

Review

Water Pollution and Agriculture Pesticide

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Abstract: The agricultural industry uses substantial amounts of water (the highest in the world) mostly for irrigation purposes. Rapid population growth and, consequently, growing demand for food have increased the use of pesticide to have higher yield for crops and other agricultural products. Wastewater generated as a result of excessive use of pesticides/herbicides in agricultural industry is becoming a global issue specifically in developing countries. Over 4,000,000 tons of pesticides are currently used in the world annually and high concentrations above their threshold limits have been detected in water bodies worldwide. The generated wastewater (contaminated with pesticides) has negative impacts on human health, the ecosystem, and the aquatic environment. Recently, biodegradable and biocompatible (including plant-based) pesticides have been introduced as green and safe products to reduce/eliminate the negative impacts of synthetic pesticides. Despite positive advantages of biopesticides, their use is limited due to cost and slow interaction with pests compared to chemical pesticides. Pesticides may also react with water and constituents of soil resulting in formation of intermediates having different physical and chemical properties. Diffusion, dispersion, and permeation are main mechanisms for transfer of pesticides in soil and water. Pesticides may degrade naturally in nature; however, the time requirement can be very long. Many mathematical models have been developed to simulate and estimate the final fate of pesticides in water resources. Development of new technologies and environmentally friendly pesticides to reduce water contamination is becoming increasingly important.

Keywords: wastewater; agriculture; pesticides; treatment; modeling



Citation: Rad, S.M.; Ray, A.K.; Barghi, S. Water Pollution and Agriculture Pesticide. *Clean Technol.* **2022**, *4*, 1088–1102. <https://doi.org/10.3390/cleantechnol4040066>

Academic Editor: Patricia Luis

Received: 15 September 2022

Accepted: 18 October 2022

Published: 20 October 2022

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1. Introduction

Pesticides/herbicides use in agriculture is very common to increase production and ensure sufficient high quality affordable food for the growing population. These pesticides are mostly produced synthetically and like almost all chemicals pose a potential risk to human health and the environment. Pesticide use is inevitable in agricultural systems. New pesticides are being introduced continuously with enhanced properties for selective use and less negative impacts. Spraying is a common way of introducing pesticides over large areas of land, most of which can be carried away by wind, water runoff, and atmospheric weathering processes, and thus up to 95% of herbicides and over 98% of insecticides may not reach the targeted pests [1]. Physical and chemical interactions in the atmosphere can lead to formation of intermediates with negative impacts. Nevertheless, these pesticides eventually find their way to surface and ground water as well as lakes and oceans through different mechanisms. Uncontrolled application of pesticides in agriculture may result in alteration of products' quality and changes in the level of different enzymes in human body, leading to various health problems [2]. Traditional pesticide formulations generally have a high concentration of organic solvents with low dispersion, remaining in soil for a long time, and moving through the environment and putting biological systems at risk. Those who work in agricultural open fields and greenhouses and the pesticide industry are usually exposed to higher concentration of pesticides.

The world population is estimated to be 9–10 billion by the year 2050 [3], increasing the need for more food. The agriculture industry is the highest user of clean water, mainly used for

irrigation purposes, which can be easily contaminated by pesticides. More than 1200 pesticides and herbicides, some of which are banned in Europe, are currently in use in the world [4].

Although some of these herbicides can be degraded naturally in the soil, many of them are not easily degraded and remain in the environment for extended periods of time [5]. Municipal, industry, and agricultural wastes are discharged directly to various water bodies in many countries. Drugs, dyes, herbicides, pesticides, and other products of daily use have been detected in ground/underground water. Irrigation and rain also facilitate transportation of pesticides into ground/underground water especially those which are soluble in water [6]. Health issues such as hematologic and hormonal abnormalities, infertility, fetal malformation, neurological diseases, and cancer are commonly observed among those exposed to these pesticides. The underlying mechanisms of these effects are genotoxic, neurotoxic, and endocrine-disrupting actions [7–9].

The maximum consumption per hectare of pesticides is about 25 kg and Asia is the highest in the world. Global use of pesticides is comprised of 47.5% herbicides, 29.5% insecticides, 17.5% fungicides, and others account for only 5.5% [10]. Pesticide use is crucial in modern agriculture. Without proper use and management of pesticides, there would be a substantial loss of agricultural products to pests (for example, about 40% in crops). Exposure to pesticides used in agriculture has been related to autoimmune diseases such as systemic lupus erythematosus [11]. It has also been linked to neurodegenerative and respiratory diseases and various forms of cancer [12].

Skin and respiratory irritations as well as diseases such as Parkinson's, leukaemia, and autism were found to be higher in residential areas close to agricultural lands where pesticides were used continuously [13]. Excessive use of synthetic pesticides may also result in high concentrations of heavy metals (used in production of pesticides) in soil, which alters the biochemistry and microbial activities in soil with a negative impact on plants [14,15].

