Chapter 5

Application of zinc orthotitanates as photocatalyst

5.1 Introduction

Zn$_2$TiO$_4$ alias zinc orthotitanate (ZOT) is the stable phase of ZnO-TiO$_2$ system which has been employed for various applications like microwave dielectrics, pigment, gas sensing material, antistatic films, anti reflecting coating in solar cells.$^{1,2,3}$ Zn$_2$TiO$_4$ have been used as photocatalyst for degradation of organic compounds and water splitting under UV light irradiation.$^4$

Dyes are manufactured on large scale all over the world and widely used in industries like textile, paper, cosmetic, leather, pharmaceutical, nutrition industries. Major amount of dyestuff has been discharged from textile industry. Near about 15% dye has been lost during dyeing.$^5$ Trace amount of dye present in effluent causes serious problems to aquatic life and disorder in human health.

Azo dyes produce toxic aromatic amine and have harmful environmental effects and they are not biodegradable since they have very low degradation rate by aerobic treatment process. Many dye molecules are resistant to biological degradation.$^6$

Acid Orange -8(AO-8) is water soluble dye containing mono azo group and have been widely used for dying silk fibre. It is toxic and carcinogenic in nature hence it is essential to take systematic step for the removal or degradation of AO-8. Preeti Mehta et. al. studied photocatalytic degradation of AO-8 using TiO$_2$ under visible
light irradiation at various pH and reported highest activity at concentration $3 \times 10^{-5}$ M and pH 9.\(^7\)

Rhodamine B (RH-B) is a xanthene dye widely used as colorant in textile and water tracer fluorescent. RH-B is harmful if swallowed by human being and animals and causes irritation to skin, eyes and respiratory track. The carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity towards human and animals have been experimentally proven.\(^8\)

H\(_2\)S is harmful to human health as well as environment and one of the pollutants in waste water as well as in air. Various techniques have been employed for removal of H\(_2\)S form water like adsorption of H\(_2\)S on Zn\(_2\)TiO\(_4\), Claus process, photocatalytic degradation etc. Various researches have attempted to remove H\(_2\)S from aqueous solution by photocatalytic degradation which generates clean and eco friendly hydrogen fuel using sulphides as photocatalyst. Use of oxides for the same purpose has been less explored.

Photocatalytic degradation of AO-8 is rarely studied and observed that photocatalytic activity of ZnO towards degradation of AO-8 is less than TiO\(_2\) under visible light irradiation.\(^9\)

Many researchers have attempted photocatalytic degradation of Rhodamine-B dye by using doped and undoped ZnO and TiO\(_2\),\(^{10,11,12}\) and other photocatalysts.\(^{13,14}\) However, very limited study was performed for photocatalytic degradation by Zn\(_2\)TiO\(_4\). Phase pure Zn\(_2\)TiO\(_4\), synthesized by solid state reaction route was found to be inactive towards photocatalytic degradation of Methyl Orange under UV region.\(^{15}\) Zn\(_2\)Ti\(_{1-x}\)Fe\(_x\)O\(_4\) visible light photocatalyst was employed for H\(_2\) generation from water- methanol solution under visible light radiation.\(^{16}\) While, thin film of Zn\(_2\)TiO\(_4\) –ZnO was found to be active for Photocatalytic degradation of Methylen Blue under UV region.\(^{17}\) It is reported that Photocatalytic activity towards degradation of Acid Orange-2 has been decreased with increase in content of Zn\(_2\)TiO\(_4\) in the composite of ZnO-TiO\(_2\)– Zn\(_2\)TiO\(_4\) when irradiated at 365 nm radiation.\(^{18}\)

Zn\(_2\)TiO\(_4\) has been effectively used for removal of multiple constituents of hot stream gases being an efficient adsorbent of gases at high temperature.\(^{19}\) The regeneration of Zn\(_2\)TiO\(_4\) was found to be fast with negligible loss as well as its
thermal stability is higher than single metal oxides.\textsuperscript{20} Shiqiang Hao et. al. reported surface reaction of H\textsubscript{2}S on 010 surfaces of Zn\textsubscript{2}TiO\textsubscript{4} on the basis of DFT calculation and showed that 010 surface is having a large fraction of the total surface area of Zn\textsubscript{2}TiO\textsubscript{4} and having two distinct terminations one oxygen rich and other metal rich. H\textsubscript{2}S forms bond with metal, hence adsorbed on 010 surfaces which is oxygen as well as metal rich.\textsuperscript{21} The adsorption energy of H\textsubscript{2}S at the Zn site is -0.75 eV so adsorbed effectively at Zn sites leading to dissociation of H\textsubscript{2}S due to low adsorption energy. These theoretical findings suggest that Zn\textsubscript{2}TiO\textsubscript{4} can be used as visible light photocatalyst for dissociation of H\textsubscript{2}S to generate H\textsubscript{2}, if band gap tuned to the visible region. Zn\textsubscript{2}TiO\textsubscript{4} being good adsorbent for H\textsubscript{2}S and having band gap around 3.1 eV could be candidate for photocatalytic degradation of H\textsubscript{2}S. Hence, zinc orthotitanates may have good potential as photocatalyst for dye degradation and water/ H\textsubscript{2}S splitting. These findings led us to attempt H\textsubscript{2}S splitting using zinc orthotitanates.

Considering the stability of the spinel Zn\textsubscript{2}TiO\textsubscript{4} there is wide scope to doped Zn\textsubscript{2}TiO\textsubscript{4} as a visible light active photocatalyst for dye degradation and more significantly for H\textsubscript{2} production. In view of this, we have made attempt to synthesize nanostructured spinel zinc orthotitanates and their photocatalytic study.

In this chapter, photocatalytic degradation of Acid Orange -8 and Rhodamine –B dyes under sunlight and H\textsubscript{2} generation via H\textsubscript{2}S splitting under visible light source have been studied. Zinc orthotitanates synthesized by combustion method are employed for H\textsubscript{2}S splitting to produce H\textsubscript{2}. Photocatalytic degradation of AO-8, RH-B and H\textsubscript{2}S splitting by zinc orthotitanates has been reported for the first time.

