Photocatalytic Oxidation of Pollutant Dyes in Wastewater by TiO_2 and ZnO nano-materials – A Mini-review

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Abstract

In recent years, photocatalytico oxidation processes with ultra violet (UV) radiation and semiconductor photocatalyst like titanium dioxide (TiO_2) and zinc oxide (ZnO) have gained immense research interest as an effective wastewater purification method because of its efficacy in decomposing and mineralising the hazardous organic pollutants as well as the opportunity of utilizing the solar UV and visible spectrum. A comprehensive review of the UV assisted heterogeneous photocatalytic oxidation process is conducted with a border perspective into the photocatalytic reaction mechanism involved, different form of TiO_2 and ZnO catalysts, effective application towards waste water treatment by immobilized on surface or as suspension. Photocatalytic decomposition with ZnO and TiO_2 catalysts is mainly applied for treating organic contaminants dyes in wastewater because of their ability to attain fully mineralization of the organic contaminants under mild reaction conditions such as ambient pressure and temperature. One hundred and eighty seven published papers are reviewed and summarized here with the center of attention being on the photocatalytic oxidation of organic dyes present in waste water effluent. Most recently, photocatalytic degradation of oraganic molecules using TiO_2 and ZnO have been studied extensively due to the degradation of persistent organic pollutants, PAH (Polycyclic Aromatic Hydrocarbons) dyes and other organic chemicals which are known to be endocrine disruptors. Treatment of wastewater in a titanium and zinc dioxide suspended reactor has been widely used due to its simplicity and enhanced photodegradation efficiency.

Keywords : ZnO nanofiber, TiO_2 nanoaprticles, photocatalysis, wastewater, oxidation.

1. Introduction

The significance of the wastewater treatment, management and its disposal gradually increases in the modern times and it becomes a major concern for public health scientific interest. All existing protocols for treatment of wastewater are categorized as physical, chemical and biological processes[1]. The sequential and concurrent use of those processes combinedly tends to create a greater efficient method in removing the pollutant aspects in liquid residues. Restrictions in terms of execution, efficiency, and price are a factor, however, biological processes, as an example, have been extensively used and show potential towards dairy and agricultural wastewater treatment[2]. The chemical process deals with the photocatalysts like TiO_2, ZnO *etc.* mediated degradation of the industrials waste waters[3]. These processes have limitations which can potentially affect degradation efficiency through control pH range, rapid organic-load variations, and also the effluent's physicochemical behavior[4].

The use of a heterogeneous photocatalyst is a conventional method for water purification which includes reduction and oxidation reactions from adsorbed wastewater, oxygen molecules and hydroxyl anions, or other organic molecules[5-8]. Uses of semiconductors like TiO_2, ZnO *etc.* in photocatalysis employ semiconductors in suspension[9]. However, this method could be a more expensive when it is scaled-up because particle-recovery of the photocatalyst particles is a difficult task and leads to an amplification in process costs. A feasible alternative is the preparation of photocatalyst layers in different substances or uses the catalytic support without hampering the photocatalyst activity. Many efforts have been made in which few studies have demonstrated continuous flow reactors with fixed-bed photocatalyst[10]. Integral to this study was an assessment of the efficiency of heterogeneous photocatalyst processes for dairy and agricultural wastewater treatment with immobilized TiO_2 and ZnO to reduce organic pollutant load[11]. The immobilization was carried out by the application of a coating containing the catalysts[12]/photocatalyst[13] or by suing the porous carbon or silica as a supporter for the catalysts to prevent agglomeration of catalyst during catalytic/photocatalytic reactions in solution. Moreover, solar emission was used as UV source[13-15].

Recent review is focused on the most important photocatalysts titanium dioxide and zinc oxide and their photocatalytic activity towards wastewater treatment. Recently, Xiaobo and Samuel reviewed the broad applications of titanium dioxide as a photocatalysts[16]. These applications were comprised of photodecomposition of various industrial pollutants, killing tumor cell and killing bacteria in cancer treatments[17]. Semiconductor catalysts TiO_2 and ZnO have been widely used to mineralize harmful organic pollutants in wastewater into less damaging inorganic nontoxic compounds like CO_2, HCl and water[18]. Several studies have been carried out for decolorization of industrial wastewater by using photocatalysis and bacteria treatment[19-21]. The elimination of color from wastewaters is more necessary than the removal of other colorless organic compounds[19]. Because of aesthetic and environmental concerns the decolorization of effluent from textile dyeing and finishing industry has given most importance[22,23].

