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Bulk and Nanocatalysts Applications in Advanced Oxidation Processes

Luma Majeed Ahmed

Abstract

Advanced oxidation processes (AOPs) are considered to be vital methods for treating the contaminations produced mainly by the human activations. In present-day, UV light or solar light, bulk and nano- photocatalysts are often used to enhance this technology by creating the highly reactive species such as the hydroxyl radicals. Extreme hydroxyl radical is considered as a key to start the photoreaction. Photoreaction is widely used in treatment of Lab and industrial contaminations, preparation of compounds and produced the renewable energy, so it's classified as green technique. In order to improve the efficiency of this reaction with fabrication the surface of the used photocatalyst such as metal doped, sensitized and produced a composite as bulk catalyst or nano catalyst.

Keywords: nanocatalysts, bulk catalyst, advanced oxidation processes, wastewater treatment, photocatalysis, Fenton reaction, photo-Fenton

1. Introduction

In this section, the advanced Oxidation Processes concepts will be related to use of the bulk and the nano- catalysts as vital materials for easily generating a highly oxidizing species and reactive oxygen species (ROSs) such as in aqueous or alcoholic solution [1]. ROSs are contains three primary kinds: superoxide anion ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2) and the hydroxyl radical (HO^{\bullet}) [2], which produced from reaction of adsorbed oxygen molecule on catalyst's surface with one electron in conductive band under illumination by light as UV, or visible or solar light, this mechanism is useful to reduce the recombination process and increased the life time of hole in valance band [3, 4]. As explained in **Figure 1**.

The ROSs are having the electron configurations as tabled in **Table 1** [5–8].

2. Advance oxidation process applications

In the last few years, several researches have predominated in many universities and research centers on the scientific ventures to mainly treat the contaminations that produced by textile factories [9–11], reduced the degradation of food's

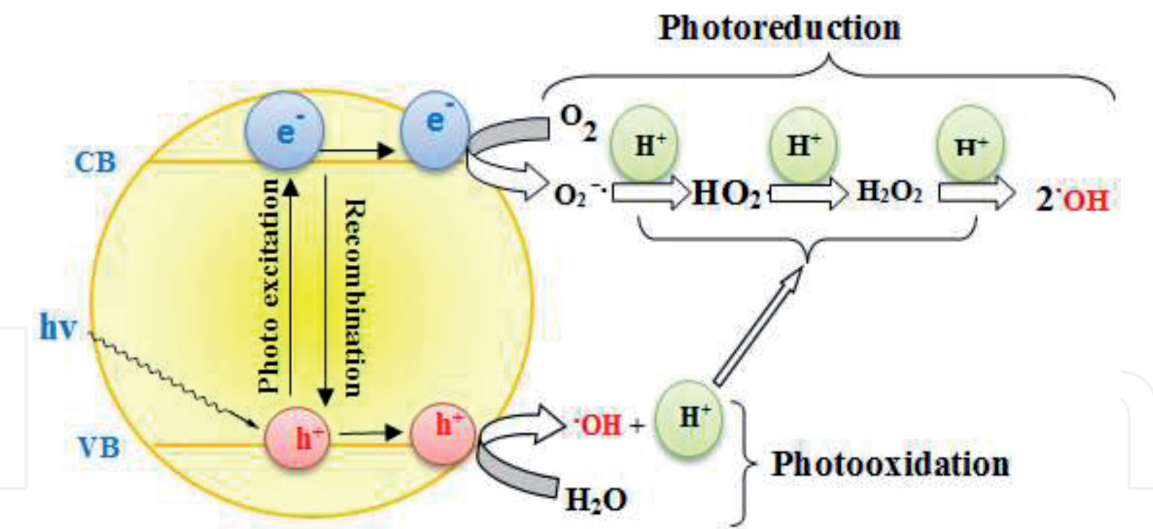


Figure 1.
Essential mechanism for generating the ROSs under illumination of photo-catalyst particles [1].

