growth activities of the plant (Rajmohan et al., 2020).
Pesticide accumulation on the soil surface is required for plant transformation and phytovolitisation. Soil properties, plant properties, and possibly indoor plants are needed to increase ideal plant treatment potential. Effective phyto-treatment not only aims to achieve phytoaccumulation, but it can also be accomplished without the use of endogenous phytobacterials. To maintain soil fertility, however, the metabolic dissociation of pollutants within soil levels is also required (Alekhya et al., 2013; Vila et al., 2007).

Also, contamination can be reduced or avoided through the utilization of the biobed (Dias et al., 2020). They are bioreactors designed to treat pesticide residues leftover from farming activities (Castillo et al., 2008; Diez, 2010), and are a system for protecting water resources, environmentally friendly and effective (Dias et al., 2020). It's a hole in the ground filled with a biomix of 25 percent peat, 50 percent of wheat straw, and 25 percent of agricultural soil, and covered with turf. It's developed to dispose of pesticide residues from accidental spills so that the pesticides are degraded by the microorganisms established in the substrate, at the same time, the uptake of pesticide residues also takes place in the bio-mix, reducing their chemical availability (Castillo et al., 2008; Cooper et al., 2016). The biobeds are distinguished by their cheapness, ease of construction, and scientifically proven efficiency of over 20 years. Optimal temperature, humidity, microbial communities, and bioreactor efficiency assessment methods, are variables that affect the efficiency of bioreactors (Dias et al., 2020). A study by Diez et al., 2013 stated that in Chile each bio cell can be used for up to 5 years. It should be noted that this period is not fixed but depends on the climatic features of each country, and it can be monitored through modifications in the depth of the substrate. As a result, it is critical to understand and determine the time required for each country before implementing this technology as an environmentally safe system in the field.

6.3.2.2. Remediation with a biological mixture enriched ligninolytic fungi

Fungi that secrete embryolytic enzymes that depolymerize and mineralize the embryo are known as embryolytic fungi. Because some pesticides are included into lignin-based compositions, ferrolytic fungus can be added to a biomix that targets pesticide breakdown. This bio-matrix mix's often includes dahlia-rich materials, soil, microorganisms, and a lignocellulosic substrate that allows embryolytic fungi to colonize (Castillo et al., 2008).

6.3.2.3. Bio-augmented activated sludge treatment

Activated sludge is a very suitable treatment technique that requires less acreage and is less expensive than AOPs, but it does require a sludge disposal location as well as specialized manpower for maintenance and operation (Luo et al., 2014). Quan et al., 2004 created activated sludge that was supplemented with 2,4-DCP degrading bacteria obtained from 2,4-DCP-polluted soil. 2,4-DCP is a chlorinated phenol derivative that serves as a forerunner to the pesticide 2,4-D. When the starting concentration was between 10 and 100 mg/L, bio-augmentation of the sludge boosted the sludge removal effectiveness from 88 percent to 89 percent. Fluoxil was digested from the water using activated sludge made from wastewater from an oil refinery. Fluoxil is a herbicide whose active ingredient is organochlorine (oxyfluorfen). Initial values varied from 85 to 500 mg/L. Despite the fact that oxyfluorfen was not completely removed, the herbicide was removed at an 80 percent rate after 70 hours of exposure (Carboneras et al., 2018). Activated sludge has also been used to remove glyphosate from water. The aforementioned pesticide was completely eliminated at 4, 13, and 18 hours, respectively, at low starting concentrations (0.1, 0.5, and 1 g/L). However, in sludge, larger concentrations of herbicides (2 and 5 g/L) hampered cell growth (Tazdaït et al., 2018). The difficulty
of treating water with high COD in big quantities due to the restricted amount of dissolved oxygen under atmospheric pressure is one of the limits of activated sludge; the aeration process raises the technology expense. By increasing total air pressure in the pressured activated sludge, the amount of soluble O$_2$ increases. Increases in operating pressure, aeration time, and sludge concentration resulted in more COD removal, with an ideal level of 85.0 percent to 92.5 percent COD elimination (Jin et al., 2010).

