Chemosphere 352 (2024) 141283

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

A review on the management of rinse wastewater in the agricultural sector

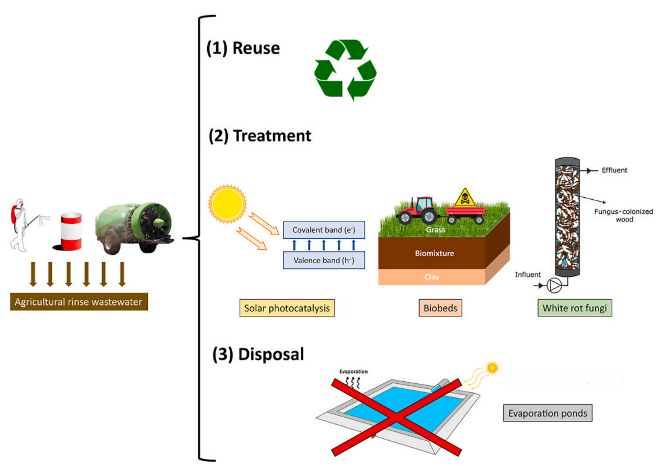
Eduardo Beltrán-Flores, Montserrat Sarrà *, Paqui Blánquez

Departament d'Enginyeria Química Biològica i Ambiental, Escola d'Enginyeria, Universitat Autònoma de Barcelona, 08193, Bellaterra, Barcelona, Spain

HIGHLIGHTS

- Good agricultural practices should include the management of rinse wastewater.
- Large farms can generate excessive volumes of rinse wastewater for direct reuse.
- Biobeds and solar photocatalysis have been applied in full-scale treatments.
- Fungal treatment is a promising option for treating agricultural rinse wastewater.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling editor: A Adalberto Noyola

Keywords:
Washing water
Agricultural wastewater
Pesticide
Solar photocatalysis
Biobed
White rot fungi

ABSTRACT

Pesticides have become indispensable compounds to sustain global food production. However, a series of sustainable agricultural practices must be ensured to minimize health and environmental risks, such as eco-friendly cultivation techniques, the transition to biopesticides, appropriate hygiene measures, etc. Hygiene measures should include the management of rinse wastewater (RWW) produced when cleaning agricultural equipment and machinery contaminated with pesticides (among other pollutants), such as sprayers or containers. Although some technical guidelines encourage the reuse of RWW in agricultural fields, in many cases the application of specialized treatments is a more environmentally friendly option. Solar photocatalysis was found to be the most widely studied physical-chemical method, especially in regions with intense solar radiation, generally using catalysts such as TiO_2, $Na_2S_2O_8$, and H_2O_2, operating for relatively short treatment periods (usually from 10 min to 9 h) and requiring accumulated radiation levels typically ranging from 3000 to 10000 kJ m^{-2}. Biological treatments seem to be particularly suitable for this application. Among them, biobed is a well-established and robust technology for the treatment of pesticide-concentrated water in some countries, with operating periods that typically range from 1 to 24 months, and with temperatures preferably close to 20 °C; but further research is required for its implementation in other regions and/or conditions. Solar photocatalysis and biobeds are the only two systems that have been tested in full-scale treatments. Alternatively, fungal bioremediation using white rot fungi has shown excellent efficiencies in the degradation of pesticides from agricultural wastewater. However,

* Corresponding author.
E-mail address: montserrat.sarra@uab.cat (M. Sarrà).

https://doi.org/10.1016/j.chemosphere.2024.141283
Received 19 June 2023; Received in revised form 15 January 2024; Accepted 21 January 2024
Available online 26 January 2024
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greater efforts should be invested in gathering more information to consolidate these technologies and expand their use in the agricultural sector.

1. Introduction

Pesticides are substances intended to prevent, destroy, or control any pest, including insects, rodents, weeds, and fungi (FAO, 1990). The increase in world population and the economic growth experienced since the mid-20th century were largely due to the increasing expansion of intensive agricultural practices. Nowadays, pesticides are still vital to meet the global food demand (EC, 2019, 2009). Over the last decades, the use of these compounds has increased significantly worldwide (Fig. 1), being widely applied in many industries, commerce, homes, parks, and gardens, although by far the largest pesticide use is in the agricultural sector, which accounts for approximately two-thirds of the global pesticide (Atwood and Paisley-Jones, 2017).

Nevertheless, prolonged exposure to some pesticides (even at low concentrations) is believed to be associated with numerous health disorders in many species, including humans, such as reproductive syndromes, respiratory dysfunctions, endocrine disruption, diabetes, neurological alterations, and cancer (Pathak et al., 2022; Rani et al., 2021; Sabarwal et al., 2018). Some pesticides can also be degraded into transformation products (TPs) that can be even more toxic than the parent compounds (Ueyama et al., 2007). In addition, interactions between pesticides (and their TPs) can trigger synergistic mechanisms with unpredictable toxicological effects (Hernández et al., 2017).

In addition, a low proportion of the applied pesticides is believed to act effectively against target pests, while the remaining amount is released into the environment (Tudi et al., 2021). Once applied, pesticides can reach water bodies by spray drift, crop-runoff (endo-drift), sub-surface drainage, and leaching through the soil, especially after rainfall and during fumigation campaigns, which is known as "diffuse contamination" (Rabiet et al., 2010; Triegel and Guo, 2019). In contrast, "point-source contamination" is a type of pollution that originates from a specifically identifiable source where toxic substances or pollutants are released at high concentrations and can easily be traced back to the source, and includes activities such as pesticide mixing, rinse wastewater, leaks, improper handling of mix left-overs, fruit washing, etc (Gikas et al., 2018). Although point-source contamination can be prevented by applying appropriate management practices and routines, it is still estimated to represent 40–90 % of pesticide pollution in surface waters. Examples of point-source contamination include spills during the handling of agrochemicals, leaks from storage containers, leachates from machinery cleaning, etc (De Wilde et al., 2007).

The occurrence of pesticides in the water resources of the European Union (EU) member countries has been a problem of growing concern during the last decade. Water bodies near areas of intense agricultural activity are particularly prone to pesticide contamination. Increasing concentrations of pesticides have been detected in surface waters near agricultural fields (Ccanccapa et al., 2016; Köck-Schulmeyer et al., 2019; Pascual Aguilar et al., 2017; Postigo et al., 2021). Given the environmental risk posed by the increasing presence of pesticides in water, the European Water Framework Directive and Groundwater Directive established a permissible limit of 0.1 μg L^{-1} for individual active substances and 0.5 μg L^{-1} for mixtures (including in both cases their major metabolites) in surface water and groundwater (EC, 2006, 2000). However, between 10 and 25 % of the samples analyzed in the surface waters (10,219 samples in total) had one or more pesticides exceeding the threshold limit, with an increasing trend observed from 2013 to 2020, as shown in Fig. 2 (EC, 2022a). Periodic renewals of pesticide approvals for use in member states are carried out by the EU and can be consulted in its updated pesticide database (EC, 2022b). Despite being banned, recent studies have reported the detection of pesticides not approved by the EU in the surface waters of some member states. This fact, rather than their illegal use, has been attributed to the persistence of these compounds in the environment (Calvo et al., 2021; Paíga et al., 2021).

Furthermore, the European Commission adopted a package of proposals to align EU policies to reduce net greenhouse gas emissions by at

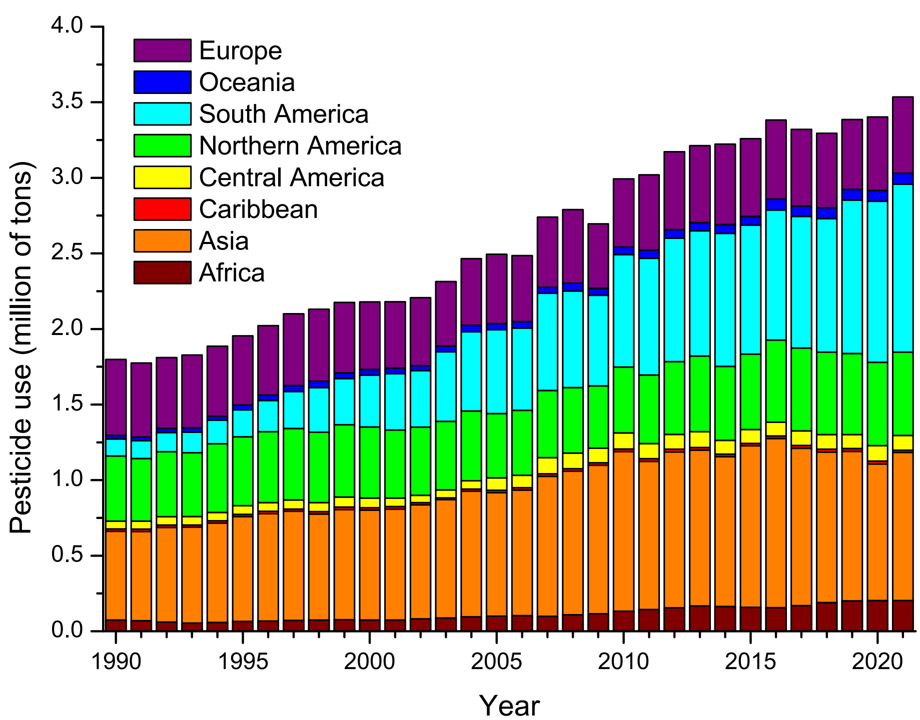

Fig. 1. World use of pesticides (adapted from FAOSTAT, 2022).

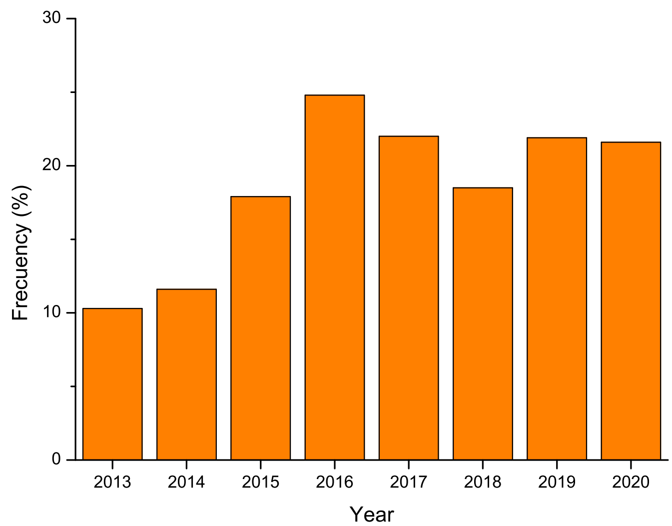

Fig. 2. Frequency at which pesticides detected at the monitoring points exceeded thresholds from 2013 to 2020 (10,219 samples in total) (EC, 2022a).

least 55 % in 2030, known as the European Green Deal (EC, 2019). This program includes the target of reducing the use and risks of chemical pesticides by 50 % in 2030 through three action plans: 1. The Zero Pollution Action Plan, which sets out a vision for a pollution-free environment in Europe and outlines a series of actions to achieve this goal. The plan recognizes the negative impact of pesticides on human health and the environment and calls for a reduction in their use through the promotion of non-chemical alternatives and the implementation of integrated pest management practices (EC, 2021); 2. The Farm to Fork Strategy, which is a comprehensive plan for making the EU's food system more sustainable. One of the key objectives of the strategy is to reduce the use and risk of pesticides in agriculture, while also promoting more sustainable farming practices (EC, 2020a); and 3. The Biodiversity Strategy, which aims to protect and restore biodiversity in Europe. One of the key objectives of this strategy is to reduce the use and risk of pesticides, particularly those that are harmful to pollinators and other beneficial organisms (EC, 2020b).

The Food and Agriculture Organization of the United Nations (FAO) created a methodology known as Integrated Pest Management (IPM), which is a coordinated approach that combines a set of sustainable agricultural practices to ensure effective pest control and crop safety. IPM is widely promoted by the scientific community, which is beginning to materialize in the pesticide regulatory policies of many developed countries. The EU has adopted IPM as a central pillar of action in the 2009 Directive on the sustainable use of pesticides (EC, 2009). Practices encouraged by IPM include the use of proper cultivation techniques, hygienic measures, pesticide monitoring, promotion of biopesticides, and the use of synthetic pesticides with high selectivity and at reasonable doses (Chandler et al., 2011).

The good agricultural practices proposed by the IPM program can be applied by farmers to significantly limit the risk of pesticide contamination. These practices should include the proper management of agricultural rinse wastewater (RWW), a concentrate with a high pesticide content produced while washing agricultural equipment and machinery (Papaevangelou et al., 2017). Nevertheless, farmers often spray pesticides incorrectly or dispose of the residues generated unsafely, especially in developing countries (Bagheri et al., 2021). In fact, in the questionnaires on attitudes and habits in the handling and disposal of pesticides, most farmers report little knowledge of the correct handling and application of pesticides. Health problems are more frequent in people over 65 years of age, with little education, low income, accustomed to using very hazardous products, and untrained in pesticide usage (Sharafi et al., 2018). Furthermore, social awareness campaigns aimed at the general public have proven to be ineffective in ensuring proper management of agrochemicals and their residues in the agricultural sector. That is, the fact that farmers belong to a society concerned about environmental issues does not necessarily guarantee safe pesticide use. Improving agricultural practices requires programs and strategies specifically designed for farmers (Karasmanaki et al., 2021).

2. Management of pesticide containers and packaging

One of the main sources of RWWs is the rinsing of plastic containers and bulk containers, which are two of the main formats used to distribute pesticides to consumers. These materials usually contain chemical residues after application, making them hazardous wastes that must be properly managed (EC, 2015). Nevertheless, a common practice is to uncontrollably burn or bury these agricultural residues, which pose a serious risk to the environment (Blanco et al., 2018; Briassoulis et al., 2013).

Alternative management of agricultural packaging is encouraged in certain regions, but it is administrated under different protocols depending on the legislation of each country (Briassoulis et al., 2013). Among the countries with the most developed packaging return systems are Germany (Pamira, 2017), France (Adivalor, 2018), and Spain (Sigfito, 2018), although each system has its particularities. The most relevant difference is regarding the category of the rinsed container, as in countries such as Germany and France it is declared as non-hazardous waste, whereas in Spain it is designated as hazardous waste (Picuno et al., 2020). This classification is important in determining the recycling value of such waste, as non-hazardous materials are considered raw materials rather than wastes (Fig. 3). In this regard, FAO and CropLife recommend the recognition of rinsed containers as non-hazardous materials (CropLife, 2010).

