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REVIEW

A review on remediation of harmful dyes through visible light-driven WO_3 photocatalytic nanomaterials

M. B. Tahir[1] · S. Ali[2] · M. Rizwan[2]

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Abstract
Environmental pollution has become a matter of great concern in the age of modern industrialization. Severe contamination in the form of dyes can cause serious health hazard in the community, killing fishes inside water, damaging fertility of the land and aquatic lives as well. All possible treatment methods are discussed to critically assess the technologies for obtaining ecofriendly discharge. High cost, technical hurdles, potential environmental and human risk are the major challenges faced by different physical, chemical and biological techniques. To overcome these barriers, photocatalysis with semiconductor nanostructured materials is a green technology approach that has been widely functional particularly in environmental remediation field. Nanostructured WO_3 used as a photocatalyst that is within the visible light responsive up to ca. 480 nm having multifunctional advantages of cost-effective, harmlessness, durability and stability in acidic conditions as well. It makes us confident that WO_3-based nanostructured materials by prudently steering its direction while evading accidental concerns can offer healthy solutions to wastewater treatment challenges.

Keywords Environmental pollution · Photocatalyst · Remediation · WO_3

Introduction

Due to overpopulation and rapid industrialization, wastewater generation has increased both in industrial and domestic sector and, as a result, the supply of drinking and nonportative water has a matter of concern nowadays (Singh et al. 2013, 2014). Environmental conservation, pollution control and effluent management are also emerging for decisive problems of residential civilization. It is worth mentioning that reduction in fossil fuels assets, increase in global warming and other environmental issues like water pollution (Potti and Srivastava 2012), energy crises (Chan et al. 2011) and toxic gases (Tsai et al. 2018) have become a matter of serious concern, and researchers are now anticipated more strongly than ever to contribute to the realization of sustainable development—a society that balances the economy with the natural environment to overcome major problem, i.e., water pollution (Cho et al. 2011; Wang et al. 2012a, b). Contamination for this watery system transport is very important issue to the universe worldwide, social and economic system of this universe. Market effluents impart a small part of chemical fraction to the environment; its integrity reduces the quality of environmental fairly (Chatterjee and Dasgupta 2005; Zhang et al. 2009). With the prompt development in industries, large quantity of fresh and pure water used as impure material in fabricating purposes. During industrial processing, raw materials in the form of processing material and effluents are discharged into the water. Therefore, the textile wastewater is an "essential by-product" of the industry and is the principal source of the effluents in the pollution of industry.

A foremost environmental threat existing in textile industrial dye markets is the expulsion of unwanted sewage to the environment, initiating pollution of proximate soil and water as well (Potti and Srivastava 2013). Approximately seven lakh tons of various dyes are produced per year worldwide. Moreover, a secondary reaction of its wide utilization is that only twelve percent of dyes are squandered while the dying

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✉ M. Rizwan
mrazi1532@yahoo.com

[1] Department of Physics, Faculty of Science, University of Gujrat, Hafiz Hayat Campus, Gujrat 50700, Pakistan

[2] Department of Environmental Sciences and Engineering, Government College University, Allama Iqbal Road, Faisalabad 38000, Pakistan

method and about 20% of this wastage mixed with environment (mostly into source of water (Kumar and Rao 2015; Mu et al. 2014). This kind of wastage can cause main problems regarding pollution in the environment and instigated negative impact to the environs and human's life as well. The low concentration of organic dye even 1×10^{-3} mg/L has very toxic effect on humans (Benedek et al. 2018). The surface and subsurface of water contain many types of dyes. These dyes are shaped by water and claimable also causes number of diverse water diseases, viz. dermatitis, and severe irritation of breathing expanse and infection on nasal septum (Lou and Zeng 2003; Qi et al. 2003).

It was noticed by WHO and UNICEF that the non-purified water and lack of the sanitation are the reasons for the death of children which ranges from 4500 to 5000 per day. It was also remarked that almost billions of people do not have access to the safe and purified water. The other significant points are about the pollution is that the need for purified water supply for the agriculture use (Altuntaş and Turan 2018). It was mentioned by Food and Agriculture Organization that about 70% of pure and fresh water is used in the agriculture industry which exceeds to 95% in the developing countries like Pakistan, Bangladesh, India, etc. (Gu et al. 2002; Su et al. 2010; Korotaeva et al. 2018). In Fig. 1a, countrywise colored profile of withdrawal of fresh water is given which is based on the water used in agriculture, industrial and domestic applications. In this profile, distribution of industry, agricultural and home use water can be assessed clearly. With the passage of time, due to population increase and development of industrial zone, removal of the fresh water is increasing that may cause disturbing condition and adverse effects on human life.

Raising social recognition of the use of industrial wastewater is crucial to moving forward. This is the significance of education and training, and new forms of awareness-raising, to change discernments of health risks and address sociocultural concerns, to strengthen public acceptance. The necessities of clean water are one of the major challenges of the twenty-first century for humans. In this regard, the access to the low-cost purified water is the main concern and was a main goal for the humans (Gu et al. 2002; Vacchi et al. 2017). Thus it is necessary to promote environment-friendly methods involving dealing of water for all the living creatures as well as human to be facilitated with clean water in the future. The number of ongoing researches examines the new ways and concepts to treat the wastewater effluents of many industries.

Important effort conceded on the elimination of a dye by wastewater through electrochemical, coagulation, precipitation, oxidation/corrosion, filtration, adsorption and flocculation processes, etc., are common techniques conveyed for reduction in dyes from sewages/effluent (Jin et al. 2004). In addition to the benefits, all these methods have several drawbacks containing inability to degrade the dyes entirely and large functioning costs (Chakrapani et al. 2009). The promptly increasing world population and the changing of the living style of humans increased the demands of dyes. The distribution of water was disturbed according to the environmental changes which disturb the supply also (Liu et al. 2011; Wang et al. 2012a, b). The currently used technologies as well as setup are at their peak to provide fresh and purified water for the human beings and the world needs. The established countries widely spread the water treatment plants and introduce the new technology to the existing systems after the very rigorous progress in the purification quality of water (Smith et al. 2011). At this stage, the new system used for the treatment of water not only uses the technology plants and overcomes the main goals of purification of water but also makes development in these plants which can be used to increase the water supply by using the unconventional sources that was beneficial to economy (Zhang et al. 2011).

