Chapter 4

Photocatalytic Degradation of Herbicides

4.1. Introduction

Contamination of the earth’s environment by toxic chemicals from various sources to a larger extent is a serious threat to the entire world. Major part of the total environmental pollution is coming from contaminated aquatic environment [1]. Removal of these recalcitrant chemicals for a clean, vivid and salubrious environment is the main aim of Green chemistry. Cost effective, recyclable and environmentally benign materials have got immense significance in environmental pollution control. The present research is pertained to the mineralization of water contaminants by advanced oxidation processes (AOPs) using metal and non-metal co-doped TiO₂ systems. Here we specifically discuss the photodegradation of herbicides, Atrazine and Metolachlor in the visible region. Various parameters are also discussed for the same.

4.1. Introduction

Among the various organic pollutants, herbicides are a major pollution source for both underground and surface waters. Contamination of herbicides in water due to agricultural, non-agricultural and industrial activities is a serious worldwide problem. The environmental fate of these pollutants depends a lot on their mobility in soils and their tendency to
intrude into other environmental compartments such as air and water [2]. Movement of water and dissolved chemicals through soil is known as leaching and the physico-chemical properties of the agrochemicals used as well as soil properties play a decisive role in this process [3, 4]. The transfer of these pollutants from soil to water mainly depends on its life time in soil [5]. Sorption of organic pollutants by soils from aqueous solutions is quantitatively measured in terms of soil organic adsorption coefficient ($K_{OC}$). $K_{OC}$ is a universally accepted measure of the relative mobility of pesticides in soils and also describing the partitioning of pesticides in soil/water/atmosphere systems [6]. Generally, compounds having higher log $K_{OC}$ values will be less mobile than those with lower values. The extensive use of herbicides in agriculture fields to control weedy plants and to increase the quality and quantity of crop productivity has become an important tool to the detriment of the environment. The herbicides and their degradation products may alter the natural habitats of different plant and animal species depending on how they are transported in the environment [7]. The release of toxic, recalcitrant and persistent organic pollutants such as pesticides, dyes, polychlorinated biphenyls (PCBs), halogenated organic solvents and polycyclic aromatic hydrocarbons (PAHs) into aquatic environment from industrial, wastewater treatment plants, agricultural run-off has drawn much attention and is considered as one of the arduous problems facing environmental scientists today [8]. Due to their chemical stability, resistance to biodegradation and sufficient water solubility, these organic pollutants penetrate deep into the ground water [9, 10]. The chemical properties of the pesticides affect their durability in the soil and their rate of movement from the surface soil to the ground water. Water solubility determines a pesticide's propensity to dissolve in
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water making the chemical more amenable to migrate through the soil and into an aquifer.

Once the soil and pesticides begin to interact, their combined chemical properties create molecular reactions forming new molecular bonds. This propensity for soils and pesticides to interact affects the rate of pesticide migration in different types of soils. Once pesticides are introduced onto a field, they have the potential to migrate deep into the soil and into the aquifers below. If the chemical is degraded by biological or chemical processes before it leaches, it never reaches the aquifer. If the chemical has high persistence, it is not degraded, and also does not bind with soil, it is very likely to leach into and contaminate the ground water. Hydrolysis is the rate of degradation of a pesticide in water. If the pesticide leaches below top layers of soil beyond biological activity, hydrolysis becomes the only process available to decompose the pesticide. But this technique is not sufficient for the effective removal of the pollutants.

Ubiquitous use and improper disposal of herbicides cause serious ecological consequences. As a result, if these xenobiotic organic chemicals are introduced into water ecosystems, they can make water quality worse and threaten human health [11]. So it is very mandatory to curtail these recalcitrant and persistent chemicals for a hygienic environment. A lot of methods have been employed for this purpose and some are found to be effective. Conventional waste water treatments such as adsorption onto granular activated carbon, air stripping, incineration, chemical remediation, pyrolysis, reverse osmosis etc. are very slow or non-destructive for these kinds of compounds [12,13]. Degradation of pollutants is also possible through photochemical and biological processes but most of these require
long treatment periods [14]. Among various techniques, Ultrasonic irradiation is an attractive technique as the degradation of contaminants may occur under ultrasonic irradiation without the addition of other chemical substances [15]. Adsorption of these pollutants onto clays or other high surface area materials transfers them but cannot degrade them into harmless substances. Ozonation is also less effective due to its selectivity towards some organic pollutants. So it is very beneficial to apply a highly effective and sophisticated technique in the field of environmental protection. Here comes the importance of advanced oxidation process [16-18].