The triple rinse technique for pesticide containers is recommended by the main international agencies, such as CropLife, the FAO, and the World Health Organization (WHO). This method applied immediately after emptying the containers can significantly reduce contamination (UN, 2021). Sequential washes have been shown to exponentially reduce the concentration of pesticides in containers, typically reaching 95 % removal after the third rinse cycle, hence the use of the recommended personal protective equipment during cleaning is essential to avoid exposure to contaminants (Osborne et al., 2015).

Pesticide containers can also be sent to specialized plants for treatment. For example, in Spain there is a non-profit association called Sigfito. This company is responsible for the management of empty packaging, which may still contain pesticide residues, at the end of its life span (Sigfito, 2018). For this purpose, Sigfito uses the triple rinsing technique to subsequently recycle empty containers. Sigfito is associated with two companies that deal with the waste produced: FCC Medioambiente (FCC Medio Ambiente, 2022), which specializes in solid waste management, and SITA SPE IBÉRICA S.L.U. (Agbar, 2022), experts in semisolid management.

3. Management of rinse wastewater

Not only the cleaning of agrochemical containers but also of agricultural equipment, machinery, and products (such as fruits and vegetables) can produce RWW with a potentially high content of pollutants, such as fertilizers or, especially, pesticides, and must be subsequently managed (Beltrán-Flores et al., 2023a). Three basic strategies can be used to deal with agricultural RWW: direct reapplication on the field as a diluted phytosanitary product or reuse as a diluent for subsequent pesticide dosing, disposal as waste, and treatment to improve water quality (Felsot et al., 2003).

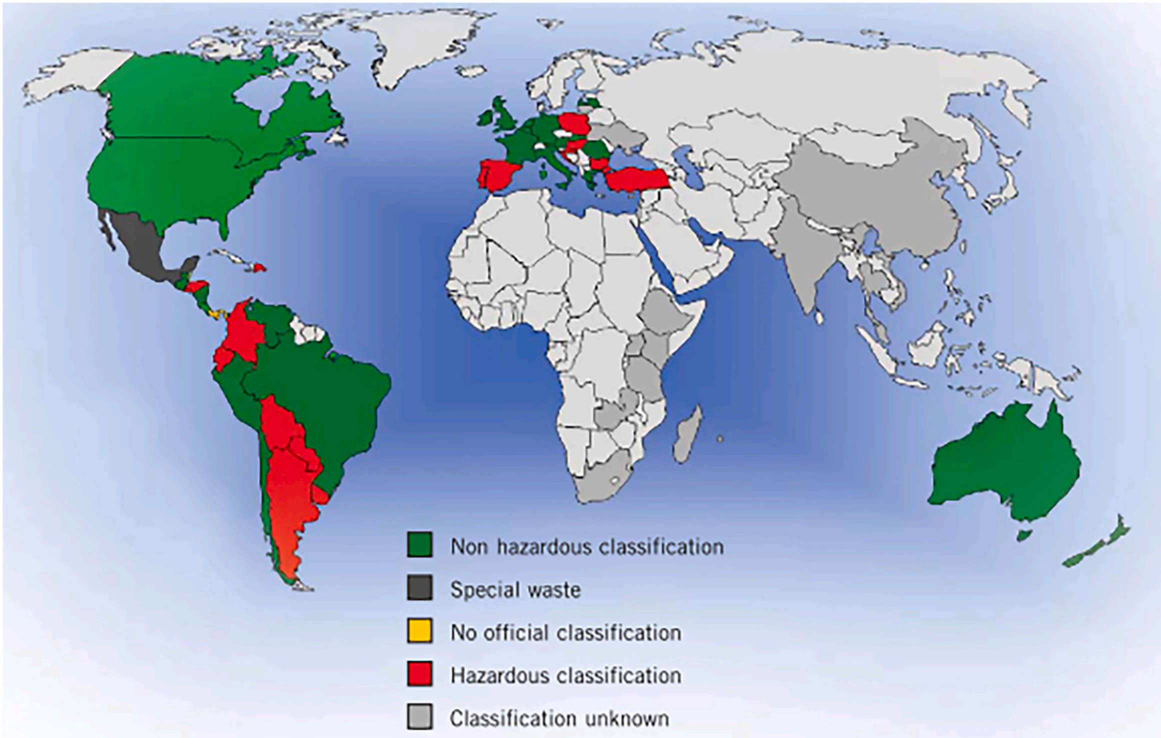

Fig. 3. Hazard classification of rinsed pesticide containers (CropLife, 2010).

3.1. RWW reuse

RWW reapplication is sometimes possible as pesticides are considered to be diluted below suboptimal concentration (Kuo and Regan, 1999). In these cases, RWW is recommended to be reused in the same season and crop in which it was first applied, avoiding mixtures and cross-contamination (Minnesota Department of Agriculture, 2016). In fact, some recognized guidelines suggest RWW reuse on the same field (or on its margins) as the cheapest and simplest option for many farms (EPA, 2012; Life aquemfree, 2018; Shukla et al., 2001).

Nevertheless, RWW reapplication is mainly limited to single/small-scale farms, as large farms can generate excessive volume for direct reuse and thus must be treated (preferably) or disposed of instead (Felsot et al., 2003). While RWW reuse may be a more economical solution for small farms, an incorrect implementation can cause contamination of the surrounding water, crops, and soil, causing adverse effects on the environment and human health, and leading to significant losses and costs not only for the particular farmer but for the entire society. There are 4 main costs associated with pesticide pollution (Bourguet and Guillemaud, 2016):

- Regulatory costs: investment in public research, regulations, decrees, laws, handling and disposal guidelines, etc.
- Human health costs: preventive medicine, annual check-ups, health problems in agriculture, etc.
- Environmental costs: pesticide resistance, soil degradation, decreased pollination, health and product quality risks for livestock, health issues for domestic animals, etc.
- Protective costs: protective clothing, glasses and masks, purchase of organic food and bottled water, etc.

Of particular concern are the so-called "hidden costs", which are costs that are not considered in the economic evaluation of pesticide use and farmers are not aware of them (Bourguet and Guillemaud, 2016). However, most of these costs can be avoided by proper management of pesticide-contaminated agricultural residues, such as RWW.

3.2. RWW disposal methods

Traditionally, farmers have developed very simple and low-cost methods intended for accumulation and confinement rather than decontamination of RWWs. In some cases, these systems have been enhanced by incorporating uncontaminated soil or sludge to promote RWW remediation. These techniques include land cultivation, disposal pits, and evaporation ponds.

Land cultivation consists of dispersing the RWWs in uncontaminated soil to promote the degradation of the compounds using natural physical-chemical and biological processes. In this regard, microbes present in the soil have exhibited some capacity to degrade multiple pesticides. In a pilot-scale bioremediation study, soils contaminated with DDT (35.37 mg kg^{-1} to 6.97 mg kg^{-1}) were treated with *Chryseobacterium* sp. PYR2 for a period of 45 days, reducing its concentration by 80 % (Qu et al., 2015). In another study, Singh et al. (2016) reported 82 % degradation of chlorpyrifos (50 mg kg^{-1}) in 10 days using a bacterial consortium of species typically present in soil (*Pseudomonas* sp., *Klebsiella* sp., *Stenotrophomonas* sp., *Ochrobactrum* sp., and *Bacillus* sp.). In this respect, microbial consortia are usually more effective at degrading pesticides than using an isolated pure culture (Raffa and Chiampo, 2021).

Regarding disposal pits, there are three main types: soil, plastic, and concrete pits. Soil pits are basically holes dug in the ground without any lining to prevent the liquid from leaking out. This method can have negative consequences for the environment, such as soil and groundwater contamination (Vryzas, 2018). Improved systems to prevent leakage are plastic or concrete pits. Plastic pits are open systems that facilitate the evaporation of water into the atmosphere, while concrete pits are commonly closed and contain a certain proportion of soil to enhance the degradation of pollutants. Junk and Richard (1984) studied a 90.000 L polyethylene-lined pit in which 150 kg of 24 different pesticides had been deposited for two years, highlighting the negligible dissemination of these contaminants into the surrounding air and water. Another study evaluated the disposal of 45 types of commercial pesticides over 6 years in a concrete pit, achieving evaporation of the liquid phase and partial degradation of the pollutants (Hall, 1984). In the same study, previous experiments using plastic, fiberglass, and other materials were unsuccessful due to freezing, thawing, and rupture problems in winter. In this regard, concrete pits are often considered the safest type of pits against leakage, but they are generally too large and expensive systems for most farms. These methods are considered obsolete and dangerous for the environment, and other more advanced and sustainable systems should be considered (Al Hattab and Ghaly, 2012).

Evaporation ponds (EVP) typically collect and contain the RWW while the water evaporates naturally (Fig. 4 a). These systems are among the most cost-effective and simple engineering approaches for RWW disposal and are especially used in developing countries with high levels of solar radiation. EVP has not only been used in the management of agricultural drainage wastewater, but also for other purposes, such as oil mill wastewater, salt production, industrial wastewater, mine wastewater, and landfill leachate, among others (Izady et al., 2020). However, evaporation and leaching of the accumulated waste pose a serious threat to the environment, as it can potentially lead to contamination of surface water bodies, aquifers, and the surrounding soil (George and Patil, 2021).

EVPs are usually constructed with impermeable geomembrane liners, such as high-density polyethylene lines, which are usually selected based on their ability to resist chemical corrosion, ultraviolet radiation, low infiltration, and their long durability. However, even when a geomembrane liner is used there is a risk of infiltration and environmental contamination; for example, carbamate pesticide wastewater accumulated in EVP in India (Bhopal) could percolate into underlying aquifers due to leaks from the low-density polyethylene flexible geomembrane liner, affecting the well water quality (George et al., 2001). Furthermore, as in the case of disposal pits, these systems are designed to retain rather than treat pesticides, e.g., Fujii (1988) analyzed bottom sediments caused by agricultural wastewater seepage from EVPs for one year and detected the persistence of pesticides such as dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE), both with maximum levels of 0.8 g kg^{-1} in the sediment. These results highlight the leaching potential of EVPs, which can act as hot spots for the release of pesticides into the environment (George and Patil, 2021).

EVPs may include a certain proportion of soil/lime to promote the degradation of pesticides, and in this case, are called evaporation beds (EVBs). In this regard, an EVB with lime provided better results than an EVP without lime in terms of removal of diazinon, 78 vs. 63 % respectively, and of 70 vs. 45 % ethyl parathion, respectively (Hodapp and Winterlin, 1989). Another study also evaluated the ability of EVBs to degrade pesticides from RWWs. The addition of lime to the bed soil also accelerated degradation, but only for some pesticides (Winterlin et al., 1984).

A more advanced evaporation technique consists of applying a decentralized and optimized dehydration process. In Spain, a company called Syngenta has developed and installed several systems to manage RWWs (Syngenta, 2022). This system is based on natural dehydration, thus producing solid waste as a by-product. Although this is an enhanced approach, it is still based on the reduction of water content, as in the case of the EVPs described above, and a post-treatment must be applied to the concentrate or solid residues. Accordingly, the solid or paste generated is typically stabilized by different chemical agents and finally disposed of in landfills (BOE 646/2020). Landfill management cannot be considered a genuinely environmentally friendly treatment option and other sustainable alternatives must be explored.

3.3. RWW treatment

In this scenario, the development of effective treatments for the removal of pesticides from RWWs is mandatory. Decentralized treatment of RWW is presumably the most appropriate strategy, although a viable treatment for this type of waste should be developed. Several treatment techniques, whether physical, chemical, physical-chemical, biological, or combinations of the above, have been described to remediate different types of pesticide-contaminated matrices (Marican and Durán-Lara, 2018). Physical-chemical methods have been extensively studied for pesticide removal, such as sorption using activated carbon and advanced oxidation processes (AOPs), which are

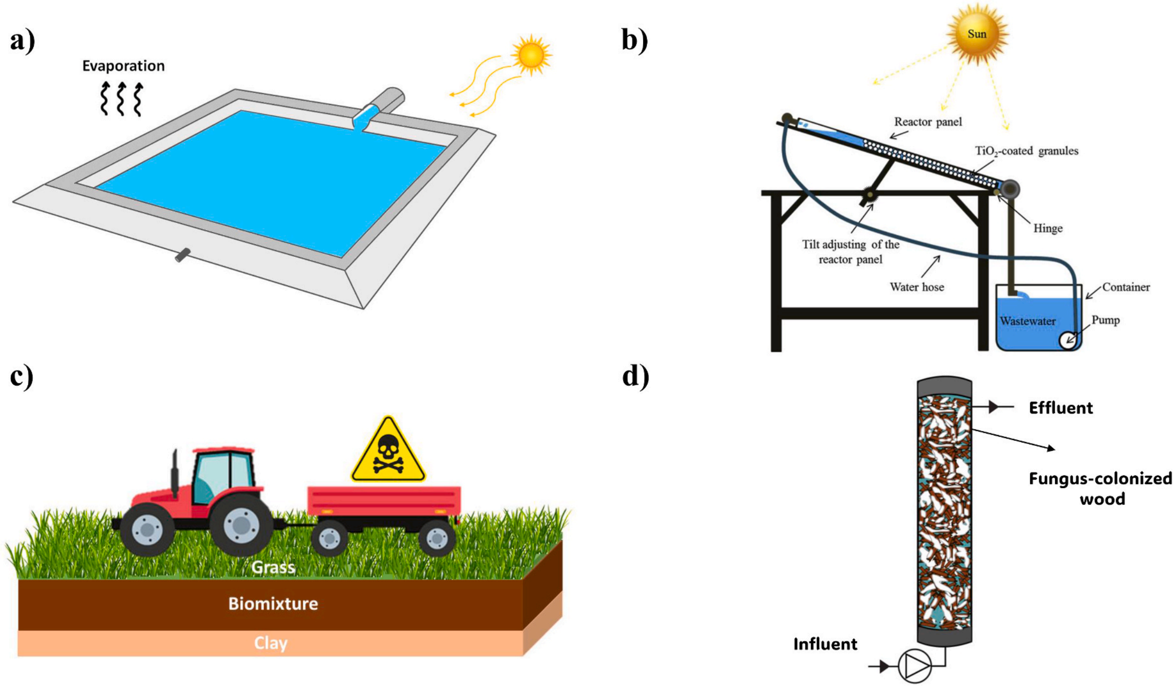

Fig. 4. RWW management by disposal methods: a) evaporation pond (based on Adam et al. (2023)), b) solar photocatalysis (Sutisna et al., 2017); and treatment systems: c) biobed (based on (Castillo et al., 2008)) and d) fungal bioreactor (based on Beltrán-Flores et al. (2023b)).

well-established, fast, and effective techniques. However, these approaches often involve high operating costs and the potential generation of residues or TPs (Ahmed et al., 2017). In contrast, despite the complications associated with biomass handling and the longer operational periods required, bioremediation has proven to be a reliable, sustainable, and cost-effective technology, and hence it may be considered a more suitable approach for low-cost applications needed on farms (Marican and Durán-Lara, 2018). Nonetheless, some of these approaches adequate for treating pesticide-contaminated agricultural effluents may be ineffective for dealing with RWW, which have particular characteristics, e.g., relatively high organic load and toxicity (Beltrán-Flores et al., 2023a; Moreira et al., 2012). This section presents the information reported in the scientific literature to date regarding the specific treatment of RWW (Table 1).