Agricultural water pollution may be due to fertilizers as they have a high concentration of nutrients (containing specifically nitrogen and phosphorus). When fertilizers are utilized in crop production more than the required amount, the excess amounts will remain in soil particles and finally be washed off the soil during irrigation or by rain, finding their way to water resources. Phosphates, which are not as soluble as nitrates, may get adsorbed onto soil particles and pollute the water thorough soil erosion.

Animal wastes are also rich source of nutrients and can be used as fertilizer. In aquaculture industry, excess nutrients and animal wastes may pollute the water. Table 1 summarizes most common water contaminants in agriculture.

Table 1. Categories of major water pollutants in agriculture and the relative contributions of the three main agricultural production systems [16].

Pollutant Category	Indicators/Examples'	Crops	Relative Contribution by:	
			Livestock	A
Nutrients	Primarily nitrogen and phosphorus present in chemical and organic fertilizers as well as animal excreta and normally found in water as nitrate, ammonia, or phosphate	***	***	*
Pesticides	Herbicides, insecticides, fungicides, and bactericides, including organophosphates, carbamates, pyrethroids, organochlorine pesticides, and others (many, such as DDT, are banned in most countries but are still being used illegally and persistently)	***	–	–
Salts	E.g., ions of sodium, chloride, potassium, magnesium, sulphate, calcium, and bicarbonate. Measured in water, either directly as total dissolved solids or indirectly as electric conductivity	***	*	*
Sediment	Measured in water as total suspended solids or nephelometric turbidity units—especially from pond drainage during harvesting	***	***	*

Table 1. Cont.

Pollutant Category	Indicators/Examples'	Crops	Relative Contribution by: Livestock	A
Organic matter	Chemical or biochemical oxygendemanding substances (e.g., organic materials such as plant matter and livestock excreta), which use up dissolved oxygen in water when they degrade	*	***	**
Pathogens	Bacteria and pathogen indicators., e.g., <i>Escherichia coli</i> , total coliforms, faecal coliforms, and enterococci	*	***	*
Metals	E.g., selenium, lead, copper, mercury, arsenic, and manganese	*	*	*
Emerging pollutants	E.g., drug residues, hormones, and feed additives	–	***	**

Pesticides can have detrimental impacts on weeds and insects, which indirectly affect the production yield. Therefore, new pesticides which are more selective and less toxic are being produced and gradually replace the older ones.

Vaccines, antibiotics, growth hormones, and drug consumption have increased in recent decades by humans or use in livestock, which can reach water resources in different ways.

Heavy metals which exist in pesticides and animal feed are considered as emerging pollutants and more than 700 of them and their metabolites have been detected in European aquatic environments [17]. Agricultural activities may reintroduce these pollutants into aquatic environments through the generated wastewater. An estimated 35.9 Mha of agricultural lands are subject to indirect use of the wastewater [18].

Generally, pests become resistant to pesticide when used for a long period of time, and therefore new pesticides need to be developed continuously, requiring new treatment methods and/or modification of existing ones. Pesticides have been classified based their functionality, lethal dose (LD50), type of impact on health, mode of action, etc. Pesticides have been classified in three categories as shown in Table 2 [19].

Table 2. Classification of Pesticides [19].

Pesticide	Class: Substance
Insecticide	Organochlorine: Endosulfa
	Organophosphate: Diazinon, Malathion, parathion, chloropyrifos
	Carbamate: Aldicarb, carbofuran, carbaryl
	Pyrethroid: Deltamethrin, Fenpropathrin
	Neonicotinoid: Acetamiprid, thiamethoxam
Herbicide	Phenylpyrazole degradate: Aldicarb sulfoxide, Endosulfan sulfate
	Triazine: Atrazine, cyanazine
	Cloroacetamide: alaclor, butachlor, dimethenamid, metolachlor
Fungicide	Benzamide: Fluopicolide, zoxamide
	Carboxamide: Boscalid captofol
	Chlorinated hydrocarbon: Hexachlorbenzene
	Organophosphate: Edifenphos, iprobenfos
	Chlorophenyl: Dichloran, quintozone

These pesticides have different characteristics with specific impacts on human health [20]. Pesticide characteristics and their effects are shown in Table 3.

Table 3. Type of pesticide pollutants in water [20].

