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REVIEW ARTICLE

REVIEW ON THE REMOVAL OF ORGANIC DYES BY PHOTOCATALYTIC DEGRADATION USING NANOCOMPOSITE OF TRANSITIONAL METAL OXIDES UNDER VISIBLE-LIGHT

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ABSTRACT

Varieties of wide organic and inorganic pollutants especially pesticides, poisonous metals, and dyes are introduced in to the water system from various sources such as: industrial effluents, agricultural runoff and chemical spills. The new treatment methods (Photocatalytic degradation method) are necessary for the removal of persistent dye chemicals or converting them into harmless compounds in water. The photocatalytic technique with metal oxide semi conductors has become one of the most promising methods for waste water treatment. In particular, ZnO has attracted much attention with respect to the degradation of various pollutants due to its being relatively cheap, stable, high photocatalysis, non-toxicity, and wide band gap. One of the main problems associated with the feasibility and viability of ZnO Semiconductor photocatalytic oxidation is: Recombination of photo-generated electrons and holes in the semiconductor and high band gap energy (>3.0 eV) that requires radiation in the UV range for electron excitation from VB to CB. To overcome this problem it can be achieved by: doping transition metal, quantum dot photosensitization, carbon nano structure and improving the catalytic efficiency of the semiconductor photocatalyst by minimizes the electron-hole recombination. The factors affect photocatalytic degradation and synthesis methods for nanocomposites were summarized. For example Ternary system of Fe_2O_3-ZnO-MnO_2, to improve the photocatalytic activity of wide band gap photocatalysts was discussed. But the difficulties in recycling and preconcentration restricted the utilization of finer nanoparticles. To overcome this limitation, the nanoparticles have been supposed to be fixed on the inert supports such as zeolite for practical applications in order to improve the recovery efficiency of photocatalysts.

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INTRODUCTION

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. About 1–20 % of the total world production of dyes is lost during the dyeing process and is released in the textile effluents (Houas *et al*., 2001). Some dyes are toxic and even at very low concentrations may significantly affect aquatic life. Some other dyes may cause allergy, skin irritation and cancer to humans (Arami *et al*., 2006; Yang *et al*., 2008). The removal of organic pollutants in wastewater is an important measure in environmental protection (Vinodgopal. *et. al.,* 1996). Photodecomposition over semiconductors oxides is initiated by the absorption of a photon with energy equal to or greater than the band gap of semiconductor producing electron – hole pairs (U.I. Gaya, A. H. Abdullah., 2008).

It is crucial to prevent electron –hole recombination before a designated chemical reaction occurs on the semiconductor surface. Many semiconductors have been tested that utilize UV –vis irradiation to degrade a high number of recalcitrant materials in aqueous system. Titanium dioxide (TiO_2) is the most active photocatalyst studied for this purpose (R. Saravanan, H. Shankar, T. Prakash, V. Narayanan, A. Stephen., 2011). However, zinc oxide (ZnO) has recently been receiving attention due to its environmental stability and low cost, as compared to other metal oxides (C. Hu, Y. Lan, J. Qu, X. Hu, A. Wang., 2006). The photocatalytic activity of ZnO is limited to the irradiation wavelengths in the UV region because ZnO has a wide band-gap of about 3.2 eV and can only absorb UV light with wavelength below 387 nm (C. Shifu, Z. Wei, Z. Sujuan, L. Wei, 2009). The photocatalytic activity of ZnO has been improved by various techniques such as doping (Z.Wang, W. Cai, X. Hong, X. Zhao, F. Xu , C. Cai, 2005 and , S. Chen, J. Zhang, C. Zhang, Q. Yue, Y. Li, C. Li, 2010), coupling or a combination of both (R. Saravanan, et al., 2011, , K. Karásková., et al 2012, K. Biswas, et al, 2010 and L. Ruiping, 2009).

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Combining some semiconductors with different band gaps to form heterojunctions in photocatalytic systems has become a primary focus of researchers in recent years because of their somewhat unique properties not existed in the individual nanomaterial arising from the interfacial interaction at the nanoscale. For example, it can efficiently reduce the recombination rate of the photogenerated charge carriers in the use of environmental purification and remediation. It also can significantly enhance the optical absorption of photocatalyst (G. Yang, Z. Yan, T. Xiao, 2012). Among the combinations reported, ZnO has been successfully fabricated combined together with Fe_2O_3 (D. Sarkar, G.G. Khan, A. K. Singh, K (2012) and with MnO_2 (D. Sarkar, G.G. Khan, A. K. Singh, K. Mandal, (2013). showing in both case enhanced properties. Recently, in Fe_2O_3-ZnO-MnO_2 coupled system, the band gap energy is 2.53 eV. This band gap energy reduced compared with band gap energy of ZnO 3.2 eV (H. Tedla, et al (2015). This decreasing band gap energy is as the result of combining ZnO and Fe_2O_3 semiconductor nanoparticles with band gap widths. One of the most effective application is to reduce the electron-hole pairs recombination (Wang et al., 2009). This because when the visible light hit the VB of combined semiconductor , CB electron can be ejected from the low band gap semiconductor (Fe_2O_3) to the band gap semiconductor (ZnO) and on the contrary, hole transfer can take place from the VB of high band gap semiconductor (ZnO) to the VB of low band gap semiconductor (Fe_2O_3). Additionally, the presence of electron accepter Mn(IV) could scavenge the excited electrons and altogether prevent the recombination of electron-hole pairs and the charge separation of the carriers.

