Synergistic impact of photocatalyst and dopants on pharmaceutical-polluted waste water treatment: a review

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ABSTRACT
In last few decades, pharmaceutical waste management emerged as one of major environmental concern. These contaminants have shown their severe impact on living being. Several methods for their treatment such as UV degradation, nano-filtration, reverse osmosis and Photocatalysis are being used. Photocatalysis is a favourable and environmentally safe method for remediation of organic pollutants. Photocatalytic oxidation process involves destruction of the organic pollutants in presence of an oxidizing agent like oxygen, light source and the semiconductor photocatalyst. Metal oxides have shown greater capability towards treatment of Pharmaceutically Active Compounds (PhACs). In present review, authors have discussed about diverse metal oxides (TiO₂, ZnO, CuO, Fe₂O₃, Ag₂O, WO₃, Bi₂O₃ and Pt), their physical and chemical properties and unique ability to recycle waste water, mechanism of action, applications and their efficiencies along with possible solutions to make them more efficient. Metal oxides do have limitations like faster recombination rate, lower ability for the full usage of light and lesser migration of photo-generated electrons. Therefore, different doping materials, those are metals, non-metals and metalloids can be applied for improving their performances is suggested. In nutshell, it can be concluded that doped metal oxides can be used as potential tools for the treatment of organic pollutants.

Introduction
In the current scenario, rapidly increasing global population and industrialization is one of the major causes for the degradation of fresh water resources [1]. This panic situation ultimately increases the paucity of drinking water. Since the available fresh water resources (FWR) on earth is only 2.5%, in this some percentage is in the form of glaciers and ice sheets. Due to some reasons, available FWR is also depleting, consequently in the upcoming decades world is going to face major difficulties in fulfilling fresh water demands. In present observations, an attention has been drawn towards Pharmaceutically Active Compounds (PhACs) and promising methods for their treatment [2]. The antibiotics provided substantial advancement in the cure of infectious diseases and irriational enhancement, worldwide over the past years [3]. In order to release the antibiotics in the environment on a regular basis with inadequate facilities to treat wastewater, PhACs cause serious intimidation to both aquatic and terrestrial ecosystem, respectively, and acts as pollutants if not treated properly [4]. The bacteria are capable enough of developing resistance towards antibiotics after continuous exposure for longer duration. Pharmaceutical compounds are immune from biological degradation, they are able to maintain their chemical configuration for longer duration and pose harmful effects. The common antibiotics, present in wastewater eflluents are; antacids, steroids antidepressants, analgesics, anti-inflammatories, antipyretics, beta-blockers, lipiddowering drugs, tranquilizers and stimulants [5]. The whole ecosystem gets disturbed due to this, as they are capable enough in polluting water, soil and air. The healthcare personals are very ignorant towards the efficient disposal of excreted waste in the hospitals. The source of these PhACs is generally through excretion else, through direct scrapping of expired or unused pharmaceuitals. In both cases, they invade in water bodies and wastewater treatment plants, due to less stable and highly polar nature [6,7]. Classification of persistent pharmaceutical pollutants is discussed in Figure 01.

Therefore, treatment of waste water generated from pharmaceutical industries is mandatory, as they are highly toxic [8]. However, there are different chemical treatment methods available, but the oxidizing agents are struggling in decomposition and mineralization of the complex pollutant structure. Photocatalysis is an advanced oxidation process (AOP) and is an economical and sustainable method for treating pharmaceutical pollutants [9].

Apart from photocatalysis, there are various techniques which are adopted to treat wastewater; they are divided into four categories, as follows [10]. Physical treatment consists of – (a) Flow equalization, (b) Sedimentation, (c) Floatation, these methods are not
1. Photocatalysis

Photocatalysts are highly efficient methods of removing contaminants from waste water, and it is a technique which is found to be very efficient for in situ treatment of waste water and make it reusable. It is capable of converting refractory organics into rapidly biodegradable compounds and ultimately mineralizes them into non-toxic carbon dioxide and water.

List of some efficient metal oxide photocatalysts and dopants, to make them more efficient are discussed below. However, there are diverse non-metals and metalloids that are being used as photocatalytic material.

1.1. Effects of dopants on the physical and chemical properties of photocatalysts

Plenty of research works are being carried out towards the refinement of photocatalysts to overcome these concerns such as doping. The doping agents (such as WO$_3$, Pt, Bi$_2$O$_3$, etc.) inside the bulk photocatalysts (ZnO, TiO$_2$, CuO, etc.) provide a great dipole moment to change the shift of electron kinetic, and more number of electron can be shifted from valence band (VB) to conduction band (CB) of the photocatalyst, hence reducing the $E_g$ value [19]. By introducing heteroatoms in crystal lattice points, photocatalytic activities can be enhanced. Due to addition of dopants, the separation and transfer of photo-generated charge carriers upgraded and thus over-potential for driving effective redox reactions is minimized. Additional active sites are created after doping. In case of metal, metal and semiconductor are in direct contact with

### Figure 01. Classification of persistent pharmaceutical pollutants [4].
each other, along with the formation of electric field and transferring electrons due to Fermi level differ-
ence, hence resulting in shifting of energy band edges [20]. Electrons usually shifted from materials
with high Fermi level to that of low Fermi level until thermodynamically equilibrium state not created.
Therefore, a barrier at the metal-semiconductor inter-
face called Schottky barriers is constructed and per-
forms as an effective electron trap. So, the electron and
whole recombination are minimized [20].