TiO_2/ZnO photocatalysis, in the presence of UV irradiation can disintegrate the pollutant dyes into non-toxic simple compounds like CO_2, HCl and water[24]. Nanosized TiO_2 and ZnO photocatalysts in the form of nanorods, nanospheres, thin porous films, nanofibers and nanowires have been utilized in various applications, including photocatalysis because of their high activity, low cost and environmental safety[25-27]. Interestingly, very high surface to volume ratio of nanostructures make them efficient for photocatalysis and other application. In recent studies[13,24], authors have reported that zinc oxide and titanium dioxide have excellent photocatalytic properties and both catalysts are designated to be capable substrates for photodegradation of dyes water pollutants as they exhibit the acceptable activity in the range of ultraviolet radiation.

Various studies have focused on treatment of industrial wastewater using different treatment methods; however, most of these treatments have intricacy in realistic uses[5,9,26,28,29]. In recent year, investigation on different systems have been carried out, such as, advanced oxidation processes (AOP)[30], ozonation[31,32], sonolysis[33], gamma–radiolysis[34], electro-coagulation[35,36], H_2O_2/UV[37], photocatalysis[24], photo-Fenton[38], biological and combined anaerobic–photocatalytic treatment[21,29,39]. The aim of the present investigate is to investigate photocatalytic oxidation process for the decomposition wastewater using TiO_2 and ZnO as photocatalysts irradiated with artificial ultraviolet radiations.

Photocatalytic oxidation processes[30], which involve the generation of highly reactive hydroxyl radical (HO), have emerged as a promising water and wastewater treatment technology for the degradation or mineralization of a wide range of organic contaminants[30,40,41]. The photoactivated reactions are characterized by the free radical mechanism initiated by the interaction of photons of a proper energy level with the catalyst (TiO_2, ZnO semiconductor catalysts)[42,43]. The efficiency of a photocatalytic system is also affected by the form of TiO_2 and ZnO nanoparticle catalysts used as immobilized on surface or as colloidal suspension[44-46]. The photocatalysis reaction effective for the degradation of various organic impurities in waste water; however, its practical application as slurry type suspensions is limited due to the difficulty in separating the nanocatalysts particles after the photocatalytic reaction[47-49].

The present review aims to provide a comprehensive analysis on the mechanism of UV-TiO_2 and ZnO photocatalytic oxidation process, photocatalyst material, irradiation sources, effect of pH, temperature, dye concentration, catalyst mass and type of catalysts on photocatalysis and the application towards wastewater treatment.

2. Photocatalytic Oxidation Process

In a typical photocatalytic system, photo reaction or photo-induced molecular transformation occurs on the photocatalyst surface[37]. The basic mechanism of photocatalytic reaction is governed by the generation of electron–hole pair into the semiconductor and its transportation to destination (i.e., reaction with organic pollutants). Frank and Bard[50] first examined the possibility of using a titanium dioxide-TiO_2 catalyst for the decomposition of cyanide, Ollis and co-workers[51] extensively studied the potential application of photocatalysis for organic degradation[52]. Semiconductor photocatalysts generally absorb different colour light depending on their bandgap energy and used as photocatalysts because of their interesting electronic configurations, light absorption ability, charge carrier transport property, and excited-state lifetimes[25,53-55]. The principal reaction mechanism of a semiconductor photocatalyst (Fig. 1) is described as follows. When a photocatalytic surface is exposed by a radiation of energy equal to or greater than the bandgap energy (bandgap

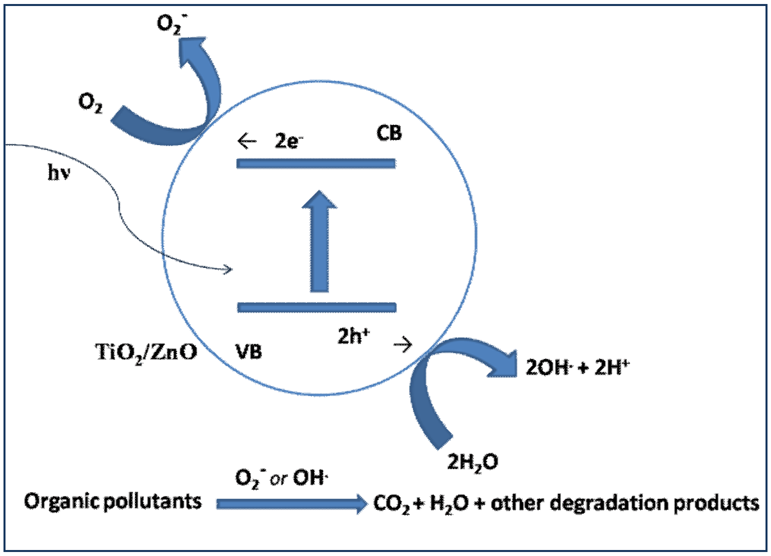

Fig. 1. Schematic of the photocatalytic mechanism for TiO_2/ZnO photocatalysts.