Presently, photocatalysis dye degradation is imaginary to deliberate having best procedure for excluding the hazardous dyes available within wastewater because of the ability of this method to perfectly mineralize the contaminants (Seabold and Choi 2011). Various semiconductors metal oxides like ZnO, TiO_2, CuO, etc., have been used for the said application (Gillet et al. 2004; Singh et al. 2014). All such catalysts faced limitations due to less absorption of visible light and others (Gillet et al. 2004). The visible light was analyzed and had a cost-effective role and prevalence in the sunlight; it is hoped that the development in the photocatalysis semiconductors gives the good response to the visible light. To overcome the limitation, tungsten trioxide (WO_3) is a semiconductor photocatalyst of *n* type, having tremendous contribution toward the degradation of organic compounds (Gerand et al. 1979). WO_3 is getting a lot of attention, and different researchers are suggesting WO_3 an efficient visible light reaping photocatalyst. WO_3 is preferred because of its non-toxic nature along with small fluctuating bandgap varying from 2.4 to 2.8 eV, just because of this size of E_g it excites in visible region of solar spectrum absorbs lighter and refrain recombination and enhances the photocatalytic efficiency (Balaji et al. 2009; Boulova and Lucazeau 2002; Sadek et al. 2008). High photocatalytic performance under visible region, moderate cost as well as constancy toward corrosion procedure of WO_3 has acceptable this substantial component as a photocatalyst for the profitable implementations. Owing to these exclusive characteristics, WO_3 is very effective to visible light photocatalyst and widely searched to the prospective fields in secondary batteries, photochromic and electro-chromic (Kuti et al. 2009; Liu et al. 2011).

In the last few years, a no. of excellent reviews on WO_3 materials focusing on the gas-sensing property (Hemberg et al. 2012), solar hydrogen generation (Janáky et al. 2013),

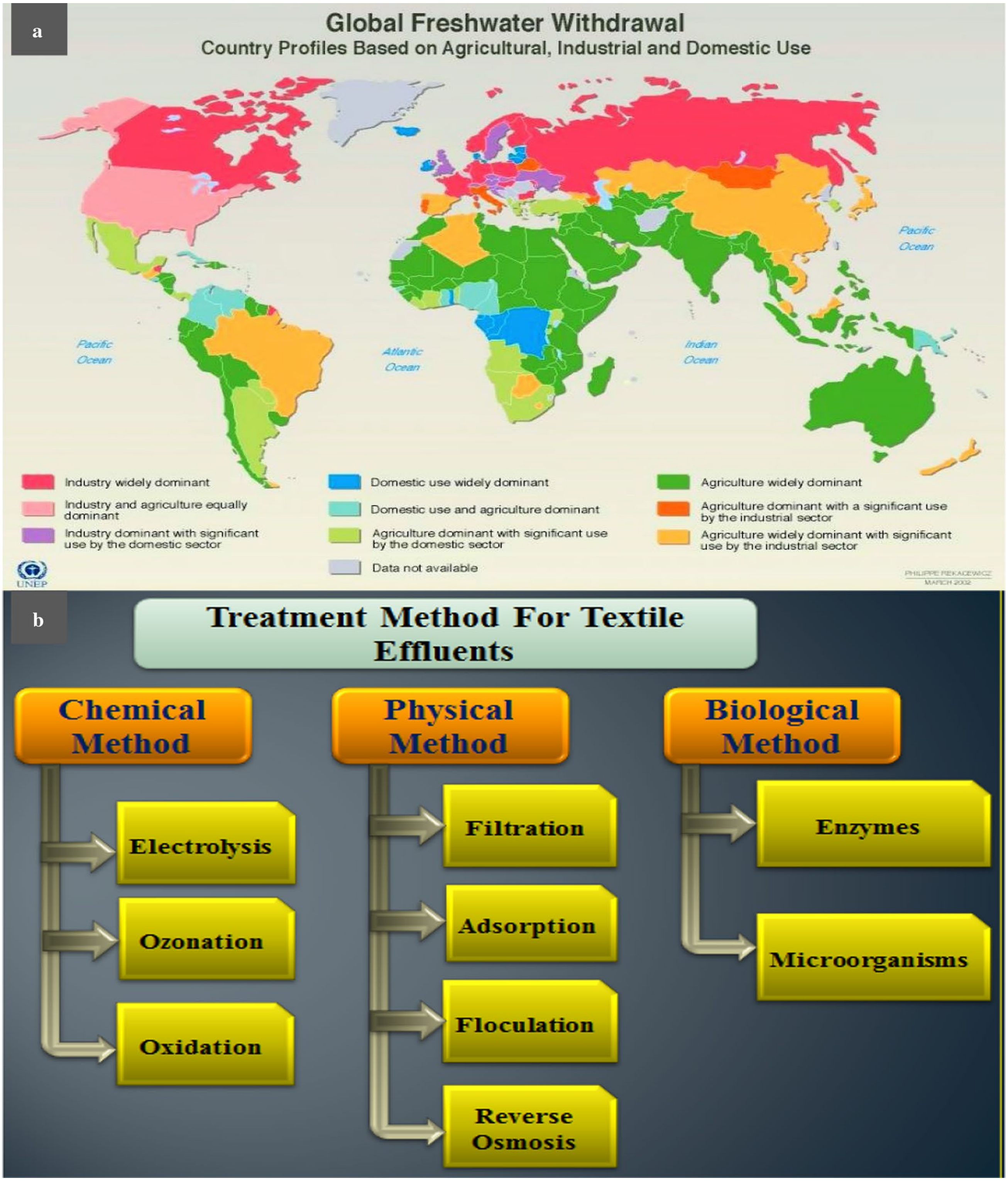

Fig. 1 Schematic diagrams of **a** global freshwater withdrawal, **b** various treatment methods for treatment of textile dyes

nanostructured thin films for photocatalytic water oxidation and density functional theory (DFT) computation (Di Valentin et al. 2013) have been published. There is also an extensive review on the fabrication methods, characteristics and implementations of WO_3 materials (Zhang et al. 2011). However, an extensive review focusing on the WO_3-based photocatalysts for the treatment of textile industrial wastewater is still required to deliver for readers for improvement and understanding of the latest research development in this field. To the best of our information, up to now, there is no review on the WO_3-based photocatalysts for wastewater treatment. In this review, we focused on the needs of clean environment by taking into consideration the dangerous dyes emitted from textile industries. The probable effect of toxic effluents on humans and ecological community and also probable conflict has been reviewed. Furthermore, different remediation techniques and their limitations are reviewed and discussed. WO_3-based nanostructured photocatalytic ingenious way that used for the elimination of large amount of dyes from the wastewater is now a very broad research area. Moreover, some approaches for enhancing photocatalytic performance of WO_3, for example, noble metal deposition, coupled semiconductors and surface hybridization are described briefly and systematically. Finally, an instant of the present research/study position as well as tasks having the aspects of WO_3-based photocatalysts is described.