6.3.2.4. Membrane Bioreactor

The Membrane Bioreactor (MBR) is a relatively new wastewater treatment technology. It is widely used to mineralize a variety of toxic contaminants; it mixes membrane filtration and biological treatment approaches. Spite of the high efficiency, but is consumes a lot of energy, not to mention the cost of anti-fouling treatments to keep it running (Ahmed et al., 2017; Khan and Pathak, 2020; Saleh et al., 2020). It also demands a lot of vitality and ventilation, in addition to another flaw is membrane peeling and roughness (Marican and Durán-Lara, 2018, Qi et al., 2018). Organic contaminant removal using an anaerobic MBR reported that pesticides were difficult to treat anaerobically, where the elimination rates was 6.8% for atrazine and 10.5% for linuron (Monsalvo et al., 2014), while, for a wide specter pesticide such as ametryn with an initial concentration of 1 to 4 mg/L, a hypoxic MBR exhibited an elimination rating of 65 percent within 15 hours. This rate climbs to 83 percent, 92 percent, and 99 percent, respectively, as the retention duration is increased to 1.5, 2.5, and 7.5 days (Navaratna et al., 2016).

6.3.3. Physical techniques

Physical remediation is the process of solving the issue using physical means (Tan, 2009). There are numerous techniques of that type (Marican and Durán-Lara, 2018), some of which are mentioned below:

6.3.3.1. Membrane filtering technology

Septic treatment plants frequently employ membrane filtering technology. Depending on the membrane and the impurities to be filtered, it can be filtered at any point during the water treatment process. Reverse osmosis (<1 nm), nanofiltration (1-10 nm), ultrafiltration (11-100 nm), and microfiltration (100-10000 nm) are all membrane filtration systems controlled by hydraulic pressure (Chiam and Sarbatly, 2011; Hylling et al., 2019; Saleh et al., 2020). The most suited methods for the elimination of organic compounds as pesticides are nanofiltration and reverse osmosis (RO), where the technology of RO is the most used (Joseph et al., 2000; Ozcan et al., 2009).

Bacteria, viruses, and big organic compounds are easily removed using nano-filtration membranes (Asad et al., 2020). Ahmad et al., 2008 used four different types of polyamide nano-membranes to investigate the filtration of two pesticides (dimethoate and atrazine) which have adverse health consequences. The filtration ability of the examined membranes was assessed in a laboratory experiment in where the quantities of pollutants were measured using HPLC. The NF90 membrane was the best of the four tested membranes, with an 85 percent retention rate for dimethoate and a 95 percent retention rate for atrazine; the pesticides' starting concentrations were evaluated at 2 and 20 mg/L, respectively (Ahmad et al., 2008; Nikbakht Fini et al., 2019; Taghizade Firozjaee et al., 2018), also, another study found that nanofiltration may effectively extract the pesticide glyphosate from brine effluent (Kenny et al., 2018; Song et al., 2013). Using interfacial polymerization technology, researchers synthesized poly(piperazinamide) thin film composite (TFC) nanofiltration membranes
and investigated the effect of triethylamine (TEA) as an accelerator on the membrane. The results showed that adding TEA to the membrane improved water rejection and flux when compared to other membranes, with diazinon rejection and water permeability increasing by 95.2 percent and 22 L/m²/h for the roughly 98.8% unmodified membrane and 41.56 L/m²/h for the TEA modified membrane, respectively. Poly (piperazine amide) TFC nanofiltration membranes for pesticide removal have shown considerable improvement (Karimi et al., 2016). Another study investigated the elimination of atrazine, simazine, and diuron in the presence of humic acid using two flat sheets negatively charged organic nanofiltration membranes (poly(piperazine amide nanofiltration (NF) and OPMN-K membrane). The results revealed that the NF membrane absorbed more pesticides than the OPMN-K membrane because of its smaller molecular cut-off. In compared to the NF membrane, OPMN-K has a lower solute retention and a higher permeate flux. Furthermore, raising the applied transmembrane pressure resulted in a significant drop in the OPMN-K membrane's solute rejection and a little rise in the NF membrane's solute retention (Pinto et al., 2018; Musbah et al., 2018; Vieira et al., 2020). Furthermore, the effect of humic acid on pesticide residues varies depending on how the solute is formed and how membrane molecules are retained. Diuron was the lowest absorbed by both membranes of all the pesticides studied, owing to its high molecular mass, higher dipole moment, and linear shape, although this is especially visible in the presence of humic acid. Importantly, poly(piperazine amide nanofiltration and OPMN-K membrane demonstrated a high ability to remove chemicals (Power et al., 2018; Wang et al., 2017). Diuron and isoproturon (phenyl urea insecticides) were eliminated from agricultural field water at a concentration of 2 mg/L in another study, using a thin-film composite polyamide reverse osmosis membrane, the pesticides were eliminated at a rate of more than 95%. The results demonstrated that the isoproturon filtration membrane caused more fouling than the diuron filtration membrane; nevertheless, diuron's membrane rejection was consistently lower than isoproturon's(Mehta et al., 2015).

