



Review Article

Non-TiO₂ Based Photocatalysts for Remediation of Hazardous Organic Pollutants under Green Technology-Present Status: A Review

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Accepted on 19th July 2015

ABSTRACT

Significant amounts of synthetic organic dyes are being used in leather, textile, paper, pharmaceutical, cosmetic and food industries. The remnant dyes disposed in to aquatic sources cause serious ecological concerns because of their less biodegradability and mutagenic/carcinogenic nature. Advanced oxidation process involving heterogeneous photocatalysis offers a cost effective green technology for remediation of several organic pollutants in industrial effluents. TiO₂ has been extensively studied for this purpose because of its ease of synthesis, chemical and biochemical inertness, and good quantum efficiency under UV irradiation. The present review is the first attempt to discuss non TiO₂ based photocatalysts projected for this purpose.

Keywords: AOP, Photocatalysis, TiO₂, Ternary metal oxides, Green Technology.

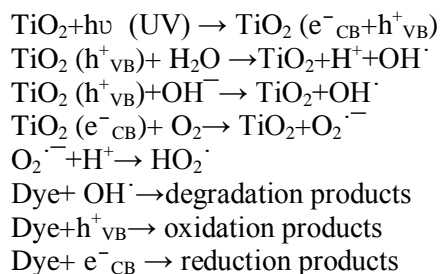
INTRODUCTION

Just like the discoveries of BaTiO₃ and YBa₂Cu₃O₇ revolutionised the respective fields of ferroelectricity and high T_C superconductivity, projection of TiO₂ as a heterogeneous photocatalyst has made a similar impact on the world wide scientific community dealing with remediation of organic pollutants from industrial effluents. Despite a large number of research publications that were reported on TiO₂ besides the excellent reviews [1-14], not even a single review has appeared on alternate non TiO₂ based ternary metal oxides as photocatalysts. This prompted us to summarize several randomly reported works on mixed metal oxides as potential photocatalysts, but prior to this discussion, highlights in earlier reviews on TiO₂ are briefly presented here for the benefit of the reader.

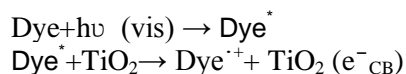
Over 70,000 tones of commercial dyes are produced annually for use in textile, paper, leather, pharmaceutical, cosmetic and food industries, and an estimated 1-15% of these dyes make their way into various aquatic sources as effluents in the form of unused dyes. Several studies indicated that the remnant dyes form a persistent class of health hazards since they are less biodegradable. Also their presence renders the aquatic sources intensely coloured and blocks the penetration of sun light which hamper the natural growth ability of aquatic life. Even when present in ppm levels, the commonly used dyes can cause serious health risks to both human beings and to animals due to their toxic, mutagenic or carcinogenic nature, and

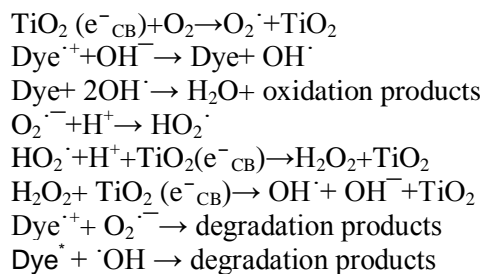
therefore detoxification of aquatic sources has become a prime ecological concern. Though several methods such as adsorption, ultrafiltration, reverse osmosis, ion exchange, biosorption, chlorination and ozonation were proposed for remediation of industrial waste waters, these processes have their own advantages and disadvantages. For instance, adsorption, filtration, ion-exchange and biosorption result in transfer of pollutant from one phase to another and lead to more serious secondary pollution, where as chlorination and ozonation are not cost effective. So, in addition to conventional primary and secondary treatment processes, scientific community has been in the search for complete degradation methods of toxic pollutants into environmentally benign and non-hazardous products. Recently, advanced oxidation processes (AOPs) have emerged as more promising alternative methods for removal of organic pollutants from industrial effluents. AOPs comprise of all methods which utilize hydroxyl radicals for carrying out oxidative degradation of organic pollutants irrespective of the method of generation of hydroxyl radicals. AOPs include photolysis, ozonation, O₃/UV, Fenton, H₂O₂/UV, photo Fenton and photocatalysis techniques. Of these different methods, heterogeneous photocatalysis is an inherently destructive process and is widely studied because of the associated advantages, namely (i) quick and non selective ability of degradation of several toxic organic pollutants into CO₂ and H₂O without any hazardous intermediates (ii) ease of performing the reaction at ambient temperature (iii) ability to effect degradation of pollutants even at trace or ppm level (iv) involves no mass transfer (v) uses solar radiation which is inexhaustible (vi) avoids expensive process of coagulation and subsequent filtration and (vii) a cost effective green technology. In this technique, a selected semiconductor when irradiated with suitable electromagnetic radiation causes excitation of an e⁻ from valance band to conduction band and simultaneously leaves a hole (h⁺) in the valance band. Both the excited e⁻ and h⁺ formed take part in the disintegration of dye structure. In this regard TiO₂ has been projected to be highly prospective because of its ease of synthesis, low cost, strong oxidizing ability, good chemical and biological inertness, and stability towards photo corrosion. Nevertheless, its poor photo conversion efficiency in the visible region and rapid recombination of photo generated electrons and holes limit its use as cost effective photocatalyst. TiO₂ exists in three polymorphic forms anatase, rutile and brookite of which anatase is the active phase.

Work done on TiO₂: Amy L. Linsebigler, G. Lu and John Yates Jr. [1] reviewed principles, mechanisms and selected results relating to photocatalysis on TiO₂ surfaces. Karthnan Rajeshwar et al [2] reviewed preparation and performance of semiconductor based composite materials. Konstantinon and Albanis [3] reviewed kinetic and mechanistic investigations of TiO₂ assisted photocatalytic degradation of azodyes in aqueous solution. These authors discussed photodegradation mechanism in terms of photocatalytic oxidation and photosensitized oxidation. According to photocatalytic oxidation, the relevant reactions at the semiconductor surface causing degradation of dyes were given as follows:



Photosensitized oxidation mechanism is different from the pathway of photocatalytic oxidation. In this case, adsorption of visible light causes excitation in the adsorbed dye with subsequent electron transfer from the excited dye molecule to conduction band of TiO₂ while the dye is converted to cationic dye radicals (Dye^{•+}) and degradation mechanism shall be as follows.





Kazibite Hashimsl, Hiroqli Irie and Akire Fujishma [4] reviewed a historical overview and future prospects of TiO₂ photocatalysis. These authors explained why nitrogen doped TiO₂ becomes visible light sensitive. Xiaoho Chen and Samuel S. Mao [5] reviewed synthesis, properties, modifications and applications of titanium dioxide nanomaterials in terms of sol-gel, micelle and inverse micelle, sol, hydrothermal, solvothermal, oxidation, chemical vapour deposition, physical vapour deposition, electro deposition, sonochemical and microwave methods. Ying Cui, Hao Du and Lishi Wen [6] reviewed doped TiO₂ photocatalysts and synthesis methods to prepare TiO₂ films. Adrina Zaleska [7] reviewed mechanism of photoactivity of pure TiO₂ and TiO₂ doped with metal and non metal species. Akpan and Hameed [8] reviewed parameters affecting the photocatalytic degradation of dyes using TiO₂-based photocatalysts. Fang Han et al [9] reviewed tailored titanium dioxide photocatalysts for the degradation of organic dyes in waste water treatment. Their review presents novel achievements in the modification of TiO₂ photocatalytic systems with noble metals, lanthanide metals, alkaline metals, CdS, Bi₂S₃ and non metals aimed at enhancing catalytic efficiency. Rauf and Salman Ashref [10] reviewed fundamental principles and applications of heterogeneous photocatalytic degradation of dyes in solution and discussed degradation pathway of an azo dye. A.R. Khateer and M.B Kasiri [11] reviewed influence of chemical structure in photocatalytic degradation of organic dyes in presence of nanostructured TiO₂. These authors discussed the influence of methyl group, nitrite group, alkyl side chains, chloride group, carboxylic group, sulfonic substituent and hydroxyl groups on photocatalytic process efficiency and concluded that (i) photocatalytic degradation rate of mono azo dyes is higher than that of dyes with anthra quinine structure, (ii) presence of methyl and chloro groups in the dye molecules decreases slightly the process efficiency while a nitrite group acts in an opposite direction (iii) dyes containing more

sulfonic substituents are less reactive while hydroxyl groups intensifies degradation rate of the dye and (iv) adsorption of the target molecule on TiO₂ surface forms a critical step towards efficient photocatalysis. Gupta Shipra Mital and Tripathi Manoj [12] discussed various methods used to enhance the photocatalytic characteristics of TiO₂ in terms of dye sensitization, doping (with transition metal cations, addition of noble metals, doping with metalloids, anion codoping), coupled composites and capping. Yong Nian Tian, Chung Leng Wong and Abdul Rahman Mohamad [13] presented a overview on the photocatalytic activity of Nano-doped TiO₂ in the degradation of organic pollutants. These authors discussed effects of metal, non metal, metalloids and codoping in the formation of nano-doped TiO₂ as well as operational factors effecting the photocatalytic degradation. Inam Ullah et al [14] reviewed the use of nano science for environmental remediation in which synthetic techniques such as ball-milling, hydrothermal, sol-gel, co-precipitation, reverse micelle techniques and dye degradation techniques were discussed. Table 1 gives a list of dopants studied on TiO₂.

