

CHAPTER-2

BACKGROUND AND PREVIOUS RESEARCHES

This chapter has a summary of literature reported about dyes, classification of dyes, TiO₂ photocatalysts, methodologies for synthesis of TiO₂ photocatalysts and application of TiO₂ photocatalysts.

2.1 Introduction

At present, there are more than 1,00,000 dyes available commercially and over 1 million tons dyes are produced per year (Ajmal et al. 2014). In India alone, dyestuff industries produce around 60,000 metric tons of dyes, which is approximately 6.6% of total colorants used worldwide. The largest consumer of the dyes are the textile industries accounting for two-third of the total production of dyes (Patra 2003). Besides textile industries, carpet industries are also a big consumer of dyestuff. In India, carpet industries are clustered in Bhadohi, Uttar Pradesh. These carpet industries discharge huge amount of dye-loaded water in waterbodies. The significant use of dyes by various industries is causing severe damage to the environment and human life due to its non-biodegradability and high toxicity.

In India, dye workers are at higher risk of tumors. Deaths amongst factory workers from several cancers, cerebrovascular disease, and lung disease are significantly 40 times higher, for same diseases than in the general population (Alwan 2011). Therefore, the removal/reduction of dye from the industrial effluent/water becomes necessary before discharge. So, before starting our discussion regarding removal of dye from waterbody, a brief literature about dye and its types given here.

2.2 Dye

Dye is a colored substance that has an affinity to the substrate at which it is being applied. Langhals (2004) defined the dye as “Dye is an organic or inorganic compound that imparts colour to substances such as textile, carpet, leather, paper, plastic materials or wax either in solution or dispersion”. A dye molecule has two components, chromophores and auxochromes. Chromophores are responsible for producing the colour whereas auxochromes supplement the chromophore and render the molecule soluble in water and enhance affinity (to attach) toward the fibers.

2.3 Classification of dyes

Dyes can be classified in several ways such as source of materials, chemical compositions, structure, solubility and application. Though, structural classification of dye is most appropriate since group and characteristics of dye can be readily identified. Moreover, based on chemical structure colour index number (C.I. number) is assigned to a dye. A dye with C.I. number has some basic details such as name, purity, chemical composition and price etc. Based on uses, dyes are classified as given below (Hunger et al. 2003; Christie 2007).

2.3.1 Acidic dyes

Acidic dyes are highly water-soluble dyes and have better light fastness. They contain sulphonic acid groups, which are usually present as sodium sulphonate salts. These increase solubility of dye in water. The principle chemical classes of these are azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso. These dyes are used to colour nylon, wool, silk, modified acrylics, paper, leather, food and cosmetics.

2.3.2 Vat dyes

Vat dyes are insoluble in water but may solubilize by alkali reduction with sodium dithionite (a reducing agent) in the presence of sodium hydroxide. These dyes have principal chemical class containing anthraquinone (including polycyclic quinones) and indigoids. Vat dyes have multi-ring systems which help to strengthen the Van der-Waals forces between dye and fiber. These dyes are used for colouring cotton, cellulosic fibers, rayon and wool.

2.3.3 Basic dyes (cationic dyes)

Basic dyes are water-soluble dyes yield coloured cations in solution and that is why these are known as cationic dyes. These dyes possess cationic functional groups in their structure, such as $-NR_3^+$ or $=NR_2^+$. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine. These are used to colour paper, polyacrylonitrile, modified nylons, modified polyesters and medicines.

2.3.4 Reactive Dyes

Reactive dyes have chromophoric group such as azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc. These dyes form a covalent bond with fiber. The covalent bonds that attach reactive dye to natural fibers make them most permanent dyes. Reactive dyes, such as Procion MX, Cibacron F and Drimarene K are very easy to use because the dye can be applied at room temperature. Reactive dyes are the best choice for dyeing cotton and other cellulose fibers at home or in the art studio.

