

Tailored functional materials as robust candidates to mitigate pesticides in aqueous matrices—a review

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Abstract

Pesticides are among the top-priority contaminants, which significantly contribute to environmental deterioration. Conventional techniques are not efficient enough to remove pollutants from environmental matrices. The development of functional materials has emerged as promising candidates to remove and degrade pesticides and related hazardous compounds. Furthermore, the nanohybrid materials with unique structural and functional characteristics, such as better material anchorage, mass transfer, electron-hole separation, and charged interaction make them a versatile option to treat and reduce pollutants from aqueous matrices. Herein, we present the current progress in the development of functional materials for the abatement of toxic pesticides. The physicochemical characteristics and pesticide-removal functionalities of various metallic functional materials (e.g., zirconium, zinc, titanium, tungsten, and iron), polymer, and

carbon-based materials are critically discussed with suitable examples. Finally, the industrial-scale applications of the functional materials, concluding remarks, and future directions in this important arena are given.

Keywords: Environmental pollution; Pesticides; Functional materials; Adverse impact; Mitigation

Introduction

Water is among the most indispensable constituent of various biotic ecosystems. The vulnerable and uninterrupted exploitation of water resources, off-the-cuff utilities of the human-made chemicals, and growing population have instigated the mitigation of the environment (Sahoo and Gupta, 2012). The traces of pesticides protect them from recognition and obstructs the development of an operative treatment methodology. Micropollutants such as pesticides contributed a lot to the deterioration of the environment. These toxicants are acutely dangerous even in a trace amount, e.g., simazine in $\mu\text{g/L}$ in water bodies can potentially cause kidney congestion, low blood pressure, heart, adrenal gland and lung related consequences (Boruah et al., 2021). These contaminants are present in unprocessed discharge from domestic wastewater, industrial effluents, cultivated fields, wetlands, and polluting natural resources (Figure 1). The United States Environment Protection Agency (USEPA) and European Environment Agency (EEA), both have declared pesticides as priority contaminants on the bases of their harmful and persistent environmental impacts (Wade et al., 2003; Rani et al., 2017). The foreseeable harmfulness of the pesticides is because of the presence of micro compounds such as dioxins, phenols, and cyanides, etc. The toxicity of these micro compounds owes to the fact that they are resilient to the conventional treatment methodologies (Debnath and Gupta, 2018; Vaya and

48 Surolia, 2020; Bayantong et al., 2021; Hashimoto et al., 2021). Their hydrophobic character has
49 facilitated the assimilation of the pesticides in fatty tissues for a more extended period. The
50 persistence of these contaminants and their accumulation in more significant concentration
51 outcome adverse impact on living organisms. This increased level further obstructs the normal
52 functioning of the endocrine system by disturbing the hormones (McKinlay et al., 2008). The
53 resistive nature of these contaminants has significantly challenged the quality of usable water
54 resources. This urges the scientists and researchers to develop advanced technologies to meet the
55 challenge (Pillai and Gupta, 2016). Recently, the investigations are centered around the
56 development of cutting edge tailored functional materials such as clay composites, core-shell
57 structure, doped metal oxides, composite heterojunctions non-metal modified oxides, metal-
58 organic framework and metal-organic framework/carbon-based hybrid nanocomposite, etc. to
59 overcome the deficiencies (Lin et al., 2006; Cui et al., 2018). These hybrid nanomaterials are
60 instituting their advanced applications to remove and degrade the pesticides as they exhibit better
61 material anchorage, mass transfer, electron–hole separation, and charged interaction.

62 This review presents functional materials as potential candidates to mitigate toxic pesticide
63 contamination in wastewater. Furthermore, the work focuses on the functional materials that
64 create a lesser amount of sludge, prevent the production of secondary pollutants, and can be
65 reused for several operations. Additionally, the basic removal pathway, negative consequences of
66 pesticides, and their efficient handling have been discussed in detail. The fundamental
67 sustainable developments in the manufacturing of various metallic functional materials, carbon-
68 based materials, and polymer-based functional materials are discussed along with their
69 advantages, such as low-cost alternatives for managing pesticides. Finally, the industrial-scale

applications of the functional materials with future prospects and recommendations are discussed.

Categories of the pesticides

The category and chemical profile of pesticides are decided based on their structure and function. , They are categorized as bactericides, fungicides, herbicides, and insecticides, based on their action on bacteria, fungi, herbs, and insects, respectively. In contrast, the organic residues of pesticides are classified based on functionalities present in their structure. They may be categorizing as pyrethroids, organophosphorus, carbamates, and organochlorine (Konstantinou et al., 2006). The pesticides are employed aerially in the form of aerosols and sprays in household areas and agricultural lands. The aerial application of pesticides may lead to the contamination of the distant regions through transboundary movement (Aktar et al., 2009). Mainly, the unpointed discharge of the pesticides from domestic wastewater and agricultural fields is hard to observe, obstructing their control (Yadav et al., 2015).

The environmental concern of the pesticides

Widespread usage of pesticides is responsible for different adverse environmental consequences and their ultimate biological effects (Figure 2). According to the Drinking Water Directive (98/83/EC) regulation, the permissible level of a single active constituent is 0.1 mg/L and for all collectively active components, the permissible level should be 0.5 mg/L in any drinking water, which is used by the humans (Karabelas et al., 2009). The documented reports reveal that the long-time intake of insecticides is responsible for interfering with the signaling of the nervous system by hindering the sodium and potassium channels and inhibiting the cholinesterase (McKinlay et al., 2008). Strong soil adsorption and resistance to biodegradation of heptachlor epoxide made them highly toxic, and its consumption causes vomiting and nausea (Grundlingh et

al., 2011). Pyrethroids are known as endocrine disruptors, and they cause various disorders as amyotrophic lateral sclerosis, dementia, genetic diseases, and Parkinson's disease. They increase the risk of childhood cancer (Slotkin, 1999; Ishihara et al., 2003). Pesticides have accumulated property. They may reside in the body from few months to several years, so even at very low concentration (ng/ml) they are dangerous for health (Graymore et al., 2001; Yadav et al., 2015). Due to their interference with cell signaling, cell shocks occur, which may cause nausea, vomiting, and muscle miscoordination (Ogut et al., 2015). Different functional moieties as amides, phosphate, phenolics, and chlorine assist the uptake of pesticides on the lipophilic membranes of lungs and kidneys responsible for irreversible adverse effects (Tomer et al., 2015). Pesticide exposure may cause reproductive diseases, congenital disabilities, cancer, malignant tumors, miscarriages, genital deformations, abnormalities in behavior stunted growth of offspring (McKinlay et al., 2008; Tayour et al., 2019; Gutiérrez-Jara et al., 2020; Yang et al., 2020). Pesticides also affect the reproductive system of fishes and affect the egg-shells thickness of different birds (Al Hattab and Ghaly, 2012).

Functional materials to remove pesticide

Conventional methods have several limitations for removing the pesticides, which urged the scientists to develop advanced functionalized materials and subsequent processes. The functionalization of hetero-structures enhances the physical and chemical characteristics of materials. Photoactive materials exhibit enhanced efficacy because the restricted movement of electrons and the appearance of discrete energy-levels are responsible for improving the material property. The significant properties of functional materials may be due to their improved surface defects, enhanced surface-area to volume ratio, excellent mobility of electrons, greater absorption of light, and excellent affinity for metabolites sorption in aqueous form (Lin et al.,

2006). These materials can be easily tailored to polymers, zeolites, and membranes to assist their operation with ease. Functional materials play a significant role in treating dangerous waste materials, sustainable products and sensor developments, *etc.* (Mohmood et al., 2013; Qu et al., 2013).

Modified structures are responsible for improving the physical characteristics of materials and enhancing the catalytic, magnetic, adsorbing, electrical, luminescence, and filtration characteristics of the material (Reddy and Kim, 2015). So far, various functional materials have been tailored and established to remove pollutants and incorporate characteristics of photocatalytic oxidation. Those functional materials suitable for treating broad spectrum molecules of pesticides also do not cause any pollution in aqueous media. These challenges regarding functional materials urged the scientist to research non-toxic benign templates of carbon, zinc, iron, titanium, tungsten, zirconium, and polymers. For instance, graphene, carbon-nanotubes, different oxides of iron as magnetite and hematite, titanium dioxide (TiO_2), zirconium oxide (ZrO), zinc oxide (ZnO), and tungsten oxides are found efficient in the removal and degradation of pesticides from aqueous media (Khajeh et al., 2013; Al-Hamdi et al., 2016). To decrease the treatment cost, different biomaterials can be used as alternatives to expensive adsorbents. Natural sources may provide carbon and biomaterials, which are obtained from polymers. They provide an excellent template to produce functionalized membranes. The dendrimers with functional surface modified and surface plasmonic species effectively adsorb the contaminants (Adachi et al., 2004). In water treatment, materials have been found actively involved in photocatalytic degradation and adsorption of organic pollutants on their porous surface (Pillai et al., 2015; Reddy et al., 2016). The active sites on porous surface materials are responsible for the interaction of solid-phase with pesticide. Attempts are being to fabricate functional materials

with overcome loopholes as surface-passivation, high aggregation, and high-surface energy. Tungsten, zinc, and titanium metal oxides have great potential to absorb a specific light spectrum.

Pesticide catalysis is a new methodology to mineralize pollutants by generating low amounts of by-products, usually water and carbon dioxide. Their light absorption capability aids the catalytic property of functional materials. After functionalization, the catalytic properties and photon capture capacity of catalysts are enhanced so that they can be re-used many times to treat pesticides. The light absorption depends on the photocatalyst band gap. When light energy exceeds the material band-gap, an electron-hole pair generates only (Lam et al., 2014). The transfer of charge and channeling on the surface of the catalyst is enhanced by a greater specific surface area (Zangeneh et al., 2015). Functional materials may overcome bottlenecks of photo-oxidation as plasmonic-species, metal, and non-metal complexes charge recombination by coupling photoactive materials with polymers and sensitized dye molecules. Charge-transfer within the semiconductors increases by the formation of additional discrete band-state. The plasmonic species like gold and silver decrease charge carrier recombination. Electrons are pumped into the conduction band by these species, and life time of positive holes increases in valence-band, which completes the oxidative species generation (Luo et al., 2015). The electrons generation is facilitated by dye-sensitization of photo-catalyst, which is ascribed for the process of photo-reduction. This phenomenon can enhance the efficacy of photo-catalyst by inserting electrons from the highest occupied molecular orbital (HOMO) to the CB of semiconductor through the lowest unoccupied molecular orbital (LUMO) (Albay et al., 2016; Alam et al., 2017). Figure 3 presents various tailored functional materials for the treatment of pesticides and related environmental pollutants.

