Role of Metal Oxides as Nanoscale Semiconductors for Photocatalysis

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Abstract - *Pollution of water bodies by various pharmaceutical, industrial, agricultural waste, and sewage has become a significant concern. Though a large number of chemical and biological methods have been developed they are not cost-effective and, in some cases, have side products that could cause harm to the environment. Photocatalysis represents one of the greener and novel approaches in which semiconductor materials in form of nanocomposites help in decomposing the pollutants. Metal oxides have a wide range of physical and chemical properties which make them effective catalysts. Modification by use of dopants or conjunction with other semiconductors makes them versatile catalysts that can function in the visible range. TiO2 and ZnO are the most widely used followed by other metal oxides. The present review summarizes the various metal oxides and their composites that have been synthesized and utilized in the treatment of pollutants from aqueous solutions.*

Key Words: photocatalysis, titanium oxide (tio2), zinc oxide (zno), iron oxide (fe3o4), doping, nanocomposites, nanoparticles

1.INTRODUCTION

Metal oxides in form of nanocomposites have become extremely useful in ecological applications such as adsorption of toxic materials and photocatalysis. Nanosized materials of metal oxides have the high surface area and high binding capacity which helps them in being very effective as detoxifying agents. Nanocomposites of metal oxides have very unique properties that make them suitable for application in a wide range of fields such as medicine, ecology, and oncology. The metal oxide nanomaterials that are widely used include of TiO_2, ZnO, SnO_2, ZrO_2, and Fe_3O_4. The surface of the crystals of the metal oxides plays an important role in determining the functionality of the crystal. The interaction of the surface with environment results in altering the various properties which are mainly associated with the chemical composition, size, surface area, defects, and morphology of the crystal structures [1].

Nanostructured Ti (IV) has very high chemical and thermal stability. This feature is useful in doping the crystals thus giving rise to materials that have superior functions. Tin (IV) oxides have very high electrical conductivity, transparency in the visible range, and thermal stability which makes them suitable for transparent solar cells and gas sensors. Oxides of Zinc (Zn) and Zirconium (Zr) depending upon their use as nano dispersion or nanomaterials shows unique properties which is based on the nature of crystal structure utilized particularly in the case of Zr. The physical and chemical properties of nanoparticles of metal oxides are directly related to particle size. The smaller the particle size the higher is Gibbs free energy resulting in different chemical and photocatalytic activities of the material. One such enumeration includes that of Titanium. As its size decreases anatase form has more oxygen vacancies in structure resulting in higher photocatalytic activity than rutile form. Nanoparticles of metal oxides have a high number of active sites that are exposed which results in enhanced activity of these. The conversion of macromolecular oxide forms to nanomaterials results in quantum dimensional effects such as increased defects, change in morphology, and particle size being smaller than DeBroglie wavelength which results in a unique dielectric, optical and electromagnetic properties [2].

Photocatalysis involves the activation of the semiconductor material by irradiation with UV-Visible light. Electrons in the atomic structure occupy two distinct positions namely the valence band and the conduction band. Band gap is the energy difference between the valence band and conduction band. Upon irradiation with a light electron from valence band gets excited and transferred to conduction band resulting in the formation of an electron-hole in the valence band. Migration of this charge from the core to semiconductor surface can initiate chemical reactions with the molecules adsorbed onto the surface. This principle is widely utilized for various redox phenomena in photocatalysis. The efficiency of converting the material adsorbed is dependent upon the inherent properties of the crystal. Metal oxides have been widely used in photocatalysis. TiO_2 was the first photocatalyst used for the production of hydrogen from water. Later a large number of photocatalysts have been utilized as gas sensors, detoxicants, wastewater treatment and adsorption of various gases [3].

Pure water availability is one of the major concerns for mankind. Contamination of water with sewage, industrial waste, medical and radioactive waste has resulted in water that is unfit for consumption. Water contamination poses a serious threat to human survival and hence needs to be addressed at the earliest. A large number of physical, chemical, and biological methods exist for the decontamination of water. However, all these have limited success and cannot remove the contaminants completely. Nanotechnology is a new arena that is being actively pursued removing contaminants as it is cheaper, has a higher capacity, and easy to operate than traditional methods. Nanoparticles provide extremely high catalytic efficiency and can remove contaminants not removed by traditional methods [4]. The present review is aimed at summarizing the various studies that have been done on waste water treatment utilizing metal oxide-based nanostructures.

