Effect of Number and Position of Nitrogen Atoms on Photocatalytic Degradation of Six Membered Heterocyclic Compound

A

Thesis Submitted
in partial fulfillment of the requirements for the Degree
M.Sc. (Chemistry)

Submitted by:
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Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled **"Effect of Number and Position of Nitrogen Atoms on the Photocatalytic Degradtion of Six membered Heterocyclic Compounds ",** in partial fulfillment of the requirements for the award of the degree of Masters in Chemistry, School of Chemistry and Biochemistry (SCBC), Thapar University, Patiala, is my own work during the period of Jan to July 2010, under the supervision of Dr. Bonamali Pal. I have not submitted the matter embodied in this dissertation for the award of any other degree.

Patiala

Date: 15-07-2010

Jasmeet Kaur

This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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Certificate

This is to certify that the project entitled **"Effect of Number and Position of Nitrogen Atoms on the Photocatalytic Degradation of Six membered Heterocyclic Compounds"**, being submitted by Ms Jasmeet Kaur in partial fulfillment of the requirement for the award of degree of Master of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonifide work carried out under the supervision of Dr. Bonamali Pal and that no part of this project has been submitted for the award of any other degree by me.

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Regards:
Jasmeet Kaur

Contents

Introduction

1.1 Photocatalysis

The term photocatalysis consists of two terms; photochemistry and catalysis. The phenomenon of photocatalysis is defined as the acceleration of a chemical reactions or the generation of some chemical reaction under the action of light in presence of substance called photocatalyst[1-2]. So the term photocatalyst refers to a substance or a catalyst which absorbs quanta of light to perform some chemical transformations of reactants used in the reaction. The phenomenon of photocatalytic water splitting on TiO_2 electrode under UV light was first studied by Fujishima and Honda in 1972[3].

In photocatalysis, light is being absorbed by the semiconductor material and the photocatalytic activity (PCA) depend upon the capability of the photocatalyst material to generate electron-hole pairs which react with the species being absorbed on the semiconductor surface through oxidation-reduction reactions. Each semiconductor which is being used as a photocatalyst corresponds to the absorption of specific light wavelength with which electron-holes may be induced[4-10].

Semiconductor materials have properties in between those of conductors and those of insulators i.e the main difference lies in the band gap energy. They have conductivity intermediate that of insulator and conductors. Common semiconducting materials are crystalline solids. TiO_2 has band gap of 3.2 eV. At 0K the valence band is occupied by electrons and conduction band is empty. The conductivity of semiconductors can be increased by increasing the temperature or by metal doping. CdS, Fe_2O_3, ZnO and TiO_2 are some of the semiconductor photocatalysts but the primary focus in photocatalysis is the TiO_2. TiO_2 mainly exits in two crystallographic forms anatase, and rutile. Degussa P-25, produced by a German company is the most popularly used TiO_2. It is composed of 80 % anatase form and 20 % rutile form, and it is very active. The BET surface area of TiO_2 is 50±15 m^2/gm and its particle size is around 21 nm. It has strong oxidizing power at ambient temperature and pressure. It also posses properties like physical stability, chemical inertness, superhyrophilicity and is cheap and readily available.

When light incident on the semiconductor material; The photons with the right energy are absorbed by the semiconductor material.The electrons from the valence band have enough energy

to jump to conduction band and then an electron is promoted to the conduction band. The hole will oxidize the absorbed species (some organic compound or some inorganic species also)

The electrons present in the conduction band reacts with other compounds present in the solution such as oxygen. These electrons can be absorbed by the oxygen to form superoxide ion or in a reaction together with oxygen and H^+ to form hydrogen peroxide[11-16].

All these species formed all highly reactive in nature. The oxygen present in the solution prevents the electron to drop back to the valence band, thus making hole free for the reactant species to being get oxidized. For the valence band hole and conduction band electron there is possibility of recombination of electron–hole pair and dissipate energy as heat. This recombination can be avoided by decreasing the size of semiconductor. From the studies it was found that if we decrease the particle size, the distance that photogenerated electrons and holes have to migrate to reaction sites on surface become short or we can say the electron-hole pair have to travel less distance as compared to that in which particle is of higher size. And this decrease of size results in a decrease in the recombination probability[1].