Functional materials based on Titanium

The photocatalyst TiO_2 has high mobility of electrons and can quickly generate the electron-hole pair, which enhances its capacity to effectively degrade the organic contaminants (López-Ayala et al., 2015; Sivagami et al., 2016). TiO_2 has UV sensitivity, and its band gap falls in the range of 3.2-3.4 eV (Lee and Park, 2013; Justh et al., 2017). Different titanium oxides exist in different phases as rutile, anatase, and brookite (Chitose et al., 2003; Follut and Leitner, 2007).

The charged electrons (e_{CB}^-) and holes (h_{VB}^+) are generated when the light having more energy than the band gap falls on the surface of TiO_2 as presented in Equation (1) (Chen et al., 2011).



Superoxides and hydroxyl radicals are generated on the surface of the catalyst when material mobilizes electrons (photo excited) from the valence to the conduction band. Available chlorine and sulfur are oxidized to chloride, and the generated holes trigger sulfide radicals and this process. While energy dissipation causes hindrance to photocatalytic efficacy, this occurs due to quick recombination of charge carriers and less visible light capability (Gupta et al., 2006; Sahoo and Gupta, 2013). Different hybrids of titanium oxides with enhanced efficiency in the visible light spectrum have been synthesized. Mainly functionalization comprises impregnating TiO_2 to the mesoporous materials like graphene, glass surface, clays, polymeric molecules, and carbon nanotubes etc. The materials strive to minimize the electron-hole pair recombination and generate additional band state, which helps absorb the visible light (Linsebigler et al., 1995; Lee et al., 2015; Cho et al. By using $\text{AgCl}/\text{Ag}/\text{TiO}_2$ (silver chloride/ silver/titanium oxide) a sandwiched type structure has been reported which enhanced the capability of TiO_2 to absorb in the visible range (Figure 4) (Tian et al., 2014).

184 Silver (Ag) and gold (Au) have plasmonic properties and can pump the electrons into the
185 conduction band of TiO₂. Because of this, they are of great interest for the development of
186 photocatalyst with enhanced qualities. The electron flow is induced by silver (Ag) surface, and
187 silver chloride (negative surface) increased the radicals (active chlorides) generation and
188 entrapment of holes (Wang et al., 2012; Dong et al., 2013). Simple TiO₂ nanoparticles have 5%
189 less efficiency to degrade pentachlorophenol under visible light irradiation compared to Ag/TiO₂
190 hybrid nanoparticles, which can degrade 80% pentachlorophenol (Zhang et al., 2012). Modified
191 TiO₂ with metals like gold, copper, palladium, and zirconium showed enhanced formation of p-n
192 hetero-junction and interfacial transfer of charge at the solid-liquid interface (Lee and Jang,
193 2014; Hernández-Gordillo and González, 2015; Naraginti et al., 2015). Yu et al. (2010) reported
194 that gold coupling provides improved photo-electrons' localization and prohibits recombination
195 loss. As compared to TiO₂, the metals favor the generation of holes and are responsible for
196 promoting oxidation. Dopped material replaced the base atoms, so the modified doped TiO₂ has
197 many surface defects, and these defects increase the separation of charges responsible for
198 entrapping the lighter energy. The *n*-type semiconductors are converted to the *p*-type when
199 doping is done with non-metals and this increase the sensitivity of visible-light (Zangeneh et al.,
200 2015). Interfacial surface tension on the TiO₂ surface caused by the metal impregnation increase
201 the mesoporous surface area. This also enhances the transfer of the electrons from the metal
202 conduction band to the TiO₂ surface, reducing the divalent oxygen to the superoxide (Hossaini
203 et al., 2014; Sahoo and Gupta, 2015). In the absorption spectrum of TiO₂, the activity of visible
204 light is monitored by red shift, which increases the apparent quantum-yield (Linsebigler et al.,
205 1995). TiO₂ has been modified with Cetyl Trimethyl Ammonium Bromide (CTAB) surfactant to
206 enhance the stability of the photo-excited species and also to give the best anchorage for the

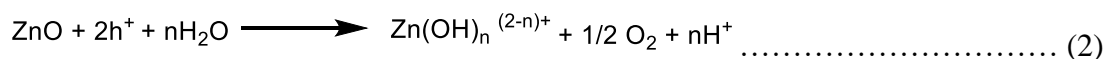
interaction of solid-liquid phase with organic compounds (Zhu et al., 2007). Increased removal and degradation of the pesticides may be due to the co-adsorptive capability of surfactant-bilayer (Senthilnathan and Philip, 2010). Enhanced dispersion of particles was also provided by surfactants which give a homogeneous surface for the degradation and adsorption of metabolites. Modification of TiO_2 particles with iron particles or silica beads has been carried out to better separate TiO_2 particles from aqueous phase both magnetically and physically. Organophosphorus based pesticides have been degraded by the immobilization of TiO_2 on silica beads (Shifu and Gengyu, 2005). Liu and his co-workers synthesized the Fe/TiO_2 nano-particles for the degradation of 2,4-dinitrophenol (Liu et al., 2012).

$\text{Fe}_2\text{O}_3/\text{TiO}_2$ has been employed for 2,4-dichlorophenoxyacetic acid degradation (Figure 5) (Lee et al., 2017). Photogenerated electrons get excited from the valence band to the conduction band of TiO_2 after exposure of photocatalyst to UV light, and holes left are left in the valence band. 2,4-dichlorophenoxyacetic acid oxidized directly to 2,4-dichlorophenol through these photogenerated holes. Reduction of oxygen takes place because holes and superoxide radicals are generated. Heteroconjunction formation between Fe_2O_3 and TiO_2 nanoparticles led to the promotion of charge transfer, which also suppressed the electron-hole recombination. Table 1 presents the efficiency of different titanium-based materials for the degradation and removal of different pesticides

Functional materials based on Zinc

Zinc-based materials with novel crystalline and characteristics have been developed with efficient photo-catalytic properties. These materials have the property of reusability for many degradation processes. Low toxicity, economic values, less light scattering, easy tailored-surface characteristics, and good mobility of E-H pair made zinc the best option for pesticide

degradation. The inhibition of recombination of E-H pair, quantum entrapment, and loss of heat energy are the main factors responsible for the efficacy of photocatalysis (Shanmugam and Jeyaperumal, 2018). The Refractive index of ZnO is 2, and it has a band gap of 3.2 eV. It has an efficiency of maximum light absorption. As compared to TiO₂, ZnO produces more reductive species due to the excellent mobility of electrons, and similarly, the oxidative potential of hydroxyl radicals is higher in ZnO (3.0 V) in comparison to TiO₂ (2.7 V) (Kumar and Rao, 2015). Despite being a promising photocatalyst, ZnO also has potent antimicrobial properties (Navarro et al., 2009; Bechambi et al., 2015). Photo-corrosion, photo dissolution, fast E-H pair recombination, and also at alkaline pH, the creation of the surface-passive-layer (Zn(OH)_n⁽²⁻ⁿ⁾⁺) are the limitations of ZnO, which decreases its efficacy and versatility (Panthi et al., 2015). Equation (2) presents the reaction process (Kumar and Rao, 2015) where ‘n’ is dependent on the solution pH. Initially, the ZnO photo dissolution involves the hole trapping (h⁺) on the surface, resultantly oxygen molecules are generated (O₂), and then the creation of the surface-passive-layer (Zn(OH)_n⁽²⁻ⁿ⁾⁺) happens.



By incorporating carbon-nanotubes, polymers, metals, non-metals, and surfactants, researchers have developed modified ZnO materials to overcome these limitations. These modifications can inhibit Photo-corrosion and the formation of the passive layer. Divband et al. (2013) presented the importance of the fermi-level for the potential transfer of the electrons from the conduction-band of ZnO to silver, which consequently entraps the oxygen and forms the super-oxides. ZnO complexes with HCA (hydrocitric acid)/TBPA (tetra-bromophthalic anhydride) increased the visible-light sensitivity of ZnO (Comparelli et al., 2005). Complexation of ZnO with chitosan to degrade the permethrin (pesticide) has been reported (Dehaghi et al., 2014). The polymer-zinc

oxide composite at the dose of 0.5 g/L degraded the 99% pesticide. After 3 cycles, the composite showed 56% efficacy. Coating the polymer on ZnO gives strength to functional material against the photocorrosion, and also polymer may also act as an electron-pumping agent. Pei and co-workers (Pei et al., 2014) described the increased photocatalytic efficacy of coupled ZnO with poly-aniline. And this attributed the process to the excellent capture of the electrons. Dyes and polymers have mobile charge carrier potential and may help in the easy transfer of electrons. In the acidic media, the polymers protonate conveniently, which protects ZnO's dissolution in acidic media and helps efficient binding of negative charge containing organic contaminants (Khatamian et al., (2012). In the continuous-flow reactor, the composite of ZnO-bentonite having an approximate size of 20-30 nm degraded the phenol (70%) with an adsorption potential of 14.7 mg/g (Meshram et al., 2011). Bentonite clay has many layers of silicate and aluminum hydroxide, which probably responsible for the removal mechanism. They have excellent absorbing power and enhance the surface area of the catalyst, which is attributed to improving the solid-liquid mass transfer operations. ZnO has been hybridized with rare earth metals as nobelium and lanthanum to control the E-H pair recombination (Anandan et al., 2007a; Anandan et al., 2007b; Lam et al., 2014). Doping of lanthanum in ZnO enhanced the space charge potential more than 0.2 V which gave the effective E-H pair separation (Anandan et al., 2007a). ZnO modified with ferric oxide provided enhanced surface-area and also showed enhanced absorption of visible light to efficiently degrade the penta-chlorophenol (Xie et al., 2015). Fast diffusional metabolites transfer occurs to the mesoporous structure (flower like) which then reacts with radicals.