energies of common semiconductors are given in Table 1) of the semi-conductor photocatalyst material, it creates a positively charged hole in the valance band and negatively charged electron in the conduction band by exciting the electrons in the valance band to the conduction band[55].

$$\text{Photocatalysts } (TiO_2/ZnO) + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$h^+ + H_2O \rightarrow H^+ + OH^\bullet \tag{2}$$

$$h^+ + OH^- \rightarrow OH^\bullet \tag{3}$$

$$e^- + O_2 \rightarrow O_2^- \tag{4}$$

$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2 \tag{5}$$

$$e^- + H_2O_2 \rightarrow OH^\bullet + OH^- \tag{6}$$

$$\text{Organic} + \bullet OH + O_2 \rightarrow CO_2 + H_2O + \text{other degradation productions} \tag{7}$$

The conduction band electron reduces oxygen (into O_2^-) adsorbed to photocatalyst surface (TiO_2/ZnO) whereas the positively charged hole oxidizes either organic pollutants directly or indirectly by water to produce hydroxiyl free radicals (HO·). The photocatalytic reaction mechanism shown above (Figure 1) can be described by Eq. (1)-(7) as shown below[25,56-58]; In the photocatalysis of the organic pollutants, the oxidation of pollutants and the reduction process of oxygen do not occurs concurrently, there is an accumulation of electrons in the conduction band of the photocatalyst, thus helping a recombination of negatively charged electron and positive hole. Therefore, efficient utilization of electrons is necessary to encourage photocatalytic oxidation process. Semiconductors can also be used as photocatalysts for environmental remediation. Here, the photon-induced electron-hole pairs helps in redox reactions at the semiconductors catalyst surface and produces hydroxyl free-radicals (OH•) and superoxide ions (O_2^-). These generated species act as powerful oxidizer to disintegrate harmful organic pollutants in wastewater and convert them into CO_2 and H_2O. The most significant and fundamental components for a proficient photocatalytic system are the photocatalyst, the light source the reactor configuration[25].

Table 1. Bandgap energies for some common semiconductor materials at 0 K[54,59].

Semiconductors	**Bandgap energy (eV)**
Diamond	5.4
Cu_2O	2.172
ZnS	3.6
TiO_2	3.03
SnO_2	3.54
ZnO	3.36
CdSe	1.7
WO_3	2.76
Si	1.17
Fe_2O_3	2.3
PbS	0.286
PbSe	0.165
ZrO_2	3.87
Ge	0.744
CdS	2.42

The photocatalytic oxidation reaction depends on generation and recombination of electrons and holes in the semiconductor photocatalyst. Adsorbed oxygen on photocatalyst surface acts as an electron captor, which can control the recombination of photo induced electron-hole recombination. The nanosized catalysts have larger photocatalytic efficiency as compared to than normal photocatalyst materials[60,61]. The reasons behind this are:

(i) **Quantum Size Effect :** One of the most direct effects happens when the particle size becomes less than a certain critical limit (*i.e.,* size reduces to the nanometer range), this give rises to quantum size effects due to the confinement of the electronic movement. This leads to the valence band and conduction band of the semiconductor change into discrete energy levels, depending on the size of the material structure, which means that the electric potential of valence band changes more positive; otherwise the conduction band electric potential changes more negative. Then the oxidation-reduction potential of the electrons and holes is increased, and therefore the oxidation activity of nanosized TiO_2 and ZnO photocatalyst is enhanced[62,63].

(ii) **Higher Specific Surface Area:** If there are more number of atoms resides on the surface, it enhances the adsorption capacity of the photocatalysts towards organic pollutants. The activity of photocatalysis is associated with the time exhausted by electrons and holes to get to the surface of the particles. When the particles are nano sized their diameter becomes very miniature, so it is then very straightforward for the charge carriers moving from the inside to the surface, and starting red-ox reaction. Higher the surface to volume ratio, smaller the particle diameter and the smaller time may be used up by charge carriers diffusing to the surface from inside. This can provide lesser probability of electron and hole recombination. Therefore, the superior photocatalytic activity can be achieved. Consequently, the nano-titanium and zinc oxides have greater photocatalytic efficiency than the common (bulk) titanium or zinc oxides[64-66].