The overall photo efficiency of TiO_2 can be increased by the addition of metals[17-18]. The reason behind this enhancement is the decrease in the recombination rate of electron-hole pair, which is due to better charge separation between the electrons and holes. Electrons get accumulated on the metal and holes remain on the photocatalyst surface, being used by the oxidizing species. The general mechanism for photocatalysis can be represented as:

$$TiO_2 \longrightarrow e^- + h^+$$

$$M^{n+} + TiO_2(ye^-) \longrightarrow M^{(n-y)+}$$

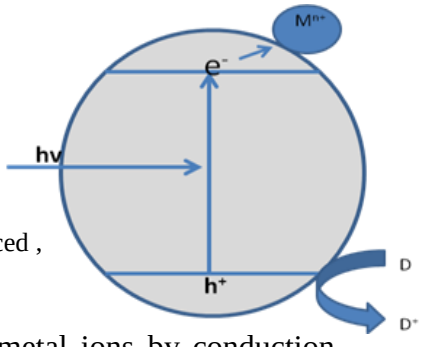


Figure. 1. Mechanism of metal loading to photocatalysis (M^{n+} is to be reduced , D is donor species)

The metal photodeposition process involves the reduction of metal ions by conduction band electrons of photocatalyst, and the oxidation process is being the oxidation of water by valence band holes. To increase the photodeposition, sacrificial electron donor are added (methanol, formaldehyde etc). The metal-ion implanted titanium dioxide, has been found to be shifted the absorption to the visible region. Different metals have different effect on this shift called

the red shift. And also the activity of metal photodeposited TiO_2 depends upon the number of metal photodeposited TiO_2 particles not on the amount of metal deposition[20-21].

2. Work done on degradation of pyridine, pyrazine and pyridazine: Though there has been much work done on photocatalysis using TiO_2 for oxidation and reduction reactions like oxidizing alchols into ketones, reducing nitrobenzene, or for synthesizing compounds, treating waste water or environmental cleaning purposes but not much work has been done on degradation of heterocyclic compounds. These compounds are also present in the structure of many pesticides and herbicides. Specially, pyridine is present in many waste water and regarded as carcinogenic compounds. Pyridine was degraded using ZnO[22-24.] It follows the same mechanism of TiO_2. With ZnO pyridine was degraded within 5 hours. According to mechanism proposed the pyridine first oxidizes to 2-hydroxypyridine which on ring cleavage leads to the formation of dialdhydes and formaide which mineralizes to nitrate ions. Also pyridine was degraded using TiO_2 within 70±5 min[25-26]. The degradation pathways reveal the existence of multiple intermediates. Complete mineralization of organic nitrogen was observed which was analyzed by High Performance Liquid Chromatography.

The thermal decomposition of pyrazine, pyrimidine and pyridine in shock waves have been investigated using the technique of laser and densitometry and time of flight measurements[27]. It was found that various forms of NO_x species were formed during the time of pyrolysis. The free radical path was proposed for the pyrolysis of these compounds. Also the products obtained were HCN, C_2H_2. These decomposition were considered to follow free radical mechanism. It was found from the photocatalytic processes taking place on TiO_2 that nitrogen containing compounds on mineralization leads to the formation of N_2 gas, ammonium and / or nitrate ion through the photooxidation and /or photoreduction pathways. The final fate of organic N_2 under photocatalytic processes has been reported to be related essentially to the initial oxidation state of nitrogen in the organics to the presence/ absence of oxygen and in few cases to the structure of the organic molecules, which has been rationalized on the basis of the nature of N-N and C-N bonds in which the organic nitrogen is involved[28-31].

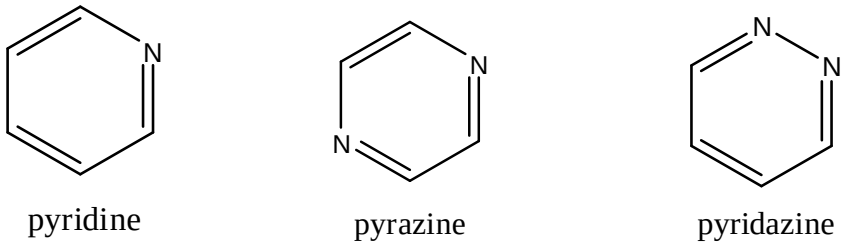
The biodegradation of pyrazine derivatives were studied and it was found that P450 enzyme oxides the alkyl group to form the corresponding alchol or carboxlylic acid or the ring can be hydroxylated by molybedenum- containing oxidases of the xanthin oxidase type[32].