The ZnO has been coupled with silver to efficiently remove the phosphamidon (an organo-phosphorus pesticide) (Korake et al., 2012). Catalyst at conc. of 1 g/dm³ (at pH = 7) degraded the

phosphamidon (at initial conc. of 5×10^{-2} mol/L) within 150 minutes. Widespread use of ZnO is hindered because of low quantum yield due to out-ward electron diffusion. To prevent the recombination and entrapment of holes, the formation of p-n hetero-junction is an efficient method (Pirhashemi and Habibi-Yangjeh, 2017). Improvement in visible-light activity of ZnO has been made by grapheme, which potentially enhances the shelf-life of radicals and provides a larger surface area for pesticide interaction (Darwish et al., 2017). The doping of nitrogen and silver obtained the modulation in the ZnO bandgap in the ZnO lattice (Debnath and Gupta, 2018). And this tailored functional material increased the degradation of 2,4-di-nitrophenol (2,4-DNPH). Co-doping with metal and non-metal and decrease in the band gap helped generate the bulk attributed to enhancing the photo-catalytic potential of ZnO by absorption of the wide light spectrum and low dissipation of heat. Role of different Zinc based functional materials for degradation and removal of pesticides has been presented in Table 1.

Functional materials based on Tungsten

Ultra-violet (UV) active photocatalysts cannot absorb in the visible light region, which is a significant part of the solar light spectrum. While many semiconductors have wider band-gaps which UV light energy activates only. Tungsten oxides have a narrow band-gap (2.3-2.5 eV), activated in visible light energy. The tungsten trioxide (WO_3) complexes with different materials or semi-conductors are under consideration to explore its photo-catalytic potential. The WO_3 was found in mono-clinic I and mono-clinic II phases (Tahir et al., 2017). Recombination, dissipation of absorbed energy, and generation of E-H pairs are processes that decrease the efficacy of WO_3 due to its small bandgap. Mesoporous $\text{WO}_3\text{-TiO}_2$ degraded the imazapyr, phenolics, and malathion with efficient removal greater than 100, 98, and 76%, respectively (Aslam et al., 2014; Ismail et al., 2016). The mechanism may be due to less light scattering and increased diffusion of

organic motifs in catalyst surface (porous). Convenient transfer of oxidative holes from WO_3 to TiO_2 produces radicals that increase the oxidation. Surface impregnation with Pd (palladium) metal enhanced the surface response of WO_3 (Mkhalid, 2016). Graphite electrodes have been coated with WO_3 for efficiently removing the 2-nitrophenol around 82%. Figure 6 showed the mechanism of the photo-assisted activity of the WO_3 -EG composite electrode for the degradation of 2-nitrophenol. (Umukoro et al., 2017). Table 1 presents the efficiency of different tungsten-based materials for the degradation and removal of different pesticides

Functional materials based on Iron

Iron has a mesoporous surface and exists in different forms in the earth's crust. It has both reductive and oxidative properties. Iron-based nano-materials have a surface area of $82 \text{ m}^2 \text{ g}^{-1}$ and a band gap of 2.2 eV (Pei et al., 2014). Iron-based materials are adequate for water treatment as they are easy to separate from aqueous solutions because of their magnetic characteristics. Complexes of iron as Fe/Pd, Fe/Ni transformed the chlorinated pesticides, PCBs (polychlorinated-biphenyls), HCH (hexa-chlorocyclohexane), and hydrocarbons by de-chlorination process (Cao et al., 2005; Elliott et al., 2009). Iron materials get agglomerated in aqueous media, leading to less dispersion and low surface contact with the pesticides. The incorporation of metals (Pd, Ni, Pt, and Zn) may counter the agglomeration by promoting association and dissociation of H_2 gas into the atomic hydrogen, which inhibits the oxide layers formation on iron (Tee et al., 2009). Table 1 presents the efficiency of different modified iron-based materials for the degradation and removal of various pesticides. Copper-maghemite mineralized the 4-nitrophenol efficiently (Feng et al., 2013). Zero-valent iron in nano form has significant reducing characteristics and good surface area, resulting in agglomeration, but metals and organic stabilizer compounds can stabilize it (Ayad et al., 2017). The reduction of organic

322 molecules may release the active radicals (bromide, sulfate, and chloride), and these radicals may
323 indirectly oxidize the pesticides. The metal nano-particles adorned on the surface of iron oxide as
324 Ni/Fe-Fe₃O₄ dechlorinated the di-chlorophenol within 3 hours (Xu et al., 2016a). Pesticides are
325 mostly hydrophobic and adhere to the porous surface of the iron. Impregnation of iron oxide with
326 either gold or silver plasmonic-species increased the *p*-nitrophenol reduction (Jiang et al., 2015).
327 The coordination of adsorption and reduction was effective at the surface of Ag/Fe₂O₃. The
328 electrons transfer from silver (Ag) to iron (Fe) formed the depletion-layer at the interface of
329 Ag/Fe₂O₃ enhanced the fast organic species reduction (Chiou et al., 2013). Iron-based materials
330 have significant porosity and permeability, which may be responsible for the potent diffusion of
331 metabolites. The transfer of mass between the solid-liquid phase offers enough time for effective
332 degradation. Magnetic-silica nanoparticles modified with palladium effectively degrade and
333 remove the DDT (Tian et al., 2015). In this process, electron-channeling from the Pd-donor
334 followed by adsorption of magnetic particles. The presentation of the Core-shell structure has
335 been provided in Figure 7. Bimetallic iron-palladium (Fe-Pd) nano effectively degraded the
336 lindane at an initial conc. of 5 mg/L (Tian et al., 2015). The iron-palladium (Fe-Pd) potential is
337 attributed to the fast de-hydrohalogenation of C-Cl bond in lindane (Joo and Zhao, 2008). The
338 amount of palladium is effective for inhibiting the agglomeration of iron (Xu et al., 2005). The
339 coupling of magnetic particles with polymers (*e.g.*, starch) and surfactants (*e.g.*, CTAB) provided
340 excellent coherence of contaminated materials (Zhao et al., 2008; Gao et al., 2013). Magnetic
341 particles coated with the starch effectively reduced the 98% of tri-chloroethylene (TCE) in the
342 period of 1 hour (He and Zhao, 2005). Zeta-potential played a role in glyphosate removal by the
343 MnFe₂O₄-graphene-nanomaterial (Yamaguchi et al., 2016). Incorporation of Fe₂O₃ on the carbon
344 nano-tubes enhanced the surface area which increased the atrazine (pesticide) removal within

120 minutes using H_2O_2 (Yu et al., 2015). Fast de-alkylation, alkylic-oxidation and de-chlorination and available adsorption sites on the carbon-nanotubes attributed to the removal of the pesticide (Graymore et al., 2001). Iron-based materials are reported to degrade nitro-aromatic pesticides which may convert the anilines to respective amine or various other nitroso compounds (Keum and Li, 2004).

Functional materials based on Carbon

A primal element, carbon, formulae the fundamental construction unit of life expectancy. In water treatment, the actuated carbon material is extensively used as an adsorbent. The nanoscale dimension and the adaptable characteristics of carbon are significantly improved, such as high thermal and mechanical properties, improved electrical conduction, etc. Various carbon-based materials, including carbon quantum dots, g-C₃N₄, carbon nanotubes, and graphene, are available as various nanomaterials based on their architectural properties. Such materials have a high volume to surface area and a particularly closer band gap (Yue and Economy, 2005). Carbon is hydrophobic and has a great affinity for non-polar phenols and pesticides. On the other hand, because of the absence of chemical activity, graphene and carbon nanotubes take a long time to adsorb organic pollutants. Conventionally, to ensure the cost-effective removal of pesticides from water, carbon-based activated materials with its increased characters of improved porosity and surface area have been investigated. Besides, carbon materials demonstrate considerable high-temperature stability, making the expended adsorbent readily available after adsorption. The production of carbon-based activated materials from waste tyres and rubber and its successive usage for atrazine, methyl parathion, and methoxychlor extraction were stated by Gupta and co-workers (Gupta et al., 2011). Carbonaceous materials based on hydrogen bonds, π - π interactions, porous nature of the surface, and covalent bonds, making it an excellent

hydrophobic contaminant removal substrate. Biomaterials can sometimes be fabricated by carbon-based materials that afford cheaper alternatives to treat pesticides, such as banana peel, rice husk, olive stone, coconut shell, eggshell, etc. The oil seed matrix as an innovative material for the collaborative elimination of hydrophobic pollutants based on the water/octanol partition coefficient has been examined for this purpose (Boucher et al., 2007). The successful elimination of chlorpyrifos DDE and endosulfan owes because of reduction in compounds by halogen group oxidation accompanied by adsorption on RGO exfoliated sheets by π - π graphene surface interactions. (Yue and Economy, 2005; Cho et al., 2018). Previous studies have also examined the successful removal of nitrophenols, pesticides, and chlorobenzene from carbon nanotubes (Peng et al., 2003; Cai et al., 2005). Based on structure, the carbon nanotubes are normally multi-walled or single-walled. In developing solid-phase extraction systems, the flexible properties of nanotubes have also been used. Even at low concentrations (4-13 ng/L), pesticides, such as sulphonyl urea and DDT, have been eliminated. This elimination owes to the extraordinary, which can be due to the unusual attraction of CNTs with functionalities present in the structure of pesticide (Zhou et al., 2006). It is worth mentioning here that the sheet purity, degree of twist, diameter of the tube, geometric character, physical/chemical character, and the synthetic method ascertain remarkable properties to the CNTs (Debnath et al., 2019). The polar and nonpolar bonds present in different molecules (COOH, NH₂, C-C, C-O) interact with these π - π interactions (Pan and Xing, 2008). Therefore, the symbiotic structure of adsorbing catalysis can effectively eliminate pesticides, and designing such functional materials is imperative. Carbon-based particles can be very easily modified by cationic and anionic surfactants on the surface. This modification leads to ionic modulation of the carbon-based surface, which can easily interact with the oppositely charged surface of pesticide (Park and Bae, 2015). Wang and

Coworkers documented MWCNT conjugated TiO_2 based material to mitigate dinitrophenol (Wang et al., 2009). Shi et al. documented the CNT-based materials conjugated with Ag/AgCl through the ultrasonication-based deposition-precipitation method to remove tribromophenol (Shi et al., 2013). The new materials resolve the issues related to the low reactivity of CNTs against intransigent carbon assisted compounds by plasmon action of silver. Electrons are injected by plasmon into the silver bromide conduction band, whose conduction band is more negative than silver (0.065 V vs. 0.2 V). Moreover, the electrons guide the flow to the mobile surface of CNTs. Often, silver-based compounds can enhance the activity of visible light. Compounds such as Ag_2S with a 0.9-1.05 eV band gap have been stated to cause the reaction under visible light reaction (Huo et al., 2018). Recently, to catalyze the degradation of 4-nitrophenol, g- C_3N_4 coupled with nickel has been effectively synthesized. In this degradation process the impregnated Ni is the major cause of degradation process as it donates electron and enhances the effectiveness of the process. This matrix (g- C_3N_4 -Ni) contains highly oxidative holes which can enhance the degradation mechanism. The improved character of Pd-mesoporous carbon based materials engineered by irradiation for the degradation of nitrophenol has also been documented in a few studies (Veerakumar et al., 2014). Guo et al. (2016) indicated that mesoporous carbon coupled plasmonic gold nanoparticles coupled with NaBH_4 function as an outstanding catalyst for the transformation of p-nitrophenol to p-aminophenol. The hybridization with other plasmonic organisms, non-metals and metals of graphene and carbon nanotubes improves the nanomaterials' reactivity and reusability. Studies investigating the applicability of carbon functional materials have been published previously. Further various carbon-based materials are tabulated in Table 2.