6.3.3.2. Zeolites
Zeolites are a family of crystalline aluminosilicate materials with interconnected micropores that demonstrate an extremely tight distribution of pore-size (Pham et al., 2016; Yang et al., 2016). Due to its unique physicochemical characteristics, accessibility, and low price, zeolite has drawn considerable attention in the scientific community. It is employed widely to remove pesticides and heavy metals in agriculture, industry, and pollution management (Huong et al., 2016; Wen et al., 2016). De Smedt et al., 2015 showed that zeolite can be used as an adsorbent to treat water contaminated with pesticides like imidacloprid, isoproturon, bentazon, and metalaxyl-m, but the rate of adsorption is reliant on two main factors, namely the polarity and mobility of the pesticides. Immobile pesticides like imidacloprid, isoproturon, and metalaxyl-m tend to be bound to zeolites, whereas more mobile pesticides like bentazon partitioned in water. Isoproturon and metalaxyl-m (non-ionic pesticides) have a greater affinity for zeolites owing to their polarity. Valičková et al., 2013 assess the effectiveness of the zeolite in removing chlorinated pesticides (hexachlorobenzene, heptachlor, hexachlorobutadiene, pentachlorobenzene and lindane). The highest removal efficiency observed during the contact time was 93.8% for hexachlorobenzene. The second highest removal efficiency of 92.1% was achieved for heptachlor, trailed by hexachlorobutadiene (83.7%), pentachlorobenzene (72.9%) and lindane (25.8%).

7. Hybrid techniques for pesticide removal
Experimental studies on wastewater treatment often focus on a mixture of one to four pesticides, but in real life, however, this is not the case. Although one method achieves a high removal rate, the
effluent may still have a total pesticide content that exceeds the requirements set by the Environmental Protection Agency in the Water Framework Directive (WFD) on environmental quality standards (EQS). Hence, there is a need to establish wastewater treatment plants that combine multiple techniques like physical, biological, and/or chemical treatment procedures to ensure that heat-tolerant pollutants such as pesticides are reduced to the required level before being released into the environment (Goodwin et al., 2018).

Some hybrid technologies have proven to be successful, such as: Based on chemical oxygen demand, the efficiency of pesticide removal when activated carbons were combined with ultrafiltration and coagulation treatments was around 84 and 88 percent (Acero et al., 2012). The use of magnetic activated carbon (MAC) and powder activated carbon (PAC) in combination with an ultrafiltration (UF) membrane as a pretreatment for paraquat and linuron removal from water was examined by Zahoor, 2013a. Due to its large surface area, PAC showed a high percent retention of paraquat and linuron. The production of cake on the membrane surface, as well as the blackening of pipes and flow meters, resulted in long backwash periods and a decrease in permeate fluxes for PAC. The MAC hybrid approach, on the other hand, uses a magnet to remove MAC from a slurry, resulting in no cake formation and minimal backwash delays. A study used a granular activated carbon (GAC)/UF hybrid system to remove 2,4-D from water and found that 2,4-D had a high retention percentage and low permeate flux, with the hybrid system achieving 100% retention of 2,4-D (Zahoor, 2013b). In addition, Zahoor and Mahramanlioglu, 2011 evaluated the removal of 2,4-D from water utilizing MAC as a pretreatment in combination with the UF membrane vs PAC as a pretreatment. The results showed that the MAC impregnation procedure blocked the micropores in the activated carbon, resulting in a reduction in the adsorbent's surface area, and hence a decreased pollutant adsorption capability. Furthermore, when the MAC was utilized as a pretreatment and was removed from the slurry via the magnetic process before entering the membrane system, no cake formed on the membrane surface. In comparison to the PAC, where some pieces of the PAC were carried into the membrane, creating extra washing time, the MAC required less backwashing time, making it more cost-effective. Finally, because of its high adsorption capacity, cost efficiency, and simplicity of removal from the medium, MAC was regarded a good pretreatment in UF systems (Saleh et al., 2020).