5.2 Experimental

5.2.1 Development of equipments for photocatalytic dye degradation and H\textsubscript{2}S splitting

The equipments required for photocatalytic reactor for dye degradation under sunlight, microscale H\textsubscript{2}S generator and gas measuring cylinder have been developed in the laboratory. The details are given in the results and discussion.
5.2.2 Photocatalytic dye degradation

Photocatalytic dye degradation was studied under the sunlight using photocatalytic reactor designed in our laboratory. The desired quantity of the photocatalyst was added in 40 ml aqueous solution of the dye (AO-8 and RH-B) and ultrasonically sonicated and magnetically stirred for 20 min in dark to establish adsorption-desorption equilibrium. The suspension was irradiated under sun light during 11.00 am to 3.00 pm in the month of March and April. Intensity of sunlight was recorded using Lux meter (Lutron, LX-107HA). Concentration of dye in the aqueous solution was measured by sampling small quantity of suspension at specific time interval. The solid catalyst was separated by centrifugation at 5000 rpm for 10 min. The concentration of dye was determined from absorbance at $\lambda_{\text{max}}$ of the Acid orange 8 (492 nm) and Rhodamine B (552 nm) using UV-Vis spectrophotometer.

The method employed for absorbance measurement has been illustrated in figure 5.1 and 5.2. Figure 5.1a and 5.2a shows the absorbance plots of the AO-8 and RH-B over the region 400-700 nm for photocatalytic degradation using Ag@Zn2TiO4 catalyst (10 mg).

![Graph of O.D. Vs \(\lambda\) for measurement of absorbance B) Samples of AO -8 withdrawn at regular time interval during degradation.](image-url)
**Figure 5.2:** A) Graph of O.D. Vs λ for measurement of absorbance  b) Graph of C/Co Vs time  B) Samples of RH-B withdrawn at regular time interval during degradation.

Figure 5.1b and 5.2b shows photograph of the samples of AO-8 and RH-B with drawn at regular time interval.

**5.2.3 Photocatalytic H₂S splitting for H₂ generation**

H₂S splitting was carried out on photocatalytic system developed in our laboratory (Figure 5.3) under visible light source 300 W (Lot Orel group, Europa, LSH302). The in-house designed photocatalytic system consist of H₂S gas generator, bubble trap, water jacketed photocatalytic reactor, H₂S gas trap and graduated H₂ gas measuring cylinder. 100 mg photocatalyst was uniformly mixed in 175 ml 0.25 N KOH by magnetic stirring followed by purging with Ar gas for about 15 min. Reactor was maintained at room temperature by continuous water circulation through water jacket surrounding the reactor. H₂S gas was prepared using microscale gas generator was bubbled into the suspension at the rate 2.0 mlmin⁻¹ for about 90 min for the purpose of saturation. Irradiation of the reactor started after the saturation of the suspension with H₂S. Gas generated was allowed to pass through H₂S traps charged with 50 ml 0.5 N NaOH to ensure the collection of pure H₂ gas. The H₂S flow rate at 2.0 ml min⁻¹ was maintained constant throughout the process carried out for 3 h. Volume of the gas generated was measured at suitable time interval. H₂ gas was immediately transferred into rubber bladder. H₂ gas evolved
was confirmed by GC analyses (Model : Shimadzu(GC-14B), MS- 5 °A Column , TCD, Ar carrier).

![Diagram of the setup](image)

**Figure 5.3: Set up for photocatalytic splitting of H$_2$S to produce H$_2$.**

Details of the parts of the set up are:

| A: Microscale H$_2$S gas generator | B: Bubble trap (water) |
| C: Trap to remove moisture (CaCl$_2$) | D: Reactor |
| E: Magnetic stirrer | F: Light source |
| G: H$_2$S trap (NaOH) | H: H$_2$S trap (NaOH) |
| I: Gas measuring cylinder | J: Beaker containing water |
| S1: Three way stop cock |

### 5.3 Results and Discussion

#### 5.3.1 Development of equipments

**5.3.1.1 Set up for photocatalytic degradation under sunlight**

A special apparatus (Figure 5.4) has been designed for photocatalytic degradation of organic dyes under sunlight. The apparatus consists of water jacketed 125 ml flat bottom flask and vertical water condenser. The purpose of this is to perform the photocatalysis at room temperature and to avoid reduction in volume due to thermal evaporation during exposure to sunlight. Reduction in volume results in increase
concentration thereby increase in optical density. Since optical density is measure of the concentration of organic dye in the solution, change in concentration should be only due to photocatalytic degradation. Increases in concentration due to solvent loss will give inaccurate change in concentration. The set up is as shown in the figure 5.4.

![Set up for photocatalytic degradation of dye under sunlight.](image)

**Figure 5.4 : Set up for photocatalytic degradation of dye under sunlight.**

5.3.1.2 Set up for H$_2$S generation on microscale

Many gas generators are reported as per type of the gas and purpose of the gas generation. *Gregg M Evans* and *Baker et. al* developed simple and economical gas generator for laboratory purpose.(Figure 5.5 a and b )
Figure 5.5: Various gas generator equipments – a) Gregg Evan’s gas generator b) Baker’s gas generator c) D. I. Walker’s gas generator d) D. K. Alern’s gas generator.

D. Irvine Walker\textsuperscript{24} (Figure 5.5c) developed gas generator in which bottom of the test tube is perforated and two holes are made in the sides at certain distance. The test tube is fitted with one hole rubber stopper containing right angle tube fitted with stop cock. This test tube is fitted in another test tube and whole assembly is fitted in wide mouth glass bottle with a rubber stopper having small hole for the purpose of admitting air. When stop cock is opened, the acid or liquid rises into tube and gas is generated. When stop cock is closed pressure increases due to gas evolution and liquid forced down and gas generation is stopped. D. K. Alpern\textsuperscript{25} developed test tube automatic gas generator based on similar principle applied by Irvine Walker Figure 5.5d).