2.3.5 Disperse dyes

Disperse dyes have low solubility in water, but they can interact with the polyester chains by forming dispersed particles. The general structure of disperse dyes is planar and non-ionic with attached polar functional groups like $-\text{NO}_2$ and $-\text{CN}$. The shape makes it easier for the dye to slide between the tightly-packed polymer chains and the polar groups improve the water solubility, improve the dipolar bonding between dye and polymer and affect the colour of the dye. They generally contain azo, anthraquinone, styryl, nitro, and benzodifuranone groups. Main use of these dyes is to colour polyesters and they find minor use dyeing cellulose acetates, acrylic fiber and polyamides.

2.3.6 Solvent dyes

Except water, these dyes are solvent soluble and these are generally non-polar or little polar i.e. they do not have sulfonic acid, carboxylic acid group in their structure. Sudan III (solvent red 23), Sudan IV (solvent red 24), Sudan black B (solvent black 3) and oil red O (solvent red 27) are commonly known solvent dyes. The principal chemical classes are predominantly azo and anthraquinone. Solvent dyes are used for plastics, gasoline, lubricants, oils, and waxes.

2.3.7 Direct dyes

The name 'direct dye' alludes to the fact that these dyes do not require any form of 'fixing'. These dyes are mostly polyazo compounds, along with some stilbenes, phthalocyanines and oxazines. They also have sulphonate functionality, which improves its solubility in water. The main problem with direct dyes is their lack of fastness during washing. However, they are cheap, so they are popular for items which are less likely to require fastness during washing. Wash fastness may

be improved by the application of such direct dyes which contain $-NH_2$ functional groups as well as sulphonate groups. These dyes are used in the dyeing of cotton and rayon, paper, leather and nylon. They have high affinity for cellulosic fibers.

The dyes mentioned above are used frequently by the various industries like textile, carpet, paint, paper, lather, food and medicine etc. which discharge a huge amount of dye-loaded wastewater. So, an efficient and cheap technique is required to remove/reduce the dyes from the waterbody and make dischargeable water under permissible limit of environmental norms.

Several methods have been investigated to treat dye contaminated wastewater such as Biodegradation, aerobic degradation, anaerobic degradation, electrochemical methods, adsorption, ozonation, coagulation and flocculation, filtration, ion exchange and advanced oxidation processes (photodegradation) etc. Among these methods, advanced oxidation processes (AOPs) have been found to be the best method for the degradation of dye since it is a clean and economical technique that oxidize the dyes by facilitating the highly oxidizing free radicals OH^\bullet and anions (O^{2-} and OH^-) which break dyes in simpler compounds such as H_2O , CO_2 etc. (Amreetha et al. 2016).

Many photocatalysts such as SiC (Yamashita et al. 2007), CdSe (Andrew Frame et al. 2008), TiO_2 (Schneider et al. 2014), GaP (Zeng et al. 2014), GaAs (Qiu et al. 2015), ZnO (Chen et al. 2017), CdS (Cheng et al. 2018) etc. are reported and used in AOPs for degradation of dye. Among these photocatalysts, TiO_2 is one of the most suitable photocatalysts due to its unique photoresponse towards UV/vis light. A brief literature regarding TiO_2 and its synthesis methods are given below.

2.4 TiO₂ photocatalysts

TiO₂ has got great attention from last three decades due to its high physicochemical stability, nontoxicity, and low cost (Liang et al. 2011; Chen et al. 2012). The physicochemical stability and activity of TiO₂ depends on its morphology and crystalline phase. There are three different phases of TiO₂, namely anatase, rutile and brookite (Fujishima et al. 2008). Both anatase and rutile phase have tetragonal crystal structure while brookite has orthorhombic crystalline structure (Fig 2.1). Thermodynamically, rutile is the most stable phase of the TiO₂, whereas anatase and brookite are metastable. At high temperature, anatase and brookite phase of TiO₂ can be converted into rutile phase (Hanaor and Sorrell 2011). Anatase phase has only one indirect band gap of 3.2 eV, whereas rutile has both direct and indirect band gap of 3.06 and 3.10 eV, respectively (Ren et al. 2007). Higher band gap energy represents better electron transport rate. The stability of TiO₂ depends on its particles size (Ranade et al. 2002). Rutile phase shows more stability for larger particle size whereas anatase is more stable for smaller one. Rutile is most stable phase of TiO₂ beyond 35nm while anatase phase shows stability below 11nm (Zhang and Banfield 2000). The brookite phase has stability between the ranges of 11-35 nm (Zhang and Banfield 2000). Brookite phase of TiO₂ is very rare and it is difficult to synthesize.