3. TiO2 and ZnO as Efficient Photocatalyst for Wastewater

3.1. TiO_2 as a Photocatalyst

Being a member of metal-oxide semiconductor photocatalysts family, there is a general agreement among researchers that TiO_2 is more superior because of its high phocatalytic activity, large chemical stability and robustness against photocorrosion, low price, and nontoxicity[67]. Particularly, titanium dioxide is largely used for many applications such as air and water purification, as an agent for antifogging and self-cleaning surface, whereas, zinc oxide has not been used like TiO_2 for such applications[13,68]. Wu has studied that TiO_2 has greater photocatalytic activity than ZnO and SnO_2[69]. For the decomposition of phenol as target organic species, Okomoto studied that TiO_2 has greater photocatalytic activity as compared to cadmium sulfide (CdS)[70]. Sakthivel proved that under similar study conditions, TiO_2 is a superior photocatalyst than WO_3, α-Fe_2O_3, SnO_2 and ZrO_2[71]. On the other hand, Augugliaro established that, TiO_2 has better photochemical stability than ZnO in aqueous solution; however, zinc-oxide is photochemically more active (although its surface to volume ratio was less)[72]. Significant amount of work has been carried out for investigating the photocatalytic activity of titanium dioxide based on its phase composition, size and crystal structure[73-75]. Three different phases of TiO_2 exist: anatase, rutile and brookite[76]. There are still very few reports on brookite while anatase and rutile phases of nanostructured TiO_2 are the most studied phases[77-79]. The position of oxygen ions on the exposed anatase TiO_2 particle surface possesses a triangular arrangement which allows significant absorption of organic molecules[80]. Whereas, the orientation of titanium ions in the anatase TiO_2 creates an advantageous reaction condition with the absorbed organic pollutants[81]. Interestingly, these favorable structural arrangements of oxygen and titanium ions are not present in the rutile phase of

TiO_2. Due to this reasons anatase phase of titania shows higher photocatalytic activity than rutile[82]. Although, anatase phase is reported to be the most photochemically active form of titaniumdioxide, but several researchers believed that a pure anatase phase has less photocatalytic performance[83]. The rutile phase present in the anatase TiO_2 introduces some percentage of mesoporosity and a wider pore size distribution which probably be accountable for the enhanced photocatalytic activity for this phase[84]. These reports have been suggested that anatase-rutile mixtures/composites would be the best combination to synergistically enhance photocatalytic efficiency[85-87].

Various strategies have been taken to prepare commercial samples of TiO_2 by varying purity, particle size, and crystal structure and phase composition to enhance photocatalytic efficiency with Degussa P25 grade (generally, it is a mixture of 30% rutile and 70% anatase TiO_2 powder samples)[88,89]. There is a general believe that commercial grade Degussa P-25 TiO_2 sample shows significant photocatalytic degradation efficiency towards organic dye degradation as compared to other commercial forms[89,90]. The effect of particle size on the photocatalysis can be explained in terms of available surface area of TiO_2 for the reaction. Usually, for the smaller particle size, surface area would be larger and surface to volume ration increases which intern increases expected photocatalytic activity. This larger available surface area thus increases the number of active photocatalytic sites per unit area, as well as enhances the adsorbability of the organic pollutants on the TiO_2 photocatalyst surface[91]. However, several shortcomings of the conventional TiO_2 powder catalysts, such as difficulty in separation after synthesis and stirring throughout reaction, make powder TiO_2 less photocatalytic efficient and prevent form being used in the practical applications[92]. Hence, several studies have been focused on the synthesis and modification of TiO_2 nanostructured by making composite photocatalysts with ceramics like SiO_2, ZrO_2, Al_2O_3 and

TiO_2 coated polymer nanostructures to eliminate the previous difficulties[93-95]. Tryba *et al.* has also been reported that TiO_2-mounted activated carbon could increase the photocatalytic degradation of organic dyes[96]. Interestingly, different form of carbons like porous carbon, carbonnanotube (CNT)[97], carbonnanofiber (CNF)[98], graphene[99], exfoliated graphite[100] and graphene oxide[101] have been reinforced with TiO_2 to make TiO_2/carbon composites for superior photocatalytic activity.