Oxidation and reactive radical species types	Electronic configurations	Chemical formulas	Oxidation potential V
Oxygen molecule	$\sigma^* 2p$ — $\pi^* 2p$ $\pi 2p$ $\sigma 2p$	O_2	1.23
Molecular singlet oxygen	$\sigma^* 2p$ — $\pi^* 2p$ $\pi 2p$ $\sigma 2p$	$^1O_2^*$	2.42
Superoxide radical anion	$\sigma^* 2p$ — $\pi^* 2p$ $\pi 2p$ $\sigma 2p$	$O_2^{\cdot-}$	-0.33
Peroxide ion	$\sigma^* 2p$ — $\pi^* 2p$ $\pi 2p$ $\sigma 2p$	O_2	1.78

Table 1.
Electronic configurations and chemical formulas for the ROSs types.

dye [12], decolorization of colored organometallic complexes [13], degradation of toxic cyclic compounds [14] and produced a hydrogen from alcohol as renewable energy [15]. The effective materials for all above mention research are generated the hydroxyl radical in aqueous solution with maximum oxidation power equals to 2.8 V [1]. Based on to the AOPs, the common sources for creation

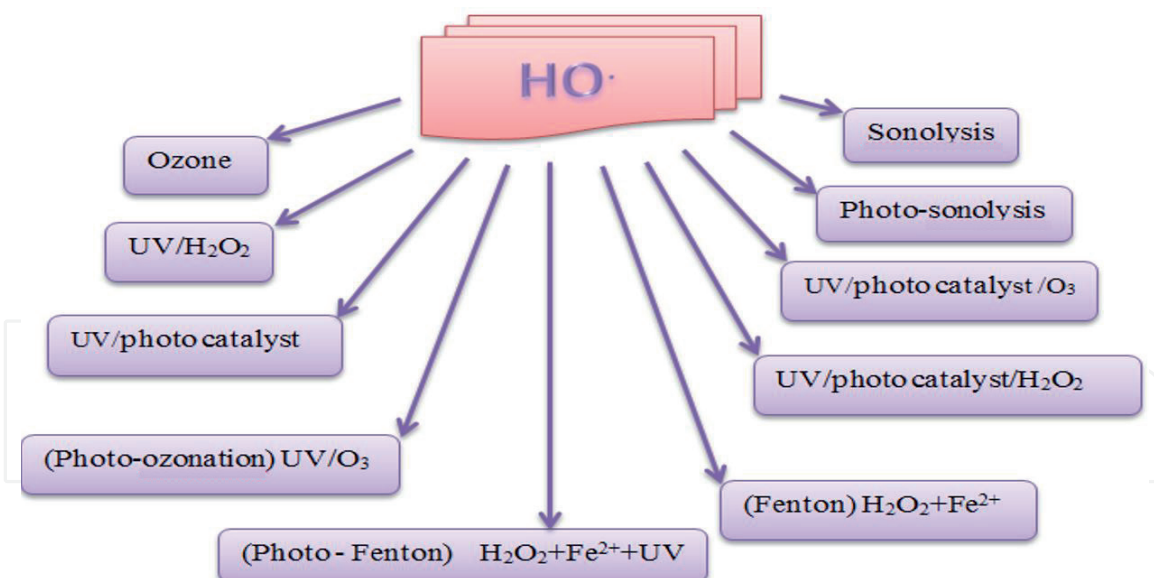


Figure 2.
 Schematic diagram of common sources of OH in advanced oxidation processes.

of OH in AOPs are illustrated in **Figure 2**, which regards as power to star the dark or photo reactions [1, 16–19].

Fortunately, the benefits of AOPs are more than those of drawbacks. The benefits of AOPs are summarized up as [1, 20] follows to:

1. Create a large number of free radicals species.
2. Have the appropriate potential to depress the hazardous organic pollutants by complete their mineralization and producing CO₂ and H₂O.
3. Reduce the time of dark or photoreaction.
4. Have low economic cost.

Whereas, the drawbacks of AOPs [1, 21] are quenching the reaction rate with increasing the scavenger contains (mostly peroxide ion) and may be generated the undesirable hazardous products that prevented the complete of mineralization process, hence, the altered of pH or using further cost steps may be essentially to treat their problems.