2. LITERATURE REVIEW

Nanomaterials are one of the most widely applicable reagents for treatment of waste water samples. Nanomaterials for photocatalysis have excellent properties which make them a perfect choice for waste water treatment. These are cheap, fast and highly reliable. However, scaling up of these methods possess a distinct problem and the utilization in large volumes need to be incorporated thoroughly [4]. A large number of nanomaterials include carbon based nano structures, nano particles and nano composites have been utilised for treatment. Graphene and its derivatives have excellent stability, safe to be used and have good adsorption capacity due to their large surface area. Graphene oxides, fullerenes and carbon nano tubes have been utilised for binding many of organic pollutants and in effective purification of water materials. Some of the reactions are effective in UV light and few of them are functional in visible light. Metal oxides based nano particles show excellent photo excitation and have been used as photocatalysts for long time [5] . TiO_2 and ZnO have highest activity and have been used in most of the cases where environmental samples have to be cleaned. Nano composites such as metal-metal, metal-metal oxide, metal oxide- oxy acids have been utilised for synthesizing effective photocatalysts for removal of pollutants [6],[7]. Fe_3O_4@graphene nanocomposites have been synthesized and test for purification. The ability of these in removal of oxytetracycline and tetracycline from water was demonstrated. The nano composite had good adsorption rate of 0.974 and 0.834 $mg^{-1}h^{-1}$. Oxy tetracycline and tetracycline were removed at efficiency of 81%-98% and 80.7-99%. However, application of these nanocomposites at large scale in presence of various other contaminants need to be checked [8].

Heterogenous and homogenous photocatalysis have become an important area for effective synthesis and utilisation in waste water treatment. Core- shell based nanoparticles have been extensively investigated in this regard. Metal- semiconductor nano shell core structures have been synthesized efficiently and have been tested for their ability for effective photocatalysis. TiO_2, SnS_2 and ZnO core shell with metal semiconductors could help in better photocatalytic conversion than the oxides alone. Such core shelled TiO_2 nanocomposites have been prepared and demonstrated to have excellent photocatalysis in UV range predominantly. Metal-ZnO based core shells have shown good catalytic efficiency in visible light [9],[10],[11].

Zn-Fe_2O_4@ZnO core shell nanoparticles were synthesized and utilised for removal of methylene blue. ZnO had around 20-30% removal efficiency whereas Zn-Fe_2O_4 had efficiency of around 30-40% in visible light. However, core nano shell composites showed up to 80% or higher removal of methylene when used in 1:1 molar ratio of each of the components. Thus, core shell nanoparticles are effective in removal of pollutants from water utilising solar light [12]. Co_3O_4/Fe_2O_3 composite nanofiber-based structures have been used as effective solar photocatalyst. These composites have been shown to effectively degrade acridine orange and brilliant cresyl blue from water sources [13].

SiO_2 tetrahedra can be easily distorted and could be polarized in a manner which could make it highly conductive and in efficient photocatalysis. Hetero composites of Ag, Si and WO_3 have been tested for ability as effective photocatalyst in removal of methylene blue from contaminated water. $Ag_6Si_2O_7$/WO_3 (1:1) showed 97.4% efficiency of methylene blue from water when compared to WO_3 or $Ag_6Si_2O_7$. The heterojunction of $Ag_6Si_2O_7$/WO_3 (1:1) was effective in removal of methyl orange, rhodamine B and 2,4-dichlorophenol from water samples. Thus, such heterojunctions could be effective photocatalysts and suitable replacement for Titanium based photocatalysts.[14] Silver nanoparticle integration into metal oxides enhances their photocatalytic efficiency. Such metal oxides effectively remove 4- chlorophenol and methyl orange from contaminated waters [15].

