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Degradation of pesticides in wastewater using heterogeneous photocatalysis

Simranjeet Singh[a,b,c*], Vijay Kumar[d*], Daljeet Singh Dhanjal[a*], Shivika Datta[e], Sukhmanpreet Kaur[f], Romina Romero[g], Joginder Singh[a]

[a]Department of Biotechnology, Lovely Professional University, Phagwara, Punjab, India. [b]Punjab Biotechnology Incubator (PBTI), SAS Nagar, Punjab, India. [c]RAWTL, Department of Water Supply and Sanitation, SAS Nagar, Punjab, India. [d]Regional Ayurveda Research Institute for Drug Development, Gwalior, Madhya Pradesh, India. [e]Department of Zoology, Doaba College, Jalandhar, Punjab, India. [f]Department of Chemistry, Rayat Bahra Institute of Engineering and Nano-Technology, Hoshiarpur, Punjab, India. [g]Technological Development Unit (UDT), University of Concepcion, Coronel, Chile

1 Introduction

Water is the prerequisite to sustain life on Earth; however, the reality is that the level of groundwater and the number of water bodies are declining globally (Ola and Maroto-Valer, 2015; Hunter et al., 2010). In addition, the condition worsens as various human activities recklessly pollute the scarcely available water resources (Inyinbor et al., 2018). One of them is the use of pesticides, as pesticides have a tendency to leach out directly into the soil system and thus contaminate the surface and groundwater (Székács et al., 2015). The metabolites of pesticides are also highly persistent in the environment and have harmful effects on soil fertility as well as aquatic and terrestrial ecosystems (Lushchak et al., 2018).

Pesticides are widely distributed in shallow groundwater and streams, and their occurrence follows the patterns of seasonal and geographic use of pesticides (Zhang et al., 2018). Most of the pesticides or their byproducts are highly resistant to photochemical and/or chemical degradation under distinctive

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*Equal contribution.

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environmental conditions (Katagi, 2004). Pesticide poisoning emerges either from regular intake of pesticides in minute quantities, called “chronic,” or in a single dose, called “acute” (Dawson et al., 2010). Acute intake includes hypersensitivity, giddiness, allergies, dermal abrasions, double vision, headaches, etc. (Tomer et al., 2015), whereas chronic intake includes damage to the central and peripheral nervous system as well as sarcomas, lymphomas, soft tissue sarcomas, reproductive disorders, leukemia, death, disruption of the immune system, birth defects, and cancers of the brain, bone, and stomach (Mostafalou and Abdollahi, 2013). LD50 and LC50 are the most common toxicity terms for defining levels of toxicity (Erhirhie et al., 2018). Pesticide pollution of groundwater and surface water becomes an issue of concern due to their long half-life and highly persistent nature (Jablonowski et al., 2011). Some pesticides result in the hydrolysis of acetylcholine to choline and acetic acid and also have an adverse effect on the activity of inhibiting other esterases (Colovic et al., 2013). Regular contact with pesticides over a short period may produce headaches, weakness in muscles, and sweating while protracted exposure to pesticides damages the liver, kidney, central nervous system, thyroid stimulating hormone, and bladder (Kamel and Hoppin, 2004; Rastogi et al., 2010). Pesticides have an adverse effect on cellular respiration, especially when they come in contact with the human population (Nicolopoulou-Stamati et al., 2016). Long-term exposure causes damage to the immune system as well as skin sensitization and cancer (Gangemi et al., 2016). Some pesticides are axonic toxic substances and cause a loss of motion to a living being (Jayaraj et al., 2016). The sodium channel comprises a layer protein with a hydrophilic inside. This hydrophobic inside is a viable minor gap that is formed precisely to strip away the incompletely charged water atoms from a sodium particle and make a thermodynamically great route for sodium particles to go through the membrane, enter the axon, and proliferate an activity potentially. The organisms gets incapacitated when they come direct contact with the pollutant (Silver et al., 2014). The pyrethroids are intense inhibitors of mitochondrial complex I (Field et al., 2017). Scientists nowadays have shown great concern about the effects of pesticides and their residues in humans as well as soil and water ecosystems (Carvalho, 2017). Therefore, the removal of pesticides from aqueous streams has become an issue of immense environmental significance in recent years (Huang et al., 2018). To overcome this problematic scenario, advanced oxidation processes (AOPs), homogeneous and heterogeneous photochemical oxidation have proven their efficiency (Muruganandham et al., 2014).