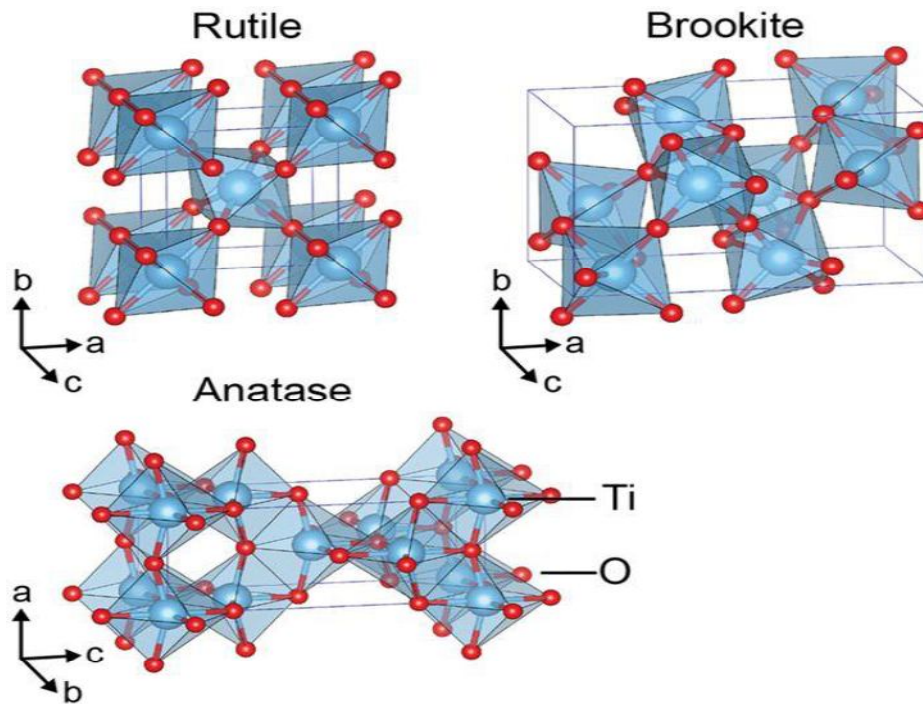


Fig 2.1 Crystal structures of TiO₂ rutile (tetragonal), brookite (orthorhombic) and anatase (tetragonal) polymorphs (Haggerty et al. 2017).

All the three phases of TiO₂ (anatase, rutile and brookite) have three crystal faces. The faces (101), (001) and (100) are the faces of anatase. The first two of them, i.e. (101) and (001) are low energy surface. These faces very are common for natural crystals (Hengerer et al. 2000; Liang et al. 2001). The face (101) is most popular face of anatase nanocrystal while the surface (100) is very rare (Ruzycki et al. 2003).

The crystal faces (110), (100) and (001) belong to rutile structure. In this phase also first two, i.e. (110) and (100) are low in energy surface. Thermally, the face (110) is most stable while (001) is less stable and restructuring occurs above 450°C (Burnside et al. 1998).

The three crystal faces of brookite are (010), (110) and (100). Among these faces, the face (010) has low stability, whereas (100) is highly stable (Beltrán et al. 2006).

Presently, TiO₂ has wide application in various products such as electro-chemical electrodes (Morozova et al. 2012), paint-pigments (Al-Kattan et al. 2013), sunscreen lotions (Jacobs et al. 2010), capacitors (Hudec et al. 2011), solar-cells (Burke et al. 2008) and toothpaste (Rompelberg et al. 2016) etc.

