



Review Article

Perovskite Based Photocatalyst for Wastewater Treatment: Green Approach of Environmental Sustainability

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Abstract: Persistent organic substances in wastewater are creating serious problems to the living world as well as to the environment, thereby creating huge detrimental impact on the ecosystem. In view of the grave situation, removal of the persistent organic substances from wastewater effluent holds a great promise to balance the ecosystem and to sustain societal impact value. In this respect, perovskite based photocatalysts have achieved remarkable attention to the scientific community due to their unique structural features and flexibility of composition. Again, surface polarization and electric dipole-dipole interaction in the perovskite material make them attractive for photocatalytic application. This review paper summarized the photocatalytic activity of perovskite materials and their modification to enhance catalytic activity for wastewater treatment. The modification in perovskite has been done to reduce bandgap energy for enhanced visible light activity, separation of charge carriers for their long lifetime, and fast photocatalytic reaction. The recent investigation of ABO₃ type perovskite, layered perovskite, and halide type of perovskite photocatalysts have been discussed detailly. The modification of corresponding perovskites by doped and formation of heterojunction is investigated carefully. The formation and identification of reactive oxygen species (ROS) and their degradation mechanism by trapping experiment and ESR technique has been summarized here. Finally, large scale with energy and environmental related research should be processed for a permanent solution of wastewater problem.

Keywords: Perovskite, Photocatalyst, Wastewater Treatment, Reactive Oxygen Species

1. Introduction

Water pollution and its proper treatment show a huge impact point in current time due to rapid growing population, urbanization, and industrial development [1]. Pollutants in water cause serious hazards to the ecosystem and also create severe health issues for humans like respiratory problems, asthma, dermatitis, mutagenicity, cancer, etc [2]. Renewable green energy is considered for future sustainability of human civilization due to limited non-renewable sources of fossil fuel and its polluted nature. In this respect, solar energy is much attractive due to easy handling, free availability, and cleanliness [3, 4]. Solar energy based photocatalysis systems show much affectivity for the treatment of wastewater without

generation of secondary pollutants. Photocatalysis is a rapidly growing field for potential application with clean environmental nature [5]. In the photocatalytic system, the advanced oxidation process (AOP) is much more effective through the production of ROS [6]. Highly active ROS species lead to the degradation and mineralization of pollutant compounds in wastewater [1, 7].

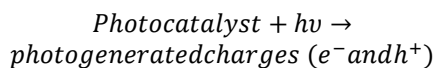
In the photocatalytic application, perovskite materials show much interest due to their common availability as oxide, narrow band gap, wide wavelength for solar light absorption, structural flexibility and high power conversion efficiency [8–11]. The above characteristics lead perovskite material to high density research for wastewater treatment. ABO₃ is the general formula of perovskite oxide structure, where ‘A’ is

alkali metal or alkaline earth metal or rare earth metal and 'B' is usually transition metal. In the structural feature of perovskite, 'A' atom reside at the corner of the lattice with 12 oxygen atoms coordination and 'B' atom reside at center position with 6 oxygen atoms coordination [12, 13]. The main problem of a perovskite material is the large bandgap that only prefers UV light absorption. A good photocatalyst should have absorbance near 520 nm as the major portion of solar light consists of visible and NIR region [14]. The photocatalytic activity of perovskite material may be tuned in different ways of design due to their chemical stability and band structure characteristics [13, 15, 16]. The band gap of perovskite can be modified by the replacement of 'A' or 'B' or 'O' atoms or introduction of different kind atoms [14, 17].

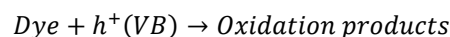
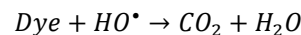
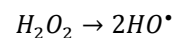
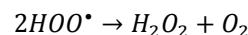
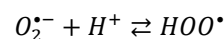
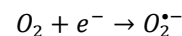
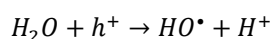
In this review article, recent reports of perovskite photocatalytic materials are summarized on basis of their organic pollutant removal capability. Modified and unmodified ABO_3 type perovskite, layered perovskite, and halide perovskite photocatalytic materials are discussed according to their photocatalytic efficiency. The degradation mechanism and role of reactive oxygen species to identify the degradation path is also reviewed here.

