ABSTRACT

Wastewater streams are posing a serious threat to human life, plants and animals and eco-systems of receiving water bodies. One of the main causes of surface water and ground water contamination is industrial discharge from various industries viz. textile, pulp and paper, pharmaceutical and other chemical industries. Organic pollutants such as alkanes, haloalkanes, aromatics and haloaromatics, polymers, surfactants, herbicides, pesticides and dyes are commonly present in industrial effluents. These compounds are quite toxic and degrade slowly in the environment. Moreover, these substances persist in the environment for long time and result in number of adverse effects and disorders in human life. Therefore it becomes imperative to completely degrade these organic compounds. The complete degradation of these recalcitrant organic compounds present in wastewater is not possible by well established techniques like flocculation, precipitation, adsorption on granular activated carbon, air stripping or reverse osmosis, combustion and aerobic biological oxidation. The incapability of conventional wastewater treatment methods to effectively remove many bio-recalcitrant pollutants leads to explore the new efficient and cost effective treatment systems for the complete degradation of these pollutants.

Textile manufacturing produces large volumes of effluents that are toxic, resistant to physiochemical treatment and not easily biodegradable. About 115–180 m$^3$ of wastewater per ton of product is generated in dyeing and finishing section and about 12-63 m$^3$ of wastewater per ton of product is produced in printing. The main contaminants present in textile effluents are sulphur compounds, colourants, textile polymers like acrylic, natural gum, polyvinyl, surfactants, starch, bleaching chemicals such as sodium hypochlorite, calcium hypochlorite and hydrogen peroxide. It is reported that production of one ton of fibre produces 10 kg sulphur, 1 kg zinc and 40 kg COD (Textile Research Association, 1989). As azo dyes represent the largest class of organic colorants
listed in the colour index (C.I.) (60–70% of the total) and their relative share among reactive, acid and direct dyes is even higher, it can be expected that they make up the vast majority of the dyes discharged by textile-processing industries. Anthraquinone dyes are second largest class (~15% of the entries in the C.I.), followed by triarylmethanes (~3%) and phthalocyanines (~2%).

Various types of synthetic dyes like reactive dyes, direct dyes, mordant dyes, acid dyes, basic dyes, azoic dyes etc. are used in the production of textiles. These organic compounds are very toxic and bioresistant and show a great stability and solubility in water.

Various treatment technologies have been developed over the last 15 to 20 years in order to meet environmental regulation requirements. The recent developments in water decontamination processes are concerned with the oxidation of these bio-recalcitrant organic compounds. These methods rely on the formation of highly reactive chemical species/radicals that degrade number of recalcitrant molecules into biodegradable compounds. These radicals have high oxidizing power superior to other usual oxidants and are able to oxidize almost all organic compounds present in wastewater to carbon dioxide and water, which confirms the total degradation. These methods are called advanced oxidation processes (AOPs).

AOPs include homogeneous and heterogeneous photocatalytic processes, however the latter being more promising novel technique for the degradation of these organic compounds present in industrial effluents. Heterogeneous photocatalytic process relies on the application of various semiconductors like titanium dioxide (TiO2), zinc oxide (ZnO), cadmium sulfide (CdS) and zinc sulfide (ZnS). Activation of semiconductor photocatalyst is achieved through the absorption of the photon of ultraviolet band gap energy, which results in promotion of an electron e\(^{-}\) from the valence band into conduction band with the generation of hole h\(^{+}\) in the valence band. The resulting hole is an oxidizing agent.
and the electron is a reducing agent. According to the accepted mechanism for the photocatalytic process, the hole can react with water to generate the hydroxyl radical and the electron can reduce the molecular oxygen or other oxidizing agent in the solution. TiO$_2$ in suspension or fixed to various supports in aqueous solutions containing organic pollutants, creates a redox environment capable of destroying these pollutants and has been demonstrated to be an excellent catalyst and its behavior is well documented in the literature. The overall process can be summarized by the following reaction equation:

\[
\text{Organic pollutants} + \text{OH}^* \xrightarrow{\text{Semiconductor} \ \text{Ultraviolet band gap light}} \ CO_2 + H_2O + \text{Mineral acids}
\]

As the catalytic and other properties of semiconductors strongly depend on the crystallinity, surface morphology, the particle sizes and preparation methods, nanostructured materials have attracted considerable attention due to their unique physical and chemical properties.

ZnO with a wide band gap (3.2 eV) has aroused an explosion of interest in the past few years because of advances in its synthesis and because of its unique optoelectronic, catalytic and photochemical properties. The quantum efficiency of ZnO is also significantly larger than that of TiO$_2$. In some cases, ZnO has actually proven more effective than TiO$_2$. The ZnO-mediated photocatalysis process has been successfully used to degrade dye pollutants for the past few years. Also it has an additional advantage of being cheaper than other semiconductors.

