Chapter - 2

Review of Literature
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Natural dyes have been in use since ancient times until they were replaced by synthetic dyes in the late 19th century. Synthesized dyes transformed the textile industry since they were cheaper and readily available. This transformation sparked great exploration of synthetic dyes and helped to create a commercial market that continues to grow, even today (Lacasse and Baumann, 2004).

However, the wastewaters generated by the textile industry dyeing process contain significant amounts of dissolved dye, mostly azo dyes. It is believed that up to 15% of dyes used for production are released in the dyeing process effluent stream (Lachheb et al., 2002).

Studies of late have demonstrated the presence of dyes in the aquatic environment. Azo disperse dyes are hydrophobic and are not expected to be found in the water column but adsorbed on the sediment. However, since the dyes are combined with dispersing agents, the hydrophilic properties of the products are much higher than the dyes alone, allowing for an increased presence of dyes in waters that receive effluents from textile processing plants (De-Aragao et al., 2005).

There are several reasons why the colors of dyes cause problems in textile waste water. Acute or chronic effects can occur from direct exposure. Even small amounts of released colorant cause aesthetic changes due to the coloration of surface waters. The absorption and reflection of sunlight entering the water is changed by the presence of dyes. This change interferes with growth of bacteria and can significantly change the
level of biological impurities in the water (Slokar and Marechal, 1998). In addition, international environmental standards are heightening, creating the need for more technology to remove the azo dye pollution (Lachheb et al., 2002). Although much research is in progress to develop effective treatment technologies containing industrial dyes and coloured textile wastewaters, no single solution has been satisfactory in degrading or removing the dyes from waste waters.

Over the last few decades, heterogeneous semiconductor photocatalysis using nanoparticle as the photocatalyst has received considerable attention for water and wastewater treatment (Surpateanu and Zaharia, 2004; Grzechulska and Morawski, 2002). Photocatalysis is an emerging wastewater treatment technology with key advantages including the lack of mass transfer limitations, operation at ambient conditions and the possible use of solar irradiation. The catalyst itself is inexpensive, can easily prepare various crystalline forms and examine the particle characteristics, non-toxic and photochemically stable. The process can easily decolourize and reduce considerably the organic load of textile wastewaters and similar effluents (Elaziouti et al., 2011; Reutergardh and Iangphasuk, 1997).

In recent years many researchers have worked on the photocatalytic processes and have achieved very good results with a new route for the photocatalytic processes. Where, metal oxide nanoparticles gain more attention because of its special physical and chemical features, and is applied in each realm gradually (Aruna and Mukasyan, 2008; Stella and Nesaraj, 2010). The nanoparticle granule size lies in the 1-100nm and gains some special capabilities on magnetism, light, electric and sensitivity etc. The nano-zinc oxide grains latent importance is indubitable, some developed nations all throw great deal
of funds to the research work, many local academies and institutes, universities also organizes research strength, opening the research work of the nanomaterials (Ni et al., 2011).

Kumar and Bansal, (2010), have reported that Photocatalysts have been found useful not only in the oxidation and in the degradation of some organic molecules, but also in the synthesis of organic compounds, isomerization/transformation, wastewater treatment, self cleaning, sterilization, and so on. The conventional wastewater treatment does not always satisfactorily cleanse the wastewater containing dyes. In order to cleanse water of these extra-stable organics, so called advance oxygen processes (AOPs) is the order of the day. The aim of these methods is to mineralize the pollutants to CO$_2$, H$_2$O and mineral acids and salts. Titanium dioxide photocatalysis belongs to the group of AOPs and has been extensively studied over the last 20 years.

Parsons (2004), observed that Advanced Oxidation Processes (AOPs) has shown a great potential in treating pollutants at both low and high concentrations and have found applications as diverse as ground water treatment, municipal wastewater sludge destruction. Advanced Oxidation Processes for water and wastewater treatment will be invaluable to researchers interested in water and wastewater treatment processes.

Barrett (1997), suggested the Advanced Oxidation Processes, since they have been proven to be effective in the removal of wide spectrum of organic and inorganic contaminants from wastewater. Also they addressed to researchers and professionals with a background in environmental science and engineering about the solar driven Advanced Oxidation Process and its multiple advantages.
Bai et al. (2011), synthesized the nano powders successfully via a solution combustion process using starch as fuel and nanoporous agglomerates are formed in the powders. Similarly, Aruna and Mukasyan, (2008), reported that the profound interest in combustion synthesis is due to the simplicity and cost effectiveness of the process followed by the superior nature of the particulate properties of the products. Promoters of nanotechnology, an approach defined on the basis of a length scale, have done a great job of selling the idea that 'smaller is better'. Similarly, now to commercialize a solution combustion method by selling the reality of 'simpler is smarter and better'.

