Water Conservation & Management (WCM)

DOI: http://doi.org/10.26480/wcm.01.2024.97.108

ISSN: 2523-5664 (Print)
ISSN: 2523-5672 (Online)
CODEN: WCMABD

RESEARCH ARTICLE

TOXICITY AND HEALTH IMPLICATIONS OF PESTICIDES AND THE NEED TO REMEDIATE PESTICIDE-CONTAMINATED WASTEWATER THROUGH THE ADVANCED OXIDATION PROCESSES

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ARTICLE DETAILS

Article History:

Received 20 November 2023
Revised 24 December 2023
Accepted 27 January 2024
Available online 07 February 2024

ABSTRACT

Pesticides are widely used in homes, industries and agricultural sector, and can travel through water and the air to pollute places far from their point source. Pesticides can find their way into water bodies via industrial wastewater and runoff from agricultural areas and can emit persistent chemicals that contaminate the water system. Since pesticides have a tendency to build up in the body and pose health risks to animals, human and the ecosystem, the issue of pesticides in aquatic environments is one that is causing concern worldwide. Thus, the need to remediate pesticides contaminated wastewater before release into the environment. The removal of pesticides could be accomplished using a variety of conventional treatment techniques, however, these methods have a number of drawbacks, including operating complexity and sludge production, they do not present total removal of pesticide, hence, the need to couple the advanced oxidation treatment processes (AOPs) with existing techniques to achieving close to zero release of organic and inorganic contaminants into the environment. AOPs are suitable as tertiary water treatment techniques and are based on the generation of hydroxyl radicals, which results in their non-selective reactivity with water pollutants, allowing for the mineralization of contaminants and their conversion to CO_2 and water. AOPs may be utilized as an additional treatment method and may be employed to oxidize contaminants in pesticides contaminated wastewater. The review will include the most recent information on the use of AOP to treat organic and inorganic contaminants and enable researchers and scientists to pinpoint areas that still require more study.

KEYWORDS

pesticides, industrial wastewater, health hazards, agricultural runoff, advanced oxidation processes.

1. INTRODUCTION

A rising amount of new toxins are entering the environment as a result of anthropogenic activities and industrial outputs (Arihilam & Arihilam, 2019). Emerging pollutants are a worry for public health, and despite extensive research being done on the subject worldwide, no definitive remedies have been proposed. Pesticides, pharmaceuticals (antibiotics, hormones, and other drugs), cosmetics, and artificial colors are some of the emerging contaminants that are causing the most worry throughout the world (Gomes et al., 2018). Each year, these micro-contaminants are produced throughout the world in around 500 million tons (Thomaidis et al., 2012). Numerous pesticides are also stable over time, allowing them to travel through water and the air to pollute places far from their point of origin (Lofrano et al., 2020). The inconsistent application of pesticides harms ecosystems and endangers fish, cattle, domestic animals, birds, and other species (Coppock & Dziwenka, 2020). For instance, a number of studies have demonstrated the dangers pesticides pose to both people and the environment (Rasheed et al., 2019). For instance, prolonged exposure to the herbicide atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) can cause cancer, heart problems, and degenerations of the retina and various muscle tissues. When applied to vulnerable plants, atrazine inhibits photosynthesis, acting as a selective herbicide. Oxyfluorfen is a herbicide that inhibits protoporphyrinogen oxidase, causing irreparable damage to cell membranes. Oxyfluorfen exposure in humans can result in anemia and difficulties with the liver (EPA, 2002). In addition, azoxystrobin, a broad-spectrum fungicide that prevents the germination of fungal spores, is among the pesticides that pose a threat to the environment because it is particularly harmful to freshwater fish and estuarine organisms (Sutherland & Ralph, 2019). Between 1900 and 2000, the world population rose from 1.5 to 6.9 billion people, which boosted food demand and put strain on agricultural sectors. Pesticides are used in modern agriculture to raise production to a level that is commercially viable. Agricultural and landscaping pesticides are being released in greater amounts into rivers due to industrial, agricultural, mining, and urban wastewater pollution (Mushtaq et al., 2020). Pesticide enrichment of wastewater is caused by a variety of sources, including pesticide residues in gray water left over from washing tainted fruits and vegetables and washing pesticide preparation and application equipment (Manasa & Mehta, 2020). Pesticide treatment from water sources is an important study area because of their abundance and resistance in wastewater (Goodwin et al., 2017; Vela et al., 2019). A few of the challenges in removing pesticides from water include the content of the influent, the diversity of the pesticides' physical structures, and the pH of water, which can range from extremely acidic to extremely alkaline. According to the literature, the range of the biological oxygen demand (BOD) is 30 to 11590 mg/L, whereas the chemical oxygen demand (COD) of wastewater used in the manufacturing of pesticides ranges between 150 and 33750 mg/L. Pesticide concentrations in diverse water sources range from 0.1 to 107

Quick Response Code	Access this article online	
	Website: www.watconman.org	**DOI:** 10.26480/wcm.01.2024.97.108

Cite The Article: Sulaiman O. Adewuyi, Babatunde T. Ibigbami, Augusta O. Mmuoegbulam, Felix S. Abimbade, Oluyide M. Abiodun, Michael J. Klink, Simphiwe M. Nelana, Dosu Malomo, Olushola S. Ayanda (2024). Toxicity and Health Implications of Pesticides and the Need to Remediate Pesticide-Contaminated Wastewater Through the Advanced Oxidation Processes. *Water Conservation & Management, 8(1): 97-108.*

mg/L. (Goodwin et al., 2017; Rodriguez-Narvaez et al., 2017). However, the problem of removing pesticides from water has been initiated and clarified using the current treatment approaches, which combine physical, chemical, and biological methods. Each treatment process has advantages and disadvantages of its own, not only in terms of initial costs and ongoing costs but also in terms of efficiency, operability, reliability, environmental impact, pre-treatment requirements, production of sludge, and hazardous byproducts. Chlorination is a low-cost and straightforward chemical treatment approach, although pre-chlorination can cause microcontaminants to oxidize into more dangerous and less removably by-products (Ahmed et al., 2017). The biological treatment approach known as activated sludge is less expensive to implement, requires less land, and is less harmful to the environment than chlorination. However, it needs a location to dispose of the sludge and qualified personnel to operate and maintain it (Luo et al., 2014). The membrane bioreactors have been successful at removing pesticides, it have a number of drawbacks, including membrane fouling and roughness (Ahmed et al., 2017). Thus, the need to combine these treatment techniques with the advanced oxidation processes (AOPs). Although, AOPs have high capital, operational, and maintenance costs but produces less sludge, has quick response rates, and requires less retention time (Marican and Duran-Lara, 2018). Fenton's reaction has a wide range of applications, is straightforward to carry out, does not produce any bromated byproducts, and can degrade both soluble and insoluble colors in industrial effluents. Photochemical degradation, another kind of AOP, has little chance of producing byproducts that are bromated. However, a separation step is necessary if the catalyst is introduced as a slurry.

The purpose and objectives of the study is to carry out a detailed review of the toxicity and health implications of pesticides. The necessity of AOPs for the removal or as additional treatment methods of pesticides contaminated wastewater was emphasized. Subsequently, the current trends and future considerations associated with the toxicity of pesticides and applications of AOPs were discussed.