Group	Chemical Composition	Characteristics	Effects
Organochlorine (DDT, aldrin, lindane, chlordane)	Non-polar and lipophilic atoms including carbon, chlorine, hydrogen atoms.	Lipid soluble, toxic to variety of animals and long-term persistence.	Tend to accumulate in fatty tissue of animals, biomagnification effect via food chain.
Organophosphate (Malathion, diazinon, parathion)	Aliphatic, cyclic, and heterocyclic possess central phosphorus atom in molecule.	Soluble in organic solvent as well as water. Less persistence than chlorinated hydrocarbons.	Tend to infiltrate into aquifers and reach groundwater. Affects central nervous system.
Pyrethroids (pyrethrins)	Alkaloid obtained from petals of plant species, namely Chysanthemum cinerariefolium.	Less persistent than other pesticides, therefore safest to be used as household insecticides.	Affects nervous system.
Carbamates (Carbaryl)	Chemical structure based on alkaloid of a plant species, namely Physostigma venenosum.	Relatively low persistence.	Only killed limited spectrum insects but highly toxic to vertebrate species.
Biological (Becillus thuringiensis, Bt and its subspecies)	Microorganism, viruses, and their metabolic products.	Applied against forest pests (butterflies) and crops.	Affect other caterpillars.

Insoluble chlorinated hydrocarbon pesticides have the potential to remain in soil for a longer time. Therefore, organophosphorus compounds such as Diazinon and Malathion were used instead. The main reason for their use is their rapid degradability so that they do not pollute water. Carbamate pesticides are used as a replacement for chlorinated hydrocarbons. Their active ingredients are not easily adsorbed to soil particles, thus reaching surface/subsurface waters. Pesticides undergo different processes in the environment, as shown in Figure 1 [21].

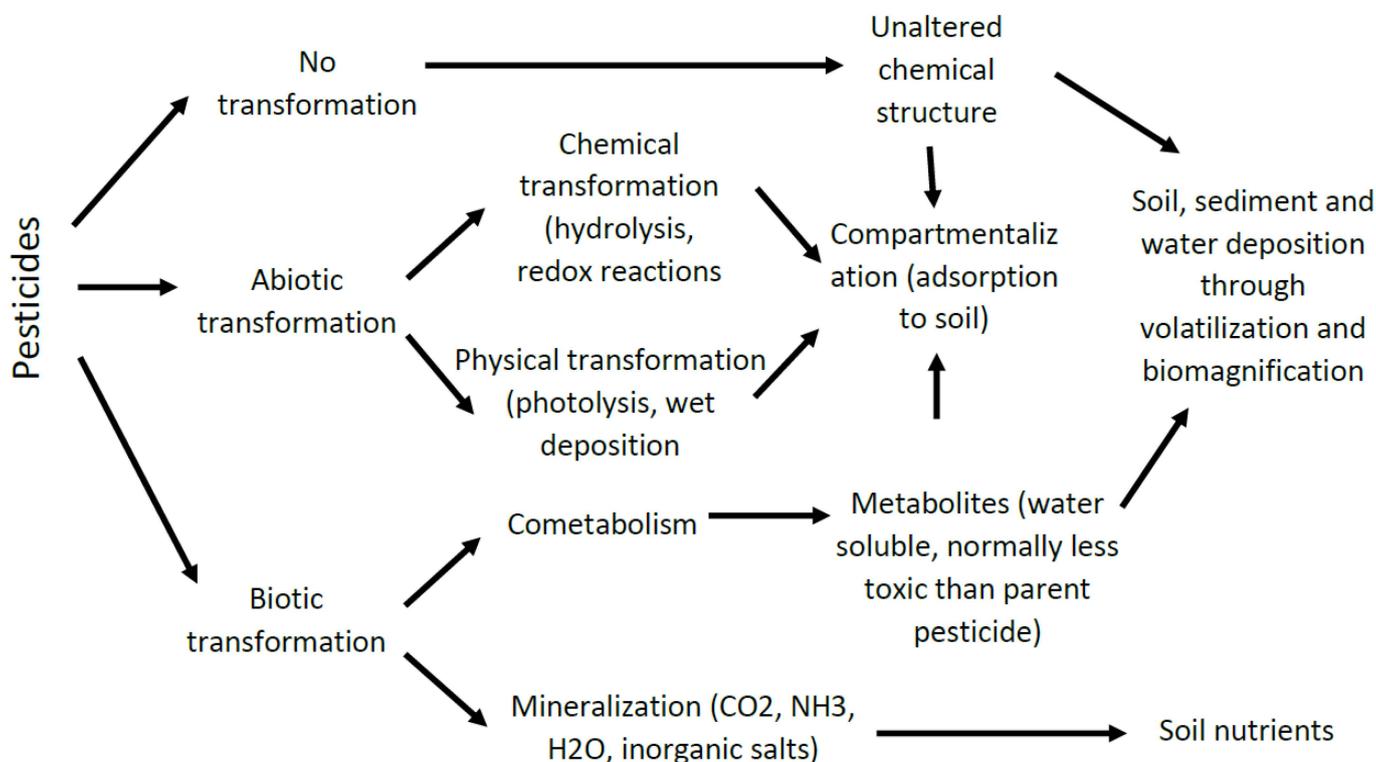


Figure 1. Transformation process of pesticides and their effect [21].

