CHAPTER TWO
LITERATURE REVIEW
CHAPTER - II

LITERATURE REVIEW

2.1 AOP’S - HOMOGENEOUS AND HETEROGENEOUS

Growing public concern on the contamination of drinking water supplies and the aquatic environment with organic pollutants has stimulated vigorous research activities in the development of various wastewater treatment technologies.

Fundamental and applied research on this subject has been performed extensively during the last 25 years all over the world as documented by more than 2000 publications (Blake, 2001). Earlier research in the 70’s and 80’s was devoted to photovoltaic conversion and energy storage. Later, synthesis, processing and characterization of new semiconductors materials became the main interest in industrial sector like electronics industry etc. Nowadays, the main goal of research and development is the use of AOPs.

A growing interest in the purification of water by semiconductor photocatalysis especially in the removal of toxic organic pollutants is evident by ever increasing number of studies in this area (Inel and Okte, 1996; Mills et al., 1993; Ollis et al., 1991, 1989; Matthews, 1988).

Frank and Bard (1977) reported the photocatalysed oxidation of cyanide ion, a frequent industrial pollutant with oxygen in the presence of TiO$_2$ in both the anatase and rutile forms. Four forms of TiO$_2$ were investigated: undoped anatase (the white form of the untreated commercial material), anatase reduced in a hydrogen gas stream at 700 °C, anatase converted to 70% rutile by heating in air at 1200 °C and 70% rutile reduced in H$_2$ at 700 °C. Undoped anatase was demonstrated to be the most active form.
Various authors have conducted studies on wastewater treatment by using UV/H$_2$O$_2$, UV/O$_3$ and photoassisted fenton degradation techniques (Shen and Wang, 2002; Alaton and Balcioglu, 2001; Herrera et al., 2000; Wang et al., 2000; Ho and Bolton 1998; Venkatadri and Peters, 1993; Prat et al., 1988). Wu (1999) discussed basic principles and advantages of typical AOP systems.

Murphy et al. (1994) analyzed the advanced oxidation treatments (ozonation, H$_2$O$_2$ and UV irradiation) for the treatment of pulp and paper mill wastewater. Esplugas et al. (2002), Chiron et al. (2000), Andreozzi et al. (1999), Bandara et al. (1997), Perez et al. (1997) and Mansilla et al. (1997) have also explored the use of AOPs for wastewater treatment.

Homogenous and heterogeneous photocatalytic oxidation systems have been employed for wastewater treatment. The principles and the advantages of several typical homogeneous and heterogeneous AOP’s system are summarized by Wu (1999) and Vogelpohl and Kim (2004).

Among heterogeneous AOP, TiO$_2$-mediated photocatalytic oxidation appears to be a promising alternative. There are number of general reviews which cover aspects of the TiO$_2$ photocatalytic destruction of organic compounds in water (Fox and Dulay, 1993; Hoffman et al., 1995; Linsebigler et al., 1995; Fujishima et al., 2000).

Fujishima et al. (2000) have discussed progress in the area of TiO$_2$ photocatalysis mainly for photocatalytic air purification, sterilization and cancer therapy, together with some fundamental aspects and have presented a novel photo-induced super hydrophilic phenomenon involving TiO$_2$ and its applications.

Herrmann et al. (1999) have described the basic fundamental principles as well as the influence of the main parameters like mass of the catalyst,
wavelength, initial concentration, temperature and radiant flux governing the kinetics of heterogeneous photocatalysis in wastewater treatment.

Few researchers have reported the use of other semiconductors such as ZnO (Neppolian et al., 2001; Pardeshi and Patil, 2008), CdS (Reutergardh and Iangphasuk, 1997; Davis and Huang, 1990), Fe°, Zn° (Agarwal et al., 2002) and WO₃ (Poulios and Tsachpinis, 1999).

ZnO appears to be a suitable alternative to TiO₂. The biggest advantage of ZnO is that it absorbs a larger fraction of solar spectrum than TiO₂ (Sakthivel et al., 2003).

Photocatalytic degradation of various azo dyes in water using slurry reactor in the presence of ZnO as a photocatalyst under UV light irradiation has been studied and the effect of various process variables on the degradation performance of the process has been investigated (Akyol et al., 2004; Lizama et al., 2002).

Studies have also been done using catalysts like ZnO under sunlight (Neppolian et al., 2002; Chakrabarti and Dutta, 2004) and good results have been obtained but their applications remain limited only by pH (Fanchiang and Tseng, 2009).

Kansal et al. (2008) investigated the photocatalytic degradation of lignin obtained from wheat straw kraft digestion by using TiO₂ and ZnO semiconductors. ZnO has been found to be a better photocatalyst than TiO₂. The different variables studied, include catalyst dose, solution pH, oxidant concentration and initial concentration of the substrate. The degradation of lignin was favorable at pH 11. The degradation of the organic compound was also evaluated as COD removal and increase in the COD removal was observed with increase in degradation rate. The applicability of ZnO in immobilized mode for
the degradation of lignin under solar light for industrial scale application has been explored. Further the comparative evaluation of ZnO in slurry/immobilized mode has been discussed.

Rao et al. (2009a) studied the photocatalytic degradation of salicylic acid by a batch process using ZnO as the catalyst on irradiation with UV light. The effect of process parameters such as pH, catalyst loading and initial concentration of salicylic acid on the extent of degradation was investigated. The degradation of salicylic acid was found to be effective in the neutral pH range. The optimum catalyst loading was observed at 2.0 g/L. The process followed first order kinetics and the apparent rate constant decreased with increase in the initial concentration of salicylic acid. The mechanism for the degradation of salicylic acid could be explained on the basis of Langmuir–Hinshelwood mechanism. The complete mineralization of salicylic acid was observed in the presence of ZnO photocatalyst. The ZnO was found to be quite stable and it underwent photocorrosion only to a negligible extent.

Shafaei et al. (2010) investigated the photocatalytic degradation of terephthalic acid (TPA) using titania and zinc oxide nanoparticles. UV–Vis spectrophotometer and high performance liquid chromatography (HPLC) were used to study the TPA degradation. The effect of influential parameters such as initial pH, catalyst loading, initial TPA concentration and H₂O₂ were studied. It was found that the photocatalytic degradation of TPA obeyed the pseudo-first order kinetic reaction in the presence of both photocatalysts. The results showed that TiO₂ and ZnO photocatalysts could be employed as effective photocatalysts for the elimination of TPA from wastewater but in optimized conditions, zinc oxide was a more efficient catalyst than TiO₂.

