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A survey on the present status of sustainable technologies for water pollutant abatement

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ABSTRACT

Safe drinking water is the most serious global challenge and demand for efficient technologies to clean water. Advanced Oxidation Processes aim at the complete mineralization of water pollutants including calcitrants rather than a phase separation and are considered as a sustainable technology. Most of the photochemical processes under this operate under UV in the presence of ozone and/or H_2O_2 and/or catalysts and derive many limitations. Such processes although attractive however the process cost limits their applications. In this regard, heterogeneous photocatalysis as a sustainable technology seems to be promising. It is regarded as a green technology and consists of many advantages over other photochemical processes. This article describes the merits and demerits of both non-photochemical and photochemical processes; particularly the heterogeneous photocatalysis, the developments of photocatalytic materials done so far for pollutant abatement, their limitations, and need for visible light active photocatalytic materials.

Keywords: Water; AOPs; Photocatalysis; Sustainable; Pollutant

1. Introduction

Energy and environment are the two biggest challenges of the twenty-first century. Pollutants generated by the rapid industrialization pose a great health hazard to human beings causing physical disabilities, psychological, and behavioral disorder [1]. The impact can be different depending upon the exposure and intensity of pollution. The contaminants may be in the form of solid, liquid, or gaseous. They can be divided into three types: water pollutants, soil pollutants, and air pollutants. The water pollutants constitute organic as well as inorganic pollutants [2]. Organic pollutants constitute a major part of water pollutants. Major organic pollutants are dyes, persistent organic pollutants (POPs), pesticides, oils etc. A wide variety of organic pollutants are introduced into the water system from various industries such as Textile, pharmaceutical, printing, leather tanning, Food, Agriculture, cosmetic, paper, petroleum, plastic, wood, paint, military etc. It is estimated that (a) 2.2 million people in developing countries die every year from diseases associated with lack of safe drinking water, (b) 1.2 billions of people are lacking safe drinking water (one quarter of the world population), and (c) more than 80 countries are suffering from a lack of water (>40% of the world population) [3].

Water is a pre-requisite to human existence and an adequate water supply in both quantity and quality is essential. Water covers three quarters of the earth surface but only 2.5% is not salty. Of this 2.5% world's fresh water, less than 1% is readily available for human use and is unevenly distributed [3]. Therefore, even a small shortage of water could become a threat

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to mankind. Therefore, the safe drinking water is the most serious global challenge and demands for efficient technologies to effectively clean water.

Conventional treatment of environmental pollutants involves collection, concentration, and incineration. This process needs vast quantity of water, air, oil, and large amount of fossil fuels. The process also produces a large amount of carbon dioxide and other harmful substances like dioxin. Many technologies such as physical methods, chemical methods, and biological methods have been developed in this regard [4]. Physical methods are non-destructive in nature, need larger contact time and huge quantity of adsorbents, transfer the contamination from one phase to another causing secondary pollution and require further treatments like regeneration of adsorbents, sludge disposal etc. [5]. Biological methods are slow and need longer detention time, do not allow for high degrees of removal, not suitable for compounds that are toxic for the micro organisms, less resistant to calcitrants, culture maintenance is cost-intensive, not suitable for large volume of effluents, and disposal of sludge creates additional expenses and environmental problems [5,6]. However, chemical oxidation destroys the contaminants and aims at the complete mineralization of the contaminants to carbon dioxide, water and at least into harmless products giving a complete solution to the problem of pollutant abatement. A lot of researches have been addressed to this aim in the last decade to develop a special class of oxidation techniques defined as advanced oxidation processes (AOPs) that operate at or near ambient temperature and pressure [7].

2. Advanced oxidation processes

AOPs involve a combination of oxidants, such as O_3, H_2O_2, UV, catalysts, photocatalysts (in presence of O_2, air), and have been developed to generate hydroxyl free radicals by different techniques [7–13]. The main mechanism of AOPs function is the generation of highly reactive hydroxyl free radicals ($OH^\bullet$). These radicals are reactive electrophiles and react rapidly and non-selectively with nearly all electron-rich organic compounds. They have an oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions compared to conventional oxidants such as H_2O_2 or $KMnO_4$. A goal of wastewater purification by means of AOPs procedure is the reduction in the chemical contaminants, biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in wastewater to such an extent that the cleaned wastewater may be reintroduced into receiving streams. These techniques include both non-photochemical and photochemical methods (Table 1) [7].