Figure 5.6: Gas generator by Hall W. T.
Hall W. T.\textsuperscript{26} has developed gas generator using wash bottle in which glass wool bed or asbestos platform is provided at midway (Figure 5.6). When liquid touches the platform gas generation begins and if gas is not consumed pressure develops in the bottle which forces liquid level down and automatically gas generation stops. Kipp’s apparatus is being used on large scale for H$_2$S generation in laboratories (Figure 5.7). This apparatus was invented by P. J. Kipp in 1844.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{kipp_apparatus.png}
\caption{Kipp’s apparatus}
\end{figure}

The apparatus consists of three vertically stacked cylinders. The iron sulphide is placed into middle cylinder; the acid is put into top cylinder. A tube extends from top cylinder to bottom. The middle cylinder has tube with stopcock attached for gas outlet. When pressure increases in the middle cylinder, the acid level in the middle cylinder falls down at the same time acid level rises in top cylinder and iron sulphide gets separated from acid and gas generation is stopped. The acid generation starts again as soon as H$_2$S is withdrawn from cylinder.
Figure 5.8: a) Shiziu Asakura’s gas generator b) Jinhua Wang’s gas generator

Shiziu Asakura [29] developed constant rate gas generator by reversing usual procedure of Kipp’s generator and dropping the liquid reagent on to the solid (Figure 5.8a). With this modification, constant rate gas generation may be possible. The rate of gas generation can be adjusted with funnel stopcock. Jinhua Wang, et al. [28] designed microscale gas generated which include horizontal annular base of which, one end connected to spherical reactor and other end to spherical funnel (Figure 5.8b). The controlled gas generation is based on the principle of rise and fall of liquid level due to change in pressure. Many chemists have redesigned gas generators as per their requirement. [29, 30, 31, 32, 33, 34, 35]

The Microscale gas generator has been developed in laboratory for the generation of H₂S with desired and constant flow rate. After performing various attempts using Kipp’s apparatus it was observed that H₂S with constant flow rate in the range of 2-3 ml min⁻¹ is somewhat inconvenient and such set up requires large quantity of liquid and solid reagent. So we have developed the microscale H₂S generator through series of attempts. In the first attempt dropping funnel with pressure equalizer (figure not shown) has been connected to round bottom flask which has provision for gas out let at the side and for draining slurry formed after gas generation. In the second attempt U tube dropping funnel was used (figure not shown). But both attempts could not serve the purpose.

In the third attempt U tube dropping funnel with pressure equalizer at one arm has been used (Figure 5.9a). The extent of gas generated can be understood from the drop in acid level due to pressure developed in the side arm of the U tube. Flow rate can be controlled by adjusting acid drop rate and opening stop cock partially. Flow rate remains constant in the certain range of acid level in the side
arm. Acid drop rate is controlled so as to maintain the acid level in the certain range.

![Diagram](image)

**Figure 5.9:** a) Gas generator having U tube with pressure equalizer. b) Gas generator having U tube with horizontal dropping provision.

Further, this U tube with pressure equaliser has been modified since it needs to control the acid drop rate. In the modified equipment (Figure 5.9b), one of the side arm has been connected through horizontal tubes to the central tube. The horizontal tubes are provided with stopcocks. Central tube is also connected to the top of the other side arm. This outlet is for the removal of excess gas generated during the experiment so that it will not affect on constant rate of H$_2$S generation.

**Mechanism:** Acid is filled in to the U tube. Top of the left side arm is kept open to the atmosphere. Level in both side arms is initially equal. One of the stopcocks is slightly opened to drop the acid into the flask. Acid level in the right arm goes down as soon as H$_2$S gas generation begins and dropping the acid automatically stops. Outlet of the round flask is partially opened as per requirement of the flow rate. When acid level rises and reaches up to the horizontal tube of which stopcock is opened, acid drops again into the flask and immediately acid level goes down and
dropping of acid stops. If gas generated is not consumed. The acid level will not rise up and no acid will drop into the flask. It means, unless and until gas is consumed, gas will not be generated. This process continues till H₂S gas generated and consumed continuously.

This technique is economical as well as an environmental friendly since, i) It avoids excess addition of acid. ii) Excess generation of gas is avoided iii) Air pollution is avoided iv) Wastage of acid and iron pyrite is avoided due to which cost of H₂S gas has been reduced.

5.3.1.3 Gas measuring cylinder

The gas measuring cylinder is designed to measure gas generated during the experiment. The earlier method of volume of gas over water is shown in the figure 5.10 (a - c). Measuring cylinder filled with water is inverted in water bath and gas outlet tube is inserted through bottom (Figure 5.10a). Modified version of this equipment is known as eudiometer as shown in the figure 5.10b. Figure 5.10c shows equipment for volume measurement using pressure equalizer. Drawback of these measuring equipments are i) Purging with N₂ or Ar cannot be done, which is essential prior to H₂ generation. ii) There is no provision for transfer of the gas into other storage device.

![Figure 5.10: Gas measuring equipments a) inverted measuring cylinder b) Eudiometer c) gas burette with pressure equalizer](image)

To overcome these drawbacks, measuring gas cylinder has been developed. The gas measuring equipment designed in laboratory measures the gas accurately over the water by displacement mechanism. The apparatus is equipped with three stopcocks
as shown in the figure 5.11. Gas tube is connected to S2. The bottom outlet S3 is immersed in water. The stopcock S3 is closed and S1 provided at the top of the cylinder is kept open while purging the setup. After purging stopcock S1 is closed and S3 is opened. When gas enters in the measuring cylinder equivalent volume of water comes out of the cylinder through S3.

**Gas storage:** The gas can be withdrawn from the cylinder through S2 with the help of syringe as when required. After the completion of the process all three stopcocks are closed and cylinder is detached from the setup. Rubber bulb or balloon is attached to the S2 and S1 is connected to water reservoir. The stopcock S2 is opened and then water is introduced through S2 which is will force gas to fill into the balloon.

![Figure 5.11 : Gas measuring equipment](image)

5.3.2 Photocatalytic degradation of dyes

5.3.2.1 Photocatalytic degradation of Acid Orange-8 (AO-8)

Photocatalytic degradation of Acid Orange family was performed by many researchers while very few reports are available on photocatalytic degradation of AO -8 \(^{7,9}\).
We have attempted photocatalytic degradation of AO-8 in aqueous medium without using H₂O₂ or maintaining pH of the solution. Photocatalytic degradation of 40 ml aqueous solution having concentration 10 ppm was carried out under sunlight. The intensity of sunlight has been measured using Lux meter and observed to be in the range 1.0 x 10⁵ to 1.1 x 10⁵ lux. (15-15.5 eV) The graph of C/Co Vs time for Zn₂TiO₄, Ag@Zn₂TiO₄ and Co@Zn₂TiO₄ is as shown in the figure 5.12. From graph depicted in the figure 5.12, it is observed that photocatalytic activity increases due to Ag doping while decreases due to Co doping into Zn₂TiO₄. Complete degradation takes place in ~ 75 min and 210 min using Ag doped and undoped Zn₂TiO₄, respectively. In other words photocatalytic activity of Ag@Zn₂TiO₄ increases almost three times as compared to that of Zn₂TiO₄. Half life period (Table 9.1) for the photocatalytic degradation was determined from graph of C/Co Vs time and found to be 14.9, 52.1 and 126.6 min for Ag@Zn₂TiO₄, Zn₂TiO₄ and Co@Zn₂TiO₄ respectively. The degradation of AO-8 in absence of catalyst (blank) under sunlight has not been observed.