Acetamiprid is a widely used pyridine-based insecticide. Its degradation was carried out using UV light in presence of TiO_2. The process of photocatalytic degradation was conducted under

controlled conditions at 43^0C with constant stirring and O_2 bubbling through. The proposed pathway of hydroxylation of the aromatic ring is probably due to OH^0 radical formation, which is the main oxidant attacking substrate, which yields the hydroxylation products and quinonidol structures and opening of the ring. It was found from analysis that during degradation, acetaldehyde, formic acid and acetic acid, pyridine containing intermediates are formed. The HPLC/MS measurements also proved the presence of aromatic degradation intermediates.

3. Objective: TiO_2 has many applications but its main application is in environmental pollution control. The rings of herbicides and pesticides contain heterocyclic compounds like pyrazine, pyridine, quinoline, indole etc which are main toxic components present in them. TiO_2 mediated photocatalysis gives an easy way to degrade these pollutant materials from the water and soil. There is a class of heterocyclic compounds which contain hetero atom in their ring, example includes indole, quinoline , pyridine, furan etc. Pyridine is a toxic, odoriferous compound and gives unpleasant smell. . Pyridine sticks to soil particles. It contaminates air and water[22-23]. Exposure to pyridine more than 1000 ppm cause health problems or death.

Pyrazine and pyridazine are class of compounds that occur in nature. In humans and animals, pyrazines are excreted as glucuronates or bound to glutathione via kidney after hydroxylation but the ring is not cleaved. When these wastes containing pyrazines goes to drains they act as source of food for some bacteria or viruses. Also some pyrazines have been found to have pharmacological effects, such as diuretics, tuberculostatic effects. . Alkylpyrazines are component of flavour of fried meat, potatoes, coffee, cocoa and some cheese. It is used as flavoring agent. Pyrazine and its derivatives possess herbicide and antibiotic activity[32]. The harmful effects includes eye irritation, may cause respiratory tract irritation**.** Our aim is to study the photocatalytic degradation kinetics of six membered heterocyclic compounds having one nitrogen atom compared with more than one nitrogen atoms versus the position of nitrogen atoms in the aromatic ring using TiO_2 mediated photocatalyst and to study the effect of number and position of nitrogen atom present in the heterocyclic ring structure during their degradation. The compounds which were studied for degradation were pyridine, pyrazine and pyridazine. Their structure are as follows:



pyridine pyrazine pyridazine

Fig. 2. Structure of heterocyclic compounds to be studied.

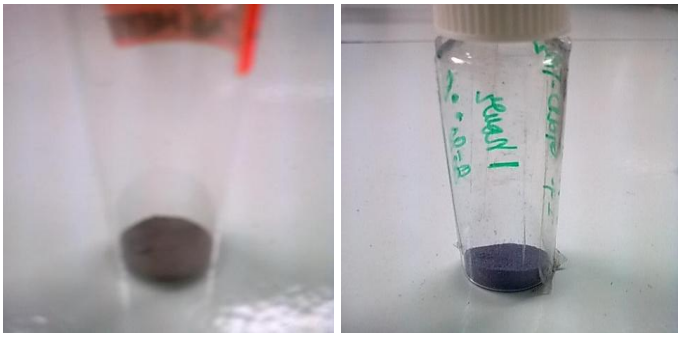
It is expected that due to different aromatic stability and resonance energy of the above compounds, the primary step of photocatalytic degradation, namely, hydroxylation will be in different extent and as a result, their degradation rate will be structure dependent as a function of number and position of nitrogen atoms in the aromatic ring.

4.Experimental section

Pyridine used for the experimental work was purchased from Loba Chemie. Pyrazine and pyridazine was purchased from Sigma Aldrich.