2. Water Pollution and Challenges

Water pollution is particularly important since it has become a worldwide problem, with emerging nations suffering considerably as a result of their drive for growth (Inyinbor et al., 2016; Rana et al., 2017). Water pollution is a severe concern to both people and aquatic ecology, and a considerable rise in population leads to climatic changes (Palmate et al., 2017). For instance, numerous human activities as well as the release of greenhouse gases by commercial companies considerably contribute to global warming, an increase in the planet's surface temperature, and a deterioration in the quality of the atmosphere. The fight for sustainable development must incorporate strategies to lessen water pollution. By effectively treating wastewater before its final discharge, one method to enhance the prevention of water pollution is used. Various corrective climate change mitigation measures against water pollution might also be researched. In any civilization, a good level of life for the populace can be started through sustainable development. In order to solve the economic, environmental, and sociological challenges without jeopardizing human and environmental future development, we must keep the future in mind while we make decisions now. Additionally, these include social progress and equality, environmental protection, natural resource conservation, and sustainable economic growth (Ilin et al., 2016). There are several instances of urbanization harming the ecology and jeopardizing its chances of survival. How the natural environment could be protected and preserved should be taken into consideration for sustainable development. Because most established or growing civilizations presently regenerate numerous natural resources on a regular basis, sustainability is one of the major problems with urbanization. Although most of these resources meet human requirements, they are limited in number. Sustainable development is often used to strike a balance between competing social demands. Many scientific organizations and organizations have recognized the need for sustainable development in accomplishing this and have established objectives and aims to meet it. This has also compelled these organizations to play a part in measuring and assessing the effects of these objectives on society. But scientists should contribute to sustainable development in more ways than only the environment. To ensure that no aspect of life suffers, it should also address the population's health (Frone and Frone, 2015). Even though various people may have different definitions of sustainable development, environmental sustainability is all-encompassing. It describes how we should protect and manage the sustainability of resources, air quality, water quality, and ecosystems, all of which are crucial for the survival of mankind. It also helps prevent any environmental damage brought on by technological advancement. One way to achieve environmental sustainability is through efficient wastewater treatment. There are a variety of traditional wastewater treatment methods that may be employed; among its drawbacks are operational complexity and sludge formation. The expensive equipment, convoluted processes, and need for expert workers are commonly cited as the causes of their financial disadvantages. Due to their cost drawbacks, traditional wastewater treatment methods are ignored by many industries, resulting in the release of untreated or only minimally treated effluent into water bodies. Therefore, a simple and inexpensive wastewater treatment system will enable effective wastewater treatment and protect the aquatic environment from contamination.

2.1 Harmful Risks of Water Pollution

Water is a fundamental requirement for life and unquestionably has an effect, either directly or indirectly. Every industrial, environmental, and physiological process requires water. According to Hanslmeier (2011), water serves a multitude of purposes in living organisms, including those of a solvent, temperature buffer, metabolite, environment, and lubricant. However, the term "contaminated water" refers to water that is inappropriate for its intended use because some components of the water quality requirements have been impacted by unplanned and anomalies from several anthropogenic activities. Water pollution poses a major risk to both the environment and human life. The pollutant's effects might vary depending on its type and source. For instance, although certain organic pollutants, like heavy metals and dyes, have been connected to cancer, others, including hormones and medicines, as well as waste from cosmetics and personal care items, have been categorized as endocrine disruptors (Adeogun et al., 2016). Because these toxins pose so many threats to the ecosystem, environmentalists are quite concerned about them. Through a variety of routes, they get to the water body, although they are mostly man-made channels.

2.1.1 Human Exposure to Pesticides

Man through the quest for proper food security and vector control, is always exposed to some kinds of pesticides like herbicides, fungicides and insecticides through different routes such as occupation, water, food, soil, air, etc (Kim *et al*., 2017). Thus, people can be exposed either by breathing pesticide (air), getting it into the mouth by eating (food) or drinking (water), or by contact with the skin or eyes. However, according to the U.S. Environmental Protection Agency (1999), drift in pesticide may be the major potential source of pesticide exposure to the general public. It is of great public health concern to know that pesticides used in the control of food crop pests can be harmful to the consumers of those foods as researchers have reported that many food crops such as fruits and vegetables still have pesticide residues even after washing or peeling. This is so because many pesticide chemical components which are resistant to breakdown though no longer in use, may persist in the soil and water and then find their way in foods (Cornell University, 1999). According to the US Centers for illness Control and Prevention (2018), there were about 18.4 million adult and 6.2 million pediatric cases of asthma in the United States in 2015. Asthma is a chronic inflammatory illness that affects breathing. With increased prevalence and severity of asthma in the last two decades (Brozek *et al*., 2015; Ding *et al*., 2015; Hartert and Peebles, 2000; Tarlo, 2015), lots of hypotheses were proposed to establish cause of the susceptibility increase and attention has been drawn to organophosphorus pesticides (OPs) exposure as a factor associated with occupational asthma in qgriculture (Hernández *et al*., 2008; Hoppin *et al*., 2014; Mamane *et al*., 2015a, Ye *et al*., 2013) in the context of urban asthma (Hernández *et al*., 2011; Mamane *et al*., 2015b; Ye *et al*., 2016). Occupational exposure to OPs occurs during its production, distribution and application through dermal absorption and inhalation (Fenske, 2012; Hernandez, 2010).

2.1.2 Toxicity of Pesticides

Pesticides are chemicals that are used to eradicate pests, weeds, rodents, insects, and other creatures that are hazardous to both domesticated plants and animals. Due to food security and control of vectors, the use of pesticides will continue even in future despite their toxic side effects which result to severe health problems. It is evident that an increased pesticide long-term effects result from parental exposure, adolescent or early life exposures. Most of the human disease conditions resulting from pesticide exposure are Parkinson's disease, asthma, bronchitis, infertility, birth defects, Alzheimer, autism, respiratory diseases, organ diseases just to mention but a few. Pesticides have been reported by Stockholm Convention on persistent organic pollutants (POPs) (2001) to be 9 out of the 12 most dangerous chemicals that are persistent in the environment (POPs, 2014; Gilden *et al*., 2010). Pesticides vary in their mechanism of action and are made to harm living things. Various types of pesticides exist, including organochlorines (OCPs), also known as POPs, organophosphates, carbamates, phyrethroids, and triazines. Although pesticides are known to have adverse effects, OCPs health effects are known by their dissolution in fatty tissues with resultant harmful accumulation in these tissues. Some of the OCPs due to their structural similarity to estrogen tend to exhibit the effects of endogenous estrogen by recognizing and binding on estrogen surface receptors (Kim *et al.*, 2017). The toxic effects of such OCPs are caused by hormonal homeostasis interference which leads to hormonal dysregulation, consequently encouraging aberrant growth and development of reproductive tissues, which can lead to negative consequences on reproductive health or cancer (Yilmaz *et al.*, 2020).

Pesticides can also alter gene expression and cellular function by interfering with cell receptors and ion channels, blocking important signaling pathways in cells, and altering DNA methylation and histone modifications. These actions can all have a negative impact on human health (Kalyabina *et al.*, 2021). Although the majority of OCPs or POPs used in the 1950s have been outlawed in many nations, the soil still contains residues of their persistent breakdown products (Kalyabina *et al.*, 2021).