Functional materials based upon zirconium

In the field of high-surface porous materials, zirconium-derived materials have expressed demanding promise in the rapid growth of material engineering. The zirconium (Tetragonal), architecture consisting of zirconium and benzenedicarboxylate, has been employed to engineering a metal-organic framework UiO-66. Due to its π - π interactions and ionic interactions, the substance has shown similar characteristics to carbon. Besides, these MOFs have excellent detection capabilities for organophosphates. The UiO-66 and 67 Zr-OH groups display a preference for pesticides such as glyphosate phosphates (Bugaev et al., 2018). Subsequently, the materials based on zirconium were used to enhance the photocatalyst's mesoporous property. Goswami and Ganguli (2013) stated the mitigation of quinalphos by zirconia/titania composite. The effect of zirconia doping allows oxygen vacancies to trap electrons and zirconia to trap holes, making them excellent electron separators. High activity zirconium content has also been reported to be involved in hydrogen production and photocatalysis by doping platinum (An et al., 2018).

Polymeric derived functional materials

In the field of water treatment, functional polymeric materials have gained a lot of interest. These materials can be synthetic or natural and can be modified to other components (Wang et al., 2013; Hu et al., 2015). In membrane preparation, many polymers are often used as immobilization substrates and resins to target particular pollutants in waste water (Halake et al., 2014). The extraction of materials such as chitosan, cellulose, alginate, and Cyclodextrins from plant, seashell residues such as shells, wood, leaves, etc. (Ding et al., 2009; Ngo et al., 2015). The functional biomaterials display more significant interaction of the adsorptive properties, functional group, and greater pollutant piling. Besides, these polymeric materials exhibit extraordinary stability and porosity and can be adjusted on the surface to improve their

437 interaction with pesticides. The formation of a layer from core shells allowing improved
438 diffusion of pesticides, the simple design of biomaterials can be used for the layer. For the
439 efficient removal of 2,4-Dinitrophenol, previous investigations have documented the adaptation
440 of the NH_2 group of functionalized carbon coated with polyacrylonitrile. The adsorption of the
441 anionic contaminants on the polymer cationic amino group is the intrinsic mechanism (Zhao et
442 al., 2017). The adsorption of cationic contaminants as pesticides is strongly regulated by the
443 molecule's pKa as negative charges that can interfere with the positive polymer are revealed by
444 the greater dissociation of molecules above pKa. A versatile structure for contaminant removal
445 and easy separation from the aqueous medium has also been documented for functional polymer
446 materials such as β -cyclodextrin-chitosan-magnetic material, β -cyclodextrin-silica nanomaterial (
447 Zhao et al., 2017). Metal-integrated polymers are successful in sorption execution as well as
448 acting as a porous catalysis substrate. Advanced oxidation of organic contaminants occurs in
449 functional polymers impregnated with gold and silver. Gold-polythiophene core-shell and silver
450 citrate polymer materials are some of those materials (Pradeep, 2009). The model for casting
451 flexible porous membranes that can be used as ultrafiltration and nano-filtration membranes can
452 be made from biomaterials (Mukherjee et al., 2018). Besides, certain materials have been
453 mimicking the sediment sorption mechanism of hydrophobic contaminants with natural clay
454 minerals such as montmorillonite (MMT) (Sahithya et al., 2015; Foo, 2016; Shabtai and Mishaël,
455 2017). Specific conductive polymers including polyaniline, polypyrrole, and polythiophene have
456 flexible properties that can be used in photocatalytic membranes, such as electrical conductivity
457 and semiconductor-based properties (Sarkar and Das, 2017; Khan et al., 2018). However, the
458 problem of biofilm formation that leads to surface passivation is faced by polymeric materials
459 used in membranes. Because of its antibacterial property, materials such as silver loaded

polymers may prohibit biofilm development. Biomaterials provide a low-cost alternative for developing flexible pesticide removal filters and membranes. In order to formulate unique biopolymers for targeting overdosed pesticides, the properties of membranes need to be examined in detail. The studies that developed carbon, zirconium and polymer based functional materials to treat pesticides consisting of are presented in Table 2.

Application of functional nanomaterials in industry

The application of polysaccharides and polymers can well be found via integrated membranes in oil separation mechanisms. In the manufacture of membranes, hydroxyethylcellulose, xanthan gums, guar gum, scleroglucan, cellulose, carboxymethylcellulose, etc. were used (Subash et al., 2013). For the elimination of inorganic and organic compounds from industrial waste water, the membranes may be used selectively. Industrial wastewater treatment requires that usable materials be tolerant of hazardous conditions. Fouling due to its antimicrobial nature is avoided using functional materials such as silver embedded carbon or polymers. The effect of high interfering ion concentrations induces shock loads to the effluent treatment easily controlled by practical material models for high surface area. Moreover, the spectrum of photocatalytic hybrids overcomes the conventional limitations that can be built to use solar light that degrade organics and hydrocarbons that are permanent. Besides, the regeneration of usable materials permits repeated reuse in industrial applications, lowering running costs (Grandclément et al., 2017). The use of materials in wastewater treatment as fine powders and pellets helps them absorb a wide variety of contaminants found in industrial wastewater, such as heavy metals, pesticides, antibiotics, surfactants, etc. (Kuśmierk and Świątkowski, 2015). In addition to the innovative production of usable materials from synthetic sources, industrial waste can also be developed to provide a sustainable alternative for sludge handling and reuse (Edathil et al., 2018).

Concluding remarks and future prospects

In conclusion, pesticide development and their effective utilization as per standard regulations have noteworthy contributions in fulfilling the ever-rising food demand. However, the disproportionate and inconsistent/irregular use of any or many pesticides that include bactericides, fungicides, herbicides, insecticides, and so on pose severe environmental and biological effects on plants, animals, and humans. Such massive consumption avoiding the standard regulations creates havoc on living beings and alters the whole ecological structure. In this context, the short and long-term consequences of pesticide compounds and/or their active by-products or residues that ultimately get discharged into water matrices should be considered with care before their agricultural or aquacultural exploitation. Moreover, the environmental and water matrices are at substantial threat of contamination due to pesticide drift, such as vapor drift and leaching drift after post-application into air or water bodies, respectively. After years of negligence, now the adverse consequences are evident in several diseases, such as cancer and other chronic diseases, and these are still emerging at a high pace. As discussed above in respective sections, many of these diseases are attributed to the consistent use and bioaccumulation of pesticide compounds in our system, which act as a catalyst to carcinogens and other disease-stimulating active agents.

There is a dire need to mitigate pesticide contamination for a safe and better tomorrow. Thus, keeping this in mind, this article spotlights the functional attributes of tailored functional materials as robust candidates since conventional methods have several limitations for removing the pesticides. The work is enriched with several functional materials with suitable examples and their exploitation against different pesticidal compounds. Based on the above-discussed literature with relevant examples, it is evident that integrating tailored functional materials as robust

candidates could be useful to mitigate pesticides from wastewater matrices. However, their large-scale implementation in bulk seems a formidable challenge, and intensive research investigations and cost-effective models are of supreme interest for future studies. Given that increasing the exploitation of tailored functional materials-based mitigation systems for pesticides drives at the cost of low reliability and efficacy and that such mitigation systems are still in their infancy and urge substantial advancement in the coming future.

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1131 **List of Tables**

1132 **Table 1** Role of Ti, Zn, W, Fe based functional materials for removal of the pesticides in
 1133 aqueous media.

| Metal based Functionalized materials | Contaminants | Removal efficacy and Time | References |
|--|---------------------|----------------------------------|---|
| Titanium based materials | | | |
| AgCl/Ag/TiO ₂ | 2,4-Dichlorophenol | 94.0 %, 60 min | (Tian et al., 2014) |
| Ag/TiO ₂ | Pentachlorophenol | 100 %, 160 min | (Zhang et al., 2012) |
| Fe/TiO ₂ | 2,4-Dinitrophenol | 97.0 %, 120 min | (Liu et al., 2012) |
| Ag/Zr/TiO ₂ | 4-nitrophenol | 100 %, 8 mint | (Naraginti et al., 2015) |
| Ag/Cu/TiO ₂ | 4-nitrophenol | 96.0 %, 30 min | (Hernández-Gordillo and González, 2015) |
| Ti-AC np | Dicofol | 97.3%, 89.12 min | (Vali et al., 2021) |
| Ag/TiO ₂ | Acetamiprid | -, 40 min | (Cao et al., 2008) |
| FeFNS/TiO ₂ | Diazinon | 87.6 %, 100 min | (Hossaini et al., 2014) |
| TiO ₂ /Fe ₂ O ₃ | Diazinon | 95.1 %, 45 min | (Mirmasoomi et al., 2017) |
| CTAB-TiO ₂ | Pyridaben | 100 %, 560 min | (Zhu et al., 2007) |
| TiO ₂ -SiO ₂ | Dichlorovos, | 100 %, 420 min | (Shifu and Gengyu, 2005) |
| Fe ₂ O ₃ /CuO/TiO ₂ | 2,4-D | 97.0 %, 300 min | (López-Ayala et al., 2015) |
| Fe/TiO ₂ | Thiacloprid | 96.0 %, 240 min | (Banić et al., 2011) |
| Fe ₂ O ₃ -TiO ₂ | Propachlor | 96.0 %, 50 min | (Belessi et al., 2009) |
| Au-Pd-TiO ₂ | Malathion | 98.2 %, 240 min | (Yu et al., 2010) |
| Zinc based materials | | | |
| Chitosan-ZnO | Permethrin | 99.0 %, 90 min | (Dehaghi et al., 2014) |
| ZnO-bentonite | Phenol | 80.0 %, 90 min | (Meshram et al., 2011) |