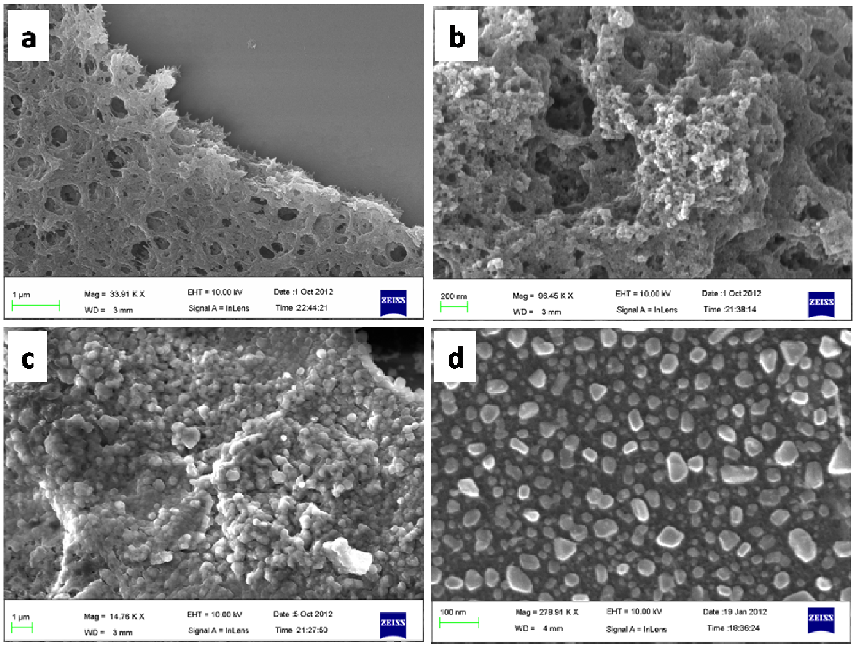

Fig. 2 : Degradation of RhB dye contaminated water with TiO_2/porous carbon films. The porous structure results in improved catalytic support for the photocatalyst as discussed in [13] :Fe-SEM micrographs of the TiO_2/polymer and TiO_2/carbon porous films: (a) Porous polyacrylonitrile (PAN) polymer and TiO_2 composite film, (b)Higher magnification images of 'a' showing the presence of TiO_2 nanoparticles on the polymer films, (c) Porous carbon and TiO_2 composite films after pyrolyzation of TiO_2/polymer film, and (d) Higher magnification images showing 'bead' like titanium dioxide particles on the porous carbon film.

Even though, in photocatalysis anatase phase of titania has more efficiency than rutile but, this phase is thermodynamically metastable[102] and it may undergoes irreversibly transformation from anatase to rutile phase at relatively high temperatures ~ 800°C and above[103]. Moreover, studies have shown that rutile pahse of TiO_2 exhibit superior photocatalytic activity compared to pure anatase TiO_2 for the photodecomposition of *p*-coumaric acid[104], photo-oxidation of H_2O with Fe^{3+},[105] and photodecomposition of H_2S[106]. Besides that, rutile TiO_2 has better light scattering properties, chemical inertness and cost efficient which makes it a potentially candidate for several applications like dye sensitized solar cells, solar photocatalytic, electrochemical and catalysis[107-110].

In a recent study[13], authors have developed an *in-situ* synthesis method for pure rutile TiO_2 nanoparticles impregnated macroporous carbon film and found efficient for the photocatalysis of Rhodamine B dye. This may be advantageous for the applications of TiO_2 when there is a requiring of pure rutile phase and the working temperature is higher.

3.2. ZnO as a Photocatalyst

Till to date, many types of semiconducting systems have been studied for photocatalysis including TiO_2, ZnO, ZrO_2, CdS, WO_3, and so on[111-116]. Most of them have band gap in the UV (ultraviolet) region, *i.e.*, equal to or greater than 3.36 eV (λ = 388 nm)[59]. Thus, these catalysts promote photocatalytic reactions under the illumination of UV radiation[117]. Surface area, surface defects and bangap of the metal oxide nanostructured catalysts play a significant role in the photocatalysis[118]. 1D- nanostructures like nanowires, nanorods, nanospheres and nanofibers are potential candidates for application to photocatalysis because they have offered a very high surface to volume ratio than nano-particles[62,119,120].

Zinc oxide is an excellent wide band gap, natural n-type semiconducting material with binding energy (60 MeV), abundant in nature, nontoxic nature and environmental friendly photocatalyst[121]. It can absorb wider range of spectrum of radiation which also makes it more applicable for dye sensitized solar cells and solar photovoltaic applications[122-124].

The nanosized ZnO oxides are most efficient functional materials for photocatalytic applications which are available at low cost, exhibit mild reaction conditions and high photochemical reactivity, while affording the use of sunlight[125]. Amongst all metal oxide semiconductors, zinc oxide, most functional material find application for many fields including biosensors, light-emitting diodes, field-emission, and gas sensing[126].

The photocatalytic efficiency of ZnO nanomaterials is believed to be much better than normal photocatalysts[127]. It is extensively used to treat wastewater, such as printing and dyeing wastes, dairy and food wastewater, drugs and pesticides wastewater, textile wastewater, papermaking wastewater, and so on[128-132].