In Single, binary and ternary systems of nanoparticles there is difficulties in recycling and preconcentration restricted the utilization of finer nanoparticles. To improve the applicability of nanoparticles for water treatment, nanocomposite materials have emerged as suitable alternatives to overcome limitations of growth nanoparticles by employing porous supports materials of large area as a matrices or stabilizers to obtain hybrid nanocomposite adsorbents (Pan B, Pan B, Zhang W, Lv L, Zhang Q, Zheng S. Chem Eng J, 2009) Among the various matrixes, zeolites are considered to be promising hosts and stabilizers due to their unique features such as: large surface area, high ion exchange capacity cavities with 1.3 nm diameter, hydrophilic, ecofriendly nature, easily tunable chemical properties and the highly thermal stability (Xu X, Ni Q. 2010 and Posada Y. 2013. Recently, for example Zeolites-y supported ZnO-Fe_2O_3-MnO_2 (Haileyesus, 2015) have been reported on dyes to increase the wave length of excited light that improve light utilization efficiency and catalytic activity. This appears to have produced in a combined effect greater than the sum of their separate effects of photocatalytic activity for the photocatalytic degradation of dyes. This study provides a unique perspective on basic research of nanotechnology for water/wastewater treatment and reuse by focusing on challenges of future research.

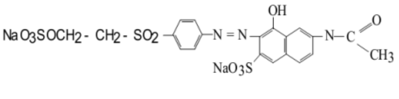
Electron-Hole Pair Recombination: The absorption of a photon with sufficient energy of the catalyst is leads to a charge separation due to promotion of an electron from valance band the conduction band of the semiconducting materials. This excited electron in conduction band comeback across a band gap into the empty state represented by hole in the valence band (Linsebigler et al., 1995), this process is known as electron-hole pair recombination (EHP). Recombination of the photoexcited electron-hole pair needs to be retarded for an efficient charge transfer on the photocatalyst surface. Charge carrier trapping would be suppressing the recombination and increase the lifetime of the separated electron and hole, which improve the photocatalytic efficiency (Jing et al., 2006; Hamadanian et al., 2010). The oxygen molecule over photocatalyst surface traps the electrons, that present in the conduction band (e^- CB) and generate the superoxide radical anion (O_2•-) which have prevents the recombination of electron-hole pairs (Ilisz et al., 1997).

Role of photogenerated electrons in photocatalysis: For a semiconductor to have high quantum efficiency, its photoinduced charges must be freely migrate to the surface of the catalyst, which has participated in reaction with adsorbed species. The migration of electrons to the surface of catalyst is not only reducing the EHP recombination but also trapping coordination defects on the surface of catalyst and lattice defects in the bulk particles. The photogenerated electrons that are able to migrate to the surface catalyst reduce the oxygen molecule (O_2) into superoxide radical (O_2•), which is powerful species for decolorization of organic compounds (Cavicchioli and Gutz, 2002).

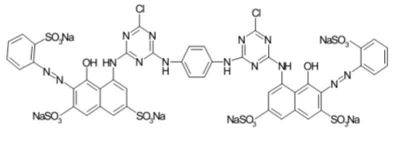
Textile organic dyes: The dyes are natural and synthetic compounds that make the world more beautiful through coloured products. The textile dyes represent a category of organic compounds, generally considered as pollutants, presented into wastewaters resulting mainly from processes of chemical textile finishing (Suteu et al., 2011a; Zaharia et al., 2009). The textile coloration industry is characterised by a very large number of dispersed dyehouses of small and medium size that use a very wide range of textile dyes.

Textile organic dye classification: The nature and origin are firstly considered as criteria for the general classification in natural and synthetic textile dyes. The natural textile dyes were mainly used in textile processing until 1856, beginning in 2600 BC when was mentioned the use of dyestuff in China, based on dyes extracted from vegetable and animal resources. It is also known that Phoenicians were used Tyrian purple produced from certain species of crushed sea snails in the 15th century BC, and indigo dye produced from the well-known indigo plant since 3000 BC. The dyes from madder plants were used for wrapping and dyeing of Egyptian mummies clothes and also of Incas fine textures in South America. The synthetic dyes were firstly discovered in 1856, beginning with ‚mauve' dye (aniline), a brilliant fuchsia colour synthesed by W.H. Perkin (UK), and some azo dyes synthesed by diazotisation reaction discovered in 1958 by P. Gries (Germany) (Welham, 2000). These dyes are aromatic compounds produced by chemical synthesis, and having into their structure aromatic rings that contain delocated electrons and also different functional groups. Their color is due to the chromogene-chromophore structure (acceptor of electrons), and the dyeing capacity is due to auxochrome groups (donor of electrons). The chromogene is constituted from an aromatic structure normally based on rings of benzene, naphthaline or antracene, from which are binding chromofores that contain double conjugated links with delocated electrons. The chromofore configurations are represented by the azo group (-N=N-),ethylene group (=C=C=), methine group (-CH=), carbonyl group (=C=O), carbon-nitrogen (=C=NH; -CH=N-), carbon-sulphur (=C=S; ≡C-S-S-C≡), nitro (-NO2; -NO-OH), nitrozo (-N=O; =N-OH) or chinoid groups. The auxochrome groups are ionizable groups, that confer to the dyes the binding capacity onto the textile material. The usual auxochrome groups are: -NH2 (amino), -COOH (carboxyl), $-SO_3H$ (sulphonate) and -OH (hydroxyl) (Suteu et al, 2011; Welham, 2000). Five examples of textile dyes are presented in Fig. 1. The textile dyes are mainly classified in two different ways: (1) based on its application characteristics (i.e. CI Generic Name such as acid, basic, direct, disperse, mordant, reactive, sulphur dye, pigment, vat, azo insoluble), and (2) based on its chemical structure respectively (i.e. CI Constitution Number such as nitro, azo, carotenoid, diphenylmethane, xanthene, acridine, quinoline, indamine, sulphur, amino- and hydroxy ketone, anthraquinone, indigoid, phthalocyanine, inorganic pigment, etc.) (Cooper, 1995).