TiO₂ morphologies include many nanostructure like nano-particles (Reyes-Coronado et al. 2008), nano-tubes (Cheng et al. 2013), nano-wires (Wang et al. 2011a) nano-rods (Zhang et al. 2001) and mesoporous structure (Wang et al. 2011b). Various routes have been reported for the synthesis of TiO₂ based photocatalysts such as sol-gel (Venkatachalam et al. 2007; Yang et al. 2006) chemical vapour deposition (Lee et al. 2011; Xie et al. 2009) hydrothermal (Pavasupree et al. 2006; Thapa et al. 2012) and micro-emulsion route (Hosseini Zori 2011; Li and Wang 1999) etc. In following paragraphs, literature regarding the synthesis technique is briefly discussed.

2.5 Synthesis technique of TiO₂ nanoparticles

2.5.1 Biological method

In this technique, nanoparticles are synthesized with the help of micro-organisms including bacteria (*Pseudomonas deceptionensis*, *Weissella oryzae*, *Bacillus methylotrophicus*, *Bhargavaea indica* etc.), fungi (*Neurospora crassa*, Actinomycetes) and yeasts (*Yarrowia lipolytica* NCYC 789, *Rhodospiridium diobovatum*, Extremophilic yeast) etc. Micro-organisms have the ability to reduce metal salts to metal nanoparticles with a narrow size distribution and less polydispersity due to various reductase enzymes (Singh et al. 2016).

Jha et al. (2009) reported a biosynthesis of TiO₂ nanoparticles by a reproducible microbes (*Lactobacillus* sp. and *Sachharomyces cerevisiae*). The synthesized nanoparticles had particles size range from 8-35 nm.

Kirthi et al. (2011) reported the TiO₂ nanoparticles preparation using bacterium *Bacillus subtilis*. Pure forms of TiO₂ nanoparticles were produced by abundantly available micro-organism. The sizes of synthesized nanoparticles were 66-77 nm and shape was spherical.

Dhandaoani et al. (2012) reported the microbial-mediated synthesis of TiO₂ nanoparticles by *Bacillus subtilis* and used for destruction of bacteria within a biofilm through H₂O₂. The synthesized photocatalysts had anatase phase with particle size range from 10-30 nm.

2.5.2 Hydrothermal method

Hydrothermal method is used to synthesize nanoparticles in the presence of water at high temperature and pressure from the substances which are insoluble in water at ordinary temperature and pressure (<100°C and 1 atm). TiO₂ nanoparticles which are synthesized by this route are influenced by various parameter like temperature, pressure, experimental duration, solvent type, pH and the initial charge of the product.

Qian et al. (1993) reported the preparation of TiO₂ nanoparticles by hydrothermal method. In this study, TiO₂ nanoparticles were synthesized in two steps. In primary step, a gel of TiO₂H₂O was formed by the oxidation of titanium with an aqueous solution of H₂O₂ which was followed by hydrothermal treatment of the gel under various condition (with distilled water and with nitric acid) at 140°C to get TiO₂ nanoparticles. Hydrothermal treatment of the gel with distilled water gave anatase

phase of TiO₂ with average particles size of 10 nm × 3 nm while with nitric acid, rutile phase with average particles size of 30 nm × 5 nm were obtained.

Wu et al. (2011) reported the synthesis of various TiO₂ structure like nano-rods, nano-flower and nano-wire etc. via alkaline hydrothermal method. The synthesized nanostructures had anatase phase of TiO₂ at 600°C. The prepared nanomaterials were used for photodegradation of Rhodamine B in water.

Thapa et al. (2012) reported the synthesis of TiO₂ nanoparticles by hydrothermal method for photodegradation of various dyes like Orange II, Methyl Orange and Rhodamine B. The synthesized nanoparticles have anatase phase with average particles size of 12 nm with indirect band gap of 3.09 eV.