2.1.3 Mechanism of Action of Pesticides

OPs is one of the most extensively used pesticides in the world, OPs are applied not only in agriculture but are also used to control insects in the urban and suburban settings (Costa, 2018). OPs are found to be ubiquitous in human chemosphere and the metabolites were found in urine samples taken from members of the broader US population (Barr *et al.*, 2005; Center for Disease Control and Prevention (CDC), 2014; Eskenazi *et al.*, 1999). Lung inflammation is a key characteristic of human asthma which has been attributed to OPs exposure. Type 2 (T_H2) immune response associated with allergy plays an important role in asthmatic conditions (Fahy, 2015; Gillissen and Paparoupa, 2015). This T_H2 immunity is regulated by interleukin-1 (IL-1), IL-5 and IL-13 all of which are secreted by T_H2 cells and are known to have high immunoglobulin E titers and eosinophilia (Annunziato *et al.*, 2015). There is a clear link between eosinophilic airway inflammation and atopic asthma (Azzawi *et al.*, 1992, Bousquet *et al.*, 1990, Drake *et al.*, 2018). Severe asthma is characterized by an elevated and persistent eosinophil count in the lungs in the absence of any exacerbations (Wenzel, 2003). This was demonstrated in an antigen sensitization guinea pig model employing antigen-induced airway hyperreactivity (AHR), which attracted eosinophils to the lungs to cluster around airway nerves (Costello *et al.*, 1997; Elbon *et al.*, 1995) as seen in human asthma (Costello *et al.*, 1997). This causes blockage of eosinophil influx with IL-5 (Elbon *et al.*,1995) or migration of eosinophil to the nerves, causing low doses of dexamethasone (Evans *et al.*, 2001) which prevents AHR and M2 receptor dysfunction in the antigen-challenged guinea pigs. To block M2 receptor activity, eosinophils on activation by antigen challenge release major basic proteins (MBP) (Costello *et al.*, 2000; Costello *et al.*, 1997). MBP inhibits the neuronal M2 receptor function by binding at its allosteric site (Jacoby *et al.*, 1993), and stimulating bronchoconstriction. MBP protects the M2 receptor function by blocking antibody through its allosteric binding so as to inhibit AHR (68), while its removal from the M2 receptor by heparin restores M2 receptor function and reverses AHR (Fryer and Jacoby, 1992) in an antigen-induced AHR guinea pig model.

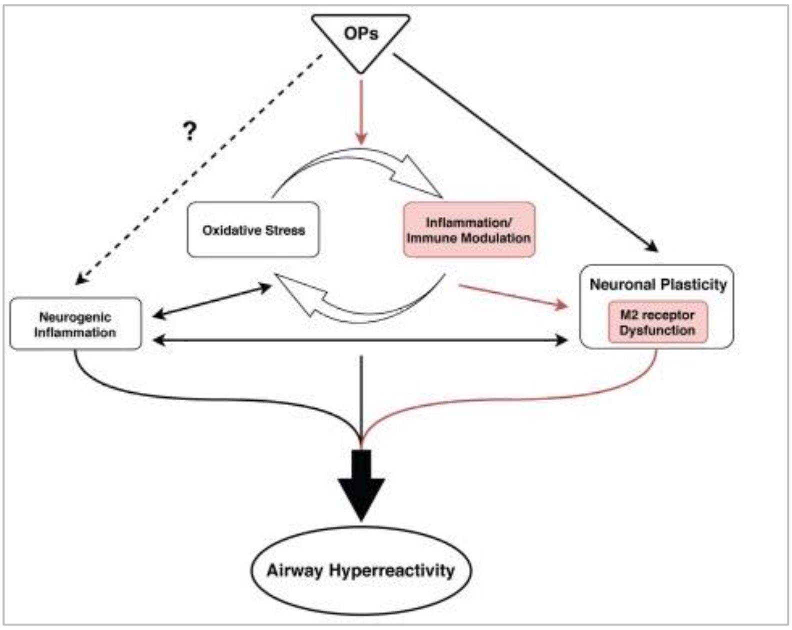

Figure 1: Several toxicological pathways for organophosphorus pesticides that cause OP-induced airway hyperreactivity (AHR) (Shaffo *et al.*, 2018).

2.1.4 Health Implications of Pesticides

Pesticides can have a negative impact on human health by interfering with cell receptors and ion channels, blocking important signaling pathways, altering DNA methylation, and altering histone modifications, which can influence gene expression and cellular function (Kalyabina et al., 2021). Pesticides can have immediate negative consequences on their users' health, including stomach discomfort, headaches, nausea, and vomiting as well as issues with their skin and eyes (Ecobichon, 1996). Insecticides such as pyrethrins have been reported to result to a potential deadly condition when inhaled (Medline Plus, 2006). In China, approximately 500,000 human pesticide poisoning cases with 500 deaths have been reported (Lawrence, 2007).

2.1.4.1 Cancer

Cancer has been proven by research as a health challenge attributable to pesticide exposure. Pesticide exposure has been associated with lymphoma, brain, pancreas, stomach, kidney, breast, prostrate, liver, lung, esophageal and skin cancers (Gilden *et al.*, 2010, Mostafalou and Abdollahi, 2013). Both residential and occupational exposures to pesticides have been associated with the increased cancer risk (Gilden *et al.*, 2010) especially among workers in the farm who use pesticides (McCauleyet *et al* 2006). Several studies have established associations between glioma and meningioma and carbamate exposure, laryngeal cancer and alachlor exposure together with B-cell lymphoma and glyphosate exposure (Curl *et al.*, 2020). Gilden et al. (2010) and Van Maele-Fabry et al. (2010) linked a pregnant mother's exposure to pesticides to an increased risk of leukemia, Wilm's tumor, and brain cancer in her offspring, while Chen *et al.* (2015) associated children blood cancer with exposure to both herbicides outside and insecticides at home. Systematic review in 2007 by Bassil *et al.* (2007) reported a positive association between leukemia and non-Hodgkin lymphoma with pesticide exposure and thus demanded for a decrease in cosmetic use of pesticides. However, a link between pesticide use and the onset of cancer at the molecular level suggested damage to genetic components like DNA, chromosomes, and histone proteins as well as to cell organelles like the endoplasmic reticulum, mitochondria, nuclear receptors, and endocrine networks (Mostafalou and Abdollahi, 2013).

2.1.4.2 Neurological Effects

Exposure to pesticides have resulted to neurological effects, with acute exposure to high concentrations of neurotoxicants (pesticides) influencing the central nervous system, which causes neurotoxicity such as cognitive and motor impairments (Richardson *et al.*, 2019; Sanborn *et al.*, 2007). According to Fucic et al. (2021), certain pesticides and their metabolites that have not fully evolved in a fetus penetrate the placenta and the fetal blood-brain barrier, hence the association of neurodevelopmental impairment health challenge in-utero and early-childhood organophosphate exposure (Sanborn *et al*., 2007, Rani *et al*., 2021, Fucic *et al*., 2021). Furthermore, the development of neurodegenerative disease at a later stage in life has been attributed to chronic exposure and accumulation of pesticides (Sanborn *et al*., 2007; Rani *et al*., 2021; Mostafalou and Abdollahi, 2013). According to research by Raji et al. (2021) and Mostafalou and Abdollahi (2013), chronic pesticide exposure may have direct toxic effects on dopaminergic neurons, which are typically depleted in Parkinson's disease patients, which may increase the risk of developing Alzheimer's disease and Parkinson's disease. Exposure to high pesticide levels among agricultural workers that make use of pesticides is associated with neuropsychiatric, neurologic and neurodegenerative disorders (Curl *et al*., 2020, Mostafalou and Abdollahi, 2013). Among these disorders are attention-deficit hyperactivity disorder (ADHD), depression, anxiety, dizziness, headache and olfactory impairment normally used as an early indication of neurodegenerative disorder (Curl *et al*., 2020).