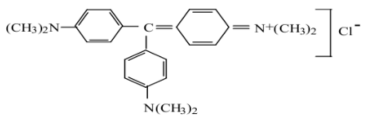
Excepting the colorant precursors such as azoic component, oxidation bases and sulphur dyes, almost two-third of all organic dyes are azo dyes (R_1-N=N-R_2) used in a number of different industrial processes such as textile dyeing and printing, colour photography, finishing processing of leather, pharmaceutical, cosmetics, etc. The starting material or intermediates for dye production areaniline, chloroanilines, naphthylamines, methylanilines, benzidines, phenylenediamines, and others. Considering only the general structure, the textile dyes are also classified in anionic, nonionic and cationic dyes. The major anionic dyes are the direct, acid and reactive dyes (Robinson et al., 2001), and the most problematic ones are the brightly coloured, water soluble reactive and acid dyes (they cannot be removed through conventional treatment systems). The major nonionic dyes are disperse dyes that does not ionised in the aqueous environment, and the major cationic dyes are the azo basic, anthraquinone disperse and reactive dyes, etc. The most problematic dyes are those which are made from known carcinogens such as benzidine and other aromatic compounds (i.e. anthroquinone-based dyes are resistant to degradation due to their fused aromatic ring structure). Some disperse dyes have good ability to bioaccumulation, and the azo and nitro compounds are reduced in sediments, other dye-accumulating substrates to toxic amines (e.g. $R_1\text{-N=N-}R_2 + 4H+ + 4e- \rightarrow R_1\text{-}NH_2 + R_2\text{-}NH_2$). The organic dyes used in the textile dyeing process must have a high chemical and photolytic stability, and the conventional textile effluent treatment in aerobic conditions does not degrade these textile dyes, and are presented in high quantities into the natural water resources in absence of some tertiary treatments.



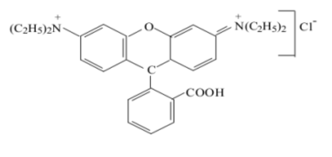
Reactive Orange 16
C.I. 18097
Anionic monoazo reactive dye;
MW = 617.54 g/mol;
λ_{max} = 495 nm



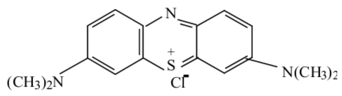
Brilliant Red HE-3B
(Reactive Red 120)
C.I. 25810
Anionic, bifunctional
azo reactive dye;
MW = 1463 g/mol;
λ_{max} = 530 nm



Crystal Violet
(Basic Violet 3)
C.I. 42555
Cationic triphenylmethane dye;
MW = 407.99 g/mol;
λ_{max} = 590 nm



Rhodamine B
(Basic Violet 10)
C.I. 45170
Cationic, Xantenic dye;
MW =479.2 g/mol;
λ_{max} = 550 nm



Methylene Blue
(Basic Blue 9)
C.I. 52015
Cationic, phenothiazine dye;
MW =319.85 g/mol;
λ_{max}= 660 nm

Nature of Organic Pollutants: Our environment is being polluted by several toxic chemicals through the wastewaters released from industries and municipal sewage system. These chemicals cause harmful ecological effect. Most of the conventional wastewater treatment methods are not designed to completely remove trace organic contaminants. Dyes and pigments, Pesticides and Herbicides, Phenols, carboxylic acids and their derivatives, Polycyclic Aromatic Hydrocarbons (PAH), Surfactants, etc.

Photodegradation of organic dyes: Removal of color in wastewater generated by the textile industries is major issue of discussion and regulation all over the world. Among the dyes, the textile azo dyes with synthetic intermediates as contaminant and its degradation products have undoubtedly attracted the most attention with regard to their high environmental impact, because of their widespread use, their potentiality to form toxic aromatic products (carcinogenic it and mutagenicity properties) and their low removal rate during primary and secondary with treatment. Therefore, it is important to develop effective wastewater remediation technologies for these compounds (Senthikumaar *et al.,* 2010*).*
Reactions involved in the photocatalytic degradation of organic pollutants

Mechanism of photocatalytic Degradation of Pollutant on a semiconductor

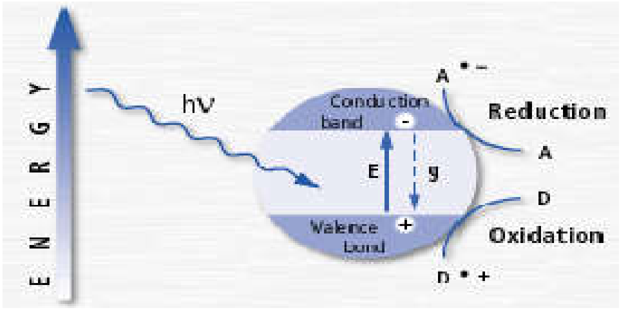


Figure 1. Dye/semiconductor/UV light system (Hussein, 2011)

$ZnO + hv \rightarrow h^+ + e^-$
$H_2O \rightarrow H+ + OH^-$
$h^+{}_{VB} + OH^- \rightarrow OH^-$
$h^+{}_{VB} + H_2O \rightarrow H^+ + OH^-$
$e^-{}_{CB} + O_2 \rightarrow O_2{}^{\cdot-}$
$H^+ + O_2{}^{\cdot-} \rightarrow HO_2$
$2HO_2 \rightarrow O_2{}^{\cdot-} + H_2O_2$
$O_2{}^{\cdot-} + H_2O_2 \rightarrow 2HO^- + O_2$
$H_2O_2 + hv \rightarrow 2{}^{\cdot}OH$

Organic pollutant +. OH + $O_2 \rightarrow$ CO2 + H2O + Other production. The processes in this pathway can be summarized by the above equations (Hussein and Alkhateeb, 2007).