| | | | |
|---|-----------------------|-----------------|-------------------------------|
| WO ₃ -ZnO | Diazinon | 99%, 180 min | (Maleki et al., 2020) |
| rGO-ZnO | Chlorpyrifos | 75%, 70 min | (Gulati et al., 2020) |
| PANI/ZnO-CoMoO ₄ | Imidacloprid | 97%, 180 min | (Adabavazeh et al., 2021) |
| Fe ₃ O ₄ /CdS-ZnS | Chlorpyrifos | 72%, - | (Soltani-nezhad et al., 2020) |
| Ag/ZnO | Phosphamidon | 100 %, 150 min | (Korake et al., 2012) |
| ZnO/TiO ₂ | Diazinon | 99.9 %, 60 min | (Jonidi-Jafari et al., 2015) |
| ZnO/Fe ₂ O ₃ | Dicamba | 100 %, 300 min | (Maya-Treviño et al., 2014) |
| Ag/ZnO | 4-nitrophenol | 100 %, 180 min | (Divband et al., 2013) |
| Ln/ZnO | 4-nitrophenol | 83.4 %, 200 min | (Khatamian et al., 2012) |
| CuO/ZnO | 4-nitrophenol | 99.0 %, 180 min | (Qamar et al., 2015) |
| Graphene/ZnO | Nitrophenol | 98.0 %, 150 min | (Darwish et al., 2017) |
| La/ZnO | Metasystox | 90.0 %, 150 min | (Korake et al., 2014) |
| | 2,4,6-Trichlorophenol | 100 %, 120 min | (Anandan et al., 2007b) |
| | Monocrotophos | 100 %, 120 min | (Anandan et al., 2007a) |
| Fe ₂ O ₃ /ZnO | Pentachlorophenol | 98.0 %, 240 min | (Xie et al., 2015) |
| W/ZnO | Chlorophenol | 100 %, 150 min | (Aslam et al., 2015) |
| Sm/ZnO | Phenol | 89.5 %, 480 min | (Sin et al., 2013) |
| Nb ₂ O ₅ /ZnO | Phenol | 100 %, 40 min | (Lam et al., 2014) |
| Tungsten based materials | | | |
| WO ₃ | 2-Chlorophenol | 98.0 %, 180 min | (Aslam et al., 2014) |
| WO ₃ -TiO ₂ | Malathion | 99.0 %, 300 min | (Ramos-Delgado et al., 2013) |
| | Imazapyr | 100 %, 120 min | (Ismail et al., 2016) |
| ZnSe-WO ₃ | Bisphenol A | 99.0 %, 90 min | (Kumar et al., 2017) |
| Pd-WO ₃ | 2,4-D | 100 %, 50 min | (Mkhalid, 2016) |
| P/W@UiO-66-NH ₂ MOFs | 4-Nitrophenol | 100%, - | (Roshdy et al., 2021) |

| | | | |
|--|--|--|---|
| WO ₃ /Fe ₃ O ₄ | Thiacloprid | 91.3%, - | (Banić et al., 2019) |
| Iron based materials | | | |
| CuFe ₃ O ₄ | 4-Nitrophenol | 95.0 %, 40s | (Feng et al., 2013) |
| SDS-coated Fe ₃ O ₄ chitosan NPs | Diazinon | 99% | (Ranjbar Bandforuzi and Hadjmohammadi, 2019) |
| | Phosalone | 98% | |
| | Chlorpyrifos | 96% | |
| Fe/Pd | Lindane | kobs =1.02x0.16 min ⁻¹ ,5 min | (Nagpal et al., 2010) |
| Fe ₂ O ₃ /MWCNT | Atrazine | 81.4 %, 2h | (Yu et al., 2015) |
| Starched Fe/Pd | Trichloroethylene | 98.0 %, 1h | (He and Zhao, 2005) |
| Ag/iron oxide | Nitrophenol | 30 min | (Chiou et al., 2013) |
| FeOOH/Fe ₂ O ₃ | Atrazine | 95.0 %, 30 min | (Ali et al., 2016) |
| Ag/Fe microbox | Nitrophenol | kobs = 11.4x10 ² s ⁻¹ , 150 min | (Jiang et al., 2015) |
| MnFe ₂ O ₄ -graphene | Glyphosate | 97.0 %, 8h | (Yamaguchi et al., 2016) |
| Fe-ZnIn ₂ S ₄ | Tribromophenol | 95.0 %, 60 min | (Gao et al., 2013) |
| CTAB-Fe ₃ O ₄ | Bisphenol A | 95.0 % | (Zhao et al., 2008) |
| CuFe ₂ O ₄ | Tetrabromobisphenol-A | 99.0 %, 30 min | (Ding et al., 2013) |
| GO-Fe ₃ O ₄ | 2,4-D | 67.2 mg/g | (Nethaji and Sivasamy, 2017) |
| Fe ₃ O ₄ @nSiO ₂ @mSiO ₂ | DDT | 97.0 %, 60 min | (Tian et al., 2015) |
| CoFe ₂ O ₄ @TiO ₂ -GO | Chlorpyrifos | -, 60 min | (Gupta et al., 2015) |
| Ce _x Fe _{1-x} O ₂ | Chlorophenol, Dichlorophenol, 2,4-D | 58.7 %, 90 min, 42.4 %, 90 min, 45.8 %, 60 min | (Kurian et al., 2017) |
| FeO/activated carbon | Chlordecone | 79.8 µg/mg, 1400 min | (Rana et al., 2017) |

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|---|---|---|-----------------------------|
| Pd/Fe-Fe ₃ O ₄ @MWCNT | 2,4-Dichlorophenol | 92.3 %, 300 min | (Xu et al., 2016b) |
| Fe ₃ C@N-GE-Fe ₃ O ₄ | 2,6-dichlorobenzamide (BAM), 2-methyl-4-chlorophenoxy acetic acid (MCPA), 2-methyl-4- chlorophenoxy propionic acid (MCPD) | 84%, 93%, 93% respectively | (Ghanbarlou et al., 2020) |
| Fe turnings | Heptachlor, endosulfan, dieldrin, endrin | 5.7, 13.2, 23.3, 39.4% respectively, 10 min | (Abbas et al., 2020) |
| CaFu MOFs | Imidacloprid | 467.23 mg/g | (Singh et al., 2021) |
| TiO ₂ @LaFeO ₃ | myclobutanil | 100%, 180 min | (Garcia-Muñoz et al., 2020) |

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1151 **Table 2** Functional polymeric materials for the removal of pesticides.

| Functional Group | Material | Target analytes | Experimental conditions | Removal efficacy | Ref |
|------------------|------------------------------------|--|---|---|------------------------------------|
| Carbon-based | MWCNT/TiO ₂ | Dinitrophenol | Dose: 8 g/L, C0: 38 ppm, pH: 6, Sunlight | 99% | (Debnath et al., 2019) |
| | Ti/MWCNT | Atrazine | Dose: 0.2 mg/L C0: 4.6 104 9.3 102 mmol/L | - | (Chen et al., 2011) |
| | Biochar | Tricyclazole, Isoprothiolane, Malathion | - | 63.81, 46.72, 98.08 % | (Tong et al., 2019) |
| | Silver@graphene oxide | Imidacloprid | - | 63% | (Keshvardoostchokami et al., 2018) |
| | Activated Coconut Charcoal (AcCoC) | monocrotophos | pH 7 | 103.9 mg/g | (Kodali et al., 2021) |
| | Plain chitosan | Imidacloprid | pH 6 | 70% | (Moustafa et al., 2021) |
| | AgNPs@chitosan | Imidacloprid | pH 6 | 95% | (Moustafa et al., 2021) |
| | Nanoporous activated carbon | Imidacloprid | - | 80-99% | (Mohammad and El-Sayed, 2020) |
| | Ag/AgBr/CNT | Tribromophenol | Dose: 30 mg/50 mL, C0: 100mmol/L pH: 10, 250 W metal halide lamp | 100% | (Shi et al., 2013) |
| | GAC (granular active carbon) | Atrazine, Prometryn, Chlorpyrifos, Dipterex, Acetamiprid, Imidacloprid, Thiamethoxam, Azoxystrobin, Carbendazim, Dimethomorph, Difenconazole, Prochloraz | - | 80, 100, 100, 93.33, 84.95, 100, 72.41, 88.89, 92.80, 83.33, 100, 100 % | (Tang et al., 2020) |
| | Au/mesoporous carbon | p-Nitrophenol | Dose: 75 mg C0: 200 ppm pH: | 87% | (Guo et al., 2016) |

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|------------------|---|---|---|--|---|
| | | | 10.1, 0.06 M NaBH ₄ | | |
| | Ag/graphene-dopamine MWCNT-O (0.85%) | 4-Nitrophenol Atrazine | NaBH ₄ Dose: 5 mg/25 mL C0: 4.2 ppm 0.01 M NaNO ₃ + 0.1 g/L NaN ₃ , pH: 6 | 17.3 mg/g | (Chen et al., 2009; Jeon et al., 2013) |
| | RGO-ZnS RGO-Ag Fe ₃ O ₄ /graphene | Nitrophenol Lindane Ametryn | Solar light simulator C0: 2 ppm, Dose: 0.5 g/L, C0: 10 ppm | 87% 99% 93.6% | (Boruah et al., 2017; Ibrahim et al., 2017) |
| | Fe ₄ O ₃ -GO-β-cyclodextrin | Thiamethoxam Imidacloprid Acetamiprid Nitenpyram Dinotefuran Clothianidin Thiacloprid | Dose: 5 g/L C0: 10 ppm | 2.8 mg/g 3.1 mg/g 2.9 mg/g 2.5 mg/g 2.5 mg/g 1.7 mg/g 2.8 mg/g | (Liu et al., 2017) |
| | β-FeOOH-RGO | 2-Chlorophenol | Dose: 1 g/L C ₀ : 100 ppm 0.1 M H ₂ O ₂ pH: 4 | 100% | (Xiao et al., 2016) |
| | Ag/AgCl-activated carbon | Thidiazuron | Dose: 0.3 g/L C0: 20 ppm 23 W Philips LED, 20 mW/cm ² pH: 7 | 91% | (Yang et al., 2017) |
| | CoO/TiO ₂ /GO | Chlorophenol | Dose: 0.5 g/L C0: 10 ppm, 0.01% H ₂ O ₂ , 200 W Xenon lamp, pH: 6 | 97.5% | (Sharma and Lee, 2016) |
| | Ag/Ag ₂ CO ₃ -rGO | Phenol | Dose: 0.05 g/25 mL C0: 10 ppm 350 W Xenon lamp, 40 mW/cm ² | 82% | (Song et al., 2016) |
| | Graphene quantum dot | Oxamyl | Dose: 0.6 g/20 mL C0: 150 ppm pH: 8 | 125mg/g 95.7% | (Agarwal et al., 2016) |
| Zirconium | Zirconium-benzene dicarboxylate | Methylchloro-phenoxy propionic | pH: 4, C0: 20 ppm Dose: 0.1 g/L | 85% | (Seo et al., 2015) |