Nanomaterials of various metal oxides have not found extensive commercial application. This is mainly associated with their tendency to form agglomerates or due to other interactions. TiO_2 has high band gap, high recombination between electron hole pairs and very low photocarrier separation. Due to such unique features the anatase form of TiO_2 shows stimulation only in UV light. Since UV light is only a fraction of solar light the oxides of Titanium are ineffective as catalyst for solar light driven reactions. ZnO based photocatalysts are effective substituent for Titanium since they are cheap, highly stable and non-toxic. Though Zinc based nanomaterials are effective in removing the pollutants from water they still have their own short comings. ZnO does not absorb in visible range like Titanium. It is difficult to recycle ZnO from waste water. It aggregates during photocatalysis and undergoes corrosion in UV light. Various other metal oxides such as SnO_2, Fe_3O_4 and ZrO_2 have been tested with limited success due to their limited ability to decontaminate the chemical in solar light [2]. Photocatalytic degradation utilising metal oxides has been actively pursued for longest time. TiO_2 has been most widely studies. However, it suffers from disadvantages such as poor sensitivity for solar irradiation, high band gap and aggregation of TiO_2 nanoparticles. ZnO is very effective in photocatalysis when compared to TiO_2 however it suffers from being unstable and precipitates in catalyst form. ZnO can find wider application it needs to be stabilised for better working. Tungsten and Copper based photocatalysts have been developed but they suffer with their own limitations. In both cases the photocatalytic efficiency is weak since the conduction of energy is not optimal upon excitation resulting in loss of efficiency. Thus, a lot of work is needed in terms of optimizing Titanium and Zinc oxides as effective photocatalysts [7],[16].

Native TiO_2 is not active in visible light and hence does not possess any distinct photo catalytic activity. Modification of oxide by making nanocomposites is one of the methods to enhance its activity in solar light driven degradation of chemicals. Preparation of composites with WO_3 and WO_3/Fe_3O_4 helps enhancing its photocatalytic activity. An increase in surface area from native 36.5m2g-1 to 210.3 m2g-1 in composites helps in enhanced adsorption of pollutants thus helping in better photodegradable characteristics. This is also associated with enhanced rate constant from 0 .01 min-1 to 0.071 min-1 in composites which helps in enhancing the catalytic efficiency of composites [17]. TiO_2 and ZnO are the most widely used photocatalysts for degradation of toxic organic pollutants. A large number of parameters influence the overall degradation which include pH, concentration of the catalyst, temperature and nature of light source. UV as light source is the most widely used on for photocatalytic degradation however solar light is far more abundant and easier to utilise for degradation. However, both TiO_2 and ZnO have very low efficiency in solar light for being an effective catalyst. Modification of the structures in both by making nano composites could help in shifting the band gap for effective functioning in solar light [1],[18].

TiO_2 is very stable and chemically inert. It resists both photo corrosion and chemical corrosion. Thus, TiO_2 is effectively utilised in degradation of dyes from water. Of the various oxides of metals that have been utilised for water purification TiO_2 showed maximum degradation of Rhodamine blue, methylene blue and acridine orange in dose dependent manner. ZnO on other hand showed enhanced activity in dose dependent manner however was extremely unstable making it less effective as catalyst. Various other catalysts of metals such as MoO_3, WO_3, RuO_2, CO_3O_4, α-Fe_2O_3, Mn_2O_3 and Fe_3O_4 are ineffective as photocatalyst in removal of dyes. Substitution of TiO_2 for ZnO results in decreasing the efficiency of photoconversion in solar light [19].

TiO_2 has been studied for effective removal of p,p' DDT from contaminated waters. Undoped TiO_2 was checked for photocatalysis in both UV and visible light. Undoped TiO_2 showed a kinetic constant of 0.0278 min-1 with 68% removal of the contaminant under UV irradiation. However, Undoped TiO_2 showed 57.45% removal under visible light with a rate constant of 0.0197 min-1. The undoped TiO_2 powder exhibited a higher absorbance of the pollutant due to its larger surface area. The surface area of TiO_2 was observed to be 11.78 m2 g-1 [20].

Immobilized TiO_2 on surface of filter membranes enhances its ability to adsorb organic pollutants from water. TiO_2 coated membranes were utilised for degradation of methylene blue and chlorhexidine digluconate from water samples in presence of solar light. Of the various methods utilised for coating TiO_2 nanoparticles on hollow membranes sol gel method was the best. Such coated membranes were found to be effective in removal of 30% of methylene blue and 40% of chlorhexidine digluconate from water samples. However, the amount of extraction is not very high since there is still significant amount of the pollutant in water. Further optimization is required for achieved 100% removal of pollutants from water [21].