De-Andrade et al. (2006), synthesized the Nanocrystalline pirochromite spinel through solution combustion synthesis using glycine and urea for the first time. By using urea the crystalline nano powders have yielded a size of 9nm during the synthesis. Producing metal oxide catalysts with nanometer crystal sizes offers an attractive means of controlling catalytic behavior in selective oxidation reactions.

Patil et al. (1997), synthesized advanced materials (both oxide and non oxide) in various forms (nanosize, films, and whiskers) have been made by a combustion process. The materials arise from the combustion residues (ash) like a 'Phoenix', the mythological bird that burnt itself on pyre and arose from the ashes with renewed youth to live again. The combustion process being simple, fast and energetically economic is attracting the attention of material scientists and engineers to prepare new and exotic materials for special applications under corrosive high-temperature and high pressure conditions.

Park et al. (1998), devoted their work for the synthesis of combustion synthesis which is the method that most commonly used to obtain powders with compositional
uniformity. As the particle size increases, the strength of the agglomerates increases. In the same way, Patil et al. (2002), showed that the combustion synthesis has emerged as a facile and economically viable technique for the preparation of catalysts and nanomaterials. Recent innovations in the combustion and processing parameters have resulted in a better understanding of combustion phenomena and control of microstructure and property of the products.

Kingsley et al. (1990), worked on the combustion synthesis of fine particle metal aluminates using metal nitrates (oxidizers) and urea or carbohydrazide (fuels) at 500 or 350°C in a short span of 5 minutes. The solid combustion products were identified by their characteristic X-ray powder diffraction patterns. The fine-particle nature of these metal aluminates was investigated using SEM, XRD, particle size analysis and Spectroscopic methods.

Giwa et al. (2012), using semiconductor oxides they have worked on the photocatalytic degradation of dyestuffs in presence of natural sunlight. Their report states that, photocatalytic degradation of dyes is mainly due to the hydroxyl radical attack on the dye molecule. The production of hydroxyl radicals in an acidic medium is different from what occurs in a basic medium. In an acidic medium, photogenerated holes react with water molecules to produce hydroxyl radicals. At alkaline pH the negative surface of the TiO₂ with OH⁻ ions acts as an efficient trap for the photogenerated holes and hydroxyl radicals are produced. Thus, the TiO₂ surface is positively charged in acidic media (pH<6.8), whereas it is negatively charged under alkaline conditions (pH>7). Secondly, hydroxyl radicals can be formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the major oxidation species at low
pH, whereas the hydroxyl radicals are considered as the predominant species at neutral or high pH levels. Finally, it has also been argued that the greater photo effectiveness of TiO$_2$ degussa photocatalyst can be attributed to three factors. The smaller band gap of rutile extends the useful range of photo activity into the visible region. The stabilization of charge separation by electron transfer from rutile to anatase slows the recombination. The small size of the rutile crystallites facilitates the electron transfer.

Zayani et al. (2009), reported on the visible light induced photodegradation of the studied dyes. Accordingly, dyes absorb strongly in the visible range, the energy harvesting efficiency should be enough high to make the photo assisted treatment of dye contaminated wastewater feasible. Here the mechanism suggests that dye molecules adsorbed on the photocatalyst surface may be excited by visible light photons to produce singlet and/or triplet states. Then the degradation occur rapidly following charge injection from the dye into the semiconductor. The electron from the excited dye molecule is injected into the conduction band of the semiconductor, and the cation radical formed at the surface is likely to be the major reactive one quickly undergoes degradation to yield stable products.

Konstantinou and Albanis (2004), discussed the photocatalytic oxidation mechanism. The conduction band electrons (e$^-$) and valence band holes (h$^+$) are generated when aqueous TiO$_2$ suspension is irradiated with light energy greater than its band gap energy (3.2 eV). The photogenerated electrons could reduce the dye or react with electron acceptors such as O$_2$ adsorbed on the dissolved in water, reducing it to superoxide radical anion O$_2^{\cdot-}$. The photogenerated holes can oxidize the organic molecule to form R$^\cdot$, or react with OH$^-$ or H$_2$O oxidizing them into OH$^-$ radicals.
Together with other highly oxidant species (peroxide radicals) they are responsible for the heterogeneous TiO$_2$ photodecomposition of organic substrates as dyes. According to this, the relevant reactions at the semiconductor surface causing the degradation of dyes can be expressed.

Bandara et al. (2004), worked on the role of TiO$_2$/MgO composite photocatalyst and showed that the coating of thin layer of MgO particles on TiO$_2$ particles enhances the photocatalytic activity of the composite system for the oxidation of chlorophenols and aminobenzoic acid in aqueous solution. The photocatalytic activity enhancement originated as a result of trapping of photogenerated electron on MgO defect sites and holes on TiO$_2$ particles, allowing wider charge separation and lesser recombination.