Mechanism of photocatalysis: A nanophotocatalyst when exposed to light valance band electrons absorb energy and transfer to conduction band producing an electron-hole pair (Konstantinou and Albanis., 2004).

h^{+}_{vb} reacts with H_2O to give OH and e^{-}_{eb} react with dissolved O_2 to give $O^{-}_{2}{}^{\cdot}$ These active radicals are responsible to decompose dye. The mechanism of the photocatalytic degradation is as under. The basic mechanisms of the photocatalytic process include these reduction and oxidation reactions as well as some secondary reactions, which forms the driving force of a number of important photocatalytic applications.

$\text{Catalyst} + hv \rightarrow e- + H^{+}$
$H_2O + h^{+}_{vb} \rightarrow {}^{\cdot}OH + H^{+}$
$e^{-}_{cb} + O_2 \rightarrow O_2{}^{-\cdot}$
$O_2{}^{-} {}_{+} H^{+} \rightarrow HO_2{}^{\cdot}$
$2HO_2{}^{\cdot} \rightarrow H_2O_2 + O_2$
$H_2O_2 \rightarrow 2OH$
$\dot{OH} + \text{Dye} \rightarrow CO_2 + H_2O$

In the heterogeneous catalysis, the overall process can be decomposed into five independent steps (Herrmann, 1999). These are:

- Transfer of the reactants from the fluid phase to the surface
- Adsorption on the catalysis surface.
- Reaction of the adsorbed molecules
- Desorption of the reaction products.
- Transfer of the products from the interface region to the solution.

The mass transfer steps (1) and (5) depend on reactant/product concentration as well as photocatalyst loading and particle size. Steps (2), (3), and (4) depend on the chemical compatibility of reactant and product molecules with the active sites. One of these steps will control the overall reaction rate. It is essential to understand which is controlling so that the photocatalyst or operating conditions can be varied to obtain optimum performance. The photocatalytic reaction occurs in the step (3); upon absorption of a photon, semiconductor acts as photocatalyst forming a hole and an electron which produce reactive radicals (mainly hydroxl radicals). The hole reacts with water to generate the hydroxyl radical and the electron can reduce molecular oxygen, hydrogen peroxide or some other oxidizing agent in the solution or over the semiconductor surface. Several steps are involved in photochemical mechanisms in solid semiconductor. These steps are described in details by (Hoffmann *et al.*, 1995). Firstly, the light energy (hv), greater than the band gap energy (Eg), strikes the surface of the catalyst and excites an electron from the valence band to the conduction band. A valence-band hole, VB h^{+}, is created, which migrates to the surface and initiates a reduction reaction. The valence-band hole and conduction-band electron can recombine in the bulk material and on the surface.

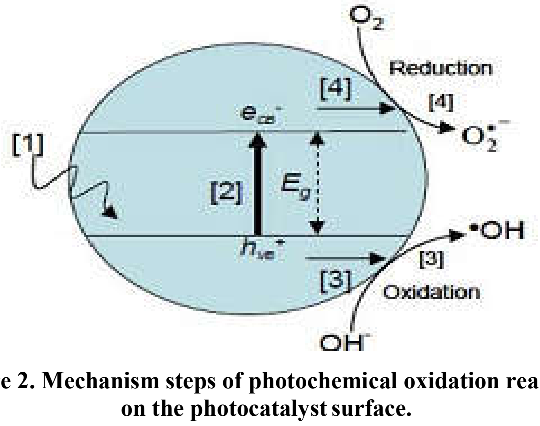


Figure 2. Mechanism steps of photochemical oxidation reaction on the photocatalyst surface.

Charge-carrier generation

$\text{Semiconductor} + hv \longrightarrow \text{Semiconductor}\ (h^{+} + e^{-})$

- Incident light energy photon (hυ) greater than band gap energy.
- It excites electron from valence band to conduction band leaving a hole in the conduction band.
- Charge-carrier trapping
- valence-band hole that successfully migrates to surface initiates oxidation reaction (Hoffmann et al., 1995)
- conduction-band electron that successfully migrates to surface Initiating reduction reaction

(Garcia and Takashima, 2003; Carp et al., 2004; Lifongo et al., 2004).

Production of hydroxyl radicals

$H_2O_{ads} \longrightarrow OH^{-}_{ads} + H^{+}_{ads}$ (oxidation rxn)
$H^{+}_{vb} + OH^{-\cdot} \longrightarrow OH$

Production of super-oxide

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

(c) Charge-carrier recombination. The recombination of e–-h+ pairs is reported as the main factor for limiting the oxidation rate of organic substrates.