Date and location of the research

The research work was conducted at Department of Physics, University of Gujrat, Gujrat and Department of Environmental Sciences and Engineering, GC University Faisalabad, 38000, Pakistan.

Treatment of dyes in wastewater: different methods

Textile effluents change the properties of the water so we have to purify that wastewater. Treatment of textile wastewater is very important to avoid the hazards on human body as well as environment. There are three basic treatment methods for this purpose that are chemical, physical and biological method as shown in Fig. 1c (Bratkova et al. 2018). Different types of effluents are present in textile wastewater that has to remove from the water then water will be useable. Figure 1b illustrates the flowchart of different method utilized for treatment of toxic dyes within wastewater discharged from textile industries.

Chemical method

In this method, chemical reaction occurred just like precipitation method. The chemical methods are depending on the contamination (want to remove) interaction and chemicals that are used for separation of contaminants/used to remove harmful effect of contaminants. The chemical methods are used separately and also used as the combination with that of the physical methods (Hossain et al. 2013). The chemical treatment could oxidize dyestuff during dyeing as well in bleaching of effluents. Fenton oxidation and ozone oxidation are examples of chemical oxidation processes.

Oxidation processes are mostly used chemical methods in treatment of wastewater. Decolorization is the main thing to do in oxidation process. The hydrogen peroxide (H_2O_2) is the strongest and mostly used oxidizing agent and can decolorize a large amount of dyes. It forms the hydroxyl radicals in the activated form which was the strongest agent used for decolonization. The hydroxyl radicals are activated in this method using hydrogen peroxide for the first time (Teh et al. 2016; Vacchi et al. 2017). The ozone oxidizing process is very effective and well-known process used for decolorizing the dyes in wastewater. It can also break the double bond easily in organic compounds. Ozonation process can remove and ruins the dyes foaming behavior. Large portion of COD also oxidized. This process can increase the ecological ability of those chemicals that have a very low part of non-degradable. It can also improve the ecological ability of the toxic component through radical components into intermediate ecological components (Barka et al. 2006; Jia et al. 2014). TiO_2 semiconductor and ozone get combined and undergo a process called normally photocatalytic ozonation. This can decrease the rate of the recombination of the electron–hole pairs. The oxidation in the TiO_2 valance bands can produce the hydroxyl radicals (Djurišić et al. 2014; Yu et al. 2009). This process was very awful method for decomposition of organism and compounds in wastewater. The basic advantage of this method is that when it was established in industries and treated water was ejected in the rivers which is free of toxic effluents and has a very good impact on the living organisms, and on humans the hazardous effect reduced. Figure 2 exemplifies the schematic diagrams of various methods (physical, chemical and biological) used for the treatment of dyes emitted from textile industries.

Physical methods

Flocculation is the most basic physical method used for the textile wastewater. It is the removal of effluent charges from the wastewater with the help of electrolytic metal. Metal is used from the electrolytic products like ferric chloride, ferric sulfate and aluminum sulfate. These products give a metal in the solution of wastewater that metal will remove the effluents charges and makes mater pure. This method is suitable for the insoluble effluents not for the soluble effluents (Yu et al. 2014). Filtration is the process to remove solid particles and suspensions from liquid solution. This removal can be taken with various methods. These methods are commonly known as straining, flocculation and sedimentation processes. These methods categorized on the basis of removal