For carrying out the photocatalytic degradation solution of pyridine, pyrazine and pyridazine were prepared (0.5 mM) in distilled water. For irradiation, 5 ml of this solution and 50 mg of TiO_2 was taken in a test tube. Then it was irradiated for 1 hour, 2 hour, 4 hour and 6 hours and analyzed . Similar procedure was followed for different weight percentages of Fe^{+2} –TiO_2, gold photodeposited TiO_2, silver photodeposited TiO_2 and for gold nanoparticles (50 µl, 100 µl, 200 µl, surface plasmon band 528 nm and average particle size 3 nm) addition to TiO_2 . For different weight percentages of Fe^{+2}-TiO_2, calculated amount of salt was directly added to the test tube containing TiO_2 (50 mg) and 5 ml aqueous solution (3.5 mg Fe^{+2} salt for 1 %, 1.8 mg for 0.5 wt % and 7 mg for 2 wt % Fe^{+2}-TiO_2). Silver and gold loaded TiO_2 samples were prepared by photodeposition method. Analysis of irradiated samples were done by UV-Vis Spectrophotometer (Analytikjena Specord 205) in the range 200 nm-600 nm and using HPLC (Agilent technologies, with C-18 column gradient pump, 250mm× 4.5mm, 5µM). Mobile phase was 50:50 methanol and water for three of the compounds. For pyridine the detector signal was set at 250 nm, for pyrazine it was 260 nm and for pyridazine the detector signal was 240 nm. Flow rate was 0.5 ml/min for pyridine and 1 ml/min for pyrazine and pyridazin.

Photodeposition of gold and silver: For 0.5 wt % photodeposition of gold and silver, amount of TiO_2 taken was 100 mg and then calculated amount of metal salt solution was added to test tube containing 100 mg TiO_2 and 10 ml of 1:1 methanol and water (for gold photodeposition 255 µl of 0.01 M gold solution was added, for silver photodeposition 926 µl of 0.01M solution was added). Nitrogen gas was purged from this mixture for 20 min and test tube was tightly closed by rubber cap and irradiated for 1 hour. Then this metal deposited solution was centrifuged, washed and dried at 80^0C and used for photocatalytic reaction.

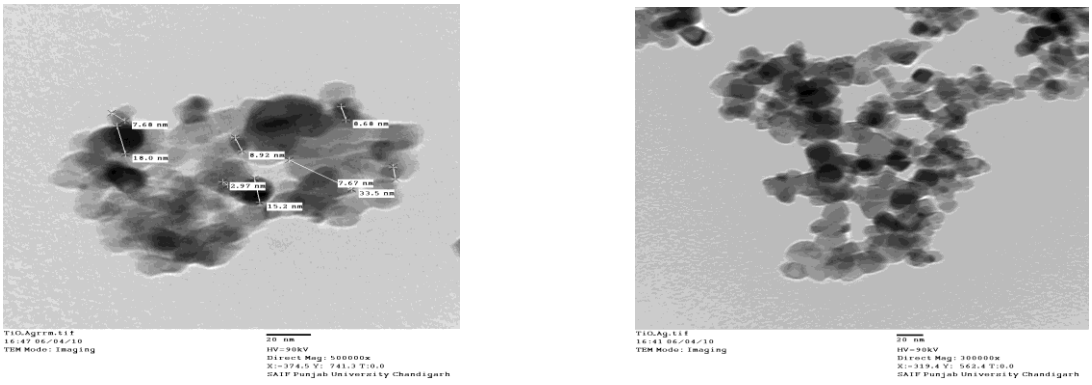


(a) (b)

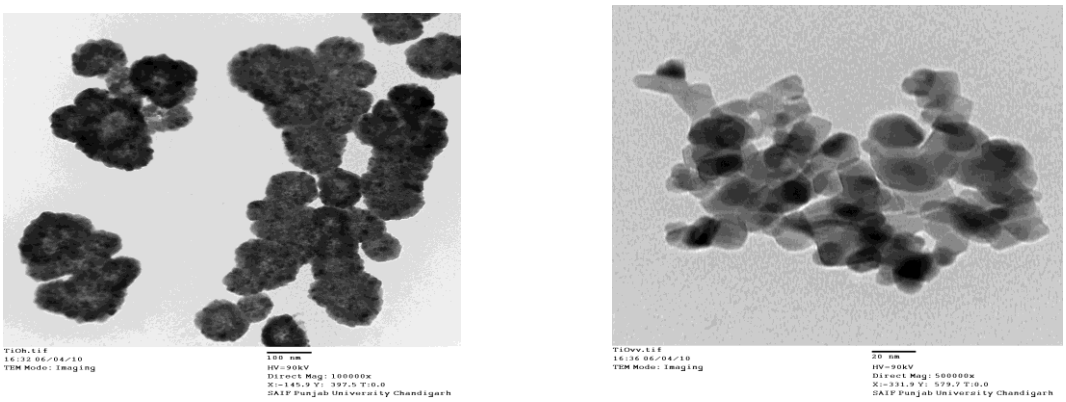
Fig. 3. Picture of (a) silver photodeposited TiO_2 (b) gold photodeposited TiO_2 (0.5 wt percentage both).