$e^{-} + h+ \longrightarrow \text{Semiconductor} + \text{heat}$

Photocatalytic degradation

$\text{pollutant} + OH. \longrightarrow POH.$

$POH. + (O_2, H_2O_2, OH) \longrightarrow nCO_2 + mH_2O$

Hydroxyl radicals and superoxide ions produced from steps [3] and

Can attack any organic compound and can lead to chemical reactions (Redox). (Hoffmann et al. 1995; Doll and Frimmel, 2004)

Approaches of making photocatalysts Visible Light Active: Photo-catalytic efficiency of generally used semiconductors (TiO_2, ZnO) is low under solar radiation due to the following reasons-(1) Recombination of photo-generated electrons and holes in the semiconductor (2) High band gap energy (>3.0 eV) that requires radiation in the UV range for electron excitation from valence band to conduction band, whereas, UV in the solar light is only upto 3-4 percent. Recently, most of the researchers in this area is focused on- (a) To minimize electron-hole recombination to enhance photo-catalytic efficiency (b) To reduce the band-gap energy of the semiconductor to make it visible light responsive (Rockafellow *et al.*, 2009). For example, the radiation that ZnO can utilize is limited to UV fraction of the entire solar spectrum. Modification of ZnO surface is one of the promising routes to enable ZnO sensitive to visible light for its use in water purification. Metal ion doping and co-doping with non-metals can improve trapping of the photo - excited conduction band electrons at the surface where by minimizing charge carrier recombination (Rockafellow *et al.*, 2009).

A number of approaches have been suggested to enhance the photocatalytic activity of ZnO in the visible light. The efficiency of Photocatalyst can be improved by the

Metallic doping: ZnO has been doped with various transition metals. When these transition metal ions substitute for Zn^{2+} ions with tetrahedral O coordination in ZnO lattice, the band gap narrows by sp–d exchange interactions between conduction band electrons (CB made up of 4s 4p orbitals of Zn) and d electrons of these transition metals (Naeem *et al*., 2008). High visible light activity has been observed with Co and Cu doped ZnO. With an increase in Co content in ZnO the absorption of visible light and content of surface oxygen vacancies increased. Co doped ZnO showed better visible light activity than Mn and Ni doped ZnO photocatalysts owing to comparatively better crystallinity and narrower band gap (Ekambaram *et al*., 2007).

Non metallic doping: Recent investigations indicate that the desired band gap narrowing of ZnO can be better achieved by employing non-metal elements such as N, F, S, P and C. Such modified ZnO showed stronger absorption in the visible region owing to band gap narrowing and enhanced the degradation of organic pollutants under visible light irradiation, especially under solar light. Mechanochemical methods were employed to dope non-metal elements into oxide fine particles (Wang *et al*., 2007).

Dye sensitization: Dye sensitization is widely used to utilize visible light for energy conversion. Some dyes having redox property and visible light sensitivity can be used in solar cells as well as photocatalytic systems. Under illumination by visible light, the excited dyes can inject electrons to CB of semiconductors to initiate the catalytic reactions. Dye sensitization has been demonstrated as a useful tool to induce visible light photocatalysis on the surface of wide band gap semiconductors like ZnO which are otherwise inactive under visible light (Bandara *et al*., 2002). Dye sensitization facilitates electron transfer between the dye molecules and the host semiconductor (Zhao *et al*., 2005). The dye sensitization process involves the excitation of dye molecules with visible light and the subsequent electron injection into CB of a semiconductor and followed by a back reaction:

$\text{Dye}\ h\nu \rightarrow \text{Dye}^*$ Excitation of dye molecules (1)

$\text{Dye}* \rightarrow \text{ZnO}\ \text{Dye}^+ + e^-$ Electron injection (2)

$\text{Dye}^+ + e^-$ dye Dye $\longrightarrow$ regeneration (back reaction) (3)

If the back reaction (3) is prevented, dye undergoes irreversible degradation while photo injected electrons in CB form active oxygen radicals yielding overall degradation of the sensitized dye (Wu *et al*., 1999):

$\text{Dye}^{+\cdot} + OH^- \rightarrow$ Oxidized products (4)

$e^-_{(CB)} + O_2 \rightarrow O_2^{\cdot -}$ (5)

$O_2^{\cdot -} + e^-_{(CB)} + 2H^+ \rightarrow H_2O_2$ (6)

To obtain a higher efficiency in converting absorbed light into direct electrical energy (for solar cells) or hydrogen energy, fast electron injection and slow backward reaction are required. Based on the literature on electron/hole recombination of dyes, the recombination times were found to be mostly in the order of nanoseconds to microseconds, sometimes in milliseconds, while the electron injection times were in the order of fem to seconds. The fast electron injection and slow backward reaction make dye-sensitized semiconductors feasible for energy conversion (Ni *et al*., 2007).