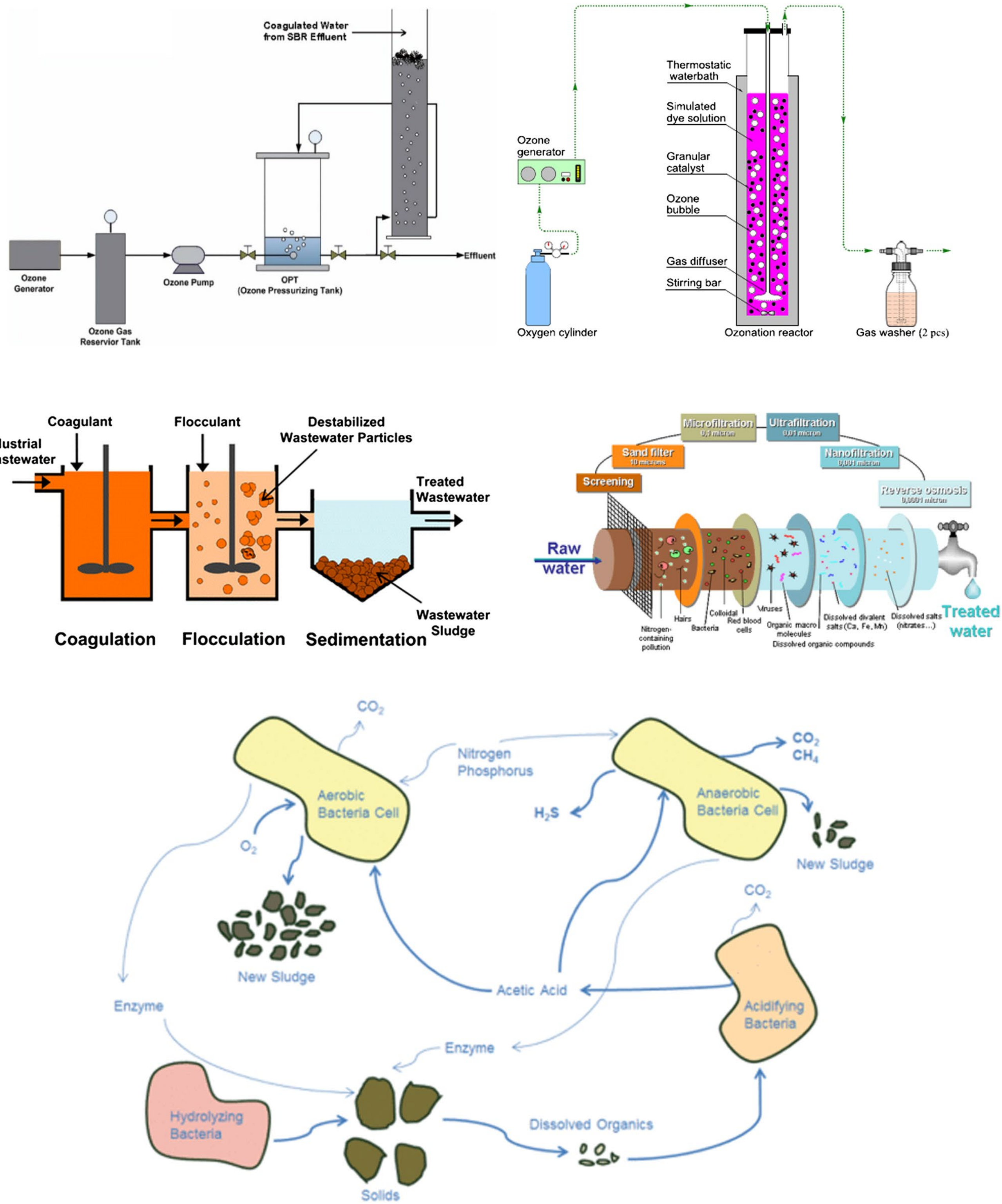

Fig. 2 Schematic diagrams of various methods (physical, chemical and biological) used for treatment of textile dyes

process like particles can be removed from the surface of the filtrate. Naturally, the filtration is done at the lower level water when it passes through the layers of soil while upper-level water should be treated to save the animals and other living organisms and preserved them from illness and other diseases in humans (Gürses et al. 2014). In filtration process, 99.9% removal is achieved. It is a very simple and cheap process (Yang et al. 2014). It was not suitable for high turbidity water and requires a good maintenance in its procedure equipments. To remove dyes, adsorption process was very useful and an effective technique (Tsai et al. 2014). It was very successful techniques for the removal of coloring dyes. Many adsorbents are used to remove dyes from water. Activated carbon is very effective but high-cost adsorbent (Xu et al. 2018). Other than activated carbon, some other adsorbent used in this process like natural phosphate, silica, perlite and some other natural biosorbents. Some parameters used in adsorption are time, pH concentration and temperature (Noureddine Barka et al. 2013; Hayat et al. 2015).

Biological methods

During the biological process, matter that is dissolved is removed from that of the fabric/textile wastewater. The ratio of dyes, microorganisms, there temperature and concentration of water decides the efficiency of removal of effluents from wastewater. The biological methods are categorized into (1) aerobic, (2) anaerobic, (3) anoxic/facultative or their combination on the basis of oxygen usage. The selection capability of microbes and enzymes tells about the efficiency to degrade the effluents using biological methods (Batista et al. 2017; Chen and Ting 2015). A large number of organic microorganisms and enzymes are used for the degradation process for many dyes. These microorganisms and enzymes are segregated (Chen and Ting 2015). The efficiency related to the biological methodology for the degradation purpose is dependent on the acceptability and on the microorganisms with enzymes. The enzymes (intra- and extracellular) are mostly used to remove the dyes in wastewater and help in metabolic activity for fungal culture (Chen and Ting 2015; Kulkarni et al. 2014). The LiP and MnP enzymes can degrade the wastewater in a very good manner. The fugue having the white rot is suitable for the azo dyes removal. Table 1 shows the fungal culture used for degradation of dyes. In this table, fungi, type of dye and photocatalytic efficiencies can be analyzed easily (Benghazi et al. 2014; Viswanath et al. 2014). Microorganisms are a type of wastewater treatment in which microorganisms like bacteria are used to remove pollutants from textile wastewater by biochemical reaction. The Microbial Fuel Cell (MFC) is also used for this purpose. The basic phenomenon in MFC was to minimize the oxygen level in water by using microorganisms that react with wastewater compound to form oxides, the electron and proton generate during this reaction which then goes toward cathode to remove oxygen. A membrane has been utilized to separate the anode and cathode chamber (Ayyaru and Dharmalingam 2014; Choi et al. 2017; Hernández-Fernández et al., 2015). Low resistance and cost membranes are used in MFC at commercial level. The stableness of these membranes is high and used for the transportation of ions between chambers (Daud et al. 2015; Leong et al. 2013; Song et al. 2015). Thick sheet (aromatic sulfonic acid) membrane along KOH/phosphoric acid is used in MFC.

All above methods have plethora of drawback in different concerns. Table 1 (Gogate and Pandit 2004) gives the complete information about different treatment methods for various dyes including Azo, Anthraquinone, Phthalocyanine, Triphenylmethane dye, Stilbene dye Thiazine, Xanthene and many others discharged from textile industries. Moreover, different treatment conditions and degradation efficiencies can also be observed. Therefore, it is essential and thrilling need to manufacture extremely effective, active catalyst of visible light active materials to solve difficulties regarding concerns of environment smoothly. Photocatalysis technique is associated with the elimination of water pollutants that can be stay long time chemically and resists the biodegradation as well. This method compromises profit over ordinary methods utilized for wastewater treatment like adsorption as well as oxidation, organic compound, dyes, membrane separation, inorganic compounds, biological treatment and heavy metals. The comprehensive discussion on photocatalytic mechanism, catalysts used for dye degradation, visible light-driven WO_3 catalyst with its properties, limitation, and activity enhancement ways is given below.

Photocatalytic approach: dye degradation

The development of very well-ordered architectures of the semiconductor metal oxide photocatalyst has accredited excessive contemplation for the excellent typical expansion along exceptional embryology and potential appliances including solar fuel production, high T_c superconductivity, catalysis of other chemical reactions, water splitting and the photodegradation of pollutants, e.g., for the production of fine chemicals and cleaning concerns of environment (Gillet et al. 2004). In the past few years, the photocatalytic semiconductors are remarked to be very low cost and ecofriendly and feasible treatment plants with the removal of the azo dyes. In past, energetic semiconductor photocatalysts like metallic oxides, sulfides, oxynitrides (Aslam et al. 2014; Theerthagiri et al. 2015) and graphitic carbon nitride ($g\text{-}C_3N_4$) synthesized and implemented to treat the biological pollutants having aqueous environment. Moreover, scientists have motivated the growth of materials used in photocatalytic process, used in the synthesis methods in environment conciliation. Various photocatalytic materials including ZnO, TiO_2, Cr_2O_3, V_2O_5, MoO_3, CdO, Sb_2O_4, CdS, CuS, nickel oxide (NiO), $\alpha\text{-}Fe_2O_3$, PbO, WOx/TiO_2, CuO–ZnO, tin oxides (SnO_2), molybdate (MoO_4), indium oxide (In_2O_3), cerium oxide (CeO_2) (Gu et al. 2005; Monllor-Satoca et al. 2006; Sun et al. 2015) have been utilized for the degradation