(1) Advantages and disadvantages of diverse metal oxides photocatalysts: In metal oxide
based semiconductors, a closely packed structure
formed when metal ions form coordination bonds with oxides and shows wide range of applications
due to their unique physical and chemical properties [21]. Metal oxides are highly
investigated to understand their physical (i.e. electron transport, transparency and magnetism)
and chemical (i.e. gas sensing photocatalysis) phenomena due to their characteristics of having
strong electron-electron interaction along with their simple composition and diverse stoichio-
metry [22]. Metal oxides also create interest because they can be modified by chemical
and structural changes, doping of hetero-
atoms and preparation of nanocomposites. They have notable recycling property and good
stability making them more efficient [23]. Hence,
metal oxides have various applications such as
heavy metal removal, gas sensing, textile coating
for wearable electronic devices, biomedical
applications and photocatalytic degradation of
organic contaminants. They also show non-
toxicity and high stability in water [24]. The
major disadvantage of metal oxide semiconduc-
tors is photocatalysts have some drawbacks,
such as wide band gap energies (E_g), lower
light absorption, photo-induced electron and
holes recombine at a faster rate; this inhibits
the practical utilization of technology [25].This
limitation could be overcome by the modifications
in the metal oxides through chemical and
structural changes to widen the band gaps, doping
of hetero-atoms and preparing nanocompo-
sites are done to overcome this concern.

2.2 General mechanism for photocatalytic treatment

Photocatalytic oxidation process involves destruction of organic pollutant in presence of an oxidizing agent
like oxygen, an energetic light source and semicon-
ductor photocatalyst. The photons having larger energy
than the band-gap energy (ΔE) may result in the exci-
tation of valence band (VB) electron which promotes
the further possible reactions. The energy lower than
(ΔE) or longer wavelengths would cause, energy dissipa-
tion while absorption of photons in the forms of
heat. The formation of a positive hole (h+) in the
valence band (VB) and electron in the conduction
band (CB) is leaded due to the illumination of the
photocatalytic surface in the presence of sufficient
energy. The electron in the conduction band reduces
adsorption of oxygen on catalyst, whereas positive
hole in valence band oxidizes pollutant either directly
or OH• radicals are produced through water.

The following steps represent the activation of photocatalyst [23]:

Catalyst + visible light (hv) → e^-CB + h^+VB

e^-CB + O_2 → O_2^-

O_2^- + 2e^-CB + 2 H^+ → 2OH^- + OH^-

h^+VB + H_2O → H^+ + H^+ + OH^-

Dye + -OH → Degradation products (CO_2, H_2O etc)

(Figure 02).

If advancement in reduction process of oxygen
and oxidation process of pollutants does not occur
simultaneously in photocatalytic degradation of pol-
lutants, then there will be an increase in the rate of
hydrogen and electron recombination. The photo-
catalytic method itself divided into two categories such
as homogeneous and heterogeneous photocatalysis,
respectively. Homogeneous photo-Fenton photocata-
lysis does not involve irradiation of light; it requires
a light of up to wavelength 600 nm. In 1960s, it was
recognised as most applied AOPs for its capability of
degrading organic pollutants in highly saline
conditions [34–36]. Heterogeneous photocatalysis is a phenomenon in which photoreaction is accelerated in the presence of a catalyst. It is an appreciable chemical catalysis technique for waste water treatment. In this, the phase of catalytic variant differs from reactant. Heterogeneous photocatalysis consists of various kinds of reactions; hydrogen transfer, water detoxification, metal deposition, deuterium-alkane isotopic exchange, gaseous, aqueous pollutant removal, dehydrogenation and effective oxidations [37].

2.3. Photocatalyst materials

Synthesis of photocatalyst can be performed from various elemental categories: noble metals, transition metals and non-metals and metalloids according to their physical and chemical properties [38]. The development of highly efficient photocatalysts follows two major key methods for degrading antibiotics: (a) the photocatalyst should consist of narrow band gap so, it could afford to absorption on both UV light and visible light and (b) a suitable surface defect state or separating medium is needed, which has capability of trapping the photoexcited electrons or holes to stop their recombination. The photocatalytic materials can be used in two forms, as follows:

Undoped photocatalytic materials

The metal oxide photocatalytic materials are sustainable and promising applicant in removing organic pollutants from waste water. The metal oxides having lower recombination rate of charge carriers are considered as promising metal oxides and can be applied in organic pollutant degradation without any doping or modification.

Doped photocatalytic materials

The quick recombination of charge carriers and electrons at conduction band could not be trapped accurately by O₂ to yield superoxide radicals. Due to this property, use of metal oxide nanomaterials as photocatalysis has been prohibited. To overcome this drawback, researchers performed doping or modifying the band gap energy of the pristine materials with other metal oxide materials to reduce recombination of charge carriers and thus enhancing its photocatalytic rate [39–41].

3.1. Metal-oxides based photocatalyst materials

Metal oxides have wide range applications due to their unique physical and chemical properties [42], and they have strong electron-electron interaction [43]. In addition, metal oxide can be modified by changing their chemical and structural properties, hetero-atomic doping, or preparing nanocomposites [44]. Moreover, they have remarkably high recycling rate and high stability and it makes them efficient for various applications [23]. Hence, metal oxides have various applications such as, heavy metal degradation, poisonous gas sensing, textile coating for wearable electronic devices, biomedical applications and photocatalytic degradation of organic contaminants. Nanomaterials based on metal-oxides having well-controlled, structural, crystalline and surface features function as...
semiconductors with wide band gaps. They also exhibit favourable characteristics such as non-toxicity and high stability in the water [45].

3.1.1. Titanium oxide (TiO₂)

Fujishma and Honda was pioneer to explore different photocatalytic aspects of TiO₂. It is widely used material due to its exceptional characteristics of band positions, photo stable, electron-shift, charge separation and non-toxic [46]. It has anatase, rutile and brookite crystal structures. AnataseTiO₂ display more photocatalysis than rutile and brookite. In anatase phase, the mean effective mass of photo-generated electrons is lesser than rutile and brookite phases, consequently facilitating charge transfer and lower recombination rate [47]. TiO₂ has wide band gap of 3.0 to 3.2 eV. It can be synthesized by hydrothermal method. Niu et al. synthesized it using titanium (IV) tetraisopropoxide (TTIP) as Ti precursor along with calcination [48]. Although, it has two limitations, firstly it can only be triggered by UV light, and it only uses about 4% solar light and second, this most photoactive anatase phase has bad thermal stability and because of that it is vulnerable to high temperature [49]. This limitation can be overcome through metal doping such as Cu [50,51] Co [52], Mn [53], Fe [54] and Ni [55,56].