5. Results and discussion

Characterization of Ag and Au photodeposited TiO_2 samples was carried out using TEM technique (using Hitachi-7500 Model, resolution = $2A^0$, power = 120 KV). The images obtained are shown below



(a) (b)



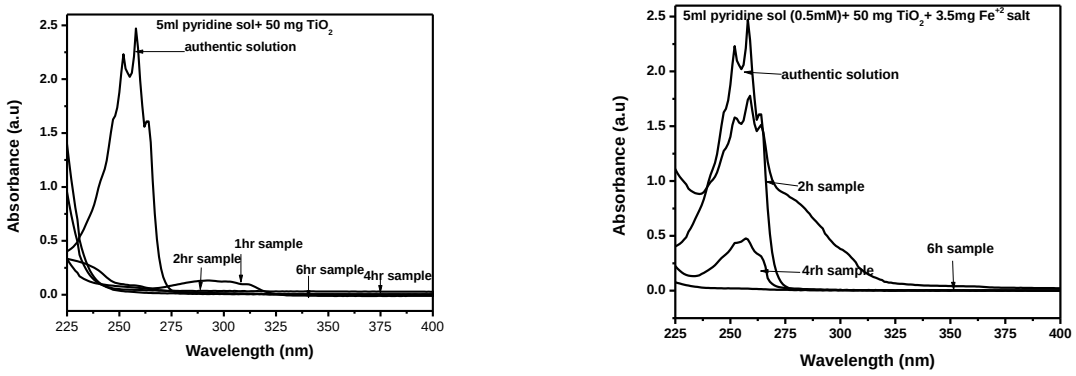
(c) (d)

Fig. 4. TEM images of (a,b) Ag photodeposited TiO_2 (0.5 wt %) (c,d) Au photodeposited TiO_2

The black colored particles in figure 4 (a, b) represent the silver metal photodeposited on TiO_2. The average particle size for silver photodeposited TiO_2 comes out to be 8.28 nm. Figure 4 (c, d) shows the gold photodeposited TiO_2. In 4 (c) aggregated particles are shown in which black colored gold particles are deposited on the large aggregated TiO_2 particles.

5.1 Pyridine degradation results: The degradation samples were analyzed using UV-Vis and HPLC technique as also mentioned in previous section. The peak of authentic sample comes around 252 nm, 258 nm and 262 nm. Since pyridine is heterocyclic, it is expected to have several peaks due to π-π^* and n- π^* transitions[22,25].

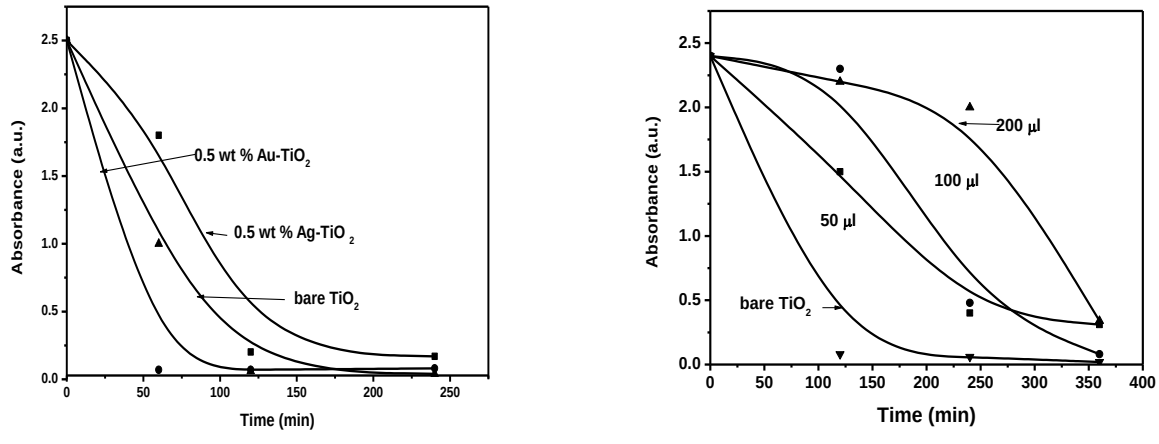
As mentioned in previous section, pyridine was degraded using TiO_2, with different weight percentage of Fe^{+2}-TiO_2. With TiO_2 and with Fe^{+2} –TiO_2 (1 wt %) added in it, the degradation results are shown in figure 5 (a) and 5 (b). With TiO_2, pyridine almost degraded in 2 hours and a new peak is seen around 280 nm, due to formation of 2-hydroxypyridine. When 1 wt % Fe^{+2}-TiO_2 used, the activity of the photocatalyst decreases and complete degradation occurs after 4-6 h irradiation, as can be seen from the UV spectra compared with bare TiO_2 which degraded within 2 h illumination