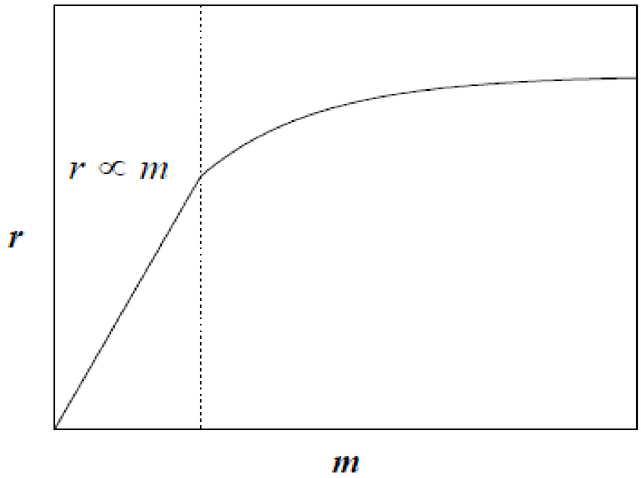


Fig.2. Influence of the mass of catalyst on the reaction rate, *r*

Role of nano-adsorbents in water/waste water treatment: Nano-adsorbents are fast emerging as potent candidates for water/wastewater treatment in place of conventional technologies which, notwithstanding their efficacy, are often very expensive and time consuming (Amin et al., 2014). This would be in particular, immensely beneficial for developing nations like India where cost of implementation of any new removal process could become an important criterion in determining its success. Qualitatively speaking nano-adsorbents can be substituted for conventional materials that require more raw materials, are more energy intensive to produce or are known to be environmentally harmful (Bhattacharya et al., 2013). Employing green chemistry principles for the production of nano-adsorbents can lead to a great reduction in waste generation, less hazardous chemical syntheses, and an inherently safer chemistry in general. There is also a wide debate about the safety of nano-adsorbents and their potential impact on the environment. There is fervent hope that nanotechnology can play a significant role in providing clean water to the developing countries in an efficient, cheap and sustainable way (Gupta et al., 2011).

Synthesis of mixed nanosized photocatalysts: There are different methods for synthesis of the nanosized photocatalyst used for the photo degradation of organic pollutants which may pollute the environment. Some of these are given below.

Hydrothermal technique: Nanoparticles can also be synthesized by this technique which is also known as solvo-thermal technique (Wang *et.al*,. 2009). The reactions are carried out in an autoclave at a pressure of 2000 pounds per square inch and a temperature of 200 °C or higher. Nanoparticles prepared by this method show better crystallinity and grain size. Nano photocatalyst with specific sizes and morphology can be synthesized by continuous hydrothermal technique. Reaction kinetics can be increased by microwave heating during hydrothermal technique (Komarneni *et. al*.,2002). Microwave hydrothermal technique needs lower temperature as 150 °C and shorter time as 25 min as compare to conventional hydrothermal technique.

Sol-gel technique: The sol gel method is one of the alternative methods to prepare the semiconductor oxide nanoparticles. This process needs a low-temperature chemical precursors to produce fine particles with desired structural characteristics such as compositional homogeneity, grain size, particle morphology and porosity, high purities, able to control the particle size in nanometric range (Buasri et al., 2008; Wang et al., 2010). Well established particle size is one of the important parameter for improving the photocatalytic activity of a semiconductor catalyst. The photocatalytic activity of materials is affected by particle size, since smaller particle size has lager number of surface area which degrade organic molecules photocatalytically when in contact with it and this leads to the less risk of charge carrier recombination (Beydoun et al., 1999). In sol gel method, appropriate precursors (such as metal salts or metal organic compounds) will be added into water and alcohol under controlled temperature and pH which to form sol followed by conversion into homogeneous oxide networks (gel) after hydrolysis and condensation.

Chemical Co-precipitation: A facile and convenient method to prepare nanoparticles is chemical co-precipitation technique. Two or more soluble salts solutions are mixed in a definite ratio and co-precipitated with a base solution under inert atmosphere (Faraji, *et al*., 2010). Solutions of two or more water soluble salts of metals are dissolved in water, mixed and co-precipitated with alkali very slowly (in approximately 2 hours). Afterwards the resulting solution was stirred for 6 hours. The precipitate thus formed were filtered, washed, dried and sintered at about 400-600 °C for 4-6 hours (Abdollahi *et al*., 2011). Composition shape and size of nano photocatalyst can be controlled by the following factors:

- Type of the base and mixing rate.
- Ionic strength of mixture solution and addition sequence
- Bubbling of nitrogen gas
- PH of the medium
- Reaction temperature
- Nature of salts used (chlorides, sulphates or Nitrates)

An increase in mixing rate decreased the size of nano photocatalyst (Abdollahi *et al*., 2011). It is a simple method which takes place at lower temperature than hydrothermal or thermal decomposition. Solvent used is environmental friendly and yield is high.

Reverse Micelle technique: Microemulsion of oil in water is used to prepare uniform sized nanoparticles (Santra *et al* ,.2001). This emulsion contains three components oil, water and surfactant which form thermodynamically stable, single phase, isotropic transparent solution. The reacting reagents are present in nano water droplets surrounded by surfactant molecule. These water droplets containing reagents coalesce rapidly allowing mixing and precipitating the nanoparticles. The size of precipitated molecule changes with size of water pool in micelle (Abdollahi *et al*., 2011). Mono dispersed nanoparticles of different morphologies and sized can be synthesized by this technique. This method is costly and have low yield.

Mechanosynthesis technique: Mechanochemical synthesis can work in the absence of solvent. Solvents are nearly always added to reactions to facilitate the diffusion and collision of the components. However, solvent is not always necessary. Transition metal oxides, borides, carbides and silicides can be synthesized by mechanochemical method. Different alloy composite can also be obtained by mechanical activation in ball mills e.g. metal alumina composites (Basset and Miani, 1993). We can prepare nanosized particles by alloying mechanically in ball mills. High energy ball mills are indispensable in material science and engineering. Nano crystalline powders with new and unusual properties can be prepared by ball milling which is a good state processing method (Dutta and Pradhan, 2007). Powdered particles are broken and welded repeatedly forming nano structured alloys in ball mills.

Factors affecting photocatalytic degradation: The solution pH is an important variable in aqueous phase photocatalytic reactions. The pH of a solution influences adsorption and dissociation of substrate, catalyst surface charge, oxidation potential of the valence band and other physicochemical properties of the system (Shankar *et al*. 2004). In accordance with Nerst's law, varying the solution pH would shift the energy of the valence and conduction band edges, by 0.059 per pH unit (at ambient temperature). This results in the valence band electron becoming more effective and the conduction band holes less effective at higher pH. Moreover, low degradation rate at higher pH is attributed to the fact that when the concentration of OH^-ion is higher in the solution, it prevents the penetration of UV light to reach the catalyst surface (Hoffmann *et al*., 1995). Furthermore, high pH favours the formation of carbonate ions which are effective scavengers of OH^- ions and can reduce the degradation rate (Akbal and Onar, 2003).