Heterogeneous semiconductor photocatalysis is a highly effective technique for the degradation and mineralization of pollutants in water and waste water to environmentally harmless compounds. Heterogeneous photocatalysis is a part of a family of techniques called Advanced Oxidation Processes and has got immense attention because of complete oxidation of pollutants, removal of inorganic compounds, heavy metals, bacteria and viruses from water [19-22]. However, in the treatment of biorefractory compounds such as pesticides, pharmaceuticals and other complex molecules, it is more logical and economical to perform the oxidation process only up to the point at which the intermediate products become biodegradable [23,24]. Among various oxide semiconductor photocatalysts, TiO₂ has proven to be the better choice for widespread environmental applications due to its chemical inertness, strong oxidizing power, lower cost and long-term stability against photo corrosion and chemical corrosion. The photocatalytic degradation of various organic systems using irradiated TiO₂ and its modified forms and the basic principles of photocatalytic oxidation are well established [25-29].
The current chapter discusses the photocatalytic degradation of some herbicides using metal, non-metal co-doped TiO$_2$ systems. Five different co-doped catalytic systems and for each catalysts, three compositions were prepared by varying the concentration of metal and checked its photocatalytic activity in the degradation of herbicides. The organic pollutants selected are Atrazine and Metolachlor. According to environmental protection agency, these two chemicals are toxic and affect the ecosystem adversely. The selection of these compounds is based on its solubility in aqueous medium and toxicity. Various parameters like effect of time, effect of different catalysts, effect of catalyst amount and reusability were monitored for the degradation. Here we could not identify the by-products obtained after degradation due to lack of instrumental facility and the reports are based on the percentage degradation calculated from the data obtained from HPLC analysis. The light response of our co-doped catalytic systems is purely in the visible region. So we use a dichoric mirror of wavelength between 420-630 nm in order to get visible radiation specifically.

### 4.2. Activity Studies

#### 4.2.1. Photocatalytic Degradation of Atrazine

![Structure of Atrazine](image)

**Fig.4.1. Structure of Atrazine**
Atrazine is a tri-azine based compound. Chlorinated tri-azines are herbicides widely used for the control of annual and perennial grass and annual broad-leaved weeds and are amongst the most commonly used herbicides all over the world [30,31]. The main compound of this family is the atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and it is found in the environment contaminating soil and water reserves [32]. This herbicide belongs to the persistent organic pollutants because of its poor biodegradability and long half-life in water. Atrazine, which has been found in both deep and superficial waters, presents a moderate solubility in water (1.6x10^{-4}M at 20 °C) and it is relatively stable in aqueous environments and soils where it possesses a half-life of one hundred days [33]. Several methods have been employed to remove atrazine from aqueous wastes such as adsorption on activated carbon and its combination with ozone [34,35], adsorption onto carbon nanotubes [36] etc. But all these methods have got a lot of disadvantages. Advanced oxidation process based on semiconductors is found to be better alternative for the conventional methods for the removal of herbicides. During this process, oxidation of the lateral chains and subsequent disappearance of the initial compound is very fast but the formation of the final product (cyanuric acid) may require a long irradiation time [37]. Due to the stability of the s-triazine ring, complete mineralization of atrazine could not be attained at shorter periods of time via oxidation which only affects the lateral chains with 5 of the 8 carbons removed as CO₂. The photocatalytic oxidation of s-triazine herbicides and their pathway of degradation have been scrutinized by various researchers and suggested that the degradation of the s-triazines occurred in a complex way with
cyanuric acid as the end product [37,38]. In this work, metal, non-metal modified TiO$_2$ were used for the effective degradation of this herbicide.