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|----------------------|--|---------------|---|------------|-----------------------------|
| - based | (UiO-66) | acid | | | |
| | Zirconium-benzene dicarboxylate (UiO-67) | Glyphosate | Dose: 0.03 g/L pH: 4, C0: 0.1 mmol/L | 537 mg/g | (Zhu et al., 2015) |
| | UiO-67 | Glyphosate | - | 540 mg/g | (Pankajakshan et al., 2018) |
| | NU-1000 | Glyphosate | - | 1500 mg/g | (Pankajakshan et al., 2018) |
| | yttria-stabilized ZrO ₂ (8YSZ) | Carbofuran | - | 89% | (Qin et al., 2020) |
| | MIL-140A | Nitrophenol | - | 91 mg/g | (Lee et al., 2018) |
| | Zirconium-benzene dicarboxylate (UiO-67) | Glufosinate | Dose: 0.03 g/L pH: 4, C0: 0.1 mmol/L | 360 mg/g | (Zhu et al., 2015) |
| | TiO ₂ /ZrO ₂ | Quinalphos | Dose: 4 g/L, pH: 3 C0: 105 M | 62% | (Goswami and Ganguli, 2013) |
| | WO ₃ /ZrO ₃ | Carbofuran | Dose: 1 g/L pH: 8, C0: 20 ppm UV flux 50 W/m ² | 100% | (Alalm et al., 2016) |
| | TiO ₂ /ZrO ₂ | Chloridazon | Dose: 3 g/L, pH: 8 C0: 5 105 M, 150W Xenon lamp | - | (Mbiri et al., 2018) |
| Polymer-based | β-Cyclodextrin-chitosan-Fe ₃ O ₄ | Bisphenol A | pH: 6 C0: 200 ppm | 133 mg/g | (Huang et al., 2017) |
| | Polyvinyl-pyridine-co-styrene-montmorillonite clay composite | Diazinon | Dose: 0.5 g/L pH: 3.5 0.13 mM | 100% | (Shabtai and Mishaël, 2017) |
| | β-Cyclodextrin | Bisphenol A | Dose: 1 g/L 0.1 mmol/L | 113 mg/g | (Wang et al., 2017) |
| | Carbon coated polyacrylonitrile | 2,4-D | Dose: 50 mg/80 mL pH: 3, 70 ppm | 61.02 mg/g | (Zhao et al., 2017) |
| | Montmorillonite-CuO-chitosan | Dichlorovos | Dose: 1.5 g/L pH: 8, 80 ppm | 93% | (Sahithya et al., 2015) |
| | Montmorillonite-CuO- polylactic acid | Monocrotophos | Dose: 15 g/L pH: 5, 100 ppm | 80% | (Foo, 2016) |

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| | Starch polymer-laponite clay | Dicamba | Dose: 30 mg/25 mL pH: 7, 500 ppm | 251 mg/g | (Pinto et al., 2016) |
| | Polyaniline-zeolite | Glyphosate | Dose: 50 mg/5 cm ³ 400 ppm | 98.5 mg/g | (Debnath et al., 2019) |
| | Polyaniline-silica gel | 2,6-Dichlorophenol | Dose: 1 g/L pH: 7, 80 ppm | 31.9 mg/g | (Pan et al., 2011) |
| | Polyvinylpyrrolidone-magnetic nanoparticles | Bisphenol-A | pH: 7 50mg/L | 90 mg/g | (Fard et al., 2017) |
| | Bentonite/P.HE MA-MMA | methyl parathion | 240 min | 868.5 mg/g | (Abukhadra et al., 2021) |
| | poly (ε-caprolactone) | Endosulfan | 30 min | 99.97% | (Mourabit and Boulaid, 2019) |
| | Nano-organoclay composite based on carboxy methyl cellulose and two nano-organobentonites (DMDA, ODAAPS) | Atrazine, butachlor, cabendazim, cabofuran, imidacloprid, isoproturon, pendimethalin, thiophanate methyl, thiamethoxam | - | 57.6, 99.6, 66.6, 74.8, 75.3, 96.2, 98.5, 99.9, 76.3% | (Narayanan et al., 2020) |

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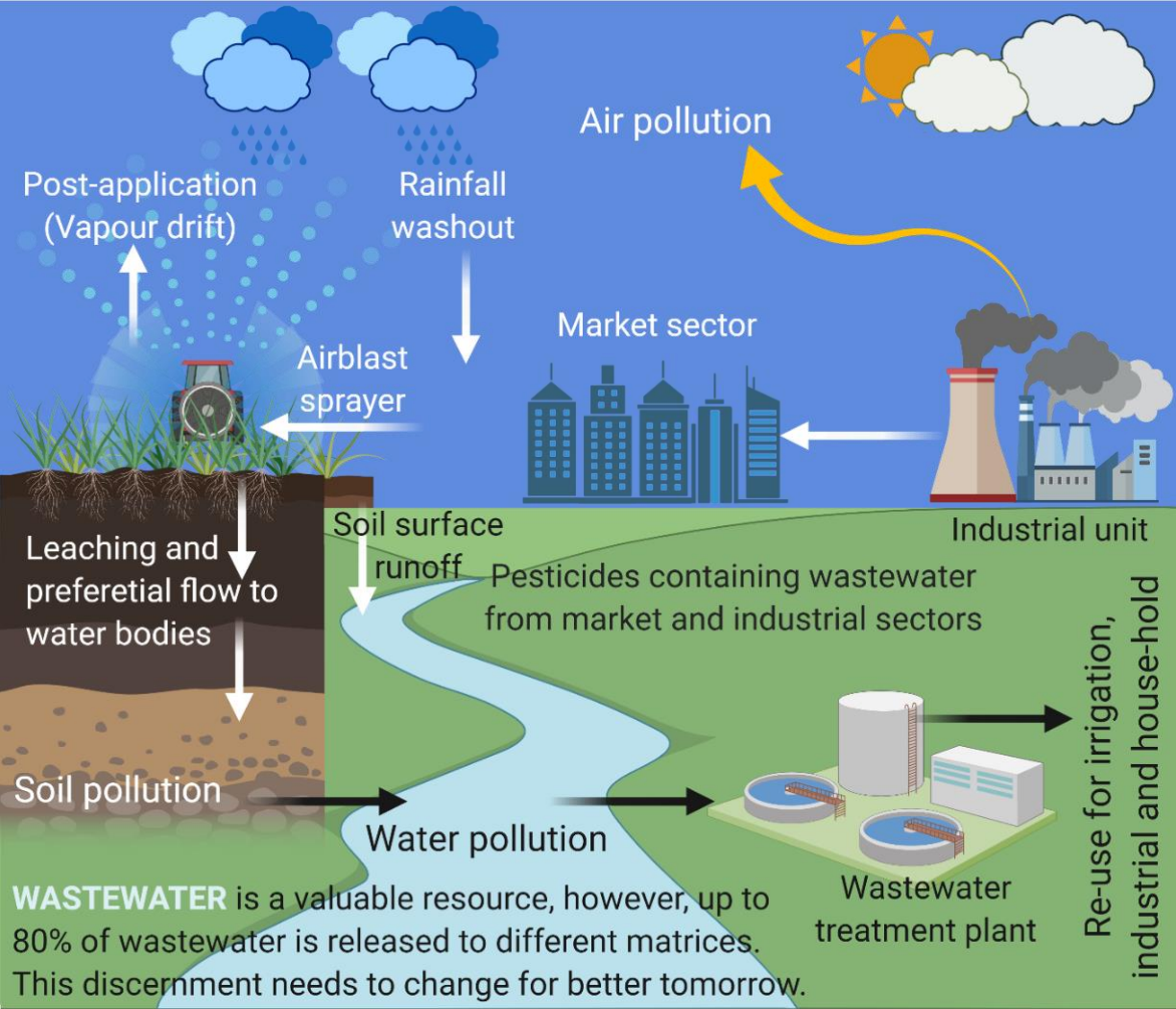
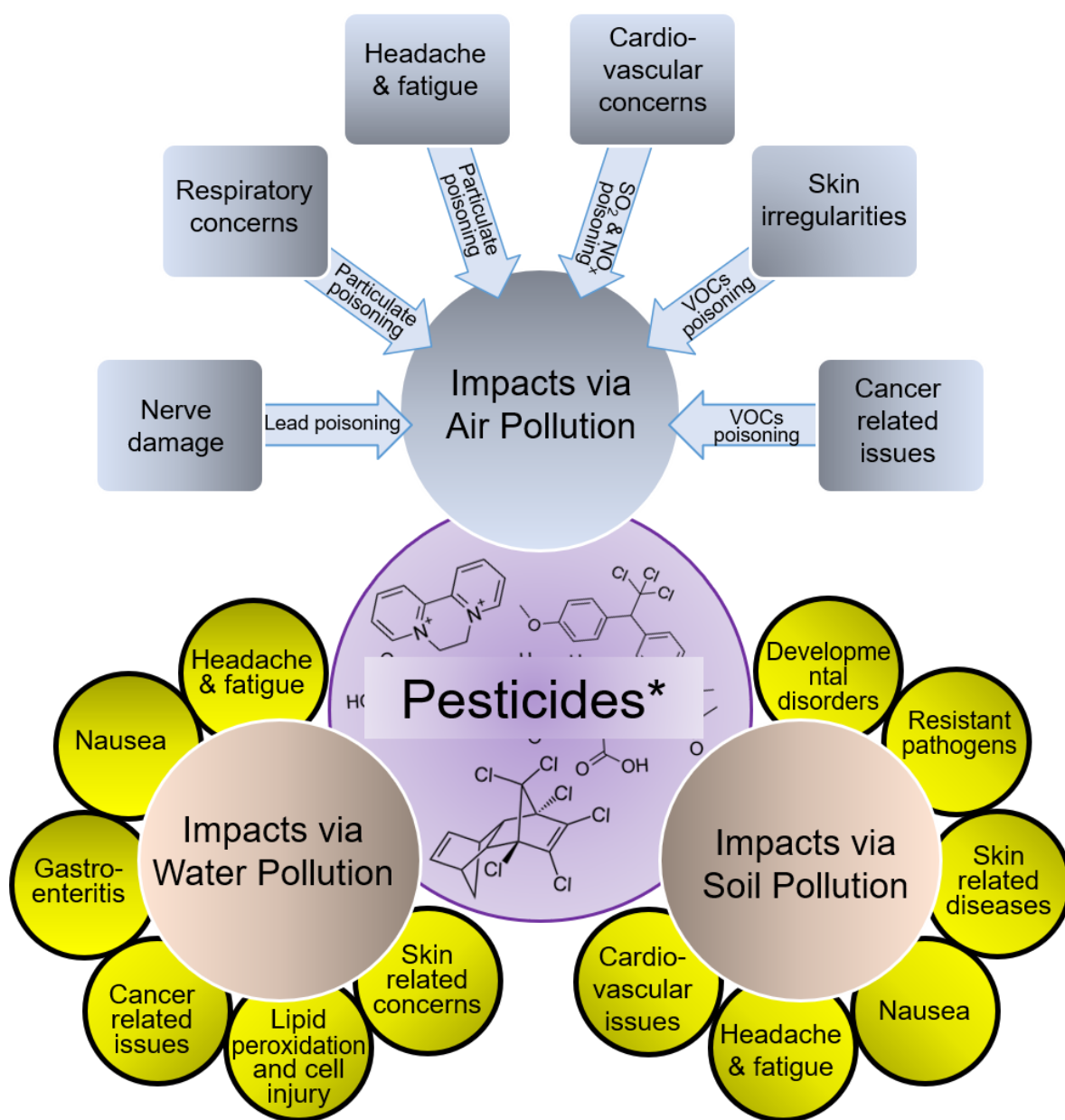