Li et al. (2014) reported the synthesis of iodine doped TiO₂ photocatalysts by hydrothermal method. An excellent photoresponse and high photocatalytic activity was observed after the iodine doping TiO₂. The synthesized photocatalysts were used for photodegradation of Methylene Blue and found that the degradation followed pseudo-order-first kinetics with the degradation rate constant of $7.92 \times 10^{-3} \text{ min}^{-1}$.

2.5.3 Micro emulsion technique

In this technique, two phases consisting of two immiscible liquids are mixed and stabilized with the help of a surfactant and with or without a cosurfactant. Micro-emulsions are thermodynamically unstable and have droplets in the range of 5-100 nm. Depending on the properties of the surfactant, micro-emulsions can be made as water-in-oil (W/O) or O/W. In water-in-oil (W/O) micro-emulsions, droplets of water are surrounded by a continuous oil phase whereas oil-in-water (O/W) micro-emulsions, oil droplets are surrounded by

an aqueous phase. In both combinations, the droplets are stabilized due to the presence of surfactants and cosurfactant since they act to reduce the interfacial tension between the two phases to almost zero. The stability of micro-emulsion depends upon the particle size, particle-particle interaction and particle-water interaction.

Deosola and Vallauri (2009) reported the synthesis of TiO₂ nanoparticles by water in oil (W/O) micro-emulsion technique. Both phase of TiO₂ (anatase and rutile) were obtained with particles size range from 10-100nm. The shape and size of the synthesized nanoparticles were controlled by parameters such as emulsifier content, water/oil weight ratio, stirring rate and concentration of Ti⁴⁺ in the aqueous phase. Zubieta et al. (2011) reported the preparation of TiO₂ nanoparticles by reverse micro-emulsion technique. The synthesized photocatalysts had mix phase (anatase and rutile) of TiO₂ and it was used to degrade Methylene Blue dye at different pH. The results showed that degradation of Methylene Blue follow the pseudo-second-order kinetics and maximum degradation was achieved at 10 pH.

Sanchez-Dominguez et al. (2015) reported the synthesis of Zn doped TiO₂ nanoparticles by oil-in-water (O/W) micro-emulsion method and found that the synthesized nanoparticles had 100% anatase phase of TiO₂ with particles size lower than 20nm. In 5 h under irradiation, 82-93% degradation of phenol was reported by the synthesized nanoparticles.

2.5.4 Co-precipitation method

Co-precipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening, and/or agglomeration processes. The formation of precipitate from a homogeneous liquid phase occurs due to physical change in

temperature, pH and reactants concentration etc. The composition of precipitate depends on the differences in solubility between component and reaction. In the typical co-precipitation reaction, two or more water-soluble salts are used that react with each other. One or more salts that are water-insoluble are formed in the liquid phase. When the concentration of this product crosses the solubility product value in the reaction media, precipitation takes place (Chaudhuri et al. 2012). Slow precipitation form small particles, whereas fast precipitation form large particles of the photocatalysts.

Namin et al. (2008) reported the preparation of TiO₂ nanoparticles by precipitation of aqueous TiCl₄ solution with NH₄OH as precipitating agent. Both phases of TiO₂ (anatase and rutile) were synthesized by this technique between the calcination range from 400-1000°C for 4h. Anatase phase with particles size of 4.5 nm was achieved up to 600°C.

Anandan et al. (2013) reported the synthesis of N doped TiO₂ photocatalysts by co-precipitation method and used it for photodegradation of plasticizer (di-ethylhexyl phthalate) by coupling with ozone and visible light from the waterbody. The synthesized photocatalysts had pure anatase phase with lower band gap energy (2.63 eV) and average particles size of the synthesized photocatalysts was ~13 nm. Buraso et al. (2018) reported the synthesis of TiO₂ photocatalysts by precipitation method using titanium (IV) isopropoxide as a precursor and used for degradation of Methyl Orange. The crystallite size and crystallinity of the synthesized photocatalysts increases (11.3 to 27.4 nm) with increasing the calcination temperature. The anatase phase of synthesized photocatalysts was achieved between temperature ranges of 400-600°C after that anatase converted to rutile

phase at 700° C. The kinetic study of dye (Methyl Orange) degradation with synthesized photocatalysts followed the pseudo-first order kinetics.