(a) (b)

Fig. 5. UV-VIS spectra for pyridine degradation using (a) TiO_2 (b) TiO_2 - Fe^{+2} (1wt %) .

Pyridine solution was irradiated with silver photodeposited TiO_2 and gold photodeposited TiO_2 (0.5 wt % each). The absorbance decreases to 94% in 6 hours for silver photodeposited TiO_2 and to 97 % in 4 hours for gold photodeposited TiO_2. The graph is shown in figure 6 (a). The rate of degradation in case of gold is more than that of silver. It can be explained on the basis of standard redox potential of the gold couple related to V_{fb} because only those species with reduction potentials much more positive than the cb edge can be photoreduced. Gold having more positive reduction potential (+1.0) than silver (+0.5) can be more easily photoreduced, giving higher degradation rates. Also the degradation was carried out using gold nanoparticles with different concentration i.e. 50µl, 100µl, 200µl. The result obtained with gold nanoparticles is shown in fig 6 (b)

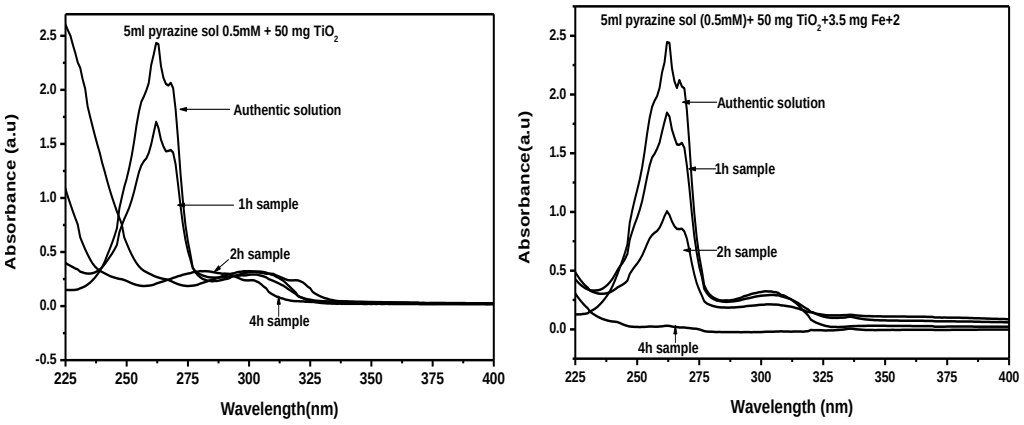


(a) (b)

Fig. 6. Absorbance vs Time graph of pyridine solution degraded (a) with silver and gold photodeposited TiO_2 (0.5 wt % each) (b) with different amount addition of gold nanoparticles.

The possible explanation of the trend for gold nanoparticles is that for 50-100 µl gold nanoparticle addition is just optimum TiO_2 photoactivity. As the concentration of Au nanoparticles addition increases (> 200 µl), the photocatalytic activity decreased.

5.2 Pyrazine degradation results: The peaks obtained for pyrazine were at 262 nm, 268 nm and 304 nm. Since pyrazine is also heterocyclic, n-π* and π-π* transitions occurs. Figure 7 (a) shows the amount of pyrazine degraded at different time with TiO_2 catalyst. Figure 7 (b) shows the UV-Vis spectra for pyrazine degradation using 1 wt % Fe^{+2} -TiO_2. Comparative rate of degradation by various (0.5, 1, 2 wt %) Fe^{+2} loaded TiO_2 is shown in figure 7 (c).