**Mechanism of action**

When TiO₂ nanoparticle is irradiated with hν, the wavelength of light for the photonic energy is λ < 400 nm. The excited photon leaves behind the vacant valence band, creating an electron-hole pair (e⁻–h⁺). Oxidative-reductive reactions series which occur at activated photon surface is as follows (Figure 03) [1]:

\[
\text{TiO}_2 + h\nu \rightarrow e^- + h^+ \\
e^- + O_2 \rightarrow O_2^-
\]

In the above reaction the h⁺ and e⁻ are powerful oxidizing and reducing agents respectively. The oxidative and reductive processes can be expressed as:

**Oxidative reaction:**

\[
h^+ + \text{Organic} \rightarrow \text{CO}_2 \\
h^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + H^+
\]

**Reductive reaction:**

\[
\cdot\text{OH} + \text{Organic} \rightarrow \text{CO}_2
\]

There are various metal ions are reported, for the enhancement of photocatalytic properties of TiO₂. For instance, oxidation state of Cu doped TiO₂ plays an important role in the production of H₂ through the process of intermediate reduction from CuO (Cu²⁺) to Cu₂O (Cu⁺). The excited electrons jump from conduction band of Cu₂O to conduction band of TiO₂, and the electrons assembled on TiO₂ conduction band are finally reduced to H₂ molecules [57]. When metal oxide such as ZnO is doped in TiO₂ oxygen vacancies gets created in the TiO₂ crystals and this is helpful in reducing charge recombination phenomena by catching excited electrons [58].

![Figure 03](image.png)  
*Figure 03. Representation of excitation of semiconductor illumination of band gap inducing‘electrons’ creation in the conduction band and ‘holes’ in the valence band [57,58].*
Applications

TiO$_2$ nanoparticles showed 95% efficiency in removing acetaminophen observed by Wu et al. in the presence of halide lamp source (250 W) for 100 min [59]. Khalaf et al. reported photocatalytic degradation of mefenamic acid using TiO$_2$ nanoparticles supported on borosilicate tubes (cut-off) 290 nm [60]. Calza et al. showed the photocatalytic degradation of diclofenac through TiO$_2$ nanoparticles under solar light irradiation [61]. Rayes et al. reported photocatalytic degradation of tetracycline using TiO$_2$ nanoparticles (0.5 g/L) under UV light irradiation [62]. Jalouli et al. evaluated the degradation of ibuprofen (600 mg/L) using TiO$_2$ nanoparticles (1 g/L) in the presence of UV light [63]. Liu et al. modified TiO$_2$ by adding Bi$_2$MoO$_6$ through solvothermal-calcination method and found that activity of Bi$_2$MoO$_6$ enhanced effectively in the presence of visible light towards the removal of antibiotics in aqueous solution. Here, conduction band of TiO$_2$ nanoparticle serves as the electron transfer platform which promotes effective charge separation at the TiO$_2$/Bi$_2$MoO$_6$ heterojunction interface. The degradation of ciprofloxacin, tetracycline and oxytetracycline reached 88%, 78% and 78%, respectively, within 150 min under visible light by using TiO$_2$/Bi$_2$MoO$_6$ heterojunction [64]. Lin and Yang reported the degradation of paracetamol by using Cu-doped TiO$_2$ photocatalyst [65]. Mugunthan et al. found that TiO$_2$-WO$_3$ showed degradation of diclofenac under visible light irradiation. The results disclose that the catalysts were efficient in the removal of diclofenac with degree of mineralization reach in 92%. It was noted that the photocatalytic efficiency of TiO$_2$-WO$_3$ mixed oxide catalysts have been approximated to be greater than that of the pure TiO$_2$ [66]. Liao et al. used Ag modified TiO$_2$ in the presence of ozone for the degradation of atenolol. Ozone facilitated formation of -OH radical through Ag nanoparticle, which acted as an electron extractor. Due to photo-induced charge separation efficiency of Ag$_2$O/TiO$_2$ fabricated heterojunction on zeolite composite reported an unprecedented photocatalytic performance for the degradation of norfloxacin [67]. Wei et al. showed that the Sr/Ag-TiO$_2$ nanoparticles have great photocatalytic stability and excellent reusability cycles of up to 94% for degrading 7α-ethinylestradiol (EE2) [68].

3.2 Zinc oxide (ZnO)

ZnO is explored universally, because of exceptional physical and chemical property which includes its firmness against photochemical corrosion; capacity to elevate antibacterial activity [69,70]. Usually ZnO exist in hexagonal wurtzite, cubic zinc-blend and rocksalt crystal structures. Thermodynamically most stable phase of ZnO is wurtzite along with hexagonal symmetry [71]. ZnO has large band gap of 3.37 eV and binding energy of 60 meV. Photo-induced charges recombine quickly in ZnO, which is identical to TiO$_2$ and decreases the photocatalytic quantum efficiency of ZnO. Although, this could be recovered, by doping or adding various materials like, TiO$_2$ [72,73], Cu$_2$O [74], SnO$_2$-x [75], Ta$_3$N$_5$ [76] and graphene oxide [77,78].