2.5.5 Spray pyrolysis

It is a process in which a nano-structure is synthesized when solution of a precursor is sprayed or injected onto the hot substrate in the furnace using a nano-porous nebulizer, leading to decomposition of the precursor to form the final desired material on the substrate. The nanostructural parameters such as particle size, shape and thickness are controlled by controlling the spray energy (gas inlet to nebulizer, gas flow pressure), droplet size of the precursors, duration of spray, distance between the spray gun and the substrate, temperature of the furnace and substrate using manual or automated control systems. If the above parameters can be maintained constantly, then this technique is most suitable for preparation of nano-thin films and clusters at large scale (Rane et al. 2018).

Wang et al. (2005) reported the preparation of TiO₂ nanoparticle directly from various precursor namely Titanium Tetraisopropoxide (TTIP), water-soluble titanium source TC-300 and TC-400 by low-pressure spray pyrolysis technique. Three solvents (water, ethanol and nitric acid) were used for synthesis of the nanoparticles where ethanol dramatically improved the preparation of nanoparticles in comparison to water/nitric acid since it has lower surface tension and lower boiling point. The synthesized nanoparticles has crystallite size about 10 nm with anatase phase.

Haugen et al. (2011) reported the synthesis of TiO₂, TiO₂/Ag and TiO₂/Au photocatalysts by spray pyrolysis method using titanium citrate complex and titanium oxalate as precursor. The crystallite size range from 12 to 120 nm, with phase compositions from 10 to 100% rutile were obtained by subsequent heat

treatment. The synthesized photocatalysts were used to oxidize Methylene Blue under UV-irradiation.

Matsubara et al. (2016) reported the synthesis of TiO₂ powder by double-nozzle electro-spray pyrolysis method and used for H₂ evolution from water splitting reaction. Aqueous solution of titanium (IV) bis (ammonium lactato) dihydroxide (TALH) was used as the precursor. The TiO₂ powder was synthesized with and without ultra-sonication. Characterization results shows that both type of particle had anatase phase but had different shape and size. The TiO₂ powder which was synthesized with ultra-sonication had irregular shape with particles range from 40 nm-10 μm whereas the synthesized powder without ultra-sonication had spherical shape with particle range from 100 nm-7 μm.

2.5.6 Sol-gel method

Sol-gel route is the most appropriate route for the synthesis of TiO₂ photocatalysts since photocatalysts produced via this route have high crystallinity, high purity, better quality and homogeneity at lower processing temperatures than traditional powder synthesis techniques. Sols are dispersions of colloidal particles in a liquid whereas gel is an interconnected, rigid network with pores of sub-micrometer dimensions and polymeric chains whose average length is greater than a micrometer. Sol-gel processing enables the control of the structure of a material on a nanometer scale from the earliest stages of processing due to mixing in atomic scale.

This method is based on inorganic polymerization reaction. In sol-gel method, four steps are involved.

1. Hydrolysis of precursors.
2. Condensation (gel formation).
3. Drying.
4. Calcination.

In hydrolysis step, precursors dissolved in water or alcohol. Acid or base also helps in the hydrolysis of the precursor. In condensation step, gel is formed due to continuous mixing of precursor and solvent. In drying step, solvent is removed from the gel at any specific temperature while organic precursor decomposes at higher temperature in calcination step. In sol-gel method, the size of nanoparticles can be tuned by controlling the solution composition, pH and temperature. High product homogeneity, good control over size and shape, formation of sol and gel at ambient temperature are the main advantage of sol-gel technique.

Sugimoto et al. (2003) reported the synthesis of anatase phase TiO_2 nanoparticles via sol-gel method. Shape of the synthesized photocatalysts were controlled from cuboidal to ellipsoidal by Triethanolamine (TEOA) and Diethylenetriamine (DETA) at 11 and 9.5 pH, respectively.