4.2.1. (a) Effect of Various Catalysts

Table 4.1. % Degradation of Atrazine against different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd(0.5wt%)-N-Ti</td>
<td>57</td>
</tr>
<tr>
<td>Gd(1wt%)-N-Ti</td>
<td>73</td>
</tr>
<tr>
<td>Gd(1.5wt%)-N-Ti</td>
<td>68</td>
</tr>
<tr>
<td>Pd(0.5wt%)-N-Ti</td>
<td>58</td>
</tr>
<tr>
<td>Pd(1wt%)-N-Ti</td>
<td>63</td>
</tr>
<tr>
<td>Pd(1.5wt%)-N-Ti</td>
<td>60</td>
</tr>
<tr>
<td>Ag(0.5wt%)-N-Ti</td>
<td>49</td>
</tr>
<tr>
<td>Ag(1wt%)-N-Ti</td>
<td>62</td>
</tr>
<tr>
<td>Ag(1.5wt%)-N-Ti</td>
<td>57</td>
</tr>
<tr>
<td>Pr(0.5wt%)-N-Ti</td>
<td>44</td>
</tr>
<tr>
<td>Pr(1wt%)-N-Ti</td>
<td>54</td>
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<tr>
<td>Pr(1.5wt%)-N-Ti</td>
<td>47</td>
</tr>
<tr>
<td>Cd(0.5wt%)-N-Ti</td>
<td>43</td>
</tr>
<tr>
<td>Cd(1wt%)-N-Ti</td>
<td>51</td>
</tr>
<tr>
<td>Cd(1.5wt%)-N-Ti</td>
<td>49</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>31</td>
</tr>
</tbody>
</table>

Here we evaluated the degradation of Atrazine using various co-doped TiO$_2$ catalysts having different concentration of metal content. In all these cases, the concentration of N is fixed. In this study, around 10 ml of $10^{-4}$ M aqueous solution of the substrate was taken and 0.1 g (1g/L) of the catalyst was added to it. The irradiation time was limited to 60 minutes based
on the lamp life. Before irradiation, the entire system was magnetically stirred for 30 minutes in order to attain the adsorption/desorption equilibrium between the catalyst surface and the substrate. Then the suspension was irradiated with a 150 W Xenon ozone free lamps. The dichoric mirror of 420-630 nm was used as the source for visible light which excludes all other radiations. The suspension was centrifuged and filtered after irradiation and the concentration was analyzed using HPLC technique. The mobile phase used was a solution of water/1 mmol ammonium acetate in the ratio 50:50 at flow rate of 1.4 ml/min with UV detection at 226 nm. The percentage of degradation was measured using the relation \((C_0-C) \times 100/C_0\), where \(C_0\) and \(C\) are the initial and final concentrations of the herbicide. Five different co-doped catalytic systems were prepared and compared its activity with pure TiO\(_2\) in the degradation of the herbicide Atrazine. For each catalyst, three different versions were prepared by varying the metal content and observed its activity. From the table it is clear that all the co-doped catalysts showed better activity than pure TiO\(_2\). After irradiation, no huge degradation was observed for pure TiO\(_2\) due to its specified spectral response in the UV region. In these co-doped systems, one element (N) is responsible for changing the light response and metal part reduces the electron-hole recombination. Effective band gap narrowing of TiO\(_2\) can be achieved by using non-metal elements such as ‘N’ due to its comparable potential with oxygen in the lattice [46]. Liu et al. also observed the reduction in band gap of N-doped TiO\(_2\) by using ammonia as the nitrogen source [47]. Among various catalysts, all the 1wt% metal doped co-doped systems showed superior activity than other systems. It is believed that the metal induces greater enhancements in the photocatalytic activity of TiO\(_2\) by creating a Schottky junction.
between metal and semiconductor. The metal particle acts as a sink for photogenerated electrons thereby reducing the rate of their recombination with holes [48]. There is an increase in the degradation efficiency with increasing metal content up to 1wt% then a decrease for the sample having higher metal content. The dosage level is an important factor influencing the enhancement of photo activity in metal doped systems. Below an optimum dosage, the metals can act as charge separation centers and thus enhance the photo activity of modified TiO₂ systems. However, as dosage levels exceed optimum loading they can act as electron-hole recombination centers which adversely affect the photocatalytic activity [46]. This may also be due to the population of the photosensitive surface of TiO₂ by the metal dopant. This observation led to the conclusion that the optimum amount of metal dopant for effective photocatalytic activity is 1wt%. Higher metal levels (1.5wt%) led to lower photodegradation rates as these become recombination centers and thus short circuiting the system. In pure TiO₂, the rate of electron-hole recombination is very high. Nitrogen and metal content have synergistic effects which is also responsible for improving the photocatalytic activity under visible light irradiation. Introduction of substitutional or interstitial nitrogen in the TiO₂ results the formation of new level above the valance band. So upon irradiation with visible light, electrons can be excited from the newly formed level to the conduction band of TiO₂ [49]. Generally, metals can be existed on the surface of the semiconductor material as an island. If the work functions of the metals present are higher than the semiconductor material, the photogenerated electrons are trapped by them leading to electron-hole separation. Then the holes are free to migrate to the surface and react with surface adsorbed water or hydroxyl groups generating highly reactive
hydroxyl radical species. On the other hand, the electrons scavenge the oxygen molecules to form very reactive superoxide radicals [50]. Both these radicals are very reactive and non-specific in nature that results the better degradation of herbicide. The metal content and nature of the metals affect the electron scavenging ability which in turn influence the photocatalytic activity. Here the activity follows as Gd-N-Ti > Pd-N-Ti > Ag-N-Ti > Pr-N-Ti > Cd-N-Ti > TiO₂. Complex formation between titania and f-orbitals of rare earths improve the absorptivity and electronic properties. The resulting Rare Earth-O-Ti bond will cease the transformation from metastable anatase to rutile phase [51, 52]. Among all the co-doped titania systems, Gd doped system shows lowest band gap and particle size thereby increasing the surface area and pore volume which positively affects the photocatalytic activity [53].