Mechanism of action

Photo-induced ZnO through sunlight having photonic energy ($h\nu$), which is equal to or greater than excitation energy ($E_g$), electrons are promoted from filled valence band (VB) to an empty conduction band (CB). This process produces electron-hole ($e^-/h^+$) pairs. The electron-hole pair emigrates at the surface of ZnO and incorporates in the redox reaction; thereupon $H^+$ reacts with water and hydroxide ions; hydroxyl radicals are produced while $e^-$ reacts with oxygen for the production of superoxide radical anions then hydrogen peroxide. Afterwards, formation of hydroxyl radicals takes place by the reaction of hydrogen peroxide with superoxide radicals. The pollutants adsorbed on the surface of ZnO, for rapid production of intermediate compounds, are attacked by resulting hydroxyl radicals, which are powerful oxidizing agents. Eventually, intermediates get converted into intermediate compounds as CO$_2$, H$_2$O and mineral acids. The mechanism of photodegradation of organic compounds in the presence of sunlight via redox reaction is as follows (Figure 04)[79,80]

\[
\begin{align*}
\text{ZnO}^{0/2} &\rightarrow \text{ZnO}(e^-_{\text{CB}}) + (h^+_{\text{VB}}) \\
\text{ZnO}(h^+_{\text{VB}}) + H_2O &\rightarrow \text{ZnO} + H^+ + \cdot OH \\
\text{ZnO}(h^+_{\text{VB}}) + OH^- &\rightarrow \text{ZnO} + \cdot OH \\
\text{ZnO}(e^-_{\text{CB}}) + O_2 &\rightarrow \text{ZnO} + \cdot O_2^- \\
\cdot O_2^- + H^+ &\rightarrow HO_2^- \\
\text{HO}_2^- + \cdot HO_2^- &\rightarrow \text{H}_2\text{O}_2 + O_2 \\
\text{ZnO}e^-_{\text{CB}} + \text{H}_2\text{O} &\rightarrow \cdot \text{OH} + \cdot \text{OH}^- \\
\text{H}_2\text{O}_2 + \cdot \text{O}_2^- &\rightarrow \cdot \text{OH} + \cdot \text{OH}^- \\
\text{H}_2\text{O}_2 + h\nu &\rightarrow 2\text{OH}^- \\
\text{Organic pollutants} + \cdot \text{OH} &\rightarrow \text{Intermediates} \\
\text{Intermediates} &\rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{When ZnO were grown on Cu@Cu}_2\text{O/ZnO, the} &\text{photo-excited electrons in surface plasmon state of Cu are introduced into the conduction band of Cu}_2\text{O by surmounting the Schottky barriers at the Cu@Cu}_2\text{O interface. Later, the generated active electrons in the conduction band of ZnO and the holes created in the valence band of ZnO are transferred to valence band of Cu}_2\text{O [74].}
\end{align*}
\]

Applications

Silva et al. reported pristine ZnO nanoparticles’ high degradation efficiency for ciprofloxacin at 300 mg/L under UV light [81]. According to Mugunthan et al., ZnO-WO$_3$ nanocomposite showed better efficiency in the
degradation of diclofenac, a pharmaceutical compound, a very common water pollutant. The mixed oxide material showed ~76% removal of diclofenac in the presence of visible light, and it displayed a better photocatalytic performance than the pure ZnO. It is also found that this nanocomposite is more stable and showed no significant change in performance after multiple photodegradation cycle [82]. Kaur et al. fabricated ternary photocatalysts, i.e. Ag/Fe$_2$O$_3$/ZnO heterostructures for the treatment of pharmaceutical wastewater in the presence of solar-light. These heterostructures showed enhanced photocatalytic activity for the degradation of ciprofloxacin which is degraded ~76.4% in comparison with pristine Fe$_2$O$_3$ nanorods (43.2%), ZnO nanoplates (63.1%), and Ag/ZnO (64.5%) under solar irradiation [83]. Zhang et al. reported the improved degradation of 7α-ethinylestradiol by Ag/ZnO hollow spheres as catalysts under UV illumination [84]. Ce-doped ZnO nanoparticles showed enhanced photocatalytic activity for the degradation pharmaceutical contaminants [85].

### 3.3 Copper oxide (CuO)

CuO is a p-type semiconductor which is used as heterogeneous photocatalytic material as it has huge availability, simple procedure for coating semiconductor, cheap and good photocatalytic activity [86,87]. CuO/Cu$_2$O is used as photoelectrode because it has small band gap of 2.17 eV, its photocatalytic performance is strongly dependent on the crystal structures and shapes CuO, which is of two different types: octahedral and cubes, where octahedra exhibits good performance over cubes [88]. According to Huang et al., when Cu$_2$O nanoparticles and microcrystals were tested for degrading the methyl orange, it was found that the stability of nanoparticles existed at ambient temperature. The Cu$_2$O/Cu nanocomposites showed photocatalytic activity at a much higher rate comparatively Cu$_2$O [89]. The narrower band gap leads to the fast recombination of charge carrier and it lowers photocatalytic performance; however, this problem can be overcome by doping and co-doping of Cu photocatalyst which increases shift in charge carrier interface and visible light absorption range by fabricating defects in its band gap position. When CuO (10%) doped on rare earth, perovskite material like samarium orthoferrite (SmFeO$_3$) showed photodegradation of RhB at a higher rate and enhanced photocatalytic activity [23,90].

