

CHAPTER-1

SUMMARY, OBJECTIVE AND APPROCH

1.1 Background

Colours (dye) and pigments have fascinated human being since the dawn of civilization. There are more than 1,00,000 commercially available dyes and over 7×10^5 tons of dyestuff are produced annually. Today, colours has a major role in human's life and it is an extensively used material for various industries like textile, carpet, pharmaceuticals, paper, plastics, leather, cosmetics and food industries etc. Among the above industries, carpet industry uses the dyes in carpet manufacturing process to colour the carpet's yarn. So, during the carpet manufacturing process, a huge amount of dyes contaminated water is generated by the carpet industries during dyeing stage (Fig 1.1).

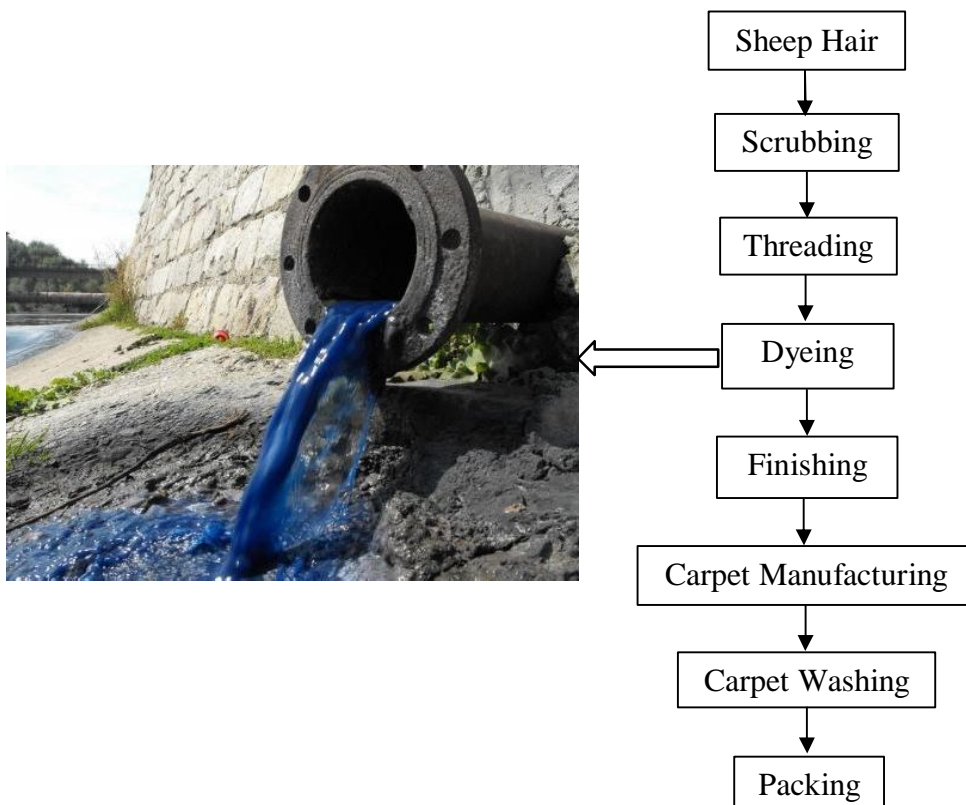


Fig 1.1 Flow diagram of carpet manufacturing process and photo of a carpet industry effluent.

Dyes are of mainly two types, namely natural and synthetic. Natural dyes are used to colour food products and pharmaceutical items whereas garments and carpets etc. are coloured by synthetic dyes. The common synthetic dyes which are used by carpet industries are direct, reactive, acid and basic dyes etc. In present work, direct dye (Direct Blue 199; molecular formula $C_{32}H_{16}N_8Cu$) was selected for the study since blue is a versatile colour. Direct dyes dissolve in water without any acidic or basic medium. It is used by carpet industries very frequently. The appearance and structure of Direct Blue 199 dye is shown below in Fig 1.2.

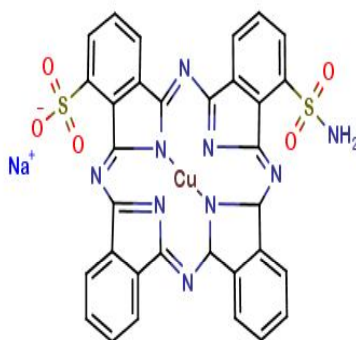


Fig 1.2 Appearance and structure of Direct Blue 199 dye.

As shown in Fig 1.2, the dye (Direct Blue 199) has N, O, H, S, Na and Cu elements in his structure which make molecular structures of dye more complex and stable which in turn create difficulties in degradation of the dye. Moreover, the

dye generates blue colour into the water body, which is not only aesthetically unpleasant but also inhibits sunlight penetration into the water stream that affects aquatic ecosystem. Furthermore, many dyes have carcinogenic properties and are toxic to some micro-organisms or inhibit the capabilities of micro-organisms.