2 Oxidation process to degrade pesticides in water

In general, pesticide removal from water can be achieved by oxidation. The traditionally used oxidation methods are wet oxidation, electrochemical oxidation, chemical oxidation, and biological oxidation (Rasalingam et al., 2014). This is followed by the AOPs, which use ultraviolet irradiation catalysts and a combinations of oxidants to generate hydroxyl radicals (OH•) in solutions; they have attracted interest for pesticide degradation in water or wastewater (Brienza and Katsoyiannis, 2017).

2.1 Wet oxidation

In this process, both organic and inorganic compounds get oxidized in the aqueous phase, with the presence of oxygen or air, at high temperature and high pressure conditions (Leonhauser et al., 2014). The temperature oscillates between 150°C and 350°C for the degradation of compounds, and it also depends upon the nature of the compounds. The pressure during the process ranges from 20 to 200 bars, which results in a COD removal of 75%–90% (Li et al., 1991). The mechanism underlying its process is simply a free radical process. Nitro functional groups and halogenated compounds have been found difficult to degrade by the wet oxidation process (Scott and Ollis, 1997).

2.2 Electrochemical oxidation

The removal of organic compounds in water solutions via electrochemical oxidation has been reported in some pilot-scale studies. The mechanism underlying electrochemical processes involves three main stages: electrooxidation, electrocoagulation, and electroflotation (Selva et al., 2017). Few studies have been found in the literature regarding the electrochemical oxidation of pesticides. However, phenolic compounds can be easily disintegrated by this method. This method is proven to remove COD, turbidity, and color when integrated with coagulation processes (Lebik-Elhadi et al., 2018).

2.3 Biological oxidation

The use of activated sludge in biological oxidation has numerous advantages in the degradation of organic compounds (Butler et al., 2017). However, various pesticides cannot be effectively degraded by this process in the treatment of natural, residual, or municipal wastewaters (Giannakis et al., 2017). The major drawback of this process is the generation of highly toxic sludge, which comes from treating phenolic, ether aliphatic, and nitroaromatic compounds (Bartolomeu et al., 2018). Biological treatment involves two kinds of processes: anaerobic and aerobic. Out of these, aerobic processes are used overall because of their high operational simplicity and high efficiency. These processes can efficiently decrease the COD value to an extent and result in the generation of useful byproducts (Puyol et al., 2017).

2.4 Chemical oxidation

The chemical oxidation process involves the transfer of electrons from one substance to another to obtain different oxidation potentials. Chemical oxidation processes are regarded as reliable techniques for the degradation of both organic and inorganic contaminants in wastewater (Chiron et al., 2000).

2.5 Advanced oxidation processes

AOP technologies were first designed and reported by Glaze et al. (1987). They are defined as a process that involves the generation of highly reactive oxidizing species capable of degrading organic contaminants (Glaze et al., 1987). AOPs have significant importance in the removal of pollutants and in the restoration of environmental applications. They are regarded as highly efficient physicochemical processes having good thermodynamic viability with the anticipation of free radicals that are able to degrade the chemical structure of compounds or contaminants (Wang and Xu, 2012). AOPs rely on hydroxyl radicals that have good oxidation capability. Besides hydroxyl radicals, AOPs are also reported to generate various oxidizing species (Deng and Zhao, 2015).

In photochemical reactions, hydroxyl radicals are generated during the photolysis of water molecules (Cervera and Esplugas, 1983).

$$H_2O\ h\nu\ H^{\bullet} + OH^{\bullet}$$

Photolysis mostly involves the interface of molecules with light to dissociates them into fragments. This process generates a large number of reaction intermediates that lower the kinetics of the contaminants (Steinberg and Paul, 2008).

Photochemical treatment also has some drawbacks or negative aspects in its application, partly because the cost of UV production is very high (Reza et al., 2017). In a photochemical reaction or degradation, only the absorbed and a fraction of light are used, which brings chemical changes. This makes photochemical treatment a slow kinetic and low yield process (Nome et al., 2017). Sometimes other oxidants such as ozone, hydrogen peroxide, or semiconductors or metallic salts such as titanium dioxide are used to catalyze the photochemical reactions, and this is an AOP (Gautam and Chattopadhyaya, 2016). Sometimes, solar lights are used instead of a UV lamp to degrade the contaminants, although no effect was observed during the degradation of contaminants (Gautam and Chattopadhyaya, 2016).