Elmolla and Chaudhuri (2010) examined the effect of operating conditions (zinc oxide concentration, pH and irradiation time) of the UV/ZnO
photocatalytic process on degradation of amoxicillin, ampicillin and cloxacillin in aqueous solution. pH had a great effect on amoxicillin, ampicillin and cloxacillin degradation. The optimum operating conditions for complete degradation of antibiotics in an aqueous solution containing 104 mg/L, 105 mg/L and 103 mg/L amoxicillin, ampicillin and cloxacillin, respectively were: zinc oxide 0.5 g/L, irradiation time 180 minutes and pH 11. Under optimum operating conditions, complete degradation of amoxicillin, ampicillin and cloxacillin occurred and COD and DOC removal were 23.9% and 9.7%, respectively. The photocatalytic reactions under optimum conditions approximately followed a pseudo-first order kinetics with rate constant (k) 0.018 min\(^{-1}\), 0.015 min\(^{-1}\) and 0.029 min\(^{-1}\) for amoxicillin, ampicillin and cloxacillin, respectively. UV/ZnO photocatalysis could be used for amoxicillin, ampicillin and cloxacillin degradation in aqueous solution.

2.2 DEGRADATION OF DYES AND TEXTILE WASTEWATER

Various types of synthetic dyes like reactive dyes, direct dyes, mordant dyes, acid dyes, basic dyes etc are used in the production of textiles. These dyes are organic pollutants and very toxic, bio-resistant and show a great stability in water.

A number of research groups have dealt with photocatalytic decomposition of this class of materials in the presence of UV-A or visible light with very encouraging results (Zhang et al., 1998; Vinodgopal and Wynkoop, 1996; Davis et al., 1994). With the aim of elucidating the potential applications of advantageous photocatalytic processes, the kinetic and mechanistic aspects of dye design have been investigated and reported in literature (Galindo et al., 2002; Bauer et al., 2001; Houas et al., 2001).
Wastewater containing dyes can be treated biochemically in combination with photocatalytic, chemical, thermochemical and physico chemical treatment methods (Zhang et al., 1997; Gopalakrishnan and Mohan, 1997; Subrahmanyam, 1996; Nasr et al., 1996; Lakshmi et al., 1995; Zang et al., 1995; Vinodgopal and Kamat, 1995; Vinodgopal et al., 1994; Davis et al., 1994; Subrahmanyam, 2003).

Subrahmanyam et al. (1998) studied the photocatalytic degradation of various dyes such as Vat Blue, Fast Orange GC Base, Drimarene Yellow, 3 GLI and Bromothymol Blue using batch reactor. They used TiO$_2$ based catalysts immobilized on ceramic beads and SiO$_2$. Various metal ion dopants were also used in preparing TiO$_2$-based photocatalysts for testing.

The photocatalytic decolorization of Reactive Orange 16, a textile azo dye, in aqueous heterogeneous solutions containing TiO$_2$ as photocatalyst was explored by Poulios and Aetopoulou (1999).

Various commercial photocatalysts were compared with respect to their decolorization efficiency and production of CO$_2$. The effect of pH and H$_2$O$_2$ on the reaction was ascertained.

Gomathi and Krishnaiah (1999) investigated the photocatalytic degradation of two azo dyes (p-amino-azo-benzene and p-hydroxy-azo-benzene) using heat treated TiO$_2$ as the photocatalyst. Anatase form TiO$_2$ (annealed at 600 °C–650 °C) was proved to be efficient catalyst as compared to the rutile form (annealed above 700 °C) and also to Degussa P-25 sample for the degradation of these dyes.

Zhao (2000) examined the direct photocatalytic degradation of dye pollutant Sulforhodamine B (SRB) in aqueous TiO$_2$ dispersions and compared it with the photosensitization process. The mineralization extent of SRB
degradation, the formation of intermediates and final products were monitored to assess the degradation pathways caused by direct photocatalysis.

Wang (2000) investigated the photocatalytic degradation of eight commercial dyes with different structures and containing different substitute groups using TiO₂ as photocatalyst in aqueous suspension under solar irradiation.

Sivakumar and Shanthi (2001) reported the decolorization of reactive textile dyes namely Procion Brilliant Orange M-2R (PBO), Procion Brilliant Magenta M-B (PBM), and Procion Brilliant Yellow M-4G (PBY) using TiO₂ semiconductor as catalyst under sunlight illumination.

Selva et al. (2002) investigated the photocatalytic degradation of Reactive Red 22 (RR 22) dye in the presence of a thin film of ZnO photocatalyst using a thin film flat bed flow photoreactor under solar irradiation. The effects of reaction parameters such as pH, amount of ZnO coating, flow rate and concentration of the dye solution on the percentage removal of dye were examined.

Lizma et al. (2002) reported the photocatalytic discoloration of Reactive Blue 19 (RB-19) in aqueous solutions containing TiO₂ or ZnO as catalysts. The reactions were described as function of parameters like pH, amount of catalyst and dye concentration modeled by the use of response surface methodology. It was concluded that ZnO was a more efficient catalyst than TiO₂ in the color removal of Reactive Blue RB-19 and its use was limited only by pH.

Agarwal et al. (2002) discussed kinetic studies on the photocatalytic decolourization of water-soluble crown dyes using Fe° and ZnO catalyst. The characteristics such as BET surface areas of Fe° and ZnO was determined by using micromeritic pulse chemisorbs 2700 system and found to be 7.47 m²/g and particle size was 0.44 microns. The decolourization studies of all the dyes were
conducted under different conditions: (a) dark (b) sunlight (c) UV (d) sunlight + Fe°
(e) UV + Fe° (f) sunlight + ZnO and (g) UV + ZnO condition. Decolourization of
dyes with Fe° and ZnO in presence of UV light was more efficient than others. The
decolourization was described by pseudo-first order kinetics.

Guillard et al. (2003) studied the influence of chemical structure of dyes,
pH and inorganic salt on their photocatalytic degradation using TiO₂ as
photocatalyst. Comparison of the efficiency of powder and supported TiO₂ by
using anionic (Alizarin S, azo-Methyl Red, Congo Red and Orange G) and
cationic (Methylene Blue) dyes either individually or in mixtures was done. The
photocatalytic efficiency of TiO₂ coated on glass by sol-gel method was found
comparable to that of TiO₂ powder.

Noorjahan et al. (2003) reported the photocatalytic degradation of H-acid,
a dye intermediate in TiO₂ suspensions and TiO₂ thin film fixed bed reactor
(TFFBR). The immobilization method used was simple and did not require
thermal treatment of the catalysts at high temperatures and it was concluded that
this type of treatment method might be used for the photocatalytic treatment of
effluents at a higher scale.