Figure 5.12: Photocatalytic degradation of AO-8 using a) Ag@Zn₂TiO₄, b) Zn₂TiO₄, c) Co@Zn₂TiO₄ and d) blank.
Since, photocatalytic activity of Ag@ Zn$_2$TiO$_4$ was found to be highest amongst the zinc orthotitanates synthesized, it has been chosen for the detailed study. Effect of concentration of AO-8 and amount of catalyst on the rate of degradation was studied for the Ag@ Zn$_2$TiO$_4$. Effect of concentration of AO-8 was studied at 5, 7.5 and 10 ppm concentration (Figure 5.13). Half life period determined from the graph was found to be 14.9, 22.0 and 57.0 min for 5, 7.5 and 10 ppm solutions, respectively.

It is observed that, reaction time increases with increase in concentration of AO-8. Half life period (t$_{1/2}$) for 5, 7.5 and 10 ppm was found to be 14.9, 22.0 and 57.0 min which show that t$_{1/2}$ is directly proportional to the concentration of the AO-8. Effect of the concentration of the catalyst on the rate of the reaction has been studied by taking 10, 20 and 30 mg Ag@ Zn$_2$TiO$_4$. Figure 5.14 indicates reaction time decreases with amount of the catalyst. Half life period (t$_{1/2}$) determined from graph of C/Co versus time was observed to be 14.9, 9.6 and 8.3 min for 10, 20 and 30 mg catalyst. Decrease in half life period (t$_{1/2}$) with amount of the catalyst also

![Figure 5.13: Effect of concentration of AO-8](image)
indicates that rate of reaction increases with amount of the catalyst. In other words, rate of photocatalytic degradation increases with increase in amount of the catalyst.

![Figure 5.14: Effect of amount of Ag@Zn₂TiO₄ on the rate of degradation of AO-8](image)

Figure 5.14: Effect of amount of Ag@Zn₂TiO₄ on the rate of degradation of AO-8 a) 30 b) 20 and c) 10 mg

It is observed that half life period decreases with increase in amount of the catalyst which is quite obvious since rate of the reaction depends upon extent of the adsorption which in turn depends on the amount of the catalyst.

5.3.3.2 Photocatalytic degradation of Rhodamine B (RH-B)

The as synthesized nanostructured zinc orthotitanates were also employed for the photocatalytic degradation of RH-B dye in aqueous medium. Variation of C/Co with time of the reaction for 5 ppm solution is shown in the figure 5.15, which indicates that rate of photocatalytic degradation of RH-B increases due to Ag doping while decreases due to Co doping into zinc orthotitanate. It is clearly observed that trend of effect of doping of Ag and Co on efficiency of photocatalytic dye degradation is same as observed in case of AO-8. There is no appreciable decrease in concentration of the RH-B in absence of catalyst (blank) indicates no degradation due to photolysis.
Figure 5.15: Photocatalytic degradation of RH- B using a) Ag@Zn$_2$TiO$_4$, b) Zn$_2$TiO$_4$ c) Co@Zn$_2$TiO$_4$ and d) blank

Effect of concentration of the RH- B on the rate of photocatalytic degradation was studied at 2.5, 5.0 and 7.5 ppm RH-B solution using 10 mg Ag@ Zn$_2$TiO$_4$. The variation of C/Co with time is shown in the figure 5.16. In this case also rate of photocatalytic degradation decreases with increase in concentration of the RH-B. Half life period ($t_{1/2}$) determined from the graph was found to be 4.4, 7.3 and 13.2 min for 2.5, 5.0 and 7.5 ppm, respectively.
Figure 5.16: Effect of Concentration of RH- B a) 2.5 b) 5 c) 7.5 ppm solution.

Effect of the amount of catalyst on rate of photocatalytic degradation was studied for 10 and 20 mg catalyst for 5 ppm solution and 20 and 30 mg catalyst for 7.5 ppm solution. Variation of C/Co with time is as shown in the figure 5.17 and 5.18.

Figure 5.17: Effect of concentration of catalyst for 10 and 20 mg Ag@Zn₂TiO₄ for 5 ppm solution
Figure 5.18: Effect of amount of Ag@Zn2TiO4 (20 and 30 mg) catalyst for 7.5 ppm RH-B solution.

Rate of photocatalytic degradation increases with increase in amount of the catalyst. Half life period \( t_{1/2} \) was observed to be 7.4 and 3.6 min for 10 and 20 mg catalyst, respectively for 5 ppm solution (Figure 5.17) While, half life period was observed to be 4.2 and 2.8 min for 20 and 30 mg catalyst, respectively for 7.5 ppm concentration of RH-B (Figure 5.18).

5.3.2.3 Explanation for effect of catalyst and dye concentration on rate of the degradation

The enhancement in degradation rate can be rationalized in terms of available active sites and penetration of photo activating light into the suspension. The availability of active site increases with increase in concentration of catalyst up to certain limit. At high concentration of catalyst, i) light penetration decreases which affect photo activated volume of suspension ii) deactivation of activated catalyst molecule due to collision with ground state molecules. Hence, decrease in rate of degradation at higher concentration of catalyst is quite justifiable.

\[ \text{ZOT}^* + \text{ZOT} \rightarrow \text{ZOT}^\# + \text{ZOT} \]

Where * represents activated molecule and # represents deactivated molecule of Zinc orthotitanate (ZOT). Hence, an optimum amount should be employed to
ensure the utmost absorption of solar light photons for efficient photo mineralization.  