2.1.4.3 Reproductive Effects

Lots of pesticides have been implicated and proven to disrupt the endocrine, with long-term exposure affecting reproductive health, which is linked to altered maturation patterns, reduced fertility, and higher miscarriage rates (Shaffo *et al*., 2018). Carbamate insecticides as well as triazines exposure have anti-androgenic effects which impacts male causing developmental issues in testicular size, sperm and androgen productions (Mostafalou and Abdollahi, 2013). Furthermore, dibromochlorophane and 2,4-D pesticides have been associated with male fertility impairment (CDC, 2014), genetic alteration in sperm, reduction in sperm count. Germinal epithelium damage and hormone function alteration (Environmental Impacts on Reproductive Health- EIRH, 2022). However, endocrine disruption is determined by the period of pesticide exposure as disease manifestation is dependent on the susceptibility variation window (Mostafalou *et al*., 2013). Due to the ability of pesticides to cross the placenta, it has been reported that congenital disorders which includes fetal death, altered fetal growth and physical and/or mental disabilities are associated with pre- and post-natal pesticide exposures (Sanborn *et al*., 2007, Fucic *et al*. 2021, Mostafalou and Abdollahi, 2013).

2.1.4.4 Respiratory Effects

Pesticide exposure has been implicated in long-term respiratory problems (Doust *et al*., 2014). Reduced lung function and associated symptoms of the airways like airway hyperreactivity (AHR) have been found to result from pesticide exposure (Curl *et al*., 2020). Pesticide exposure has been linked to airway symptoms including; wheezing, coughing, shortness of breath, runny nose, sore throat, inflammation of the throat, and difficulty breathing (Curl *et al*., 2020, Ye *et al*., 2013). Ye *et al*. (2013) has reported carbamate and OPs exposure to cause reduction or impairment of lung function due to inhibition of cholinesterase by pesticides, as POs exposure is associated with decline in lung function through a restrictive driven process (Ye *et al*., 2013).

3. Industrial Wastewater

Water is a valuable resource that was formerly practically free to use. But times have changed, and today, neither society's citizens nor business has free access to water. In fact, the price of water has increased to the point where industry now views it at the same level as any other raw commodity. In many kinds of enterprises, water serves a variety of purposes. Nearly 90% of the water utilized in industry ends up as industrial effluent. The discharge of this industrial effluent into the environment leaves a huge environmental legacy and could lead to a number of other risks. This is particularly true for the chemical industry and other related process sectors. Therefore, every effort must be made to decrease water usage and treat wastewater so that it is at the very least reusable or safe to release into the environment. Chemical and related process industries utilize a lot of water, making them industries with a high water intensity. Water is utilized to fill these demands from sources including surface water, groundwater, ocean, and recycled water (industrial wastewater and urban sewage). In many businesses, the amount of wastewater produced varies greatly from process to process and is significantly larger in underdeveloped nations. This also depends on the kind of pollutants present and how concentrated they are in the wastewaters. For instance, India's steel sector uses 25–60 m^3 of water for every ton of steel produced, which is 8–10 times more than in industrialized nations. As a result, cooling fluids from the steel and coke industries make up a large volume and may include pollutants in the form of hazardous substances including cyanide, ammonia, phenols, and metals. Wastewater in the pharmaceutical industry is mostly produced by cleaning machinery. Despite the relatively small amounts, the resulting effluent is seriously contaminated due to the high levels of organic pollutants contained in solvents, pharmaceutical compounds, and other materials.

3.1 Reuse, Recover, and Recycle (3R)

Industrial wastewater can be recycled, reused, or recovered if it is correctly handled, which can significantly reduce the amount of water needed and have a positive influence on the environment (Anderson, 2002; Jana et al., 2018). Although most current operations in industrial wastewater treatment do not seek to reuse, recover, and recycle (3R) until they are faced with strict restrictions, this has lately received more attention (Mohapatra & Kirpalani, 2019). However, given that trash is not recovered to be recirculated in present practices, resource industrial cycles are usually linear systems (Piadeh et al., 2014; Ranade & Bhandari, 2014). Due to the industry's rapid growth, which generates competition for water between industry and agriculture as well as the rising cost of water, more emphasis must be placed on the 3R scheme of industrial wastewater and derived sludge treatment. This calls for more effective water use practices as well as the prevention of pollution (Levine & Asano, 2002; Ranade & Bhandari, 2014). As a result, more companies are becoming aware of the financial implications of water consumption and the benefits of reuse versus waste. As resource costs, water supply restrictions, and effluent limitations rise, along with a significant reduction in the environmental impact of industry, the cost of recovering, recycling, and reusing the water, valuable materials, and energy found in industrial wastewater is also becoming more and more profitable (Ranade & Bhandari, 2014; Smol et al., 2020). With the primary goal of resolving environmental issues, unit operations and procedures in wastewater treatment are critical for increasing cost competitiveness, boosting energy efficiency, creating new employment, and rising productivity. Consequently, wastewater treatment is now more than just a way to make water purer (Safferman et al., 2017).

Financial gain and stability are the two main goals of the sector. From this angle, wastewater management ought to help achieve these objectives. In general, optimizing water consumption and emissions instead of reducing them has become the norm in recent years. In this situation, it is often assumed that industrial wastewater treatment's sole purpose is to remove contaminants to levels that comply with discharge standards in an effort to keep treatment costs to a minimum (Ranade & Bhandari, 2014). Unfortunately, because it restricts the potential of the 3R method, this strategy has an extremely constrained and impractical scope. Not simply availability and cost considerations, but also the quality of the water must be taken into account. As previously highlighted, economics nearly totally determines how much value is placed on the industrial wastewater (Crini & Lichtfouse, 2019). However, increased treatment technology diversity, intensity, and efficacy have made effluent reuse and recovery increasingly feasible to address these issues. A more stringent environmental regulations has created a hostile economic environment for the industry (Mpofu et al., 2021). Reusing industrial wastewater while still in operation, with or without treatment; recycling industrial wastewater in connection with the recovery of water for potable use by modifying or replacing the current plant; resources recovery from wastewater including industrial products, energy, heavy metals, salts, organic fertilizers, biogas, biopolymers, inorganic nutrients, etc. are some of the different ways that the 3R scheme can be implemented (Smol et al., 2020). These industrial water cycle closure and valuable component acquisition plan solutions will often call for a combination of wastewater treatment activities. However, due to the wastewater's unique contaminants, high levels of organic matter, and poorly biodegradable components, this is a challenging task (Morales-arrieta et al., 2021). Because of this, industrial wastewater treatment encompasses a wide range of physical, pharmacological, and biological treatment modalities (Ranade & Bhandari, 2014). The potential combinations of processes, but not just, are often categorized according to the severity of treatments (Drewes et al., 2017). The choice of these, however, is the biggest problem and will be highly influenced by the wastewater's characteristics, such as its quality, the pollutants it contains, and the extent to which these pollutants should be reduced or recovered. There is no one or universal methodology or method for these given that, unlike urban wastewater, the quality of industrial wastewater differs greatly among itself, even in the same category of industries (Crini & Lichtfouse, 2019). The task is to find solutions and open doors for sustainable growth. The 3R approach still requires significant technology advancement in terms of maturity, dependability, demonstration, and quality control, as well as social and economic advancement in terms of public acceptability and expenses, reimbursements, and financial risks (Baawain et al., 2020; Jana et al., 2018; Mohapatra & Kirpalani, 2019). As a consequence, the state of the art examines any shortcomings and unrealized potential for the implementation of the 3R scheme in the industrial sector, as well as the advantages and disadvantages of unit operations and processes in the field of industrial wastewater treatment.