Taking all these facts into consideration, in the present study, the photocatalytic decolorization of three different dyes viz. Biebrich Scarlet (BS), Pararosaniline Chloride (PC) and Rhodamine B (RhB) dye in unhydrolysed and hydrolysed forms and their simulated dyebath effluent has been investigated by employing heterogeneous photocatalysis process. The photocatalytic activity of different semiconductors viz. TiO$_2$, ZnO, CdS and ZnS has been compared in order to select the most active catalyst for the decolorization of each dye.
The degradation of these organic compounds has been investigated in terms of change in concentration of the compound by measuring the absorbance and reduction in COD under optimized conditions. The experiments were performed with different photocatalysts in slurry mode under UV light irradiation. Various process parameters like catalyst dose, pH and initial substrate concentration were varied and their effects have been analyzed. In an attempt to relate our present study to the real situation arising with effluent from the commercial dyeing of cotton/textiles with dyes, it was decided to formulate the simulated dyebath effluent and to test its response to photocatalytic decolorization.

Further the ZnO nanostructures were synthesized by using three different methods viz. precipitation, hydrothermal and sol-gel method. The characterization of the synthesized samples was done with different techniques such as XRD, FT-IR, TGA, SEM and TEM, PL spectrum and BET surface area analyser. It was found that the synthesized ZnO nanostructures were in accordance with the zincite phase of ZnO. Then the photodecolorization of the model compounds was investigated by using synthesized ZnO under optimized conditions. Thereafter the comparative evaluation of the photocatalytic activity of the synthesized ZnO and commercial ZnO powder was made. Experiments were also performed to investigate the reusability of the synthesized ZnO.

The work done has been presented in four chapters. After introducing the problem and its contents in the first chapter, the study begins with the literature review on photocatalytic degradation of various compounds in the second chapter. The relevant literature regarding the synthesis of nanophotocatalysts and their application for the treatment of organic compounds has also been discussed in this chapter. In the third chapter experimental procedures, description of reactor, instruments used, catalyst synthesis methods and their characterization techniques have been discussed in detail. Chapter four deals with the results and discussion of photocatalytic decolorization/degradation of various dye compounds and
simulated dyebath effluents with different types of catalysts (commercial/synthesized).

The photocatalytic decolorization of each dye was investigated in the presence of different catalysts under UV light irradiation. ZnO showed better photocatalytic activity than the other catalysts. The variables studied were: catalyst dose, solution pH and substrate concentration. The favorable pH value for the degradation of all the three dyes was found to be alkaline. The optimum value of catalyst dose was 0.75 g/L for BS dye and 1 g/L for other two dyes. The disappearance of the model compounds obeyed first order kinetics with the apparent rate constant values being $3.4 \times 10^3$ s$^{-1}$, $1.6 \times 10^3$ s$^{-1}$ and $9.48 \times 10^4$ s$^{-1}$ for BS, PC and RhB dyes respectively. COD analysis indicated the complete mineralization of organic compounds on the catalyst surface. The complete decolorization of BS, PC and RhB dyes was achieved in 16, 30 and 75 minutes respectively with commercial ZnO. Further the comparative evaluation of the photocatalytic activity of synthesized catalysts and commercial ZnO was done for the decolorization of these dyes. It was observed that the decolorization of each dye took place in a shorter duration with synthesized catalysts as compared to the commercial catalysts. 97% decolorization of BS dye was achieved in 10 minutes using synthesized ZnO whereas only 84% decolorization was observed with commercial ZnO for same duration. Similarly almost complete decolorization of PC and RhB dyes was achieved in 18 minutes and 30 minutes with synthesized ZnO whereas with commercial ZnO, only 85% and 82% decolorization was noticed in the same time duration.

Further the study was extended to explore the applicability of this system for the decolorization of each dye in its hydrolysed form and its simulated dyebath effluent. The decolorization rate as well as chemical oxygen demand (COD) reduction of the hydrolysed dye solutions was higher than that of the unhydrolysed dye solutions, whereas the simulated dye bath effluent decolorized at a somewhat
slower rate than hydrolysed and unhydrolysed dye solutions. From the results, it was seen that the synthesized catalyst showed better photocatalytic activity for the decolorization of hydrolysed dye solutions and their simulated dyebath effluent in terms of percentage decolorization and percentage COD reduction than the commercial ZnO.

In order to assess the stability of the synthesized catalysts, the experiments were performed to evaluate the reusability of the synthesized ZnO samples for the decolorization of these dyes. It was observed from the results that the synthesized ZnO samples show considerable photocatalytic activity up to three/four cycles.

After testing the photodecolorization efficiency of the synthesized nanophotocatalysts for each of the three dyes and their simulated dyebath effluent individually, studies on the photocatalytic decolorization of simulated dyebath effluent of all the three dyes (BS, PC and RhB) were carried out using commercial ZnO and ZnO synthesized by different methods (precipitation, hydrothermal and sol-gel) under optimized conditions. It was concluded that in case of simulated dyebath effluent also, synthesized ZnO exhibited better photocatalytic activity than the commercial one.

The results of the photodegradation of various dye compounds present in textile mill wastewater as well as of simulated dyebath effluents showed that heterogeneous photocatalysis process could be used as an efficient and environmental friendly technique. The investigations demonstrate the importance of selecting the optimal degradation parameters and appropriate nanophotocatalyst for practical applications of this process. The complete destruction of recalcitrant compounds present in wastewater will offer the opportunity to reuse the wastewater in the production processes of the concerned textile mill.