2. Photocatalytic Pathway

In a photocatalytic process, a photocatalyst uses photon as a source of energy to enhance chemical reaction rate without being involved in the reaction. TiO_2 was discovered as a photocatalyst in 1972 during water splitting in a photo-electrochemical reaction [18]. Under light irradiation on a photocatalyst, the electrons absorb energy from the valence band (VB) and excited to the conduction band (CB). The excitation of electrons from VB to CB creates a hole (h^+) at the conduction band. The capability of a photocatalyst depends on the excitement of the electron, separation of the electron and hole, and photo-oxidation reduction reaction at the catalyst surface [19]. In such reactions, the light energy should be greater than the bandgap energy of the material ($h\nu \geq E_g$, where $h\nu$ is the light energy and E_g is the bandgap energy).



The photogenerated holes is then react with water and form hydroxyl radical ($\cdot OH$) at the surface of the material. $\cdot OH$ is a powerful oxidizing agent and attacks organic molecules non-selectively and mineralizes them according to their structure and stability. Photoexcited electron in the conduction band reacts with oxygen to form superoxide anion radical ($\cdot O_2^-$) and take part in the oxidation process of organic molecules. The $\cdot O_2^-$ also react with proton to form hydroperoxyl radical ($\cdot OOH$), which is responsible for the formation of hydrogen peroxide (H_2O_2). Dissociation of H_2O_2 again generates highly reactive $\cdot OH$ [20].



The degradation mechanism is schematically given in Figure 1. The accurate assessments of an active photocatalyst can be measured through apparent quantum efficiency (AQE) [14].

$$AQE = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$

In ABO_3 type perovskite, the 2p orbitals of oxygen atoms are responsible for the formation of lower energy level valence band and 3d orbitals of 'B' atoms constitute the conduction band [13].

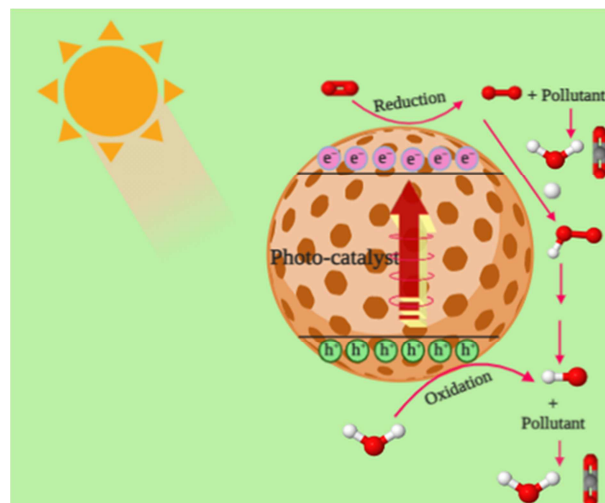


Figure 1. Schematic representation for the photocatalytic degradation of organic pollutant.

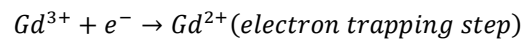
3. Importance of Perovskite Photocatalyst

3.1. ABO_3 Type Perovskites

Visible light driven $LaNiO_3$ is modified with TiO_2 to form heterojunction composite catalysts that exhibit superior photocatalytic efficiency for the degradation of methyl orange (MO) and ciprofloxacin. The combination of n-type TiO_2 and p-type $LaNiO_3$ form S-scheme heterojunction that shorten the electron transfer route from inner to surface [13]. Hexahydroxy-stannates ($MSn(OH)_6$ ($M=Cu, Zn$)) show photocatalytic properties for the degradation of methylene blue (MB). In this perovskite material, the 'A' site induces

lattice distortion through d^{10} - d^{10} configuration though the ionic radius of Cu, Zn is almost the same. In the degradation mechanism, scavengers study shows that photo-generated holes play a dominant role for MB degradation, where superoxide and hydroxyl radicals take an assistant role [21]. Visible light active BaBiO₃ shows good photocatalytic activity for the decomposition of rhodamine B (RhB) and water splitting. BaBiO₃ that annealed at 800°C showed higher catalytic study than low temperature hydrothermal synthesized material due to higher crystallinity, smaller particle size, lower recombination rate of charge carriers, and lower resistance [22]. Green capping agent, corn assisted LaFeO₃ perovskite nanostructured show high catalytic efficiency for the degradation of organic pollutant erythrosine and eriochrome black T. Under UV light irradiation, the photocatalyst degrade 96% erythrosine and 84% eriochrome black T in 90 min [23]. Lanthanum and Chromium codoped SrTiO₃ (SrTiO₃(La, Cr)) has removed 83% tetracycline in 90 min under photocatalytic reaction. In the degradation mechanism, the presence of Cr³⁺ enhances the formation of superoxide radical, which is the main active species [24]. Gong *et al.* have been used LaFeO₃ to decorate TiO₂ nanotube arrays through an electrochemical method to enhance quantum efficiency under sunlight irradiation. Involvement of