3.2 Industrial Wastewater Treatment Technologies

Wastewater treatments have a number of well-established procedure (Ranade & Bhandari, 2014). Each of the procedure has its own drawbacks, including those related to feasibility, equipment or space availability, removal effectiveness, dependability, environmental impact, generation of sludge and byproducts, operational difficulty, pretreatment needs, and the development of potentially dangerous residues (Crini & Lichtfouse, 2019). Only a small number of unit treatment options are frequently used in industrial wastewater treatment, and regrettably, as was already indicated, their primary selection factor is economic (Crini & Lichtfouse, 2019). The following are many operations and unit procedures for wastewater treatment that, when used in the right order, can result in a 3R scheme technology system.

3.2.1 Conventional Physicochemical Treatment Units

This comprises all typical treatment unit operations whose elimination principles are based on phase separation, molecular separation, or chemical conversion and which are not dependent on biological conversion. Normally regarded as the primary process or pretreatment units in wastewater treatment, however in a 3R scheme, these might potentially be considered secondary or tertiary. Each technology's full technical specifications have already been covered elsewhere (Mai et al., 2018; Nidheesh et al., 2021). One of the most popular treatment modalities is coagulation/flocculation, which is well established, affordable, useful, and reasonably effective in the context of today (Zhao et al., 2018). Depending on the effluent quality, it is often used as a main or secondary treatment step, either in the conventional approach (chemically induced coagulation) or somewhat less frequently in the unconventional way (electro-coagulation or cavigulation). However, depending on the business, this technology may possibly be the main barrier to system reuse and recovery (Zheng et al., 2021). In the past, biological processes along with settling and filtration were the principal methods used in industrial wastewater treatment plants (Ranade & Bhandari, 2014). Due to their considerable experience and straightforward operation, they are still widely employed in industry today. When recovering pollutants from industrial wastewater, other technologies like flotation or chemical precipitation are frequently applied. These offer the advantages of a straightforward process, inexpensive investment, established technology, substantial large-scale experience, and a high level of automation (Wang, 2018).

Adsorption is an efficient treatment method for resistant contaminants that are challenging to remove by biological alternatives in industrial wastewater treatment units (Mai et al., 2018). Similar to the previously described processes, this process has a strong commercial presence and is technologically advanced, demonstrating its wide adoption in the sector. Due to its straightforward deployment, cheap cost, great availability, and excellent removal efficiency even at low pollution concentrations, it has also continued to be one of the most promising recovery solutions (Dawn & Vishwakarma, 2021; Wang, 2018). In the intermediate and tertiary treatment stages, other common unit processes including absorption, evaporation, and crystallization are typically taken into account (Ranade & Bhandari, 2014). However, these are typically utilized in traditional wastewater recycling and reuse systems and are not thought of as unconventional or advanced unit treatment operations (Muhammad & Lee, 2019). Adsorption techniques are the technology with the most progress, interest, and potential for exploitation. When compared to other traditional technologies, these processes are able to create high-quality effluents at cheap operational costs because of the strong adsorption potential of fresh material and the speedy adsorption of metals, hazardous contaminants, and persistent organic pollutants. Ion exchange and precipitation are two more technologies that have a particular interest in industrial wastewater treatment with a potential eye toward a 3R scheme.

3.2.2 Unconventional Physicochemical Treatment Units

The operation and procedures of conventional wastewater treatment units have somewhat successful in treating effluents for release throughout the past few decades. Nevertheless, in order to contemplate recovery and make treated wastewater re-usable for industrial and other sector applications, innovations and integration with unconventional technologies are absolutely necessary (Ezugbe & Rathilal, 2020). These novel, non-biological water treatment techniques are equal to these non-conventional physicochemical treatment units. Unusual physicochemical treatment techniques, such as membrane processes, are usually considered to be more energy-efficient, simpler to utilize, and to produce water and products of superior quality with no negative environmental effect. A possible method for recovering metals, nutrients, and other components in industrial wastewater is membrane technology (Ali et al., 2021; Shrestha et al., 2021). However, there are several restrictions, especially in industrial wastewater reclamation, which is severely hampered by membrane fouling. This may not always be the case (Ranade & Bhandari, 2014). Membrane processes are still a relatively new type of industrial wastewater treatment, despite the fact that pressure-driven membrane processes like reverse osmosis (RO), nano filtration (NF), ultrafiltration (UF), and microfiltration (MF) are currently used in industrial wastewater treatment on a large scale (Cui et al., 2010). They are frequently used in tertiary treatment as a fine polishing step as well as a main treatment. These are actually some of the procedures that have a great chance of producing pure water that may be reused and recycled. Forward osmosis (FO), membrane distillation (MD), and electrodialysis (ED) are examples of newly developed membrane processes. Other electrochemical membrane methods include capacitive membrane deionization (MCDI), electro-electrodialysis (EED), bipolar membrane electrodialysis (BMED), membrane-assisted electron ionization (EDI), and membrane electrolysis (ME). The selectivity of these processes is favorable (Wei et al., 2013). Even while almost all of these new membrane technologies have tremendous potential, there are still issues that hinder their widespread industrial adoption. Although numerous studies on the recovery in the industry have been conducted, the majority of these have concentrated on synthetic matrices, which are frequently significantly different in quality from the genuine ones (Perez et al., 2019). But generally, it is anticipated that research into and use of all membrane alternatives would increase.

3.2.3 Biological Treatment Unit

When somewhat comprehensive treatment is needed and it can be made to work, biological treatment is typically seen as being more affordable than any other type of treatment. However, industrial wastewaters frequently include concentrations of organic molecules that are more than 10 times greater than those in municipal wastewater, as measured by biological oxygen demand (BOD) and chemical oxygen demand (COD). Therefore, the existence of inhibitory or resistant biological molecules, and the biological treatment of some industrial wastewater are all potential issues (Ranade & Bhandari, 2014). Similar to how adsorption technologies have firmly established themselves in terms of commercial use and technological maturity, biological processes such as conventional activated sludge (CAS), membrane bioreactor (MBR), and biological nutrient recovery have done the same, indicating their wide acceptance in the industry. This contrasts with AOPs, which are more technologically developed but are nevertheless likely to be used more frequently in the future due to the intensification of refractory pollutants (Ranade & Bhandari, 2014).