3. Bulk and nano-catalysts

In general, the catalysts may be metal or alloy or semiconductor. Semiconductor is wide used as catalyst and can be element or compound as amorphous or crystalline or rock salt crystal. Because of semiconductors have intermediate properties between metal and insulator, which has given them rescannable electronic and structural properties, hence, semiconductor is classified as a better-known kinds, as mentioned in **Figure 3** [22–24].

The usages of the bulk and nano catalysts are increment with increasing the development of life activations. The catalysts were known for the long time to increase the rate of reaction with decreasing the time of reaction and the activation energy in dark reaction or photoreaction. In order to use the catalyst in

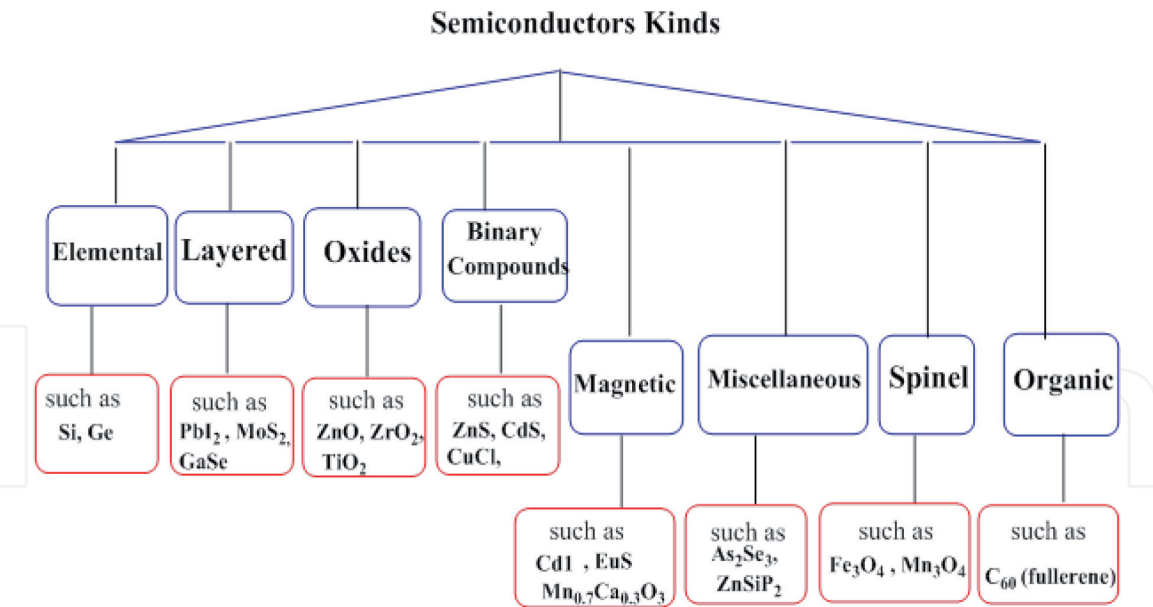


Figure 3.
Better-known kinds of semiconductors.