2.1. Non-photochemical methods

The non-photochemical methods include the oxidants such as O_3 and/or H_2O_2 and/or catalysts.

2.1.1. Ozonation (O_3)

Ozone is unstable in an aqueous medium and decomposes spontaneously by a complex mechanisim to hydroxyl free radicals. The degradation of the compound occurs through the action of the ozone itself as well as through the radicals generated in the alkaline medium. When the pH is increased, the production rate of $OH^\bullet$ radicals also increase because of the reaction given in (1) [14–16]:

$$3O_3 + OH^- + H^+ \longrightarrow 2OH^\bullet + 4O_2 \tag{1}$$

2.1.2. $O_3 + H_2O_2$

Hydrogen peroxide in an aqueous solution is partially dissociated to hydroperoxide anion (HO_2^-) which reacts with ozone giving rise to a series of chain reactions including hydroxyl radicals [17–19]. Addition of hydrogen peroxide to ozone can initiate the decomposition cycle of ozone, resulting in the formation of $OH^\bullet$ radicals as shown in reaction (2). This method can be used for the degradation of practically all compounds.

$$H_2O_2 + 2O_3 \longrightarrow 2OH^\bullet + 3O_2 \tag{2}$$

2.1.3. O_3 + catalyst

Another opportunity to accelerate ozonation reactions is to use heterogeneous or homogeneous catalysts. Several metal oxides and metal ions (Fe_2O_3, Al_2O_3-Me, MnO_2, Ru/CeO_2, TiO_2-Me, Fe^{2+}, Fe^{3+}, Mn^{2+} etc.) have been studied and sometimes a significant acceleration in the decomposition of the target compound has been achieved, although the reaction mechanism in most cases remained unclear [17,20,21].

2.1.4. $H_2O_2 + Fe^{2+}$ (Fenton's process)

The H_2O_2/Fe^{2+} system known as Fenton process was reported by Fenton [22–25] already over a hundred years ago for maleic acid oxidation. The rate constant for the reaction of ferrous ion with hydrogen

Table 1
List of non-photochemical and photochemical methods

Non-photochemical methods	Photochemical methods
(1) Ozonation at elevated pH (>8.5)	(1) O_3/UV
(2) O_3/H_2O_2	(2) H_2 O_2/UV
(3) Ozone + catalyst (O_3/CAT)	(3) UV/O_3/H_2O_2
(4) Fenton system (H_2O_2/Fe^{2+})	(4) UV/TiO_2/O_3
	(5) Photocatalytic oxidation (UV/TiO_2)

peroxide is high and Fe(II) oxidizes to Fe(III) in a few seconds to minutes in the presence of excess amounts of hydrogen peroxide. The Fenton process is very effective for $OH^{\cdot}$ radicals generation; however, it involves consumption of one molecule of Fe^{2+} for each $OH^{\cdot}$ radical produced, demanding a high concentration of Fe(II) (reaction 3) for pollutant degradation [26,27].

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^{\cdot} \qquad (3)$$

2.1.5. Disadvantages

Although, ozonation was found to be effective due to its high reactivity with many azo dyes and providing good color removal efficiencies, however, it has limitation of short life time (20 min), low COD removal, as well as the high cost of O_3. The major operating cost for the O_3 oxidation process is the cost of electricity for O_3 generation. The energy requirement for O_3 synthesis using air as a feed gas ranges from 22 to 33 kWh/kg of O_3 including air handling and ozone contacting with water [7]. The energy requirement for O_3 production from pure O_2 is in the range from 12 to 18 kWh/kg O_3 to which the cost of O_2 should be added. The cost of H_2O_2 is also added to the cost of ozone. It is produced by electrolysis of ammonium bisulfate or by oxidation of alkyl hydroanthraquinones. The electrolytic process consumes approximately 7.7 kWh per 1 kg of H_2O_2 [7]. The main drawback of catalytic ozonation is limitations on the transfer of matter since it takes place in three phases. An increase in catalyst concentration above a critical value does not involve a corresponding increase in oxidation efficiency. The major disadvantages of Fenton process are the generation of iron hydroxide sludge and the necessity of a very low pH value (2.5–3.0). Besides the above, conventional O_3 and/or H_2O_2 and/or catalysts oxidation of organic compounds does not completely oxidize organics to CO_2 and H_2O in many cases. In some reactions, the intermediate oxidation products remaining in the solution may be as toxic as or even more toxic than the initial compound.