3.2.4 Sludge Treatment Unit

Despite being considered to be "thrown away," sludge, a solid waste produced by industrial wastewater treatment, should be considered as part of the economics of water treatment systems since it has a cost (Fytili & Zabaniotou, 2008). In order to make the transition to the adoption of 3R schemes in industrial processes, it is common to evaluate only the water while ignoring solid wastes. However, it might be conceivable to optimize the entire wastewater treatment plants at the same time, leading to increased economic output and diminished environmental effect (Elalami et al., 2019). On the one hand, the CAS and its various configurations produce a significant amount of surplus sludge that needs to be removed because they are the most widely utilized technology for wastewater treatment in the world (Yoshino et al., 2020). This sludge produces extraordinarily high volumes of residual solids and incurs significant disposal expenses due to its high volatile solids fractions and water retention. In fact, between 25 and 65 % of a wastewater treatment plant's overall operating expenses can be attributed to the treatment and disposal of this extra sludge. As a result, the majority of traditional physicochemical and biological techniques convert an industrial wastewater problem into a problem with solid waste management (Salehiziri et al., 2018). Because of this, the management of these solid wastes must be done in a way that is environmentally friendly and complies with certain standards for effective resource recycling (Fytili & Zabaniotou, 2008). As a result of the numerous physicochemical reactions occurring in industrial wastewater, inorganic sludge, chemicals made from metal cations, fluoride anions, cyanides, and phosphates, as well as synthetic organic compounds including phenols, detergents, and oily emulsions, are commonly created. Although preventing the generation of residual sludge is the easiest approach to handle it, when there are no other ways to minimize it, it must be treated in order to be reused, recycled, revalued, and finally disposed of (Golomeova et al., 2013). Environmental quality criteria are quite rigorous for the most popular industrial solid waste treatment options, such as landfilling or incineration. Additionally, regulations for this application are becoming stricter in order to prevent threats to the health of people and the environment from potentially hazardous substances in sewage sludge. Although there are other options, such is the creation of nanomaterials and the creation of building materials (Guerra-Rodriguez et al., 2020; Martnez-Martnez et al., 2020), sludge management trends have gained a lot of scholarly attention since they relate to technologies like wet oxidation, pyrolysis, gasification, and combustion for use as an energy source in the future (Elalami et al., 2019; Fytili & Zabaniotou, 2008). The wastewater treatment plants in the industry should switch to recovering water resources from sludge and wastewater itself as part of the implementation of the 3R plan in the future. Therefore, sludge ought to be taken into consideration as a feedstock for future renewable energy and materials. Emerging biological technologies are actively being researched for this purpose, including dark fermentation, bio-electrochemical systems (BES), and others (Elalami et al., 2019).

4. Advanced Oxidation Processes

AOPs are described as oxidation processes that result in the production of hydroxyl radicals ($OH^\bullet$) in sufficient quantities to impact water purification. In the 1980s, it was first suggested that they be used to purify potable water (Glaze, 1987). AOP eventually included oxidative reactions employing $SO_4^\bullet$ sulfate radicals. As opposed to traditional oxidants like chlorine and ozone that have a dual function of decontamination and disinfection, AOPs are primarily employed to remove organic or inorganic pollutants from water and wastewater. The inactivation of pathogens and pathogenic markers by AOP has been the subject of investigations (Cho et al., 2005; Ikai et al., 2010), however further research is needed, they are rarely used for disinfection since the needed detention lengths for disinfection are prohibitive due to the extremely low radical concentrations (Tchobanoglous et al., 2003). Being a strong oxidizing agent, these radicals are anticipated to effectively destroy wastewater contaminants and convert them into less hazardous or even non-toxic products when AOPs are used for wastewater treatment, hence offering the best possible outcome (Huang et al., 1993).

4.1 Hydroxyl Radical-Based Advanced Oxidation Processes

The hydroxyl radical is the most reactive oxidizing agent in water treatment, with an oxidation potential ranging from 2.8 V (pH 0) to 1.95 V (pH 14) vs. saturated calomel electrode, the most used reference electrode (Tchobanoglous et al., 2003). The behavior of $OH^\bullet$ is incredibly non-selective and responds swiftly with a variety of species at rates of 10^8–10^{10} $M^{-1}\ s^{-1}$. Hydroxyl radicals eliminate organic contaminants through four different processes: radical addition, hydrogen abstraction, electron transfer, and radical combination (System, 1994). They combine with organic molecules to produce carbon-centered radicals ($R^\bullet$ or $R^\bullet$-OH), which, in the presence of oxygen, transform into organic peroxyl radicals ($ROO^\bullet$). All of the radicals continue to react, producing more reactive species including super oxide ($O_2^\bullet$) and H_2O_2, which causes chemical breakdown and even mineralization of these organic molecules. Since hydroxyl radicals have a very brief lifetime, they can only be created in-place during application using various techniques, such as a combination of oxidizing substances (like H_2O_2 and O_3), irradiation (like ultrasound or UV light), and catalysts (like Fe^{2+}) (Huang et al., 1993).

4.2 Ozone-Based Advanced Oxidation Processes

Organic molecules undergo chemical disintegration and even mineralization as a result of all the radical reactions that follow, which produce more reactive species including super oxide ($O_2^\bullet$) and H_2O_2. Below is a summary of the key AOPs for wastewater treatment's hydroxyl radical generating mechanisms.

$$3O_3 + H_2O \rightarrow 2OH^\bullet + 4O_2 \qquad (1)$$

In the presence of extra oxidants or radiation, the $OH^\bullet$ production can be significantly boosted. For instance, in the so-called peroxone (O_3/H_2O_2) system, hydroperoxide (HO_2), which is formed from H_2O_2 decomposition, promotes O_3 decomposition and $OH^\bullet$ generation.

$$H_2O_2 \rightarrow {HO_2}^- + H^+ \qquad (2)$$

$$HO_2 + O_3 \rightarrow OH^\bullet + {O_2}^- + O_2 \qquad (3)$$

H_2O_2 is produced during the O_3/UV irradiation as an additional oxidant, predominantly via O_3 photolysis.

$$O_3 + H_2O + hv \rightarrow 2OH^\bullet + O_2 \qquad (4)$$

As a result, at least three processes such as ozonation (Eq. 1), O_3/H_2O_2, and photolysis of H_2O_2 (Eq. 5) can produce $OH^\bullet$.

$$H_2O_2 + hv \rightarrow 2OH^\bullet \qquad (5)$$

4.3 UV-Based Advanced Oxidation Processes

Photons have the ability to initiate the production of hydroxyl radicals in the presence of catalysts or oxidants. The most well-known catalyst is TiO_2, a semiconductor of the RO type. TiO_2 particles are energized as follows to create positive holes with an oxidative capacity in the valence band and negative electrons with a reductive capacity in the conduction band:

$$TiO_2 + hv \rightarrow e_{cb}^- + h_{vb}^+ \qquad (6)$$

At the surface of TiO_2, these holes and electrons can further interact with OH, H_2O, and $O_2^\bullet$ to produce hydroxyl radicals.

$$h_{vb}^+ + OH_{surface}^- \rightarrow OH^\bullet \qquad (7)$$

$$h_{vb}^+ + H_2O_{absorbed} \rightarrow OH^\bullet + H^- \qquad (8)$$

$$e_{cb}^- + O_{2\,absorbed} \rightarrow O_2^\bullet \qquad (9)$$

When exposed to UV light with oxidants like H_2O_2 (Eq. 5) or O_3, more $OH^\bullet$ may be generated. Moreover, it is possible for $OH^\bullet$ to be created at a wavelength less than 242 nm by photolyzing water.