3.3.1. Sorption

Dhaouadi et al. (2010) removed 97 % rotenone (initial concentration 39 mg L^{-1}) from RWW originating from the cleaning of agricultural application equipment by adsorption on chemically modified activated carbons. Gikas et al. (2022) studied the removal of pyraclostrobin from contaminated water from spray equipment rinsing sites using three filters filled with bauxite, carbonate gravel, and zeolite, obtaining 33 %, 37 %, and 61 % of pesticide removal, respectively. However, sorption seems hardly suitable for the treatment of RWW, as its high organic load might lead to a potentially rapid saturation of the sorbent material (Table 2) (Heidarinejad et al., 2020; Rivera-Utrilla et al., 2011; Yin et al., 2007).

3.3.2. Advanced oxidation processes

Among the AOPs, the most developed technique to date for the treatment of RWWs is solar photocatalysis (Fig. 4 b), which has been considerably reported in the literature (Table 1). Titanium dioxide (TiO_2) photocatalyzed degradation of pesticides in RWW of agricultural sprayers demonstrated high degradation efficiency for multiple pesticides in 10 h of treatment (91 % dichloroaniline, 70 % benzopyran, 78 % atrazine, 50 % propazine, 70 % alachlor, 56 % prometryn, 63 % bromacil, 67 % cyanobenzoate) (Muszkat et al., 1995).

A Fenton-like photosensitization process using dye significantly improved the degradation efficiency of carbofuran residues (Kuo and Ho, 2010). The COD degradation efficiency of the RWW increased from 37 to 61 % and 66 % with the addition of methylene blue (MB) and alizarin red S (ARS), respectively. Nevertheless, better results were obtained by the addition of ARS in terms of mineralization and toxicity reduction, reaching 57 and 90 %, respectively.

In another study, direct photolysis by ultraviolet C (UVC) and UVC/H_2O_2 radiation was applied for the degradation of three pesticides, azoxystrobin, difenoconazole, and imidacloprid, commonly found in the tomato RWW (Cunha and Teixeira, 2021). Direct photolysis achieved total removal of azoxystrobin and imidacloprid in 15 min using 21.8 and 28.6 W m^{-2}, respectively, while the highest percentage degradation of difenoconazole was 52 % at 28.6 W m^{-2} UVC. Concerning UVC/H_2O_2, total pesticide removal was achieved after 10 min working at $[H_2O_2]_0 =$ 130 mg L^{-1} and 26 W m^{-2}.

Some experiments have also been performed using solar photocatalysis treatment at pilot scale. A titania-based photocatalysis system was used for RWW treatment and successfully mineralized the herbicide 2,4-D (dichlorophenoxyacetic acid), and insecticides tetrachlorvinphos, fenitrothion, pirimiphos-methyl, and fenamiphos (Herrmann and Guillard, 2000). In another study, solar photocatalysis using sodium persulfate was conducted to treat RWW contaminated with another series of pesticides (pymetrozine, flonicamid, imidacloprid, acetamiprid, cymoxanil, thiachloprid, spinosad, chlorantraniliprole, triadimenol, tebuconazole, fluopyram, difenoconazole, cyflufenamid, hexythiazox, spiromesifen, folpet and acrinathrin) using sodium persulfate ($Na_2S_2O_8$) under natural sunlight (Vela et al., 2019). After treatment, almost complete degradation (97 %) of the target pesticides was achieved, although dissolved organic carbon (DOC) remained at 13 % of the initial content. In addition, the treated water was used for growing broccoli (*Brassica oleracea* L. spp. *Italica* cv. Parthenon) with no evidence of general quality reduction.

Garrido et al. (2020) evaluated the elimination of traces of pesticides (acetamiprid, cyproconazole, cyprodinil, difenoconazole, fenhexamid, hexythiazox, myclobutanil and thiamethoxam) in RWW, using natural sunlight and TiO_2 in tandem with sodium peroxydisulfate ($Na_2S_2O_8$) as photocatalytic/oxidizing agents. The pilot scale results show that the use of solar irradiation, together with a commercial photocatalyst such as TiO_2 and $Na_2S_2O_8$, represents an excellent technique to degrade the pesticide residues studied, obtaining on average ($n = 5$) a final amount of about 13 % of the initial mass of pesticides present in the RWW. The same approach was used to treat other pesticides detected in similar RWW, yielding removals in the range of 0–47 % for thiamethoxam, 0.1–33 % for imidacloprid, 2–66 % for acetamiprid and 0.02–60 % for thiacloprid (Fenoll et al., 2019). A similar study evaluated the reuse of RWW treated by solar photocatalysis with TiO_2 and $Na_2S_2O_8$ for the cultivation of lettuce (*Lactuca sativa*), in which no significant deterioration in general quality parameters was observed (Aliste et al., 2020). The same system was used for the treatment of another series of pesticides detected in RWW, achieving eliminations of 96 % in winter and 98 % in summer (Kushniarou et al., 2019).

Based on the good results, a few studies have tried to apply solar photocatalysis in a full-scale system. RWW produced in a vineyard of area $A = 0.15$ km^2 was treated by solar photocatalysis on a corrugated steel inclined plate of area $S = 1$ m^2 on which a thin TiO_2-coated material was adhered (Pichat et al., 2004). After 8 days of treatment, a considerable improvement of the overall water quality in terms of TOC, toxicity, and BOD_5 was observed, but it was concluded that better operability and treatment efficiencies could be obtained by using an S/A ratio about three times higher. In addition, to improve the characteristics of treated water not only in terms of pesticide content but also in terms of overall quality, this technology has been combined with activated sludge processes in pilot-scale treatment trains, obtaining promising results (Section 3.3.9).

Therefore, solar photocatalysis is positioned as the best alternative within AOPs for the treatment of agricultural RWW, which has demonstrated remarkable pesticide removal efficiencies and improvements in overall water quality while reducing inherent costs by using solar energy, although this application has some disadvantages (mainly high operating costs and the production of TPs) and is recommended mainly in regions with abundant solar radiation (Table 2). This technology generally employs catalysts such as TiO_2, $Na_2S_2O_8$, and H_2O_2, operates for relatively short treatment periods (usually from 10 min to 9 h), and requires typical accumulated radiation levels ranging from 3000 to 10000 kJ m^{-2} (Blanco-Galvez et al., 2007; Malato Rodríguez et al., 2004; Meng et al., 2020).

3.3.3. Biobeds

While physical-chemical treatments can be effective, in most cases they are unaffordable for the average farmer. For agricultural purposes, treatment systems must be inexpensive, simple, reliable, labor-saving, low time-consuming, and with limited waste disposal costs. In this regard, bioremediation systems have proven to be cost-effective strategies, which in many cases are farmer-friendly and flexible to adapt to local conditions (De Wilde et al., 2007). Bioremediation is the process by which pollutants are biologically degraded or transformed into less or non-toxic forms (Abatenh et al., 2017). The main bioremediation techniques are: (a) promotion of the activity of indigenous microorganisms (biostimulation); (b) inoculation with degrading microorganisms (bioaugmentation); (c) application of immobilized enzymes; and (d) use of plants with biotransforming activity (phytoremediation) (De Wilde et al., 2007). The best-developed bioremediation systems for the treatment of agricultural RWW are the biobed, the biobac (or Phytobac®), and the biofilter. The concept of the three systems is similar: they

Table 1
Reported studies on RWW treatment.

Technique	Scale	RWW origin	Pesticides	Initial concentration	Removal (%)	Source
Sorption						
Filtration with bauxite, carbonate gravel, and zeolite	Bench-scale	Sprayers	Pyraclostrobin	1.3 mg L^{-1}	33–61	Gikas et al. (2022)
Ammonia-impregnated activated carbon	Bench-scale	Agricultural application equipment	Rotenone	39 mg L^{-1}	97	Dhaouadi et al. (2010)
Advanced oxidation process						
Direct photolysis UVC	Bench-scale Bench-scale	Tomatoes (simulated) Tomatoes	Azoxystrobin, difenoconazole and imidacloprid Azoxystrobin, difenoconazole, imidacloprid, fenitrothion, pirimiphos-methyl, fenamiphos	1.5–2.8 mg L^{-1} 1.5–2.9 mg L^{-1}	52–100 100	Cunha and Teixeira (2021).
Solar photo-Fenton	Bench-scale	Rinsate (simulated)	Carbofuran	100 mg L^{-1}	100	Kuo and Ho (2010)
Solar photocatalysis with sodium persulfate	Pilot-scale	Containers and phytosanitary treatment equipment	Acetamiprid, acrinathrin chlorantraniliprole, cyflufenamid cymoxanil, difenoconazole fluopyram, folpet, hexythiazox, imidacloprid, pymetrozine, spinosad A & D, spiromesifen, tebuconazole, thiachloprid and triadimenol Flonicamid	0.02–1.17 mg L^{-1} 0.51 mg L^{-1}	99–100 59	Vela et al. (2019)
Solar photocatalysis with TiO_2	Bench-scale	Sprayers	Dichloroaniline, benzopyran, atrazine, propazine, alachlor, prometryn, bromacil, and cyanobenzoate	6–273 μg L^{-1}	56–91	Muszkat et al. (1995)
Solar photocatalysis with TiO_2	Full-scale	Sprayers used in a vineyard	Folpet, triadimenol, tebuconazole, quinoxyfen, chlorpyriphos, dinocap amd mancozeb	0.3–38 mg L^{-1}	52–100	Pichat et al. (2004)
Solar photocatalysis with TiO_2 and $Na_2S_2O_8$	Pilot-scale	Tanks, containers, machinery, and equipment	Thiamethoxam, imidacloprid, acetamiprid, and thiacloprid	0.1–11.6 mg L^{-1}	40–100	Fenoll et al. (2019)
Solar photocatalysis with TiO_2 and $Na_2S_2O_8$	Pilot-scale	Tanks, containers, machinery, and equipment	Acetamiprid, myclobutanil, thiamethoxam, cyprodinil, difenoconazole, cyproconazole, hexythiazox and fenhexamid	0.2–6.0 mg L^{-1}	48–100	Garrido et al. (2020)
Solar photocatalysis with TiO_2 and $Na_2S_2O_8$	Pilot-scale	Tanks, containers, machinery, and equipment	Azoxystrobin, cyproconazole, cyprodinil, fludioxonil, kresoxim-M, metalaxyl, metribuzin, pendimethalin, propyzamide, pymetrozine, pyriproxyfen, and rimsulfuro	Total: 1.2–1.4 mg L^{-1}	96–98	Kushniarou et al. (2019)
Solar photocatalysis TiO_2 and $Na_2S_2O_8$	Pilot-scale	Containers and phytosanitary treatment machinery	Chlorpropham, flutolanil, methoxyfenozide, prochloraz, iso-xaben, boscalid, propyzamide, napropamide, azoxystrobin, triadimenol, flutriazol, myclobutanil and propamocarb	8.1–7.8 mg L^{-1} DOC	100	Aliste et al. (2020)
Bioremediation						
Biobed	Bench-scale	Rinsate	39 pesticides	≈1,5 μg L^{-1}	97–99	Bergsveinson et al. (2018)
Biobed	Bench-scale	Rinsate (simulated)	2,4-D	56 mg L^{-1}	100	Cessna et al. (2017)
Biobed	Pilot-scale	Rinsate (simulated)	Isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate	2–22 mg L^{-1}	99	Fogg et al. (2004)
Biobed	Full-scale	Machinery	Propyzamide, chloridazon, triclopyr ethofumesate, chlorotoluron, bromoxynil, 2,4-D, mecoprop, MCPA, fluroxypyr, dicamba, carbetamide, clopyralid, MSM and Metazachlor	0.1–27 mg L^{-1}	98	Cooper et al. (2016)
Biofilter	Pilot-scale	Sprayers (simulated)	Atrazine, carbofuran, diuron, lenacil, simazine, isoproturon, chloridazonand and chlortoluron	100 mg L^{-1}	>95	Pussemier et al. (2004)
Biofilter	Pilot-scale	Sprayers (simulated)	Atrazine, azoxystrobine, carbofuran, chloridazon, diuron, ethofumesate, flupyrsulfuron-methyl, lenacil, MCPP, metalaxyl, metconazole, metolachlor, nicosulfuron, iprodione and simazine	≈67 μg L^{-1}	92	Pigeon et al. (2005)
Biofilter	Pilot-scale	Rinsate (simulated)	Chlorpyrifos, metalaxyl and imazamox	750 mg L^{-1}	100	Vischetti et al. (2004)
Biobac	Pilot-scale	Rinsate (simulated)	Atrazine, simazine, lenacil, metalaxyl diuron and carbofuran	10 mg L^{-1}	61–100	Spanoghe and Steurbaut. (2004)
Horizontal subsurface flow CW	Pilot-scale	Sprayer (simulated)	Fluopyram	1.40 mg L^{-1}	25–71	Parlakidis et al. (2022)
Horizontal subsurface flow CW	Pilot-scale	Rinsate (simulated)	Boscalid	2 mg L^{-1}	49–100	Papaevangelou et al. (2017)
Horizontal subsurface flow CW	Pilot-scale	Rinsate (simulated)	Pyraclostrobin	1.3 mg L^{-1}	57–75	Gikas et al. (2022)
Horizontal subsurface flow CW	Pilot-scale	Rinsate (simulated)	Terbuthylazine	0.4 mg L^{-1}	74–98	Gikas et al. (2018)
Fungal treatment	Bench-scale	Rinsate	Azoxystrobin, chlortoluron, tebuconazole and thiacloprid	5–19 mg L^{-1}	81–100	Beltrán-Flores et al. (2023a,b)

(*continued on next page*)

Table 1 (*continued*)

Technique	Scale	RWW origin	Pesticides	Initial concentration	Removal (%)	Source
Treatment train						
Activated sludge/solar photo-Fenton/activated sludge	Pilot-scale	Plastic containers washing	S-Metolachlor, 2,4-D, MCPA imidacloprid, alachlor, terbuthylazine, isoproturon, bentazone, tebuconazole, atrazine, linuron, metobromuron, dimethoate, diuron, metribuzin, metalaxyl, chlortoluron, simazine, and terbuthylazine-desethyl	20 μg L^{-1} – 45 mg L^{-1}	86 % of 18/19 pestides	Vilar et al. (2012)
Activated sludge/solar photocatalysis TiO_2/UV system with preliminary acidification	Pilot-scale	Plastic containers washing	S-Metolachlor, 2,4-D, MCPA, imidacloprid, alachlor, terbuthylazine, isoproturon, bentazone, tebuconazole, atrazine, linuron, metobromuron, dimethoate, diuron, metribuzin, metalaxyl, chlortoluron, simazine and terbuthylazine-desethyl	20 μg L^{-1}–45 mg L^{-1}	90 % of 18/19 pesticides	Moreira et al. (2012)
Solar photo-Fenton/activated sludge	Pilot-scale	Shredded and washed containers	Oxamyl, methomyl, imidacloprid, dimethoate and pyrimethanil	40–175 mg L^{-1}	100	Zapata et al. (2010)
	Full-scale	Shredded and washed containers	Oxamyl, methomyl, imidacloprid, dimethoate and pyrimethanil	40–110 mg L^{-1} DOC	100	Zapata et al. (2010)

Note: 2,4-D is 2,4-dichlorophenoxyacetic acid, MCPA is 2-methyl-4-chlorophenoxyacetic acid, UVC is ultraviolet C, H_2O_2 is hydrogen peroxide, TiO_2 is titanium dioxide, $Na_2S_2O_8$ is sodium persulfate, MSM is metsulfuron-methyl, AOPs advanced oxidation processes, CW constructed wetlands and DOC dissolved organic carbon.

contain an active biological matrix that retains the pesticides and promotes microbial degradation (De Wilde et al., 2007).