A critical survey of literature on TiO₂ suggests that three different approaches have been developed to shift the absorption edge from U.V to visible region and thereby improve the photocatalytic efficiency of TiO₂ namely (i) doping/ codoping of metal atoms/ anions/ cations (ii) dye sensitization and (iii) formation of heterostructures with materials of suitable band potential in the form of nano composites. These three approaches are shown pictorially as follows

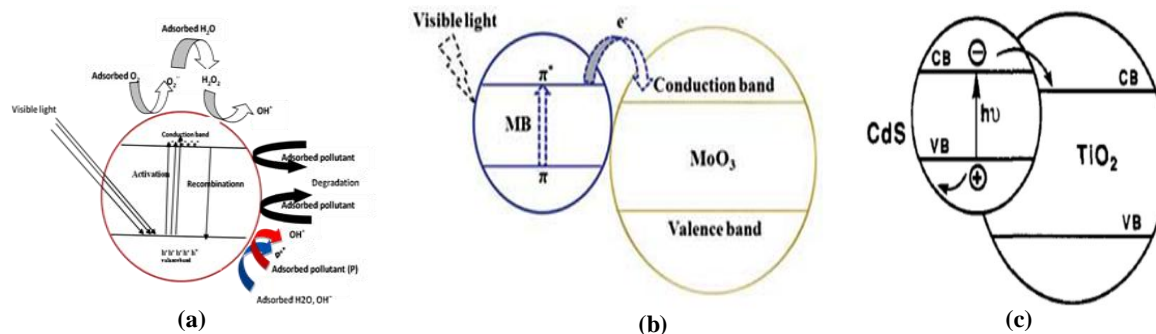


Fig. 1 Schematic representation of (a) redox reactions of a dye in presence of photocatalyst under visible light irradiation. (b) transition of electrons from excited dye molecule to photocatalyst and (c) energy band structure and electron-hole pair generation in CdS/TiO₂ heterostructure

Of these three approaches, doping of TiO₂ has been extensively studied followed by nanocomposite fabrication. Dye sensitizations have been found to be more useful in water splitting than in photocatalysis.

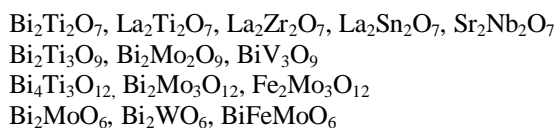
Table. 1 Dopants reported in TiO₂

S.No	Dopant	References
1.	Be	[15]
2.	Si	[16]
3.	V	[17]
4.	Cr	[18-20]
5.	Fe	[21-34]
6.	Co	[35-38]
7.	Ni	[39-44]
8.	Cu	[45-47]
9.	Nb	[48]
10.	Ag	[49-56]
11.	Au	[57]
12.	Pt	[58]
13.	Pd	[59]
14.	Ce	[60, 61]
15.	Zr	[62]
16.	La	[63-65]
17.	Gd	[66]
18.	W	[67]
19.	N	[68-89]
20.	C	[90, 91]
21.	B	[92, 93]
22.	F	[94, 95]
23.	S	[96]
24.	P	[97, 98]
25.	Mn ²⁺ and Mo ⁶⁺	[99]
26.	Sc ³⁺ and V ⁵⁺	[100]

S.No	Dopant	References
27.	La ³⁺ and Eu ³⁺	[101]
28.	Cr ³⁺ and Fe ³⁺	[102]
29.	Fe ³⁺ , Ni ²⁺	[103]
30.	Cu, Fe, Al	[104]
31.	Cu, Zn	[105]
32.	Cu, Fe, Pt, Pd, V, W, Ce, Zr	[106]
33.	Ce, Si	[107]
34.	Ag, Al, Ce, Nb	[108]
35.	Zn ²⁺ and V ⁵⁺	[109]
36.	W/Mo	[110]
37.	Mn, Fe	[111]
38.	Cu, Ce	[112]
39.	Fe, Cu	[113]
40.	Mn ²⁺ , Ni ²⁺ , Zn ²⁺	[114]
41.	Ag, N	[115]
42.	W, N	[116]
43.	Ga, N	[117]
44.	Mn, P	[118]
45.	Ce, N, S	[119]
46.	Mn, N	[120]
47.	Au, N	[121]
48.	La, N	[122, 123]
49.	Ni, B	[124]
50.	Ni, N	[125]
51.	S, N	[126-129]
52.	B, N	[130, 131]
53.	N, S, C	[132]
54.	N, F	[133]
55.	C, N	[134]
56.	N, P	[135]

Alternate non-TiO₂ based ternary metal oxide semiconductor photocatalysts: In view of the photo absorption of TiO₂ being restricted to U.V. region which is hardly 4% of the solar radiation, focus on alternate photo catalytic materials is now shifted to non-TiO₂ based semiconductors that show significant absorption in visible region comprising of ~ 43% of the solar radiation. For a semiconductor photocatalyst, bottom of the conduction band and top of the valance band determine the reducing ability of electrons and oxidizing ability of holes respectively. Besides possessing a suitable band gap, a good semiconductor photocatalyst must also be photo stable, non-hazardous towards humans and environment, show good quantum efficiency of solar radiation, easily seperable after use and, be able to catalyze effectively. Though some of the semiconductors fulfil the band gap requirements; they suffer from other limitations which restrict their use in practice. For instance although GaAs and CdS possess excellent band gaps for use under visible radiation, they are not stable enough in aqueous solutions. Likewise ZnO is also unstable in water, while Fe₂O₃ and SnO₂ need an external bias since the conduction band edge lies below the reversible hydrogen potential. Besides TiO₂, several binary and ternary metal oxides have been studied as photocatalysts. These include, ZnO, Fe₂O₃, Cu₂O, V₂O₅, MoO₃, WO₃, ZrO₂, SnO₂, FeWO₄, ZnWO₄, BiFeO₃, BiVO₄, CoFe₂O₄, BaMoO₄, Bi₂MoO₆, Bi₄Ti₃O₁₂, Bi₂Ti₂O₇, Fe₂Mo₃O₁₂, KNb₃O₈ etc. On suitable substitution, both binary metal oxides and ternary metal oxides yield new materials with different band gaps as can be seen from the following examples.

TiO₂, Cd₂SnO₄, CrNbO₄, AlPO₄
 MoO₃, NaBiO₃, SrTiO₃, BiFeO₃, LaFeO₃, La₂FeTiO₆
 BaMoO₄, BaBi₂Mo₄O₁₆, SrTiMo₃O₁₂, ZnWO₄
 BiVO₄, FeVO₄, LaVO₄, SrMoO₄, FeWO₄, NdVO₄



Recent studies indicated that some ternary metal oxides are better photocatalysts compared to binary metal oxides or sulphides. These mixed metal ternary oxide photo catalysts can be broadly classified into different categories based on chemical composition or on metal ion families as shown in tables 2 and 3. For a detailed description of crystal structures based on composition, the reader may refer to Major ternary structural families by Muller and Roy [136]. Classification based on crystal chemistry is useful for material scientists whereas the other classification is a general one suitable for researchers from different backgrounds. Development of suitable non-TiO₂ based photo catalysts has indeed potential applications in terms of green technology for environmental remediation of industrial waste waters.