$$H_2O + hv \rightarrow OH^\bullet + H \qquad (10)$$

4.4 Fenton-Related Advanced Oxidation Processes

The most popular of these metals that may activate H_2O_2 and produce hydroxyl radicals in water is iron. In the so-called Fenton reaction, H_2O_2 reacts with Fe^{2+} to create strong reactive species. Although other compounds, such ferryl ions, have been proposed. There have been extensive discussions on the Fenton-related chemistry for the treatment of water and wastewater (Pignatello et al., 2006). The reactions (Eq. 11-13) make up the core of a traditional Fenton radical mechanisms.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \qquad (11)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {HO_2}^\bullet + H^+ \qquad (12)$$

$$2H_2O_2 \rightarrow OH^\bullet + {HO_2}^\bullet + H_2O \qquad (13)$$

In a conventional Fenton wastewater treatment settings, Fe^{3+} produces iron sludge. The complexity of the treatment and operational costs are increased because the sludge must be disposed of separately. It should be noted that the Fenton reaction only produces hydroxyl radicals when the pH level is acidic. Therefore, the practical use of the Fenton reaction to wastewater treatment is limited. The Fenton-like system, the photo-Fenton system, and the electro-Fenton system are three modified Fenton procedures that are offered as expansions of the conventional Fenton treatment method. Fe^{3+} replaces Fe^{2+}in the Fenton-like reaction, which means that the series of reactions in the Fenton system are started from Eq. 12. With the classic Fenton system, UV irradiation is used in the photo-Fenton reaction with the primary goal of accelerating the UV-induced reduction of dissolved Fe^{3+} to Fe^{2+}. Both or each of the Fenton reagents can be produced electrochemically in the electro-Fenton process.

4.5 Utrasound-Based Advanced Oxidation Processes

Other AOPs, such as ultrasonic (US) irradiation and electronic beam irradiation, have been investigated for various wastewater treatment applications. Under US irradiation (16 kH - 100 MHz), alternating compression and rarefaction cycles of the sound waves can result in three sequential phases of cavities formed of vapor and gas-filled micro-bubbles (nucleation, growth, and implosive collapse). The micro-bubble collapse can produce high temperatures (4200–5000 K) and pressures (200–500 atm) immediately and under these harsh circumstances, gaseous water molecules within bubbles are broken apart, producing hydroxyl radicals.

$$H_2O+))) \rightarrow OH^\bullet + H^\bullet \qquad (14)$$

The hydroxyl radicals is able to mineralize water and wastewater contaminants. The modified US processes include H_2O_2 assisted US, nano catalyst assisted US, and the nano catalyst/ H_2O_2 assisted US (Ayanda et al., 2018).

4.6 Sulfate Radical-Based Advanced Oxidation Processes

Strong oxidant $S_2O_8^{2-}$ has a typical oxidation potential by itself. Heat, UV light, transitional metals, or a higher pH can all activate $S_2O_8^{2-}$ to produce a more potent sulfate radicals ($SO_4^{\bullet}$), which can then start advanced oxidation processes based on sulfate radicals.

$$S_2O_8^{2-} + hv\ (or\ heat) \rightarrow 2SO_4^{\bullet-} \quad (15)$$

When the sulfate radical generated from the ion peroxydisulfate and UV radiation is combined with oxygen or H_2O_2, a higher amount of $OH^{\bullet}$ is produced and thus promote the oxidation of organic contaminants. Although high pH can also activate persulfate, the underlying processes are still unclear (Tsitonaki et al., 2010). The temperature used in a thermally activated persulfate technique typically falls between 35 and 130 °C (Tsitonaki et al., 2010). According to Eq. 15, the metal activation approach only produces 50% of the sulfate radical yield obtained by the heat- or UV-activated persulfate method at the same molar persulfate concentration. Hence, logically speaking, the metal activation method is not effective. Fe(II) and Fe(III) ions are the most often used metals, although other metals, including Cu(I) and Ag(I), have been demonstrated to be capable of activation (Anipsitakis and Dionysiou, 2004). Like hydroxyl radicals, sulfate radicals are highly reactive, short-lived creatures, but they respond in different ways. In their interactions with organic compounds, hydroxyl radicals choose to add to C=C bonds or take H out of C-H bonds (Neta et al., 1977). On the other hand, sulfate radicals typically strip electrons off organic molecules and transform them into organic radical cations (Forsey, 2004).

4.7 Multiple Mechanisms Occurring During Advanced Oxidation Processes

Several mechanisms concurrently happening during the AOP treatment may remove target contaminants in wastewater. Non-radical oxidative reactions may or may not be dominant in the removal of pollutants, depending on the kind of AOP and the circumstances of the reaction. Table 1 provides a summary of the mechanisms concurrently occurring in various AOP treatment processes.

Table 1: Major mechanism for organics removal during wastewater treatment by different AOPs

AOP types	Oxidant for AOPs	Other occurring mechanisms
O_3	$OH^{\bullet}$	Direct O_3 oxidation
O_3/ H_2O_2	$OH^{\bullet}$	Direct O_3 oxidation
O_3/UV	$OH^{\bullet}$	UV photolysis
UV/TiO_2	$OH^{\bullet}$	UV photolysis
UV/ H_2O_2	$OH^{\bullet}$	UV photolysis H_2O_2 oxidation
Fenton reaction	$OH^{\bullet}$	Iron coagulation iron sludge-induced adsorption
Photo-Fenton reaction	$OH^{\bullet}$	Iron coagulation Iron sludge-induced adsorption UV photolysis
Ultrasonic irradiation	$OH^{\bullet}$	Acoustic cavitation generates transient high temperatures (≥5000 K) and pressures (≥1000 atm), and produce $H^{\bullet}$ and $HO_2^{\bullet}$, besides $OH^{\bullet}$
Heat/persulfate	$SO_4^{\bullet-}$	Persulfate oxidation
UV/persulfate	$SO_4^{\bullet-}$	Persulfate oxidation UV photolysis
Fe(II)/persulfate	$SO_4^{\bullet-}$	Persulfate oxidation Iron coagulation
OH^-/persulfate	$SO_4^{\bullet-}$/$OH^{\bullet}$	Persulfate oxidation

4.8 Photocatalysis

Over the past three decades, semiconductor photocatalysis has drawn a lot of attention as a potential remedy for issues relating to energy production and the environment. Since Fujishima and Honda found that water may be photo-electrochemically splitted into hydrogen and oxygen using a semiconductor (TiO_2) electrode under UV irradiation, several investigations have been carried out to manufacture hydrogen from water splitting utilizing a variety of semiconductor photocatalysts. Environmental applications including water treatment and air purification have been a recent focus of scientific and engineering interest in heterogeneous photocatalysis. In the literature, there are numerous review articles on semiconductor photocatalysis (Hoffmann et al., 1995; Linsebigler, 1995). After band gap excitation, electron-hole pairs start semiconductor photocatalysis. When exposed to light with an energy level equal to or higher than the band-gap energy, the valence band electrons in a photocatalyst can be driven to the conduction band and leave a positive hole there. The excited electron-hole pairs can recombine without having any chemical repercussions, releasing the energy as heat. Yet if the electrons (and holes) go to the semiconductor's surface without recombining, they can take part in a variety of oxidation and reduction processes with adsorbed species like water, oxygen, and other organic or inorganic species. Valence band (VB) holes are crucial components that stimulate the oxidative breakdown of environmental contaminants in photocatalytic water/air cleanup as an environmental application. Pollutants can be oxidized by the positive hole directly, but most of the time they react with water to form $OH^{\bullet}$, an extremely aggressive oxidant with an oxidation potential of 2.8 V. (NHE). Pollutants are quickly attacked by $OH^{\bullet}$ both on the surface and in solution, where they might be mineralized into CO_2, and H_2O. Numerous studies have demonstrated the capacity of the most widely used photocatalyst, TiO_2, to thoroughly oxidize a range of organic molecules, including persistent organic pollutants. TiO_2's comparatively high activity, chemical stability, availability, low manufacturing costs, and lack of toxicity are the reasons for this. By using a photocatalytic reaction to produce hydrogen from water splitting, the decreasing conduction band (CB) electrons become increasingly significant. To begin hydrogen production, the conduction band level has to be lower than the level at which hydrogen is produced.