4.2.1. (b)Effect of Catalyst Amount

Fig. 4.2. % Degradation of Atrazine against amount of catalysts
The effect of different catalysts revealed that co-doped TiO$_2$ systems containing 1wt% metal are very good candidates for degradation of Atrazine. So we evaluated the effect of catalyst amount by considering only the 1wt% metal doped catalysts. 10 ml of $10^{-4}$M aqueous solution of the herbicide was taken and different catalyst amounts varying from 1 g/L to 4 g/L were added. Before irradiation the suspension was stirred for about 30 minutes in order to attain adsorption/desorption equilibrium and then the time of irradiation was limited to 60 minutes. The dichoric mirror of 420-630 nm was used as the source for visible light. After irradiation, the percentage degradation was analyzed using HPLC technique. Maximum degradation of about 91% was observed with Gd(1wt%)-N-Ti system with a catalyst amount of 3 g/L. From the results it is clear that photocatalytic degradation increases with increase of catalyst amount and reaches a maximum. Further increase of catalyst amount does not have much effect on degradation. Active surface sites increase as the catalyst amount increases which improves the photocatalytic efficiency through the formation of activated photoexcited species. Increase of catalyst concentration beyond the optimum value made the suspension very thick for the light to transmit and resulted in a reduced photocatalytic activity. So catalyst amount is a significant parameter to be determined to avoid the catalyst loss and ensure the effective absorption of photons. Here also the activity follows the same trend as before.
4.2.1. (c) Effect of Time

![Graph showing % Degradation of Atrazine against time](image)

In this case a total of 50 ml aqueous solution of Atrazine was taken in a beaker and catalyst amount of 3 g/L was added. The suspension was magnetically stirred for 30 minutes in order to achieve adsorption/desorption equilibrium. Dichoric mirror of 420-630 nm was used as the light source. After starting the lamp, 10 ml of the suspension was pipetted out from the solution at an interval of 15 minutes up to 60 minutes. The concentrations of the collected samples were monitored by HPLC technique. It is clear from the figure that the percentage of degradation increases with increase of irradiation and reaches above 90% with an irradiation time of 60 minutes. Here also maximum degradation was observed with Gd(1 wt%)-N-Ti system. The degradation follows the same pattern as before. Increase of irradiation time allows more light energy to fall on catalyst surface which enhances the generation of photoexcited...
species. The formation of these intermediate species facilitates the generation of reactive oxygen species responsible for the degradation of adsorbed substrates.

4.2.1. (d) Recyclability Studies

Recyclability studies were conducted with two of the most active catalysts. The catalysts were removed from the reaction mixture by centrifuging the suspension. Then it was washed with various solvents and calcined at 500°C for 1 hour. The reactivated catalysts were active in the second cycle without appreciable loss in its activity. Here the catalyst amount used was 3 g/L and the time of irradiation was 1h. The catalysts employed were Gd(1wt%)-N-Ti and Pd(1wt%)-N-Ti. The results are shown in the table below.