Table2. Classification of ternary metal oxide photocatalysts based on composition

S.No	General compositions *	Examples of photo catalysts reported	Observed crystal structures
1.	ABO ₃	SrTiO ₃ , BaTiO ₃ , CaTiO ₃ LaFeO ₃ , YFeO ₃ BiFeO ₃ AgNbO ₃	Pervoskite ” Orthorhombic Pervoskite
2.	ABO ₄	BiNbO ₄ BiVO ₄ LaVO ₄ FeVO ₄ BaMoO ₄ , MWO ₄ (M= transition metal ions)	Triclinic Tetragonal Zircon, Monoclinic scheelite, Tetragonal scheelite Tetragonal Zircon, Monoclinic monazite Scheelite, Wolframite ”
3.	AB ₂ O ₄	CoFe ₂ O ₄ , MnFe ₂ O ₄ , NiFe ₂ O ₄ CuFe ₂ O ₄ , ZnFe ₂ O ₄	Normal/ inverse Spinel
4.	A ₂ BO ₆	Bi ₂ MoO ₆ , Bi ₂ WO ₆	Koehlinite, Russellite
5.	A ₂ B ₂ O ₉	Bi ₂ Mo ₂ O ₉	Monoclinic
6.	A ₂ B ₃ O ₁₂	Bi ₂ Mo ₃ O ₁₂ Fe ₂ Mo ₃ O ₁₂	Monoclinic Orthorhombic Hexagonal Monoclinic Orthorhombic
7.	A ₂ B ₂ O ₇	Bi ₂ Ti ₂ O ₇	Pyrochlore
8.	A ₄ B ₃ O ₁₂	Bi ₄ Ti ₃ O ₁₂	Aurvillus type

* where A and B are different metal ions

Table3. Classification of ternary metal oxide photocatalysts based on metal ion family

S.No	Metal ion family	Examples
1.	Titanates	SrTiO ₃ , BaTiO ₃ , Bi ₂ Ti ₂ O ₇ , Bi ₄ Ti ₃ O ₁₂ , La ₂ Ti ₂ O ₇
2.	Niobates	AgNbO ₃ , BiNbO ₃ , InNbO ₄ , KNb ₃ O ₈ , NiNb ₂ O ₆
3.	Ferrates	LaFeO ₃ , BiFeO ₃
4.	Ferrites	CoFe ₂ O ₄ , CuFe ₂ O ₄ , MnFe ₂ O ₄ , ZnFe ₂ O ₄ , Fe ₃ O ₄
5.	Vanadates	BiVO ₄ , LaVO ₄ , FeVO ₄
6.	Molybdates	BaMoO ₄ , (Bi/Fe) ₂ MoO ₆ , Bi ₂ Mo ₂ O ₉ , (Bi/Fe) ₂ Mo ₃ O ₁₂
7.	Tungstates	ZnWO ₄ , Fe ₂ W ₃ O ₁₂ , FeWO ₄ , Bi ₂ WO ₆

Titanates

i) Alkaline earth metal titanates: These compounds with general formula $MTiO_3$ where $M = Ca, Sr$ and Ba crystallize in perovskite type of structure and show photocatalytic activity for degradation of dyes under UV irradiation. Shuang Song et al [137] studied the photocatalytic activity of $SrTiO_3$ and $SrTiO_3/CeO_2$ for the degradation of C.I. Direct Red 23 (4BS) under UV irradiation and reported that $SrTiO_3/CeO_2$ powders exhibited more photocatalytic activity for decolorisation of 4BS. Sydoruk, Khalameida and Zazhigalov [138] reported photodegradation of safranin-T over mechano chemically synthesized nano $BaTiO_3$ under UV irradiation. Tao Xian, Hua Yang [139] reported photocatalytic degradation of Congo red, Rhodamine B, Methyl orange and Methylene blue over sol-gel prepared nano $SrTiO_3$ particles. Sharad S. Gaikwad, Ashok V. Borhade and Vishwas B. Gaikwad [140] reported 98% degradation of Methylene blue in 8 hr under UV irradiation using $CaTiO_3$ prepared by mechano chemical method as photocatalyst. Loghman Karimi and Salar Zohoori [141] studied photodegradation rate of azo dyes (Dark Green 6 and Reactive Orange 7) over $SrTiO_3$ and $SrTiO_3/TiO_2$ composite under UV irradiation and their results indicated that adding nano $SrTiO_3$ to nano TiO_2 showed more promising photocatalytic activity toward dye degradation. Loghman Karimi, Salar Zohoori and Mohammad Esmail Yazdanshenas [142] reported photocatalytic degradation of azo dyes (Dark Green 6 and Reactive Orange 72) using nano- $SrTiO_3$ under UV irradiation.

ii) Bismuth Titanates: These are $Bi_2Ti_2O_7$, $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$.

a) $Bi_2Ti_2O_7$: Compounds with $A_2B_2O_7$ composition represent a family of phases isostructural to the mineral pyrochlore. The structure is composed of two types of cation coordination polyhedra. The A cations are eight coordinated of which 6 are located in distorted cubes that contain equally spaced anions while the smaller B cations are six coordinated and are located within trigonal antiprism with all six atoms at equal distances from the central cation. $La_2Ti_2O_7$ and $Sr_2Nb_2O_7$ have been reported for water splitting while $Bi_2Ti_2O_7$ is reported to exhibit photocatalytic activity. Wei. F. Yao et al [143] reported a band gap of 2.95 eV for $Bi_2Ti_2O_7$ which showed higher photocatalytic activity for Methyl orange degradation compared to TiO_2 . Li Yue-Jun et al [144] reported the synthesis of $Bi_2Ti_2O_7/TiO_2$ composite fibers which showed enhanced photocatalytic activity for degradation of Rhodamine B. Jungang Hou et al [145] synthesized $Bi_2Ti_2O_7$ with well defined spherical structures by hydrothermal process which showed higher photocatalytic activity than commercial P25 TiO_2 for the degradation of Rhodamine-B under visible light irradiation. Zuyun Zhang et al [146] synthesized $Bi_2Ti_2O_7/TiO_2$ composites with different shapes by a glycerol assisted alcohol thermal method and reported higher photocatalytic activity for Petal shaped composite which was ascribed to higher surface area and larger pore volume.

b) $Bi_4Ti_3O_{12}$: $Bi_4Ti_3O_{12}$ belongs to the family of compounds that can be represented by the general formula $(Bi_2O_2)^{2-} (A_{m-1}B_mO_{3m+1})^{2+}$ in which $A=Bi$, $B=Ti$ and $m=3$. Ever since its discovery by Aurvillus, $Bi_4Ti_3O_{12}$ has been studied by many investigators for its ferroelectric, piezoelectric and electrolytic switching behavior. The special structure is beneficial in reducing recombination of the charge carriers and is helpful for enhancing photocatalytic oxidation of organic pollutants because it stimulates the separation of electron-hole pairs and facilitate the mobility of photogenerated carriers to the surface of the photocatalyst crystallites. Sankaran Murugesan, Vaidyanathan Subramanian [147] reported synthesis of pyrochlore $Bi_4Ti_3O_{12}$ nanorods and studied the photodegradation of Methyl orange over this substitute under UV-visible radiation from a 450 W commercial immersion type mediation pressure quartz mercury vapour UV-visible lamp. Liu Xue et al [148] reported controllable synthesis and photocatalytic activity of layered flower like and Rock like $Bi_4Ti_3O_{12}$ nanostructures for the degradation of Methyl orange under visible light. Pin Hao et al [149] synthesized $Bi_4Ti_3O_{12}$ nanobelts by a low temperature nanoscale solid state reaction and studied photodegradation of Methyl orange over it under UV irradiation. Andre Nogueira et al [150] synthesized $Bi_4Ti_3O_{12}$ with two different structures via peroxo method and studied photodegradation of Rh-B under UV irradiation from mercury vapour lamp source. Lingli Wang et al [151] reported synthesis of $Bi_4Ti_3O_{12}$ by high temperature solid-state method and studied its photocatalytic activity for the degradation of 4-chlorophenol and microcystic -RR under visible light irradiation.

c) **Bi₁₂TiO₂₀**: Bi-containing Ti (transition metal ion with d⁰ configuration) based Bi₁₂TiO₂₀ is one of the important Sillimite compounds due to its useful properties such as high electro optical coefficient, low optical activity, high photosensitivity in the visible region. Zhou et al [152] demonstrated the potential of Bi₁₂TiO₂₀ as a visible light photocatalyst for the oxidation of methanol to CO₂. Jinkai Zhou et al [153] reported synthesis of Bi₁₂TiO₂₀ and its photocatalytic decomposition of methanol under visible light irradiation. Jia Liu et al [154] reported photodegradation of Crystal violet over Bi₄Ti₃O₁₂+ Bi₁₂TiO₂₀ mixed oxide under UV irradiation. Jungang Hou et al [155] reported Hiererachial assemblies of Bi₁₂TiO₂₀ coupled architectures and their visible light degradation of Rh-B. York Saith et al [156] reported photodegradation of MO using hydrothermally synthesized Bi₁₂TiO₂₀ under UV irradiation.