Xin et al. (2005) reported the preparation of Ag-doped TiO_2 photocatalysts by sol-gel method using titanium butoxide as starting material and determine its photocatalytic activity by photodegradation of Rhodamine B solution. It was reported that Ag-doping in TiO_2 reduces the combination of photogenerated electron-hole pairs and enhances the activity of TiO_2 photocatalysts.

Hung et al. (2008) reported the synthesis of TiO_2 and Fe doped TiO_2 photocatalysts by sol-gel method using titanium-isopropoxide as precursor and used for

photodegradation of 1, 2-dichloroethane. A mixture of anatase and rutile phase was obtained with anatase phase being dominant. The synthesized photocatalysts have spherical shape with 10-20 nm crystallite size.

Sergio Valencia (2010) reported the synthesis of TiO₂ nanoparticles using tetraisopropyl orthotitanate as precursor by sol-gel method followed by hydrothermal treatment. The synthesized photocatalysts had anatase phase with band gap energy of 3.27 eV and it was used to degrade Methyl Orange.

Hussain et al. (2010) reported the synthesis of 10-20 nm TiO₂ nanoparticles by sol-gel process in vortex reactor under optimize operating condition. The prepared nanoparticles had majority of anatase phase with small rutile phase, higher BET surface area, confined band gap energy and higher OH group. The activity of the synthesized nanoparticles was compared with P-25 in the respect of oxidation of ethylene and found that the synthesized nanoparticles have better activity than P-25.

Behnajady et al. (2011) prepared anatase TiO₂ nanoparticle by sol-gel method using titanium (IV) isopropoxide as precursor under different synthesis condition such as solvent percent, water percent, reflux time, reflux temperature, sol drying method and calcination temperature. The synthesized photocatalyst was used to degrade Acid Red 27. The degradation results show that the activity of TiO₂ photocatalyst strongly depends on type of precursor, type of solvent and synthesis conditions.

Muneer et al. (2012) reported the synthesis of TiO₂ nanoparticles by sol-gel route using titanium-isopropoxide as precursor. A transformation of phase from anatase to rutile was observed above 500°C. The synthesized photocatalysts were utilized for degradation of chlorophenols. The degradation results reveal that 99% of

chlorophenols was degraded in 90 min and degradation of chlorophenols follow the pseudo-first order kinetics.

Abdulla et al. (2012) reported the synthesis of 1-10% Fe-doped TiO₂ nanopowder by sol-gel method using Titanium (triethanolaminate)-isopropoxide as precursor. Metallic Ag nanoparticles were successfully deposited on the surface of the synthesized nanopowder. Activity of the synthesized photocatalysts (Ag and Fe doped TiO₂) was determined through killing of cancer cell. The highest activity of the synthesized photocatalysts in terms of cancer cell killing was observed at 5%.

Perumal et al. (2014) reported the preparation of Fe²⁺ doped TiO₂ nanoparticles via sol-gel technique using titanium tetraisopropoxide as starting material. The synthesized photocatalysts have pure crystalline anatase phase with average particle size of 14nm and band gap energy of the synthesized photocatalysts was lowered from 3.2 eV to 2.8 eV.

Amreetha et al. (2016) reported the synthesis of C-N-S tri-doped TiO₂ nanoparticles by sol-gel method using titanium tetra-isopropoxide as precursor at different temperatures of 300, 400, 500 and 600°C. Thiourea was used as a compound source of elements C, N and S. An inhibition in phase transformation from anatase to rutile, lowering of band gap energy and enhancement in activity of TiO₂ was observed after the doping of C-N-S in TiO₂. In 180 min, 99% of dye (Rhodamine B) degradation was reported by the synthesized tri-doped nanoparticles.

Ali et al. (2017) reported synthesis of Fe doped (0, 3, 5, 7 and 10 mole %) TiO₂ via sol-gel technique using titanium tetraisopropoxide as precursor. Pure anatase phase with tetragonal crystal structure was found in the synthesized photocatalysts. The synthesized photocatalysts was used to degrade Methylene Blue under visible light

illumination where the highest photocatalytic activity was observed at 3% of dopant concentration.