Daneshvar et al. (2003) investigated photocatalytic degradation of azo dye
Acid Red 14 in water using TiO₂ suspension, which was irradiated by a UV-C
lamp of 30 W. The effect of pH, amount of TiO₂ and initial concentration of dye
under three different conditions under TiO₂, TiO₂/UV and UV alone was
examined. Combined TiO₂/UV treatment supported the highest decolourization
rate than TiO₂ and UV alone.

Chakrabarti and Dutta (2004) found ZnO as an effective catalyst for the
photodegradation of two model dyes: Methylene Blue and Eosin Y. The effects
of parameters like catalyst loading, initial dye concentration, air, flow rate, UV
irradiation intensity and pH on the extent of photodegradation were investigated. They proposed a rate equation for the degradation based on the Langmuir-Hinshelwood model.

Bouras et al. (2004) demonstrated the photodegradation of Basic Blue by highly efficient nanocrystalline titania films. Transparent nanocrystalline titania films were deposited on glass slides by using sol-gel procedures carried out in the presence of surfactant, Triton X-100. Films were calcined at 550 °C to ensure destruction of all organic residues. These films were found to be very efficient for photodegradation of Basic Blue dye, in aqueous solutions.

Konstantinou and Albanis (2004) reviewed the photocatalytic degradation of azo dyes containing different functionalities using TiO₂ as photocatalyst in aqueous solution under solar and UV irradiation and stated that the mechanism of the photodegradation depends on the irradiation used. Charge injection mechanism took place under visible irradiation whereas charge separation occurred under UV light irradiation.

Daneshvar et al. (2004) reported that ZnO appears to be a suitable alternative to TiO₂ since its photodegradation mechanism has been proven to be similar to that of TiO₂ for Acid Red 27. Central composite rotatable design (CCRD) experiment technique was used to study the effect of ozone treatment for acid dye effluents and to optimize the variables such as salt concentration, pH and time. It was observed that the treatment time plays a major role in decolorization and COD removal of the dye effluent.

Qamar et al. (2005) investigated the photocatalytic degradation of two selected dye derivatives Chromotrope 2B and Amido Black 10B in aqueous suspensions of TiO₂ under a variety of conditions. which is essential from an application point of view. The degradation was monitored by measuring the
change in substrate concentration as a function of irradiation time employing UV spectroscopic analysis. A number of byproducts are formed during the photooxidation process which can potentially be harmful to the environment, therefore, they have studied the mineralization of the pollutants by measuring the total organic carbon (TOC) as a function of irradiation time. The degradation of dyes were studied using different parameters such as types of TiO$_2$, reaction pH, catalyst concentration, substrate concentration and in the presence of different electron acceptors such as hydrogen peroxide (H$_2$O$_2$), potassium bromate (KBrO$_3$) and ammonium persulphate (NH$_4$)$_2$S$_2$O$_8$ besides molecular oxygen. The degradation rates were found to be strongly influenced by all the above parameters. They found that the Degussa P-25 is more efficient photocatalyst than the others.

Comparelli et al. (2005) immobilized ZnO nanocrystals with different surface organic coatings and commercial ZnO powder onto transparent substrates and comparatively examined the photocatalysts for the UV induced degradation of two azo dyes, Methyl Red and Methyl Orange in water.

Hasnat et al. (2005) examined photocatalytic degradation of Methylene Blue, a cationic dye and Procion Red, an anionic dye in TiO$_2$ dispersions under visible light and discussed the extent of degradation in terms of Langmuir-Hinshelwood model. The degradation pathway of Procion Red was found to be somewhat different from Methylene Blue.

Zhu et al. (2009) studied photocatalytic degradation of Congo Red (CR) under visible light irradiation. The influences of catalyst amount, initial CR concentrations, pH of the reaction solution and different anions on CR decolorization and degradation reaction kinetics were investigated. The photocatalytic degradation was found to follow a pseudo-first-order kinetics according to Langmuir–Hinshelwood (L–H) model. The dye could be
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decolorized more efficiently in acidic media than alkaline media. UV-vis spectra were analyzed to indicate that degradation of CR in the solution was due to the break up of the N=N bonds and degradation of aromatic fragment in this reaction system. The recycling experiments confirmed the relative stability of the catalyst.

Kansal et al. (2007) studied the photocatalytic degradation of Methyl Orange (MO) and Rhodamine 6G (R6G), employing heterogeneous photocatalytic process. Photocatalytic activity of various semiconductors such as titanium dioxide (TiO₂), zinc oxide (ZnO), stannic oxide (SnO₂), zinc sulphide (ZnS) and cadmium sulphide (CdS) has been investigated. An attempt has been made to study the effect of process parameters viz., amount of catalyst, concentration of dye and pH on photocatalytic degradation of MO and R6G. The experimental results indicated that the maximum decolorization (more than 90%) of dyes occurred with ZnO catalyst and at basic pH and the maximum adsorption of MO was noticed at pH 4 and of R6G at pH 10. The percentage reduction of MO and R6G was estimated under UV/solar system and it was found that COD reduction took place at a faster rate under solar light as compared to UV light. In case of R6G, highest decolorizing efficiency was achieved with lower dose of catalyst (0.5 g/L) than MO (1 g/L) under similar conditions. The performance of photocatalytic system employing ZnO/solar light was observed to be better than ZnO/UV system.

Kaur and Singh (2007) investigated the photocatalytic degradation of an aqueous solution of azo dye (Reactive Red 198) used in textile industries by UV-irradiation. The effect of initial dye concentration, TiO₂ loading, pH and H₂O₂ on degradation rate was ascertained and optimized conditions for maximum degradation were determined. The kinetics of photocatalytic degradation was found to follow a pseudo-first order according to
Xu et al. (2009) prepared flowerlike cadmium sulfide (CdS) nanostructure via the controllable solvent thermal method by using ethylenediamine as the structure directing template. The average crystal size was calculated to be about 3.1 nm. The petals were about 30 nm thick and 1 μm wide. The specific surface area of flowerlike CdS nanostructure was found to be 20.77 m²/g, higher than CdS powder (10.18 m²/g). The photocatalytic activity of CdS was investigated for the decolorization of Methyl Orange (MO) under high-pressure mercury lamp illumination. It was observed that the flowerlike CdS showed better results as compared to other CdS materials.

Rao et al. (2009b) studied the photocatalytic degradation of Direct Yellow 12 (DY12) by a batch process using ZnO as the catalyst on irradiation with UV light. The influence of pH, catalyst weight and initial concentration of the dye on the degradation of the dye was investigated. The degradation of the dye was found to be effective in alkaline media. The dye degradation obeyed first order kinetics and was explained on the basis of Langmuir–Hinshelwood mechanism. The oxidants involved were identified as positive hole, hydroxyl radical and superoxide anion radical.