Biobeds are bioreactors designed to deal with pesticide residues produced during agricultural activities, such as agricultural washing wastewater (Fig. 4 c). The original Swedish biobed was developed by Torstensson and Castillo (1997), was intended to deal with pesticide spills on farms, and consisted of three different layers: clay at the bottom (10 cm), followed by a biomixture (50 cm) of soil, peat, and straw (25:25:50 v/v, respectively), and a top cover of grass. Nowadays, this structure is still quite respected, although certain modifications are implemented for each specific use and location. Each component plays a role in the biobed. The clay layer has low permeability and high sorption capacity, thus acting as a barrier that slows the downward flow and extends the pesticide retention time. The biomixture is composed of three widely available components: a lignocellulosic substrate, aimed at enhancing the growth and enzymatic activity of ligninolytic fungi with a proven ability to degrade some pesticides, a humic-rich material (commonly peat and compost), which enhances pesticide retention capacity and provides potentially degrading microbiota to the matrix, and soil, which is considered to be the main source of pesticide degrading communities. Finally, the grass layer aids in regulating moisture and contributes to the retention and degradation of pesticides.

Bergsveinson et al. (2018) studied biobeds effective in removing pesticides from up to four different rinses, achieving an average removal of up to 99 %. The different characteristics of the RWW caused changes in the composition of the microbial population but maintained a core of 60–70 % of the prominent orders of the bacterial and fungal assemblage. Bacterial communities exhibited greater variation in diversity, while fungal populations remained more stable. In any case, the biobeds achieved high pesticide removal regardless of the microbial assemblage, which establishes them as a robust system for rinsate bioremediation. Note that high concentrations of pesticides, frequently found in RWW, could negatively affect the degradative activity of the consortium, especially when treating compounds of high toxicity.

A study conducted in the Canadian prairies evaluated the effect of temperature on the performance of biobeds for the treatment of a simulated sprayer tank rinsate containing seven herbicide-active ingredients (Cessna et al., 2017). In this study, the half-lives of all herbicides were found to be <70 days at 20 °C. However, temperatures in this region are considerably lower than 20 °C, thus the temperature of the biobeds would not be high enough to achieve complete dissipation of the herbicides, even over a long period. In such cold regions, supplementary heating is recommended to maintain incubation temperatures of approximately 20 °C, thus optimizing herbicide degradation. Therefore, given that RWWs are produced in agricultural fields, where considerable temperature variations can occur, the degradative activity of the consortium could be adversely affected unless the biobed is adequately protected, such as inside covered or even temperature-controlled facilities.

Larger scale studies have also been reported. Two semi-field scale biobed systems were compared in the treatment of pesticides from farmyard spills, as well as from tank and sprayer washing activities: a lined system, in which the biomix was contained in a closed column, and an unlined system, in which leachate was able to filter out from the bottom of the biomix (Fogg et al., 2004). Although line systems prevent contaminant leachates, they tend to accumulate a high moisture content in the deepest parts of the bed. In contrast, unlined biobeds showed that only the most soluble pesticides leached out and that the system removed 99 % of all pesticides, with most being degraded within 9 months. Thus, this study showed that biobeds can perform better without sealing or covering, to favor the aeration and degradative activity of microorganisms. However, a possible leakage may pose a serious risk of contamination due to the high pesticide content of RWWs. Cooper et al. (2016) evaluated the effectiveness of three-stage on-farm biobed for RWW treatment. Monitoring of water quality over two years revealed that individual pesticide concentrations were reduced by 68–99 %, with an average decrease in total pesticide concentrations of up to 98 %. No indication of seasonality in pesticide removal efficacy or decline in biobed performance was reported over the two-year monitoring period. Nevertheless, high concentrations of pesticides were detected at the deeper sampling points, which could pose a risk to groundwater quality.

Biobeds seem to be a very appropriate technology for RWW treatment since it is a simple, economical, and effective remediation method for pesticide removal. Despite their proven effectiveness under certain conditions, the standardization of biobed-like systems for the treatment of RWW still has to be optimized:

- Selection of the appropriate substrate in the biomixture. Lignocellulosic substrates are readily available on farms and hence are widely used in biobeds. However, other materials, such as peat, may not be sufficiently accessible or affordable in other countries and should be substituted by more suitable alternatives (Diez et al., 2013). In fact, compost is the most applied humic-rich material in tropical regions of Latin America and the Mediterranean instead of peat (Karanasios et al., 2010; Rodríguez-Rodríguez and Rodríguez-Saravia, 2023). Substrate replacement must be well studied, as it can affect the pH level or the structure of the biomixture, e.g., forming preferential flow paths or floodings. For example, peat-based biomixtures enhance the co-metabolic degradation of pesticides by providing a low pH habitat to favor fungal growth and enzyme production. In contrast, compost-based biomixtures can induce neutral or basic pH

Table 2
Advantages and disadvantages of the main treatments applied to the remediation of RWWs.

Technique	Advantages	Disadvantages	Source
Activated carbon	✓ High pesticide removal efficiency ✓ Relatively low cost ✓ Short treatment period ✓ Safety: no transformation products are produced ✓ High availability	X Saturation due to high organic matter content in RWWs X Material regeneration required X Adsorption capacity depends on the pesticide properties	Heidarinejad et al. (2020); Rivera-Utrilla et al. (2011); Yin et al. (2007).
Solar photocatalysis	✓ High removal efficiency and even mineralization of pesticides ✓ Operating cost savings due to the use of solar energy ✓ Short treatment period	X High operating costs X Radical scavenging by the high content of organic material X Potential production of transformation products X Sunlight dependence X Sensitive to pH X Post-treatment is required	Blanco-Galvez et al. (2007); Malato Rodríguez et al. (2004); Meng et al. (2020).
Biobed-like systems	✓ Effective for many pesticides, especially for non-polar compounds ✓ Sustainable and cost-effective option ✓ Simple operation ✓ Reuse of agricultural residues as substrate	X Pesticide persistence X Sediment accumulation, especially in lined systems X A large area is usually required X Lixiviation risk, especially polar compounds X A long treatment period is normally required X Biomixture aging X Production of metabolites X Biomass maintenance X Climate dependence	Aguilar Romero, (2021); De Wilde et al. (2007); Rodríguez-Rodríguez and Rodríguez-Saravia (2022)
Constructed wetlands	✓ High pesticide removal efficiency ✓ Sustainable and low operating and maintenance costs ✓ Versatility	X Large area required X Climate dependence X Long treatment period X Persistence of some pesticides	Gorgoglione and Torretta (2018; Hadidi (2021); Kennedy and Mayer (2002).
Fungal treatment	✓ High capacity for degradation of pesticides ✓ High toxicity resistance ✓ No prior acclimatization period is required ✓ Simple operation ✓ Reuse of agricultural residues as substrate	X Slow metabolism X Substrate supply is necessary X pH control X Aeration may be desirable X Climate dependence X Biomass aging	Beltrán-Flores et al. (2023a); Mir-Tutusaus et al. (2018)

environments, which stimulate the metabolic degradation of pesticides by bacteria (Karanasios et al., 2010). In addition, the C/N ratio must be evaluated, as low N levels favor fungal co-metabolic activity, i.e., extracellular enzyme production, over metabolic activity, and fungal growth (Dias et al., 2020). Given that RWWs are generally treated on-site in agricultural fields, agricultural residues produced by the farm could be used as substrate, considerably reducing operating costs.

- Substrate size and biomixture homogeneity. In general, a reduced substrate size is desirable, as it increases the specific surface area and thus the pesticide retention capacity of the biomixture. In this regard, milling and/or crushing processes are recommended to reduce the substrate size, but they entail additional costs. Furthermore, the biomixture should be distributed homogeneously to avoid dead zones or low-efficiency regions in the bioreactor (Castillo et al., 2008).
- Biomixture aging. One of the most critical parameters is biomixture maturity. Young biomixtures tend to have lower pesticide retention, thus it is recommended to incorporate a pre-composting period. The mature biomixture produced in the pre-composting stage should be applied not only at the beginning but also throughout the treatment to compensate for substrate consumption, which can lead to increased economic cost and operational complexity. However, an over-mature biomixture is also undesirable and can lead to oxygen deficiency, thus reducing the degradation capacity of the system (Castro-Gutiérrez et al., 2017). In fact, old substrates resulting from biobeds must be subsequently managed, generally by composting or vermicomposting, which adds more complications (Masin et al., 2018).
- Long operating periods are commonly required to achieve the complete removal of adsorbed pesticides. In the original Swedish biobeds, periods of 1 year were reported to reduce the pesticide content below the detection limit (Torstensson, 2000). However, the required duration may change depending on the characteristics of the biobeds, climatic conditions, and RWW characteristics. In fact, RWWs typically have high levels of organic matter, thus part of the degradation potential of the biobed can be used to remove compounds other than pesticides, reducing efficiency and increasing treatment time. Nevertheless, treatment time is not usually a limiting factor for the bioremediation of RWWs, since they are commonly generated in small volumes and only during spraying campaigns, thus having long periods available for their treatment.
- Climatic conditions are one of the key variables influencing the performance of biobeds. For example, higher temperatures can enhance the enzymatic and metabolic activity of the microbial community, as well as increase the solubility of pesticides, leading to higher bioavailability (and biotransformation) and consequently better treatment efficiency. Rainwater is another factor that must be controlled to avoid solubilization and dilution of pesticides and may require additional infrastructure costs (Castillo et al., 2008).
- This type of process can generate metabolites, which may be even more toxic than the original compounds. In this regard, a useful approach to evaluate and monitor the performance of biobeds is the use of ecotoxicological tests, which measure the toxicity of all remaining pesticides and their potential transformation products, and thus determine the detoxification capacity of the treatment. The detoxification efficiency of the biobed depends on many factors, such as environmental conditions, the biomixture, the pollutants, among others (Acosta-Sánchez et al., 2020; Pérez-Villanueva et al., 2022). Bioaugmentation of certain microorganisms with proven degradation capabilities, such as the white rot fungi (WRF) *T. versicolor*, has shown good performance in terms of degradation of some metabolites (Lizano-Fallas et al., 2017; Rodríguez-Rodríguez et al., 2018).
- Limited local legislation, technological development, and full-scale experience. As previously described, the potential functionality of biobeds depends on each region and application. This specificity encourages further studies of the possibilities of this technology. The role of local legislation is a key constraint, as this type of technique requires a certain regulatory framework to be applied by farmers. For example, Guatemala is the only country in Latin America in which biobeds have been recognized as an official technology for pesticide management. However, other countries are already moving towards the inclusion of this technology in the agricultural sector (Dias et al., 2020).

Therefore, biobeds are considered efficient and robust systems for the treatment of RWW. According to the reported studies, biobeds usually employ different materials as lignocellulosic substrate (depending on the region), work in operation periods that typically range from 1 to 24 months and with temperatures preferably close to 20 °C. The main advantages and disadvantages of biobeds are also summarized in Table 2 (Aguilar Romero, 2021; De Wilde et al., 2007).

Despite the strong potential of biobeds for the treatment of RWWs, these systems still face major challenges, such as the determination of their life span and their subsequent disposal. The life span of the biobeds seems to be significantly influenced by climatic conditions, reaching 5–6 years in cold regions such as Sweden, and 3–4 years in warmer or tropical locations such as Costa Rica (Arbeli and Fuentes, 2007; Torstensson, 2000). One of the most recommended measures to extend the durability of the biobed is to progressively replenish the volume of biomixture lost during treatment. Regarding the disposal of spent biomixture, various approaches have traditionally been proposed, such as incineration, landfill disposal, or simple storage, although nowadays the most widely accepted practice is composting, which requires a minimum period of 6 months and toxicity monitoring to evaluate its eventual disposal on the soil (Rodríguez-Rodríguez and Rodríguez-Saravia, 2023). In any case, further rigorous studies on these topics are needed to adequately address the challenges that still face this technology. An interesting option for this type of treatment can be its combination with other complementary methods, such as solar photocatalysis, in a treatment train, which should be explored in future research.

3.3.4. Biobacs (or Phytobac®)

Biobeds have been used in several countries as a sustainable and cost-effective strategy for the treatment of highly polluted water. However, the configuration and composition of biobeds must be adapted to the specific characteristics of each region, which requires a comprehensive study of the available materials, climatic conditions, legislation, and agricultural practices (Rodríguez-Castillo et al., 2018). Such modifications may include the replacement of some biobed materials or even changes in the bioreactor configuration, leading to the development of new variants of biobeds, renamed as biomassbed in Italy, biofilter in Belgium, Phytobac and biobac in France, and biotable in Guatemala (Castillo et al., 2008). Biobac is based on the biobed concept but features a watertight concrete or plastic foil cistern that limits water removal to evaporation only. Unlike unlined systems, biobacs allow leachate recovery but generally require large volumes of substrate to avoid saturation or even flooding of the bed. Simulated RWW spiked with 10 ppm atrazine, simazine, lenacil, diuron, metalaxyl, and carbofuran was treated for 1 year in two pilot plants of bioremediation systems based on the Phytobac® concept for in situ retention and/or degradation of pesticides (Spanoghe and Steurbaut, 2004). These compounds were retained for at least one month by the Phytobac® filler, allowing enhanced microbial populations to degrade the pesticides. None of the pesticides leached out, except metalaxyl, which was detected at a concentration of 3.5–3.9 mg L^{-1} in the biobac drain. Nevertheless, biobacs have some common drawbacks, such as difficulty in protecting from precipitation, complex mixing and homogenization, and low treatment capacity.