**Mechanism of action**

Electrons in the conduction band and protons in valence band are generated at NPs surface, when CuO NPs are irradiated by sunlight. The holes counter with water are attached to the surfaces of CuO NPs to generate most reactive hydroxyl radicals (OH·). Meanwhile, oxygen acts as an electron acceptor by generating superoxide radical anion (O$_2^-$). The direct oxidation by the OH radicals and O$_2^-$ radicals destroy the dye. The mechanism of photocatalytic degradation of dyes through CuO NPs is as follows [91]:

$$\text{CuO} + h\nu \rightarrow e^-_{CB} + h^+_{VB}$$

$$h^+_{VB} + H_2O \rightarrow H^+ + OH$$

$$e^-_{CB} + O_2 \rightarrow O_2^-$$

$$O_2^- + H^+ \rightarrow H_2O_2 \rightarrow O_2 \rightarrow HO_2^+ + O^-$$

$$H_2O_2 + H^+ \rightarrow HO + OH^+ + O_2$$

$$H_2O_2 + e^- \rightarrow HO + OH^-$$

$$H_2O_2 + h\nu \rightarrow 2HO$$

$$O_2^- + OH + \text{dye} \rightarrow \text{degraded}$$

The hybrid CuO photocatalyst (10 wt%) doped on rare earth perovskite type oxide like samarium orthoferrite (SmFeO$_3$) showed increase in photocatalytic activity for photodegradation of RhB under the

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**Figure 04.** Degradation of organic pollutants through ZnO in the presence of solar light.
irradiation of visible light. In this, electron-hole pairs are generated on CuO and (SmFeO)₃ in the presence of visible light. As the conduction band edge potential of SmFeO₃ is more negative comparatively CuO, so the photo-generated electron will be moving towards the conduction band of CuO. Besides this, photo-induced holes will get transferred to CuO, because of more positive valence band of SmFeO₃ than CuO. Consequently, the charge carrier recombination effect will be delayed [92].

**Applications**

Yu et al. showed Zn doped Cu₂O displayed increased efficiency in degrading ciprofloxacin [93]. Zn doping enhanced the band gap of Cu₂O, increasing the charge separation and transmission efficiency [94]. Zn doped Cu₂O having oxygen vacancies may produce more -OH, h⁺ and -O₂⁻ active species. So, this increases specific surface area of Zn doped Cu₂O and can increase in more reaction sites [95].

### 3.4 Iron oxide (Fe₂O₃)

The ferum oxide has various crystallographic structures. They are α-Fe₂O₃ (hematite), β-Fe₂O₃, γ-Fe₂O₃, and ε-Fe₂O₃, among them the α-Fe₂O₃ is most stable one and it has hexagonal arrangement of iron atoms having six localised oxygen atoms [31,96]. Nevertheless, Fe₂O₃ is more advantageous over TiO₂, Bi₂O₃, ZnO, etc. as it has narrower band gap of ~2.2 eV, chemically stable, cheap, abundance and nontoxic. Apart from this, it has good capability of absorption. Fe₂O₃ has ferromagnetic behaviour which makes it advantageous in separating photocatalyst from the solution after the photocatalytic treatment [97]. α-Fe₂O₃ can be synthesized by different methods such as hydrolysis, hydrothermal, solvothermal, co-precipitation, thermal decomposition, ionic liquid assisted synthesis, combustion methods, etc. α-Fe₂O₃ and Fe₂O₃ were synthesized through the solid-state reaction expressed impressive photocatalytic activity than virgin Fe₂O₃ [98,99]. Fe₂O₃ has certain drawbacks like holes have lower diffusion length, recombination rate of electrons is high and conductivity is poor, various attempts have been approached by the scientists such as lowering the rate of recombination, use of nanostructures, alternating the doping material, increase in the conductivity and ability to shift the charge [100].

**Mechanism of action**

Hydrogen peroxide (H₂O₂) is decomposed by the Fe³⁺ ions those are present in aqueous phase, in the absence of light source, hydroxyl radical is generated as a result. The photo-Fenton reaction takes place in the presence of light source. Consequently, decomposition of H₂O₂ by ferrous or ferric ions takes place rapidly, resulting in the creation of radicals. All these soluble iron complexes are capable in absorption of UV radiation as well as visible light. The mechanism for the Fenton reaction is shown in the following equation:

\[
\text{Fe}^{2+} (aq) + H_2O_2 \rightarrow \text{Fe}^{3+} (aq) + OH^- + HO^- \\
\]

The Fe²⁺ can be converted back into Fe³⁺ through different mechanisms:

\[
\text{Fe}^{3+} (aq) + H_2O_2 \rightarrow \text{Fe}^{2+} (aq) + HO_2^- + H^+ \\
\text{Fe}^{3+} (aq) + HO_2^- \rightarrow \text{Fe}^{2+} (aq) + O_2 + H^+ \\
\]

In the presence of light source, the rate of photo-Fenton was found to be positively enhanced as compared to the dark condition. This is due to the simultaneous generation of the OH⁻ radicals in the system and regeneration of Fe²⁺ (aq) from the photochemical effect of light. Such an inversion cycle of Fe²⁺ (aq) → Fe³⁺ (aq) → Fe²⁺ (aq) continuously produces OH⁻ radical, it is provided that the concentration of H₂O₂ in the system is significant. If iron is present in small amount, then regeneration of the Fe²⁺ (aq) from Fe³⁺ (aq) is the rate-limiting step in the catalytic iron cycle [1].

The catalysts are capable in influencing efficiency of photodegradation processes. For instance, when the ZnO is doped in Fe₂O₃, change in energy levels occurs, the change in energy levels between Fe₂O₃ and ZnO causes the electron generation that was transferred from the ZnO to Fe₂O₃. The main driving force behind the migration of electrons is potential difference between the conduction band electrons or the valence band holes of two semiconductors. The photogenerated electrons transfer from the conduction band of ZnO to conduction band of Fe₂O₃ and the holes from valence band of ZnO to valence band of Fe₂O₃ were favourable thermodynamically. The recombination rate of photogenerated electrons and holes was decreased effectively because of that the life of the material gets extended and photocatalytic performance also increases [101].