this p-type third generation perovskite photocatalyst enhances charge carrier lifetime and their separation efficiency through the improvement of photocatalytic activity. The formation of heterojunction between LaFeO₃ and TiO₂ leads to Fermi energy level apt to align in equilibrium and built-in an electric field at the interface of heterojunction. In the degradation mechanism, under visible light irradiation, the photogenerated electrons are transferred from the CB of LaFeO₃ to the CB of TiO₂ that reduces the recombination rate of charge carriers [17]. 3.2 at.% Ti substitution in LaFeO₃ leads to the 100% total organic carbon (TOC) removal from the 4-chloro phenol aqueous solution under UV-A light irradiation [25]. Undoped and Gadolinium-doped MTiO₃ perovskites (M=Co, Cu, and Ni) show photocatalytic activity for the degradation of MB dye under visible light irradiation. CoTiO₃, CuTiO₃ and NiTiO₃ degrade 31.42%, 61.12% and 30.10% MB within 120 min whereas, this degradation efficiency increase to 43.64%, 74.19%, and 88.64% by doping 2% of Gd in the perovskite material respectively. The enhancement of degradation efficiency is due to the reduction of electron hole recombination rate by the introduction of Gd. The presence of partially filled 4f orbital of Gd facilitates to trap conduction band electron and leads to the formation of superoxide anion radical according to the following way [26]:



Subramanian *et al.* have been synthesized BiFeO₃-Bi₂S₃, BiFeO₃-NiS₂, and BiFeO₃-NaNbO₃ heterostructured visible light active photocatalyst for the degradation of organic pollutants. Among the heterostructured, BiFeO₃-Bi₂S₃ show reduced band gap energy (1.4) and able to degrade 97% MB upto 3 cycle [27]. Microwave-ultraviolet (MW-UV) double response active Z-scheme SrTiO₃/MnFe₂O₄ photocatalyst successfully degrades tetracycline as a target pollutant. In the

Z-scheme system, n-type semiconductor SrTiO₃ (E_g=3.40 eV) has used photosystem-I where MnFe₂O₄ (E_g=1.74 eV) has used photosystem-II. The combined 300W microwave and 200W ultraviolet system is eligible to completely degrade tetracycline pollutants within 20 min in pseudo first order pathway [28]. Mn- and Ce- codoped BaTiO₃ [29] show photocatalytic activity for the degradation of congo red and titan yellow dye solution as shown in Figure 2.

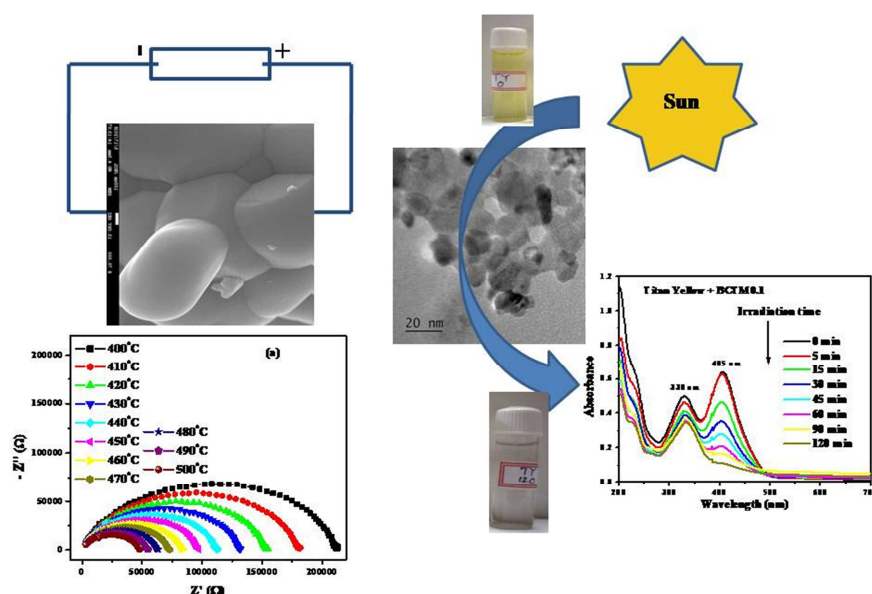


Figure 2. Schematic diagram for the photocatalytically degradation of titan yellow by -Mn and -Ce doped BaTiO₃ (reprinted with permission from ref [29]. Copyright © 2020, Elsevier).