3.3.5. Biofilters

Biofilters usually consist of two or three units of plastic containers (1 m^3) filled with a biomixture, stacked vertically, and connected with plastic valves and pipes. Biofilters were first developed in Belgium and were intended to modify the biobed concept to a smaller, more flexible, and modular configuration, but capable of treating large volumes of effluent. Eight different pesticides (atrazine, carbofuran, diuron, lenacil, simazine, isoproturon, chloridazonand, and chlortoluron) from RWW were monitored during one year of treatment in a biofilter. An average removal of more than 95 % was achieved, with none of the target compounds detected in the effluent during this period, except for lenacil (Pussemier et al., 2004). In another study, twenty different biofilter installations demonstrated pesticide removal efficiencies from RWWs higher than 92 % (Pigeon et al., 2005). However, leaching problems were observed for the more hydrophilic pesticides, such as carbofuran and chloridazon, compared to the more hydrophobic pesticides that tended to be adsorbed by the organic substrate, such as metconazole and iprodione. The relatively high concentration of pesticides frequently found in RWWs poses a high environmental risk in case of leaching losses, thus biofilter application should be limited to RWWs with low polar pesticide content or should incorporate an impermeable collection system to prevent leakage, although the latter may result in undesirably high moisture levels in the deeper layers. In addition, 75 % of the biofilters showed pesticide degradation above 95 %. A modification of a biobed, called biomassbed, was used as a biofilter to treat simulated RWW by Vischetti et al. (2004). Up to 100 % removal of chlorpyrifos, metalaxyl, and imazamox was achieved after 4 weeks of treatment when using citrus peels and garden compost.

3.3.6. Phytoremediation

Constructed wetlands (CWs) are man-made ecosystems designed to mimic natural wetlands that typically consist of shallow basins filled with various types of vegetation and treat polluted water sources. The effectiveness of CWs is mainly determined by some key design parameters, such as the type of flow (horizontal or vertical), plant species, and porous media (Tsihrintzis et al., 2010). In this regard, Parlakidis et al. (2022) applied CWs with horizontal subsurface flow (HSF) to remove fluopyram from the RWW produced during the cleaning of pesticide spraying equipment. Five units of CWs were studied: WG-C was planted with *Typha latifolia*, WG-R with *Phragmites australis*, WGZ-R with *Phragmites australis* and contained gravel and zeolite as porous media, WG-R-P with *Phragmites australis* and bioaugmented with plant growth-promoting rhizobacteria, and WG-U was left unplanted as a control. Mean removal efficiencies obtained for fluopyram were 25 %, 36 %, 60 %, 62 %, and 71 % for WG-U, WG-R, WG-C, WGZ-R, and WG-R-P units, respectively. *Phragmites australis* bioaugmented with PGPR *Pseudomonas putida* (WG-R-P unit) was the most effective, doubling fluopyram removal compared to the WG-R unit.

In addition, two HSF CW units with *Phragmites australis*, one with cobbles and one with fine gravel, were used to treat water containing boscalid at concentrations similar to those commonly detected in RWW (Papaevangelou et al., 2017). The results showed high removals in both reactors, which in the first two months ranged between 75-94 % and 95–100 % for CW with cobbles and fine gravels, respectively.

Gikas et al. (2022) studied two pilot-scale CWs filled with a porous medium of cobbles and fine gravel and planted with *Phragmites australis* to remove pyraclostrobin from contaminated water from spray equipment wash sites. The unit with a fine gravel porous medium achieved the highest pyraclostrobin removal efficiency, 75 vs. 57 %, indicating that the grain size of the porous medium is a key design parameter in CWs. In another study, both a CW and a biobed were used for the treatment of the herbicide terbuthylazine from wastewater in which RWW conditions were simulated (Gikas et al., 2018). The CW and BPS achieved maximum removals of 74 % with a hydraulic retention time (HRT) of 6 days and 98 % in 28 days, respectively. However, the matrix was poorly detoxified, as demonstrated in seed germination assays, so the authors proposed the combination of the CW and the BPS to increase the removal efficiency for future work.

Therefore, CWs seem to be a sustainable and effective alternative for the treatment of RWW. Nonetheless, their application may be limited to certain meteorological conditions, some pesticides may be resistant to this type of treatment, and they usually require large spaces and operating periods, as presented in Table 2 (Gorgoglione and Torretta, 2018; Hadidi, 2021; Kennedy and Mayer, 2002).

3.3.7. Bacterial treatment

Numerous studies in the literature deal with the use of bacteria to biodegrade pesticides from synthetic RWW. For example, a new *Stenotrophomonas acidaminiphila* strain, *Y4B*, was able to completely degrade glyphosate at high concentrations (50–800 mg L^{-1}) with a degradation efficiency of more than 98 % within 72 h (Geed et al., 2017). In another publication, Geed et al. (2017) studied the biodegradation of synthetic wastewater containing atrazine, malathion, and parathion in a two-stage Integrated Aerobic Treatment Plant using *Bacillus* sp. isolated from the agricultural field. The treatment succeeded in reducing the initial pesticide content (COD of 1232 mg L^{-1}) of the influent stream by 90 %. Regarding real RWW, Ben Salem et al. (2019) evaluated the degradation potential of two bacterial strains previously isolated from Tunisian soil (*Enterobacter cloacae and Serratia rubidaea*) as biological agents in the formulation of a bio-detergent for cleaning empty pesticide containers. In summary, the triple rinse with bio-detergent proved to be a new, simple, and effective method, which resulted in lower levels of residues in the rinse effluent than those obtained from the triple rinse recommended by FAO. This work also suggests the use of bio-detergent to enhance the microbial treatment of phytosanitary effluents, particularly through its application in the Phytobac® system.

3.3.8. Fungal bioreactors

An alternative type of process that has shown good results in eliminating pesticides is fungal treatment by WRF (Fig. 4 d). In recent years, there has been a growing interest in WRF bioremediation because of the unique characteristics of these microorganisms, which include a powerful enzymatic system capable of degrading numerous micropollutants, such as pesticides, and its strong resistance to toxicity (Gao et al., 2010).

Several fungal bioreactors have been investigated to remove pesticides (Table 3). In continuous mode, more than 85 % aerobic biodegradation of chlorpyrifos by *Aspergillus* sp. was reported in packed bed bioreactors (Yadav et al., 2015). *Aspergillus niger* was also able to continuously degrade 60 % of the herbicide atrazine from wastewater in a bioreactor (Marinho et al., 2017). One of the most widely used WRFs is *T. versicolor* due to its proven ability to degrade multiple xenobiotics. For example, Nguyen et al. (2013) explored the degradation of several pesticides in a fungus-augmented MBR inoculated with *Trametes versicolor*, achieving removals of 29 % ametryn, 11 % atrazine, 57 % fenoprop, 92 % pentachlorophenol, and 20 % propoxur.

Nevertheless, the consolidation of fungal bioremediation using WRF requires overcoming a key limitation, microbial contamination. When operating under non-sterile conditions, other microorganisms compete for substrate consumption and may compromise the dominance and survival of WRF. In recent studies, one strategy particularly effective is the immobilization on lignocellulosic supports. These materials constitute a specific substrate for WRF, thus benefiting their activity against bacteria (Torán et al., 2017).

The immobilization strategy has already been explored for the fungal treatment of pesticides. Hu et al. (2021) recently compared the pesticide removal efficiencies achieved by *T. versicolor* immobilized on pine wood in sequencing batch mode in two different bioreactors, a fluidized-bed and a trickled bed reactor. The latter reactor showed higher yields even for lower contact times, which was partially attributed to the sorption capacity of the wood. A recent study reported the ability of *T. versicolor* immobilized on pine wood to remove up to 94 % of diuron during an operating period of 35 days in a rotating drum bioreactor.

Table 3
Reported evidence of pesticide abatement with fungal bioreactors.

Reactor	Fungus	Water	Matrix	Pollutants	Sterility	Period	HRT	pH	C_0	Pesticides	Removal (%)	Source
Bottle reactor	*A. niger*	Synthetic water	Vishniac solution	Spiked	Sterile	8 days	Batch	3.5	30 mg L^{-1}	Atrazine	72	Marinho et al. (2017)
	T.. versicolor	Real water	WWTP effluent	Spiked	Sterile	12 h	Batch	4.5	350 μg L^{-1}	Atrazine and DEET	0	Shreve et al. (2016)
Fixed-bed bioreactor	*T. versicolor*	Real water	Agricultural wastewater	Spiked	Non-sterile	20 days	1 day	4.5	10 mg L^{-1}	Bentazon and diuron	6–42	Beltrán-Flores et al. (2021)
	T. versicolor	Real water	Agricultural wastewater	Spiked	Non-sterile	40 days	3 day	4.5	10 mg L^{-1}	Bentazon and diuron	18–61	Beltrán-Flores et al. (2021)
Fluidized-bed reactor	*T. versicolor*	Synthetic water	Defined medium	Spiked	Sterile	7 days	Batch	4.5	4 mg L^{-1}	Acetamiprid and imidacloprid	20–65	Hu et al. (2022)
	T. versicolor	Real water	Agricultural wastewater	Spiked	Non-sterile	30 days	3 days	4.5	10 mg L^{-1}	Bentazon and diuron	30–37	Hu et al. (2021)
	T. versicolor	Real water	Rinse wastewater	Non-spiked	Sterile	17 days	Batch	4.5	5–19 mg L^{-1}	Azoxystrobin, chlortoluron, tebuconazole and thiacloprid	77–100	Beltrán-Flores et al. (2020)
					Non-sterile	17 days	Batch	4.5	5–19 mg L^{-1}	Azoxystrobin, chlortoluron, tebuconazole and thiacloprid	38–87	
Membrane bioreactor	*T. versicolor*	Synthetic water	Malt extract-based	Spiked	Non-sterile	110 days	2 days	4.5	5 μg L^{-1}	Fenoprop, pentachlorophenol, propoxur, Ametryn, and atrazine	11–92	Nguyen et al. (2013)
Packed bed reactor	*Aspergillus* sp.	–	–	Spiked	Sterile	45 days	–	7	180–250 mg L^{-1}	Chlorpyrifos	90	Yadav et al. (2015)
	Verticilium sp. and *Metacordyceps* sp.	Synthetic water	Define medium	Spiked	Sterile	10 days	9.8 h	5.5	50 mg L^{-1}	Atrazine, chlorpyrifos and iprodione	59–96	Levio-Raiman et al. (2021)
Packed-bed channel bioreactor	*T. versicolor*	Synthetic water	Tap water	Spiked	Non-sterile	35–49 days	3 days	4.4	10 mg L^{-1}	Diuron	89–94	Beltrán-Flores et al. (2020)
Rotating drum bioreactor	*T. versicolor*	Real water	Agricultural wastewater	Spiked	Non-sterile	225 days	3–5 days	4.5	10 mg L^{-1}	Bentazon and diuron	14–33	Beltrán-Flores et al. (2022)
	T. versicolor	Real water	Agricultural wastewater	Spiked	Non-sterile	16 days	3 days	4.5	10 mg L^{-1}	Diuron	61	Beltrán-Flores et al. (2020)
	T. versicolor	Real water	RWW	Non-spiked	Non-sterile	34 days	Batch	4.5	5–19 mg L^{-1}	Azoxystrobin, chlortoluron, tebuconazole and thiacloprid	81–100	Beltrán-Flores et al. (2022)
Slurry reactor	*Bjerkandera adusta*	Real water	Slurry	Spiked	Sterile	30 days	Batch	4.5	25 mg kg^{-1}	α,β,γ,δ-HCH	95	Quintero et al. (2007)
Trickle-bed reactor	*T. versicolor*	Real water	Agricultural wastewater	Spiked	Non-sterile	30 days	3 days	4.5	10 mg L^{-1}	Bentazon	48	García-Vara et al. (2021)
	T. versicolor	Real water	Agricultural wastewater	Spiked	Non-sterile	36 days	3 days	4.5	10 mg L^{-1}	Diuron	63	Hu et al. (2020)
	T. versicolor	Real water	Agricultural wastewater	Spiked	Non-sterile	30 days	3 days	4.5	10 mg L^{-1}	Diuron	69	Hu et al. (2021)

Note: HCH is hexachlorocyclohexane and C_0 is the initial concentration.

However, part of the biomass was detached from the wood throughout the treatment (Beltrán-Flores et al., 2020). Biomass washing was solved by replacing pine wood with holm oak wood and by modifying some operating parameters, which allowed operation over a long period of several months (Beltrán-Flores et al., 2022).

Immobilization on lignocellulosic support seems to improve pesticide removal performance. This can be attributed to two main reasons: the addition of a more favorable substrate for WRF and the sorption capacity of these materials. For example, wood is a very porous material, with a high capacity to retain pesticides inside. Recent studies showed that contaminated substrate could be further treated by *T. versicolor* in a biopile-like system, although better biodegradation efficiencies could be expected by improving the treatment (Beltrán-Flores et al., 2021, 2022). In this regard, more research should be conducted on the biodegradation of pesticides adsorbed on wood.

Based on all these previous results, a recent study applied a rotary drum reactor inoculated with *T. versicolor* immobilized on holm oak wood for RWW treatment at real pesticide concentrations (Beltrán-Flores et al., 2023a). The treatment was highly effective in terms of pesticide removal, achieving 100 % azoxystrobin, 84 % chlortoluron, 100 % tebuconazole, and 81 % thiacloprid after 17 days. Nevertheless, a considerable increase in DOC and color was observed in water resulting from the extraction of soluble organic compounds from the wood. This drawback might be addressed by using a wood with a lower content of soluble organic compounds and also by combining this technology with other treatment techniques, such as AOPs or activated sludge processes.

Despite the limited scientific evidence of WRF technology for RWW treatment, this approach has demonstrated high pesticide removal efficiency in multiple studies (Table 3). Fungal bioremediation is especially appropriate for the treatment of relatively small volumes since fungi have a slow metabolism that requires long HRT and high concentrations to take advantage of their high resistance to toxicity and powerful enzymatic system, which makes this technology a promising solution for the treatment of RWW. The main advantages and inconveniences of WRF for RWW treatment are also listed in Table 2 (Beltrán-Flores et al., 2023a; Mir-Tutusaus et al., 2018). Future research should address the application of this technique for RWW remediation, with the dual objective of eliminating pesticides and achieving an effluent with sufficient quality to be reused, complying with current regulations. In addition, the risk posed by the use of the WRF to surrounding crops should be assessed.