2.6 Photocatalytic oxidation

The photocatalyst producing surface oxidation is the main phenomenon of photocatalytic oxidation, which removes both the pathogen bacteria and the organic compounds when exposed to a fluorescent lamp or direct sunlight (Tsydenova et al., 2015). A photocatalyst can also be used in combination with NOx to purify the contaminated environment. This process has been proven to be the best for the mineralization of organic and inorganic pollutants in wastewater (Ameta et al., 2013). They offer several advantages over other oxidation systems as they result in the complete oxidation of pesticides and other hydrocarbons within a few hours. The catalysts used in the photocatalytic oxidation system are cost effective and are adaptable to designed reactor systems, resulting in the oxidation of contaminants in ppb value (Bagheri et al., 2017). Photocatalytic oxidation doesn't form polycyclized compounds after mineralization. The various catalysts used as potent photocatalysts have been reported and studied, and include ZnS, CdS, ZnO, Cr_2O_2, WO_3, SnO_2, ZrO_2, lanthanide tantalate, niobium oxides, TiO_2/SiO_2, etc. (Bagheri et al., 2017). Among these, TiO_2 is one of the most promising and popular materials because of its environmental stability under various conditions. The other advantages of TiO_2 over other catalysts are that they are easily commercially available, have different allotropes, have enhanced photoactive properties, can be easily coated on solid support, and easily prepared in the laboratory (Regalado-Raya et al., 2018). The photocatalytic activity of TiO_2 can be well studied in the fixed bed studies as well in suspension form. Further TiO_2-based catalysts such as TiO_2/SiO_2, TiO_2/In_2O_3, TiO_2/ZrO_2, Ru/TiO_2, Rh/TiO_2, Pt/TiO_2, etc., have proven to be good photocatalysts (Dzinun et al., 2019).

2.6.1 Properties and characteristics of different photocatalysts

The degradation of organic wastewater with the help of TiO_2 has been reported by various authors. It also decomposes various organic compounds in water (Poulopoulos et al., 2019). Matthews et al. (1990) reported the action of TiO_2 suspensions to improve the detoxification of hazardous wastewater. The spectral absorption characteristics of TiO_2 allow its extinction in UV-A, B, and C regions, giving space for the use of medium-pressure mercury arcs (Matthews et al., 1990). The catalyst exhibits good selectivity, stable performance, and good accessibility of products and reactants (Dumesic et al., 2008). Different types of photocatalysts and their light sources used in pollutant degradation are depicted in Table 1.

2.6.1.1 Catalysts and reactor systems

Most of the photocatalytic reaction involved in the purification of water is carried out using a catalyst in the contaminated water generating a low solid mass (Chong et al., 2010). The configuration of the reactor system includes a fluidized bed, a field bed, an immobilized membrane, a wall reactor, and optic fibers. It is universally accepted that maximum efficiency is obtained using this approach (Deng et al., 2019). Later on, the cost of removing the catalyst from the water offsets this advantage. Although most of the reported work was carried out in slurry reactors with high catalytic efficiencies. Using such systems in pilot-scale studies poses various challenges, especially optimum radiation absorption. The presence of scattering and the absorption of radiation in these systems make the determination of light distribution systems difficult (Ola and Maroto-Valer, 2015).

Various studies have been reported that signify the enhancement of photoactive compounds by coupling various semiconductors. This is accelerated by the separation process, followed by higher disposability of the reactive electron-hole pair. This process is complex and the chemistry of the reaction intermediates and substrates plays a significant role in determining the photoactivity of a catalyst (Ayati et al., 2014).

In the photocatalytic degradation of cellulose, bleaching effluent, and nitrobenzene, TiO_2 was reported as better than ZnO whereas ZnO exhibited higher efficiency in the mineralization of black liquor and reactive dyes (Cristina Yeber et al., 2000). Future studies are needed to determine the role of various catalysts and the process taking place during such a reaction system.

Table 1 Different types of photocatalysts and their light sources used in the degradation of pollutants.

