



**PHOTOCHEMICAL AND SOLAR LIGHT TREATMENT OF  
SOME INDUSTRIAL WASTES USING EFFICIENT  
NANOCATALYSTS**

**Thesis**

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**By**

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## **Aim of the Work**

Colour removal from textile wastewater has been a matter of considerable interest during the last two decades, not only because of the potential toxicity of certain dyes but also due to their visibility in receiving waters. Recent studies indicate that approximately 12% of synthetic dyes are lost during manufacturing processing operations and that 20% of the resultant colour enters the environment through effluents from industrial wastewater treatment plants. Colour in dye-house effluents has often been associated with the application of dyestuffs, during which up to 50% of the dyes may be lost to the effluent, which poses a major problem for the industry as well as a threat to the environment. Decolourization of dye effluents has therefore acquired increasing attention. Decolourization of dye effluent by bisulfate - catalyzed borohydride reduction has been reported earlier. During the past two decades, nanostructured titanium dioxide ( $\text{TiO}_2$ ) is a semiconductor and its chemical stability is high, thus it was extensively used as a photocatalyst and adsorbent (Hu et al., 2007 and Chen, 2010).

Earlier studies have shown that a wide range of organic substrates such as alkanes, alkenes, aromatics, surfactants and pesticides, can be completely photomineralized in the presence

of  $\text{TiO}_2$  and oxygen. Thus, one of the major advantages of the photocatalytic process over existing technologies is that there is no further requirement for secondary disposal methods.

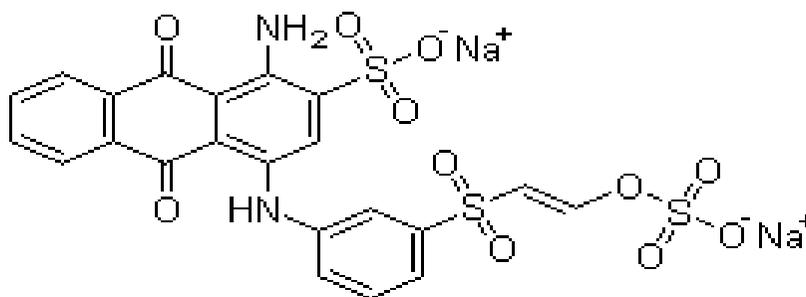
Another advantage of this process is that when compared to other advanced oxidation technologies, especially those using oxidants such as hydrogen peroxide and ozone, expensive oxidizing chemicals are not required as ambient oxygen is the oxidant (Matthews, 1993). Photocatalysts are also self-regenerated and can be reused or recycled.  $\text{TiO}_2$ -based photocatalytic oxidation techniques have received much attention due to their potential application for complete mineralization of many toxic and non-biodegradable organics (Hoffmann et al., 1995 and Fujishima, 2000).

Unfortunately,  $\text{TiO}_2$  is only responsive to ultraviolet irradiation, which greatly limits its practical applications because of its large band gap (3.0–3.2 eV) (Cao et al., 2010). Moreover, fast recombination rate of photogenerated electron–hole pairs also hamper the photocatalyst development. So, it is desirable to develop novel photocatalysts with high photocatalytic activity under visible light.

Many efforts have been exerted to extend the light absorption of  $\text{TiO}_2$  into the visible light region, such as doping  $\text{TiO}_2$  with trivalent lanthanide ions (Saif and Abdel-Mottaleb, 2007), copolymer- $\text{TiO}_2$  membranes (Essawya et al., 2008), dye

sensitization (Kaur and Singh, 2007), transition metals ion doping (Kumaresan et al., 2010), non-metals ion doping (Ananpattarachai et al., 2009 and Yang et al., 2007), ion implantation (Hou et al., 2006), metal deposition (Hidalgo et al., 2009 and Anandan et al., 2008), semiconductor composite (Kim et al., 2010 and Zhang et al., 2009) and conjugated polymer modification (Tang et al., 2007 and Wang et al., 2009).