1.2 Aim of the study

The aim of the present study is to remove/reduce the dye from the water body by a cheap and effective technique.

1.3 Conventional methods to treat dye contaminated water

Many conventional methods including physical, chemical and biological methods such as absorption, adsorption, coagulation and flocculation, precipitation, filtration and ion-exchange, etc. were investigated to remove/reduce dyes from the water body. In above techniques of decolourization, there are some drawbacks including generation of large volume of sludge and transformation of dye from the solution to solid forms.

The degradation of organic pollutant by a photocatalyst is one of the advanced oxidation process (AOP). In this, a wide range of organic pollutants from industrial wastewater can be degraded in simpler compound with the help of highly oxidizing radicals (hydroxyl radical OH^\bullet) and anions (O^{2-} and OH^-).

As a photocatalysts, nanomaterials are used very frequently in photocatalytic process since nanomaterials have large surface area, large number of reactive atoms and vacant reactive sites. Among various nano-materials, TiO_2 has attracted great attention and has been selected as a model photocatalyst due its high catalytic activity, nontoxicity, high chemical stability in an extensive pH range and low cost.

1.4 TiO₂ based photocatalysts

TiO₂ has three crystalline phase, namely anatase, rutile and brookite. Out of these phases, anatase is the most desirable phase of TiO₂ but some factors which are associated with anatase phase decrease its efficiency. First, activation energy of anatase phase of TiO₂ needs photons of UV radiation due to its high band gap energy (3.2 eV) and second, the rapid recombination of photogenerated electron-hole pair in TiO₂. So, for efficient photocatalytic activity, it is necessary to extend the photoresponse of TiO₂ from UV to visible region by modification of its optical properties and inhibit the recombination of photogenerated electron-hole pair.

Many approaches have been tried to enhance the photocatalytic activity of TiO₂ catalysts by lowering its band gap energy and inhibition of electron-hole pair. Various metals and non-metals were tried to modify the properties of TiO₂ by doping technique (Wang et al. 2000; Zhao et al. 2011; Chen et al. 2011; Lin et al. 2011; Lin et al. 2012; Lu et al. 2012; Zhang et al. 2012). The metals can acts as electron trapper and inhibit electron-hole recombination. So, the properties of TiO₂ were tuned by the doping of metal ions (Fe, Pd, Pt, Ag, Cu, W and Hf etc.) into TiO₂ lattice (Kočí et al. 2008; Yu et al. 2012; Fiorenza et al. 2018). The modification of TiO₂ by metals ions doping gives better result in charge separation but shows limited contribution in band gap lowering from UV to visible region (Zhang et al. 2011). On other hand, the doping or co-doping with non-metals ions (C, B, N and S etc.) into TiO₂ shows significant lowering in band gap energy (Hong et al. 2005; Su et al. 2008). The modification of TiO₂ by metals and non-metal doping increases the activity of TiO₂ up to a certain concentration of the doped materials since higher doping concentrations create several recombination centers for generated electron-hole pairs which suppress the photocatalytic activity of TiO₂

(Li et al. 2010; Rengaraj and Li 2006; Wu and Lee 2004; Koči et al. 2010). So, the concentration of doped materials in the TiO₂ lattice must be optimal.

The above studies suggest that the activity of TiO₂ photocatalyst can be enhanced by anion and cation doping. Among the various metal and non-metal ions, the cation (Fe³⁺) and anion (I⁵⁺) ions were selected for doping in TiO₂. The above elements have gained considerable attention as doped materials. The reason for Fe³⁺ doping are: First, d-shell electronic configuration of Fe³⁺ ion is half-filled which can inhibit the recombination of photo-induced electron-hole pair by capturing the photogenerated electron (Wang et al. 2000; Choi et al. 1994; Hoffmann et al. 1995). Second, Fe³⁺ (0.64 Å) and Ti⁴⁺ (0.68 Å) have almost identical ionic radius so; the Fe³⁺ ion can be easily incorporated into the TiO₂ lattice (Khan and Swati 2016). The reason of I⁵⁺ doping into TiO₂ is that it can shift the photoresponse of TiO₂ from UV to visible region and lowers the band gap energy of TiO₂ (Hong et al. 2005; Su et al. 2008). Further, the I⁵⁺ has ability to replace the lattice titanium and can create Ti³⁺ ions due to close ionic radii of I⁵⁺ and Ti⁴⁺ ions which increases the activity of the TiO₂ photocatalysts (Hong et al. 2005; Su et al. 2008).