Chungshin et al. (2009) studied the effects of influential factors like initial dye concentration, catalyst dosage and initial pH on degradation of Basic Blue 11 (BB-11). A ZnO-mediated photocatalysis process was used to successfully degrade BB-11 under visible light irradiation. To obtain a better understanding, the mechanistic details of ZnO-assisted photodegradation of the BB-11 dye with low watt visible light irradiation were studied. The results indicated that the N-de-alkylation and oxidative degradation of BB-11 dye took place and that N-hydroxyalkylated intermediates were generated during the process.
Zhong et al. (2009) studied the photocatalytic degradation of Rhodamine B (RhB) using TiO\textsubscript{2} supported on activated carbon (TiO\textsubscript{2}-AC) under microwave irradiation. Composite catalyst TiO\textsubscript{2}-AC was prepared and characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM) and Brunauer-Emmett-Teller (BET) techniques. In the process of microwave-enhanced photocatalysis (MPC), RhB (30 mg/L) was almost completely decoloured in 10 minutes and the mineralization efficiency was 96.0% in 20 minutes. The reaction rate constant of RhB in MPC using TiO\textsubscript{2}-AC by pseudo first-order reaction kinetics was 4.16 times of that using Degussa P25.

Soutsas et al. (2010) studied the decolorization and degradation of four commercial reactive azo dyes, namely Remazol Red (RR), Remazol Yellow (RY), Procion Crimson H-exl and Procion Yellow H-exl, using photocatalytic processes (TiO\textsubscript{2}/UV) and TiO\textsubscript{2}/UV/H\textsubscript{2}O\textsubscript{2}). Decolorization and degradation were found to be dependent strongly on the system parameters i.e. TiO\textsubscript{2} loading, dye and H\textsubscript{2}O\textsubscript{2} initial concentrations and pH. Decolorization efficiency (%) sharply increased with increasing the TiO\textsubscript{2} loading, especially up to 1 g/L, as well as with decreasing the initial dye concentration from 250 down to 50 mg/L. At pH = 3, more than 90% decolorization of all dyes could be achieved in only 15 minutes. Addition of H\textsubscript{2}O\textsubscript{2} increased the decolorization rates up to an optimum value (97.9% RR decolorization at 12 minutes irradiation, with a 0.5% w/w initial H\textsubscript{2}O\textsubscript{2} concentration and pH = 3). Among the four dyes examined, significant differences in decolorization and degradation rates were revealed, but decolorization and degradation efficiencies up to 100% (in 25 minutes and 4 hours respectively) were possible with proper combinations of the system parameters.

Wang et al. (2010) evaluated the photocatalytic activities by degradation of Acid Red B under solar light irradiation. The results showed that the
photocatalytic activity of the TiO$_2$ catalyst could be greatly enhanced by using appropriate amount of loaded biomaterials or biomimetic-material. Meanwhile, the effect of solar light irradiation time, and dye initial concentration on the photocatalytic degradation of Acid Red B dye in aqueous solution was also investigated in detail.

Talebian and Nilforoushan (2010) investigated the photocatalytic degradation of Methylene Blue in an aqueous solution, as a model compound, using different metal oxides such as Indium oxide (In$_2$O$_3$), zinc oxide (ZnO), stannic oxide (SnO$_2$) and titanium dioxide (TiO$_2$) in an attempt to compare the decomposition reaction rate. The progress of degradation was monitored using UV–vis spectrophotometry. The effects of various experimental parameters such as initial concentration of methylene blue (5–10 mg/L), pH of the solution (2–8), annealing temperature (250–550 °C) and catalyst nature and its microstructure were systematically studied in order to achieve maximum degradation efficiency.

Wastewater of textile dyeing and finishing industries consists of unbound colorants, reaction products, dye impurities, auxiliaries and surfactants. These effluents exhibit very slow degradation kinetics and resistance to conventional biological treatment processes and conventional physico-chemical treatment has not been proved as an effective method for decolorization and organic matter removal.

Juliana et al. (2009) investigated the photodegradation of real textile effluents by advanced oxidative process (AOP) using TiO$_2$/H$_2$O$_2$/sunlight system. The results were evaluated by COD reduction concomitant to the increase in inorganic ion concentration (mineralization) and the analysis of the effluent characteristic spectral wavelengths. The results indicated that solar radiation was as efficient as or even more efficient than artificial radiation as seen in previous studies and that it also allowed a reduction in effluent treatment operational costs.
Radha et al. (2009) studied the reduction of organics from textile effluents through electrochemical oxidation technique. Effect of pH and current intensity were investigated in this system. It was found that degradation was maximum at the current intensity of 0.6 A and at a pH of 1.3. Under the same experimental conditions the removal of chemical oxygen demand (COD), total solids, total dissolved solids and total organic carbon were found to be approximately 68%, 49.2%, 50.7% and 96.8%, respectively. The maximum removal efficiency (96%) was reached within 60 minutes at 0.6 A. While studying the effect of pH on COD removal, it was observed that a decrease in pH to an optimum of 1.3 showed maximum COD reduction of 68%. These results suggest an important role of these parameters in electrochemical process for removing organic pollutants.

Gozmen et al. (2009) studied the photocatalytic degradation and mineralization of C.I. Basic Red 46 (BR46) and C.I. Basic Yellow 28 (BY28) dyes in single and binary solution as a function of periodate ion concentration (IO₄⁻), irradiation time, initial pH and initial dye concentrations. First order derivative spectrophotometric method was used for simultaneous analysis of BY28 and BR46 in binary mixtures. Langmuir–Hinshelwood kinetic model was applied to experimental data and apparent reaction rate constant values were calculated. The apparent degradation rate constant values of BR46 were higher than those of BY28 for all experiments in single dye solutions. On the other hand, the significant reductions were observed for the apparent degradation rate constant values of the BR46 in the presence of BY28 in binary solutions whereas TOC removal efficiency slightly enhanced in binary system. The highest TOC removal efficiency was obtained at pH 3.0 by adding 5 mM periodate ion into the solution in the presence of 1 g/L TiO₂ for both dye solutions. After 3 hours illumination, 68%, 76% and 75% mineralization were found for 100 mg/L BY28, 100 mg/L BR46 and 50 + 50 mg/L mixed solutions, respectively.
Sermin and Ozlem (2009) studied the effect of operational parameters such as dye concentration, \( \text{H}_2\text{O}_2 \) concentration and pH on the photocatalytic degradation of Reactive Red 194 (RR194), Reactive Yellow 145 (RY145) azo dyes and synthetic textile dye-bath effluent using \( \text{O}_3 \) and \( \text{H}_2\text{O}_2/\text{UV-C} \) processes. Results indicated that the decolorization and dearomatization rate of each dye were well defined by pseudo-first order reaction kinetics. In general, decolorization reactions were faster than dearomatization reactions in both systems, though ozonation had faster reaction rates in both decolorization and dearomatization compared to the corresponding reaction rates taking place during the application of the \( \text{H}_2\text{O}_2/\text{UV-C} \) process.