There is growing interest for the photocatalytic degradation of different organic pollutants present in wastewaters comes from industrial and agricultural waste[5,24,31,92,133]. The photocatalytic reactions happens in such treatment somehow identical to heterogeneous catalysis which includes the simultaneous adsorption of oxygen and organic reactant species present on the waste, followed by the oxidation on the ZnO photocatalyst surfaces[6,10]. Zinc oxide is a photoactive semiconducting material oxide and able to activate itself by taking energy for the photocatalytic reaction from photons. Therefore ZnO photocatalyst must have to simultaneously adsorb reasonable amount of O_2 and reducing species (i.e., the organic pollutant molecules). A good photocatalyst like zinc oxide is considered to provide adsorption sites for the organic pollutants, which means that an open porous structure with high specific surface area is needed[134]. Since the thermal energy is expensive, a very important issue of a good photocatalysis is that the involving reactions have to occur at ambient temperature.

Recently, it is proven that semiconducting photocatalyst mediated photocatalytic oxidative degradation of organic compounds is a doing well[135]. This has been demonstrated as an alternative to conventional wastewater treatments for the removal of organic pollutants from various industrial wastes[136]. The uses of ZnO nanostructures as a potential photocatalyst material to decompose the environmental pollutants have also been rigorously studied[137,138]. Interestingly, to achieve better photocatalytic efficiency in many realistic applications, it is expected that ZnO photocatalyst should absorb not only ultraviolet radiation but also visible light[139]. To absorb visible spectrum of solar radiation, band gap energy of ZnO photocatalysts must have to be decreased or divided into different sub-bandgaps, which can only be obtained either by incorporating transition metal ions or by doping nitrogen, sulphur atoms[140]. The electronic and photocatalytic properties of zinc oxide solely depended on its surface morphology, size, crystal structure, aspect ratio, density of crystal and crystallographic orientation[141,142]. ZnO has known as an effective photocatalyst for water detoxification, organic pollutant decomposition and other photolysis because it produces hydrogen peroxide (H_2O_2) more proficiently[143]. Also, it has high mineralization and reaction rates, and also provides more of active sites with high specific surface photoactivity[144]. So far, many attempts have been taken to create different morphology of nanosized ZnO photocatalysts in which hydrothermal synthesis[145], sol-gel technique[146], plasma-enhanced chemical vapor deposition (PECVD)[147], Rf-magnetron sputtering[148], electrospinning[24,149] and so on[150-152]. Recently, we have reported[24] a novel synthesis protocol for the fabrication of mesoporous ZnO nanofibers by employing electrospinnig technique. In that paper, we have demonstrated an ultraviolet radiation assisted photodecomposition of PAHs dyes-naphthalene and anthracene by using free standing mesoporous ZnO nanofibers mats.

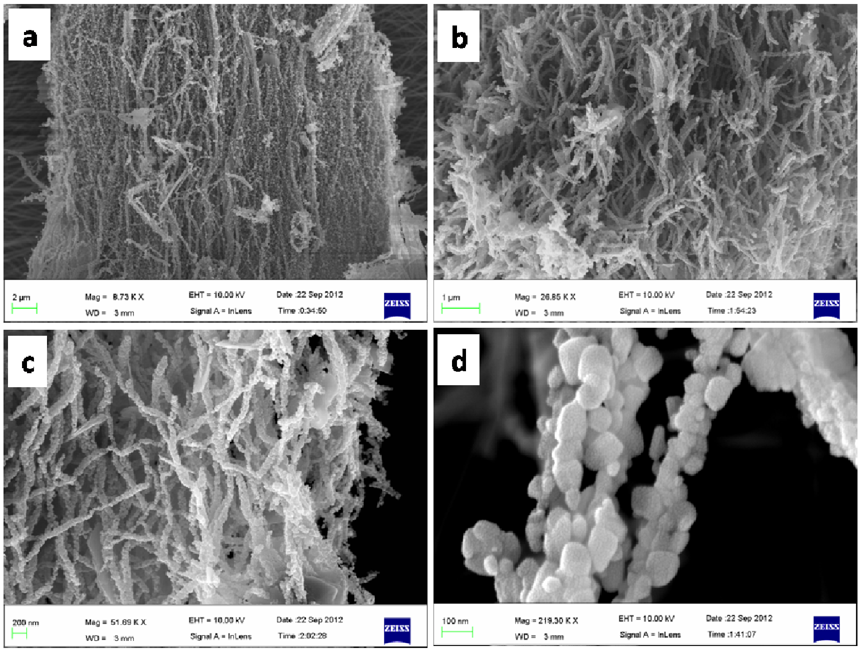

Fig. 3 : Photocatalytic degradation of polycyclic aromatic hydrocarbon dyes-naphthalene and anthracene in wastewater water with electrospun mesoporous ZnO nanofiber mats as discussed in [24]: Fe-SEM micrographs of the electrospun ZnO nanofibers: (a) free-standing fiber mats, (b) partially aligned nanofibers, (c) Higher magnification of 'b' and (d) a single mesoporous nanofiber.