S. no.	Photocatalyst	Type of pollutant	Light source	Substrate concentration	Optimum substrate concentration	References
1	Titanium dioxide	Acephate	UV	0.7–1.0	1	Rahman et al. (2006)
2	Titanium dioxide	Bentazon	UV	0.02–0.062	0.02	Pourata et al. (2009)
3	Titanium dioxide	Carbofuran	UV	0.023–0.113	0.09	Mahalakshmi et al. (2007)
4	Titanium dioxide	Daminozid	UV	0.50–1.5	0.75	Qamar et al. (2006)
5	Zinc oxide	Diazinon	UV	0.003–0.005	0.003	Daneshvar et al. (2007)
6	Titanium dioxide	Diphenamid	UV	0.1–0.6	0.6	Rahman et al. (2016)
7	Titanium dioxide	Dimethoate	UV	0.0195–0.49	0.0195	Chen et al. (2007)
8	Titanium dioxide	Erioglaucine	UV	0.006–0.02	0.006	Daneshvar et al. (2006)
9	Titanium dioxide	Indole-3-acetic acid	UV	0.2–0.6	0.3	Qamar and Muneer (2005)
10	Titanium dioxide	Indole-3-buteric acid	UV	0.18–0.6	0.3	Qamar and Muneer (2005)
11	Titanium dioxide	Isoproturon	Solar	0.25–0.75	0.75	Haque and Muneer (2003)
12	N-TiO_2	Lindane	Visible	3.45×10^{-5}–2.07×10^{-4}	3.45×10^{-5}	Senthilnathan and Philip (2010)
13	Re-TiO_2	Methamidophos	UV	0.1–0.5	0.1	Zhang et al. (2009)
14	Zinc oxide	Phenol	Solar	0.027–0.32	0.027	Pardeshi and Patil (2008)
15	Titanium dioxide	Phosphamidon	UV	0.1–0.6	0.45	Rahman and Muneer (2005)
16	Titanium dioxide	Propham	UV	0.25–1.3	0.75	Muneer et al. (2005)
17	Titanium dioxide	Prophachlor	UV	0.2–1.35	1.35	Muneer et al. (2005)
18	Zinc oxide	Resorcinol	Solar	0.05–0.272	0.05	Pardeshi and Patil (2009)
19	Titanium dioxide	Thiram	Solar	4.2×10^{-4}–16.6×10^{-4}	4.2×10^{-4}	Kaneco et al. (2004)
20	Titanium dioxide	Triclopyr	UV	0.25–1.0	0.75	Qamar et al. (2006)
21	Titanium dioxide	Tebuthiuron	UV	0.25–1.5	1.0	Muneer et al. (2005)
22	Zinc oxide	2,4-Dinitrophenol	UV	0.05–0.09	0.09	Vora et al. (2009)
23	Co-TiO_2	2-Chlorophenol	UV	0.097–0.583	0.097	Barakat et al. (2005)

2.6.2 Catalyst used in advanced oxidation processes

2.6.2.1 Hydrogen peroxide

Hydrogen peroxide, when added to ozone, initiates the degradation cycle of ozone by generating OH radicals (Gautam and Chattopadhyaya, 2016). Paillard (1988) reported the removal of atrazine in water using this process. Findings suggest that the combination of hydrogen peroxide with ozone shows better degradation compared to ozone-treated. The optimum conditions like mass ratio range from 0.35 to 0.45. Another study by Duguet et al. (1985) reported that the best results were achieved when hydrogen peroxide was added after oxidation with ozone of highly reactive compounds.

2.6.2.2 Ozone-UV radiation (O_3/UV)

The use of a UV/O_3 introduction system brings the rapid and complete degradation of organic compounds. They attack with a short molecular chain (formic acid, oxalic acid, glyoxylic acid, glyoxal) on the complex structure of pesticides, resulting in the mineralization of pesticides (Machulek et al., 2013). Various studies have been reported to demonstrate the efficiency of the O_3/UV system in the treatment of various organic and inorganic compounds (Amor et al., 2019).

2.6.2.3 Photo-Fenton and Fenton-like systems

The addition of Fe^{3+}ions to the UV/H_2O_2 process to enhance the degradation of organic compounds is called the photo-Fenton oxidation process. This oxidation process solely depends upon the pH of the solution. At low pH (pH = 3), the Fe^{3+} ions are reduced to Fe $(OH)^{2+}$ (Aramyan and Moussavi, 2017).

$$Fe^{3+} + H_2O \rightarrow Fe\,(OH)^{2+} + H^+$$

$$Fe\,(OH)^{2+} \longleftrightarrow Fe^{3+} + OH^-$$

When Fe^{3+} comes in contact with UV irradiation, it undergoes decomposition and produces Fe^{2+} and OH ions:

$$Fe\,(OH)^{2+} \rightarrow Fe^{2+} + OH$$

These two processes have been widely used with a high degradation rate of several contaminants, including pesticides. The optimum pH used in these two processes ranges from 2.5 to 4.