Da-Silva and Faria (2003), worked on the photocatalytic degradation of azo dye using UV irradiation and reported the Surface reaction between the dyestuff and the oxidizing agent. The mechanism explains the process is initiated upon UV irradiation of the semiconductor with the formation of high energy state electron/hole pairs ($e^-/h^+$), which migrate to the surface, ready to initiate redox chemistries. Oxygen is present all over the TiO$_2$ and acts as electron acceptor to form the superoxide radical ion (O$_2^{-}$) while adsorbed OH$^-$ groups and H$_2$O molecules are available as electron donors to yield the hydroxyl radical (OH'). Both species are strongly oxidizing and capable of degrading aromatic compounds. Hence, they proved that UV radiation sources are able to delivery energy very efficiently using low lamp power and match the band gap requirements of a simple active carbon modified TiO$_2$.

Swati and Meena, (2012), constantly worked on the azo dyes which are being used in the textile industries. Here, the freely available sunlight was used for the
degradation process. After examination she concluded that photocatalyst (Methylene blue immobilized resin Dowex-11) has a very good potential to degrade azo dyes into simple molecules such as CO$_2$ and H$_2$O and purify textile effluent (wastewater) which contains large amount of non fixed dyes mostly azo dyes.

Habibi and Askari (2011), have done research on the photocatalytic degradation of an azo textile dye with manganese doped ZnO nanoparticles coated on glass. According to the research, manganese doped zinc oxide thin film supported commercial glass, which is a promising and efficient catalyst to degrade organic pollutants. Glass coated manganese doped zinc oxide thin film can be used repeatedly over a long time with small loss of efficiency.

Abo-Farha (2010), has worked on the mono azo and diazo dyes in wastewater using the nano-sized TiO$_2$ where he found that the dye color removal and degradation rates are proportional to the number of azo and sulphonic groups present in their molecule. His work demonstrates that photocatalysis is a very effective technology for degrading Acid dyes with azo and sulphonic groups. Moreover, this technology can be utilized directly in dye baths before they are mixed with other textile effluents, which make their treatment difficult and costly due to dilution.

Hosseinnia et al. (2010), worked on the organic dyes with different chromophores under visible light irradiation using TiO$_2$ photocatalysts. The Single phase anatase Titania powders with size below 20nm were used for the degradation processes. Here the photooxidation reactions gave similar results when 500 W white halogen lamps were used as the light source.
Barka et al. (2010), in their article on the degradation of Reactive Yellow 84 and successfully carried out using TiO$_2$ coated on paper fibers. They studied the correlation between the adsorption of the dye onto photocatalyst material and the rate of degradation. The photocatalytic degradation was explained here in terms of Langmuir Hinshelwood kinetic model.

Meena and Rambabu (2009), worked on the Photocatalytic degradation of model textile azo dyes by Advanced Oxidation Process (AOP) and found that by using a photocatalyst to degrade a azo dye is a very good method. She also proved that it can purify the textile effluent containing mostly non biodegradable azo dyes. She also proved that on increasing the light intensity the degradation rate increases upto certain extent.

Akpan and Hameed (2009), reported in a review, the effects of operating parameters on the photocatalytic degradation of textile dyes using TiO$_2$ based photocatalysts. It further examines various methods used in the preparations of the considered photocatalysts. The findings revealed that various parameters, such as the initial pH of the solution to be degraded, oxidizing agents, temperature at which the catalysts must be calcined, dopant content and catalyst loading exert their individual influence on the photocatalytic degradation of any dye in wastewaters.

Byrappa et al. (2006), reported on the sunlight mediated photocatalytic degradation using ZnO. Textile effluent with diverse composition was effectively treated using hydrothermally synthesized ZnO. The reduction in COD of the effluent suggests that the dye molecules were completely mineralized along with colour removal. So, it is concluded that the ZnO assisted photocatalytic degradation of textile dyes and textile effluent may be a versatile, economic, environmentally benign and efficient method of treatment.
Mozia et al. (2005), have focused on the application of photocatalysis in the degradation of azo dye Acid Red 18 and found that it is a very good and effective method of degradation of azo dyes. After 5 hours of irradiation they have found around 87% degradation depending on the catalyst loading and reaction temperature.

Daneshvar et al. (2004), have devoted their research work for the commonly used textile dyes using the photocatalysts and found that using UV irradiation can efficiently degrade the dyes. They proved that the degradation was effected by the illumination time; pH and catalyst loading have helped the degradation process. Also the addition of hydrogen peroxide has helped the rate of photodegradation.

It is evident from the preliminary brief survey of literature that there are a large number of studies have been done pertaining to the photocatalytic degradation of industrial dyes and wastewaters. Thus, the above preliminary review of research and literature on dye degradation studies justifies the varied dimensions of the subject along with explaining its vastness and depth.