1. INTRODUCTION

Dyes are colored substances that have an affinity for substrates on which they are applied. Today dyes are used in several industries including textiles, paper, plastics, leather, cosmetics, food and pharmaceuticals. There are more than 100,000 commercially available dyes. Synthetic dyes quickly replaced the traditional natural dyes. They cost less, they offered a vast range of new colors, and they imparted better properties to the dyed materials. Among the various types of dyes Azo dye represent 60% of all dyes in food and textile industries. Azo dyes are synthetic dyes which contain azo group, -N=N- in their structure and give bright high intense colors compared to other class of dyes. The reactions for synthesis of azo dyes are so simple that the process can be scaled up or down easily. The reactions occurs at low temperature and hence energy requirements for the process are very less. The above factors make azo dyes cheap to produce. These dyes are stable in whole pH range of foods and are heat stable. Also, these dyes do not fade when exposed to oxygen or light. This feature makes them attractive in textile industries. But azo dyes causes skin irritation in some people especially in people with asthma or other similar disorders. As these dyes degrade to form toxic and carcinogenic products, removing these dyes form effluents is very important.

There are several techniques for dye removal and decolourisation. Each method has its advantages and demerits. Broadly, methods fall under three categories- Physical, Chemical and Biological. Developing single economical method for treatment of textile effluent still remains a big challenge (Santos et. al. 2007). Chlorination and ozonation are also being used for the removal of certain dyes but at slower rates as they have often high operating costs and limited effect on carbon content. These are the reasons why advanced oxidation processes (AOPs) have been growing during the last decade since they are able to deal with the problem of dye destruction in aqueous systems. AOPs were based on the generation of very reactive species such as hydroxyl radicals ($^{\bullet}OH$) that oxidize a broad range of pollutants quickly and non-selectively. AOPs such as Fenton and photo-Fenton catalytic reactions, H_2O_2/UV processes and TiO_2 mediated photo-catalysis have been studied under a broad range of experimental conditions in order to reduce the color and organic load of dye containing effluent waste waters. The photo catalytic purification of water by irradiated titanium dioxide particles has proven to be a very effective process, which leads to the complete mineralization of organic substrates. The deposition of metals on the surface of TiO_2 would produce traps to capture the photo-induced electrons or holes, leading to the reduction of electron-hole recombination and thus improving the photo catalytic efficiency.

$$TiO_2 + h\nu\,(UV) \rightarrow TiO_2\,(eCB^- + hVB^+) \quad (1)$$
$$TiO_2\,(hVB^+) + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet \quad (2)$$
$$TiO_2(hVB^+) + OH^- \rightarrow TiO_2 + OH^\bullet \quad (3)$$
$$TiO_2(eCB-) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \quad (4)$$
$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \quad (5)$$
$$Dye + OH^\bullet \rightarrow \text{degradation products} \quad (6)$$
$$Dye + hVB^+ \rightarrow \text{oxidation products} \quad (7)$$
$$Dye + eCB^- \rightarrow \text{reduction products} \quad (8)$$

The resulting $^\bullet OH$ radical, being a very strong oxidizing agent (standard redox potential +2.8 V) can oxidize most of azo dyes to the mineral end-products. Substrates not reactive toward hydroxyl radicals are degraded employing TiO_2 photo catalysis with rates of decay highly influenced by the semiconductor valence band edge position.

1.1 Limitations on the Application of TiO_2

Light of wavelengths below 400 nm can be absorbed by TiO_2 particles (E_g, 3.2 eV) to generate e^-/h^+ pairs.

It is known that less than about 5% of the solar energy reaching the surface of the earth is ultra violet lights.

Artificial light sources need high power.

All these factors place some limitations on the application of TiO_2 in the treatment of waste water.

1.2 Synthesis of Ag doped TiO_2 nanoparticles

Silver is particularly suitable for industrial applications due to its low cost and easy preparation. The effect of Ag dopants on the lattice or surface of TiO_2 have been examined. TiO2 loaded with silver enables the catalyst to perform more effectively and shortens the illumination period.

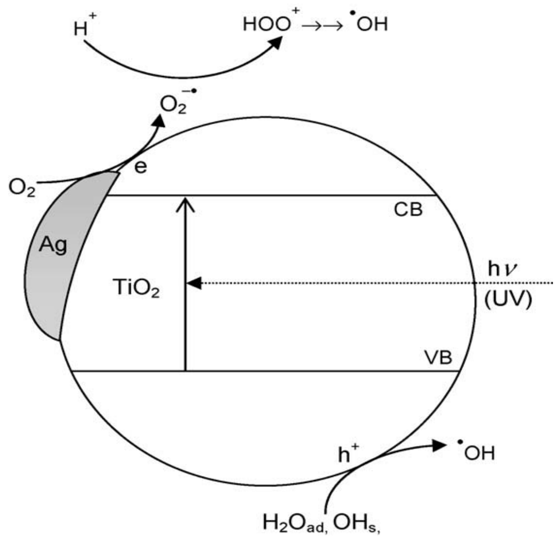

Figure 1.1 : Mechanism of catalytic action

Metals doped or deposited on TiO_2 are expected to show various effects on the photo catalytic activity of TiO_2 by different mechanisms. These noble metals act separately or simultaneously depending on the photo reaction conditions.

They may,

(i) enhance the electron–hole separation by acting as electron traps,

(ii) extend the light absorption into the visible range and enhance surface electron excitation by Plasmon resonances excited by visible light and

(iii) modify the surface properties of photo catalysts.

To overcome the high band gap and electron hole recombination the doping of TiO_2 with metals are employed (Sobana et al. 2006) Thus Ag doped TiO_2 is used in the present studies. In the present work the Ag doped TiO_2 nanoparticles is used as photocatalyst and the photocatalytic degradation of azo dye namely Congo Red dye is studied under solar light irradiation.