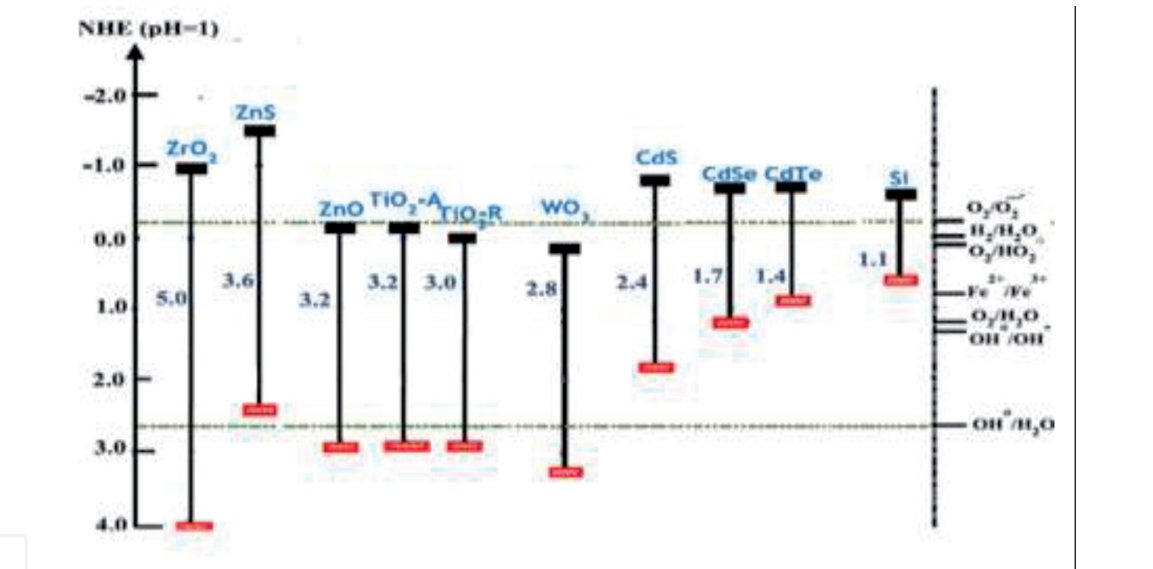


Figure 4.
Band gap energy positions of different photo-semiconductor at pH = 1.

photoreaction as photo catalyst, must have a band gap with ranged about 1.1 eV to 5.0 eV [1, 24]. Referring to **Figure 4**, several band gap energy positions of some common photo catalysts can be displayed [1, 25–27].

The mainly problem in bulk and nano catalyst is recombination process, which results in diminishing the efficiency of used photocatalyst by returning the photoelectron from conductive band to valance band and reacting with photohole immediately. The recombination includes four kinds can be followed in **Table 2** and **Figure 5** [1, 28–30].

In order to improve the activity of photocatalysts must depress the recombination with modify their surfaces with three main methods: surface sensitization, metalized photocatalyst surface and coupled for two or more photocatalysts as Composite. The details of these modification methods are mention in **Table 3** and **Figure 6** [40].

Kinds	Other name	Info	Type of photocatalyst
Direct recombination	Band-to- band recombination	In this kind, the transition occurs as a radiative transition in direct band gap semiconductor. It is created when the Free photo electron in CB drops directly into free photo hole (an unoccupied state) in the VB and associated together. Note Figure 5(A) .	ZnO have a direct band gap.
Volume recombination	Centers recombination or Trap-assisted recombination	This case obtains, when defect of semiconductor by impurities that given a new levels (as traps of photoelectron and photohole). It leads to liberate heat as phonon in indirect band gap semiconductor. Note Figure 5(B) .	Pure TiO ₂ and defect of TiO ₂ by metal, which had given an indirect band gap.
Surface recombination	Recombination of an exciton	This case occurs at low temperature, when the traps at or near the surface or interface of the semiconductor, capture the photo electron- hole as exciton. That attitude to dangling bonds caused by the sudden discontinuation of the semi-conductor crystal with energy just below the band gap value. Note Figure 5(C) .	It happed in solar cells and light emitting diode (LED) containing shallow levels.
Auger recombination	—	This recombination involves three carriers: Free photo electron, free photo whole recombine, and the emitting the energy as heat or as a photon (non-radiative process). The transition of energy deals with as intra-band transitions, which resulting when either electron elevates in higher levels of conduction band or hole deeper push into the valence band. Note Figure 5(D) .	This case can be obtained wit short lifetime when heavy doping defects (like Ag) in direct-gap semiconductors under present sunlight.

Table 2.
The most common recombination types concepts.