Zhao et al. (2010) investigated the removal of Acid Orange 7 (AO7) in simulated wastewater using a three-dimensional electrode reactor with granular activated carbon as the particle electrode. The removal of AO7 in the system was mainly dependent on the oxidation by the produced active substances ('OH, etc.) and the coagulation by Fe(II) or Fe(III) dissolved from the anode. The former mechanism was predominant. A possible pathway for AO7 degradation was proposed by monitoring the temporal evolution of intermediates in the solution, with the use of some techniques including GC/MS, FTIR and HPLC.

Baban et al. (2010) studied the highly polluted and recalcitrant azo reactive dye-baths from cotton textile dyeing processes using fixed and up-flow fluidized bed type reactors packed with brown coal. Ozone oxidation was carried out to assess the combination of biological and chemical oxidation. COD removal efficiencies ranged from 70% to 93% and up to 99% color removal was attained.

Yang et al. (2001) reported the photocatalytic oxidation of Acid Blue 9 (AB9) in water using \( \text{TiO}_2 \) under UV illumination (254 to 365 nm). Liquid phase kinetics was affected by solution pH, with the rate of oxidation
increasing as the pH decreased. A kinetic model first order, with respect to dye concentration, was deemed suitable for the liquid phase oxidation by these researchers, who stated that the apparent rate constants included contributions from the rate of mass transfer of the dye to the photocatalyst surface and the inherent surface reactions.

Nasser et al. (2011) examined the photodecolorization of azo dyes in aqueous solution by combined UV, individual and coupled photocatalysts. The model substrate employed in this work was C.I. Acid Yellow 23 (AY23) and the ZnO and ZnO/SnO2 were utilized as the photocatalysts. A 30W UV lamp was the source of UV-radiation in a batch reactor. Photodecolorization efficiency was small when the photolysis was carried out in the absence of ZnO and it was also negligible in the absence of UV light. The effects of various parameters such as catalysts loading, initial dye concentration, radiation intensity, pH, gap size and catalysts ratio on the dye removal have been investigated. The results indicated that the degree of decolorization of AY23 was obviously affected by illumination time, pH, gap size and photocatalyst amount. The decolorization efficiency was found to increase with an increase in catalyst loading, up to an optimal value.

Bansal and Sud (2011) studied the degradation of reactive dye, Procion Blue Herd (PBH) in the presence of artificial UV light and nanophotocatalyst and investigated the effectiveness of semiconductor photocatalytic treatment of real textile wastewater. For degradation of PBH, batch experiments were carried out by irradiating the aqueous solution of dye, in the presence of different semiconductors such as TiO2 and ZnO in the presence of UV light. The rate of decolorization was estimated from residual concentration spectrophotometrically. The effect of process parameters viz. pH, initial concentration of dye and photocatalyst loading on decolorization of dye were also assessed. Comparison of photocatalytic activity of catalysts clearly indicated that the ZnO was the more
efficient photocatalyst for decolorization of PBH. Experimental results indicated that the decolorization of dye was facilitated in the presence of catalyst. As the initial concentration of dye was increased, the rate of decolorization decreased. The optimum dose of the catalyst was required for the complete degradation of the known concentration of the dye solution because high as well as low catalyst dose reduced the percentage degradation of dye. When the photocatalytic degradation of real effluent containing PBH was investigated under optimized conditions with ZnO, decolorization of effluents took place and a significant decrease in the COD values of effluents with respect to their initial values was observed, indicating the removal of recalcitrant organic compounds from textile mill effluents. The application of the ZnO photocatalytic method to the real wastewater proved to be efficient in decolorizing the textile wastewater.

Tabrizi et al. (2011) studied the ozonation of wastewater containing four different textile reactive dyestuffs in a semi-batch reactor. Various ozonation conditions (ozone dose, ozone consumption efficiency, etc.) were explored and studied for these dyestuffs. The mass transfer coefficient of ozone in water and its relationship to the ozone efficiency was studied. Pseudo-first order decolouration rate constants for all dyestuffs were determined experimentally.

2.3 SYNTHESIS OF NANOPHOTOCATALYSTS AND THEIR APPLICATION FOR THE TREATMENT OF ORGANIC COMPOUNDS

Nanomaterials are defined as materials that have at least one dimension $<100$ nm ($1 \text{ nm} = 10^{-9} \text{ m}$) and they can be divided into two large groups: ultrafine nanosized particles not intentionally produced and engineered nanoparticles produced in a controlled, engineered way (Oberdorster et al., 2005a). Nanotechnologies are among the fastest growing areas of scientific research and have important applications in a wide variety of fields. The corresponding industries
would require about two million workers in nanotechnology and about three times as many jobs in supporting activities (Roco, 2005). Nanoscale materials are already being introduced for use in many commercially available products like cosmetics and sunscreens, pharmaceuticals, stain resistant clothing, sports equipment, automobile catalytic converters, dental bonding, cleanings products, dressings for specific wound care strategies and many more fields of possible future applications of nanotechnologies which include drug delivery systems, nanomedicine, environmental remediation, cell imaging etc.

Titanium dioxide (TiO$_2$) and zinc oxide (ZnO) are largely present in many sunscreens formulations to protect against UV-induced skin damage. When exposed to UV radiation, TiO$_2$ and ZnO do not undergo any chemical decomposition and for that reason they represent an alternative to chemical agents. Moreover, they offer a wider range of protection compared to other organic compounds. Actually, in many formulations TiO$_2$ and ZnO are included as nanosized particles because in this form they are transparent and more esthetically acceptable to the consumers.

Engineered nanoparticles, because of their big surface to volume ratios, exhibit chemical, physical and biological properties distinctly different from the same materials in the bulk form. Every year new products containing nanomaterials enter in the market (Woodrow Wilson International Center for Scholars, 2007) and in the next future more workers and costumers will come in contact with nanoproducts.