Niobates: Niobates are an important class of functional materials with unique properties that include chemical and electrochemical stability, ion conductivity, heterogeneous catalysis and photocatalysis. The distorted NbO₆ octahedra and the availability of 4d orbitals of Nb make them promising materials as photocatalysis. In recent years, several attempts have been made to explore niobate semiconductors such as NaNbO₃, AgNbO₃, KNb₃O₈, InNbO₄, FeNb₂O₆, Bi₃NbO₇, K₄Nb₆O₁₇, Bi₂MNbO₇ (M=Al, Ga, In), SrNb₂O₆ etc. Zhigang Zou, Jinhua Ye and Hironori Arakawa [157] reported photophysical and photocatalytic properties of InNbO₄ under visible light irradiation. Gaoke Zhang et al [158] reported photocatalytic activity of Cu-doped K₂Nb₄O₁₁ for Acid red under U.V. irradiation. Lizhi Zhang et al [159] studied visible light photocatalytic activity of InNbO₄ for the degradation of Rhodamine-B under visible light irradiation. Gaoke Zhang et al [160] reported a band gap of 3.47 eV for KNb₃O₈ and claimed photodegradation of Acid red G over KNb₃O₈ was higher compared to TiO₂. Guoqiang Li et al [161] reported compositions dependence of the photophysical and photocatalytic properties of (Ag_{1-x}Na_x)NbO₃ solid solutions for the degradation of iso propanal. Xiukai Li, Naoki Kikugawa and Jinhua Ye [162] reported a band gap of 2.7 eV for AgNbO₃ and studied photodegradation of Rhodamine-B over HNb₃O₈ under visible light irradiation. Wenjie Zhang, Xin Sun, Baihan Chen [163] reported photocatalytic degradation of Methyl orange over FeNb₂O₆ under U.V. irradiation. Wanling Wang et al [164] reported photodegradation of Rhodamine-B under visible light over AgNbO₃. Jingrui Fang [165] studied photocatalytic property of SrNb₂O₆ for the degradation of Methyl orange under U.V. irradiation. Hui Xu et al [166] reported photocatalytic activity of NaNbO₃/ZnO heterojunction for the degradation of Methylene blue. Huiming Yin et al [167] reported photocatalytic activity of Bi₃TiNbO₉ for degradation of Methyl orange under U.V. irradiation. Chao Zhou, Gang Chen, Qun Wang [168] reported high photocatalytic activity of porous K₄Nb₆O₁₇ for degradation of Rhodamine-B under U.V. light irradiation. Yongfu Qiu et al [169] studied N-doped K₂Nb₄O₁₁ for the degradation of orange G, Bisphenol A and pentachloro phenol. Guoqiang Li et al [170] reported enhanced visible light photocatalytic properties of AgNbO₃-AgSnO₃ composites for degradation of Rhodamine-B under visible light. Cheng Wang et al [171] reported enhanced visible light photocatalytic activity of AgBr/ AgNbO₃ composite for the degradation of Methylene blue under visible light. Liyun Cao et al [172] reported topstactic soft chemical synthesis and photocatalytic performance of one-dimensional AgNbO₃ nanostructures for the degradation of Methylene blue under visible light. Blain Paul, Kwang-Ho Choo [173] reported visible light active Ru-doped NaNbO₃ for degradation of phenol.

Ferrates

i) **Bismuth Ferrate (BiFeO₃)**: BiFeO₃ is known to be a multi ferroic which shows coexistence of ferroelectric and magnetic ordering in a specific temperature interval. BiFeO₃ also exhibits ferromagnetism at room temperature. Feng Gao et al [174] studied visible light photocatalytic properties of BiFeO₃ nano particles for the degradation of Methyl orange and the degradation times of 8h and 16h were reported for UV-visible and visible light irradiation respectively. Li Shun et al [175] synthesized BiFeO₃ particles with different morphologies by a KNO₃ assisted hydrothermal method and reported 80% degradation of Congo red in 90min using hydrothermal synthesized nano particles. Madhu, Manjunath and Manivannan [176] studied Bi_{1-x}M_xFeO₃ (M=Mg, Al, Y) and claimed that Y³⁺ doped BiFeO₃ exhibited higher photocatalytic effect towards degradation of Rhodamine-B as compared un doped BiFeO₃ and TiO₂. Guo-Qiang Tan et al [177] synthesized three kinds of bismuth ferrites -BiFeO₃, Bi₂₅FeO₄₀ and Bi₂₅FeO₄₀-BiFeO₃ via

Microwave hydrothermal method and reported that these catalysts exhibited 35%, 52% and 90% degradation of Methyl orange in 2h respectively. Kevin Mc Donnell et al [178] reported 28% degradation of Methyl orange over BiFeO₃. Yan-Nan Feng et al [179] synthesized Ca-doped BiFeO₃ nano fibers using electro spinning method which then used for degradation study of congo red under visible light irradiation. Xuehui Zhang et al [180] studied photocatalytic activity of BiFeO₃ nano fibers for degradation of Congo red and claimed enhanced catalytic activity for fibers compared to nano particles. Yi Liu, Zuo and ShiShun Qi [181] synthesized BiFeO₃ carbon core/shell nano fibers and reported that the photocatalysts exhibited higher activity for degradation of Methyl orange compared to BiFeO₃ nano fibers. Tayyeb Soltani, Mohammad Entezari [182] synthesized BiFeO₃ with ultra sound and reported degradation of Rhodamine-B under solar light in 35min in acetic acidic medium. Yannan Feng et al [183] studied photocatalytic behaviors of Ca, Mn, Co-doped BiFeO₃ nano fibers for degradation of Congo red. Saranyoo Chaiwichian et al [184] reported fabrication of BiFeO₃-Bi₂WO₆ composites and claimed that BiFeO₃:Bi₂WO₆ composite with 0.4:0.6 mole ratio exhibited the highest photocatalytic performance for degradation of Rh-B under visible light irradiation.

ii) Lanthanum Ferrate (LaFeO₃): Pervoskite type oxides of general composition of ABO₃ where A is rare earth ion and B is 3d transition metal ions are promising functional materials widely reported for various applications such as catalysts, solid oxide fuel cells, chemical sensors, magnetic materials and photocatalysts. LaFeO₃ crystallises in orthorhombic pervoskite structure with space group P bnm. Shudan Li et al [185] studied photocatalytic activity of nano sized LaFeO₃ under visible light irradiation for the degradation of Rh-B. Jun Yang et al [186] reported that visible light photocatalytic activity of LaFeO₃ prepared by conventional co precipitation could be markedly enhanced by post treatment method with molten KNO₃, for Acid red 18 dye. Jianlin Ding et al [187] reported synthesis of ReFeO₃ (Re: La, Sm, Eu, Gd) by microwave assisted method and studied their photocatalytic activity towards degradation of Rhodamine-B under visible light irradiation and found their activities varied as GdFeO₃ > EuFeO₃ > SmFeO₃ > LaFeO₃. Shudan Li and Xianlei Wang [188] synthesized LaFeO₃ fibers with different different morphologies and studied their photocatalytic activity towards degradation of Methylene blue under visible light irradiation. Priti Goseri, Rajesh Bini wale [189] reported synthesis of LaFeO₃ by three different wet chemical routs, namely co precipitation, combustion and sol-gel methods and observed that sol-gel method gives rise to single crystalline phase pure LaFeO₃. Haijiao Su et al [190] reported synthesis of nano sized LaFeO₃ by an impregnation process with mesoporous silica as hard template. The sample exhibited superior visible light photocatalytic activity for degradation of Rhodamine-B under visible light irradiation. Fa-tang Li et al [191] synthesized nano particles of LaFeO₃ and Ca-doped LaFeO₃ (La_{1-x}Ca_xFeO₃, x=0.05-0.20) and studied the degradation of Methylene blue using fluorescence light as a visible light sources. These researchers claimed that partial substitution of La³⁺ with Ca²⁺ enhanced visible light photocatalytic activity. Rui Shang Hu et al [192] studied photocatalytic activities of LaFeO₃ and La₂FeTiO₆ for p-chlorophenol degradation under visible light. Their experimental results demonstrated that La₂FeTiO₆ is more active compared to LaFeO₃ and this was attributed to difference in structure and surface properties. Thirumalairajan et al [193] reported controlled synthesis of LaFeO₃ microspheres via self-assembly process and their associated reactivity towards Rh-B under visible light illumination. Zhi-Xian Wei et al [194] synthesized LaFeO₃ and LaFe_{0.5}Mn_{0.5}O_{3.5} by combustion method and reported that Mn³⁺ doped LaFeO₃ showed much higher photocatalytic activity towards degradation of Methyl orange under solar radiation.