2.2. Photochemical methods

The incomplete oxidation of pollutants through the non-photochemical methods could be overcome by supplementing the reactions with UV radiations. Thus, various combinations studies have explored the synergistic effects of ozone and/or H_2O_2 based systems on the pollutant degradation in wastewater (Table 1).

2.2.1. O_3 + UV

AOPs using ozone and ultraviolet radiation begin with the photolysis of the ozone, which produces H_2O_2 as an intermediate that decomposes to hydroxyl radicals (reaction 4 and 5).

$$O_3 + H_2O + hv \longrightarrow O_2 + H_2O_2 \qquad (4)$$

$$2O_3 + H_2O_2 \longrightarrow 2OH^{\cdot} + 3O_2 \qquad (5)$$

Ozone readily absorbs UV radiation at 254 nm wavelength. The aqueous medium saturated with ozone is radiated with ultraviolet light at this wavelength. This method permits the degradation of many pollutants [25–27]. The extinction coefficient for gas-phase ozone is 3,300 M^{-1} cm^{-1} at this wavelength which is much greater than that of hydrogen peroxide (18.6 M^{-1} cm^{-1}) because of the presence of more number of available lone pairs for excitation on oxygen atoms in the structure of ozone than that of H_2O_2. Therefore, the production of H_2O_2 in reaction as shown in reaction (4) limits the yield of hydroxyl radicals.

2.2.2. H_2O_2 + UV

The photolysis of hydrogen peroxide occurs when UV radiation is applied, as shown in the reaction 6:

$$H_2O_2 + hv \longrightarrow 2OH^{\cdot} \qquad (6)$$

H_2O_2/UV process involves the formation of hydroxyl radicals generated by the photolysis of H_2O_2 and the corresponding propagation reactions [8]. The photolysis rate increases under more alkaline conditions. This is probably due to the fact that the intermediate peroxide anion HO_2^- has an absorption coefficient with a higher value at the wavelength 253.7 nm. An H_2O_2/UV system can totally mineralize any organic compound, reducing it to CO_2 and water [28,29]. One of the greatest disadvantages of this method is when the water to be treated has a higher absorbance; it may compete for radiation with the hydrogen peroxide.

2.2.3. $O_3 + H_2O_2 + UV$

When hydrogen peroxide is used in an O_3/UV process, it accelerates the decomposition of ozone and increases the generation of $OH^{\cdot}$ radicals. This process is the result of the combination of two binary systems, O_3/UV and O_3/H_2O_2. The overall reaction is given in reaction 7. This method was used by several investigators for pollutant degradation [30,31]. However, the process cost is very high. As shown in Table 2, O_3/H_2O_2/UV processes are the most expensive because of the use of two types of reagents as compared to processes that use only one.

$$2O_3 + H_2O_2 + UV \longrightarrow 2OH^{\cdot} + 3O_2 \tag{7}$$

2.2.4. $H_2O_2 + Fe^{2+}$ + UV (photo-Fenton's process)

In photo-Fenton process the formation of hydroxyl radical also occurs by the reaction (8). UV light leads not only to the formation of additional hydroxyl radicals but also to the recycling of ferrous catalyst by the reduction in Fe^{3+}. In this way, the concentration of Fe^{2+} is increased and the overall reaction is accelerated. Among the AOPs, the oxidation using Fenton's reagent and photo-Fenton's reagent has been found to be a promising and attractive treatment method for the effective decolorization and degradation of dyes [32,33]. Muruganandham and Swaminathan [34] have carried out studies where similar results were obtained. However, it is necessary to control the pH of the medium between 2.6 and 3.0 for the best performance of the system.