3.3.9. *Treatment trains*

Treatment trains can synergistically combine the advantages of several technologies, often obtaining better results than those achieved by each treatment independently. In this regard, AOPs have been used as pre-treatment to oxidize biologically persistent pollutants to more biodegradable compounds (Mansour et al., 2014). These pre-treatments usually pursue a low mineralization of the contaminants to reduce operating costs associated with this type of treatment. Afterward, a biological stage can be applied to eliminate potential TPs. Nonetheless, several studies have also reported the strategy in the opposite direction, i.e., applying first a bioremediation treatment to reduce organic matter content followed by an AOP stage to achieve pollutant removal or even mineralization (Oller et al., 2011).

Solar photo-Fenton treatment followed by a biological oxidation process was combined to treat pesticide-containing RWWs (Vilar et al., 2012). This treatment was not only able to achieve 52 % mineralization and 86 % abatement of 18 of the 19 pesticides detected but also succeeded in reducing the high intrinsic organic load (1662–1960 mg $O_2 \cdot L^{-1}$) below the discharge limits accepted by Portuguese regulations (150 mg O_2 L^{-1}). This work highlights the excellent performance of the combined AOP/biological oxidation treatment for RWWs, which is based on achieving acceptable biodegradability using the minimum time of photocatalytic oxidation, and subsequently applying biological oxidation to reduce the overall process cost and making it a more attractive approach.

In another work, Moreira et al. (2012) also studied a treatment train combining biological and AOP steps, at pilot scale and applying a preliminary biological pre-treatment process. An immobilized biomass reactor (IBR) followed by AOP was used, testing both heterogeneous (TiO_2/UV and TiO_2/H_2O_2/UV, with and without acidification) and homogeneous (UV, H_2O_2/UV, Fe^{2+}/H_2O_2/UV, and Fe^{2+}/H_2O_2) systems. In this case, a biological treatment before AOPs was chosen due to the high biodegradability of the treated RWW. This first step achieved a reduction of the chemical oxygen demand (COD), DOC, and biological oxygen demand (BOD_5) of 46–54 %, 41–56 %, and 88–90 %, respectively. The photo-Fenton reaction, conducted with an initial iron concentration of 140 mg $Fe^{2+} \cdot L^{-1}$, proved to be the most efficient process, achieving 86 % mineralization and the removal of 18 of the 19 pesticides initially detected.

ALBAIDA Recursos Naturales y MedioAmbiente S.A. is a company that recycles empty plastic pesticide containers from greenhouses in El Ejido (south-eastern Spain). These containers are crushed and washed, producing RWWs with pesticide residues that are treated by a combination of solar photo-Fenton and bioremediation. This technique was applied after comparing two alternative strategies at pilot scale, photo-Fenton/bio and Bio/photo-Fenton, mainly in terms of DOC, COD, toxicity, and biodegradability, being the most successful system scaled-up at full scale (Zapata et al., 2010). The industrial-scale combined system (photo-Fenton/bio) achieved 84 % removal, 35 % corresponding to the photo-Fenton treatment, and 49 % to the aerobic biological treatment. The Bio/Photo-Fenton combination was also tested, but it was ineffective owing to the low initial biodegradability of this RWW.

4. Conclusions

Good agricultural practices include the management of agricultural rinse wastewater, which should preferably be treated onsite before being discharged or reused. Among the physical-chemical methods, solar photocatalytic treatment has attracted particular interest due to the good performance shown in terms of pesticide elimination in short periods, especially in regions with intense solar radiation. Biological treatments, such as biobeds and fungal bioreactors, seem to be promising approaches, but their global market insertion depends on their feasibility when using different substrates, pesticides, and operating conditions, scenarios that need to be carefully studied in future research. Treatment trains are also an interesting approach, as they integrate the advantages of different treatment technologies, but new combinations of the most effective techniques have yet to be explored.

CRediT authorship contribution statement

Eduardo Beltrán-Flores: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing, Visualization. **Montserrat Sarrà:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – review & editing. **Paqui Blánquez:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – review & editing.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

Acknowledgements

Project PID2019-103989RB-100 financed by MCIN/AEI/10.13039/501100011033 and TED2021-130639B-I00/AEI/10.13039/501100011033/Unión Europea NextGenerationEU/PRTR. Eduardo Beltrán-Flores acknowledges support from a MINECO predoctoral research grant (BES-2017-080500).

References

Abatenh, E., Gizaw, B., Tsegaye, Z., Wassie, M., 2017. The role of microorganisms in bioremediation - a review. Open J. Environ. Biol. 2, 38–46. https://doi.org/10.17352/ojeb.000007.

Acosta-Sánchez, A., Soto-Garita, C., Masís-Mora, M., Cambronero-Heinrichs, J.C., Rodríguez-Rodríguez, C.E., 2020. Impaired pesticide removal and detoxification by biomixtures during the simulated pesticide application cycle of a tropical agricultural system. Ecotoxicol. Environ. Saf. 195 https://doi.org/10.1016/j.ecoenv.2020.110460.

Adam, A., Saffaj, N., Mamouni, R., 2023. A sustainable concept for recovering industrial wastewater using adjustable green resources. Environ. Sci. Proc. 25, 2–6. https://doi.org/10.3390/ecws-7-14302.

Adivalor, 2018. ADIVALOR - Agricultores, Distribuidores, Industriales para la recuperación de residuos agrícolas [WWW Document]. https://www.adivalor.fr/. accessed 6.4.22.

Agbar, 2022. Agbar - SITA SPE IBÉRICA S.L.U [WWW Document]. https://www.agbar.es/#section1/section4. accessed 6.12.22.

Aguilar Romero, I.M., 2021. Biobed Biopurification Systems with Agroindustrial Wastes to Remove Organic Contaminants from Water: Microbiological and Molecular Aspects. Universidad de Granada.

Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Thomaidis, N.S., Xu, J., 2017. Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: a critical review. J. Hazard Mater. 323, 274–298. https://doi.org/10.1016/j.jhazmat.2016.04.045.

Al Hattab, M.T., Ghaly, A.E., 2012. Disposal and treatment methods for pesticide containing wastewaters: critical review and comparative analysis. J. Environ. Protect. 3, 431–453. https://doi.org/10.4236/jep.2012.35054.

Aliste, M., Garrido, I., Flores, P., Hellín, P., Vela, N., Navarro, S., Fenoll, J., 2020. Reclamation of agro-wastewater polluted with thirteen pesticides by solar photocatalysis to reuse in irrigation of greenhouse lettuce grown. J. Environ. Manag. 266 https://doi.org/10.1016/j.jenvman.2020.110565.

Arbeli, Z., Fuentes, C.L., 2007. Accelerated Biodegradation of Pesticides: an Overview of the Phenomenon, its Basis and Possible Solutions; and a Discussion on the Tropical Dimension. Crop Protection. https://doi.org/10.1016/j.cropro.2007.03.009.

Atwood, D., Paisley-Jones, C., 2017. Pesticide Industry Sales and Usage. 2008-2012 Market Estimates. Unites States Environmental Protection Agency (EPA).

Bagheri, A., Emami, N., Damalas, C.A., 2021. Farmers' behavior towards safe pesticide handling: an analysis with the theory of planned behavior. Sci. Total Environ. 751 https://doi.org/10.1016/j.scitotenv.2020.141709.

Beltrán-Flores, E., Pla-Ferriol, M., Martínez-Alonso, M., Gaju, N., Blánquez, P., Sarrà, M., 2022. Fungal bioremediation of agricultural wastewater in a long-term treatment: biomass stabilization by immobilization strategy. J. Hazard Mater. 439, 1–11. https://doi.org/10.2139/ssrn.3991524.

Beltrán-Flores, E., Pla-Ferriol, M., Martínez-Alonso, M., Gaju, N., Sarrà, M., Blánquez, P., 2023a. Fungal treatment of agricultural washing wastewater: comparison between two operational strategies. J. Environ. Manag. 325 https://doi.org/10.1016/j.jenvman.2022.116595.

Beltrán-Flores, E., Sarrà, M., Blánquez, P., 2021. Pesticide bioremediation by Trametes versicolor: application in a fixed-bed reactor, sorption contribution and bioregeneration. Sci. Total Environ. 794, 1–11. https://doi.org/10.1016/j.scitotenv.2021.148386.

Beltrán-Flores, E., Tayar, S., Blánquez, P., Sarrà, M., 2023b. Effect of dissolved oxygen on the degradation activity and consumption capacity of white-rot fungi. J. Water Proc. Eng. 55 https://doi.org/10.1016/j.jwpe.2023.104105.

Beltrán-Flores, E., Torán, J., Caminal, G., Blánquez, P., Sarrà, M., 2020. The removal of diuron from agricultural wastewaters by *Trametes versicolor* immobilized on pinewood in simple channel reactors. Sci. Total Environ. 728, 1–10. https://doi.org/10.1016/j.scitotenv.2020.138414.

Ben Salem, A., Chaabane, H., Lahbib, N., Salghi, R., Fattouch, S., 2019. Management of phytosanitary effluent: rinsing and decontamination of empty pesticide containers by bio-detergent. Crop Protect. 116, 142–155. https://doi.org/10.1016/j.cropro.2018.10.014.

Bergsveinson, J., Perry, B.J., Sheedy, C., Braul, L., Reedyk, S., Gossen, B.D., Yost, C.K., 2018. Identifying the core bacterial and fungal communities within four agricultural biobeds used for the treatment of pesticide rinsates. J. Appl. Microbiol. 125, 1333–1342. https://doi.org/10.1111/jam.14051.

Blanco, I., Loisi, R.V., Sica, C., Schettini, E., Vox, G., 2018. Agricultural Plastic Waste Mapping Using GIS. A Case Study in Italy. https://doi.org/10.1016/j.resconrec.2018.06.008.

Blanco-Galvez, J., Fernández-Ibáñez, P., Malato-Rodríguez, S., 2007. Solar photocatalytic detoxification and disinfection of water: recent overview. J. Sol. Energy Eng. 129, 4–15. https://doi.org/10.1115/1.2390948.

BOE, 2020. BOE, Real Decreto 646/2020, de 7 de julio, por el que se regula la eliminación de residuos mediante depósito en vertedero, Ministerio para la Transición Ecológica y el Reto Demográfico (Gobierno de España). Boletín Oficial del Estado.

Bourguet, D., Guillemaud, T., 2016. The Hidden and External Costs of Pesticide Use, pp. 35–120. https://doi.org/10.1007/978-3-319-26777-7_2.

Briassoulis, D., Babou, E., Hiskakis, M., Scarascia, G., Picuno, P., Guarde, D., Dejean, C., 2013. Review, mapping and analysis of the agricultural plastic waste generation and consolidation in Europe. Waste Manag. Res. 31, 1262–1278. https://doi.org/10.1177/0734242X13507968.

Calvo, S., Romo, S., Soria, J., Picó, Y., 2021. Pesticide contamination in water and sediment of the aquatic systems of the Natural Park of the Albufera of Valencia (Spain) during the rice cultivation period. Sci. Total Environ. 774 https://doi.org/10.1016/j.scitotenv.2021.145009.

Castillo, M.D.P., Torstensson, L., Stenström, J., 2008. Biobeds for environmental protection from pesticide use - a review. J. Agric. Food Chem. https://doi.org/10.1021/jf800844x.

Castro-Gutiérrez, V., Masís-Mora, M., Diez, M.C., Tortella, G.R., Rodríguez-Rodríguez, C.E., 2017. Aging of biomixtures: effects on carbofuran removal and microbial community structure. Chemosphere 168, 418–425. https://doi.org/10.1016/j.chemosphere.2016.10.065.

Ccanccapa, A., Masiá, A., Navarro-Ortega, A., Picó, Y., Barceló, D., 2016. Pesticides in the ebro river basin: occurrence and risk assessment. Environ. Pollut. 211, 414–424. https://doi.org/10.1016/j.envpol.2015.12.059.

Cessna, A.J., Knight, J.D., Ngombe, D., Wolf, T.M., 2017. Effect of temperature on the dissipation of seven herbicides in a biobed matrix. Can. J. Soil Sci. 97, 717–731. https://doi.org/10.1139/cjss-2017-0017.

Chandler, D., Bailey, A.S., Mark Tatchell, G., Davidson, G., Greaves, J., Grant, W.P., 2011. The development, regulation and use of biopesticides for integrated pest management. Phil. Trans. Biol. Sci. 366, 1987–1998. https://doi.org/10.1098/rstb.2010.0390.

Cooper, R.J., Fitt, P., Hiscock, K.M., Lovett, A.A., Gumm, L., Dugdale, S.J., Rambohul, J., Williamson, A., Noble, L., Beamish, J., Hovesen, P., 2016. Assessing the effectiveness of a three-stage on-farm biobed in treating pesticide contaminated wastewater. J. Environ. Manag. 181, 874–882. https://doi.org/10.1016/j.jenvman.2016.06.047.

CropLife, 2010. Roadmap for Establishing a Container Management Programme for Collection and Disposal of Empty Pesticide Containers.

Cunha, I.L.C., Teixeira, A.C.S.C., 2021. Degradation of pesticides present in tomato rinse water by direct photolysis and UVC/H2O2: optimization of process conditions through sequential Doehlert design. Environ. Sci. Pollut. Control Ser. 28, 24191–24205. https://doi.org/10.1007/s11356-021-13387-7.

De Wilde, T., Spanoghe, P., Debaer, C., Ryckeboer, J., Springael, D., Jaeken, P., 2007. Overview of on-farm bioremediation systems to reduce the occurrence of point source contamination. Pest Manag. Sci. https://doi.org/10.1002/ps.1323.

Dhaouadi, A., Monser, L., Adhoum, N., 2010. Removal of rotenone insecticide by adsorption onto chemically modified activated carbons. J. Hazard Mater. 181, 692–699. https://doi.org/10.1016/j.jhazmat.2010.05.068.

Dias, L.D.A., Gebler, L., Niemeyer, J.C., Itako, A.T., 2020. Destination of pesticide residues on biobeds: state of the art and future perspectives in Latin America. Chemosphere. https://doi.org/10.1016/j.chemosphere.2020.126038.

Diez, M.C., Levio, M., Briceño, G., Rubilar, O., Tortella, G., Gallardo, F., 2013. Biochar as a partial replacement of peat in pesticide-degrading biomixtures formulated with different soil types. J. Biobased Mater. Bioenergy 7, 741–747. https://doi.org/10.1166/jbmb.2013.1376.