Thus we focus first on studying photodegradation process of a model compound Remazol Brilliant blue dye RBB using  $\text{TiO}_2$  (Degussa P25 suspensions) in different media. The aim is to determine the optimum condition to obtain the highest rate of photodegradation (optimum concentration of  $\text{TiO}_2$  and optimum pH). Secondly, we are going to fabricate and characterize different nanocatalysts such as (metal oxide  $\text{M}_x\text{O}_y$ : AgO and metal halide  $\text{M}_x\text{X}_y$ : AgI) doped  $\text{TiO}_2$ . Their photocatalytic effect will be tested using RBB and its efficiencies will be compared with that of  $\text{TiO}_2$ .



**Scheme 1.** Chemical structure of Remazol Brilliant blue RBB.

# 1. INTRODUCTION

## 1.1. Nanotechnology

### 1.1.1. What is meant by nanotechnology?

Nanotechnology is broadly defined as the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications.

Nanotechnology is expected to contribute towards improving our quality of life, in particular, for sectors such as materials sciences, healthcare, information technology and the environment. Many products have been enhanced by nanotechnology to provide improvements and are already on the market e.g. heart-valves, coatings, scratch-free paints, tyres, sport equipment etc. Other important attributes of nanomaterials include high surface areas that can be functionalized at the molecular level, new combinations of photon penetration depth with modified carrier diffusion lengths, improved light harvesting, and band-gap manipulation.

Nanotechnology is the first major worldwide research initiative of the 21<sup>st</sup> century. Nanotechnologies are general purpose technologies that act as both the basis for technology solutions across a range of industrial problems or as a nexus for the convergence of other enabling technologies like

biotechnologies, computational sciences, physical sciences, communication technologies, cognitive sciences, social psychology and other social sciences (Linton and Walsh, 2004; Kautt et al., 2007; Hyungsub and Mody, 2009 and Freitas Jr, 2010).

Nanotechnology has assumed a special status in semiconductor materials and catalysts. These two classes of materials could be considered as the key for solar energy conversion. Nanomaterials applied in solar energy conversion may be classified depending on their proposed application.

Photocatalysts are a big family of nanomaterials (semiconductors or transition metal oxides) mostly applied in water treatment and solar water splitting for hydrogen production, among other useful applications (Abdel-Mottaleb et al., 2011).

Applications employing nanotechnologies promise greater and more equal access to knowledge and information, new therapeutic interventions, improved environmental monitoring, greater safety and security, expanded communication capacities and many other industrial and societal applications.

### **1.1.2. Nanocatalysts**

Improving the performance of a catalyst is very important for economical and social aspects of society. In an

article discussing the economic contributions of catalysis noted that “one-third of material gross national product in the U.S. involves a catalytic process somewhere in the production chain” (Bell, 2003). An example is the petroleum industry. Many of their processes heavily depend on catalysts to produce oil, gasoline, and other petroleum products. If a catalyst’s efficiency improves by 3%, this may lead to an increase of millions, possibly billions of dollars for the petroleum industry. The social impact would be the price reduction of different petroleum products for the consumer. The environment also benefits since harmful by-products will subside as a result of increasing the yield of a process. In order to improve catalysts, scientists are investigating the nanocatalyst as an avenue.

By nanocatalyst being very small in size, the particle size creates a very high surface to volume ratio (Mansoori, 2002). This increases the performance of the catalyst since there is more surface to react with the reactants. Another advantage is that nanocatalysts are able to place where traditional catalysts will not fit.

These new and unique properties of nanostructured materials, nanoparticles, and other related nanotechnologies lead to improved catalysts, tunable photoactivity, increased strength, and many other useful characteristics. It is beyond the scope of this research to synthesize nanoscale catalysts for

using it in treatment of water pollution in industrial processes. Yadav et al., 2005 published a review on nanocatalysts for green chemistry.

Nanomaterials possess certain desirable properties like high catalytic activity, better stability in aqueous media, comparatively easier preparation techniques, and material economy. Still, nanomaterials suffer from certain drawbacks when they are used in photocatalytic and photoelectrochemical devices.