Table 2
Comparative operating costs of some AOPs [11]

Process	Treatment cost ($\$/m^3$)
O_3	5.35
O_3/H_2O_2	6.58
O_3/UV	8.68
H_2O_2/UV	4.56
O_3/H_2O_2/UV	11.25

$$Fe^{2+} + H_2O + UV \longrightarrow Fe^{3+} + OH^{\cdot} + H^+ \tag{8}$$

2.2.5. Disadvantages

Although photochemical processes including UV/O_3/H_2O_2/Fenton's process are successful, however suffers with many disadvantages such as capital intensive, high cost of photolysis of ozone, low molecular absorption of H_2O_2 at 254 nm that limits the OH yield in the solution, high cost of UV, control of low pH in Fenton's process etc. Production, transport and storage of ozone and H_2O_2 are expensive and require a pH adjustment. Both are corrosive, hazardous, and unstable. For some applications, quenching of excess peroxide is required; excess of H_2O_2 reacts with $OH^{\cdot}$ to form H_2O and O_2. If water solutions contain UV absorbing organic compounds, then UV radiation usually does not give any additional effect to ozone because of the screening of ozone from the UV by optically active compounds such as phenol, 5-methylresorcinol, xylenols, etc. [7]. Therefore, sustainable technologies for pollutant degradation are the thrust areas of research. In this regard photocatalysis, one of the AOPs, seems to be promising.

3. Photocatalysis

Photocatalysis is one of the AOPs which involves photocatalytic oxidation using photoactive semiconductors as heterogeneous catalysts for the rapid degradation of organic pollutants in water and air into carbon dioxide and water upon irradiation of light [35]. It is regarded as a Green technology as the environment can be purified using this technology without using fossil fuels and harmful chemicals. It provides a simple way to use light to induce chemical transformations. In comparison to homogeneous processes, such heterogeneous catalysis has the advantage of separating the product with greater ease and most commonly used these days. Photocatalysts can be reused many times without significant loss in efficiency. In 1972, Akira Fujishima and Kenichi Honda discovered the photocatalytic water splitting effect on TiO_2 [36]. Since then, many research efforts have been performed in understanding the fundamental processes and in enhancing the photocatalytic efficiency of TiO_2 and prompted a true revolution on the extensive use of photocatalyst in the generation of hydrogen fuel, and water disinfection devices and pollutant abatement [37].

3.1. Fundamental aspects of photocatalysis

The basis of photocatalysis is the photoexcitation of a semiconductor that is a solid material upon the absorption of electromagnetic radiation. Under irradiation the material may be excited by photons ($h\nu$) possessing energies of sufficient magnitude to produce conduction band (CB) electrons, and valence band (VB) holes. These charge carriers are able to induce reduction or oxidation, respectively. Most of these electron-hole pairs recombine, releasing the absorbed energy, however a small fraction of these migrate to the surface of the photocatalyst and react with absorbed species [38,39]. The process involves the use of photocatalysts to carry out the continuous generation of $OH^{\cdot}$ radicals that oxidize the pollutant molecules. The probable mechanism steps of reaction mechanism are as follows [40]:

Photoabsorption

$$TiO_2 + h\nu \longrightarrow h^+_{VB} + e^-_{CB} \tag{i}$$

Recombination

$$e^-_{CB} + h^+_{VB} \longrightarrow \text{energy} \tag{ii}$$

Charge transport and formation of free radicals

$$H_2O + h^+_{VB} \longrightarrow OH^{\cdot} + H^+ \tag{iii}$$

$$O_2 + e^-_{CB} \longrightarrow O_2^{\cdot -} \tag{iv}$$

Pollutant degradation

$$OH^{\cdot} + \text{pollutant} \longrightarrow H_2O + CO_2 \tag{v}$$

$$O_2^{\cdot -} + H^+ \longrightarrow OOH^{\cdot} \tag{vi}$$

$$OOH^{\cdot} + OOH^{\cdot} \longrightarrow H_2O_2 + O_2 \tag{vii}$$

$$O_2^{\cdot -} + \text{pollutant} \longrightarrow CO_2 + H_2O \tag{viii}$$

$$OOH^{\cdot} + \text{pollutant} \longrightarrow CO_2 + H_2\,O \tag{ix}$$

The absorption of a photon excites an electron to the CB (e^-_{CB}) generating a positive hole in the VB (h^+_{VB}) (Eq. (i)). The charge carriers either can recombine to dissipate energy (Eq. (ii)) or alternatively, can migrate to the catalyst surface and initiate redox reactions with adsorbates. CB electrons can reduce electron acceptors, like oxygen molecules or H^+ (Eq. (iv)). On the other hand, VB holes are oxidants that are able to attack donor species such as organic molecules or OH^- groups or water molecules (Eq. (iii)). The hydroxyl radicals can subsequently oxidize organic species with mineralization producing mineral salts, CO_2, and H_2O (Eq. (v)). Holes possess an extremely positive oxidation potential and should thus be able to oxidize almost all chemicals. Even the one-electron oxidation of water resulting in the formation of hydroxyl radicals should be energetically feasible. Numerous observations can indeed be explained by the intermediacy of $OH^{\cdot}$. However, due to the short life-time and high reactivity, no experimental evidence for the formation of hydroxyl radicals has been given so far. The superoxide radical anion ($O_2^{\cdot -}$) (Eq. (iv)) may further react with H^+ to generate hydroperoxyl radical ($^{\cdot}OOH$) (Eq. (vi)) and further electrochemical reduction yields H_2O_2 (Eq. (vii)). These reactive oxygen species may also contribute to the oxidative pathways such as the degradation of a pollutant (Eqs. (viii) and (ix)).

3.2. Materials research in photocatalysis

Photocatalysis with TiO_2 is considered as one of the most promising approaches for pollutant abatement and has been studied widely [41]. It is still being actively researched and has become quite well understood experimentally and theoretically both in the forms of anatase and rutile [42–44]. However, it presents some disadvantages. The major drawbacks are large band-gap of TiO_2 (3.2 eV for anatase) that requires an excitation wavelength that falls in the UV region (solar radiation contains only 7% UV light reaching the surface of the earth and pure TiO_2 is inactive in sunlight) and rapid recombination of photogenerated electrons and holes, a limiting factor that controls the efficiency of photocatalysis. This fact has prompted research in photocatalysis either to improve the efficiency of TiO_2 in the visible spectrum or to look for new visible light active (VLA) alternative materials. During the last few years, a large number of new photocatalysts has been synthesized and is tested as possible alternatives to TiO_2. Among these, mixed oxides of transition metals like Nb, V, or Ta, or with main group elements such as Ga, In, Sb, or Bi have been extensively investigated as alternative photocatalysts [45–47]. Besides, sulfides and nitrides of different metals have been frequently selected to obtain materials with photoactivity in the visible range [45]. The materials developed so far can be grouped as TiO_2-based materials, non-TiO_2 based materials, and graphene-based materials.

3.2.1. TiO_2-based materials

Considerable effort has been devoted to improve TiO_2 photocatalytic efficiency. This has been done either by morphological modifications such as increasing surface area and porosity by preparing nanoparticles, nanotubes, mesoporous phases [47–50], or by chemical modifications such as the incorporation of additional components such as metals, non-metals, or a second semiconductor phase surface sensitization by organic dyes or metal complexes [51–55]. Although morphological modifications have shown different degrees of photoactivity improvements, however the improvements are not significant. Under chemical modifications metal-doping of TiO_2 has been extensively explored as a way to improve photoactivity under visible light. Foreign cations frequently act as recombination centers. Therefore, significant improvements are only possible at low concentration of dopants, and using careful synthesis methods to limit lattice distortion. Coupling of TiO_2 with another semiconductor is another widely used approach to increase the photonic efficiency because, if the band structure of both materials is adequate, charge carriers become physically separated upon generation and therefore the recombination rate greatly decreases. Some of the semiconductors more frequently coupled with TiO_2 are SnO_2, WO_3, and Bi_2S_3, Cu_2O, Bi_2O_3, Fe_2O_3, CdSe, ZrO_2, and In_2O_3. The most promising route seems to be the partial substitution of oxygen with N and other elements like C and S [56]; $TiO_{2-x}N_x$ materials show remarkable photoactivity under visible illumination ($\lambda = 300–450$ nm). However, it is worth noting that photoactivity under visible light is often significantly lower than under UV. Although many strategies have been made, however to get solar-driven TiO_2 photocatalyst with higher activity is still promising.