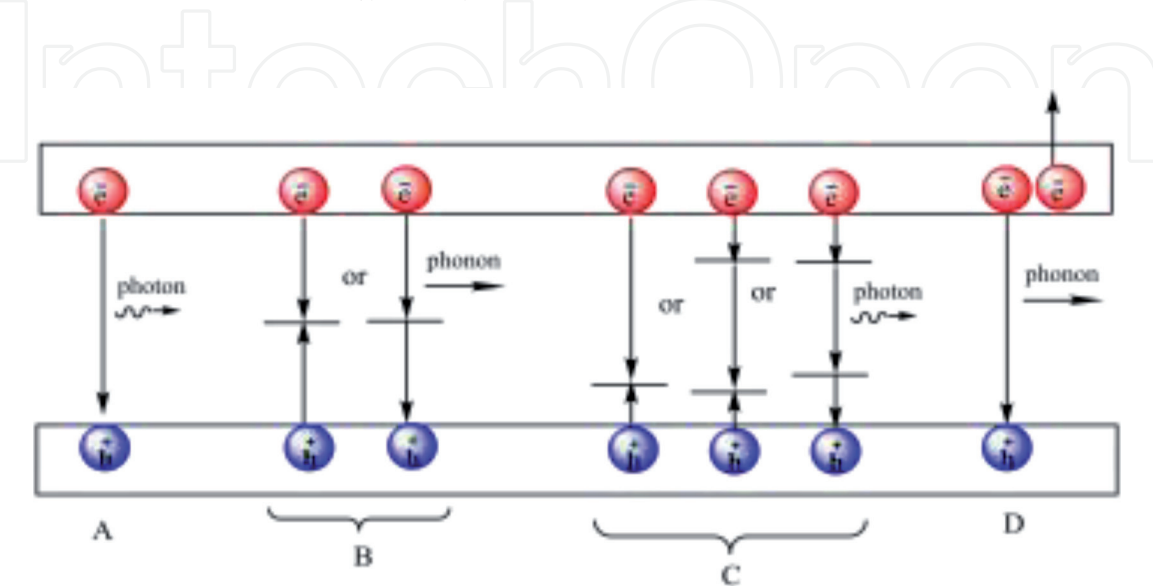


Figure 5.
The schematic diagram of the most common recombination kinds.

Kinds	Info	References
Surface sensitization	This case favors for modified the wide band gap semiconductor by physical or chemical adsorption of colored materials mostly dye. The colored material will absorb the visible or solar light after irradiation, and excite it either singlet or triplet excited state. The excited colored material will inject its electron via the conductive band of semiconductor.	[31–34]
Metalized photocatalyst surface	The metal deposits on the surface of semiconductor must choose with high work functions of metal compared to work function of the metal in semiconductor. The doped metal will act as sink of electron, with create a Schottky barrier. That will increase the lifetime of photo hole. Examples: Pt and Au doped on TiO ₂ , Ag doped on ZnO, Cr and Mn doped on ZnS .	[2, 4, 14, 35–37]
Coupled for two or more photocatalysts as composite	<p>When the energy of the irradiated light is not enough to promote electron from conductive band of the photocatalyst, that attitude to it has a big band gap, hence, can couple it with other semiconductor has a small band gap. This coupling process includes three kinds: type (I), type(II) and type(III).</p> <p>Type I</p> <p>Type II</p> <p>Type III</p> <p>Examples: CdS-ZnS (Type I), WO₃-TiO₂ (Type II). And Mn₂O₃-ZrO₂ (Type III).</p>	[16, 30, 38–39]

Table 3.
The description of the methods for modifying photocatalysts [31–39].