**Applications**

Liu et al. synthesized SrTiO₃/Fe₂O₃ for the photocatalytic degradation of tetracycline. The SrTiO₃/Fe₂O₃ photocatalysts experiences a phenomenon called as the interfacial charge transfer (IFCT) mechanism. In this mechanism the range of photocatalyst for light-capturing extends by facilitating the migration of photogenerated e⁻ from the VB of the SrTiO₃ to Fe₂O₃, which partially reduces the Fe³⁺ to Fe²⁺. The adsorbed O₂ get reduced by Fe²⁺ on the surface of catalyst by generating H₂O₂. The photogenerated h⁺ present in the valence band of SrTiO₃ takes part in the photocatalytic reactions. The separation of charge happens spatially by IFCT and the e⁻·h⁺ recombination inhibited [102]. Enhanced photocatalytic degradation of carbamazepine under visible light illumination
shown by SrFeO$_{3-x}$/g-C$_3$N$_4$. Catalyst synthesized at 500°C for 2 h exhibited the highest photodegradation activity towards carbamazepine [103]. A multicomponent containing photocatalyst (Ag/ZnFe2O4/Ag/BiTa1-xVxO4), having an iron oxide, has also been synthesized for degrading sulphanilamide antibiotic. It was observed that the presence of V and Fe ions drove enhance photocatalytic activity under visible light illumination [104].

### 3.5 Silver (Ag$_2$O)

Silver is broadly known for its antimicrobial properties which makes it prominent from other nanoparticles. According to Das et al. in the treatment of water Ag is extensively explored as an effective adsorbent, Zhou et al. says that as a co-catalyst and as a membrane nanofilter [105–107]. Normally, silver nanoparticles are synthesized through the wet chemical reduction and thermal decomposition methods, currently the green synthesis is also being explored by using different plants such as Cordia dichotomaleaf and Prosopis sp. tree (Miri et al.) [108,109]. Ag NPs can be synthesized through chemical method also in which chemical reduction, electrochemical, irradiation-assisted chemical and pyrolysis methods are involved [110]. Ag NPs biosynthesized by Kumar et al.2019 by implementing various insertion of Mortihro berry extract (MBE) (1 mg, 5 mg and 10 mg) as capping and reducing agents for degrading MB dye. In this study, it was established that by synthesizing Ag in alkali conditions with 5 mg MBE revealed the formation of Ag with the ability of photodegradation [111].

**Mechanism of action**

In presence of UV light, visible light or red/NIR light, the electrons of Ag$_2$O are transferred to the conduction band from the valence band. Three reaction paths are instigated by the photogenerated holes and electrons: recombination with each other, reacting inside with lattice Ag$^+$ and O$^{2-}$, and reacting outside with the materials to finish off the photocatalytic process. The photogenerated holes may influence four reactions. First, dissolved oxygen in the solution can be converted into ozone by generated holes. Second, photo-oxidation and mineralization of dye occur when holes react with dye. Third, recombination of holes with photogenerated electrons lowers the quantum efficiency of Ag$_2$O. Fourth, the oxidation of lattice O$^{2-}$ in Ag$_2$Ooccurs due to holes, oxygen is released and the stability of Ag$_2$O is destroyed. Three more reactions can be induced through photogenerated electrons. First, oxidation of dye through ozone anion radicals formed through electrons, captured by ozone. Second, reacting with lattice Ag$^+$ for the generation of metallic Ag, decomposing the photocatalytic performance of Ag$_2$O. Finally, it could re-join with photo-generated holes [112].

\[
\begin{align*}
\text{Ag}_2\text{O} + hv & \rightarrow \text{h}^+ + \text{e}^- \\
\text{O}_2 + 2\text{OH}^- + 2 \text{h}^+ & \rightarrow \text{O}_3 + \text{H}_2\text{O} \\
\text{h}^+ + \text{dye} & \rightarrow \text{oxidation products} \\
\text{h}^+ + \text{e}^- & \rightarrow \text{hv} \\
2\text{O}_2^- + 4 \text{h}^+ & \rightarrow \text{O}_2 \\
\text{O}_3^- + \text{e}^- & \rightarrow \text{oxidation products} \\
\text{Ag}^+ + \text{e}^- & \rightarrow \text{Ag}
\end{align*}
\]

When the metal ion Zn$^{2+}$ is doped into Ag$_2$O lattice, it leads in the widening of band gap. Usually, the d-orbitals of metal make the conduction band and oxygen 2p orbitals usually compose the valence band of a metal oxide semiconductor. In this case, the dopant (Zn$^{2+}$) 3d orbitals would fall above the conduction band of Ag$_2$O, which should lead to the widening of the bandgap of the semiconductor. It is essential to mention that there are not much report are available regarding metal oxide doping into Ag$_2$O [113].

### 3.6 Tungsten trioxide (WO$_3$)

Oxide of tungsten is another semiconductor that is inexpensive photocatalytic material because of stable physicochemical properties, and small band gap of 2.4–2.8 eV, it responses good towards solar spectrum, excessive ability of the holes to oxidize in the valence band and low toxicity [114–116]. Although, pure WO$_3$ shows low photocatalytic activity because of low recombination of photoexcited electron hole pairs and conduction band are more positive [117–119]. WO$_3$ catalysts were prepared by Sayma et al., amorphous prex- tungstic acid used for the preparation, and it was more active than WO$_3$ samples obtained with different methods [120,121]. Researchers explored various modifications to overcome the less efficiency problem in WO$_3$, such as morphological control, deposition of noble metal, element doping, coupling with other semiconductor for heterojunction formation and modified using carbon based materials [122,123]. The lower conduction band edge potential (+0.3–0.5 V vs. NHE) of WO$_3$ is a major problem towards the reduction of oxygen ubiquitously available in aqueous solution [124]. So, the photoexcited electrons are gathered on the surface are prone to recombination, due to which WO$_3$ becomes in effective for the complete mineralization of the pollutants [125]. The widening of bandgap [126,127] and applying external bias [128] are common approaches for facilitating the single electron reduction process.