The fascinating optical properties of nanostructured materials find important applications in a number of solar energy utilization schemes and devices. Nanotechnology provides methods for fabrication and use of structures and systems with size corresponding to the wavelength of visible light. This opens a wealth of possibilities to explore the new, often of resonance character, phenomena observed when the object size and the electromagnetic field periodicity (light wavelength  $\lambda$ ) match (Abdel-Mottaleb et al., 2011).

Nanotechnology has a wide range of application in different fields such as nanomaterials applied for chemical substitution, corrosion protection, coatings Anti-fouling, self-cleaning, wood preservatives, flame retardants, batteries, potential nanomaterial applications for waste minimization, dry cleaning, construction, plasticizers, pesticides and recycling.

### **1.1.3. Nanotechnology and its importance to the environment**

Nanotechnology plays an important role in environmental protection such as minimizing or eliminating the generation of wastes and effluents, reducing use of raw and manufactured materials (dematerialization) and reducing toxics.

The environment is also protected in applications that more effectively treat waste streams and remediate existing polluted sites. (Dabbousi et al., 1997; Elliott and Zhang, 2001 ; Hutchison, 2001 and Kamat et al., 2002).

### **1.2. Dyes and water pollution**

The extensive use of dyes often brings pollution problems in the form of colored wastewater and discharge into water bodies. The synthetic dyes have been commonly used in many industries such as textile, leather, tanning, paper, rubber, plastics, cosmetics, pharmaceutical and food industries.

Synthetic dyes, classified by their chromophores, have different and stable chemical structures to meet various coloring requirements and often are not degraded and/or removed by conventional physical and chemical processes (Ahn et al., 1999 and Robinson et al., 2001).

Konstantinou and Albanis, 2004, reported that 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 (Zollinger, 1991). The presence of dyes in effluents of textile industries represents a relevant problem not only for the aesthetic condition of the receiving water body, but also because their presence interferes with the oxygen solubility and the photosynthetic activity of the aquatic flora. Moreover, some dyes can exhibit characteristics of toxicity and recalcitrance. Due to the deep impact on the environment, the treatment of wastewaters from textile industries constitutes an issue of major economical and environmental concern (Chung and Stevens, 1993 and Hafez et al. 2005).

### **1.3. Textile dyeing wastewater risk**

Discharged wastewater by some industries under uncontrolled and unsuitable conditions is causing significant environmental problems. The importance of the pollution control and treatment is undoubtedly the key factor in the human future. If a textile mill discharges the wastewater into the local environment without any treatment, it will have a serious impact on natural water bodies and land in the surrounding area. High values of COD and BOD<sub>5</sub>, presence of particulate matter and sediments, and oil and grease in the

effluent causes depletion of dissolved oxygen, which has an adverse effect on the aquatic ecological system.

Effluent from textile mills also contains chromium, which has a cumulative effect, and higher possibilities for entering into the food chain. Due to usage of dyes and chemicals, effluents are dark in color, which increases the turbidity of water body. This in turn hampers the photosynthesis process, causing alteration in the habitat (Joseph, 2007).

#### **1.4. Textile wastewater treatment**

Textile wastewater includes a large variety of dyes and chemicals additions that make the environmental challenge for textile industry not only as liquid waste but also in its chemical composition (Venceslau et al., 1994). Main pollution in textile wastewater came from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs, which are generally organic compounds of complex structure. Because all of them are not contained in the final product, became waste and caused disposal problems. Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, colour, acidity, and other soluble substances (Dae-Hee et al., 1999).

The removal of colour from textile industry and dyestuff manufacturing industry wastewaters represents a major

environmental concern. In addition, only 47% of 87 of dyestuff are biodegradable (Pagga and Brown, 1986). It has been documented that residual colour is usually due to insoluble dyes which have low biodegradability as reactive blue 21, direct blue 80 and vat violet with COD/BOD ratio of 59.0, 17.7, and 10.8, respectively (Marmagne and Coste, 1996).

Conventional oxidation treatment have found difficulty to oxidize dyestuffs and complex structure of organic compounds at low concentration or if they are especially refractory to the oxidants.