Nanotoxicology is an emerging discipline (Oberdorster et al., 2005a) and there is a gap between the nanomaterials safety evaluation and the nanotechnology development that daily produce new materials, new synthesis, new applications and new products ready for the market. According to the Royal Society & the Royal Academy of Engineering report (2004), nanoparticles should be treated as new chemicals from a risk-point of view because they can overcome the body’s normal
protective barrier given their size (Nasterlack et al., 2008; NIOSH, 2007; Schulte et al., 2008). Moreover, ultrafine particles, different in sources and composition (Geller et al., 2002) are a component of the airborne particulate matter (Ntziachristos et al., 2007; Pakkanen et al., 2001) and their absorption through inhalation and skin routes must be better studied (Ayres et al., 2008).

Since the toxicological and environmental effects of these compounds are not fully known, there is a need to understand better the health and environmental impacts, the nanoparticles life cycle, the human exposure routes, the behavior of nanoparticles into the body and the risk for workers in order to use these new materials in a safe way (Dreher, 2004; EPA, 2007; Gwinn’and Vallyathan, 2006; Hoet et al., 2004; Nasterlack et al., 2008; Nel et al., 2006; NIOSH, 2007; Oberdorster et al., 2005a, b).

In order to enhance the catalytic activity and process efficiency of industry, nano-sized photocatalysts have been synthesized by various techniques such as vapor chemical deposition, sol–gel, precipitation, hydrothermal and microemulsion etc. (Byrappa et al., 2006; Daneshvar et al., 2007; Joni et al., 2009; Rautio et al., 2009; Veriansyah et al., 2010; Li et al., 2009b; Cimitan et al., 2009).

An excellent review of progress on processing, properties and applications of ZnO has been published by Pearton et al. (2005).

Byrappa et al. (2006) stated that textile effluent with diverse composition could be effectively treated with hydrothermally synthesized ZnO and concluded that ZnO assisted photocatalytic degradation of textile dyes and textile effluent may be a versatile, environmentally benign and effective method of treatment.

Jang et al. (2006) compared the photocatalytic activity of ZnO nanoparticles and its nano-crystalline particles using Methylene Blue under UV
light illumination. The photocatalytic degradation capacity of the ZnO nanoparticles was higher than that of the ZnO nano-crystalline particles.

Hong et al. (2009) synthesized ZnO nanoparticles by precipitation method. They studied its photocatalytic activity for the decolorization of Methyl Orange dye and observed that the synthesized particles showed higher photocatalytic activity.

Daneshvar et al. (2007) prepared ZnO nanocrystals by precipitation method. After aging, washing and drying, solids were calcined at 300 °C and examined as photocatalyst for UV-induced degradation of organophosphorus insecticide diazinon in aqueous solution. The effects of some operational parameters such as pH value, nanocatalyst loading and initial insecticide concentration on the degradation efficiency were discussed through the photocatalytic experiments using prepared ZnO nanocrystals. The optimized parameters were also tested for the treatment of real water containing the insecticide. A model was successfully established for the prediction of degradation of diazinon in UV/ZnO process with any concentration of insecticide. Catalytic activities of prepared and commercial ZnO nanocrystals were also compared. The diazinon photodegradation quantum yield in UV/ZnO process increased with decreasing the diameter size of ZnO from 33 nm to 14 nm. The results showed that the photocatalysis process in the presence of ZnO with mean size of 14 nm offered the best energy efficiency. Accordingly, it could be stated that 80% removal of the insecticide, after selecting desired operational parameters could be achieved in a relatively short time, about 80 minutes.

Chen et al. (2008) obtained the precursor precipitates of zinc oxide (ZnO) by a direct precipitation method via the reaction between zinc nitrate (Zn(NO₃)₂) and ammonium carbonate ((NH₄)₂CO₃) in aqueous solutions with proper concentration. The precursor precipitates of ZnO were subjected to thermal
calcination and finally yielded the nano-sized ZnO powders. The XRD results indicated that the synthesized ZnO powders had a pure wurtzite structure and the average nanoparticle sizes were about 35.2 nm. In addition, both the SEM image and the TEM photograph demonstrated that the nano-sized ZnO particles were of a pseudo-spherical shape.

Azizian-Kalandaragh et al. (2009) reported a facile route for preparation of hexagonal ZnO nanocrystallites using aqueous solution of zinc acetate dihydrate \((\text{Zn(C}_2\text{H}_3\text{O}_2)_2\cdot2\text{H}_2\text{O})\) with the aid of ultrasound irradiation. SEM images displayed the product consisting of rod-like nanocrystallites of about 70 nm width and 250 nm length, which aggregated in the form of polydispersive clusters. XRD exhibited that the particles were excellently crystallized.

Joni et al. (2009) reported the synthesis and characterization of ZnO nanoparticles prepared via pulse combustion-spray pyrolysis (PC-SP) at a high rate. Instead of using an ultrasonic nebulizer as the atomizer during PC-SP synthesis, a two-fluid nozzle was used to enhance the production rate. A high production rate was achieved by the use of a two-fluid nozzle, which efficiently generated droplets in large quantities and by controlling the rate of precursor flow. ZnO nanoparticles were characterized using XRD, SEM, TEM and UV–vis spectroscopy. The prepared ZnO nanoparticles were spherical and highly crystalline with an average size of 15.6 nm. In addition, high UV-light absorption and visible-light transparency properties were successfully obtained for a dispersion of ZnO nanoparticles in glycerol. The high UV-blocking capacity of the ZnO particle dispersion made the dispersion potentially useful in cosmetic applications.

Rautio et al. (2009) synthesized homogeneous doped ZnO nanoparticles by the Pechini method. A statistical experimental design was used to study the
effects of the synthesis method variables on the particle size. The variables were the molar ratios of the reagents and the calcination temperature. The results indicated that the calcination temperature was the only factor that had a significant effect on the particle size. The particle size of ZnO varied between 16 and 76 nm with calcination temperatures of 400–800 °C.

Chung et al. (2009) prepared suspensions of ZnO nanoparticles in water with the two-step powder dispersion process using several methods of ultrasonication. The dispersion of ZnO was found to proceed by a fragmentation process, with minimum achievable particle size in the range 50 nm to 300 nm. This was consistent with other oxide nanopowder systems, in which most primary particulates still remain in hardened aggregates that cannot be further reduced. A submersible accelerometer probe was developed and used to measure the relative ultrasonic energy field in the liquid for the various ultrasonication methods. Oscillation at the expected frequencies was identified in each case, with strong variability at different locations in the liquid volume.

Chao et al. (2009) prepared ZnO nanoparticle aggregations with porous morphology by the direct precipitation of Zn(OH)$_2$ coats on the surface of Zn powders and succedent calcination of Zn/Zn(OH)$_2$ composites. The coating and calcination reaction mechanism was given to explain the formation of the novel structure. It was found that ZnO nanoparticle aggregations were irregular porous microspheres consisting of ZnO nanoparticles with hexagonal wurtzite structure and the diameters of bores in the microspheres ranged from tens to hundreds nanometers.