**Mechanism of action**

When the electrons in valence band of a nanostructured-based WO$_3$ are irradiated by light, they transfer to the conduction band, forming an
electron-hole pair. The formation of hydroxyl radicals occurs through the oxidation process of H₂O or OH⁻ molecules through valence band holes (h⁺_{vb}), whereas formation of superoxide radicals (O₂⁻) occurs through dissolved oxygen and electrons in conduction band (e⁻_{cb}) is a reduction process. The active radicals are responsible for breaking dyes in wastewater. The photocatalytic degradation reaction mechanism is as follows (Figure 05) [129]:

\[
\text{WO}_3 + h\nu \rightarrow h^+ (VB) + e^- (CB) \\
e^- + O_2 \rightarrow O_2^- \\
h^+ + OH^- \rightarrow OH \\
O_2^- + \text{dyes (pollutant)} \rightarrow \text{Degradation of dyes} \\
OH + \text{dyes (pollutant)} \rightarrow \text{Degradation of dyes}
\]

The addition of Cu(II) nanoclusters and titanium dioxide (TiO₂) showed increase in photocatalytic activity of WO₃. Cu(II)–WO₃/TiO₂ nanocomposite, showed that the positions of conduction band and valence band of WO₃ are more positive than those of TiO₂. Resultantly, the photogenerated electrons can move from the conduction band of TiO₂ to the conduction band of WO₃ and the photogenerated holes are transferred from the valence band of WO₃ to TiO₂. Besides this, if photons do not have adequate energy to excite TiO₂ but have ample energy to excite WO₃, hole in the valence band of WO₃ is still move towards the valence band of TiO₂.

Applications

Czech et al. recently reported that elsomereite/tungsten oxide@ZnS photocatalyst are potent photocatalyst in the degradation of pharmaceutical and personal care products (PPCPs). Their study reflected that elsomereite/tungsten oxide@ZnS heterojunction are 20–70% effective in degradation and good and stability and recyclability of selected PPCPs [130]. Zhang et al. reported that WO₃ nanosheets modified with Pt exhibit enhanced photocatalytic activity for the degradation of tetracycline than the pure WO₃ [131]. Chen et al. showed Ag decorated WO₃ nanofiltrates/g-C₃N₄ nanosheets heterostructure by a solvent evaporation and in situ calcination method for photocatalytic degradation of 10 mg/L tetracycline hydrochloride [132].

3.7 Bismuth oxide (Bi₂O₃)

Bismuth oxide has a direct band gap of 2.8 eV and is a p-type semiconductor drawn a huge recognition towards the application in the photocatalytic reactions due to its narrow band gap, fine optical electronic properties, great electrical conductivity and exceptional photoconductivity. Bi₂O₃ exists in six types of polymorphs, they are, α – (monoclinic), β – (tetragonal), γ – (cubic, bcc), δ-(cubic, fcc), ε – (orthorhombic) and ω – (triclinic). It is non-carcinogenic and nontoxic photocatalytic material and useful for the degradation of pollutants under visible light irradiation. Bulk Bi₂O₃ display lower photocatalytic activity when used alone so, various structures of Bi₂O₃ are doped with metal elements (rare earth and other metals) and two types coupling of metal oxide [23]. According to Cheng et al. when the three Bi₂O₃ (α-, β – and δ-) polymorphs were by sol-gel method for determining the photocatalytic degradation of MO and 4-CP under visible light irradiation. Enhanced photocatalytic activity for β-Bi₂O₃ observed in comparison with δ-Bi₂O₃ polymorph [133].
Mechanism of action

The rapid recombination of photo-generated electrons-holes and wide band gap are the reasons behind the poor photocatalytic activity. Remarkably, the photocatalytic removal of nitrate is much higher through $\beta$-Bi$_2$O$_3$ than that of $\alpha$-Bi$_2$O$_3$ and defect-controlled $\alpha$-Bi$_2$O$_3$-X samples, they can be assigned to make the excellent optical properties and efficiency of separation of carriers arose from the unique crystal structure. In addition, the defect-controlled samples were found to be more efficient towards NO removal and they followed the sequence as $\beta$-Bi$_2$O$_3$-X > $\beta$-Bi$_2$O$_3$ > $\alpha$-Bi$_2$O$_3$-X > $\alpha$-Bi$_2$O$_3$. The activation and adsorption of the gas molecule can be achieved through constructing oxygen vacancy or the production of -OH and -OOH radicals for the photocatalytic oxidation of NO. The oxygen molecule prefers to get the electron from electron efficient areas and hence, get activated for the formation of -OH radicals. In reverse, the water molecule tends to donate the electrons to electron-deficient region and hence get activated for the formation of -OH radicals [134].

In the presence of visible light irradiation, electrons (e$^-$) in the valence bands move towards conduction band, having same amount of holes (h$^+$) left in both the valence bands of Bi$_2$O$_3$ and Bi$_2$WO$_6$ respectively. The electrons in the conduction band of Bi$_2$O$_3$ were inoculated into the conduction band of Bi$_2$WO$_6$ due to more negative Bi$_2$O$_3$ conduction band than that of Bi$_2$WO$_6$. This is beneficial in the reduction of recombination. The photogenerated electrons were then trapped by O$_2$ for yielding O$_2^-$ and H$_2$O$_2$, and then to hydroxyl radicals [135,136]. Contrastingly, the photogenerated holes in Bi$_2$O$_3$ are powerful oxidative species, which can start off some unsaturated organic pollutants, which can induce subsequent decomposition. These photogenerated holes showed great performance in degrading organic compounds over the Bi$_2$O$_3$/Bi$_2$WO$_6$ catalysts (Figure 06) [137].