Currently available water treatment technologies such as adsorption or coagulation merely concentrate the pollutants present by transferring them to other phases, but still remain and not being completely “eliminated” or “destroyed” (Padmanabhan et al., 2006). Other conventional water treatment methods such as sedimentation, filtration, chemical and membrane technologies involve high operating costs and could generate toxic secondary pollutants into the ecosystem (Gaya and Abdullah, 2008). These concentrated toxic contaminants are highly redundant and have been concerned worldwide due to the increasing environmental awareness and legislations.

Chlorination has been the most commonly and widely used disinfection process. The disinfection by-products generated from chlorination are mutagenic and carcinogenic to

human health (Coleman et al., 2005; Yang and Cheng, 2007 and Lu et al., 2009).

Degradation of dyes in industrial wastewaters has therefore received increasing attention and some methods of remediation have been preferred. Traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc.) have been used for the removal of dye pollutants (Tang and An, 1995; Konstantinou and Albanis, 2004). These methods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. This will require a further treatment of solid-wastes and regeneration of the adsorbent, which will add more cost to the process.

Microbiological or enzymatic decomposition (Hao et al., 2000), biodegradation (Sleiman et al., 2007), ozonation (Slokar and Marechal, 1998), and advanced oxidation processes such as Fenton and photo-Fenton catalytic reactions (Kuo, 1992; Konstantinou and Albanis, 2004),  $H_2O_2/UV$  processes (Ince and Gonenc, 1997) have also been used for dyes removal from wastewaters. Forgacs, et al., 2004, noted that traditional wastewater treatment technologies have proven to be markedly ineffective for handling wastewater of synthetic textile dyes because of the chemical stability of these pollutants, and went

further to verify that 11 out of 18 azo dyes selected for their investigations passed through the activated sludge process practically untreated. Most textile dyes are photocatalytically stable and refractory towards chemical oxidation (Arslan and Balcioglu, 2001), and these characteristics render them resistant towards decolorization by conventional biochemical and physico-chemical methods. All the aforementioned processes have a wide range of their deficiencies in the removal of dyes from wastewaters.

To ease the stated problems advanced oxidation processes AOPs have been developed to generate hydroxyl free radicals by different techniques. AOPs processes are combination of ozone ( $O_3$ ), hydrogen peroxide ( $H_2O_2$ ) and UV irradiation, which showed the greatest promise to treat textile wastewater. These oxidants effectively decolorized dyes, however did not remove COD completely (Tzitzis et al., 1994; Lidia et al., 2001; Stanislaw et al., 2001 and Ahmet et al., 2003).

### **1.5. Advanced Oxidation Processes (AOPs)**

Advanced oxidation process AOPs are defined as treatment processes which use the hydroxyl radical  $OH\bullet$  as the primary oxidant. AOPs are widely accepted technologies for wastewater decontamination (Andreozzi et al., 1999), which are based on the generation of hydroxyl radicals ( $OH\bullet$ ). These

radicals are strong oxidants that are able to degrade a great variety of biorecalcitrant organic compound (Hapeman and Torrents, 1998).

In general, the AOP systems generate in situ  $\text{OH}\cdot$  in very mild experimental conditions, being semiconductor heterogeneous photocatalysis (Dome`nech, 1993; Hoffmann et al., 1995 and Litter, 1999) and Fenton and photo-Fenton systems (Safarzadeh-Amiri et al., 1996 and Chamarro et al., 2001) the most widely studied. However, new approaches, such as the use of ozone and UV light and the coupling of different AOPs, have been recently investigated, with the aim to improve the rate of hydroxyl radical generation (Sa´nchez et al., 1998; Piera et al., 2000; Herna´ndez-Alonso et al., 2002 and Torrades et al., 2003).

Despite AOPs have shown to be adequate for the degradation of persistent organic compounds, they may involve considerable energy consumption, related to the UVA lamps that provide photons to the system.

In this way, cleaning up the wastewater comes at the price of consuming scarce resources and generating pollutant emissions and waste, associated to the electricity needed (Bauer and Fallmann, 1997). On the other hand, it is well known that several AOPs can be performed under solar irradiation, as the sun provides photons with the wavelength required for these