3.2.2. Non-TiO_2 based materials

Research on non-TiO_2 based photocatalysts has led to the development of many new materials as possible alternatives to TiO_2 (Table 3). In this regard, many metal oxides, metal sulfides, and complex oxides are synthesized. Although some of them are promising, however limitations with these materials arise from low mineralization yields, stability, and others too. ZnO has been frequently considered as an alternative to TiO_2 for photocatalytic applications, since it shows similar activity in certain conditions [57]. However, it suffers from anodic photocorrosion different from TiO_2; this reaction is not inhibited by water oxidation. In addition, it is soluble in strong acids and alkalis, which limits the pH range in which it can be used, as well as in the presence of Zn^{2+} chelating agents. These properties limits the photocatalytic applications of ZnO for water treatment but, in spite of this, a considerable number of works have dealt with the degradation of aqueous pollutants using ZnO [57]. Another limitation of ZnO is its wide band-gap (3.2 eV), which restricts light absorption in the UV region. Miyauchi et al. [58] studied the activities of thin films of several oxides for the degradation of methylene blue (MB) adsorbed on their surface from aqueous solutions. TiO_2, SnO_2, ZnO, WO_3, $SrTiO_3$, V_2O_5, CeO_2, CuO, MoO_3, Fe_2O_3, Cr_2O_3, and In_2O_3 were used for this purpose. Among them, TiO_2, $SrTiO_3$, and ZnO exhibited a high activity for the oxidation of MB under UV illumination, while SnO_2 showed relatively low activity and the rest of the oxides were not active for decomposing the dye molecules. CeO_2 has also received attention as a photocatalyst because of its interesting properties: stability under illumination and strong absorption of both UV and visible light. However, this material has been generally found to be less active than TiO_2 under UV irradiation [59,60]. However, in contrast with titania, this oxide can be activated by visible (violet) light. Some metal sulfides have shown high photocatalytic activities, however, these materials are not relevant for aqueous pollutant degradation due to anodic photocorrosion. Nevertheless, several works have been devoted to the study of these photocatalysts, among

Table 3
Some important alternative photocatalysts

Photocatalyst	Band-gap (eV)	Radiations	Limitations
ZnO	3.2	UV active	Anodic photocorrosion
CeO_2	2.95	Visible light active	
BiOCl	3.46	UV active	Few studies are available, scarcity and higher cost of bismuth
BiOCl nanofiber	3.2	UV active	As above
$BiVO_4$	2.38	Visible light active	As above
Bi_2WO_6	2.69	Visible light active	As above
BiOBr	2.54	Visible light active	As above
Bi_2MoO_6	2.59	Visible light active	As above
$CaIn_2O_4$	–	Visible light active	As above
CdS	2.42		Anodic photocorrosion

which the application of ZnS to the reduction of nitrates and nitrites, or the oxidation of hexafluorobenzene can be cited [61,62].

Interest has recently been dedicated to mixed oxides known as metallates for water decontamination processes, mainly under visible light illumination. The first metallate used for aqueous pollutant photocatalytic abatement was $BiVO_4$ [63–67]. A faster degradation of 4-nitrophenol (4-NP) was observed with $BiVO_4$ when oxygen was purged into the solution, while similar activities to TiO_2 were found in air-saturated medium. However, in contrast with TiO2, no CO_2 evolution was observed with $BiVO_4$. Chemical modification of $BiVO_4$ has been studied as a way to improve its photocatalytic properties. Kohtani et al. [63] have applied Ag-loaded $BiVO_4$ to the photocatalytic degradation of various aqueous pollutants. The photocatalytic activity of Bi_2WO_6 has been studied by several research groups [68–70]. Other tungstates have also been investigated for aqueous pollutants degradation [71–73]. Zhu's group compared the activities of $ZnWO_4$ and $PbWO_4$ with that of Bi_2WO_6 for RhB degradation under simulated solar light and visible light irradiation. Under both illumination conditions, $ZnWO_4$ and $PbWO_4$ exhibited lower activity than Bi_2WO_6 for this reaction. Methyl orange (MO) and RhB were used to evaluate the photocatalytic activity of $CdWO_4$ for aqueous pollutant degradation. Its activity was similar to that of $ZnWO_4$ for both reactions and was also similar to that of TiO_2 under UV irradiation, but activity slightly declined after 5 photocatalytic runs. Martı´nez de la Cruz et al. investigated the photocatalytic degradation of RhB over nanosized Bi_2MoO_6 [74].