Agriculture pesticides are generally complex molecules and undergo several different reactions to become completely degraded. Pesticide transformation/conversion to other

molecules starts when introduced at a site. Degradation is more complex for insoluble pesticides as soluble pesticides are degraded much easier in the environment. The degradation reactions may be fast or slow and the intermediate molecules formed during the degradation may have different properties and follow different pathways to be mineralized, which depends on the type, physical, and chemical properties of the pesticide. Heat and photodegradation imposed by solar radiation play a major role in the breakdown of pesticide molecules.

A large number of mechanisms have been reported in the literature for degradation of agriculture pesticides. Despite the large variety in proposed degradation mechanisms, the main reactions are oxidation, reduction, and hydrolysis. Microorganisms play a key role in the biodegradation of pesticides where complex biochemical reactions occur.

Biopesticides and Nanotechnology

Due to negative impacts of synthetic pesticide, there is an increasing interest in biodegradable and biocompatible materials for the formulation of non-toxic, safe, environmentally friendly, and efficient pesticides. They have little negative impact on the surrounding ecosystem and human health [22]. Biopesticides are generally derived from natural resources such as animals, plants, bacteria, and certain minerals and can provide an alternative to synthetic pesticides used to control pest populations in agriculture [23].

Biopesticides are more advantageous to traditional pesticides due to their low toxicity and target specific nature, effectiveness in small doses, fast biodegradability, low exposition, and negligible emission. Although biopesticides are an environmentally friendly alternative to chemical pesticides, they are not as strong [24,25]. According to the FAO definition, biopesticides include those biocontrol agents that actively and selectively invade target pests [26]. Biopesticides fall into three main categories:

1. **Microbial pesticides** are microorganisms, such as viruses, bacteria, or fungi that prey on the pests that cause harm to crops
2. **Plant-incorporated** pesticides are produced by plants that mostly have been genetically modified.
3. **Biochemical** pesticides are herbal pesticides that have naturally chemicals that possess pest-repelling properties.

Similar to other pesticides, biopesticides may develop mutations and resistances in the target pests in agriculture [26].

Development of nanotechnology in recent decades has provided solutions to many problems in production materials with different applications including pest control. Nanoscience and nanotechnology have facilitated formulation, design, and preparation of environmentally friendly biopesticides (called nano-biopesticides) with controlled release. Embedding genetic materials in biopesticides have improved their effectiveness [27]. The use of nanomaterials in the development of new biopesticides/nano-pesticides with unique features for specific targets have been increased significantly in recent years [28]. The extremely small size and large surface area of nanoparticles play a major role in their applications in different areas of engineering and science, in the fields of pest control and management in agriculture, medical, pharmaceuticals, etc. Although nanoparticles can be produced synthetically using chemical, physical, and biological methods, they can also be found in nature, in plants such as algae, in the form of superoxide nano-particles and insects. High mobility and solubility as well as low toxicity, stability, and high efficiency are other characteristics of nano-biopesticides with a promising future for their applications in the agriculture industry. High selectivity of nano-biopesticides for targets of interest can reduce the required dosage. Groups of biopesticides such as nano-herbicides, nano-fungicides, nano-pesticides, and nano-insecticides (referred to as nano-agrochemicals) have great potential to replace traditional synthetic pesticides. Several biopesticides have been approved by the European body Ecocert and some by Organic Farmers & Growers (OF&G) [29]. Although the use of nanomaterials to enhance crop production can be a breakthrough for sustainable agriculture and control of plant pathogens, their release into the environment may have negative health issues.

Plants, algae, bacteria, and fungi use their protein and metabolites to absorb inorganic metals which can be further processed in biosynthesis of eco-friendly nanoparticles. For example, the fungus *Pleurotus cornucopiae* var. *citrinopileatus* can produce silver NPs which have antifungal activity. Biopesticides may undergo nano-coating for better delivery methods for pest control in agriculture and crop production facilities [30].

2. Water Pollution by Pesticides

Water contamination is mostly the result of agricultural and urban runoff, where herbicides/pesticides find their way through leaching in soil or by direct discharge of contaminated wastewater [21].

Pesticides interact with water in different ways due to their physical and chemical properties. All pesticides have main ingredients that are mixed/dissolved in inert compounds (e.g., solvent) to adjust their concentration. Therefore, water pollution in agricultural systems may be due to the presence of active ingredients as well as fillers and impurities or intermediates during the degradation process. Diffusion, dispersion, and permeation are the main mechanisms for transfer of pesticides in soil and water. At the same time, the natural degradation of pesticides in soil or water may result in the formation of intermediates. Interaction between pesticide and soil and/or water is a complex phenomenon with little information in the literature. The stability of pesticides is generally related to their half-life. Persistent pesticides have a long half-life and pose threats for a longer time.