4.8.1 Photocatalyst Used for Pesticides Photodegradation

By absorbing light in water, photocatalysts are compounds that use solar energy to degrade persistent organic pollutants. Therefore, supported or unsupported semiconductors that use light to accelerate chemical reactions are called photocatalysts. A photocatalyst must possess photoactivity, photostability, and the capacity to use UV and visible light in addition to being accessible, nontoxic, and chemically and physiologically inert (Miguel et al., 2012). Several semiconductors have been created and employed as photocatalysts, including Fe_2O_3, SnO_2, $SrTiO_3$, TiO_2, $TiWO_5$, WO_3, ZnO, WSe_2, CdS, and Si. According to their physical and chemical characteristics, photocatalysis may be produced using metalloids, noble metals, transition metals, and non-metals. Examples of noble or rare metals include platinum (Pt), gold (Au), silver (Ag), palladium (Pd), ruthenium (Ru), cesium (Ce), rhodium (Rh), tungsten (W), and others. Transition metals include titanium (Ti), zinc (Zn), copper (Cu), tin (Sn), and strontium (Sr), whereas non-metals and metalloids include nitrogen (N), clay, graphene, and carbon dots (Ma et al., 2019). Currently, materials and matrices for supporting the photocatalysts are being developed for maximum conversion efficiency of the polluting substrate, while conventional photocatalytic materials are dopped with metal ions to improve the photocatalytic efficacy. The most common bulk photocatalysts for industrial photocatalysis processes are TiO_2 and ZnO (Jiang et al., 2021). Since the discovery of its catalytic activity, TiO_2 has been one of the compounds that have undergone the most research in terms of its photocatalytic impact. Anatase, rutile, and brookite are three distinct polymorphic forms of TiO_2 that are each active in the UV spectrum and have band gaps of 3.2, 3.0, and 3.2 eV, respectively. The two most prevalent polymorphs are anatase and rutile, with anatase having stronger photocatalytic activity than rutile and brookite (Chen et al., 2020; Antoniou et al., 2016).

4.8.2 Doped Photocatalysts

Another significant development in photocatalysis is the doping of semiconductors with metallic and non-metallic elements (such as Cu, Fe, Sn, N, S, Ag, Au, etc.) to broaden the wavelength range and activate the photocatalytic process using solar light to breakdown organic contaminants (Fiorenza et al., 2018). Such materials were produced using a variety of synthesis processes, including (a) physical mixing of prepared particles derived from the semiconductor material and the doping substance; (b) reduction of the doping agent directly on the semiconductor's surface; (c) impregnation of the support with various salt precursors, then allowing the solvent to evaporate, follow by calcination of the material (Fiorenza et al., 2018). Regardless of the synthesis technique, the concentration of the doping agent, the shape, and the size of the final photocatalysts had a key impact in boosting photocatalytic activity. Additionally, the dramatic changes in the final material's crystallite size or shape resulted in enhanced photocatalytic activities even in visible light. To reduce the energy band of semiconductors and prevent the recombination of electron hole pairs, a minimal concentration of the doping agent (i.e., 1-5% wt.) is required (Rehman, et al., 2009; Huong et al., 2022). Due consideration should be given to photocatalytic nanomaterials in light of these facts, which highlight the significance of photocatalyst particle size.

4.9 General Future Perspective

Although pesticides are mainly used in agriculture, their use in public health interventions for vector control in vector-borne disease like malaria and dengue fever, and in the control of unwanted plants cannot be over emphasized. However, with the various health effects attributed to pesticide use/exposure, efforts should be made in regulating pesticide use in both developed and developing countries where occupational exposure to pesticides are high. Users of pesticides should be aware of the dangers involved and utilize personal protection equipment and correct handling techniques to minimize harm to human health. Pesticides that cause cancer must be banned, and innovative pest control techniques must be promoted. Regulations should be put in place to stop the use of pesticides whose metabolites are recalcitrant and may persist in the environment for a long time causing major health challenges.

The bulk of the industry's wastewater treatment facilities were built with the intention of eliminating contaminants, recycling, or recovery (Ahmed & Hameed, 2018). The recovery of metals, nutrients, and other components that can be reintroduced into material cycles will still continue to be difficult in the future due to the high cost of wastewater disposal and the rapidly rising cost of resources (Verhuelsdonk et al., 2021). Furthermore, the nature of the recovered contaminant might become appealing and help add value to the current industrial process, to improve process efficiency and create fresh separation alternatives for recovery, recycling, and reuse. Industrial wastewater treatment is a broad field that encompasses a number of proven and commercially available physicochemical and biological treatment techniques that can recover resources and even generate energy. The effective implementation of these technologies might lessen pollution, lessen global climate change, and create new companies and employment since new applications for turning pollutants into valuable materials rather than merely removing and destroying them can arise (Ranade & Bhandari, 2014; Safferman et al., 2017). Even though emerging technologies are promising for 3R schemes in industrial wastewater management, they must deal with a number of significant challenges that have already been mentioned and could hinder operations or prevent them from being commercially viable options. These challenges primarily revolve around the energy consumption and general cost compared to the top established technologies. If they are not supplemented with novel, cutting-edge, or adaptive usage technologies, the 3R schemes with low potential are mostly limited for those that are already well-established. However, it was demonstrated that there is still room for advancement in these well-established technology. Because of a widespread lack of information and comprehension regarding contemporary advanced oxidation technologies and their applicability to diverse scenarios, technologies like AOP systems are not frequently employed in industry. Based on the number of publications, AOP procedures have a significant potential to enhancing the performance of industrial wastewater treatment; hence, the industry is anticipating the widespread application of these processes in new and/or updated industrial wastewater treatment plants in the future.

5. Conclusion

Pesticides tend to persist in the environment due to their complex structures and difficulty in degradation. Their persistence in the environment has a negative impact on water quality and public health. Therefore, creating technology to get rid of pesticides would be beneficial. The global world are so preoccupied with agriculture and industrial development that they neglected the environment; contaminants grew more potent, resistant, and gradually accumulated in organisms and the environment. As a result, scientists have focused their attention on creating efficient removal methods for organic and inorganic contaminants. Traditional methods are becoming less effective at removing all kinds of pollutants.

In this article, the major risks and health implications of wastewater and pesticides were highlighted. It was stressed that more emphasis should be placed on the 3R scheme of industrial wastewater due to the rapid growth of industries, which generates competition for water between industry and agriculture. Lastly, the industrial wastewater treatment technologies such as conventional, unconventional, biological and the AOP treatment methods were detailed. The AOPs, methods involving the generation of highly reactive oxidizing species able to attack and degrade organic pollutants have demonstrated greater efficacy in eliminating organic contaminants from water, therefore, AOPs could be effectively used to eliminate pesticides from aqueous environments.

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