EPA, 2012. Environment Protection Authority. Guidelines for Managing the Disposal of Pesticide Rinsate.

European Commission, 2022a. Pesticides in Rivers, Lakes and Groundwater in Europe [WWW Document]. https://www.eea.europa.eu/ims/pesticides-in-rivers-lakes-and. accessed 9.28.23.

European Commission, 2022b. EU Pesticides Database [WWW Document]. Regulation (EC) No 1107/2009. https://food.ec.europa.eu/plants/pesticides/eu-pesticides-database_en. accessed 8.28.22.

European Commission, 2021. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions 'Pathway to a Healthy Planet for All — EU Action Plan towards Zero Pollution for Air, Water and soil.'.

European Commission, 2020a. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions 'A Farm to Fork Strategy for a Fair, Healthy and Environmentally Friendly Food System'. COM(2020) 381 fi.

European Commission, 2020b. Communication from the Commission to the European Parliament, the Council, the Economic and Social Committee and the Committee of the Regions 'EU Biodiversity Strategy for 2030. Bringing Nature Back into Our Lives'. COM(2020)380 final.

European Commission, 2019. Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Regions 'The European Green Deal'.

European Commission, 2015. Replacing Decision 94/3/EC Establishing a List of Wastes Pursuant to Article 1(a) of Council Directive 75/442/EEC on Waste and Council Decision 94/904/EC Establishing a List of Hazardous Waste Pursuant to Article 1(4) of Council Directive 91/689/EEC on Ha.

European Commission, 2009. Directive 2009/128/EC of the European Parliament and the Council of 21October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides. Off. J. Eur. Union.
European Commission, 2006. Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. Off. J. Eur. Union.
European Commission, 2000. Directive 2000/60/EC of the European Parlament and of the Council of 23October 2000 establishing a framework for Community action in the field of water policy. Official J. Eur. Commun.
FAO, 1990. International Code of Conduct on the Distribution and Use of Pesticides.
FAO Statistics (FAOSTAT), 2022. Pesticide Use [WWW Document]. https://www.fao.org/faostat/en/#data/RP. accessed 8.22.22.
FCC Medio Ambiente, 2022. FCC Medio Ambiente [WWW Document]. https://www.fccma.com/fcc-iberia. accessed 6.12.22.
Felsot, A.S., Racke, K.D., Hamilton, D.J., 2003. Disposal and degradation of pesticide waste. Rev. Environ. Contam. Toxicol. 177, 123–200.
Fenoll, J., Garrido, I., Flores, P., Hellín, P., Vela, N., Navarro, G., García-García, J., Navarro, S., 2019. Implementation of a new modular facility to detoxify agro-wastewater polluted with neonicotinoid insecticides in farms by solar photocatalysis. Energy 175, 722–729. https://doi.org/10.1016/j.energy.2019.03.118.
Fogg, P., Boxall, A.B.A., Walker, A., Jukes, A., 2004. Degradation and leaching potential of pesticides in biobed systems. Pest Manag. Sci. 60, 645–654. https://doi.org/10.1002/ps.826.
Fujii, R., 1988. Water-quality and Sediment-Chemistry Data of Drain Water and Evaporation Ponds from Tulare Lake Drainage District.
Gao, D., Du, L., Yang, J., Wu, W.M., Liang, H., 2010. A critical review of the application of white rot fungus to environmental pollution control. Crit. Rev. Biotechnol. 30, 70–77. https://doi.org/10.3109/07388550903427272.
García-Vara, M., Hu, K., Postigo, C., Olmo, L., Caminal, G., Sarrà, M., López de Alda, M., 2021. Remediation of bentazone contaminated water by *Trametes versicolor*: characterization, identification of transformation products, and implementation in a trickle-bed reactor under non-sterile conditions. J. Hazard Mater. 409, 1–9. https://doi.org/10.1016/j.jhazmat.2020.124476.
Garrido, I., Flores, P., Hellín, P., Vela, N., Navarro, S., Fenoll, J., 2020. Solar reclamation of agro-wastewater polluted with eight pesticides by heterogeneous photocatalysis using a modular facility. A case study. Chemosphere 249. https://doi.org/10.1016/j.chemosphere.2020.126156.
Geed, S.R., Shrirame, B.S., Singh, R.S., Rai, B.N., 2017. Assessment of pesticides removal using two-stage Integrated Aerobic Treatment Plant (IATP) by Bacillus sp. isolated from agricultural field. Bioresour. Technol. 242, 45–54. https://doi.org/10.1016/j.biortech.2017.03.080.
George, K.V., Patil, M.P., 2021. A critical review of environmental and public health impacts from the activities of evaporation ponds. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2021.149065.
George, K.V., Patil, M.P., Swaminathan, R., 2001. Study for reclamation of land occupied by solarevaporation pond at UCIL, Bhopal, India. Waste Manag. Res. 19, 573–578.
Gikas, G.D., Pérez-Villanueva, M., Tsioras, M., Alexoudis, C., Pérez-Rojas, G., Masís-Mora, M., Lizano-Fallas, V., Rodríguez-Rodríguez, C.E., Vryzas, Z., Tsihrintzis, V.A., 2018. Low-cost approaches for the removal of terbuthylazine from agricultural wastewater: constructed wetlands and biopurification system. Chem. Eng. J. 335, 647–656. https://doi.org/10.1016/j.cej.2017.11.031.
Gikas, G.D., Vryzas, Z., Karametos, I., Tsihrintzis, V.A., 2022. Pyraclostrobin removal in pilot-scale horizontal subsurface flow constructed wetlands and in porous media filters. Processes 10. https://doi.org/10.3390/pr10020414.
Gorgoglione, A., Torretta, V., 2018. Sustainable management and successful application of constructed wetlands: a critical review. Sustainability 10, 3910. https://doi.org/10.3390/su10113910.
Hadidi, L. Al, 2021. Constructed wetlands a comprehensive review. Int. J. Regul. Govern. 9, 395–417. https://doi.org/10.29121/granthaalayah.v9.i8.2021.4176.
Hall, C.V., 1984. Pesticide waste disposal in agriculture. ACS (Am. Chem. Soc.) Symp. Ser. 27–36. https://doi.org/10.1021/bk-1984-0259.ch003.
Heidarinejad, Z., Dehghani, M.H., Heidari, M., Javedan, G., Ali, I., Sillanpää, M., 2020. Methods for preparation and activation of activated carbon: a review. Environ. Chem. Lett. 18, 393–415. https://doi.org/10.1007/s10311-019-00955-0.
Hernández, A.F., Gil, F., Lacasaña, M., 2017. Toxicological interactions of pesticide mixtures: an update. Arch. Toxicol. 91, 3211–3223. https://doi.org/10.1007/s00204-017-2043-5.
Herrmann, J.-M., Guillard, C., 2000. Photocatalytic degradation of pesticides in agricultural used waters. Comptes Rendus Acad. Sci. - Ser. IIC Chem. 3, 417–422.
Hodapp, D.M., Winterlin, W., 1989. Pesticide degradation in model soil evaporation beds. Bull. Environ. Contam. Toxicol.
Hu, K., Barbieri, M.V., López-García, E., Postigo, C., López de Alda, M., Caminal, G., Sarrà, M., 2022. Fungal degradation of selected medium to highly polar pesticides by *Trametes versicolor*: kinetics, biodegradation pathways, and ecotoxicity of treated waters. Anal. Bioanal. Chem. 414, 439–449. https://doi.org/10.1007/s00216-021-03267-x.
Hu, K., Sarrà, M., Caminal, G., 2021. Comparison between two reactors using *Trametes versicolor* for agricultural wastewater treatment under non-sterile condition in sequencing batch mode. J. Environ. Manag. 293, 1–7. https://doi.org/10.1016/j.jenvman.2021.112859.
Hu, K., Torán, J., López-García, E., Barbieri, M.V., Postigo, C., de Alda, M.L., Caminal, G., Sarrà, M., Blánquez, P., 2020. Fungal bioremediation of diuron-contaminated waters: Evaluation of its degradation and the effect of amenable factors on its removal in a trickle-bed reactor under non-sterile conditions. Sci. Total Environ. 743, 1–9. https://doi.org/10.1016/j.scitotenv.2020.140628.
Izady, A., Nikoo, M.R., Bakhtiari, P.H., Baawain, M.S., Al-Mamari, H., Msagati, T.A.M., Nkambule, T.T.I., Al-Maktoumi, A., Chen, M., Prigent, S., 2020. Risk-based stochastic optimization of evaporation ponds as a cost-effective and environmentally-friendly solution for the disposal of oil-produced water. J. Water Proc. Eng. 38 https://doi.org/10.1016/j.jwpe.2020.101607.
Junk, G.A., Richard, J.J., 1984. Pesticide disposal sites: Sampling and analyse. ACS Symp. Ser. 69–95. https://doi.org/10.1021/bk-1984-0259.ch005.
Karanasios, E., Tsiropoulos, N.G., Karpouzas, D.G., Ehaliotis, C., 2010. Degradation and adsorption of pesticides in compost-based biomixtures as potential substrates for biobeds in southern Europe. J. Agric. Food Chem. 58, 9147–9156. https://doi.org/10.1021/jf1011853.
Karasmanaki, E., Dimopoulou, P., Vryzas, Z., Karipidis, P., Tsantopoulos, G., 2021. Is the environmental behavior of farmers affecting their pesticide practices? A case study from Greece. Sustainability 13, 1–15. https://doi.org/10.3390/su13031452.
Kennedy, G., Mayer, T., 2002. Natural and constructed wetlands in Canada: an overview. Water Qual. Res. J. 37, 295–325. https://doi.org/10.2166/wqrj.2002.020.
Köck-Schulmeyer, M., Postigo, C., Farré, M., Barceló, D., López de Alda, M., 2019. Medium to highly polar pesticides in seawater: analysis and fate in coastal areas of Catalonia (NE Spain). Chemosphere 215, 515–523. https://doi.org/10.1016/j.chemosphere.2018.10.049.
Kuo, W.S., Ho, Y.Y., 2010. Treatment of pesticide rinsate towards reuse by photosensitized Fenton-like process. Water Sci. Technol. 62, 1424–1431. https://doi.org/10.2166/wst.2010.367.
Kuo, W.S., Regan, R.W., 1999. Removal of pesticides from rinsate by adsorption using agricultural residuals as medium. J. Environ. Sci. Health B 34, 431–447. https://doi.org/10.1080/03601239909373207.
Kushniarou, A., Garrido, I., Fenoll, J., Vela, N., Flores, P., Navarro, G., Hellín, P., Navarro, S., 2019. Solar photocatalytic reclamation of agro-waste water polluted with twelve pesticides for agricultural reuse. Chemosphere 214, 839–845. https://doi.org/10.1016/j.chemosphere.2018.09.180.
Levio-Raiman, M., Briceño, G., Leiva, B., López, S., Schalchli, H., Lamilla, C., Bornhardt, C., Diez, M.C., 2021. Treatment of pesticide-contaminated water using a selected fungal consortium: study in a batch and packed-bed bioreactor. Agronomy 11. https://doi.org/10.3390/agronomy11040743.
Life aquemfree, 2018. Descontaminación en fincas de aguas residuales con productos fitosanitarios procedentes de remanentes, enjuagues y limpiezas mediante fotocatálisis solar.
Lizano-Fallas, V., Masís-Mora, M., Espinoza-Villalobos, D., Lizano-Brenes, M., Rodríguez-Rodríguez, C.E., 2017. Removal of pesticides and ecotoxicological changes during the simultaneous treatment of triazines and chlorpyrifos in biomixtures. Chemosphere 182, 106–113. https://doi.org/10.1016/j.chemosphere.2017.04.147.
Malato Rodríguez, S., Blanco Gálvez, J., Maldonado Rubio, M.I., Fernández Ibáñez, P., Alarcón Padilla, D., Collares Pereira, M., Farinha Mendes, J., Correia de Oliveira, J., 2004. Engineering of solar photocatalytic collectors. Sol. Energy 77, 513–524. https://doi.org/10.1016/j.solener.2004.03.020.
Mansour, D., Fourcade, F., Huguet, S., Soutrel, I., Bellakhal, N., Dachraoui, M., Hauchard, D., Amrane, A., 2014. Improvement of the activated sludge treatment by its combination with electro Fenton for the mineralization of sulfamethazine. Int. Biodeterior. Biodegrad. 88, 29–36. https://doi.org/10.1016/j.ibiod.2013.11.016.
Marican, A., Durán-Lara, E.F., 2018. A review on pesticide removal through different processes. Environ. Sci. Pollut. Control Ser. 25, 2051–2064. https://doi.org/10.1007/s11356-017-0796-2.
Marinho, G., Barbosa, B.C.A., Rodrigues, K., Aquino, M., Pereira, L., 2017. Potential of the filamentous fungus *Aspergillus niger AN 400* to degrade Atrazine in wastewaters. Biocatal. Agric. Biotechnol. 9, 162–167. https://doi.org/10.1016/j.bcab.2016.12.013.
Masin, C.E., Lescano, M.R., Rodríguez, A.R., Godoy, J.L., Zalazar, C.S., 2018. Earthworms to assess the innocuousness of spent biomixtures employed for glyphosate degradation. J. Environ. Sci. Health B 53, 519–525. https://doi.org/10.1080/03601234.2018.1462922.
Meng, X., Eluagwule, B., Wang, M., Wang, L., Zhang, J., 2020. Solar photocatalysis for environmental remediation. In: Handbook of Smart Photocatalytic Materials. Elsevier, pp. 183–195. https://doi.org/10.1016/B978-0-12-819049-4.00013-1.
Minnesota Department of Agriculture, 2016. Pesticide Rinsate Management.
Mir-Tutusaus, J.A., Baccar, R., Caminal, G., Sarrà, M., 2018. Can white-rot fungi be a real wastewater treatment alternative for organic micropollutants removal? A review. Water Res. 138, 137–151. https://doi.org/10.1016/j.watres.2018.02.056.
Moreira, F.C., Vilar, V.J.P., Ferreira, A.C.C., dos Santos, F.R.A., Dezotti, M., Sousa, M.A., Gonçalves, C., Boaventura, R.A.R., Alpendurada, M.F., 2012. Treatment of a pesticide-containing wastewater using combined biological and solar-driven AOPs at pilot scale. Chem. Eng. J. 209, 429–441. https://doi.org/10.1016/j.cej.2012.08.009.
Muszkat, L., Bir, L., Feigelson Aro, L., 1995. Solar photocatalytic mineralization of pesticides in polluted waters. J. Photochem. Photobiol. Chem.
Nguyen, L.N., Hai, F.I., Yang, S., Kang, J., Leusch, F.D.L., Roddick, F., Price, W.E., Nghiem, L.D., 2013. Removal of trace organic contaminants by an MBR comprising a mixed culture of bacteria and white-rot fungi. Bioresour. Technol. 148, 234–241.
Oller, I., Malato, S., Sánchez-Pérez, J.A., 2011. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination-A review. Sci. Total Environ. 409, 4141–4166. https://doi.org/10.1016/j.scitotenv.2010.08.061.
Osborne, P.P., Xu, Z., Swanson, K.D., Walker, T., Farmer, D.K., 2015. Dicamba and 2,4-D residues following applicator cleanout: a potential point source to the environment and worker exposure. J. Air Waste Manage. Assoc. 65, 1153–1158. https://doi.org/10.1080/10962247.2015.1072593.
Paíga, P., Sousa, S., Vera, J., Bitencourt, L., Vieira, J., Jorge, S., Silva, J.G., Correia, M., Domingues, V.F., Delerue-Matos, C., 2021. Multi-residue analysis of fifty pesticides