Table 1 Different treatment methods of highly contaminated wastewater discharged from textile industries

Sr. no.	Process	Advantages	Disadvantages
1.	Biological process	Cost is very reasonable. Simple, absolute method, disperse and the high amount of dyes adsorbed on the sludge	The basic dyes are very harmful and have toxic nature and are opposing to the biodegradability. The reactive dyes like acid dyes are very soluble in water due to which cants be adsorbed on the sludge
2.	Coagulation process	Beneficial on economical basis, suitable for the dispersion of dyes like sulfur and vat dyes	The azo dyes and other acidic/basic dyes cannot be removed and the result was not satisfactory, the resultant sludge produced in very large amount. In this method, the removal is depending on the pH
3.	Activated C adsorption process	Azo, acidic dyes, etc., can be removed very quickly and safely, it is very good and suitable to the basic effluents dyes	The ejection of dyes is depending on the pH. The sulfur and vat dyes can not be removed totally and result was not good. The renovation of adsorbent is very costly and results in the loss of these dyes, necessitating costly disposal
4.	Ion exchange process	Without any lose the adsorbent can be renovated, dye recovery conceptually possible	In this method, the resins used are specific for every type of dyes, renovation and regeneration is a costly method, due to which at large scale dyes regeneration is exceed the normal cost
5.	Chemical oxidation process	Stimulate and begin the azo-bond cleavage	The oxidants depend on some of its limitation of thermodynamic and kinetic quantities and the secondary effluents. This was not suited for the disperse dyes. The suspected minerals are very negligible. The aromatic dyes released with chlorine
6.	Advanced oxidation processes	Reactive radicals are produced which surpass the oxidants during the decolorization process	This process produces other toxic products due to which it was not completely mineralized. It was also depending on the pH. At its present stage, the process is very expensive
7.	UV/O_3	This was very good for the removal of all dyes and very good removal for reactive dyes. No sludge is produced as a by-product and has a very low time taking reaction	It was also pH dependent; the removal of disperse dyes is very low, very important to handle it, COD removal is low, water used for ozone, expensive and have a short half-life of coupled that was generated with very dependent/limited on the mass transfer
8.	UV/H_2O_2	COD can be removed with this. The quickly reactive method and also no sludge produces	It was not suitable for all dyes and for the penetration of UV light the suspended solids and suffers should be separated. At very low pH the effects can be negligible of radicals
9.	Fenton's reagent	This involves very simple equipment's for the reaction which can be easily established. It can remove COD, suspend solid which are at very high amount. It was also useful for the removal of soluble dyes	It is very useful with pH lower than 3.5 and produces sludge. It requires a long time for the reaction
10.	Photocatalysis	It uses the solar light for the reaction and can remove a high amount of COD along with no production of sludge as a by-product	Solar light penetration was limited, coloration of catalyst used, and the catalyst can not be separated from the liquid that was used for treatment
	Electrochemical	Soluble and insoluble dyes can be removed also COD removal is possible. The salt in water was not affected on this reaction	In this method, the removal is depending on the dye type and is also a very costly procedure. In electrocoagulation process the sludge is produces as a by-product. The oxidation is responsible for the production of secondary pollutants including chlorine compounds, and heavy metals. The development in industries can be made on the direct oxidation using anodic oxidation

of different dyes emitted from textile industries. It is worth to mention that TiO_2 (among various discovered photocatalysts) has become one of the most significant semiconductor metal oxide that is widely investigated and utilized in many applications owing to ability to disintegrate the carbon-based compounds, non-toxic, less expensive, sensitive to UV light, the compound long half-life, etc. However, only 3–5% of UV light of the sun radiation is used by the TiO_2 due to the bandgap of 3.2 eV. Therefore, it is unavoidable to make the photocatalyst that utilizes the ordinary light especially to the visible light. The sunlight usage increased due to the sensitivity of the TiO_2 to visible light which has a large influence on the human beings as well as advanced the technology of treatment wastes (Wu et al. 2013).

A successful photocatalyst based on semiconductors, the CB level would exceed negatively in the sense of removal of electrons from oxygen for the photoexcited electrons to be spent by that of the molecular oxygen. The utilization of photogenerated electrons is required to inhibit charge carrier recombination as well as to permit the photogenerated VB holes in order to oxidize the organic molecules. Among available materials, to fulfill above condition, tungsten trioxide (WO_3) is a well-known and most favorable semiconductor metal oxides photocatalyst because of its superior response toward EM spectra, reasonable metallic interactions as well as mechanical strength (Huang et al. 2013).

Tungsten trioxide: properties

Tungsten trioxide (WO_3) is a semiconductor photocatalyst of *N* type, having tremendous contribution toward the degradation of organic compounds. It is worth mentioning that WO_3 is an oxygen-deficient semiconductor based on the oxides of metals with bandgap of almost 2.4 and 2.8 eV. It has been reviewed that bandgap energies strongly relies on the concentration of the defects and stoichiometry's ratio. Compound shows strong physicochemical nature and very sensitive to sunlight that's why used in photocatalytic processes. Nowadays, it is widely accepted that this compound endows some intriguing abilities like non-expensive, non-toxic, and strong stability in any condition. WO_3 has remarkable features like photosensitivity, non-toxicity, durable stability in various electrolytes, and strong stability below pH of 8 in acidic condition, large absorption ability within solar spectrum (UV–visible), indicative photoelectrons converting ability and persist to the photodecay, effortless analysis with maximum purification, almost 3.1–3.2 V beneath VB with diffusion limit of 150 nm, indicative electron passage 6.5 cm^2/Vs and long life of charges (Sánchez-Martínez et al. 2013; Zhang et al. 2011). These qualities allow WO_3 a promising substitute to TiO_2 and others that need to be enhanced in absorbing light in visible region. The crystal structure of the tungsten oxide varies with the synthesis method or operating temperature. Normally, there are three phases of tungsten oxide nanoparticles that are hexagonal, monoclinic and orthorhombic. It was demonstrated that only the monoclinic I (γ-WO_3) phase is the most stable phase at the room temperature, and many phases of WO_3 show the photocatalytic process. It moves toward orthorhombic via enhancing the operating temperature when move from bulk material to nanostructure (Xi et al. 2012; Zhang et al. 2014). Good power of light absorption, suitable rate of oxidation as well as reduction onto surface carrier's recombination control rate are manufacture WO_3 to extensively utilized it in photocatalytic degradation method. *N*-type WO_3 compounds have the ability to utilize almost 30% of sunlight.