Applications

Niu et al. used Sr-doped $\beta$-Bi$_2$O$_3$ photocatalyst for the degradation of tetracycline drug [138]. Zhang et al. found the enhanced degradation of tetracycline by Ce$^{3+}$ doped Bi$_2$O$_3$ in the presence of visible light. The Bi$_2$O$_3$ hollow needle-shaped (HNB) doped with 5 wt% Ce shows good morphology, strongly absorbs visible light and good photocatalytic property. In the visible light of 300 W, the rate of photodegradation of tetracycline over HNB-Ce exhibit 89.1%, which is higher than the commercial Bi$_2$O$_3$ nanoparticles [139]. Jiang et al. used WO$_3$/Bi$_2$O$_3$ nanocomposite for the photocatalytic degradation of norfloxacin [140]. Bismuth ternary oxides have been extensively investigated for the degradation of PhACs. Huang et al. has recently shown Bi$_2$WO$_6$ shown photodegradation towards norfloxacin and enorflaxin with the efficiency of 92.95% and 94.58% respectively in 75 min [141].

3.8 Platinum

Platinum is another promising photocatalyst as it shows lot of applications like catalyst, biomedicine, and electronics. Nonetheless, platinum is not economical as it costs very high and this is barrier for its commercialization [142]. Due to its fast electron trapping from conduction band, Pt is the most efficient co-catalyst for the extraction of photo-generated electrons, as the recombination of charge carrier prohibited and photocatalytic performance

Figure 06. Schematic diagram of charge separation in a visible light irradiated Bi$_2$O$_3$/Bi$_2$WO$_6$ heterojunction.
is enhanced [143,144]. According to Oh et al. and Jaramillo-Páez et al., Pt is efficient to enhance the visible light absorption and deliver it to the semiconductor photocatalyst, consequently enhancing the photocatalytic activity [145,146].

**Mechanism of action and application**

The mechanism of action for platinum (Figure 07) is explained along with dopant as platinum is not that much efficient when used without doping as it is mentioned above that it is a co-catalyst. Samsudin et al. in their experiment found that Pt@BIVO₄ doped with g – Ce₃N₄ showed high COD removal in comparison with BIVO₄/g-C₃N₄ in the presence of sunlight. It was observed that when pt added as an active site, it changed the conventional heterojunction-type structure to Z-scheme hetero-structure. The mechanism is proposed as the conduction band electrons of BIVO₄, move towards valence band of g-C₃N₄ and jumped to its conduction band. The Schottky contact among g-C₃N₄ and Ptelevate the amount of reduction of O₂ to

![Figure 07. Illustration of the proposed photocatalytic mechanism of Pt@BIVO4/g–C3N4 (Re-print with permission from Springer Nature [146]).](image)

| S. No. | Photocatalyst | Properties | Efficiency | Synthesis | Applications | References |
|-------|---------------|------------|------------|-----------|--------------|------------|
| 1     | NiO           | Shape-Spherical, Cubic, Size – 6 to 10 nm, High purity, increased degradation, when pH of the solution increased Band gap – 3.6 eV | Better photocatalytic efficiency compared to TiO₂ | Sol-gel, Solvothermal | Degradation of phenol at 266 nm and Acid red 1 degradation | [153,154] 150, 151 |
| 2     | Nb₂O₅         | Band gap – 3.4 eV | Similar photocatalytic activity as TiO₂ | Solvothermal | Oxidative decomposition of acetic acid and durable as catalytic activity maintained 85% in degrading dye after 10 cycles of reaction | [155,156] 152, 153 |
| 3     | Ta₂O₅         | Band gap – 3.2 eV | Good efficiency | Synthesis by using TaCl₃ as precursor | Degrades gaseous formaldehyde | [157] 154 |
| 4     | ZrO₂          | Less efficient than TiO₂ | Synthesized through high current electric arc discharge of Zr electrodes in water | Organic compounds – 2-propanol, Aniline, 4-chlorophenol and 4 – nitrophenol, RhB and for the environmental transformation of nitrite, EDTA and Cr(VI) | | [158,159] 155, 160 |
| 5     | Ce₂O₃         | n-type semiconductor, band gap – 2.94 eV | Thin films are inefficient for degrading methylene blue, commercial Ce₂O₃ able to degrade toluene when used in gaseous form, Less efficient than TiO₂ Efficient in some reductive reactions | Reverse microemulsions | For the degradation of azo dye acid orange 7, degradation of Acidic Black108 | [159–164] |
| 6     | Ga₂O₃         | Band gap – 4.8 eV | Prepared using Ga(NO₃)₃ as precursor | Decomposition of perfluorooctanoic acid is environmental persistants, organic pollutants | | [165,166] |
form ·O₂⁻ radicals. Whereas, the holes in the valence band of BiVO₄ reacted with water to produce ·OH radicals [146].

1. **Other metal oxides**

However, above mentioned, all the metal oxides are widely explored for the photocatalytic degradation of Pharmaceuticals, other less explored metal oxides, such as NiO, Nb₂O₅, Ta₂O₅, ZrO₂, CeO₂, and Ga₂O₃ discussed briefly in Table 1, have also been investigated for the treatment of PhACs. These also have displayed potential in photocatalytic degradation of pharmaceutical-polluted water; although, besides their limitation to harness visible light, other concerns include environmental safety due to nanotoxicity [147] and current higher cost [148–152] in comparison with other metal oxides.

2. **Conclusions and future prospects**

In this review diverse metal oxides, exhibiting efficient photocatalytic activities are explored. Several researches are being carried out in the direction of waste water treatment. The PhACs pollution in water is major concern as they are persistent in nature and also some bacteria have potential of developing resistance against the former so, these PhACs are very challenging to treat, the metal oxides have shown great capability in their treatment. Metal oxides are promising photocatalytic materials, some very efficient categories that are currently being explored are discussed here. They have distinctive physical and chemical characteristics; stable, economical and their band gap energy can be adjusted to make them more efficient for the absorbing light and intensifying catalytic capability. When the photocatalysts have applied alone, sometimes they show lesser efficiency but this can be overcome through doping with other metals and non-metals, it is also required that the material used for doping, should enhance photocatalytic activity as well as exhibit exceptional re-cycling ability for an efficient application. There is need of more research for the treatment of the residual heavy metal, those are resultant of metal oxide treatment, and they could act as heavy metal pollution.

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