Figure 1 Pesticide drift that can lead to contamination of different environmental matrices including air, soil, and water.



*The degree to which pesticides pose adverse consequences may depend more on the level of exposure, concentration range, and contact period.

Figure 2 Adverse biological impacts of pesticides via air, water and soil pollution.

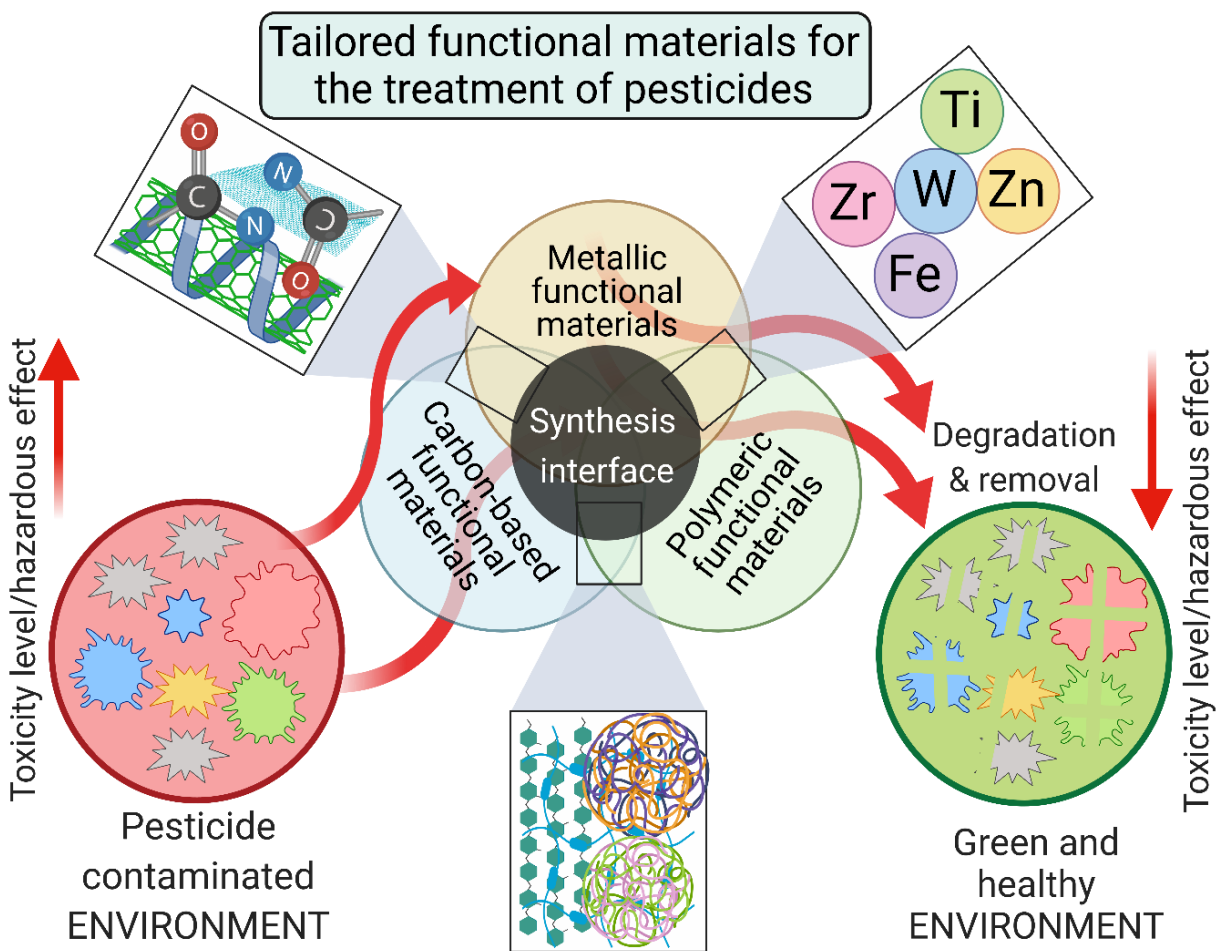


Figure 3 Schematic diagram showing tailored functional materials for the treatment of pesticides and related environmental pollutants.

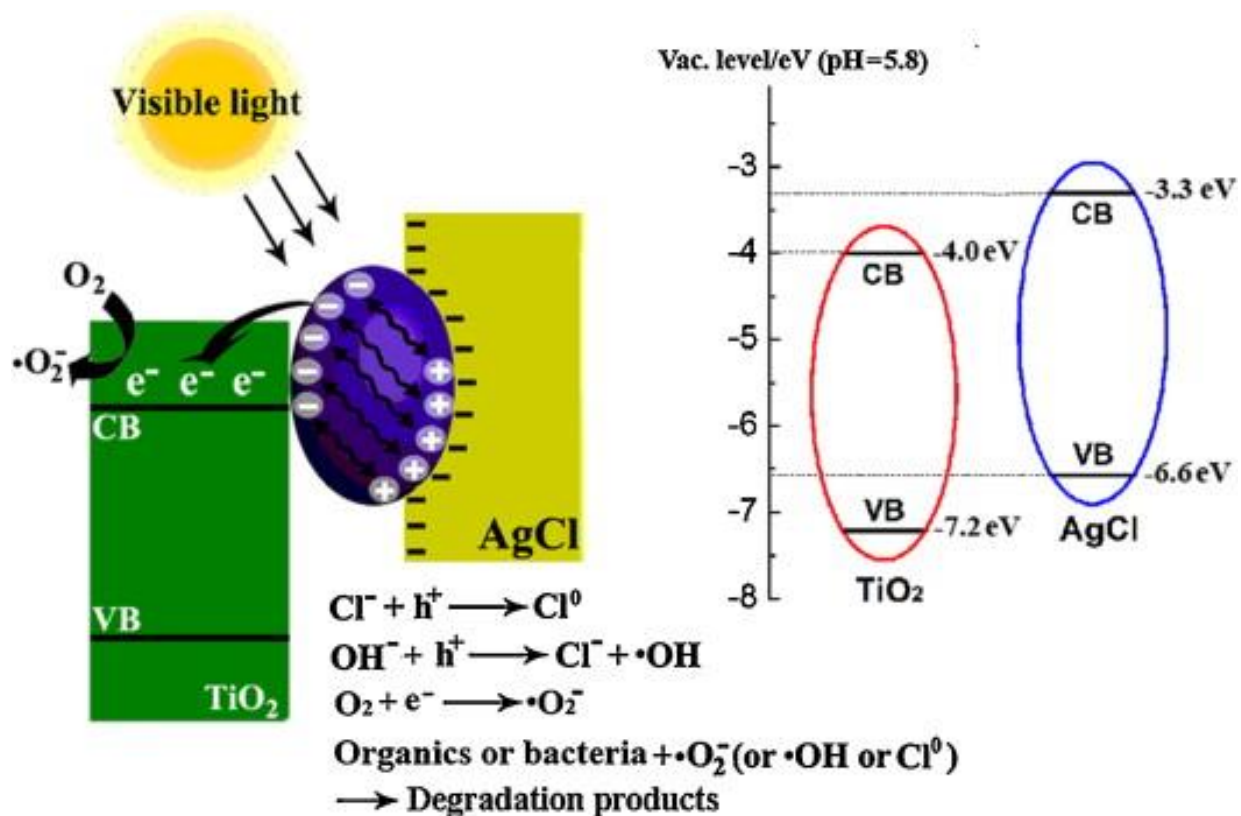


Figure 4 Proposed reaction mechanism of organics (or bacteria) over AgBr@Ag@TiO₂ photocatalyst under visible light irradiation. Reprinted from Tian et al. (2014) with permission from Elsevier. Copyright © 2014 Elsevier B.V. License Number: 5055760857679.