It is observed that degradation rate decreases with increase in concentration of dye. As initial concentration of dye increases the path length of the photon entering the solution decreases and at low concentration reverse effect is observed thereby increasing photon absorption by the catalyst. It is quite obvious that, as the initial concentration of dye increases, requirement of catalyst surface needed for the degradation also increases. Since amount of catalyst is fixed, the formation of OH radicals on the surface of Zinc orthotitanate is also relatively fixed. So the relative number of free radicals attacking the dye molecule decreases with increase in concentration of dye. The major portion of degradation occurs in the region (reacting zone) near to the irradiated sites because; the irradiation intensity in this region is much higher than at the other sites. Hence at higher concentration of dye, there is decrease in rate of degradation.

A photocatalytic process is based on the generation of electron hole pair by means of band gap radiation that can give rise to redox reaction with the species adsorbed on the surface of the catalyst. In principle, the coupling of different semiconductor oxides seems useful in order to achieve more efficient electron pair separation under irradiation and consequently the higher photocatalytic activity. It is reported that absolute pure phase Zn$_2$TiO$_4$ is photocatalytically inactive however coupling of Zn$_2$TiO$_4$ with ZnO shows an enhancement in photocatalytic activity. Cun Wang et. al. reported that photocatalytic activity towards degradation of Methyl Orange was observed for Zn$_2$TiO$_4$-ZnO composite and not for pure phase Zn$_2$TiO$_4$. In our case Zn$_2$TiO$_4$ synthesized shows photocatalytic activity towards degradation of AO-8 and RH-B. The existence of zinc orthotitanate in tetragonal phase having band gap at ~3.2 eV is responsible for photocatalytic activity.

Enhancement in photocatalytic degradation activity of dyes using Ag@Zn$_2$TiO$_4$ with respect to undoped Zn$_2$TiO$_4$ is due to Ag metal loading on the surface of the Zn$_2$TiO$_4$ which promotes the photocatalytic degradation of dyes. Enhancement in photocatalytic activity of Ag@Zn$_2$TiO$_4$ due to Ag nanoparticles is because of i) additional band gap observed at 1.62 eV with broad absorption in the visible region 400-700 nm ii) promotion of visible light absorption through
surface plasmon resonance of Ag nanoparticles iii) Ability of silver to reduce the recombination by trapping of electrons through introduction of Fermi level of silver which is just below the conduction band of Zn$_2$TiO$_4$.\(^{46,47}\)

The rate of degradation of AO-8 and RH-B is decreased in case of Co@Zn$_2$TiO$_4$. Though there is shift in band gap towards the visible region (~ 2.7 eV), there is decrease in photocatalytic activity under natural sunlight. Surprisingly, it is much less as compared to undoped Zn$_2$TiO$_4$. This decrease is may be due to induction of recombination site because of doping of Co$^{+2}$ ions into Zn$_2$TiO$_4$. In the case of Co$^{+2}$ doping, induction of recombination sites is more dominant under the solar irradiation. Since intensity of the sun light is not enough to separate the electron hole pair, so recombination increase thereby decrease in rate of degradation.\(^{48}\)

Increase in concentration of dye decreases the intensity of transmitting light through the solution which interacts with the surface of the catalyst in other words penetration of photo activating light decreases which causes decrease in rate of photocatalytic degradation with increase in concentration.\(^{49,50}\)

### 5.3.2.4 Effect of synthesis method on efficiency of photocatalytic degradation of AO-8 and RH-B.

I) Zinc orthotitanates synthesized by glycothermal method

Photocatalytic degradation of AO-8 and RH-B has been performed using zinc orthotitanates synthesized by glycothermal method. Graph of C/Co Vs time shows enhancement in rate of photocatalytic degradation of AO-8 due to Ag doping and decreases in photocatalytic degradation due to Co doping in zinc orthotitanate.

![Figure 5.19: Photocatalytic degradation of a) AO-8 and b) RH-B by using Zn$_2$TiO$_4$, Ag@Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$](image)

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\(\text{Ph. D. Thesis} \quad \text{University of Pune, 2013}\)
II) Zinc orthotitanates synthesized by template base combustion method

Zinc orthotitanates synthesized by template assisted combustion method were employed for photocatalytic degradation of AO-8 and RH-B under visible light. From figure 5.20 it is observed that rate of photocatalytic degradation in presence of Ag@Zn2TiO4 is higher than in presence of Zn2TiO4 while rate of photocatalytic degradation in presence of Co@Zn2TiO4 is lower than in presence of Zn2TiO4.

![Figure 5.20: Photocatalytic degradation by zinc orthotitanates: a) AO-8 and b) RH-B](image)

From the results obtained, it is observed that photocatalytic activity towards dye degradation has been enhanced due to Ag doping and suppressed due to Co doping irrespective of synthesis method. Comparative study has been done on the basis of order of the reaction and rate constant for photocatalyst Zn2TiO4 and Ag@Zn2TiO4. In case of Co@Zn2TiO4 complete degradation has not been observed and therefore not included in comparative study.

**Table 5.1: Order, rate constant and half life period of AO-8 degradation**

<table>
<thead>
<tr>
<th>Method</th>
<th>Zn2TiO4</th>
<th>Ag@Zn2TiO4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>K_n (con^{-n}min^{-1})</td>
</tr>
<tr>
<td>Combustion</td>
<td>0.87</td>
<td>0.011</td>
</tr>
<tr>
<td>Solvothermal</td>
<td>0.84</td>
<td>0.011</td>
</tr>
<tr>
<td>Template</td>
<td>1.40</td>
<td>0.030</td>
</tr>
</tbody>
</table>
Table 5.2: Order and rate constant of RH-B degradation

<table>
<thead>
<tr>
<th>Method</th>
<th>Zn$_2$TiO$_4$ n</th>
<th>K$_n$ (con$^{1-n}$ min$^{-1}$)</th>
<th>Ag@Zn$_2$TiO$_4$ n</th>
<th>K$_n$ (con$^{1-n}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion</td>
<td>0.82</td>
<td>0.0093</td>
<td>1.11</td>
<td>0.096</td>
</tr>
<tr>
<td>Solvothermal</td>
<td>0.84</td>
<td>0.015</td>
<td>1.10</td>
<td>0.039</td>
</tr>
<tr>
<td>Template</td>
<td>1.42</td>
<td>0.029</td>
<td>0.92</td>
<td>0.041</td>
</tr>
</tbody>
</table>