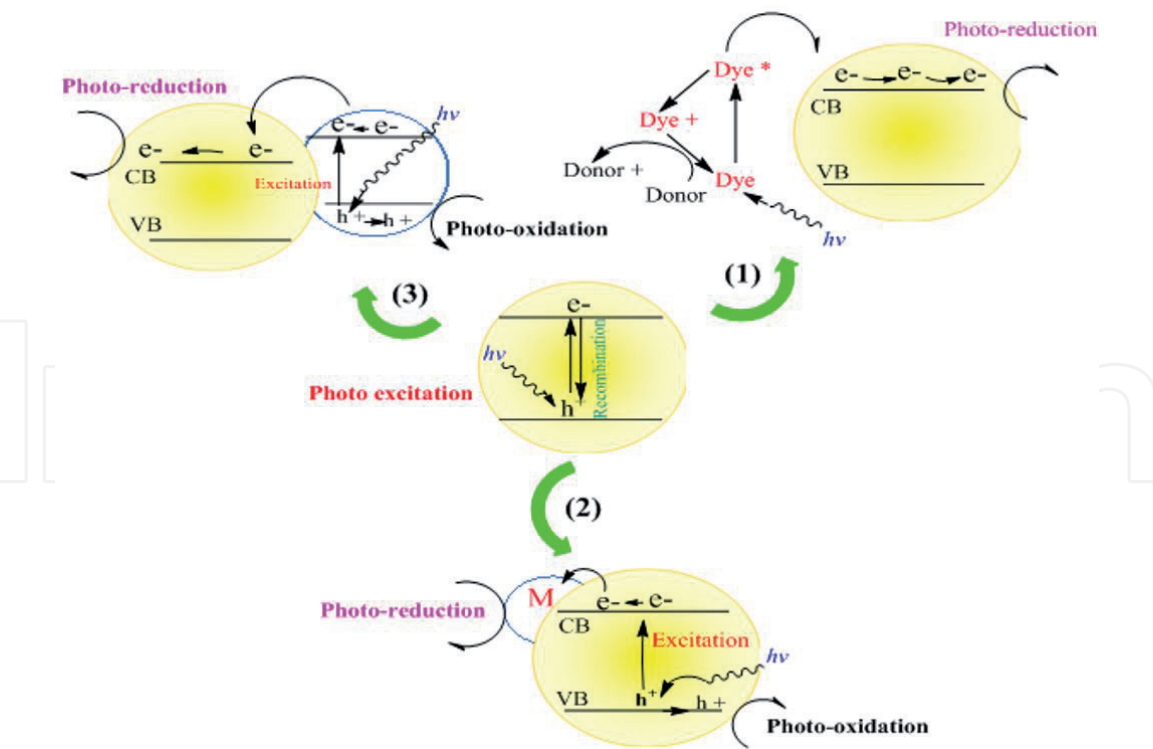


Figure 6.
Schematic diagram for modification of photocatalyst surface [40].

Application field	Type of used AOPs	Efficiency	References
Textile dye Reactive red 2 dye	O ₂ /UV-A(250 W)/ZnO/ H ₂ O ₂	89.8% (Photodecolorization) (5 mmole/L) of H ₂ O ₂ (T = 25°C), (pH = 10)	[41]
Textile dye direct orange dye	O ₂ /UV-A(250 W)/ZnO	92.7% (Photodecolorization) (T = 35°C), (pH = 6.68)	[42]
Textile dye reactive yellow 14 dye	O ₂ /UV-A(250 W)/ZnO	91.41% (Photodecolorization) (T = 38°C), (pH = 6.75)	[43]
Industrial dye Chlorazol black BH dye	O ₂ /UV-A/ZnO	99.07% (Photodecolorization) (T = 15°C), (pH = 7.63)	[44]
Industrial dye Acid Red 87(Eosin (Eosin Yellow) dye	O ₂ /UV-A(125 W)/ZnO	74.4.5% (Photodecolorization) (T = 38°C), (pH = 8.6)	[32]
	O ₂ /UV-A(250 W)/ZnO	98.5% (Photodecolorization) (T = 38°C), (pH = 8.6)	
	O ₂ /Solar/ZnO	96.5% (Photodecolorization) (T = 42°C), (pH = 8.6)	
Textile dye Dispersive yellow 42 dye	O ₂ /UV-A(125 W)/ZnO	94.40% (Photodecolorization) (T = 20°C), (pH = 7.7)	[10]
	O ₂ /UV-A(125 W)/ZnO/Fe ²⁺	60.86% (Photodecolorization) (T = 20°C), (pH = 7.7)	
	O ₂ /UV-A(125 W)/ZnO/ Fe ²⁺ +1% H ₂ O ₂	16.44% (Photodecolorization) (5 x 10 ⁻⁴ mole/L) of Fe ²⁺ (T = 20°C), (pH = 7.7)	