3.2.3. Graphene-based materials

Carbonaceous nanomaterials such as activated carbon, fullerenes, carbon nanotubes, graphene, and others have unique structures and properties that can add attractive features to photocatalysts [75,76]. Generally, the photocatalytic enhancement is ascribed to the suppressed recombination of photogenerated electron-hole pairs, extended excitation wavelength, and increased surface-adsorbed reactant. However, the underlying mechanisms are still unclear. Leary and Westwood [77] reported the recent progress in the development of TiO_2/nanocarbon photocatalysts covering activated carbon, fullerenes, carbon nanotubes, graphene and other novel carbonaceous nanomaterials. Graphene, a two-dimensional single layer of graphite as the most recently discovered carbonaceous material, has attracted immense attention due to its outstanding mechanical, thermal, optical, and electrical properties [78,79]. Especially, graphene possesses a high thermal conductivity (~5,000 $W\ m^{-1}\ K^{-1}$), offers an excellent mobility of charge carriers at room temperature (~2,00,000 $cm^2\ V^{-1}\ s^{-1}$), and exhibits an extremely high theoretical specific surface area (~2,600 $m^2\ g^{-1}$), high value of Young's modulus (1TPa), and optical transmittance (~97.7%). A variety of semiconductor photocatalysts have been used for the synthesis of graphene-based composites and/or functional graphene oxide [80,81]. They mainly include metal oxides (e.g. TiO_2, ZnO, SnO_2, Cu_2O, Fe_2O_3, NiO, MnO_2, and ZrO_2), salts (e.g. ZnS, CdS, CdSe, Bi_2WO_6, $BiVO_4$, $Sr_2Ta_2O_7$, $ZnFe_2O_4$, $InNbO_4$, and g-Bi_2MoO_6). The widely used preparation methods are *in situ* growth, solution mixing, hydrothermal, and/or solvothermal method [76]. They could be regarded as the next generation photocatalyst systems. These exciting developments have opened up new pathways to high-performance photocatalysts. The fabrication of high quality graphene-based composites is very challenging due to the existence of defects or oxidation sites in the partially restored graphene. More efficient synthetic strategies for graphene-based composites need to be developed to address these issues.

4. Future prospects

Photocatalysis is an effective method for global water purification under AOPs. TiO_2 is considered as one of the most promising approaches for pollutant abatement and has been studied widely. The major drawbacks are large band-gap of TiO_2, photoactivity under UV light and rapid recombination of photogenerated electrons and holes, hence the need for more stable, efficient, VLA active photocatalysts is now the goal of researchers. It is important to note that for a catalyst to be considered more active than TiO_2, this activity must exceed that obtained with TiO_2. The factors to be considered in photocatalysts developments are recombination of electrons and holes, amount of visible light utilized (band-gap), stability against photocorrosion, position of VB and CB i.e. band-gap, high activity, resistance to poisoning, mechanical stability, non-selectivity in most cases, physical and chemical stability under a wide range of conditions, complete mineralization of pollutants, calcitrants etc. In order to achieve significant improvements in catalytic activity using visible light, precise control of the stoichiometry of the catalytic metal oxides and mixed metal oxides, addition of dopants, particle shape, and pore topology are all critical factors for catalyst development. A significant problem is suppressing charge recombination in semiconductor materials. Although some metallates, considering their activities and stability, appear promising materials for solar photocatalysis, however limitations with these materials arise from low mineralization yields, stability. Recently the graphene-based materials are advancing fast in the field of semiconductor photocatalysis to meet the challenges of visible light activity. They are considered as the next generation photocatalyst. Coupling of TiO_2 or other semiconducting materials with graphene could introduce new enhanced properties to improve the overall photocatalytic performance of these materials. Although many important findings have been reported in this regard, however more studies are required to establish the above materials as robust materials. In summary, the limitations of TiO_2 for photocatalytic application have not been overcome up-to-date, but there are promising alternative materials that may lead to better future in photocatalysis.

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