4. Effect of Light Source on Photocatalytic Degradation

The percentage degradation of dyes in waste water improved with increasing exposed light intensity[153]. Under the elevated intensity of light irradiation, the enhancement was significantly higher since the electron–hole formation is predominant at high irradiation intensity and, therefore, electron–hole recombination probability is insignificant[154]. However, when irradiated light intensity becomes very poor, separation of electron–hole pair competes with recombination which consecutively decreases the formation of free radicals, thus, causing less result on the percentage degradation of the waste water[155-157].

The greater part of photocatalytic degradation studies have been carried out between the wavelengths 320-380 nm[59] which is related to the bandgap energy of the TiO_2 and ZnO photocatalyst[158]. Thus, the light source which produces the required radiation field can be performed by solar irradiation or by artificial lamps. In a typical photocatalytic reactor, radiation (wavelength ranging between 320-380 nm) is provided by fluorescent low-pressure and medium mercury lamps emitting low and high intensity UV light, respectively in the short, medium and long UV spectrum[59]. The higher possibility of trapping of electron-hole pairs with shorter wavelength excitation and direct photolysis were considered to be likely the reasons for a good photocatalytic system[159]. Only ~5% of the incident solar radiation is used by TiO_2 and ZnO assisted photocatalytic decomposition of dyes[59,160]. This drastically confines their practical application. Therefore, modification of TiO_2 and ZnO photocatalysts to improve light absorption capacity and photocatalytic activity under visible light irradiation is the topic of recent research[161-163].

5. Effect of pH on Photocatalytic Degradation:

The pH value of the aqueous solution is a key parameter for photocatalytic degradation of wastewater and dyes because it affects the adsorption of pollutants that happens at the surface of photocatalysts[164,165]. The wastewater produces from textile, dairy and pharmaceutical industries generally have a wide range of pH values. In addition, the generation of hydroxyl radicals which is necessary for the photocatalytic reaction also depends on pH of the solution[166]. Therefore, pH plays a significant role for both cases, in the chemical nature of wastes and generation of hydroxyl radicals[1,167]. Hence, many attempts have been taken to investigate the effect of pH in the degradation of wastewater in the ultraviolet and solar irradiations[168-170]. Photocatalytic decomposition of dyes in waste water have been studied at pH values ranging from 3 (acidic) to 13 (alkaline) for all the three (anionic, cationic and neutral) dyes in wastewater[1].

It was observed that, at optimal concentration of dyes in both acidic and alkaline pH tends to lower the degradation efficiency of some azo dye wastes[171,172]. It was studied that in presence of H_2O_2 some nonbiodegradable cationic dyes (Malachite green, Rhodamine B, and Methylene blue) degrades least effectively at both acidic and alkaline pH, but highly effective at neutral pH value of the solution[173]. The inhibitory effect found to be more prominent in the high alkaline range (*i.e.,* pH 11–13)[171]. At high pH values the hydroxyl radicals are so quickly discarded that they do not have proper time to react with dyes in waste water. The pH influences the surface properties of TiO_2 and ZnO photocatalysts, dissociation of organic pollutants (or dyes in waste water) and formation of hydroxyl radicals[25].

The greater photodegradation efficiency at neutral pH can be explained by the point of zero charge (pzc) of the photocatalysts[169]. The pzc value was found at pH 6.25[170] and 8.9[174] for the TiO_2 and ZnO respectively. The photocatalysts surfaces become negatively charged under alkaline conditions (pH > pzc), whereas it is positively charged in acid media (pH< pzc). While TiO_2 and ZnO exhibit an amphoteric nature with a zero charge in the pH range around their pzc value, the adsorption of dye pollutants is extremely good at that pH value, and consequently, higher photodegradation activity was predictable at a neutral pH value[169]. Therefore, the result indicates that pH value has a significant effect on the adsorption properties at the photocatalyst surface and hence photodegradation rates are quite insignificant with extreme pH values[175].

The interpretation of effects of pH values on the activity of the photodegradation process is a very complicated task, because there are three possible reaction mechanisms behind the organic pollutant/dye degradation process, namely, oxidation and reduction by the positive hole and negatively charged electron, respectively in the semiconductor photocatalysts and hydroxyl radical attack. The importance of each parameter strongly depends on the pH value and nature of the substrate. In the case of organic dyes and pollutants, it can be assumed that the main reaction is governed by the hydroxyl radical attack, which can be advantageous by the high hydroxyl radicals' concentration at around neutral pH values of the solution[169]. Additionally, another justification for the pH effects can be connected with ionic specification of the organic dyes because the protonation or deprotonation of the dyes can drastically alter its adsorption characteristics and oxidation-reduction activity[1,171].