The photocatalytic process needs a photocatalytic reactor to carry the photocatalytic reaction. Many photochemical reactors (UV, visible and UV-vis) have been fabricated by researchers to accomplish their respective photocatalytic processes (Ray and Beenackers 1998; Bouchy and Zahraa 2003; Abhang et al. 2011). These photochemical reactors were used to determine the activity of photocatalysts by kinetic studies in the terms of pollutants degradation rate (Natarajan et al. 2011; Sarkar et al. 2012). In present study, two types of reactors namely UV photochemical reactor (UV-PCR) and open pan reactor (OPR) were

adopted for the photodegradation study of the dye in the presence of three kinds of light (UV, visible and sunlight).

In present work, citric acid assisted undoped, cation (Iron) doped TiO₂ and anion (Iodine) doped TiO₂ photocatalysts were synthesized via sol-gel route. Addition of citric acid in the synthesis process has a unique benefit in ignition step since citric acid acts as a complexing agent which produces a complex with cations and provides the fuel for combustion.

Based on above literature following objectives were set for the present research work.

1.5 Objectives and Approach

The objective of the present investigation is to evaluate effect of anions and cations on the photocatalytic efficiency of TiO₂ for the degradation of dye (Direct Blue-199) from carpet industry waste water.

- Synthesis of citric acid assisted undoped, cation (Iron) doped TiO₂ and anion (Iodine) doped TiO₂ photocatalysts by sol-gel method.
- Photocatalytic degradation of dye (Direct Blue 199) from its simulated dye solution and real industrial wastewater using the synthesized photocatalysts in UV photochemical reactor and open pan reactor in sunlight.
- Determination of dye degradation rate in photocatalytic process by kinetic studies in both reactors.
- Regeneration of used photocatalysts and determination of its photocatalytic activity in terms of the dye degradation.
- Comparison among photocatalysts (undoped TiO₂, Fe/I doped TiO₂ and Aeroxide P-25) for dye degradation.

1.6 Systems

A system represents a combination of one photocatalysts, one reactor (UV-PCR or OPR), one light source (UV, Visible or sunlight) and a known concentration of simulated dye solution (50, 100, 200 and 300 ppm) or industrial wastewater.

For better understating of the kinetic studies of the dye by the synthesized anion and cation doped TiO₂ photocatalysts in both reactors, the photodegradation experiments are divided into following systems (Table 1.1):

Table 1.1: System numbering for kinetic study.

Light source	UV		Sunlight	Light source	UV		Sunlight
	Reactor		Reactor		Reactor		Reactor
Photocatalyst	GT	QT		Photocatalyst	GT	QT	
Undoped TiO ₂	1	12	23	Ti _{0.99} I _{0.01} O ₂	34	44	54
Ti _{0.99} Fe _{0.01} O ₂	2	13	24	Ti _{0.98} I _{0.02} O ₂	35	45	55
Ti _{0.98} Fe _{0.02} O ₂	3	14	25	Ti _{0.97} I _{0.03} O ₂	36	46	56
Ti _{0.97} Fe _{0.03} O ₂	4	15	26	Ti _{0.96} I _{0.04} O ₂	37	47	57
Ti _{0.96} Fe _{0.04} O ₂	5	16	27	Ti _{0.95} I _{0.05} O ₂	38	48	58
Ti _{0.95} Fe _{0.05} O ₂	6	17	28	Ti _{0.94} I _{0.06} O ₂	39	59	59
Ti _{0.94} Fe _{0.06} O ₂	7	18	29	Ti _{0.93} I _{0.07} O ₂	40	50	60
Ti _{0.93} Fe _{0.07} O ₂	8	19	30	Ti _{0.92} I _{0.08} O ₂	41	51	61
Ti _{0.92} Fe _{0.08} O ₂	9	20	31	Ti _{0.91} I _{0.09} O ₂	42	52	62
Ti _{0.91} Fe _{0.09} O ₂	10	21	32	Ti _{0.90} I _{0.10} O ₂	43	53	63
Ti _{0.90} Fe _{0.10} O ₂	11	22	33				

1.7 Scope of the work

The doping was carried for both Fe³⁺ and I⁵⁺ for 1 to 10% only.

Photocatalytic processes for degradation of any pollutant in water would be more economical if the applied photocatalyst can be regenerated. Few studies over the regeneration of used catalysts researcher have been reported for the TiO₂ based catalysts (Wang et al. 2019; Miranda-García et al. 2014). So, in the present study,

used anion and cation doped TiO₂ photocatalysts were regenerated. The regenerated catalysts were reused five times and their photocatalytic activity was determined in terms of the dye degradation.

The performance of synthesized undoped and doped TiO₂ photocatalysts was compared with Aeroxide (Degussa) P-25 TiO₂ nanoparticles supplied by Sigma Aldrich for photodegradation of the dye.