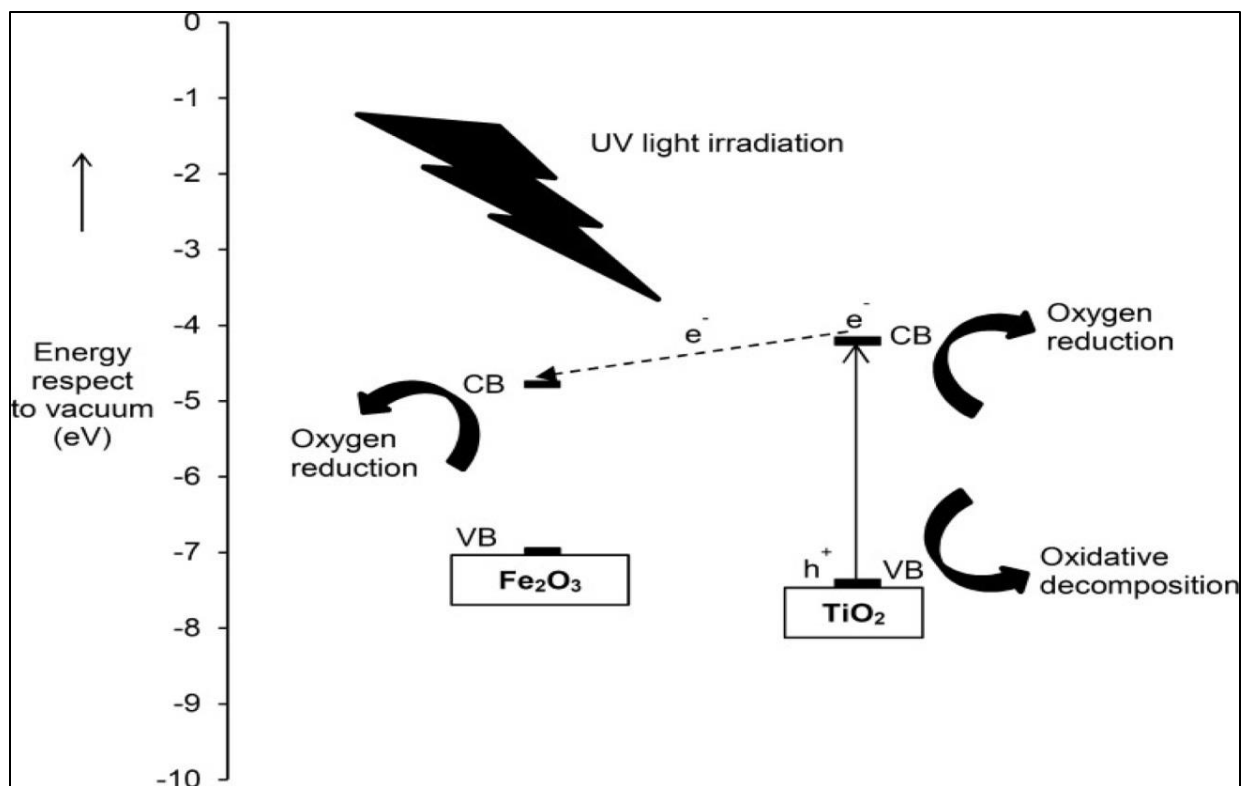


Figure 5 Illustration of the mechanism for major charge transfer pathways on $\text{Fe}_2\text{O}_3(0.5)/\text{TiO}_2$ (PD) for 2,4-dichlorophenoxyacetic acid degradation. VB stands for valence band and CB stands for conduction band. Reprinted from Lee et al. (2017) with permission under the terms of the Creative Commons Attribution License.

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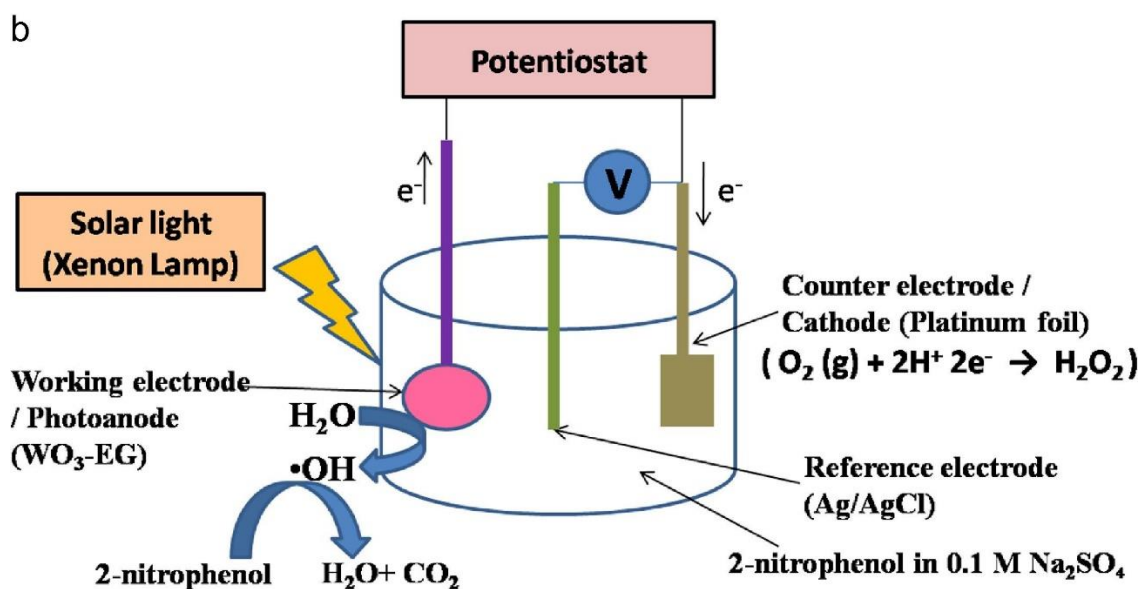
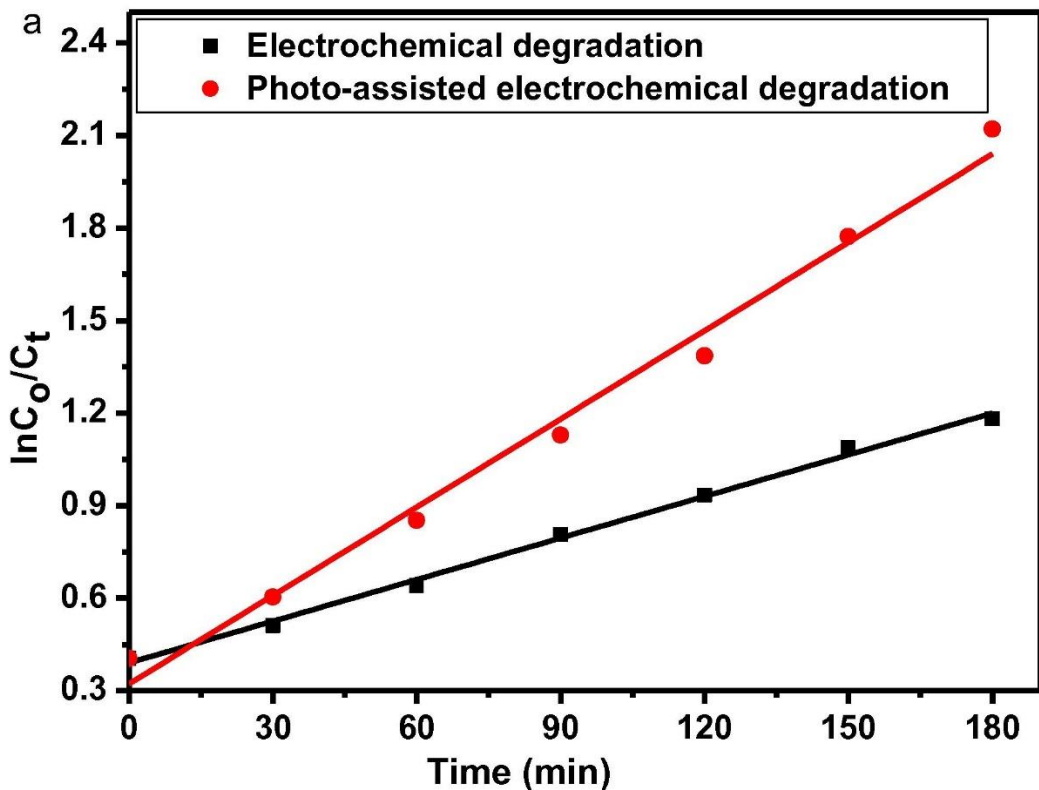


Figure 6 (a) Degradation kinetics graphs of electrochemical and photo-assisted electrochemical degradation of 2-nitrophenol dye at pH 6 and 10 mA cm⁻² using WO₃-EG composite electrode; (b) Proposed underlying charge transfer mechanism of the photo-assisted activity of WO₃-EG composite electrode for the degradation of 2-nitrophenol. Reprinted from Umukoro et al. (2017) with permission from Elsevier. Copyright © 2017 Elsevier B.V. License Number: 5055761305400.

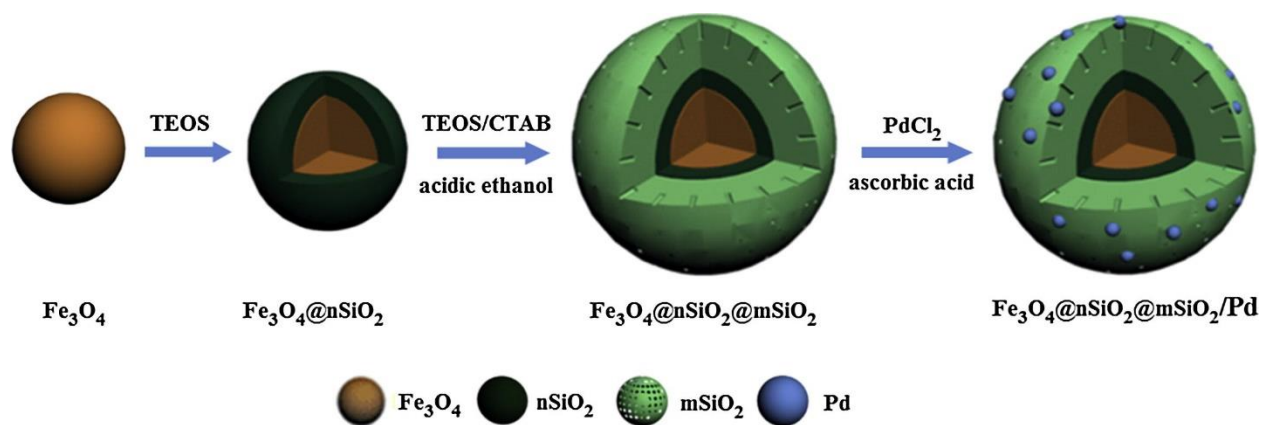


Figure 7 Schematic of $\text{Fe}_3\text{O}_4/\text{nSiO}_2/\text{mSiO}_2/\text{Pd}$ formation. Reprinted from Tian et al. (2015) with permission from Elsevier. Copyright © 2015 Elsevier Inc. License Number: 5055770011546.