Photocatalytic characteristics

A semiconductor-based material demonstrates photocatalytic process in water to energy packets emitted from light source including xenon lamp, metal halide lamp and solar light, etc., when photon energy is greater or equal to the value of bandgap of catalyst, then consequences in creation of e/h pairs which could yield $OH^\bullet$ radicals. Figure 3a shows the photocatalytic mechanism in aqueous solution. In this figure, we visualize that how energetic photon might produce e–h pairs that would tend to free radical as well as degradation of the harmful dyes later. Photocatalytic behavior of the WO_3-based catalyst strongly relies on the valance band and conduction band edge. Both conduction and valance band edges are more strongly positive than H_2/H_2O reduction potential and H_2O/O_2 oxidation potential, respectively (Tanaka et al. 2010). Therefore, it has been investigated that WO_3 was more suitable photocatalyst to removal of wastewater effluents like, textile dyes, bacteria and some organic compounds. WO_3 elevation from the blue regions of solar spectrum is because of wide bandgap energy. Moreover, it is also noted that the photocatalyst used for the analysis of the organic acidic compounds because of the long-term stable condition of WO_3 in acidic climate. Photocatalytic degradation activity of nanostructured-based WO_3 greatly enhances due to the huge surface-to-volume ratio. WO_3 was found as an auspicious material that exists in the nanostructure form, e.g., WO_3 nanowires, nanorods, nanoflake, flower-like structure, nanosheets and nanobelts (Gondal et al. 2010). Different type of WO_3-based nanostructures have been synthesized by various techniques like tungsten filament heating in environment of vacuum/argon gas, thermal vapor deposition, chemical vapor deposition, hydrothermal process, solvothermal method and sol–gel spin coating techniques (Li et al. 2014; Martínez-de la Cruz et al. 2010; Zhang et al. 2011).

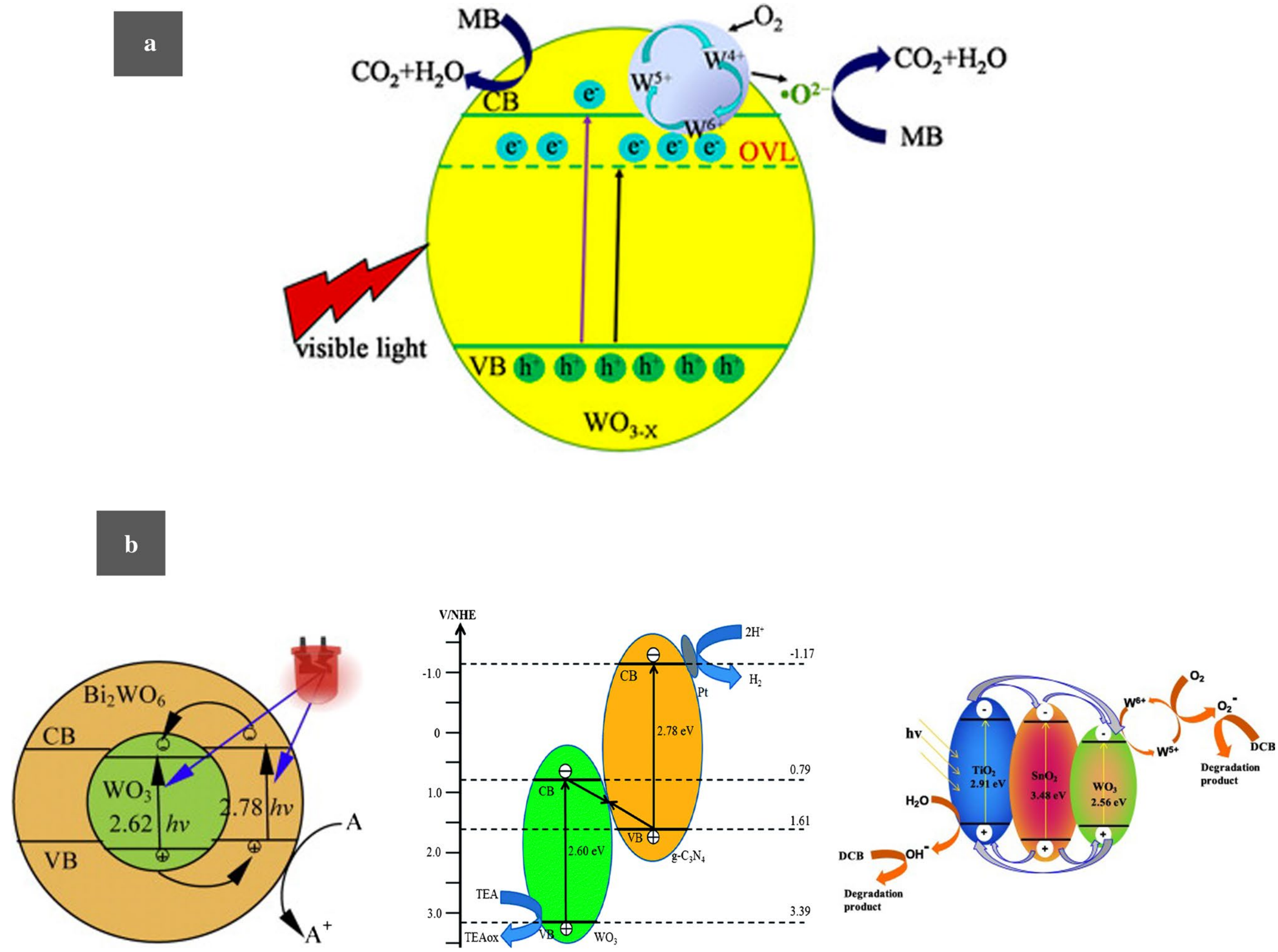

Fig. 3 A schematic diagram of the WO_3 photocatalytic activity during the treatment of wastewater (**a**) and a schematic diagram of the coupled WO_3 photocatalytic activity during the treatment of wastewater (**b**)

Limitations

Fast recombination rate of photogenerated e/h carriers, comparatively small conduction band edge as well as the indirect bandgap of WO_3 are main obstacles preventing its photocatalytic efficiency. Moreover, by taking the leveled conduction band of WO_3 is not too negative as compared to the probable reduction in single e^- from oxygen, the photogenerated e^- s in the conduction band of WO_3 cannot be utilize competently from adsorbed oxygen molecules using the single e^- elimination process to produce superoxide anion-free radical ($\bullet O^{2-}$), which refers to the aggregation of photoinduced e^- on the WO_3 photocatalyst surface using visible light and recombination of e/h pairs. The photocatalytic activity is very low as compared to normal condition in suitable escalation (Xi et al. 2012). Furthermore, a very thick film is required for the absorption of large portion of light in WO_3 semiconductors that have a direct bandgap nature. This results in reduction in e/h pair recombination due to the thick film and hence very low photon activity.