TiO_2 synthesized by sol gel method was analysed for degradation of cyanobacterial toxin Microcystin LR. The rate constant of 0.026 min-1 for degradation of toxin was optimal at acidic pH of 3.5. Degradation of toxin was seen in both UV and visible light. However, the extent of degradation in visible light was weak with TiO_2 calcined at 350°C and 400°C showing rate constant of 0.014 and 0.022 min-1. Thus, alteration of TiO_2 seems to be essential alternative to enhance its overall ability to bind and remove the pollutants [22]. Alteration of Titanium oxide to enhance its photocatalytic efficiency is one of the most widely used method. Metal doping often helps in enhancing photo catalytic activity. However, metal doping often makes the Titania unstable, causes photo corrosion and leaching of metals could cause damage to environment. Non-metals often are better choice to overcome such loop holes.

Non-metals reduce the band gap and helps in enhancing the overall photocatalytic efficiency. Doping with single or multiple non-metals is in fact an active area of study as co-doping has its own significant effects [23]. Fixed bed photoreactor was prepared for TiO_2 and its variants. The reactor was checked in visible light for degradation of methyl orange. The study observed that modification of TiO_2 in form of doping enhances the overall photocatalytic efficiency. Co doping with two or more elements further increases its photocatalytic efficiency. In the study co doping with S and N resulted in 95% removal of the pollutant under visible light in 2 hrs. Pure TiO_2 is not functional under visible light and thus such modifications greatly enhance its catalytic activity and commercial application [24].

Commercially available TiO_2 powder (AEROXIDE P25) and their nanocomposites have been evaluated in removal of diclofenac from water. Commercial TiO_2 powder, SnS_2 powder showed an efficiency of 8.9% and 0.7% in removal of diclofenac whereas nanocomposite of both showed 41.4% removal of diclofenac in solar light. The maximum removal of diclofenac was seen within 30 min for each of the components individually however upon preparation of nano composite the removal could be seen even at 60 min. The adsorption of the pollutant was much higher with nanocomposites than when compared to the individual components alone [25].

Removal of dexamethasone from water was compared using native unmodified and modified TiO_2. Comparison of degradation of dexamethasone in both UV and visible light showed that TiO_2-P25 had efficiency which is 50% lower than the modified Titania. The Kapp and r0 were 4.5 and 22.5 for TiO_2-P25 whereas modified Titania had Kapp and r0 of 3.5 and 52.5 respectively [26].

Sugar refinery waste water is a potential pollutant. Removal of various pollutants and decreasing its chemical oxygen demand (COD) can be effectively done using metal oxides. TiO_2 and doped versions of Titanium in form of thin plate reactors have been tested for effective cleaning of waste water. The COD reduction was highest with silver doped Titania when compared to Titania alone showing that it is very effective source for cleaning waste water under solar irradiation conditions [27].

Photosensitization of metal oxides enhances their photocatalysis and has been achieved utilising quantum dots, plasmonic metal nano structures and carbon nanostructures [28]. TiO2 hollow nano fibres were loaded on CdS quantum dots. Such structures were checked for effective photocatalysis under UV and visible light. Under UV irradiation conditions 19% degradation of 4-nitrophenol was observed for hollow fibres. Sensitization of TiO2 with CdS enhanced its ability for degradation of nitrophenol when compared to non-sensitized material. However, the study showed effective conversion under UV light and hence has limited importance [29]. Undoped, single and double doped TiO2 show effective photocatalysis with efficiency of degradation of dyes higher with co-doped material [30].

Modification of metal oxide-based nanocomposite to enhance its photocatalytic efficiency has been pursued actively for patent applications as well. ZnO nanoparticles when doped with Fe show effective degradation of several dyes such as cresyl blue, indigo carmine and gentian blue. At alkaline pH 100% degradation of dyes is observed in less than 2-3hrs under solar irradiation conditions [31]. Composites of TiO2-ZnO and silver coated TiO2-ZnO have been used successfully for purification of water. The light weight composites bind to pathogenic bacteria and adsorb them on surface which results in purification of contaminated water samples. Maximum decontamination is seen in sun light. Thus, these light weight composites have excellent usage in water purification and could be further tested for binding and removal of pollutants from water [32].