Pollutant Concentration: It is well documented that the initial rates of reaction are directly proportional to the mass (*m*) of catalyst (Prakash *et al.,* 2002; Rabindranathan *et al.,* 2003; Lathasree et *al.,* 2004; Shankar *et al*., 2004a). However, above a certain value of *m*, the reaction rate levels off and becomes independent of mass. The increase in the efficiency seems to be due to the increase in the total surface area (namely number of active sites) available for the photocatalytic reaction as the dosage of photocatalyst increased. However, when TiO_2 was overdosed, the number of active sites on the TiO_2 surface may become almost constant because of the decreased light penetration *via* shielding effect of the suspended particles (Burns *et al*., 2002; Sobczynski *et al*., 2004) and the loss in surface area caused by agglomeration (Chen *et al*., 2007).

Effect of electron acceptors: One practical problem in using TiO_2 as photocatalyst is the energy lost in the electron hole recombination which results in low degradation efficiency. Hence the prevention of electron hole recombination becomes very important. Molecular oxygen has been employed as an effective electron acceptor in most photocatalysis applications (Augugliaro *et al*., 1991 and Gupta and Tanaka S. (1995). In heterogeneous photocatalytic reaction, molecular oxygen (air) has been used for this purpose as an electron acceptor for prevention of electron hole recombination. One approach used to prevent electron hole recombination is to add electron acceptors into the reaction media. The presence of H_2O_2 as electron acceptor can serve as electron scavengers to prevent the recombination and enhance photodegradation efficiency. H_2O_2 has several effects including: (a) avoid recombination of electron-hole by accepting the conduction bandelectron and (b) increase the concentrations of the hydroxyl radical. (Aceituno *et al*., 2002; Burns *et al.,* 2002; Chu and Wong, 2003; Bertelli and Selli, 2006; Mahmoodi *et al*., 2006).

$H_2O_2 + hv \rightarrow 2^{\cdot}OH$
$h^+ + OH^- \rightarrow 2^{\cdot}OH^-$
$e^- + O_2- \rightarrow O_2-$
$e^- + H_2O_2 \rightarrow OH^- + {}^{\cdot}OH$
$RH +. OH \rightarrow H_2O^- +. R^{\cdot} \rightarrow$ Further oxidation

Where, RH refers to phenolic compound. Furthermore, the enhanced degradation rate observed with H_2O_2 is probably due to direct photolysis by UV light. This generates. OH radicals, which are likely to be dominant rate improving mechanism in the process. H_2O_2 has two hydrogen atoms bounded to oxygen atoms (H–O–O–H), thus it is more electropositive than O_2, suggesting that H_2O_2 is a better electron acceptor than oxygen (Chen and Liu, 2007). However, when present at high concentrations, H_2O_2 also becomes a scavenger of both the valence band holes and hydroxyl radicals as follows (So *et al*., 2002).

$H_2O_2 + 2h + VB \rightarrow O_2\ 2H^+$

$H_2O_2 + OH. \rightarrow HO_2^{\cdot} + 2H_2O$

$OH^{\cdot} + HO_2^{\cdot}. \rightarrow + 2H_2O + O_2$

Electron scavenging and the consequent recombination suppression can also be achieved by the use of other inorganic oxidants such as $S_2O_8^{-2}$ and BrO^- Naeem and Feng, 2009). In any given application, an optimum photocatalyst concentration has to be found in order to avoid excess photocatalyst and ensure total adsorption of efficient photons (Qamar and Muneer, 2005). Furthermore, according to Kabir *et al*., (2006) and Naeem and Feng (2009), phenol degradation decreases above the optimum TiO_2 loading. The optimal photocatalyst loading or effective optical penetration length, under given conditions, is then very important in designing a slurry reactor for efficient use of the photocatalyst and the reactor volume. Photodegradation rate decreases when pollutant concentration increases. It is because of at higher concentration of pollutant, the number of interacting radiation photons per pollutant molecule decreases (Pecchi *et al*., 2001).

Dissolved oxygen in solution: The photocatalytic degradation rate at semiconducting surfaces were depends on the photocatalytic generation and recombination of electron-hole pair. This electron/hole pair recombination is one of the main drawbacks in the application of photocatalysis as it causes a waste of energy. In the absence of suitable electron acceptor or donor, recombination step is predominant and thus it limits the degradation rate. Large airflow of the dissolved oxygen into the solution through air purging, enhances the separation of photogenerated electron and hole, which prevents the recombination between the hydroxyl radicals and the photo eject electrons (Hoffmann et al., 1995). As Nam et al., (2002) pointed out the increased airflow rate always brought about high degradation rate because the solution became more turbulent. Molecular oxygen is generally used as an electron acceptor in heterogeneous photocatalytic reactions. Addition of external oxidant/electron acceptors into a semiconductor suspension has been shown to improve the photocatalytic degradation of organic contaminants by: (1) Removing the electron–hole recombination by accepting the conducion band electron, (2) Increasing the hydroxyl radical concentration and oxidation rate of intermediate compounds and (3) Generating more superoxide radicals and other oxidizing species to accelerate the degradation efficiency of intermediate compounds (Saquib et al., 2008;Tariq et al., 2008). It was found that the photo catalytic activity was completely suppressed in the absence of oxygen.