From the data given in table 5.1 and 5.2 it is clearly seen that highest rate constant has been registered for Zn$_2$TiO$_4$ synthesized by template base combustion method and for Ag@Zn$_2$TiO$_4$ synthesized by combustion method. Hence, Ag@Zn$_2$TiO$_4$ synthesized by combustion method is more efficient than synthesized by solvothermal method or template based combustion method. Zinc orthotitanates synthesized by template based combustion method are more efficient than synthesized by solvothermal method. It is quite well known that efficiency of the catalyst depends upon method of the synthesis, presence of other constituents, particle size, morphology, surface area and band gap. In case of zinc orthotitanates, activity depends upon extent of cubic phase (E$_g$ = 3.7 eV) and tetragonal phase (E$_g$ = 3.11 eV) of Zn$_2$TiO$_4$, extent of ZnO and type of the doping. It is observed that there is no much difference in band gap observed for Zn$_2$TiO$_4$, Ag@Zn$_2$TiO$_4$ and Co@Zn$_2$TiO$_4$ synthesized by the method employed. Hence, the difference in activity may be due to extent of agglomeration, different types of morphology observed.

5.3.2.5 Photocatalytic degradation of mixture of dyes

Photocatalytic degradation of mixture of AO-8 (5.0 ppm) and RH-B (5.0 ppm) was performed using 10 mg of Ag@Zn$_2$TiO$_4$. These two dyes are nonreacting so their degradation in mixed state can be performed. Graph of variation of C/Co with time is shown in the figure 5.21. It’s observed that in mixture state; degradation rate of RH-B is higher than AO-8. It means trend is same as observed in case of individual dyes.
From the half life period of degradation of dyes in individual and mixed state it is clear that, rate of degradation of the dyes has been decreased (Table 5.3). This is quite obvious because total concentration of the dye has been increased to 10 ppm. In mixed state, degradation of dye takes place in presence of other dye molecules which affects on rate of the reaction.

Table 5.3: Order and half life period of AO-8 and RH-B

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Dye</th>
<th>Order (n)</th>
<th>Half life period (t½)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Individual</td>
<td>mixed</td>
</tr>
<tr>
<td>01</td>
<td>AO-8</td>
<td>1.35</td>
<td>1.41</td>
</tr>
<tr>
<td>02</td>
<td>RH-B</td>
<td>1.10</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Marginal increase in order of reaction has been observed with respect to individual state. This indicates that Ag@Zn₂TiO₄ can be employed for photocatalytic degradation of mixed dyes. The mixture of dyes affects on i) extent of light transmitted through solution and incident on surface of the catalyst, ii) number of water molecules adsorbed and dissociated to form active species like OH⁻ and O₂⁻, iii) distribution of the active species amongst the dye molecules. These factors are responsible for the decreases in rate of the degradation.

Figure 5.21: Photocatalytic degradation of mixture of dyes : a) RH-B, b) AO-8
Study of degradation of dyes in mixed state is essential in practical point of view since; effluent may include variety of pollutants. These pollutants should be degraded simultaneously by photocatalyst. Thus, the Ag@Zn$_2$TiO$_4$ can be employed effectively for degradation of mixed dyes. This type of study has been performed for the first time.

5.3.2.6 Kinetic study

Kinetics of photocatalytic degradation of organic dyes under UV and visible light has been studied by many researchers. It was reported that photocatalytic degradation follows first order kinetics based on Langmuir-Hinshelwood Model.\textsuperscript{51,10} We have also performed kinetics calculation considering the photocatalytic dye degradation obeying pseudo first order kinetics as per Langmuir-Hinshelwood Model. In case of photocatalytic degradation of AO-8 and RH-B it is observed that extent of the degradation of the dye (C/Co) decreases with increases in concentration of the dye. In other words half life period of the reaction increases with increases in concentration of the dye. As per the characteristics of the first order reactions half life period is independent of the initial concentration of the reactant (Dye) according to equation 1.

$$t_{1/2} = \frac{0.693}{k_1}$$ \hspace{1cm} (1)

Our observation indicates the discrepancy between rate constant and order of the reaction. D Zhang et. al\textsuperscript{52}, reported that the discrepancy between first order reaction and rate constant may arise due to complicated mechanism. The complicated mechanism would be influenced by many factors such as particle size, phase and chemical composition, surface properties, Intensity of light and effectiveness of charge separation.

To know the apparent order of the reaction, we have assumed that photocatalytic degradation of dye takes place in the solution phase and not on the surface of the catalyst. So we have used power rate law to determine the order of the reaction. The power rate can be applied for homogenous reactions.\textsuperscript{53}

Kinetics of the photocatalytic degradation has been studied using equation 2, which is applicable for the reaction of single reactant (A → Product)

$$Rate = -\frac{dc}{dt} = KC^n$$ \hspace{1cm} (2)
Where C, n and K are concentration of the reactant at time t, order of the reaction and rate constant of the reaction, respectively. Order and rate constant of the reaction can be determined from the logarithmic form of the equation 1.

\[ \log(-R) = \log K + n \log(C) \]  

(3)

Slope and intercept of the graph of \(\log(-R)\) Vs \(\log(C)\) gives order (n) and rate constant (k) of the reaction.

Expression for half life period of the \(n^{th}\) order reaction has been derived from equation 1.

\[ (t_{1/2})_n = \left(\frac{C_0}{2}\right)^{\frac{1-n}{n(1-n)}} \left[2^{1-n} - 1\right] \]  

(4)

Where \(K_n\) is the rate constant of the \(n^{th}\) order reaction and \(C_0\) is the initial concentration. Equation (4) is not applicable for \(n=1\).