Although municipal and industrial wastewater discharges substantial amount of wastewater into water bodies, agriculture accounts for 70 percent of water abstractions worldwide. Large amounts of agrochemicals (mostly pesticides/herbicides) are discharged into the water, endangering human health, aquatic ecosystems, and plants [31]. According to FAO, the agricultural land, which requires irrigation, has more than doubled (about 320 Mha in 2014) in recent decades [25], which has increased the use of pesticides and eventually affected ground/underground water quality.

About 85–90% of all fresh water is used for irrigation of agricultural land in Africa and Asia. Agriculture withdrew 67% of the world's total freshwater in 2000 [31].

Based on the U.S. Geological Survey (USGS) carried out in mid 1990s, 90% of major rivers' water and fish samples close to agricultural and urban land contained pesticides [32]. The herbicides 2,4-D, diuron, and prometon were among the 21 pesticides detected most often in surface and ground water across the nation with concentrations above the guidelines. High concentrations of pesticides above their threshold limits were detected at 13–30% of all surface and ground waters in Europe between 2013 and 2019, as shown in Figure 2 [33].

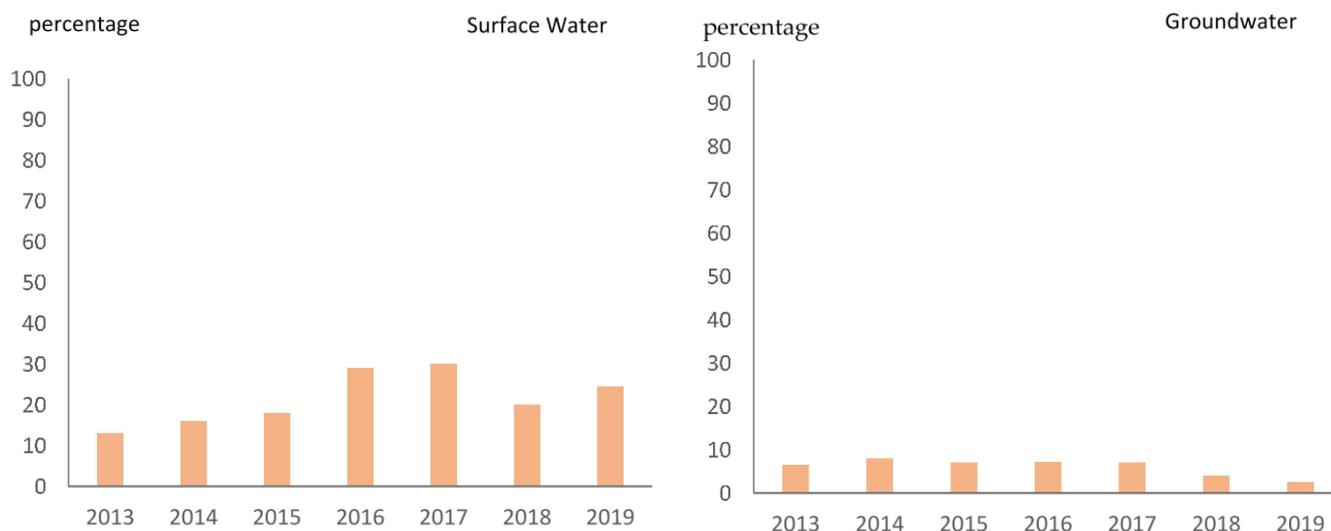


Figure 2. Pesticide concentrations in surface and ground water [34].

Figure 2 shows one or more pesticides with concentrations above their threshold for all surface water monitoring sites each year between 2013 and 2019. The number of pesticides in surface water ranged from about 10 to over 100 with the lowest being in Austria [6] and the highest in France [29].

Pesticide concentrations higher than the acceptable limit were also reported in surface waters in Mexico (Cienega area of Jalisco). In a comprehensive study on the concentration of pesticide in India, high concentrations were also observed in river water, surface water, ground water and, interestingly, rainwater [35].

An analysis of samples from 1204 wells across the United States showed the presence of 109 pesticides and 116 pesticide degradates. Among those, about two-thirds contained pesticides and three-quarters contained degradant. The most common detected pesticides were Atrazine, Hexazinone, Prometon, Tebuthiuron, four Atrazine degradates, and one metolachlor degradates, detected in >5% of the wells with 1.6% of the wells having concentrations approaching levels of potential concern [6].

The annual use of conventional pesticides in the United States between 2005–2012 was about 400–450 million kg, excluding biological and antimicrobial pesticides. Glyphosate, atrazine, metolachlor-(S), 2,4-D, and acetochlor were the most commonly used herbicides in United States between 1992–2017 [36].