UV radiation is the most widely used method for photoexcitation of metal oxides. Many of the nanoparticle semiconductors such as TiO2, SnO2 and ZnO demonstrate excellent photocatalytic activity in UV light. However due to the relatively small proportion of UV light in solar light photocatalysis in presence of solar light has gained importance. A large number of photocatalysts have been developed and many of them have been immobilized for effective purification of pollutants from water thus aiding in its purification [3].

3. RESEARCH GAP

The biggest challenge in area of photocatalysis with metal oxide-based nanocomposites is their ability to degrade the pollutant utilizing solar light. TiO2 and ZnO are the major oxides used widely for this purpose. It is essential to ensure TiO2 has excellent catalytic efficiency in solar light. Due to the large band width associated with the nature of energy transfer pure TiO2 has no catalytic efficiency in visible range. Decreasing the band width and enhancing the energy transfer is one of the best methods for making Titanium oxide a suitable material for removal of pollutants from water. The preparation of nano composites that could help in enhancing the efficiency needs to be thoroughly evaluated from literature. Apart from Titanium there are several other metal oxides such as ZnO, Fe3O4 and several others that have been reported to be effective photocatalysts. The utilisation of Titanium as the major choice for photocatalysis in spite of other metal oxides being present is not evaluated though research exists on it. Thus, significant features associated with Titanium and their nano composites needs to be highlighted properly. A comprehensive analysis of various methods of synthesis and the best method that could be used as effective photocatalyst needs to be highlighted from available literature to identify the best method for synthesis of various derivatives. This could help in utilization of such methods by researchers for better application. The significance of TiO2 based photocatalysis is not just restricted to research publications however it has been commercialized and patented successfully. A summary of the various modified Titania needs to be highlighted for effective understanding by the scientific community. Thus, in the present review paper a summary of various research papers, patents, reviews and commercial products that highlight utilisation of TiO2 based nanocomposites is highlighted. The description of other metal oxides and their role in photocatalysis is also evaluated.

4. METAL OXIDES AND THEIR SYNTHESIS METHODS

Many methods have been employed successfully for the synthesis of metal oxides. The co-precipitation method involves generating a Metal oxo-hydroxide intermediate by a reaction of the metal salt and precipitating medium. The oxo-hydroxide is converted to the metal oxide by adding NaOH, KOH, or Tetra ethyl ammonium hydroxide. The pH and nature of the alkaline solution determine the final morphology and properties of a photocatalyst. The method is economical and ZnO is widely synthesized using this method. In the Microemulsion method involves formation of an emulsion by mixing two immiscible layers of water/surfactant and oil/surfactant containing metal oxide precursor. The addition of precipitating reagent results in the formation of nanoparticles of metal oxide. Modified procedures have been adapted for the synthesis of TiO2 in the 30-50nM range by this method. Hydrothermal synthesis involves thermal decomposition of aqueous solutions of metal oxides by autoclaving or by utilizing an inactive atmosphere at ambient temperature. The addition of stabilizers helps in preventing the aggregation of the particles. In Sono-chemical methods solution of metal oxide is subjected to ultrasonic waves. This results in heating of the solution which when cooled results in formation of the crystals of metal oxides. The crystallization is achieved by a phenomenon termed acoustic cavitation. The method produces nanoparticles of uniform size, high purity, and high surface area. TiO2 nanoparticles have been synthesized by this method and have shown very high photocatalytic activity. Sol-gel process is the most widely used method that involves the decomposition of alkoxides of metals in ethanolic solution to generate hydroxides which polymerize to form a porous gel. Heating and drying of the gel results in the formation of nanoparticles, bulk material, or oxygen- deficient structures [7],[33].