Prajapati et al. (2017) synthesized the pristine and Fe doped (0.5, 1, 2, 3, 4 and 5 atom %) TiO₂ photocatalysts by sol-gel method using titanium isopropoxide as starting material. They reported that the crystallite size of the synthesized photocatalysts decreased exponentially with increase in Fe concentration. Moreover Fe concentration in TiO₂ also decreases its band gap energy from 3.2 to 2.2 eV.

A brief literature regarding synthesis of TiO₂ photocatalysts by sol-gel method with different precursor and fuels is given in Table 2.1.

Table 2.1: TiO₂ nanoparticle by sol-gel method with different precursor and fuels.

Precursor	Solvent	DRS (eV)	XRD	SEM	TEM (nm)	Application	Ref.
Titanium isopropoxide	Acetylene black	Anatase	15-20	Dye Solar Cells	(Han et al. 2008)
Titanium dioxide	Trisodium citrate	3.0	Anatase	Spherical shape	86	(Hema et al. 2012)
Titanium isopropoxide	Methanol	3.26	Anatase and	Tetragonal shape	50-60	NH ₃ monitoring	(Pawar et al. 2012)
Titanium tetraisopropoxide	Ethyl alcohol	Anatase	Spherical shape	6	(Thangavelu et al. 2013)
Titanium Tetraisopropoxide	Ethanol	3.2	Anatase	Spherical spongy shape	(Devi et al. 2014)
Titanium tetra chloride	Ethanol	3.54	Anatase	Polygonal structure	36.06±2.0	(Hayle 2014)
Titanium dioxide	Acetic acid	2.63	Anatase	11.416	(Devi et al. 2015)
Titanium tetrachloride	Ethanol	3.52	Anatase and Rutile	spherical spongy shape	20	antimicrobial activity	(Haider et al. 2017)
Titanium tetraisopropoxide	Ethanol	Anatase and Rutile	Fine powder with irregular shape	180	(Araoyinbo et al. 2018)
Titanium tetraisopropoxide	2-propanol	3.2	Anatase and Brookite	spherical shape	20 ± 5	NOx reduction	(Giampiccolo et al. 2019)

Regeneration of used photocatalysts

Regeneration of the photocatalysts make the photocatalysis process more economical. Some researchers regenerated the used photocatalysts and checked their activity through various applications.

Gandhi et al. (2012) reported the degradation of phthalic acid with the help of TiO₂ photocatalysts. The study also extended up to the deactivation and regeneration of the photocatalysts. Adsorption of organic species (carboxylic acid compounds) on the surface of the catalyst was found the reason behind the deactivation of the catalysts, not the pore blockage. To regenerate the photocatalysts various regeneration method such as washing with solvents, hydrogen peroxide (H₂O₂) and thermal treatment were tried. It was found that regeneration with H₂O₂ has better ability than others to restore the activity of the photocatalysts.

Wu et al. (2015) reported the regeneration of TiO₂ photocatalysts and check its activity and deactivation by using Congo Red dye. The used photocatalysts were regenerated at different temperature such as 250, 350, 450 and 550°C. Among the above temperature, 450°C was observed as optimum temperature for regeneration of the photocatalysts and restored the photocatalytic ability of TiO₂ by 81.4%.

Wang et al. (2019) reported the regeneration of deactivated P-25 photocatalysts by sulphur poisoning through four regeneration methods such as water washing, H₂SO₄ washing, NaOH washing, and thermal treatment. Out of above regeneration method, water washing is the simplest and effective method to regenerate the catalyst.

Conclusion form literature search

- Sol-gel method is suitable for my research to produce TiO₂ photocatalysts.
- Dye can be photodegraded by TiO₂ based photocatalysts.
- The activity of TiO₂ can be enhanced by doping of metals and non-metals.

Technical gap

- Citric acid assisted synthesis of Fe doped TiO₂ and I doped TiO₂ photocatalysts by sol-gel route has not been reported.
- Study on regeneration of Fe doped TiO₂ and I doped TiO₂ photocatalysts are rare.