Pesticides are being transported from land to ground water by rain fall and irrigation, where permeable soil is more susceptible to the process. Pesticides with high persistence and a low tendency to adsorb to soils and sediments are detected easily [37]. A higher concentration of pesticides is generally observed in shallower groundwater than deeper, and older groundwater, as drainage systems in agricultural areas can divert shallow groundwater to surface water [38].

In five studies, when evaluating up to 80 pesticide compounds and 9 degradates, Atrazine and its degradant deethylatrazine (DEA) were the most detected [33]. The eighth most detected compound was Dieldrin, an insecticide (3.1%) while Propoxur concentration was reported as 1.8%. The most detected fungicide was Metalaxyl (0.7%) [39,40].

The formulation of green, safe, and efficient pesticides is one of the ongoing challenges in the pesticide industry. Design and production of targeted environmentally friendly pesticides with controlled release through chemical modification offers great potential for new formulations. One of the emerging technologies is production of pesticides using genetically modified plants.

Wastewater Treatment

Removal of pesticides from water requires knowledge of physical and chemical properties of pesticides and their interactions with water (e.g., ionization, solubility, etc.). Therefore, different design approaches and operating conditions are necessary for the treatment.

Due to the large amount of wastewater in agriculture, physical processes are generally preferred to avoid using large volume of chemicals, which may generate new sources of pollution to the environment. The concentration of pesticides in water is low even when it is much higher than the threshold limits, therefore, adsorption is the preferred option for the separation of pesticides from water. Different adsorbents are available for different classes of pesticides in terms of hydrophobicity, molecular structure, and size, such as activated charcoal, activated carbon, organoclays, inorganics, and plant-based adsorbents (bio-adsorbents). A detailed review of different adsorbents and their selectivity for different pesticides can be found elsewhere [41].

The large diversity in size and shape of pesticide molecules has been used to separate them from water using membranes processes such as nanofiltration and ultrafiltration [42].

The combination of membrane separation and adsorption was proven to be more effective for the removal of pesticides from water [43,44].

The complete removal of carbaryl and carbofuran (micropollutants) from public water was reported using a combined technique of adsorption (fixed bed of granular activated carbon) and microfiltration from public water [45].

In recent decades, advanced oxidation processes (AOPs), which are based on formation of hydroxyl radicals (OH) to degrade pesticides in wastewater to nontoxic compounds, have been studied extensively. Hydroxyl radical is a very powerful highly reactive non-selective oxidant that can be produced in an aqueous solution using certain chemicals or photocatalysts such as titania to destruct organic molecules. Titania is the most commonly used photocatalyst that can generate electron-hole pair when irradiated by ultraviolet light to initiate reactions, leading to the formation of hydroxyl groups. Due to the large band gap of titania, doping is applied to reduce the bandgap and thus facilitate using visible light instead of UV light. AOPs have been successfully employed for decomposition of pesticides [46,47].

To enhance pesticides' degradation efficiency and selectivity, a combination of AOPs have been successfully employed. Nearly complete mineralization of pesticides in water can be achieved using H₂O₂, ozone, and metallic oxide [48].

Advanced oxidation processes can be also combined with physical processes such as adsorption to degrade pesticides. AOPs such as chlorination and ozonation, followed by adsorption using activated carbon removed over 90% of 44 pesticides from water [49].

Live microorganisms such as fungi and bacteria have been found to be effective in the degradation of pesticides in water. The process is referred to as biodegradation. Jariyal et al. (2018) used three different microorganisms (*Brevibacterium frigoritolerans*, *Bacillus aerophilus*, and *Pseudomonas fulva*) to remove organophosphate residues in water achieving biodegradation efficiencies over 97.5 percent [50]. Complete degradation of Carbaryl was reported using *Rhodopseudomonas sphaeroides* [51,52].

Recently, living plants have been used for the degradation of pesticides in water. The process is known as phytoremediation and is used for decomposition of clomazone with over 50% efficiency. Phytoremediation efficiency is challenging to determine due to the exposure of plants to other microorganisms living in soil as well as other weathering processes involved [53]. One of the most used plant-based pesticides (extensively used in agriculture crops) is derived from neem, which is a tropical Asian tree (*Azadirachta indica*) that has insecticidal and antiseptic properties. The potential benefits are that they are economical, environmentally friendly, effective, and of low toxicity to non-target organisms, including humans [53,54].

Genetically modified (GM) foods have been produced by introducing genetic material (DNA) from other organisms to the plants by genetic engineering. GM foods have been found to be more resistant to pests; for example, GM crops needed 40% less pesticide, which has a huge impact on water contamination in crop agriculture. There are sporadic reports about positive and negative impacts of GM foods but there is no solid scientific proof for that; however, it seems that GM foods are becoming crucial in feeding the world's growing population, especially in harsh environments/climates [55].

Application of the treatment processes for a very large amount of agriculture wastewater needs more research to optimize the process for an effective, feasible, and environmentally friendly treatment.