in river waters and in wastewaters. Environ. Sci. Pollut. Control Ser. 28, 66787–66803. https://doi.org/10.1007/s11356-021-15134-4.
Pamira, 2017. PAMIRA® [WWW Document]. https://www.pamira.de/. accessed 6.4.22.
Papaevangelou, V.A., Gikas, G.D., Vryzas, Z., Tsihrintzis, V.A., 2017. Treatment of agricultural equipment rinsing water containing a fungicide in pilot-scale horizontal subsurface flow constructed wetlands. Ecol. Eng. 101, 193–200. https://doi.org/10.1016/j.ecoleng.2017.01.045.
Parlakidis, P., Mavropoulos, T., Vryzas, Z., Gikas, G.D., 2022. Fluopyram removal from agricultural equipment rinsing water using HSF pilot-scale constructed wetlands. Environ. Sci. Pollut. Control Ser. 29, 29584–29596. https://doi.org/10.1007/S11356-021-15373-5/FIGURES/5.
Pascual Aguilar, J.A., Andreu, V., Campo, J., Picó, Y., Masiá, A., 2017. Pesticide occurrence in the waters of Júcar River, Spain from different farming landscapes. Sci. Total Environ. 607–608, 752–760. https://doi.org/10.1016/j.scitotenv.2017.06.176.
Pathak, V.M., Verma, V.K., Rawat, B.S., Kaur, B., Babu, N., Sharma, A., Dewali, S., Yadav, M., Kumari, R., Singh, S., Mohapatra, A., Pandey, V., Rana, N., Cunill, J.M., 2022. Current status of pesticide effects on environment, human health and it's eco-friendly management as bioremediation: a comprehensive review. Front. Microbiol. https://doi.org/10.3389/fmicb.2022.962619.
Pérez-Villanueva, M.E., Masís-Mora, M., Araya-Valverde, E., Rodríguez-Rodríguez, C.E., 2022. Fast removal and detoxification of oxytetracycline, triazine and organophosphate pesticides in a biopurification system. Biocatal. Agric. Biotechnol. 44 https://doi.org/10.1016/j.bcab.2022.102452.
Pichat, P., Vannier, S., Dussaud, J., Rubis, J.P., 2004. Field solar photocatalytic purification of pesticides-containing rinse waters from tractor cisterns used for grapevine treatment. Sol. Energy 77, 533–542. https://doi.org/10.1016/j.solener.2004.03.023.
Picuno, C., Alassali, A., Sundermann, M., Godosi, Z., Picuno, P., Kuchta, K., 2020. Decontamination and recycling of agrochemical plastic packaging waste. J. Hazard Mater. 381 https://doi.org/10.1016/j.jhazmat.2019.120965.
Pigeon, O., De Vleeschouwer, C., Cors, F., Weickmans, B., De Ryckel, B., Pussemier, L., Debongnie, Ph, Culot, M., 2005. Development of biofilters to treat the pesticides wastes from spraying applications. Commun. Agric. Appl. Biol. Sci. 70.
Postigo, C., Ginebreda, A., Barbieri, M.V., Barceló, D., Martín-Alonso, J., de la Cal, A., Boleda, M.R., Otero, N., Carrey, R., Solà, V., Queralt, E., Isla, E., Casanovas, A., Frances, G., López de Alda, M., 2021. Investigative monitoring of pesticide and nitrogen pollution sources in a complex multi-stressed catchment: the lower Llobregat River basin case study (Barcelona, Spain). Sci. Total Environ. 755, 1–11. https://doi.org/10.1016/j.scitotenv.2020.142377.
Pussemier, L., De Vleeschouwe, C., Debongnie, D., 2004. Self-made biofilters for on-farm clean-up of pesticides wastes. Outlooks Pest Manag. 60–63.
Qu, J., Xu, Y., Ai, G.M., Liu, Y., Liu, Z.P., 2015. Novel Chryseobacterium sp. PYR2 degrades various organochlorine pesticides (OCPs) and achieves enhancing removal and complete degradation of DDT in highly contaminated soil. J. Environ. Manag. 161, 350–357. https://doi.org/10.1016/J.JENVMAN.2015.07.025.
Quintero, J.C., Lú-Chau, T.A., Moreira, M.T., Feijoo, G., Lema, J.M., 2007. Bioremediation of HCH present in soil by the white-rot fungus *Bjerkandera adusta* in a slurry batch bioreactor. Int. Biodeterior. Biodegrad. 60, 319–326. https://doi.org/10.1016/j.ibiod.2007.05.005.
Rabiet, M., Margoum, C., Gouy, V., Carluer, N., Coquery, M., 2010. Assessing pesticide concentrations and fluxes in the stream of a small vineyard catchment - effect of sampling frequency. Environ. Pollut. 158, 737–748. https://doi.org/10.1016/j.envpol.2009.10.014.
Raffa, C.M., Chiampo, F., 2021. Bioremediation of agricultural soils polluted with pesticides: a review. Bioengineering. https://doi.org/10.3390/bioengineering8070092.
Rani, L., Thapa, K., Kanojia, N., Sharma, N., Singh, S., Grewal, A.S., Srivastav, A.L., Kaushal, J., 2021. An extensive review on the consequences of chemical pesticides on human health and environment. J. Clean. Prod. 283, 1–33. https://doi.org/10.1016/j.jclepro.2020.124657.
Rivera-Utrilla, J., Sánchez-Polo, M., Gómez-Serrano, V., Álvarez, P.M., Alvim-Ferraz, M.C.M., Dias, J.M., 2011. Activated carbon modifications to enhance its water treatment applications. An overview. J. Hazard Mater. 187, 1–23. https://doi.org/10.1016/j.jhazmat.2011.01.033.
Rodríguez-Castillo, G., Molina-Rodríguez, M., Pérez-Villanueva, M., Masís-Mora, M., Rodríguez-Rodríguez, C.E., 2018. Removal of two neonicotinoid insecticides and mineralization of 14C-imidacloprid in biomixtures. Bull. Environ. Contam. Toxicol. 101, 137–143. https://doi.org/10.1007/s00128-018-2370-0.
Rodríguez-Rodríguez, C.E., Castro-Gutiérrez, V., Lizano-Fallas, V., 2018. Alternative approaches to determine the efficiency of biomixtures used for pesticide degradation in biopurification systems. In: Methods in Pharmacology and Toxicology. Humana Press Inc., pp. 57–73. https://doi.org/10.1007/978-1-4939-7425-2_3
Rodríguez-Rodríguez, C.E., Rodríguez-Saravia, S., 2023. On-farm removal of pesticides: current insights on biopurification systems. ACS Agric. Sci. Technol. https://doi.org/10.1021/acsagscitech.2c00337.
Sabarwal, A., Kumar, K., Singh, R.P., 2018. Hazardous effects of chemical pesticides on human health–Cancer and other associated disorders. Environ. Toxicol. Pharmacol. 63, 103–114. https://doi.org/10.1016/j.etap.2018.08.018.
Sharafi, K., Pirsaheb, M., Maleki, S., Arfaeinia, H., Karimyan, K., Moradi, M., Safari, Y., 2018. Knowledge, attitude and practices of farmers about pesticide use, risks, and wastes; a cross-sectional study (Kermanshah, Iran). Sci. Total Environ. 645, 509–517. https://doi.org/10.1016/j.scitotenv.2018.07.132.
Shreve, M.J., Brockman, A., Hartleb, M., Prebihalo, S., Dorman, F.L., Brennan, R.A., 2016. The white-rot fungus *Trametes versicolor* reduces the estrogenic activity of a mixture of emerging contaminants in wastewater treatment plant effluent. Int. Biodeterior. Biodegrad. 109, 132–140. https://doi.org/10.1016/j.ibiod.2016.01.018.
Shukla, S., Mostaghimi, S., Lovern, S.B., McClellan, P.W., 2001. Impact of agrichemical facility best management practices on runoff water quality. Trans. ASAE (Am. Soc. Agric. Eng.) 44, 1661–1672. https://doi.org/10.13031/2013.7042.
Sigfito, 2018. SIGFITO: Sistema de recogida de envases agrarios [WWW Document]. https://sigfito.es/. accessed 6.4.22.
Singh, P., Saini, H.S., Raj, M., 2016. Rhamnolipid mediated enhanced degradation of chlorpyrifos by bacterial consortium in soil-water system. Ecotoxicol. Environ. Saf. 134, 156–162. https://doi.org/10.1016/J.ECOENV.2016.07.020.
Spanoghe, P., Steurbaut, W., 2004. Limitation of point source pesticide pollution: results of bioremediation system DISCUSS a dual indicator set for crop protection sustainability surveys View project Pesticides Use on Yam in Ghana View project. Art. Comm. Agric. Appl. Biol. Sci.
Sutisna, Rokhmat, M., Wibowo, E., Khairurrijal, Abdullah, M., 2017. Prototype of a flat-panel photoreactor using TiO2 nanoparticles coated on transparent granules for the degradation of Methylene Blue under solar illumination. Sustain. Environ. Res. 27, 172–180. https://doi.org/10.1016/j.serj.2017.04.002.
Syngenta, 2022. Syngenta | Tecnología al servicio del agricultor [WWW Document]. https://www.syngenta.es/. accessed 6.12.22.
Torán, J., Blánquez, P., Caminal, G., 2017. Comparison between several reactors with Trametes versicolor immobilized on lignocellulosic support for the continuous treatments of hospital wastewater. Bioresour. Technol. 243, 966–974. https://doi.org/10.1016/j.biortech.2017.07.055.
Torstensson, L., 2000. Experiences of biobeds in practical use in Sweden. Pestic. Outlook 11, 206–212. https://doi.org/10.1039/b008.
Torstensson, L., Castillo, M.D.P., 1997. Use of biobeds in Sweden to minimize environmental spillages from agricultural spraying equipment. Pestic. Outlook 8, 24–27.
Triegel, E.K., Guo, L., 2019. Overview of the fate of pesticides in the environment, water balance; runoff vs. leaching. In: Mechanisms of Pesticide Movement into Ground Water. CRC Press, pp. 1–14. https://doi.org/10.1201/9781351074346-2.
Tsihrintzis, V.A., Akratos, C.S., Gikas, G.D., Karamouzis, D., Angelakis, A.N., 2010. Performance and Cost Comparison of a FWS and a VSF Constructed Wetland System, pp. 621–628. https://doi.org/10.1080/09593332808618820.
Tudi, M., Ruan, H.D., Wang, L., Lyu, J., Sadler, R., Connell, D., Chu, C., Phung, D.T., 2021. Agriculture development, pesticide application and its impact on the environment. Int. J. Environ. Res. Publ. Health 18, 1–24. https://doi.org/10.3390/ijerph18031112.
Ueyama, J., Wang, D., Kondo, T., Saito, I., Takagi, Kenji, Takagi, Kenzo, Kamijima, M., Nakajima, T., Miyamoto, K.I., Wakusawa, S., Hasegawa, T., 2007. Toxicity of diazinon and its metabolites increases in diabetic rats. Toxicol. Lett. 170, 229–237. https://doi.org/10.1016/j.toxlet.2007.03.010.
United Nations, 2021. Assessment of Agricultural Plastics and Their Sustainability: A Call for Action, Assessment of Agricultural Plastics and Their Sustainability: A Call for Action. https://doi.org/10.4060/cb7856en.
Vela, N., Fenoll, J., Garrido, I., Pérez-Lucas, G., Flores, P., Hellín, P., Navarro, S., 2019. Reclamation of agro-wastewater polluted with pesticide residues using sunlight activated persulfate for agricultural reuse. Sci. Total Environ. 660, 923–930. https://doi.org/10.1016/j.scitotenv.2019.01.060.
Vilar, V.J.P., Moreira, F.C., Ferreira, A.C.C., Sousa, M.A., Gonçalves, C., Alpendurada, M.F., Boaventura, R.A.R., 2012. Biodegradability enhancement of a pesticide-containing bio-treated wastewater using a solar photo-Fenton treatment step followed by a biological oxidation process. Water Res. 46, 4599–4613. https://doi.org/10.1016/j.watres.2012.06.038.
Vischetti, C., Capri, E., Trevisan, M., Casucci, C., Perucci, P., 2004. Biomassbed: a biological system to reduce pesticide point contamination at farm level. Chemosphere 55, 823–828. https://doi.org/10.1016/j.chemosphere.2003.11.042.
Vryzas, Z., 2018. Pesticide fate in soil-sediment-water environment in relation to contamination preventing actions. Curr. Opin. Environ. Sci. Health 4, 5–9. https://doi.org/10.1016/j.coesh.2018.03.001.
Winterlin, W.L., Schoen, S.R., Mourer, C.R., 1984. Disposal of pesticide wastes in lined evaporation beds. In: ACS Symposium Series. ACS, pp. 97–116. https://doi.org/10.1021/bk-1984-0259.ch006.
Yadav, M., Srivastva, N., Shukla, A.K., Singh, R.S., Upadhyay, S.N., Dubey, S.K., 2015. Efficacy of *Aspergillus sp.* for degradation of chlorpyrifos in batch and continuous aerated packed bed bioreactors. Appl. Biochem. Biotechnol. 175, 16–24. https://doi.org/10.1007/s12010-014-1244-0.
Yin, C., Aroua, M., Daud, W., 2007. Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. Sep. Purif. Technol. 52, 403–415. https://doi.org/10.1016/j.seppur.2006.06.009.
Zapata, A., Malato, S., Sánchez-Pérez, J.A., Oller, I., Maldonado, M.I., 2010. Scale-up strategy for a combined solar photo-Fenton/biological system for remediation of pesticide-contaminated water. Catal. Today 151, 100–106. https://doi.org/10.1016/j.cattod.2010.01.034.