8. **Performance comparison of removal techniques**

Pesticide removal presents a significant concern for environmental researchers and engineers. The treatment and removal of several pesticides from the environment has been successfully accomplished using a variety of techniques. The most effective way to design methods to remove and degrade environmental and public health-related toxins, like pesticides, is to use combined techniques. This review assessed various pesticide kinds (herbicides, insecticides, and fungicides) and their water removal rates using various approaches (Table 2). The removal rates vary depending on the water treatment methods studied. It's crucial to note that removal rates alone do not determine whether a technique of water detoxification is effective and suitable in large-scale experiments. Thus, it is crucial to screen for harmful treatment byproducts, before adopting a technique, especially when using chemical treatments. A comparative analysis of removal is very important for selecting the appropriate treatment techniques. For instance, Table 2 depicts the various percentages for atrazine removal attained using different techniques. The best techniques for atrazine removal were ozonation using a pilot-scale reactor, nZnO-catalytic ozonation, adsorption by banana peel, adsorption by graphene family materials. In the same context, the study of Saleh et al., 2020 find that nano-ZnO, biological treatment utilizing a particular microbial consortium, adsorption using wood charcoal and biochar, as
well as ozonation/H2O2 and nano-filtration, were the most effective atrazine removal techniques. According to the same study, the ozonation technique combined to activated carbon shows a high performance of removing (remove 100%) for 4 pesticides such as isoproturon, diuron, methyl parathion and 2,4-D. Chlorination techniques shows also high rates of removal (100%) for isoproturon, diuron, methyl parathion. While adsorption using wood charcoal, iron-catalyzed photo-activation and ozonation, appears lower removal performance for 2,4-D, methyl parathion, and isoproturon and diuron, respectively.

**Conclusion**

Pesticide contamination is one of the most significant worldwide challenges, posing a serious threat to human health and the natural balance of the ecosystem. Pesticides do have a number of advantages, the most notable of which is that they assist farmers to boost yields in the face of increasing population expansion. Pesticides, on the other hand, are a lethal weapon with difficult-to-control effects due to their vast range and misuse. Most, if not all, pesticides are harmful, albeit to varying degrees.

This review contained sources of environmental pollution, and disorders linked to pesticide exposure were also addressed, as multiple studies have found a correlation between pesticide exposure and infection with various cancers and other diseases. Lastly, this research summarized the various pesticide analytical techniques: extraction, detection and removal techniques, as well as a presentation of some of the techniques and pesticides that can be eliminated, as well as the percentage of removal, which are reached according to well-determined conditions. Where adsorption by the graphene family materials and Ozonation using an experimental reactor, Fenton, are considered examples of technologies that have been able to remove 100% of some pesticides.

The treatment of pesticides requires a comprehensive scientific analysis in order to select appropriate treatment techniques to avoid further toxic by-products. It is also necessary to choose the treatment technologies best suited to the environmental conditions of each country, which will help increase the treatment plant profitability.

**Statements and Declarations**

**Ethical Approval**

All authors confirm that this manuscript is original and has not been published elsewhere and is not currently under consideration for publication elsewhere in any form or language.

**Consent to Participate and to Publish**

This work described has not been published before;

It is not under consideration for publication anywhere else;

All co-authors have approved its participation and publication,

**Authors' Contributions**

All authors contributed to this review article:

The idea for the article was given by Dr. Anas EL LAGHDACH.

Yousra TAIDI performed the literature search and data analysis

All authors drafted and/or critically revised the work.

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