According to the annual report of pesticides, a Fenton catalyst is possible in PSA reactors. A total of 500 mg TOC/L of pesticides are 80% destroyed in 3 h using a PSA-CPCs field. Sun and

Pignatello (1993) documented that various herbicides and pesticides, including parathion and malathion, can be fully degraded by the $H_2O_2/h\nu-\text{Fe}$ (III) process. Various other studies with higher degradation rates were also reported using these processes (Sun and Pignatello, 1993).

3 Heterogeneous photocatalysis

In heterogeneous photocatalysis, the interaction of a photon with a catalyst produces the appearance of hole pairs/electrons. Bahena and Martínez (2006) reported that heterogeneous photocatalysis is a good and valid method for the mineralization of a number of pesticides such as alachlor, atrazine, and chlorbromuron in water systems under nonexpensive solar irradiation.

The concept and mechanism of heterogeneous photocatalytic degradation are quite simple. In this process, it is used under irradiation of a stable solid semiconductor for stimulating a reaction at the solution/solid interface (Ibhadon and Fitzpatrick, 2013). In the case of semiconductor particles, the excitation of a photon provides the circumstances for carrier separation, although there is no ohmic contact to generate out the majority carriers by transferring them to the second electrode by the external conductor. This means that the two charge carriers interact at the electrolyte/semiconductor interface with the species in solution (Beranek, 2011). During steady-state conditions, the quantity of charge transported to the electrolyte must be equivalent and opposite for the two types of carriers. Hence, the semiconductor-mediated redox processes are reported to involve an electron transfer diagonally at the interface (Tan et al., 2019). When hole pairs/electrons are generated, the electron moves away to the semiconductor as the hole pairs or electrons migrates toward the surface. These charge carriers are parted quickly as they can be used for the reduction or oxidation of the pollutants (Tan et al., 2019).

3.1 Principle of heterogeneous photocatalysis

Catalyst is the substance that has a tendency to convert the reactants into products without being consumed itself (Solel et al., 2019). The main advantage of using a heterogeneous catalyst is that solid material is used as a catalyst, which is easy to separate from the gas and liquid reactants and products (Védrine, 2017). The basic principle of heterogeneous catalysis is when a semiconductor photocatalyst is illuminated in the presence of light with the intensity of photons is equal to or greater than its bandgap energy (Ibhadon and Fitzpatrick, 2013).

3.2 Kinetics of heterogeneous photocatalysis

The mechanism and kinetics of the heterogeneous photocatalytic process solely depend on experimental conditions such as the dose, type of catalyst, pH of the solution, temperature, presence of an oxidant, initial concentration, etc. Various experimental results concluded that the rate of photocatalytic oxidation of pesticides with TiO_2 fitted the Langmuir-Hinshelwood (L-H) kinetics model (AI-Ekabi et al., 1988).

$$r = \mathrm{d}C/\mathrm{d}t = kKC/(1 + KC)$$

where

r = oxidation rate of the reactant (mg/min)
C = reactant concentration (mg/L)
T = illumination time
K = reaction rate constant (mg/L)
K = adsorption coefficient of the reactant (L/mg)

4 Conclusion

This chapter focuses on the various methods and advancements in heterogeneous photocatalysis in the treatment of wastewater. The functions of another oxidation system on photocatalytic degradation of pesticides have also been explored. Out of various catalysts, TiO_2 has been recommended to be viable and efficient for the photocatalytic mineralization and degradation of multiple pesticides and other contaminants in wastewater. However, the efficiency of TiO_2 depends upon the operating parameters such as light intensity, catalyst amount, initial pH of the medium, pollutant type, etc. The optimization parameters play vital roles in the efficient design of future photocatalytic oxidation processes to ensure a safe, cost-effective, and sustainable operation. However, certain ionic components influence the photocatalytic degradation rate of phenols and pesticides. Recent advances in TiO_2 photocatalysis using doped metals and nonmetals have reported as improving the degradation rate. Future work should address the optimization of these various oxidation systems and focus on the applicability in pilot-scale reactors to collaborate with industrial partners to deliver the benefits of this technology to society.

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