5. MODIFICATIONS OF VARIOUS METAL OXIDES

Nanoscale semiconductors function effectively in UV light. However, the use of UV lamps for decontamination of water increases the cost and hence development of semiconductors that could function in visible light has gained significant importance. Most of the metal oxides have been appropriately modified to enhance their photoactivity in visible light. Nanocomposites consist of the creation of an inorganic solid core surrounded by an organic shell or vice versa. Such composites have been found to have better efficiency than nanoparticles alone. The various such combinations for a generation of nanocomposites include metal-metal, metal- metal oxide, metal oxide-metal oxide, and metal combination with oxyacids. TiO_2 when wrapped around with noble metals such as Ag and Au shows enhanced activity in the visible range. To enhance the degradation rate and to obtain high catalytic efficiency binary or ternary complexes of metal oxides have been tested successfully. ZnO/TiO_2 nanocomposites have been effectively utilized in the removal of dyes, drugs, heavy metals, and organic compounds from wastewater. CuO is nontoxic and has a low band gap which makes it a very good choice for the preparation of binary oxides with TiO_2 or ZnO. ZnO/CuO is effective in the removal of dyes, drugs, and many other pollutants. TiO_2/CuO is another binary oxide that is cheap to make and has effective efficiency in the removal of organic compounds and pollutants [6]. Another approach is a preparation of metalcore with a shell of a metal oxide semiconductor. The core could be constituted of Nobel metal or Zn or Nickel. The semiconductor nanoparticle is usually oxides of Ti, Zr, Sn, Fe, Cu, or Zn. The metal core helps in the modification of electrochemical properties of semiconductor material. The metal-metal oxide combination is highly photo-energetic and upon excitation, the transfer of electrons to metal helps in enhancing the overall catalytic reaction [9].

Doping with nonmetals is one of the common methods to change the activity to visible light. TiO_2 doped with halides or with C, N, or S show enhanced photocatalytic activity in the visible region. Doping with C or N results in reducing the band gap resulting in excitation by visible light. Doping with transition metals is another method for improving the excitation of TiO_2 in the visible range. The d electrons of transition metal help in charge transfer to TiO_2 bands resulting in shifting the wavelength. Semiconductor -semiconductor heterojunctions is another method to increase the efficiency of the photocatalyst. Conjugation of TiO_2 or ZnO with other semiconductors such as oxides of Cd, Nb, Ni, Bi, and graphene has shown to enhance photocatalytic efficiency [3].

6. APPLICATION OF METAL OXIDES IN TREATMENT OF WASTE WATER

Various nanocomposites of metal oxides such as nano-shells, nanotubes, nanospheres have all been applied for the successful purification of wastewater. Metal-metal oxide core-shell of Zn-Fe_2O_4 and ZnO core has been developed as nanospheres and utilized successfully in the removal of methylene blue from wastewater upon excitation in the visible range [12]. In another such approach, TiO_2 nanofibers incorporation with CdS quantum dots showed excellent photocatalytic activity in the visible range. The composite was useful in removing p-nitrophenol from wastewater [29]. Nano-particles of TiO_2 are immobilized on commercially available hollow fiber ultrafiltration membranes. Such membranes prepared by sol gel coating showed effective removal of methylene blue and chlorhexidine digluconate from water [21]. Nanocomposites of TiO_2 with SnS_2 have been utilized in the removal of diclofenac from water. The composite showed high activity in presence of solar light at neutral pH [25]. Silver doped TiO_2 was synthesized by chemical reduction and coated onto surface of ceramic tiles. These tiles were used for the treatment of wastewater from sugar refinery. Silver doped TiO_2 was good at reducing the COD of water and the resultant material was cleaner for reusage [27]. In [19] synthesized nanoparticles of TiO_2 and ZnO by controlled hydrolysis and sol-gel method. Particles of TiO_2 and ZnO were tested individually for removal of an organic dye such as Rhodamine B, Methylene blue, and Acridine orange from water samples under solar irradiation. Nanoparticles of Ti and Zn successfully removed the dyes in presence of solar light in time-dependent manner. In [23] investigated the effect of doping TiO_2 with C, N, and S for photocatalytic degradation of rose Bengal dye contaminated water. CNS-TiO_2 was synthesis by hydrolysis method. The catalyst was irradiated using solar light and was shown to effectively remove rose Bengal dye from aqueous solution. Heterojunction of $Ag_6Si_2O_7/WO_3$ was synthesized by ultrasound-based precipitation method. The composite was shown to very effective in removal of methylene blue, methyl orange and 2,4-dichlorophenol from water under visible light irradiation. The composite retained effective activity even after three rounds of purification [14]. $WO_3/TiO_2/Fe_3O_4$ composites with varying ratios were prepared by sol- gel method and checked for effective application in dye removal from aqueous solutions. These particles were effective in removing direct blue 71 dye from aqueous solution under visible light. The particles could be easily removed from water due to their magnetic nature and could be reused multiple times [17].