Table. 4.2. Recyclability Studies

<table>
<thead>
<tr>
<th>No. of Cycles</th>
<th>Catalysts</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gd(1wt%)-N-Ti</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>Pd(1wt%)-N-Ti</td>
<td>88</td>
</tr>
</tbody>
</table>

4.2.2. Photocatalytic Degradation of Metolachlor

![Structure of Metolachlor](image)

Fig.4.4. Structure of Metolachlor
Metolachlor is an aniline derivative. It is chemically 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide. It is structurally similar to other herbicides such as Alachlor, Butachlor etc. and the difference is manifested mainly in the methoxyalkyl side chain. This moiety controls selectivity, water solubility and other such herbicidal properties. Metolachlor is a pre-emergent germination inhibitor used to control annual broadleaf weeds, grasses in corn, soybean and other crops and is the most intensively used herbicide belonging to the chemical class of chloroacetamides [39,40]. It inhibits cell growth and induces cytotoxic and genotoxic effects to lymphocytes. Due to its high mobility and persistency in soil, it has a high potential to contaminate ground water. Among the acetanilide herbicides, Metolachlor appears to be the most persistent (t_{1/2}=200 d in highly acidic water, 97 d in highly alkaline waters) and has the potential to leach to ground water because of its relatively high water solubility (530 mg L\(^{-1}\) at 20ºC) [41]. Concentration of Metolachlor in ground and surface water was found to be in the range of 0.01 to 0.40 µg/L [42-45]. Several studies revealed the persistence of Metolachlor indicating that it is fairly resistant to hydrolysis at a wide pH range. So there is a need of some advanced and sophisticated technique for their removal from the environment. Here also we employed modified TiO\(_2\) systems for the degradation studies.
4.2.2. (a) Effect of Various Catalysts

Table 4.3. % Degradation of Atrazine against different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd(0.5wt%)-N-Ti</td>
<td>60</td>
</tr>
<tr>
<td>Gd(1wt%)-N-Ti</td>
<td>81</td>
</tr>
<tr>
<td>Gd(1.5wt%)-N-Ti</td>
<td>76</td>
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<tr>
<td>Pd(0.5wt%)-N-Ti</td>
<td>54</td>
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<tr>
<td>Pd(1wt%)-N-Ti</td>
<td>74</td>
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<tr>
<td>Pd(1.5wt%)-N-Ti</td>
<td>69</td>
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<tr>
<td>Ag(0.5wt%)-N-Ti</td>
<td>51</td>
</tr>
<tr>
<td>Ag(1wt%)-N-Ti</td>
<td>68</td>
</tr>
<tr>
<td>Ag(1.5wt%)-N-Ti</td>
<td>67</td>
</tr>
<tr>
<td>Pr(0.5wt%)-N-Ti</td>
<td>47</td>
</tr>
<tr>
<td>Pr(1wt%)-N-Ti</td>
<td>62</td>
</tr>
<tr>
<td>Pr(1.5wt%)-N-Ti</td>
<td>60</td>
</tr>
<tr>
<td>Cd(0.5wt%)-N-Ti</td>
<td>43</td>
</tr>
<tr>
<td>Cd(1wt%)-N-Ti</td>
<td>54</td>
</tr>
<tr>
<td>Cd(1.5wt%)-N-Ti</td>
<td>51</td>
</tr>
<tr>
<td>TiO₂</td>
<td>29</td>
</tr>
</tbody>
</table>

Here we evaluated the degradation of Metolachlor using various co-doped TiO₂ catalysts having varied amount of metal content. In all these cases, the concentration of N is fixed. In this study, around 10 ml of 10⁻⁴ M aqueous solution of the substrate was taken and 0.1 g (1g/L) of the catalyst was added to it. The irradiation time was limited to 60 minutes based on the lamp life. Before irradiation, the entire system was magnetically stirred for 30 minutes in order to attain the adsorption/desorption equilibrium between the catalyst surface and the substrate. Then the suspension was irradiated with a 150 W Xenon ozone free lamps with an irradiance of 96.8 mW/cm². The dichoric mirror of 420-630 nm was used.
as the source for visible light. The suspension was centrifuged and filtered after irradiation and the concentration was analyzed using HPLC technique. The mobile phase used was a solution of acetonitrile/water in the ratio 63:37 at a flow rate of 1.4 ml/min with UV detection at 220 nm. The percentage of degradation was measured using the relation \((C_0 - C) \times 100/C_0\), where \(C_0\) and \(C\) are the initial and final concentrations of the herbicide respectively. Preparation method, the doping concentration, the dopant energy level within the TiO\(_2\) lattice and the distribution of the dopant in the particle can sometimes affect the photocatalytic performance of the catalysts [54]. The metal ion dopant can act as a mediator of interfacial charge transfer or as combination centre, so there must be an optimum value for the dopant concentration in order to carry out photocatalysis effectively [55]. Compared to pure TiO\(_2\), all the co-doped catalysts showed better activity in the degradation of the substrate in visible region. The optimum concentration of metal content for effective degradation of herbicide was found to be 1wt% in all the cases. Above that concentration, the metal centers facilitate electron-hole recombination thereby reducing the photodegradation rate. Anpo and co-workers have reported that the overlap of the ‘d’ orbitals of TiO\(_2\) and ‘d’ orbital of the doped metal ions could decrease the band gap of TiO\(_2\) to absorb the visible light [56]. So upon irradiation of a co-doped system using visible light, the electrons can be excited from the impurity level of N to metal impurity level or from the N impurity level to the conduction band or from valance band to the impurity level of the metal. Therefore, the quantity of excitons is much higher than that of the pure titania which affects the photodecompositon positively. Here also the activity follows as Gd-N-Ti > Pd-N-Ti > Ag-N-Ti > Pr-N-Ti > Cd-N-Ti > TiO\(_2\). The
effect of the dopants, optimum concentration of dopants, the rate of electron-hole recombination and generation of reactive oxygen species have been explained previously.