3.2. Layered Structured Perovskites

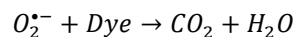
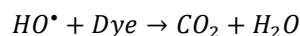
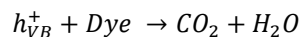
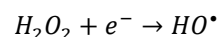
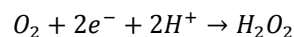
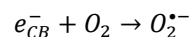
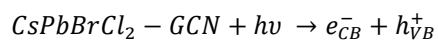
In layered perovskite structure, the network arrangement of octahedrons has boosted the mobility charge carriers with high quantum yield efficiency [30]. Hua *et al.* have been synthesized N-doped $\text{La}_2\text{Ti}_2\text{O}_7$ decorated on graphene sheets through the attachment of Ti-N bond, Ti-C bond, and oxynitrides. The composite material shows high photocatalytic activity for the decomposition of bisphenol A under visible light irradiation and degrades 81% within 300 minute. The mixing of N 2p states and O 2p states extend optical adsorption characteristics of the composite. Again, the presence of graphene enhances the ability for the charge separation and transformation that enhance catalytic activity [30]. Heterojunction formation by the combination of oxygen vacant bismuth tungstate nanosheets (BWO-OV) and oxygen-enriched graphitic carbon nitride (OCN) show high photocatalytic efficiency for tetracycline degradation. This 3D Z-scheme heterojunction built an electric field that accelerates the interfacial charge transfer. Under light irradiation, electrons are excited from Bi 4p orbital to Bi 6p orbital and form an electric field that reduce recombination rate of charge carriers [31]. Bi_2WO_6 has been grown vertically on Ta_3N_5 nanofibers to prepare visible light active $\text{Bi}_2\text{WO}_6/\text{Ta}_3\text{N}_5$ -scheme heterojunction photocatalyst. The catalyst within 120 min degrades 86.7% tetracycline hydrochloride. In presence of visible light irradiation, the catalyst follows type-II heterojunction, where CB and VB of Bi_2WO_6 are more positive than Ta_3N_5 . As a result, photoexcited electrons of Ta_3N_5 drift to Bi_2WO_6 , meanwhile holes from Bi_2WO_6 transfer to Ta_3N_5 . This type of electron-hole transportation increases the lifetime of ROS that enhance catalytic activity for pollutant degradation [32].

3.3. Hybrid Organic–inorganic Perovskites

The general formula of hybrid organic–inorganic perovskites is ABX_3 where A, B, X represent an organic cation, an inorganic metal and a halogen element respectively. Such types of hybride perovskites show much affectivity in photocatalytic application due to fast electron and hole mobility, high absorption coefficient, suitable bandgap, reduced rate of electron-hole recombination [33, 34]. This type of perovskite is also termed as revolutionized photovoltaics due to their 25.2% power conversion efficiency [35]. The perovskite show excellent properties for dye degradation, hydrogen evolution, CO_2 to CO , photo-polymerization reduction through photocatalytic pathway [35, 36].

Lead free methylammoniumiodobismuthate perovskite $((\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9)$ shows high degradation efficiency for RhB, MB, reactive blue under visible light irradiation. The presence of carbon atom in the catalyst play several role for

good catalytic activity of the sample like it increases surface acidity, decrease electron-hole recombination rate, broaden visible light absorption capability. In the degradation mechanism, photo-generated holes follow one electron oxidation step for the production of hydroxyl radicals. These hydroxyl radicals are mainly responsible for the decomposition of the chromophoric dye structure to organic acid and alcohols [34]. Narrow band gap (2 eV) characteristics cesium bismuth iodide ($\text{Cs}_3\text{Bi}_2\text{I}_9$) has been anchored with UV100– TiO_2 nanoparticles to increase visible light absorption capacity [1]. Organic-inorganic hybrid bromide perovskite shows good photocatalytic activity in aqueous media by the formation of composite with MOF. Nanocomposite $\text{MAPbBr}_3@\text{ZIF-8}$ (MA represent methyl amine, ZIF-8 represent zeoliticimidazolate framework) show excellent stability in aqueous media and visible light activity for the decomposition of organic pollutants. In-situ hydroxyl radicals are formed from the composite materials and take an important role for the degradation of methyl orange under visible or sunlight irradiation [37]. Graphitic carbon nitride (GCN) and cesium lead halide perovskite (CsPbBrCl_2) based type-II heterojunction catalyst degrade Eosin B under visible light irradiation. 30 mg GCN content GCN- CsPbBrCl_2 composite material show 94% Eosin B degradation efficiency in 120 min. The CB of CsPbBrCl_2 is more negative than GCN and VB of GCN is more positive than other. This type of position favours the separation of electron and hole for the creation of ROS at the surface of the composite material. The adsorbed dye molecule at the catalyst surface easily degrades to the non-toxic substance by the reaction with ROS. The corresponding chemical reactions are given below [36]:



Cesium lead bromide quantum dots (CsPbBr_3 QDs) show high photocatalytic activity for the degradation of methyl orange (MO) and tetracycline hydrochloride in ethanol under visible light irradiation. Here, in the pollutant degradation O_2 easily form $\text{O}_2^{\bullet -}$ and take part in oxidizing reaction [38].

Table 1. Perovskite photocatalytic materials for wastewater treatment.

Catalyst	Pollutant	Degradation efficiency	Condition	References
(CH ₃ NH ₃) ₃ Bi ₂ I ₉	RhB	98%	Neutral pH, visible light irradiation, 3h	[34]
LaNiO ₃ /TiO ₂	MO	100%	150 min, 10 mg/L	[13]
	Ciprofloxacin	54%	210 min	
ZnSn(OH) ₆	MB	88.4%	100 min, natural sunlight, 5 mg/L pollutant	[21]
CuSn(OH) ₆		73.04%		
BaBiO ₃	RhB	83%	240 min, natural pH, 450W Xe lamp, 5 mg/L pollutant	[22]
LaFeO ₃ /TiO ₂ NTAs	MB	69.7%	120 min, natural pH, 500 W tungsten-halogen lamp, 10 mg L ⁻¹ pollutant	[17]
BWO-OV/OCN	Tetracycline	96.16%	60 min, 300 W Xe lamp, 10 mg L ⁻¹ pollutant	[31]
SrTiO ₃ (La, Cr)	Tetracycline	83%	90 min, 300 W Xe lamp, 20 mg L ⁻¹ pollutant	[24]
Ti substituted LaFeO ₃	4-chloro phenol	100%	120 min, UV-A light, neutral pH	[25]
GCN-CsPbBrCl ₂	Eosin B	94%	120 min, 500 W Xenon lamp, 20 mg catalyst in 40 ml of 10 ⁻⁵ M pollutant	[36]
CsPbBr ₃ QDs	MO	70%	30 min, 10 mg L ⁻¹ pollutant	[38]
	Tetracycline	76%		
2% Gd-doped CoTiO ₃		43.64%	120 min, 300 W Xenon lamp, 0.04g photocatalyst in 100 ml 5ppm	
2% Gd-doped CuTiO ₃	MB	74.19%	Methylene blue	[26]
2% Gd-doped NiTiO ₃		88.64%		
BiFeO ₃ -Bi ₂ S ₃	MB	97%	18h, 20 mg photocatalyst in 10 ml 10 mg L ⁻¹ pollutant	[27]
SrTiO ₃ /MnFe ₂ O ₄	Tetracycline	100%	20 min, 300 W microwave-200 W ultraviolet system, 22 mg/L pollutant	[28]
Ba _{0.9} Ce _{0.1} Ti _{0.9} Mn _{0.1} O ₃	Congo red	91.95%	60 min, natural solar light, natural pH, 0.025 mM pollutant	
	Titan yellow	82.45%	120 min, natural solar light, natural pH, 0.025 mM pollutant	[29]

4. Active Species Trapping and ESR Study

In photocatalytic reaction, the identification of ROS is necessary to distinguish the path of reaction, improve

degradation efficiency, involvement of several techniques for practical application [5]. The reactive oxygen species are generally superoxide anion radical, hydroxyl radical, hydrogen peroxide, singlet oxygen, electron, hole.

Table 2. List of scavengers for several ROS in photocatalytic mechanism study.