7. DISCUSSION

TiO_2 based nanoparticles are the most widely used photocatalysts. Apart from Titanium various other metal oxides have been utilized successfully either by combining with Titanium or by combination with other semiconductors. A summary of various such metal oxide-based semiconductors that have been utilized for water treatment using solar light is summarized in table 1. Commercially a large number of photocatalysts have been developed utilizing TiO2. The fine particulate form of TiO2 is commercially available for photocatalysis (AEROXIDE® TiO2 P 25, Evonik, Germany). Highly dispersed TiO2(AEROXIDE® TiO2 P 90 and hydrophilic fumed TiO2(VP Aeroperl P25/20) are available from Nippon Aerosil Co.LTD., Tokyo. Anatase TiO2 fine powder is available from Mikroanatas and Sachtleben Chemie GmbH, Duisburgo, Germany for photocatalysis. The photocatalytic ability of metal oxides has been patented as well. Silver doped TiO2-ZnO composites have been shown to be effective in purification of contaminated water [32]. Similarly, Fe doped ZnO nanoparticles are effective in degrading cresyl blue, indigo caramine and gentian blue [31].

Table -1: Summary of various metal oxides utilised for water treatment

Material	Synthesis	Pollutant	Removal/ Adsorption	Recovery	Reference
TiO_2 nano powder and sol on hollow fibre membrane	Sol gel	Methylene blue	30%	Membrane bound and hence no recovery considered	Chakraborty *et al.*, 2017
		Chlorhexidine digluconate	40%		
TiO_2-SnS_2 nanocomposites	Sol gel and hydrothermal	Diclofenac in aqueous solution	80-90% at pH 4	Immobilised photocatalyst	Kovacic *et al.*, 2017
TiO_2 codoped with S and N	Sol gel dip coating	Methyl orange	95% at pH 2	fixed bed photoreactor	Khalilian et al., 2015
$WO_3/TiO_2/Fe_3O_4$	Chemical method	Blue 71 dye solution	19% adsorption was seen	Removal facilitated by magnetic methods	Shojaei *et al.*,2015
C, N,S doped TiO_2	Hydrolysis	Rose Bengal dye	100% degradation in 60 min at pH 6	Not evaluated in study	Malini & Raj, 2018
Silver doped TiO_2 in form of plates	Chemical reduction method	Waste water from sugar cane refinery	95% COD reduction by 8h under visible light	Plate reactors which have immobilised photocatalyst	Saran *et al.*, 2016
Ag/TiO_2 nanophotocatalyst	Sol gel method	Dexamethasone	63.8% at pH 3.0	Not estimated	Pazoki *et al.*, 2016
N-doped TiO_2 nanopowders	Sol gel method	p,p' DDT	100% degradation in visible light	Not estimated	Ananpattarachai &Kajitvichyanukul , 2015
C,N co doped TiO_2	Solvothermal method	Bisphenol A	>99% with white and blue light	LED photoreactors	Wang &Lim,2010
Mesoporous N doped TiO_2	Sol gel	Microcystin-LR	120c m^3/g at pH 3.5	Not estimated	Choi *et al.*, 2007
Fe_3O_4 @graphene	in situ precipitation	tetracycline and oxytetracycline from water	lake, tap, pool water -95%, 96% and 89% for oxy tetracycline 98,98 and	Removal facilitated by magnetic methods	Zhang *et al.*, 2017

8. CONCLUSION

Metal oxides of various transition metals have been found to have narrow band gaps that help in effective absorbance and emission of electrons that could be of use for removing various contaminants from polluted water. However due to the narrow band gap their ex-citation is in UV range. Doping these metal oxides using noble metals or by conjunction with other semiconductor helps in the catalysis by absorption of visible light. A large number of studies have been done which show effective catalysis in the visible range and helps in removing a large number of diverse pollutants. Nanoscale semiconductors are extremely useful and would be helpful in cleaning of air, water and environmental samples by reducing the time for detoxification and making the whole process eco-friendly. However, being catalysts, they could be inactivated and thus need cycles of regeneration for successful usage. Also, the recovery of the semiconductor material and the number cycles for which the photocatalysis possesses a significant challenge. In the future with in-creasing population and exhausting resources it is essential for purification of natural re-sources and hence photocatalysis utilising semiconductor nano catalysts would be in great demand. However, their large-scale application possesses a challenge as studies done till now are only at small scale.

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