Therefore, many efforts are made to tune electronic structure of WO_3 to improve the photocatalytic activity. Investigators have lessened the recombination of carriers and also improving photocatalytic activity by amended the positions of band energy of WO_3 through an increment of low bandgap material (semiconductor catalysts) (Huang et al. 2012). The conduction band potential in two different semiconductor materials can play a significant role to enhance photocatalytic performance. The lessened charge recombination was observed due to efficient electron–hole pair separation between two different semiconductors (Sun et al. 2015).

Enhancement of photocatalytic activity via doping/coupling

The surface conversion of WO_3 and doping is very important for the development in the energy band and to resist the electrons and holes to recombine. Hence, more development is required for the better result of the photocatalysts sensitive to the visible light. Two scenarios are suggested for the designing of visible light sensitive photocatalyst. The first strategy was the hybridization/coupling of bandgap photocatalysts with narrow bandgap semiconductors to form heterostructure, which has been proven an effective strategy or noble metal deposition. The dopants (low band semiconductor catalyst) and/or doping of metals on the surface modification of WO_3 plays a significant role on the removal of water–organic effluents by increasing the photocatalytic process (Sadakane et al. 2010). In the noble metal/WO_3 composite, noble metal always works like bunch of electrons and can reduction in oxygen can be catalyzed through a multi-electron reduction process to form H_2O_2 and H_2O instead of the traditional single-electron process. By studying and controlling, morphology of photocatalyst is very important point in the development of its activity increase because of the reason that these reactions are typically done on the surface, and hence it is very much dependent on the surface morphology (Li et al. 2014; Zhang et al. 2011). The second strategy is the investigation of unusual materials used for semiconductors. Generally, it is believed that increase in surface-to-volume ratio of a photocatalyst is one of the effective ways to increase the photocatalytic efficiency. Therefore, various 1D nanostructured WO_3 such as nanorods, nanofibers and nanotubes (Huang et al. 2012; Tanaka et al. 2010; Xi et al. 2012) have been fabricated for photocatalysis application (Wen et al. 2013; Wu et al. 2013).

It is widely believed that the photocatalytic performance of a photocatalyst is not only dependent on its surface area alone, but also notably dependent on the surface structure. This is because the surface atomic structure and arrangement fundamentally affects the extent and value of reactant particles sucked from the surface of a photocatalyst, hence influences the carrier handover competence from the surface to adsorbed molecules and ultimately affects its reactivity of the photocatalyst (Jianhua Huang et al. 2013; Wu et al. 2013). Owing toward the quantum size consequence, very tiny nanometer-sized particle semiconductors are quite interesting because of their attractive optical, electronic and catalytic properties (Kim et al. 2010). It was demonstrated that the nanosized WO_3 nanoparticles less than 5 nm exhibited a widened bandgap and improved photocatalytic performance enhanced by reducing potential through widening the bandgap resulting from the quantum-confinement effect (Adhikari et al. 2013). In recent years, a series of graphene hybridized semiconductor-based photocatalysts have been developed to raise the photocatalytic process with the increase in the ability of separating the separation photogenerated electron/hole pairs that involves graphene/TiO_2, graphene/ZnO, graphene/CdS, and so on. The hybridization effect is beneficial to the transfer of photogenerated charges of semiconductor photocatalyst to graphene, resulting in an enhancement of separation efficiency. This enhancement strategy could also be applied to WO_3 photocatalyst (Theerthagiri et al. 2015). Enhanced photocatalytic activity was explained as follows. Firstly, the photoexcited electrons in WO_3 were reactive toward O_2, and the process was enhanced significantly by loading of lead. Secondly, that was much easier to proceed through the multi-electron reduction process instead of single-electron process at the upper surface of lead that uses as an electron puddle and catalyze O_2 reduction. This is because the probable for multi-electron drop of O_2 is more optimistic (e.g., $O_2 + 2H^+ + 2e^- = H_2O_2$, $+0.682$ V vs. NHE; $O_2 + 4H^+ + 4e- = 2H_2O$, $+1.23$ V vs. NHE) and for single e^- (e.g., $O_2 + e^- = O^{2-}$, -0.284 V vs. NHE; $O_2 + H^+ + e^- = H_2O$, -0.046 V vs. NHE). Figure 3b shows a schematic diagram of the coupled WO_3 photocatalytic activity during the treatment of wastewater (Wu et al. 2013; Xi et al. 2012). In addition to these single noble metals, two types of noble metal were used to improve the photocatalytic activity of WO_3. It was successfully prepared Pt/Au/WO_3 photocatalyst and found that the as-prepared Pt/Au/WO_3 photocatalyst could continuously produce H_2 as well as CO_2 from glycerin and O_2 by oxidation of H_2O under visible light irradiation. Overall, the alkali hydroxide load was proved as an operative technique for enlightening the photocatalytic action of WO_3 photocatalyst despite the loading amount and the reasons. The electric possessions of doped tungsten oxide (WO_3) can be studied with DFT cunnings through cross-functional. While the place of the topmost of the VB in WO_3 is respectable for O^{-2} development in aquatic excruciating, the CB is too squat for H^{-2} creation. Moreover, the bandgap must be condensed to recover action with visible light. Doping is used to alter the location of energy levels, thus resultant in a more well-organized photocatalyst (Sun et al. 2010).