Ferrites: Ferrites exist in three different crystal structures: Cubic spinel (MFe₂O₄, M is a bivalent transition metal ion such as Mn, Fe, Co, Ni, Cu and Zn), Hexagonal, (MFe₁₂O₁₉, M= Sr, Ba, Pb) and Garnet (M₃Fe₅O₁₂, M= Al, Ga, Gd, Fe, Y) type. Of these three types of ferrites, spinel ferrites have only been studied as photocatalysts. Jum Suk Jang et al [195] reported synthesis of nano crystalline ZnFe₂O₄ by polymerized complex method and investigated the photo decomposition of isopropanol under visible light. J.S. Jang et al [196] reported that ZnFe₂O₄ was a better photocatalyst over TiO_{2-x}N_x for visible light degradation of isopropanol. Harish et al [197] studied the effect of Cd doping in ZnFe₂O₄ for the

photocatalytic degradation of MO under solar radiation and reported 80% degradation in 240min. P.H. Borse et al [198] reported that doping of co-catalyst \square 1 wt% RuO_2 over BaFe_2O_4 yield a better photocatalyst for the degradation of isopropanol. Harish et al [199] reported solar light active $\text{Zn}(\text{Fe}_{2-x}\text{Al}_x)\text{O}_4$ showed enhanced photocatalytic activity for the degradation of Methylene blue under sun light. Yongsheng Fu et al [200] reported high photocatalytic activity of MnFe_2O_4 -graphene heteroarchitectures for the degradation of Methylene blue under UV and visible light. M.M. Rashad et al [201] reported 96% degradation of Methylene blue under UV irradiation using CuFe_2O_4 . Sonal Singhal et al [202] studied degradation of Methylene blue under visible light over $\text{ZnFe}_2\text{O}_4/\text{MWCNT}$ composite and reported 99% degradation in 5h. T.K. Pathak et al [203] investigated photocatalytic degradation of aqueous nitrobenzene solution using nano crystalline Mg-Mn Ferrite. A. Sutka et al [204] studied photocatalytic activity of non-stoichiometric $\text{ZnFe}_{2+z}\text{O}_4$ ($\text{ZnFe}_{2+z}\text{O}_4$, $z= 0.05, 0.10$ and 0.15) and reported 40% degradation of Methylene blue in 3h under visible light. David Greene et al [205] reported photocatalytic studies of $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$ nano composites for the degradation of MB under UV-light. D.F. Zhao et al [206] reported fabrication of nickel ferrite-graphene nano composites which could degrade Methylene blue up to 50% in 5h under visible light. Wasim Ullah Marwat [207] reported synthesis of $\text{CdO.5MgO.5Fe}_2\text{O}_4$ for 76% degradation of Methyl orange in 90min under solar light. Borhan et al [208] reported 65% degradation of orange 1 in 45min at $\text{pH}=3$ by $\text{ZnFe}_{2-x}\text{Al}_x\text{O}_4$. Triveni Kumar Mahto et al [209] synthesized citric acid functionalized MFe_2O_4 , $\text{M}=\text{Fe, Mn}$ and Zn for the degradation of Methyl orange under visible light. Manohar R. Patil and V.S Shrivastava [210] developed polyaniline nickel ferrite nano composite for the degradation of Methylene blue under visible light 90% degradation was achieved in 140min at $\text{pH}=8.5$. Keitro Tezuka, Masahiro Kogure, Yue Jin Shan [211] reported photocatalytic degradation of acetic acid on spinel ferrites MFe_2O_4 ($\text{M}=\text{Mg, Zn}$ and Cd) under xenon lamp. Abilarasu, A. Saravanan and T. Somanathan [212] reported 96% degradation of Congo red in 80min under sun light using $(\text{Co}_{1-x}\text{Mn}_x)\text{Fe}_2\text{O}_4$. W. Zhao et al [213] reported fabrication of p-n junction photocatalyst $\text{CuFe}_2\text{O}_4/\text{Bi}_4\text{Ti}_3\text{O}_{12}$ for the degradation of Methyl orange under medium pressure Hg-lamp. Xueyan Liu et al [214] reported microwave-induced catalytic oxidation of Malachite green using CuFe_2O_4 . Katerina Zaharieva et al [215] reported synthesis of nano sized CuFe_2O_4 for the degradation of Malachite green under UV irradiation for 150min. M.P. Tsvetkov et al [216] reported photocatalytic activity of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.25, 0.5, 1.0$) for degradation of Malachite green under UV irradiation 80% degradation was believed in 120min of irradiation. Panpan Jing et al [217] reported efficient photocatalytic degradation of acid fuchsin using porous CuFe_2O_4 nano tubes. Zhengru Zhu et al [218] reported photocatalytic performances and activities of Ag doped CuFe_2O_4 nanoparticles for the degradation of 4-chloro phenol under xenon lamp irradiation. N. Nasrallah et al [219] studied photocatalytic reduction of Cr(VI) on the novel hetero system $\text{CdS}/\text{CuFe}_2\text{O}_4$. Yu-Shen et al [220] reported enhanced photocatalytic conversion of benzene over CuFe_2O_4 nano structures under xenon lamp irradiation.

Vanadates

i) Bismuth vanadate: Bismuth vanadate, BiVO_4 exhibits unique ferroelastic, acoustic-optical and ion-conductive properties. Owing to its good performance and less ecotoxicological nature BiVO_4 is a potential substitute for lead and cadmium as pigment. BiVO_4 exists in three crystalline structures-tetragonal Zircon, monoclinic (m) Scheelite and tetragonal (t) Scheelite forms [221] of which only BiVO_4 of monoclinic Scheelite structure with a band gap of 2.4eV was reported to exhibit visible light photocatalytic activity. Several synthesis methods have been reported for BiVO_4 in terms of mechanochemical assisted solid-state [222], precipitation [223], solvothermal [224], sonochemical [225], hydrothermal [226], spray pyrolysis [227], combustion [228] etc. Generally, m- BiVO_4 is obtained by high temperature processes [229] while t- BiVO_4 is prepared in aqueous media by low-temperature processes. The authors reported a simple solid state metathetic synthesis of BiVO_4 of monoclinic structure [230].

(ii) Lanthanum vanadate: Lanthanide orthovanadates, LnVO_4 crystallise in two polymorphic forms namely tetragonal (t) phase with zircon structure and monoclinic (m) phase with monazite structure. With increase in ionic radius there is a strong tendency for lanthanide ions to prefer monoclinic structure due to

its higher oxygen coordination number 9 compared to 8 of tetragonal form [231]. Since La^{3+} has the highest ionic radius among the tripositive lanthanide ions, m-LaVO₄ exists as thermodynamically more stable state while t-LaVO₄ exists as metastable state. Consequently, of the two forms m-LaVO₄ can be easily prepared by conventional solid-state reactions [232] where as t-LaVO₄ can only be prepared by soft chemical routes under specified reaction conditions [233-235]. Of the two forms m-LaVO₄ has been reported to be neither a suitable host for luminescent activators nor a good catalyst compared to t-LaVO₄. It is therefore a challenge to synthesize the metastable zircon type t-LaVO₄ by solid-state synthesis. The authors reported a simple synthesis of tetragonal LaVO₄ via solid-state metathetic reaction [230].

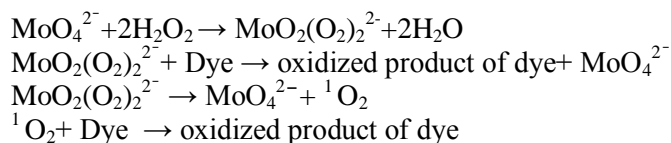
iii) Ferric vanadate: Beysim Ozturk and Gulish Selda Pozan Soyulu [236] reported synthesis of rod like pure triclinic FeVO₄ catalyst by hydrothermal method and studied photocatalytic degradation of phenol under natural solar light irradiation. Soumya kanti Biswas and Jin-Ook Beeg [237] demonstrated enhanced photo activity of visible light responsive “W” incorporated FeVO₄ photoanode for solar water splitting. Sijiang Hu et al [238] reported highly efficient degradation of methylene blue on microwave synthesized FeVO₄ nano particles under visible light irradiation. Yi Tong and Paisong Tang [239] reported synthesis of nanocrystalline FeVO₄ and its visible light photo catalytic activity. Wang Min, Zhang Lifang, Luan Haiyan [240] reported synthesis and photo catalytic property of FeVO₄ photo catalyst prepared by sol-gel method using citric acid. Yang et al [241] studied enhanced magnetic property and photo catalytic activity of UV light responsive N-doped Fe₂O₃/FeVO₄ heterojunction. Jingheng Deng et al [242] reported FeVO₄ as a highly active heterogeneous Fenton-like catalyst towards the degradation of orange II. Ag doped FeVO₄ was synthesized by Wang Min [243] and reported that the optimal photo catalytic activity is reached when the Ag doping was 1 wt% for the decoloration of methyl orange. Rao Zhi et al [244] synthesized FeVO₄ by liquid phase precipitation method and used it for the photo degradation of orange II and 2, 4-dichloro phenol in presence of H₂O₂ under visible light illumination. V.D. Nithya et al [245] reported synthesis of FeVO₄ nano particles by simple co precipitation method using various surfactants such as ethylene glycol, polyethylene glycol 200 and polyethylene glycol 400. Jingang Zhao et al [246] reported synthesis of La_{1-x}Fe_xVO₄ solid solutions and their photo catalytic activity and concluded that the Meta stable tetragonal phase exhibits higher photo catalytic activity than the monoclinic. Min Wang, Qiong Liu, Dong Zhang [247] studied the synthesis and photo catalytic property of BiVO₄/FeVO₄ composite novel photo catalysts by precipitation method. These authors indicated that when BiVO₄ doping was 22 at% optimal photo catalytic activity was reached for the degradation of methyl orange.