Application field	Type of used AOPs	Efficiency	References
Drug dye Cobalamine(Vit B12)	O ₂ /UV-A(250 W)/ZnO	79.33% (Photodecolorization) (T = 30°C), (pH = 6.5)	[19]
	O ₂ /UV-A(250 W)/ZnO/ K ₂ S ₂ O ₈	88.75% (Photodecolorization) (1 x 10 ⁻⁴ mole/L) of K ₂ S ₂ O ₈ (T = 30°C), (pH = 6.5)	
	O ₂ /UV-A(250 W)/ZnO/ 0.025% H ₂ O ₂	90.80% (Photodecolorization) (T = 30°C), (pH = 6.5)	
	O ₂ /UV-A(250 W)/ZnO/ K ₂ S ₂ O ₈ + 0.025% H ₂ O ₂	95.85% (Photodecolorization) (1 x 10 ⁻⁴ mole/L) of K ₂ S ₂ O ₈ (T = 30°C), (pH = 6.5)	
Food dye Carmoisine (E122) dye	O ₂ /UV-A(250 W)/ZnO	73.11% (Photodecolorization) (T = 18°C), (pH = 7.55)	[12]
	O ₂ /UV-A(250 W)/ZnO/ 0.1% H ₂ O ₂	62.58% (Photodecolorization) (T = 18°C), (pH = 7.55)	
	O ₂ /UV-A(250 W)/ZnO/ Fe ²⁺	36.99% (Photodecolorization) (1 x 10 ⁻⁵ mole/L) of Fe ²⁺ (T = 18°C), (pH = 7.55)	
Lab materials Co(II) Complex of Schiff Base	O ₂ /UV-A(250 W)/ZnO	99.11% (Photodecolorization) (T = 38°C), (pH = 7.55)	[13]
Industrial dye Methyl green dye	O ₂ /UV-A(400 W)/ ZnO NPS	37% (Photodecolorization) (T = 25°C), (pH = 5.4)	[35]
	O ₂ /UV-A(400 W)/Ag(2%) ZnO NPs	87.37% (Photodecolorization) (T = 25°C), (pH = 5.4)	
Liberated of hydrogen from Methanol as renewable energy	Ar/UV-B(1000 W)/ (0.5 Pt) TiO ₂ NPS	8.8% (Photo hydrogen production) (T = 25°C), (pH = 7.3)	[14]
	Ar/UV-B(1000 W)/ (0.5 Au) TiO ₂ NPS	4.5% (Photo hydrogen production) (T = 25°C), (pH = 7.3)	
Industrial dye Light Green SF Yellowish (Acid Green 5) Dye	O ₂ /UV-A(400 W)/ TiO ₂	90.2% (Photodecolorization) (T = 20°C), (pH = 7.3)	[45]
	O ₂ /UV-A(400 W)/ TiO ₂ NPS	88.1% (Photodecolorization) (T = 20°C), (pH = 7.3)	