Reaction Temperature: Due to the photonic activation process, temperature has nearly no effects in the range (20 °C $\leq T \leq$ 80 °C). At very low temperatures below 0 °C or at very high temperature above 80 °C, the photo catalytic activity decreases. Thus, a photo catalytic experimental setup does not require severe temperature control. Accordingly, no significant effect of temperature increased from 30 °C to 50 °C was observed either for photo degradation of MB (Ling *et al*. 2004) or of humic acid in the temperature range of 10-68°C (Palmer *et al*., 2002). Nevertheless, several works discussed on the secondary temperature effects. A slight benefit by using higher temperature for photocatalytic reactions was demonstrated by Trillas *et al.* (1995) and Chen and Ray (1998). It would be due to faster diffusion of OH from the surface of the TiO_2 to the pollutant at higher temperature. However, a negative effect of temperature on the concentration of dissolved oxygen in the solution may be expected. Dissolved oxygen levels below a certain point may allow for electron-hole recombination at the surface of the TiO_2. Electron-hole recombination is dominant unless there is an electron acceptor such as oxygen available to absorb the excited electron. More importantly, a temperature increase will induce species desorption from the TiO_2 surface, decreasing the rate of reaction at low species concentrations (Chin *et al*., 2006).

Light intensity: Apparently, light irradiation plays a significantly important role in all of the photo catalytic reactions and determines the number of created $e^- h^+$ pairs. Accordingly, increasing the incident photon rate would result in an increase in the photo catalytic reaction rate. Mahalakshmi *et al.* (2009) reported that the rate of degradation of propoxur increases with the increase in light intensity. When the intensity of incident light increases, the probability of excitation of electrons also increases and hence increases the degradation rate (Mehrotra *et al*., 2003). Ling *et al.* (2004) studied the effect of incident light on the photo degradation of MB; it was found that the residence time of 15.2 min was required for 50% photo degradation of 40 ml/L MB using 1.5 $mWcm^{-2}$ light intensity, whereas 11 min was needed by using 5 $mWcm^{-2}$ of light intensity. Chiou *et al.* (2008a) found an acceptably good in ear correlation exists between the apparent first-order rate constant of phenol photo degradation by TiO_2 and light intensity under the UV light intensity ranges of 20–400W.

Effect of pH: In heterogeneous photocatalytic degradation of organic dye, pH is one of the most important operating parameter that affect the charge on the surface of photocatalyst, size of photocatalyst aggregates and the positions of conductance and valence bands (Chong et al., 2010). This may be because most of the semiconductor oxides exhibit amphoteric behavior in nature. The pH effect is related to the ionization state of the surface of the photocatalyst as well as organic pollutants. Chen et al., (2007) revealed that adsorption of MG dye on the surface of nanocomposite photocatalyst was reduced during the recombination of photo generated charge carriers and accelerated the interfacial charge transfer process. Because MG dye is a cationic organic pollutant with low pH, more H^+ was available for adsorption to mask the surface of the catalyst, thus preventing the photo excitation of semiconductor particles, thereby reducing the generation of free radicals (Rauf et al., 2011). Therefore, force of electrostatic attraction between the positive semiconductor oxide surface and cationic malachite green molecules lead to the strong repulsion with each other, and it is difficult for malachite green molecules to be adsorbed on the semiconductor oxide surface under the acidic condition. Thus this repulsion decreases the degradation efficiency of photo catalyst in the acidic solution (Shimizu et al., 2007). However, in basic solutions strong adsorption of the dye molecules can take place at high pH but excessive Malachite Green adsorption might block light arriving on the surface of the photo catalyst and impede the electron-hole pair photo excitation process. Subsequently, the concentration of hydroxyl radicals in solution is decreased at high pH which would also decrease photo catalytic efficiency (Zhou et al., 2010). The point of zero charge (pzc) for Fe_2O_3 is at pH 7.3 (Kosmulski, 2009). The Fe $_2O_3$ surface is positively charged in acidic solution and negatively charged in basic solution. (Acidic solution) pH < pzc:

(acidic solution)PH<Pzc:Fe-OH + $H^+ \rightarrow FeOH_2^+$

(basic solution) PH> Pzc: Fe-OH + $OH^- \rightarrow FeO + H_2O$

Therefore, one can conclude that pH value has a significant effect on photodegradation of Malachite Green dye under high and low pH values. However, the best pH value for the photodegradation Malachite Green is near the pzc of the photocatalyst.

Conclusion

Usual physical and chemical methods for the treatment of wastewater do not completely destroy the pollutants but merely offer phase transfer of pollutant. In a photocatalytic process, a semiconductor photocatalyst is activated with UV / Visible irradiation. The activated photocatalyst promotes the formation of hydroxyl radicals, which in turn completely degrade the pollutants to give simple products such as CO_2 and H_2O. Metal doping in photocatalyst decreases electron-hole recombination thereby the photocatalytic degradation of pollutant is enhanced. Non-metal doping helps in decreasing the band gap energy of semiconductor photo-catalyst thus increasing the photo-degradation of pollutants under solar irradiation. Metal-non metal co-doping in a semiconductor shows synergetic / cumulative effect for enhancing its photocatalytic efficiency for the degradation of pollutants. Photocatalytic degradation method is fast, effective, eco-friendly, economically viable and efficient method for removing wastewater pollutants. Solar photocatalytic process is an exciting clean technology that uses only sunlight, water, and a reusable photo-catalyst to remove pollutants from wastewater.

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