Certainly, WO_3 is considering to be deliberated as a photocatalyst of visible light. It is resilient to degradation because of photocorrosion, which moves toward decrease in catalytic activity and formation of metal ions. Onto WO_3 surface supports oxidation reactions process for VB (+3.1 eV). Surfaces of WO_3 comprise of highly negative charges which are idyllic for use in adsorbing usage, mainly for cationic compounds like MB when we deeply study the promising photocatalytic aspects. Negative carriers upon exterior of WO_3 were due to the oxide's low isoelectric point (IEP = 0.2–1). Investigations utilizing other WO_3 nanostructures are also carrying advantage of strong electrostatic cooperation between methylene blue MB and WO_3. The coupling of high adsorption capacity with methylene blue MB and good photocatalytic flora of the WO_3 surface makes present oxide a strong member for subsequent conversion for adsorbed MB in aquatic systems (Ho et al. 2012; Lee et al. 2015). Table 2 illustrates the photocatalytic

Table 2 Photocatalytic degradation through pure/doped/coupled WO_3 catalyst

Sr. no.	Preparation methods	Catalyst	Morphology	Wastewater	Light Source	Removal efficiency	References
1.	Thermal heating method	WO_3	Monoclinic	RhB, IC and CR	Xe lamp: 10,000 K	93%	Martínez-de la Cruz et al. (2010)
2.	Hydrothermal reaction	WO_3	Monoclinic-rectangular nano plates	RhB	Xe lamp: 400 nm cutoff filter	100%	Huang et al. (2013)
3.	Hydrothermal method	WO_3	Monoclinic	MB	Xe lamp: 300 W	100%	Li et al. (2014)
4.	Citric acid-assisted precipitation method	WO_3	Monoclinic	RhB	Xe lamp: 10,000 K	82%	Sánchez-Martínez et al. (2013)
5.	Hydrothermal method	WO_3	Monoclinic-shell microspheres	RhB	Mercury lamp: 250 W	100	Zhang et al. (2011)
6.	Solvothermal method	WO_3	Orthorhombic	RhB	Xe lamp: 300 W	88.5%	Zheng et al. (2013)
7.	Hydrothermal method	WO_3	Multiple-Shell: Hollow Spheres	RhB	Xe lamp: 300 W	100%	Xi et al. (2012)
8.	Hydrothermal method	WO_3	Nanoparticles	Benzene	UV radiation	100% Completely decomposition into CO_2	Tanaka et al. (2010)
9.	Precipitation method	WO_3	Hollow flower-like microsphere	RhB	Xenon lamp: 300 W	100%	Huang et al. (2012)
10.	Hydrothermal method	WO_3	3DOM	Acetic acid	Visible Light	90%	Sadakane et al. (2010)
11.	Hydrothermal method	Pr-doped α-Bi_2O_3/WO_3	Monoclinic	RhB and 2,4-DCP	Xe lamp: 1000 W	85.5% RhB and 76.2% DCP	Wu et al. (2013)
12.	Template method	Fe–doped WO_3	Monoclinic	RhB	Xe lamp: 300 W	93% RhB	Wen et al. (2013)
13.	Photodeposition method	Pt/WO_3	Monoclinic	DCA, 4-CP, TMA, As(III), MB and AO7	Xe lamp: 300 W	83% decrease 4-CP and DCA but only 8% for MB and AO_7	Kim et al. (2010)
14.	Microwave assisted hydrothermal process	Ag–AgCl/WO_3	Monoclinic	RhB	Metal halide lamp: 125 W	100%	Adhikari et al. (2013)
15.	Hydrothermal method	10% CuS–WO_3	Monoclinic	MB	Tungsten halogen lamp: 100 W	100%	Theerthagiri et al. (2015)
16.	Hydrothermal method	Mo-doped WO_3	Hexagonal-nanowires	MB	Mercury lamp: 125 W	98%	Sun et al. (2010)
17.	Hydrothermal method	Cs-WO_3	Monoclinic-Crystal structure	MO	Hg lamp: 250 W	100%	Ho et al. (2012)
18.	Sol–gel method	Bi_2WO_6	Monoclinic-microspheres	MB	Xe lamp: 400 W	100%	Xu et al. (2009)
19.	Sol–gel method	Pt/WO_3	Monoclinic	Rhodamine 6G	Tungsten–halogen: 230 W lamp	100%	Qamar et al. (2010)
20.	Solvothermal method	Ag–AgCl/WO_3	Monoclinic	4-CP	Metal halide lamp: 125 W	100%	Ma et al. (2012)

degradation of various dyes through pure/doped/coupled visible light-driven WO_3 catalyst. Development of such kind of simple skills to employ sunlight irradiation is more proficiently could facilitate much pecuniary mixtures for the degradation of pharmaceutical compounds like Lidocaine by water (Hunge et al. 2016; Pudukudy et al. 2013). Tungsten trioxide WO_3 catalytic powder was synthesized using facile, cost-effective sol–gel and precipitation processes carried out from hydrothermal process at less temperature. WO_3 process of crystallization completed by calcination of specimen the temperature of 500 °C and temperature of 700 °C. Impacts of processes of synthesis along with calcination temperature onto the features of surface, structure and morphology were inquired. Using methyl blue solution having decolorization ability when placed under visible light energy source tells about the photocatalytic process of semiconductor of WO_3 models under different value of pH. It was calculated that the methyl blue ability of photocatalytic decolorization is increased along with the increase in pH of the reactions and at pH 9 the very good results are obtained (Vamvasakis et al. 2015).

Barriers and research perspectives

Although WO_3 nanostructured-based photocatalytic materials have shown great promise for remediation of dyes from industrial wastewater in laboratory studies, this green technology needs to be implemented at commercial level as well. Highly photocatalytic activity performed under UV/Visible radiation, moderate price and stability toward deterioration processes of WO_3 has justified the multifunctional applications. Due to these unique properties, WO_3 is not only a visible light active photocatalyst; it can also widely search for prospective fields in secondary batteries, photochromic, electro-chromic and many others. Study can be carried out in assessing concentration of Sn in the human body through analysis of urine or blood paired with health impact assessment to a population in certain locations, which may have been affected by high concentration of Sn in drinking water.

Conclusion

Photocatalysis technology for contamination treatment is acquiring momentum universally. The distinctive properties of nanostructured-based WO_3 photocatalytic materials and their convergence with current treatment methods present great opportunities to revolutionize wastewater treatment. It has been reviewed that dyes discharged from textile industries have hazardous effects on environment and our present treatment ways and discharge practices, which heavily rely on conveyance and centralized systems, are no longer sustainable. In this review, we provide broad interpretation of visible light-driven WO_3-based photocatalyst. The highly effective, integrated and multifunctional developments qualified by photocatalysis technology are envisioned to provide affordable and high-performance wastewater treatment solutions.

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