3. Modeling and Simulation

Large quantities of wastewater are generated in agriculture, therefore experimentation, management, and control at such levels are time consuming and costly. Models that are simplified representations of real-world systems are used to simulate the fate of pollutants and estimate the changes in water quality at different locations to an acceptable level. Due to the complexity of real-world problems, simplifying assumptions are used and therefore models cannot be completely accurate; however, they are reliable enough to help in providing policies, strategies, and actions for mitigation purposes. Models with different strengths and limitations are used in the field of water quality. These can be applied at different scales to support planners and policymakers in designing cost-effective measures for addressing water pollution in agriculture [56,57].

The models are mainly related to the flux of polluted water and transformation processes. Water transportation, quality, meteorology and hydrology, land characteristics and management and transformation processes are of main concern. Irrigation and type of agriculture as well as plants, soil, and the environment make such modeling activities a challenging task. Leaching and water runoff are generally the first stages in pesticide transportation.

A mathematical model based on a system of ordinary differential equations was developed to provide farming alertness for pest administration in crops production, considering plant biomass, type of pest, and control level. Using the local pest-free and coexistence equilibria and applying the control theory, the criteria to decrease pest contamination in crop fields were achieved [58].

To control the pest population in crop fields under different dynamic regimes, a mathematical model based on Z-type control was applied. The pest population and its fluctuation were successfully controlled and the results were verified by actual field data [59].

Despite the unique advantages of biopesticides, they suffer from time requirements as well as cost. However, a combination of biopesticides with chemical/synthetic pesticides has shown to reduce time and cost. A mathematical model was developed to show the effectiveness of such an approach to pest control for *Jatropha curcas* plantation. The model successfully predicted the optimum concentration profile for biopesticides and chemical pesticide using optimal control theory, minimizing negative impacts, and improving feasibility. The numerical simulations justified the results [60].

Bacteria, algae, fungi, protozoa, and viruses have been used as microbial pest control agents used for specific pests. Viruses such as Baculoviridae (nucleopolyhedroviruses) [NPV] and granuloviruses are among very strong biopesticides. More than 400 insect species have been reported as hosts for baculoviruses. A mathematical model was established to study the interaction between a virus and a pest. The interaction follows the Michaelis–Menten type and the virus attacks the pest population only with no recovery or immunization of the pest. A good agreement was reported compared to available data in the literature [61].

Jena and Kar proposed and analyzed an ecological system and studied the dynamics of pest control systems using the prey–predator model. They developed a mathematical model with three state variables, namely the susceptible pest, the infected pest, and the biological predator to the pest. Additional food sources were considered in the model to help the predator to survive when the prey concentration is negligible. The role of additional food is very much important in relevance to pest control because it helps to protect predator populations when the pest population is not sufficient. Considering the cost and environmental impact and using Pontryagin’s maximum principle, the optimal pest control strategy was obtained [62].

An ecophysiological model of plant–pest interaction and multi-criteria decision analysis was developed to optimize crop management when considering two contrasting objectives: (1) maximizing crop production and (2) minimizing environmental impact related to fertilization, irrigation, and pesticide deployment. A mechanistic plant growth model and a pest population model were considered [63].

Pesticide dissipation is a complex phenomenon which depends on pesticide type, environmental factors, transfer processes, degradation phase partitioning, etc. Prediction of pesticide dissipation half-life in plants is important in estimating the fate of pesticides. Over 4500 data points on pesticides’ half-lives were used with four machine learning models (i.e., gradient boosting regression tree [GBRT], random forest [RF], supporting vector classifier [SVC], and logistic regression [LR]) to predict dissipation half-life intervals using extended connectivity fingerprints (ECFP), temperature, plant type, and plant component class as model inputs. Despite successful outcomes of the model, due to the large number of variables and uncertainty involved in their prediction, more data is required to improve the models’ performance [64].

Yadav and Kumar used mathematical modeling to study an ecosystem consisting of two types of preys and their predators in agriculture. The two preys had a long time and

short time to grow (sugarcane and vegetable, respectively) with predators that can attack them both simultaneously. The various equilibria of the system were obtained, and the stability conditions were analyzed [65].

The Environment Protection Agency (EPA) offers models for evaluation of pesticides leaching. The Global Livestock Environmental Assessment Model (GLEAM) [66] and the transformation process-based model (LEACHM) [67,68] are currently in use. The most employed mathematical models have been listed in Table 4.

Table 4. List of mathematical models for pesticides fate in agriculture.