6. Effect of Temperature, Dye Concentration, Catalyst Loading and Type of Catalysts on Photocatalysis:

In a typical photocatalytic decomposition of wastewater dyes, the following operating parameters have also involved in the process.

6.1. Temperature : Abass *et al* studied[19] that decolorization of real textile industrial wastewater with time increases with increasing temperature for all types of catalysts. Their results confirm that higher temperature is significantly helpful to decompose the pollutants in wastewater. This is probably due to the fact that the activation energy gets increased with increasing operating temperature[169].

6.2. Dye Concentration : The lowering in dye (pollutant in waste water) concentration reduces the time of decomposition of the wastewater. This performance could be described as: when the concentration of real industrial wastewater is very less than of the original concentration then the catalysts active sites probably be completely exposed by dye ions[176]. The further increase in dye concentration may also be responsible for screening the exposed light so the light intensity will be reduced[177].

6.3. Photocatalyst Loading : The effect of photocatalytic degradation of wastewater dyes with different catalyst loading has been extensively explored[18,171,178,179]. Konstantinou and his co-workers have shown that, for azo dye degradation by TiO_2 assisted photocatalysis, the initial degradation rates of azo dyes in aqueous solution were directly proportional to TiO_2 catalyst concentration[171]. Interestingly, studies for UV assisted photocatalytic decomposition of industrial wastewater using different photocatalyst (anatase or rutile or zinc oxide) loading shows that for an optimum photocatalysts mass, which was required for utmost decolorization efficiency does not dependent on exposure time, type of irradiation source and characteristics of pollutant[180]. Further studies have also revealed that the decolorization efficiency increases with increase in catalysts loading and it get saturated at a certain value of loading and then it starts decreasing with further increasing the mass[19,181]. The increasing photocatalytic activity with increase in photocatalysts's masses happens may be due to increasing accessibility of photocatalyst sites and the diminish of catalytic activity after the saturation region is correlated to rising of light scattering by the much excess of photocatalyst particles[181,182].

6.4. Type of Catalysts : Considering the impact of different prospective photocatalyst on their thermal and chemical activity, stability under different working environment, accessibility and ease of handiness in many physical forms, cost effectiveness, toxicity, and environmental friendly the common widely used photocatalyst is TiO_2[31]. Amongst the three crystal structures, only rutile and anatase are established enough and can be used as a potential photocatalyst[183]. Pillai and his co-worker has reported that photocatalytic properties of different phases of TiO_2 materials might be dissimilar significantly and rutile phases exhibiting the lowest photoactivity[184,185]. Anatase phase of TiO_2 is superior photocatalyst than rutile while brookite phase has not studied much[186]. In the case of Degussa P-25, a mixture of anatase and rutile TiO_2 which prevents the recombination rate of photogenerated electrons and holes and for this reason shows more activity than anatase[187].

Further, Hussein and Abass[19] studied the decomposition of real industrial wastewater on rutile, anatase, and zinc oxide at a constant temperature and time and has proven that the efficiency of these catalysts fell in the sequences as shown below:

ZnO > Degusa P-25 >TiO_2 (Anatase) > TiO_2 (Rutile)

Interestingly, the quantity of ZnO photocatalyst required to achieve the optimal photocatalytic activity is nearly double than that for TiO_2 (anatase or rutile)[19,182].

7. Conclusions

Reviewing the recent representative publications, the function of various operating parameters on the photocatalytic decomposition of various ognaic dyes in wastewater explored in this review. TiO_2 and ZnO have been recommended to be efficient photocatalysts for the degradation and mineralisation of various toxic organic pollutants such as azo dyes in wastewater water. The investigations also suggest that the coexistence of photocatalyst and lights exposure is necessary for photocatalytic degradation of dyes. Various operating parameters such as nature light source, pH of the reaction medium, temperature, dye concentration, catalyst loading and type of catalysts have a considerable effect on degradation efficiency of dyes in wastewater. Optimization of the photodecomposition parameters is essential from the viewpoint of efficient design and the application of photocatalytic oxidation processes to guarantee sustainable wastewater purification process.

Although the UV energy gives improved efficiency in degradation of dyes, solar irradiation could appear as a substitute cost effective light source because of its abundance. Thin-film coating of photocatalyst may resolve the problems of leaching and separation. Make the naofibers of catalysts may further enhance the photocatalytic activity due to its high surface to volume ration which will facilitate the better adsorption of dyes. Metal and non-metal doped nanostructured TiO_2 and ZnO have been reported to result in improved degradation rates due to their modified band gap energy for using visible and solar radiation. So, we need to focus for developing more reliable photocatalysts which can absorb visible and solar radiation or by both. In addition, further work is essential on the designing and understanding the working parameters for oxidation of pollutant dyes in wastewater.

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