4.2.2. (b) Effect of Catalyst Amount

In a suspension, the catalyst dosage is an important controlling parameter that can affect degradation rate. The co-doped systems containing 1wt% metal content were employed for finding out the effect of catalyst dosage on degradation because higher activity of these systems has been proved in the earlier study. With a constant concentration of 10 ml of $10^{-4}$M aqueous solution of Metolachlor, the optimum catalyst amount was found by varying the catalyst dosage from 1 g/L to 4 g/L. Here 420-630 nm dichoric mirror was used as the visible light source and the time of irradiation was limited to 60 minutes depending on the lamp life. Concentration of the solution after degradation was monitored using HPLC technique. Maximum degradation of about 95% was observed with Gd(1wt%)-N-Ti system with a catalytic amount of 3 g/L. The degradation rate was found to increase with the increase in catalyst concentration which is the characteristic of heterogeneous photocatalysis [57,58]. Up to an optimum concentration, the reaction rates were found to be directly related to the catalyst concentration. But above that concentration the reaction rate decreases and becomes independent of the catalyst concentration. Surface area of the catalyst available for adsorption and degradation increase as the catalyst amount is increased. But increasing of catalyst loading beyond the optimum value increases the solution opacity leading to a decrease in the penetration of the photon flux thereby reducing the photocatalytic degradation. Curtail the use of excess catalyst
and efficient photon absorption can be attained by optimizing the catalyst concentration.

**Fig. 4.5.** % degradation of Metolachlor against catalysts amount

### 4.2.2. (c) Effect of Time

**Fig. 4.6.** % Degradation of Metolachlor against time
In this case, a total of 50 ml aqueous solution of Metolachlor was taken in a beaker and catalyst amount of 3 g/L was added. The experimental set up and the conditions used are same as before. It is clear from the figure that percent of degradation increases with increase of irradiation and reaches around 95% with an irradiation time of 60 minutes. Further increase of time does not have much effect on photocatalytic activity. Here maximum degradation was observed with Gd(1wt%)-N-Ti system and least degradation was observed with Cd(1wt%)-N-Ti system. The degradation follows the same pattern as before. Increase of irradiation time on catalyst surface enhances the generation of photoexcited species. These intermediate species facilitates the generation of reactive oxygen species responsible for the degradation of adsorbed substrates. These generated reactive oxygen species are very unstable and non-specific in nature that affects the photo reaction positively.

4.2.2. (d) Recyclability Studies

Here also we conducted the recyclability studies with two of the most effective catalysts in order to understand the stability of the catalytic systems. The same experimental conditions were used. The concentration was analyzed by HPLC technique. The catalysts were found to be active up to two cycles without appreciable loss in its activity.

Table 4.4. Recyclability Studies

<table>
<thead>
<tr>
<th>No. of Cycles</th>
<th>Catalysts</th>
<th>% Degradation</th>
</tr>
</thead>
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<td>1</td>
<td>Gd(1wt%)-N-Ti</td>
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<tr>
<td>2</td>
<td>Pd(1wt%)-N-Ti</td>
<td>89</td>
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</tbody>
</table>
4.3 Conclusion

The catalytic activity of the cost effective, sustainable and environmentally benign, metal, non-metal co-doped TiO\(_2\) systems were checked in the photodegradation of recalcitrant and persistent herbicides such as Atrazine and Metolachlor. The catalysts were found to be very active for the effective degradation of the herbicides. The percentage degradation was analyzed using HPLC technique. Various parameters such as effect of different catalysts, effect of catalyst dosage, effect of time and recyclability were monitored for the same.

References