Description	Model	Reference
Crop Pest management and control	Based on IPM * technique	Abraha et al., 2021 [69]
	Optimum control approach	Chowdhury et al., 2019 [61]
	Prey–predator based	Tang and Cheke, 2005 [70]
	pest-epidemic model	Wang et al., 2011 [71]
	microbial pesticide model	Wang et al., 2017 [72]
Watershed model, single-event capabilities	Pest Population control by infected pasts	Sun and Chen, 2009 [73]
	AGNPS	Merritt et al., 2003 [74]
Long-term effects of hydrological changes and water and soil management practices	DWSM	Borah et al., 2002 [75]
	AnnAGNPS	Bingner and Theurer, 2001 [76]
	HSPF	Donigian et al., 1995 [77]
	SWAT	Neitsch et al., 2002 [78]
Study of hydrology and non-point source pollution, small watersheds	MIKE SHE	Borah and Bera, 2003 [79]
Numerical models considering surface and subsurface hydrologic	InHM	Loague and VanderKwaak, 2002 [80]
	MOD-HMS	Panday and Huyakorn, 2004 [81]
	HydroGeoSphere	Colautti et al., 2005 [82]
Concentration of pesticides and their fate in rivers, steady state conditions	EXAMS	Burns, 2000 [83]
	the Mackay Level III Model	Mackay, 2001 [84]
	QUAL2E	Brown and Barnwell, 1987 [85]
	principal component analysis	Gramatica and Di Guardo, 2002 [86]
	MIKE11	DHI 1995 [87]
Dynamic in-stream water quality models	ISIS	HR Wallingford and HalcrowUK, 1998 [88]
	RWQM1	Reichert et al., 2001 [89]
	WASP	Wool et al., 2001 [90]
Pesticide fate modeling in surface water	TOXSWA	FOCUS, 2001 [91]
	PERPEST	Van den Brink et al., 2006 [92]

* Integrated Pest Management.

In most cases, the predictions made through modeling and simulation efforts have been supported by field and lab experiments in a relatively narrow range of parameters. More comprehensive models are required to take into account different parameters simultaneously.

4. Wastewater Treatment Cost

Similar to all industries, feasibility is one of the main concerns in wastewater treatment industries. Access to affordable clean water has been and probably will be one of the serious challenges worldwide. Population growth, industrialization, agriculture, energy production, etc. have introduced new pollutants to water that require advanced treatment processes, adding more to the cost of clean water production. Therefore, a detailed study of water treatment processes and associated costs is vital to reduce/optimize the cost, making clean water available, especially to developing countries with limited water resources. The cost of wastewater treatment plants depends on the process, design configuration, as well

as the quality of the treated water. Obviously, the cost per unit volume of the treated water decreases by increasing capacity. The detailed cost and profitability analysis including the capital cost and operating cost is out of the scope of this study. Due to the large variations and conditions in different plants, it is quite challenging to compare the cost of different wastewater treatment plants [93].

The capital cost for a 150,000 gallon per day of a typical wastewater treatment plant (including design to start-up) is estimated to be between USD 500,000 to 1.5 million, while operating costs vary considerably due to the cost of energy, labor, and local rules and regulations. The cost of an industrial wastewater treatment plant strongly depends on the type of industry and wastewater as well as the target quality [94]. Detailed information about cost estimation can be found elsewhere [95].

Advanced oxidation processes have been employed as a tertiary water treatment option. Despite variabilities of auxiliary processes (e.g., adsorption, filtration etc.) to improve efficiency, cost estimation has been carried out for some plants. It was reported that the capital cost in the range of 0.035–0.05 EUR/m³ and an operating cost of 0.04 EUR/m³ of treated wastewater for an ozonation process combined with adsorption (granular and powder activated carbon). A cost analysis of wastewater treatment plants is a complex process due to uncertainties involved, and, thus, the reported values are an approximation for the initial assessment of wastewater treatment plants [96].

5. Conclusions

Water pollution by pesticides used in agriculture is increasing at an alarming rate due to the need for more food by the growing population, requiring the use of many pesticides in agriculture. It is a multidimensional challenging problem and requires comprehensive actions and cooperation from various sectors involved. Pesticides undergo different processes in a complex fashion which makes it challenging to apply the existing mitigation processes. A high concentration of pesticides has been detected worldwide and the need for effective treatment processes is urgent. Biopesticides seems to be a promising approach, however, the limitations such as their effectiveness and cost have made their application challenging. The combination of biopesticide and chemical pesticides can increase the effectiveness of pest control strategies with less impact on the environment. Many mathematical models have been introduced for pest population control as well as treatment of agriculture wastewater. These models are applicable to certain conditions and are usually within a narrow range of variables. Physical treatment processes are preferred over chemical processes for agriculture wastewater due to use of large amount of chemicals, which may lead to generation of new pollutants. Research is needed to reduce source load and minimize water pollution along flow paths and find a feasible effective method for wastewater treatment.

Author Contributions: Original draft preparation, S.M.R., Review and editing, A.K.R. and S.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no funding.

Institutional Review Board Statement: Ethical approval not required.

Informed Consent Statement: The study did not involve humans.

Conflicts of Interest: The authors declare no conflict of interest.

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