The exercise to determine the order and rate constant of the reaction is illustrated for the photocatalytic degradation of the 40 ml 5 ppm solution AO-8 using 10 mg Ag@Zn\(_2\)TiO\(_4\) catalyst. Variation of \(\log(-R)\) with \(\log(C)\) is shown in the figure 5.22

![Figure 5.22: Graph of \(\log(-R)\) Vs \(\log(C)\) for the 5 ppm solution of AO-8 using 10 mg Ag@Zn\(_2\)TiO\(_4\).](image)

Half life period and rate constant calculated from interpreted order of the reaction, first order kinetics and experimental observations are given in Table No. 5.4 and 5.5 for AO-8 and RH-B solutions.
Table 5.4: Order, Rate constant and half life period of photocatalytic degradation of AO-8 using Ag@Zn₂TiO₄

<table>
<thead>
<tr>
<th>Conc. of dye (ppm)</th>
<th>Amount of catalyst (mg)</th>
<th>Order n</th>
<th>Rate Constant</th>
<th>Half life period (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_n$ ($\text{conc}^{1-n}\text{min}^{-1}$)</td>
<td>$K_1$ min$^{-1}$</td>
</tr>
<tr>
<td>05.0</td>
<td>10</td>
<td>1.35</td>
<td>0.064</td>
<td>0.032</td>
</tr>
<tr>
<td>07.5</td>
<td>10</td>
<td>1.30</td>
<td>0.038</td>
<td>0.027</td>
</tr>
<tr>
<td>10.0</td>
<td>10</td>
<td>1.22</td>
<td>0.013</td>
<td>0.010</td>
</tr>
<tr>
<td>05.0</td>
<td>20</td>
<td>1.41</td>
<td>0.108</td>
<td>0.048</td>
</tr>
<tr>
<td>05.0</td>
<td>30</td>
<td>1.40</td>
<td>0.124</td>
<td>0.068</td>
</tr>
</tbody>
</table>

Order of the reaction was found to be in the range 1.2 – 1.41 for AO-8 and 1.1-1.2 for Rhodamine B. Experimentally determined rate constant and half life period of the reaction indicates that rate constant of reaction decreases with increase in concentration from 2.5 to 7.5 ppm. Dependence of the rate constant of the reaction on the initial concentration of the reactant is characteristic property of the reaction having order higher than one. It is observed that half life period calculated from equation and from experimental observation i.e. graph of C/Co Vs time is in good agreement with each other. While, half life period calculated from first order kinetics is not in agreement with experimental value.

Table 5.5: Order, Rate constant and half life period of photocatalytic degradation of RH-B using Ag@Zn₂TiO₄

<table>
<thead>
<tr>
<th>Conc. of dye (ppm)</th>
<th>Conc. of catalyst (mg)</th>
<th>Order n</th>
<th>Rate Constant</th>
<th>Half life period (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_n$ ($\text{conc}^{1-n}\text{min}^{-1}$)</td>
<td>$K_1$ min$^{-1}$</td>
</tr>
<tr>
<td>02.5</td>
<td>10</td>
<td>1.20</td>
<td>0.190</td>
<td>0.121</td>
</tr>
<tr>
<td>05.0</td>
<td>10</td>
<td>1.10</td>
<td>0.096</td>
<td>0.067</td>
</tr>
<tr>
<td>07.5</td>
<td>10</td>
<td>1.20</td>
<td>0.052</td>
<td>0.040</td>
</tr>
</tbody>
</table>
Mechanism of the photocatalytic degradation

From experimental observation it is proposed that water is adsorbed on the surface of the catalyst followed by formation of $OH^-$ and $O_2^-$ radicals due to redox reaction taking place by photo excitation of electron under the sunlight irradiation. These photo generated radicals interact with the dye molecule in solution state and degradation takes place. In the review on TiO$_2$ assisted photocatalytic degradation of azo dyes in aqueous solution taken by Konstantinou et. al. also reported the mechanism which involves formation $OH^-$ and $O_2^-$ radicals.$^{52, 54, 55}$

Mechanism of photocatalytic degradation of dye is given below.

\[
\begin{align*}
Zn_2TiO_4 &+ hv \rightarrow Zn_2TiO_4 (e^-_{CB} + h^+_{VB}) \\
H_2O &+ h^+_{VB} \rightarrow OH^- + H^+ \\
O_2 &+ e^-_{CB} \rightarrow O_2^- \\
OH^- + \text{dye} &\rightarrow H_2O + CO_2 \\
O_2^- + H^- &\rightarrow OOH^- \\
OOH^- + OOH^- &\rightarrow H_2O_2 + O_2 \\
O_2^- + \text{Dye} &\rightarrow CO_2 + H_2O \\
OOH^- + \text{dye} &\rightarrow CO_2 + H_2O
\end{align*}
\]

In nut shell, the higher photocatalytic activity has been obtained for Ag@ Zn$_2$TiO$_4$ as compared to undoped Zn$_2$TiO$_4$ and Co@ Zn$_2$TiO$_4$. The kinetic study showed the dye degradation follows order of reaction in the range 1.1-1.4 with optimum concentration 2.5 -7.5 ppm.

Photocatalytic H$_2$S splitting for H$_2$ generation

Photocatalytic splitting of H$_2$S can release the hydrogen stored in H$_2$S by utilizing solar energy which is generally carried out in aqueous medium.$^{56, 45}$ Photocatalytic H$_2$S splitting has been performed using as synthesized nanostructured zinc orthotitanates. Amount of H$_2$ generated by using Zn$_2$TiO$_4$, 

<p>| | | | | | | |</p>
<table>
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<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>05.0</td>
<td>20</td>
<td>1.16</td>
<td>0.202</td>
<td>0.160</td>
<td>03.6</td>
<td>04.3</td>
</tr>
<tr>
<td>07.5</td>
<td>30</td>
<td>1.14</td>
<td>0.238</td>
<td>0.168</td>
<td>02.8</td>
<td>04.1</td>
</tr>
<tr>
<td>07.5</td>
<td>20</td>
<td>1.16</td>
<td>0.159</td>
<td>0.108</td>
<td>04.2</td>
<td>06.4</td>
</tr>
</tbody>
</table>
Ag@ Zn2TiO4 and Co@ Zn2TiO4 with time under the visible light source is shown in the figure 5.23.

**Figure 5.23: Photocatalytic Hydrogen generation by using Zn2TiO4, Ag@ Zn2TiO4 and Co@ Zn2TiO4**

The H2 evolution via H2S splitting is given in the table 5.6. It reveals from literature that Zinc orthotitanates have been employed for H2S splitting to produce H2 for the first time. The Zn2TiO4 showed H2 evolution under visible light (633 µ mol/ h/100 mg) from H2S. The necked orthotitanates showed photocatalytic activity because of its high reduction potential and low oxidation potential and it is reported that it is better catalyst than TiO2 under UV as well as visible light.57,58

Amongst the zinc orthotitanates synthesized, Ag doped Zn2TiO4 has been found to be excellent photocatalyst. The utmost H2 evolution i.e. 2820 µ mol /h /100 mg (Estimated volume: 28200 µ mol / g /h) under visible light irradiation which is much higher than the earlier report.59 Enhanced Photocatalytic activity of Ag@Zn2TiO4 as compared to undoped Zn2TiO4 could be explained on the basis of elemental doping of Ag into Zn2TiO4. Many researchers have reported that loading of noble metal on the surface of the catalyst promotes the Photocatalytic production of hydrogen.57,45 ,60.