Molybdates: Metal molybdates are an important family of functional materials that have been widely used in photoluminescence, microwave applications, optical fibers, scintillation materials, humidity sensors and catalysis.

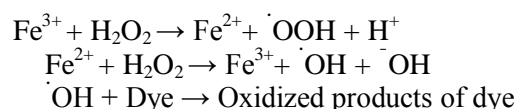
i) Alkaline earth molybdates: Among these materials BaMoO₄ is the most important. It belongs to a body centered tetragonal system with Scheelite crystal structure. MoO₄²⁻ anions are loosely bound to Ba²⁺ ions with their space-group symmetry of C_{4h}⁶ [248-253]. A Novel scheelite like structure BaBi₂Mo₄O₁₆ based BaMoO₄ structure was proposed and investigated by Muktha, Giridhar and Guru Row for photocatalytic degradation of pollutants like phenol, substituted phenols, Rhodamine-B and Rhodamine blue [254]

ii) Transition metal molybdates: Metal molybdates with general formula MMoO₄ crystallise in two different types- the Scheelite and Wolfaramite depending on the ionic radii of the cation. For scheelite structure, the ionic radii of $\geq 0.99 \text{ \AA}$ such as Fe, Mn, Co, Ni, Mg and Zn are required. Ferric molybdate Fe₂Mo₃O₁₂ crystallizes in two polymorphic forms - a low temperature monoclinic α - form and a high temperature orthorhombic β -form with structural transformation of α to β phases occurring at 518^oC on heating [255]. Fe₂Mo₃O₁₂ was reported to function as a catalyst for oxidation of methane to methanol [256], methanol to formaldehyde [257, 258], and propane to acrolein [259], but its use as a photo catalyst has been explored first time for the degradation of Bromo-Pyrogallal red [260], Acid orange II [261] and Methylene Blue [262]. In the catalytic degradation of Acid orange II at neutral pH using Fe₂(MoO₄)₃ as a

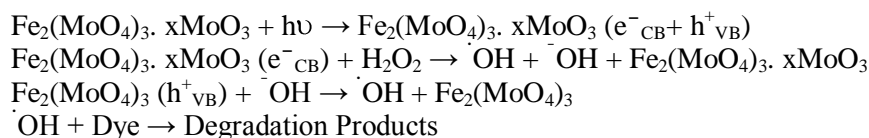
catalyst the proposed mechanism involved formation of peroxy complex (which is also a strong oxidant) as well as singlet oxygen. The different reactions were given as.



In addition to the above, $\text{Fe}^{3+} / \text{H}_2\text{O}_2$ also exhibits Fenton like reactions shown below:

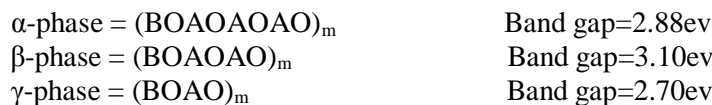


However, such mechanism is not involved in photocatalytic processes probably because photo excitation of e^- and formation of hole dominate the degradation mechanism. Recently, the authors reported facile H_2O_2 assisted visible light degradation of Rhodamine-B, Methylene blue, Methyl orange, Carmine indigo, Crystal violet, Malchite green, Congo red and Eosin-Y over suprastoichiometric $\text{Fe}_2(\text{MoO}_4)_3 \cdot x\text{MoO}_3$ [263-265] and explained the photocatalytic degradation in terms of the following sequence of reactions.



In the case of Bromo-Pyrogallal red $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ was synthesized by microwave irradiation, while for Acid orange II degradation, $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ was prepared by wet chemical process. Synthesis of $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ has been reported in terms of solid-state reactions [266], coprecipitation [267], sol-gel [268], hydrothermal [269] mechano chemical [270] and solution combustion [263-265] methods.

iii) Bismuth molybdates: Bismuth molybdates have the general chemical formula $\text{Bi}_2\text{O}_3 \cdot n\text{MoO}_3$ where $n=3, 2$ or 1 corresponding to α, β and γ -phases respectively. The three phases of Bi-Molybdates include alternative MoO_2^{2+} (A) layers, $\text{Bi}_2\text{O}_2^{2+}$ (B) layers and O_2^{2-} (O) layers [271]. Arrangement of layers in the α, β and γ -phases is as follows.

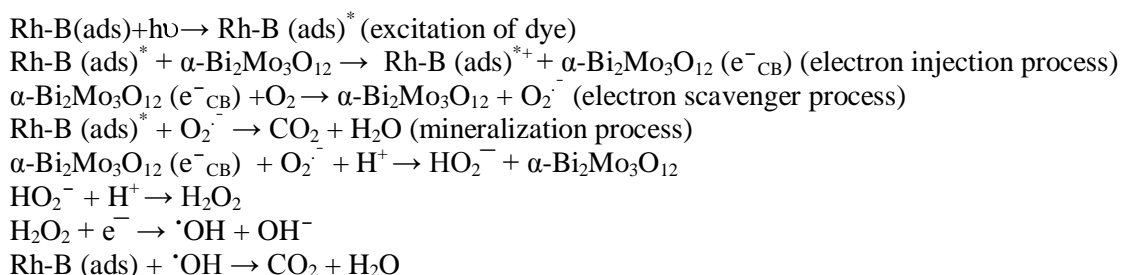


Although compositionally very similar, they are structurally quite distinct with α and β -phases described as possessing defect fluorite structures, while γ -phase is considered as a clear example of an Aurivillius structure [272]. The coordination of both Bi and Mo within these materials is also different, for instance α and β - phases contain BiO_8 units and MoO_4 tetrahedra where as both environments in γ -phase are considered to be distorted six-coordinated geometry. Pure phases of α and γ -phases were usually synthesized at 500-600^oC where as β -phase- $\text{Bi}_2\text{Mo}_2\text{O}_9$ could be obtained above 550^oC due to its decomposition at 540^oC to α and γ -phases [273].

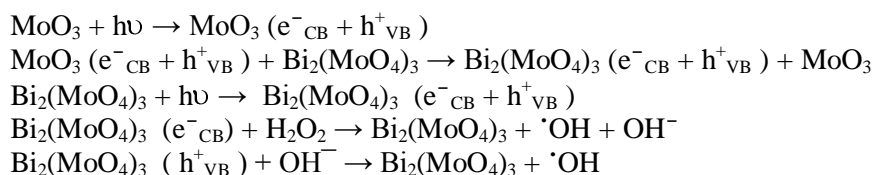
α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and γ - Bi_2MoO_6 have been widely studied because of their industrial applications in the oxidation of propylene, butene and isobutene, and in the ammoxidation of propene: yielding acrolein, butadiene, methacrolein, and acrylonitrile, respectively [274-277]. These oxides have also been used as ionic conductors [278], ammonia sensors [279] and as thin films photo conductors [280]. These are also used as photo catalysts for O_2 evolution from AgNO_3 aqueous solution and for degradation of organic

pollutants under visible light irradiation. Because of their band gaps (Bi_2MoO_6 -2.70eV and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ -2.88eV) these oxides are also useful for visible light degradation of organic pollutants [281-283]. $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ belongs to monoclinic system with space group $\text{P}2_1/\text{C}$ and its crystal structure is considered to be a distorted scheelite structure with ordered cations [284]. Synthesis of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ was reported in terms of solid-state reactions [285], Co precipitation [286, 287], pechini [288], and hydrothermal [289, 290] methods.