Li et al. (2009a) synthesized ZnO nanospindles by PVP-assisted hydrothermal growth and ZnO@ZnS core–shell microspindles were successfully fabricated by sulfidation of ZnO nanospindles via a facile chemical synthesis. The results showed that the pure ZnO nanospindles were
hexagonal wurtzite crystal structure and the ZnS nanoparticles were sphalerite structure with the size of about 40 nm grown on the surface of the ZnO nanospindles. The measurement of luminescence revealed that ZnO@ZnS core–shell microspindles integrated the luminescent effect of ZnO and ZnS. The broad blue emission of ZnO@ZnS core–shell microspindles were dramatically enhanced, while the orange emission disappeared.

Abdel et al. (2009) prepared ZnO thin film via evaporation of Zn metal on a glass sheet followed by calcination (oxidation) process. The influence of calcination parameters such as temperature and time on the surface morphology and phase structure of ZnO films were investigated by SEM and XRD, respectively. The analysis of XRD patterns indicated that the growth of ZnO nano-structure was controlled by calcination time and temperature. Optimum ZnO nano-fibers could be formed uniformly after 2 hours of oxidation at 550 °C. Nanostructured ZnO catalyst exhibited a significantly greater superiority for the photodegradation of 2,4,6-Trichlorophenol (TCP) as a model pollutant in water over photolysis via irradiation with UV of 254 nm wavelength. The role of ZnO catalyst was discussed and the chemical composition of degradation products and intermediates was identified.

Cao et al. (2009) synthesized the ZnO using zinc carbonate hydroxide (ZCH) as the precursor by chemical precipitation method and the precursor was modified in situ with silica and TMS. The modified ZnO ultrafine particles were obtained after calcinating the modified precursors. The surface properties of the modified ZnO ultrafine particles were characterized using XRD, FT-IR spectroscopy, XPS, SEM and TEM. The effects of the modifiers on the photocatalytic activity and UV shielding ability of ZnO ultrafine particles were also investigated and discussed.
Suchanek (2009) synthesized ZnO powders by the hydrothermal method at 160–280 °C for 6–24 hours, under 90–930 psi pressure, from concentrated precursors without stirring. The precursors were formed by mixing aqueous solutions of zinc acetate, chloride, sulfate, or nitrate with KOH (aq) under either controlled or rapid precipitation conditions. Comparison with several commercially available ZnO powders revealed superior purity, particle size distributions, defect structure and ultimately the UV attenuation, in selected powders synthesized hydrothermally. Results of this study enable the use of hydrothermally made ZnO powders in sunscreens or other UV absorption applications and make their hydrothermal production commercially feasible.

Verma et al. (2008) prepared nanosized-semiconductor zinc oxide–sulphide (ZnO/ZnS) core–shell nanocomposites, both formed sequentially from a single-source solid precursor. ZnO nanocrystals were synthesized by a simple co-precipitation method and ZnO/ZnS core–shell nanocomposites were successfully fabricated by sulfidation of ZnO nanocrystals via a facile chemical synthesis at room temperature. The results showed that the pure ZnO nanocrystals were hexagonal wurtzite crystal structures and the ZnS nanoparticles were sphalerite structure with the size of about 10 nm grown on the surface of the ZnO nanocrystals.

Li et al. (1993) reported the successful preparation of flower-like ZnO microstructures in one step by a simple, rapid and reliable ultrasound irradiation route, using only Zn(CH$_3$COO)$_2$ and NaOH as starting materials. The product was characterized by powder X-ray diffraction, energy-dispersive X-ray spectrometry, transmission electron microscopy and scanning electron microscopy. The UV–vis absorption and emission spectra, photocatalytic activity and electrochemical properties of the as-obtained flower-like ZnO microstructures were studied.
Lee et al. (2009a) prepared the ZnO nanostructures by reacting zinc acetate dihydrate with NaOH in water at 50–60 °C. Evolution of ZnO nanostructures with reaction time is studied using UV–Vis spectroscopy, TEM, XRD and FT-IR spectroscopy techniques. During the process of Zn²⁺ hydroxylation, well defined rod-like crystals were formed within 15 minutes. Further hydroxylation leads to the formation of a gel-like structure within about 45 minutes. However, XRD, FT-IR and energy dispersive spectroscopy confirmed that these initial products were zinc hydroxyl double salts (Zn-HDS), not ZnO. On aging the reaction mixture, ZnO nanoparticles with wurtzite structure evolved.

Lee et al. (2009b) synthesized nanometer-sized zinc oxides, ZnOs, by hydrothermal treatment at 150 °C, 200 °C and 250 °C for 8 hours and their morphologies were controlled by using different pHs, pH = 2, 3 and 4, with the addition of formic acid. The TEM results revealed that the as-prepared particles at pH = 3 were hexagonal disk-shaped and the crystallite sizes were 40 nm measured across the diagonal. However, the shapes were different at the other pHs; nanoneedles at pH = 2 and hexagonal columns at pH = 4. The patterns of the photoluminescence (PL) spectra of the ZnOs varied according to their shapes.

Mohajerani et al. (2009) synthesized ZnO nanostructures in the shape of particle, rods, flower-like and micro-sphere via facile hydrothermal methods and the effect of morphology on the decolorization of Cl Acid Red 27 solution under direct irradiation of sunlight was investigated. XRD patterns showed that the synthesized nanostructures have wurtzite-type hexagonal structure with high crystallinity and crystallite size in the range of 67–100 nm. UV–vis absorption spectra indicated that the ZnO nanorods had higher visible light harvesting as compared to the other morphologies. The decolorization obeyed the first order
kinetics rate with the kinetics constant of $4.5-19.5 \times 10^3 \text{ min}^{-1}$ dependent on the ZnO morphology and surface area.

Kong et al. (2009) prepared a novel photocatalyst ZnTiO$_3$ powder by a modified alcoholysis method, using ethylene glycol as reagent/solvent and acetylacetone as stabilizer. Results showed that the photocatalytic activity was dependent on the phase of catalysts. The product of ZnTiO$_3$ with pure hexagonal-phase calcined at 800 °C for 3 hours exhibited the maximum photocatalytic performance in the photochemical degradation of the azo dye methyl violet under solar light irradiation. The processing parameters such as the concentration of catalysts and the pH value also played an important role in tuning the photocatalytic activity. The optimal concentration and pH value of the pure hexagonal-phase ZnTiO$_3$ was around 4 g/L and 8 in a 10 mg/L dye-aqueous solution, respectively.