Loaded metal can capture the photo generated electrons on the catalyst surface so that after excitation, the electrons are effectively separated from the holes and the
life time of the electrons is prolonged. This increases the proportion of electrons
that participate in Photocatalytic reduction of protons to produce hydrogen.\(^{61}\) On the
other hand Hydrogen overpotential of noble metal is very low. Loading metal on
semiconductor can lower the electrochemical reductive potential (\(E_{\text{H}^+/\text{H}_2}\)) which
favours the Photocatalytic hydrogen production. Additionally, the reason mentioned
in dye degradation like Plasmon resonance effect and broad absorption from 400-
700 nm is also responsible for getting enhance photocatalytic activity. However, we
obtained lower photocatalytic activity for Co@Zn\(_2\)TiO\(_4\) as compared to
Ag@Zn2TiO4. The H\(_2\) evolution, i.e. 1672 µmol /h/ 100 g (Estimated volume:
16720 µmol /h/ g)

As mentioned earlier nature of the doping of Ag and Co into Zn\(_2\)TiO\(_4\) is not same
in the sense elemental Ag doping takes place in Zn\(_2\)TiO\(_4\)while Co\(^{2+}\) ion substitution
doping has been indicated by XRD analyses. It is observed that not only surface
area but also increase in recombination centre and extent of shifting of band gap
towards visible region, composition of the catalyst affects on the efficiency of
catalyst. In case of Co@Zn\(_2\)TiO\(_4\) photocatalytic dye degradation efficiency was
found to be decreased while Photocatalytic H\(_2\)S splitting observed to be increased
with respect to undoped zinc orthotitanates. It has been reported in the literature that
ZnCoTiO\(_4\) worked not only as an active site during sulfidation process but also as a
support to prevent the Zn migration to the outside of the sorbents and to minimize
the volume expansion / Contraction. Hence doping Co into Zn\(_2\)TiO\(_4\) at the Zn site
increases the efficiency of adsorption of H\(_2\)S on the surface compare to undoped
Zn\(_2\)TiO\(_4\) there by enhancement in H\(_2\)S splitting in presence of Co@Zn\(_2\)TiO\(_4\).

**Table 5.6: Rate of H\(_2\) generation using zinc orthotitanates.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Catalyst</th>
<th>Rate of H(_2) generation µmol/min/100 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Zn(_2)TiO(_4)</td>
<td>10.55</td>
</tr>
<tr>
<td>02</td>
<td>Ag@Zn(_2)TiO(_4)</td>
<td>46.40</td>
</tr>
<tr>
<td>03</td>
<td>Co@Zn(_2)TiO(_4)</td>
<td>27.87</td>
</tr>
</tbody>
</table>
Photocatalytic production of hydrogen using Ag@Zn2TiO4 (2796 µmol h⁻¹, for 100 mg catalyst in 175 ml 0.25 N KOH) is much higher than H₂ produced using CdS, CaIn₂S₄, CdLaS₄, ZnIn₂S₄, N-ZnO, Fe₂O₃, FeGaO₃ (AFM). 61,62,63,64,65,66

**Mechanism of H₂ generation by H₂S splitting**

Mechanism of H₂ generation by H₂S splitting under visible light source in basic medium has been mentioned by many researchers. 62,63,64

It is well known that H₂S is a weak diprotic acid having pKa values are 7.0 and 11.96. 67 At pH ~ 13 dissociation of H₂S takes place to form HS⁻ and S⁻². When suspension irradiated with visible light, photocatalyst generates conduction band electron (e⁻ₓ) and valence band hole (h⁺ₓ). The detailed mechanism is given below.

\[
\begin{align*}
H₂S + OH^- & \leftrightarrow HS^- + H₂O \quad [13] \\
HS^- + OH^- & \leftrightarrow S²⁻ + H₂O \quad [14] \\
ZOT + hv & \to e^-_{CB} + h^+_xB \quad [15] \\
2S²⁻ + 2h^+_xB & \to S_2 \quad [16] \\
2HS⁻ + 2h^+_xB & \to S_2⁻ + 2H^+ \quad [17] \\
2H^+ + 2e^-_{CB} & \to H_2 \uparrow \quad [18]
\end{align*}
\]

Overall reaction is given below.

\[
H₂S + 2OH^- \xrightarrow{hv \text{ ZTO}} H₂ + Polysulphide
\]

**5.4 Summary**

The zinc orthotitanates synthesized by combustion method, solvothermal method and templates base combustion method have been employed for photocatalytic degradation of Acid Orange-8 and Rhodamine B under sun light. Zinc orthotitanates synthesized by combustion method were employed for H₂S splitting under visible light source. Reactor for photocatalytic degradation of dye under sun light has been developed.

Microscale H₂S gas generator and Gas measuring cylinder for measuring volume of hydrogen generated during photocatalytic H₂S splitting have been developed.
The photocatalytic activity of dye degradation under natural sun light has been performed with kinetic study. The Ag@ Zn$_2$TiO$_4$ was found to be most efficient photocatalyst. The power rate law for $n^{th}$ order reaction in homogenous medium have been employed to determine order ($n$), rate constant($k$) and half life period ($t_{1/2}$). The order of the reaction observed to be in the range of 1.1-1.41 for Acid Orange-8 and Rhodamine–B. Half life period calculated from order and rate constant was observed to be in good agreement with experimental values. The photocatalytic activity of zinc orthotitanates synthesized by solvothermal method and template based combustion method have been tested. The Ag@ Zn$_2$TiO$_4$ was proved to be most efficient catalyst for performing photocatalytic degradation of dyes (AO-8 and RH-B).

The solar photo hydrogen production was also performed using undoped and doped Zinc orthotitanates. It is noteworthy that utmost hydrogen production (28200 µmol / h/ g) was obtained using Ag@ Zn$_2$TiO$_4$ which is much higher than the oxide photocatalyst reported so far. This catalyst may have good potential in water splitting and complex waste degradation.
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