Martinez-de la cruz and Obregon Alfaro [287] reported synthesis of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ nano particles by coprecipitation method and evaluated the adsorption parameters and photo catalytic activity for the degradation of Rh-B. According to these investigators, degradation of Rh-B occurred via successive deethylation forming N,N,N¹-triethylated Rh ($\lambda = 539\text{nm}$), N,N¹-diethylated Rh ($\lambda = 522\text{nm}$), N-ethylated Rh ($\lambda = 510\text{nm}$) and Rhodamine ($\lambda = 498\text{nm}$). Martinez-de la Cruz et al [291] reported synthesis of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ nano particles by an amorphous complex precursor and studied photo assisted degradation of Rhodamine-B over it under visible light irradiation. Those authors suggested photosensitization process as a key step in the degradation of Rhodamine-B over α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. The proposed mechanism given by those authors is as follows:



Li Hong -Hua, Li Kun-Wei, Wang Hao [289] reported synthesis of α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ nano tablet and γ - Bi_2MoO_6 nanoplate by hydrothermal method. According to them, photo physical and photo catalytic studies revealed more intense absorption band in the visible light region and better photo catalytic activity for γ - Bi_2MoO_6 than α - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ under visible light irradiation. Based on photo physical properties and photo catalytic activity of Bismuth molybdates under visible light irradiation, Yoshiki shimodaira et al [285] concluded that the corner sharing structure of the MoO_6 octahedra constituted to the visible light response and photo catalytic performance because excitation energy and/or photo generated electron and hole pairs begin to migrate easily in Aurivillius structure. Bi_2MoO_6 possesses pervoskite shape consisting of MoO_6 octahedra where as $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ has a certain connection between MoO_4 tetrahedra and MoO_6 octahedra. It results in that the photo catalytic activities of Bi_2MoO_6 and $\text{Bi}_2\text{Mo}_2\text{O}_9$ are larger than that of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. Tongxuan Liu et al [292] reported the synthesis of MoO_3 nanowire membrane and $\text{Bi}_2\text{Mo}_3\text{O}_{12}/\text{MoO}_3$ nano-heterostructural photo catalyst for waste water treatment. According to their studies, $\text{Bi}_2\text{Mo}_3\text{O}_{12}/\text{MoO}_3$ nano-heterostructure, consisting of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ nano particles attached on to MoO_3 nanowire displayed enhanced photo catalytic activity for degradation of MB under visible light which can be attributed to improved electron-hole regeneration in the nano-heterostructures. Recently, we reported visible light degradation of organic dyes with different chromophores and their binary mixtures over suprastoichiometric $\text{Bi}_2(\text{MoO}_4)_3 \cdot x\text{MoO}_3$ [293, 294] and suggested a different mechanism for $\text{Bi}_2(\text{MoO}_4)_3 \cdot x\text{MoO}_3$ photocatalyst in terms of a synergetic effect arising due to the difference in the band gaps of MoO_3 and $\text{Bi}_2(\text{MoO}_4)_3$. The proposed sequences of reactions are as given below:





Tungstates

i) Transition metal tungstates: Though nano structured tungstate materials such as CdWO_4 , ZnWO_4 and BaWO_4 are known for their applications in conventional catalysis, very few reports are available on their use as photo catalysts for decontamination of industrial waste water. Montini et al [295] reported the photo catalytic activity of transition metal tungstates MWO_4 (where $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ and Zn) for the degradation of methylene blue and methyl orange. Reported band gap energies of these tungstates in eV are as follows.



In divalent metal tungstates, hybridization of the valance states of the metal with O 2p and W 5d orbitals plays a crucial role in determining the lower edge of the conduction band of the material. As per the report of Montini et al [295], ZnWO_4 is the most active photo catalyst while CoWO_4 is the least active photo catalyst for the degradation of Methylene blue. For methyl orange, only ZnWO_4 showed a good catalytic activity while CoWO_4 , NiWO_4 and CuWO_4 are inactive. ZnWO_4 crystallises in monoclinic wolforamite structure with C_{2h} point group symmetry and consists of infinite zigzag chains of either edge sharing ZnO_6 or WO_6 octahedra parallel to [001]. Preparation of ZnWO_4 has been reported in terms of solid-state synthesis [296], Sol-gel [297, 298], hydrothermal [299-303], decomposition of polymeric complexes [304], co precipitation [305], solid state metathesis [306] and ethylene glycol combustion [307] methods. Photo catalytic performance of ZnWO_4 has been enhanced through fabrication of thin films, nano rods, nano particles doped with F, Cl, Eu, Cd, Ag and formation of heterojunctions with $\text{g-C}_3\text{N}_4$, graphite, BiOI, Bi_2WO_6 and ZnO [308-316]. ZnWO_4 has been used as photo catalyst for degradation of methylene blue [295, 309], Rhodamine-B [309], 4-chloro phenol [301], salicylic acid [317], acetaldehyde [315] and methyl orange [295]. Except for one report on Methylene blue and Methyl orange [309], all the above photo catalytic studies made use of U.V irradiation around 254 nm.

ii) Bismuth and iron tungstates: Bismuth tungstate (Bi_2WO_6) is a typical n-type semiconductor with a band gap of 2.75 eV and has potential applications in electrode materials [318], solar energy conversion [319], catalysis [320-322] and photo catalysis [323]. There are two main drawbacks which limit the application of Bi_2WO_6 as photo catalyst. First, photo response of Bi_2WO_6 is limited to light with wavelength shorter than about 450nm. Second, the recombination of photo induced electrons and hole pairs limit the light energy conversion efficiency. Bi_2WO_6 is a member of the Aurivillius family of bismuth based mixed oxides, represented by the general formula $(\text{Bi}_2\text{O}_2)^{2+} [\text{A}_{m-1} \text{B}_m \text{VO}_{3m+1}]^{2-}$. Bi_2WO_6 results when $\text{A} = \text{Bi}$, $\text{B} = \text{W}$ and $m = 1$ in the general formula and forms a layered structure consists of regular intergrowth of $[\text{A}_{m-1} \text{B}_m \text{VO}_{3m+1}]^{2-}$ perovskite slabs and $(\text{Bi}_2\text{O}_2)^{2+}$ sheets. Amano et al [324] reported facile hydrothermal synthesis and photo catalytic activity Bi_2WO_6 poly crystalline Flake like particles for decomposition of acetic acid. Ling Wu et al [325] reported rapid preparation of Bi_2WO_6 photo catalyst with nano sheet morphology via microwave assisted solvothermal synthesis and degradation of Rh-B was reported under visible light irradiation ($\lambda \leq 420\text{nm}$) for an irradiation time of 5 hrs. Jinpo Li et al [326] reported efficient visible light degradation of Rh-B to an extent of 87% by a photo electro chemical process based on a Bi_2WO_6 nanoplate film electrode in 2 hrs. Yuanyuan Li et al [327] reported synthesis and visible light photo catalytic property of Bi_2WO_6 hierarchical octahedron – like structures which degraded Rh-B in 6 hrs. Dong Yong Kim et al [328] reported synthesis of nanomaterials sheet shaped Bi_2WO_6 for the degradation of methyl orange in 4 hrs. Yilin Chen et al [329] reported the gas- phase photo catalytic mineralization of benzene over visible light driven Bi_2WO_6 @ C microspheres.

Erping Gao et al [330] reported synthesis and enhanced photo catalytic performance of graphene Bi_2WO_6 composite which degraded Rh-B in 16 min. Yue Tian et al [331] reported Bi_2WO_6 nano/micro structures with controllable morphologies which degraded Rh-B in 120min. Yu Chang-Lin et al [332] reported hydrothermal synthesis and photo catalytic performance of $\text{Bi}_2\text{WO}_6/\text{ZnO}$ heterojunction photo catalysts

which was used to evaluate photo catalytic degradation of acid orange under U.V light ($\lambda = 365\text{nm}$) irradiation. Tamar Saison et al [333] evaluated the photo catalytic activity under visible light for Bi_2O_3 , BiVO_4 and Bi_2WO_6 . According to these investigators Rh-B was degraded in 80 min by Bi_2WO_6 and presence of acid sites were attributed to be responsible for degradation mechanism. Gao Xiaoming et al [334] reported preparation of Bi_2WO_6 photo catalyst and its application in the oxidative desulfurization in presence of H_2O_2 .