Application field	Type of used AOPs	Efficiency	References
Industrial dye Safranine O Dye	O ₂ /UV-A(125 W)/ TiO ₂ NPS	90.2% (Photodecolorization) (T = 30°C), (pH = 6)	[34]
	O ₂ /UV-A(125 W)/ TiO ₂ NPS/ Fe ²⁺	85.92% (Photodecolorization) (1 x 10 ⁻⁴ mole/L) of Fe ²⁺ (T = 30°C), (pH = 6)	
	O ₂ /UV-A(125 W)/ TiO ₂ NPS/ 0.1% H ₂ O ₂	92.73% (Photodecolorization) (T = 30°C), (pH = 6)	
	O ₂ /UV-A(125 W)/ TiO ₂ NPS/ 0.1% H ₂ O ₂ + Fe ²⁺	98.83% (Photodecolorization) (1 x 10 ⁻⁴ mole/L) of Fe ²⁺ (T = 30°C), (pH = 6)	
Industrial dye Acid Red 87 (Eosin Yellow) dye	O ₂ /UV-A(250 W)/ TiO ₂ NPS	63.58% (Photodecolorization) (T = 25°C), (pH = 6.09)	[16]
	O ₂ /UV-A(250 W)/ TiO ₂ NPS+ H ₂ O ₂	50.44% (Photodecolorization) (1 x 10 ⁻² mmole/L) of H ₂ O ₂ (T = 25°C), (pH = 6.09)	
	O ₂ /UV-A(250 W)/ WO ₃ NPS	27.84% (Photodecolorization) (T = 25°C), (pH = 6.09)	
	O ₂ /UV-A(250 W)/ WO ₃ NPS+ H ₂ O ₂	21.54% (Photodecolorization) (1 x 10 ⁻² mmole/L) of H ₂ O ₂ (T = 25°C), (pH = 6.09)	
	O ₂ /UV-A(250 W)/ (0.5) WO ₃ -TiO ₂ nanocomposite	25.11% (Photodecolorization) (T = 25°C), (pH = 6.09)	
	O ₂ /UV-A(250 W)/ (0.5) WO ₃ -TiO ₂ nanocomposite+ H ₂ O ₂	73.88% (Photodecolorization) (1 x 10 ⁻² mmole/L) of H ₂ O ₂ (T = 25°C), (pH = 6.09)	
Industrial dye Methyl green dye	O ₂ /UV-A(250 W)/ZrO ₂	92.31% (Photodecolorization) (T = 30°C), (pH = 5.4)	[46]
	O ₂ /UV-A(250 W)/ ZrO ₂ + Fe ²⁺	39.93% (Photodecolorization) (1 x 10 ⁻⁴ mmole/L) of Fe ²⁺ (T = 30°C), (pH = 5.4)	
	O ₂ /UV-A(250 W)/ ZrO ₂ + 1.5% H ₂ O ₂	98.78% (Photodecolorization) (T = 30°C), (pH = 5.4)	
	O ₂ /UV-A(250 W)/ ZrO ₂ + K ₂ S ₂ O ₈	74.62% (Photodecolorization) (1 x 10 ⁻⁴ mmole/L) of K ₂ S ₂ O ₈ (T = 30°C), (pH = 5.4)	
Lab materials Fe(II)-(4,5- DIAZAFLUOREN-9- ONE 11) COMPLEX	O ₂ /UV-A(400 W)/ Mn ₃ O ₄	22.64% (Photodecolorization) (T = 15°C), (pH = 4)	[47]
	O ₂ /UV-A(400 W)/ (1)Mn ₃ O ₄ - (4) ZrO ₂ nanocomposite	40% (Photodecolorization) (T = 17°C), (pH = 4)	

Application field	Type of used AOPs	Efficiency	References
Textile dye Reactive blue 5 dye	O ₂ /UV-A(400 W)/ ZnS NPs	59% (Photodecolorization) (T = 15°C), (pH = 6.3)	[36]
	O ₂ /UV-A(400 W)/ Cr-ZnS NPs	94% (Photodecolorization) (T = 17°C), (pH = 4.1)	
Industrial dye Congo red dye	O ₂ /UV-A(400 W)/ ZnS NPs	95% (Photodecolorization) (T = 30°C), (pH = 7.5)	[39]
	O ₂ /UV-A(400 W)/ CdS-ZnS nanocomposite	98% (Photodecolorization) (T = 30°C), (pH = 7.5)	

Table 4.
Some applications of bulk and nano photocatalyds in AOPs, with environment chemistry and green chemistry.

4. Used of bulk or nano catalyst in AOPs

There are many common application of AOPs in environment fields by using the white photocatalyst or its modified such as ZnO, TiO₂ ZrO₂, ZnS, WO₃, CdS and Mn₃O₄. The efficiencies with used these photocatalysts are altered with using AOPs methods. The efficiency of the photoreaction depends mostly on the concentration of colored material, initial pH which affected on the surface of photocatalyst and the temperature. As shown in **Table 4**.

5. Conclusions

This chapter focuses on the source of hydroxyl radical which produces via the advance oxidation process. Indeed, this process interests in the forming the different species, which in the final step generates a hydroxyl radical. The photocatalyst enhances the generating of hydroxyl radicals (2.8 V) in aqueous solution under Uv- light or visible or solar. The photoexitation of photocatalyst leads to jump of electron to conductive band then return to valance band and liberates a hot this process called recombination. It is depressed the efficiency of photoreaction. However, some procedures used to modify the photocatalyst surface.

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