Tian et al. (2009) prepared the TiO$_2$/ZnO nano composite film with atomic ratios of Ti/(Ti+Zn) of 100%, 75%, 50%, 25% and 0% via sol-gel process from directly mixing TiO$_2$/ZnO sol followed by heat treatment at 500 °C for 2 hours in air. The UV irradiated degradation of MO solution using the composite film as catalyst showed a linear tendency of the photocatalytic activity of the film against the value of Ti/(Ti+Zn). An exception to photocatalytic activity was observed for the film with Ti/(Ti+Zn) of 75%, which has been attributed to the poor crystallization of the film.

Zhang et al. (2009) presented a surfactant-assisted complex sol–gel method for the controlled preparation of ZnO nanoparticles using zinc nitrate and citric acid as starting material. ZnO nanoparticles with a pure wurtzite structure were obtained after calcination at 773 K. The effects of the citric acid concentration, the pH and the surfactants on the average particle size and morphology of the ZnO nanoparticles were investigated using XRD and SEM.
techniques. Well dispersed ZnO nanoparticles with a uniform size distribution were obtained using polyethylene glycol (PEG) 2000 as a surfactant.

Thongtem et al. (2010) synthesized ZnO nanoparticles and nanorods from Zn(NO$_3$)$_2$·6H$_2$O and NaOH in H$_2$O and in different molecular weights (MWs) of polyethylene glycol (PEG) using 180 W microwave radiation. Scanning and transmission electron microscopy revealed the presence of nanoparticles with an average size of 12.7 ± 2.7 nm in water; these gradually changed into nanorods in PEG with different MWs.

Yan et al. (2010) synthesized a novel nest-like ZnO nanostructure by a solvo-thermal method, with Zn(NO$_3$)$_2$·6H$_2$O and NaOH as starting materials. The results showed that the as-synthesized samples had a wurtzite structure, with a weak UV emission at about 395 nm, a green emission at around 557 nm and a blue-green emission at 453 nm. SEM investigation revealed that the growth route of the nest-like ZnO could be considered involving three stages: nano-sized ZnO sheet could be firstly achieved, then outspreaded quickly and increasingly became a long fishbone-like strip with many branch sheets and finally these sheets curled into a nest-like structure.

Kuo et al. (2010) synthesized ZnO nanocrystalline powders for cosmetic applications by a coprecipitation process. When the Zn(OH)$_2$ precipitates were calcined at 373 K for 10 minutes, the crystalline phase comprised the major phase of Zn(OH)$_2$ and the minor phase of ZnO. XRD pattern showed that only ZnO was present, and no other phase was detected when the Zn(OH)$_2$ precipitates were calcined at 413 K for 10 minutes. The nanocrystallite size of ZnO increased slightly from 32.3 to 44.3 nm when the calcination temperature increased from 413 to 873 K.
Yang et al. (2010) synthesized ZnO–SnO₂ composite oxides with various molar ratios of Sn:Zn at different calcination temperatures via a facile cetyltrimethylammonium bromide (CTAB)-assisted co-precipitation method with Zn(NO₃)₂·6H₂O and SnCl₄·5H₂O as starting materials. The photocatalytic properties of the composite oxides were investigated using photocatalytic degradation of methyl orange as the probe reaction. The results show that the ZnO–SnO₂ composite oxide with a cube morphology exhibited the best photocatalytic activity, which was prepared with a molar ratio of Zn:Sn of 2:1 and calcination temperature of 700 °C.

Xie and Wu (2010) synthesized ZnO/Ag composite nanospheres with an average diameter of about 440 nm, through a facile one-pot solvothermal reaction, using a kind of biomolecular sodium alginate as template, H₂O and diethanolamine as solvents, followed by the assembly of ZnO and Ag nanoparticles in-situ produced. The composite spheres were characterized by XRD, SEM, TEM and energy disperse X-ray spectrum. Moreover, the results showed that the as-made ZnO/Ag assembled nanospheres exhibited better photocatalytic performance than the pure ZnO nanoparticles and this one-pot synthesis method has great potential to be extended for the synthesis of other metallic oxide/metal spheres.

Xu et al. (2010) prepared ZnO/Cu₂O compound photocatalysts by “soak-deoxidize-air oxidation” with different concentrations of Cu²⁺ (0.125, 0.25, 0.5, 1, 1.5 and 2 mol/L). The results showed that ZnO was hexagonal wurtzite structure and the crystallinity had no change with the increase of Cu²⁺ concentration. Cu₂O belonged to cubic structure and the crystallinity increased with the increase of Cu²⁺ concentration. ZnO were rods and bulks which had diameter of about 300–400 nm, some small round Cu₂O particles which had a diameter of about 50 nm adhered to these rods and bulks. The photocatalytic activities of ZnO/Cu₂O compound were evaluated using a basic organic dye,
Methyl Orange (MO). It was found that, compared with pure ZnO, the photocatalytic properties of ZnO/Cu2O compound were improved greatly and some compounds were better than pure Cu2O.

Zhu et al. (2010) synthesized bismuth titanate (Bi12TiO20) nanostructures with different morphologies by hydrothermal method using Bi(NO3)3 and Ti(SO4)2 in the presence of polyethylene glycol (PEG). XRD proved that the samples were in pure cubic phase. UV–visible diffuse reflection spectra showed the band gap of Bi12TiO20 to be about 2.7 eV. BET analysis proved that the Bi12TiO20 samples have higher surface areas than samples prepared by another methods. Photocatalytic degradation of Acid Orange 7 (AO7) under visible light illumination was used to evaluate the photocatalytic ability of samples. The photocatalytic results showed Bi12TiO20 could degrade AO7 very efficiently and had higher photocatalytic activity than traditional N-doped TiO2. In addition, they have also discussed factors that have major effect on reaction efficiency. BET surface area played the most important role in the photocatalytic degradation of AO7. The crystallinity of the samples was another important factor which could also influence photocatalysis results.

Pourretedal and Keshavarz (2010) synthesized Zn1-xCuxS and Zn1-xNixS nanocomposites by using a controlled coprecipitation. The nanocomposite materials were characterized by the use of UV–Vis spectra, atomic absorption spectroscopy, XRD, TEM image and BET method. For Zn1-xCuxS and Zn1-xNixS nanoparticles, the XRD showed the zinc-bland crystal structure. The blue shift in band-gap of ZnS was observed through incorporation of Cu2+ and Ni2+ ions. The Congo Red photodegradation was performed to study the photoactivity of prepared nanocomposites under UV–Vis irradiation. The effect of dopant mole fraction, dosage of photocatalyst and pH of samples were considered on the decolorization rate of dye and photoactivity of nanocomposites.