Murcic-Lopez, Hidalgo, Navio [335] reported photo catalytic activity of single and mixed nano sheet-like Bi_2WO_6 and TiO_2 for Rh-B degradation under sun light and visible irradiation. Yongming Ju et al [336] reported synthesis of surface surfated Bi_2WO_6 with enhanced photo catalytic performance for Malachite green. Zhou and Zhu [337] reported significant photo catalytic enhancement in methylene blue degradation of Bi_2WO_6 with graphene hybridization in 120 min. Kodols, Didrihsone, Grabis [338] reported preparation of nano sized Bi_2WO_6 and its photo catalytic activity for Methylene blue for 3 hrs irradiation. Duan et al [339] reported enhanced visible light photo catalytic activity of Bi_2WO_6 via modification with poly pyrrole which degraded Rh-B in 15 min. Ahsaine et al [340] reported synthesis and characterization of Bi_2WO_6 and its effect towards the degradation of MB in 60 min. Yang et al [341] reported enhanced photo sensitized activity of $\text{BiOCl-Bi}_2\text{WO}_6$ heterojunction by effective interfacial charge transfer which degraded Rh-B in 30 min. Zheng Lou et al [342] reported curling like Bi_2WO_6 micro discs with lamellar structure for enhanced gas-sensing properties. Yongli Li et al [343] reported titanium alkoxide induced BiOBr , Bi_2WO_6 mesoporous nano sheet composites with much enhanced photo catalytic activity with which Rh-B was degraded in 40 min. Tamar Saison et al [344] discarded new insights in to Bi_2WO_6 properties as a visible light photo catalyst which degraded Rh-B in \square 120 min.

Zhang et al [345] developed rapid sonochemical synthesis of irregular nano laminar-like Bi_2WO_6 as efficient visible light active photo catalysts which could degrade 85% Rh-B in 150 min. Yanlong Tian et al [346] reported hydrothermal synthesis of graphite carbon-nitride- Bi_2WO_6 heterojunctions with enhanced visible light photo catalytic activities for methyl orange in 120 min. $\text{Bi}_2\text{Mo}_3\text{O}_{12}/\text{MoO}_3$ Bhattacharya, Lee and Bard [347] discussed rapid screening by scanning Electrochemical microscopy of dopants for Bi_2WO_6 improved photo catalytic water oxidation with Zn doping. Ming-Sheng Gui and Wei-De Zhang [348] reported preparation and modification of hierarchical nanostructured Bi_2WO_6 with high visible light-induced photo catalytic activity for the degradation of Rh-B in 6 hrs. Sheng Jia-Yi, Li Xiao-Jin and Xu Yi-Ming [349] reported the effect of sintering temperature on the photo catalytic activity of flower-like Bi_2WO_6 for phenol degradation. Cui Yu-Min et al [350] reported photo catalytic degradation and mechanism of $\text{BiOI/Bi}_2\text{WO}_6$ toward methyl orange and phenol degradation of methyl orange took 120 min. Danjun Wang et al [351] reported AgBr quantum dots decorated mesoporous Bi_2WO_6 architectures with enhanced photo catalytic activity for Methylene blue which was degraded in 30 min. Ankita Ameta, Rakshit Ameta and Mamta Ahuja [352, 353] reported role of ferric tungstate as photo catalyst for removal of xylenol orange and photo catalytic degradation of methylene blue over ferric tungstate.

Photosensitisation vs Photocatalysis: As the dyes themselves absorb in the solar/visible radiation, it is very important to distinguish the two processes of photosensitization and photocatalysis. Characteristic absorption spectra for eight commonly used dyes in photocatalytic studies in the region 350-700nm are shown in fig. 2.

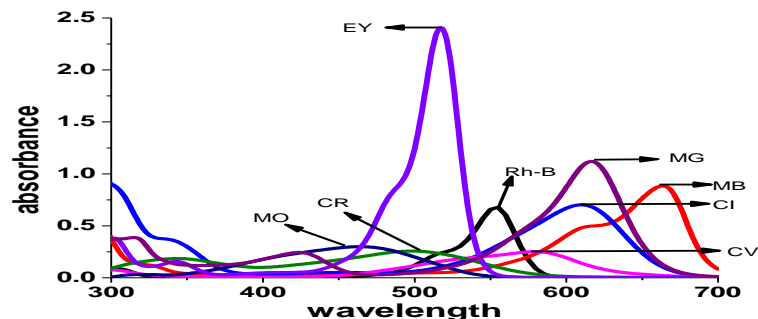


Fig 2. Absorption spectra of different dyes showing λ_{max} for each.

Variations of percentage degradation as a function of irradiation time in the visible region for these dyes in presence and in absence of H_2O_2 are shown in fig. 3.

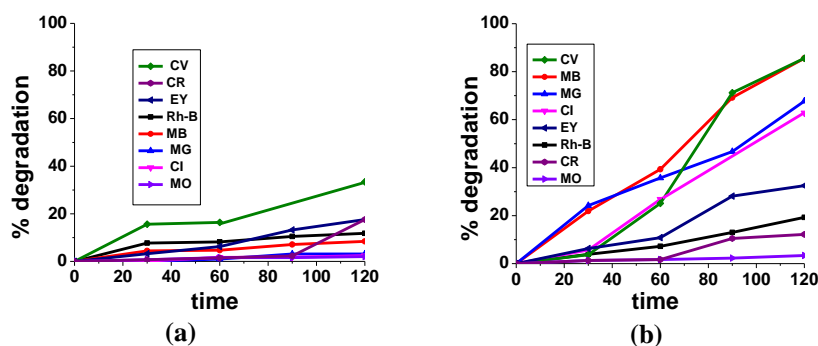


Fig 3. Variation of % degradation as a function of irradiation time for different dyes (a) in the absence of H_2O_2 (b) in presence of H_2O_2

From the figure it is apparent that some of the dyes like Malachite green show extensive decolourisation compared to other dyes which show decolorisation only to an extent of 20-25% for an irradiation time of 120 min. Figures 4 and 5 depict % degradation as a function of irradiation time for the dyes Rhodamine-B, Methylene blue, Methyl orange, Crystal violet, Carmine indigo, Congo red, Eosin-Y and Malachite green in presence and in absence of catalysts $Fe_2Mo_3O_{12}$, $xMoO_3$ and $Bi_2Mo_3O_{12}$. $xMoO_3$. The figures clearly indicate that decoloration due to photocatalysis dominates photosensitization process.

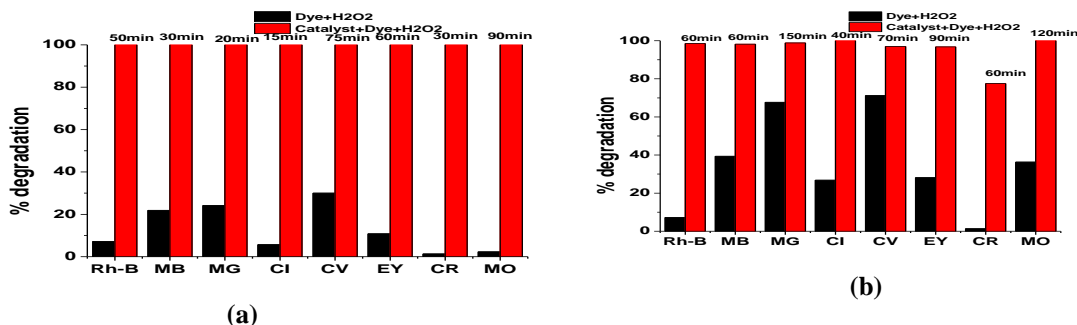


Fig 4. Variation of % degradation as a function of irradiation time for different dye solutions containing H_2O_2 in presence and in absence of (a) $Fe_2Mo_3O_{12}$ and (b) $Bi_2Mo_3O_{12}$ photocatalysts.

CONCLUSIONS

Although TiO₂ is very promising as heterogeneous photocatalyst for remediation of hazardous organic pollutants from industrial effluents, the use of TiO₂ is limited because its photoabsorption is restricted to UV region which is hardly around 4% of solar radiation, and hence not cost effective. Doping of metal atoms/anions/cations, photosensitization and composite formation methods were reported to enhance the photocatalytic efficiency of TiO₂ in the visible region. Alternately, several ternary metal oxides comprising of titanates, vanadates, ferrates, ferrites, niobates, molybdates and tungstates have been developed as potential substituents for TiO₂ in terms of rapid degradation utilizing ~ 43% of solar radiation. Supra stoichiometric Ferric and Bismuth – molybdates in presence of external oxidant H₂O₂ are reported to effect faster dye degradation compared to TiO₂. Proposed photodegradation mechanisms for Fe₂Mo₃O₁₂. xMoO₃ and Bi₂Mo₃O₁₂. xMoO₃ in terms of cooperative and synergetic effects respectively are discussed.

ACKNOWLEDGMENTS

One of the authors (P.S) is grateful to the Council of Scientific and Industrial Research, New Delhi, India for the financial support in the form of SRF.

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