Reactive species	Scavenger	Pollutant	Catalyst	Reference
•OH	Isopropanol	Tetracycline	SrTiO ₃ (La, Cr)	[24]
		Tetracycline	Bi ₂ WO ₆ /Ta ₃ N ₅	[32]
		MO	MAPbBr ₃ @ZIF-8	[37]
	tert-butanol	Tetracycline	SrTiO ₃ /MnFe ₂ O ₄	[28]
		Tetracycline	CsPbBr ₃ QDs	[38]
		MB	2% Gd-doped MTiO ₃ (M=Co, Cu, and Ni)	[26]
		MO	MAPbBr ₃ @ZIF-8	[37]
•O ₂ ⁻	p-benzoquinone	Tetracycline	CsPbBr ₃ QDs	[38]
		MB	2% Gd-doped MTiO ₃ (M=Co, Cu, and Ni)	[26]
		Tetracycline	SrTiO ₃ /MnFe ₂ O ₄	[28]
e ⁻	Silver nitrate	Tetracycline	SrTiO ₃ (La, Cr)	[24]
	Methanol	Tetracycline	SrTiO ₃ (La, Cr)	[24]
	di-ammonium oxalate	MB	2% Gd-doped MTiO ₃ (M=Co, Cu, and Ni)	[26]
Hole (h ⁺)	EDTA-2K	MO	MAPbBr ₃ @ZIF-8	[37]
	ethylenediaminetetraacetic acid	Tetracycline	CsPbBr ₃ QDs	[38]
	disodium ethylenediaminetetraacetic acid	Tetracycline	SrTiO ₃ /MnFe ₂ O ₄	[28]

Jiang *et al.* has been used isopropanol, silver nitrate, and methanol for the identification of •OH, e⁻, and hole respectively. They have done a control experiment under bubbling of N₂ gas to identify the effect of •O₂⁻. In this study, •O₂⁻ is taken an important role due to significant decrease of photocatalytic reaction rate by the time of control experiment [24]. In the photocatalytically degradation of MO by MAPbBr₃@ZIF-8, Mollik *et al.* have been used AgNO₃ (radical scavenger), EDTA-2K (h⁺ scavenger), isopropanol (•OH), p-benzoquinone (•O₂⁻ scavenger) to distinguish the

reactive species [37]. Bi₂WO₆/Ta₃N₅ heterojunction exhibits a sharp decrease of degradation efficiency for tetracycline degradation in presence of isopropyl alcohol than benzoquinone and ammonium oxalate. The activity of hydroxyl radical is also established from the electron spin resonance (ESR) technique, where DMPO-•OH signal is more contrast than DMPO-•O₂⁻ [32]. Visible light mediated tetracycline degradation by CsPbBr₃ QDs shows that superoxide anion radicals take an important role than other ROS. The less influence of hydroxyl radical is due to the

standard reduction potential of $\bullet\text{OH}/\text{OH}^-$ (+1.99 eV) is more positive than VB potential of CsPbBr_3 QDs (+1.81 eV). In the other side, the standard redox potential of $\text{O}_2/\bullet\text{O}_2^-$ (-0.33 eV) is less negative than CB potential (-0.45 eV) of CsPbBr_3 QDs [38]. In tetracycline degradation by $\text{SrTiO}_3/\text{MnFe}_2\text{O}_4$ microwave-ultraviolet system, trapping experiment shows that $\bullet\text{OH}$ takes an important and major role. ESR technique is also supported the above ROS, as the high intensity 1:2:2:1 characteristics signal of $\text{DMPO}-\bullet\text{OH}$ than 1:1:1:1 signal of $\text{DMPO}-\bullet\text{O}_2^-$ [28].

5. Future Prospectus and Conclusion

Perovskite photocatalyst materials have great interest in photocatalytic application for wastewater treatment. A huge number of research has been done on doped and undoped perovskite material to enhance the photocatalytic property. The main aim to find a suitable photocatalyst, which is based on the reduction of bandgap energy, visible light activity, separation efficiency of electron-hole, easy generation of reactive oxygen species, recyclability of photocatalyst, low cost, easy operation, large industrial application, no secondary pollutant, and environmental friendly nature. Though some disadvantages are removed but a lot of work till pending for future like (i) rate of the reaction, (ii) recovery of the photocatalyst, (iii) practical large scale based work, (iv) design of photocatalytic reactor for speedy process, (v) involvement of natural solar light. The research also takes place on the basis of the surface/interface process at atomic level to understand the action of the photocatalyst surface.

The review is based on the activity of perovskite material for wastewater treatment under light irradiation. The progress of research shows involvement of different design strategies, variation of chemical formula, morphology engineering, heterojunction formation etc. The generation of ROS and their non-selective involvement in pollutant degradation prefer no secondary pollutant generation. Most of the studies have been done in laboratory scale with artificial solar light irradiation which does not give the real impact of future applicability.

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