(a) (b)

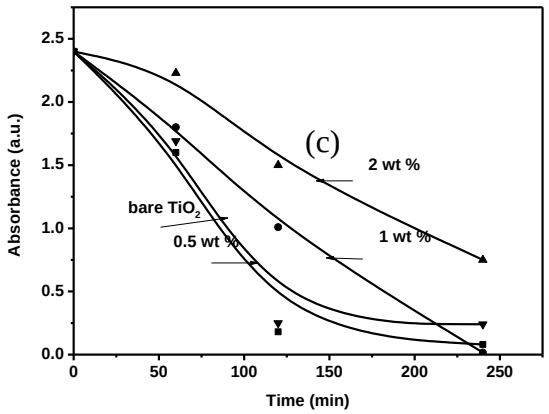
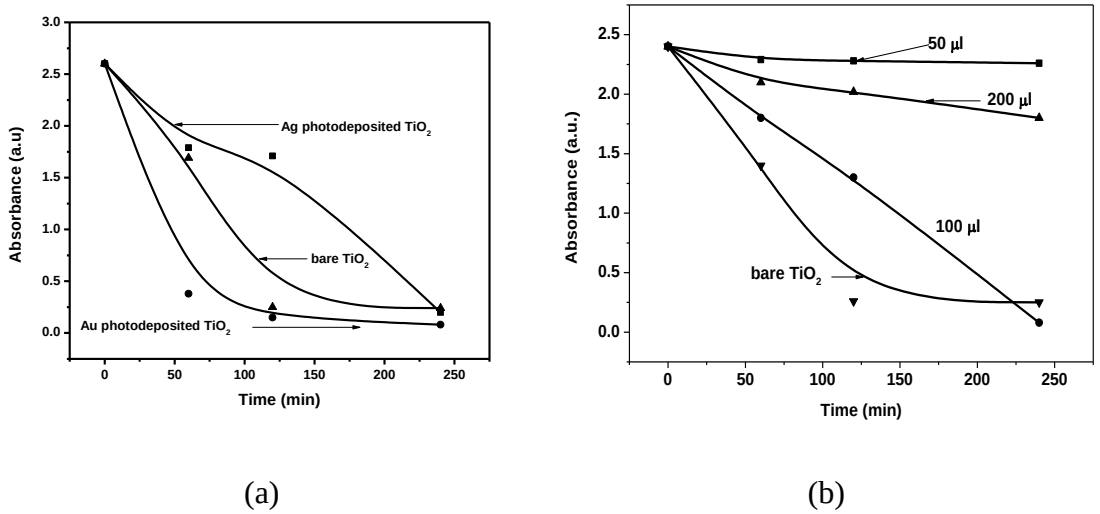


Fig. 7. UV-Vis spectra for pyrazine degradation using (a) 50mg TiO_2 (b) for Fe^{+2} added to TiO_2 (c) Concentration vs Time graph for different weight percentages added to TiO_2.

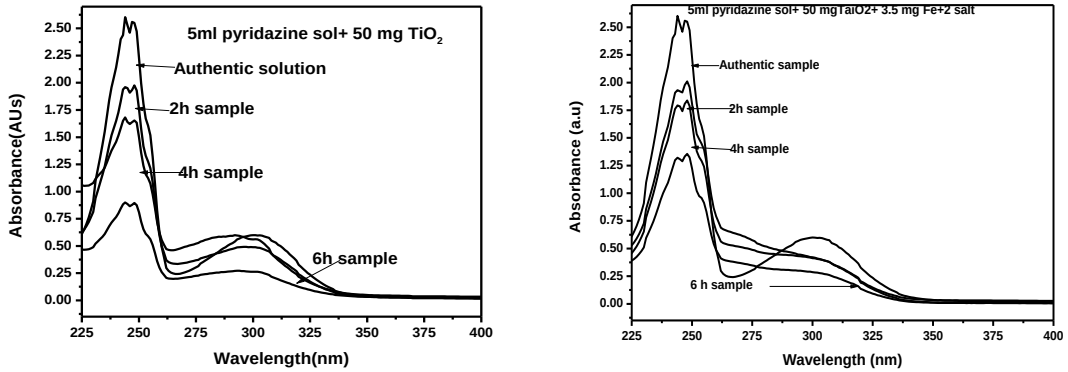
Also the degradation was carried out using gold and silver photodeposited TiO_2. The rate of degradation is higher in case of Au loading compared to Ag loading onto TiO_2. For gold nanoparticle addition to TiO_2, the best degradation results were found for 100 µl gold nanoparticles. The rate is shown in the graph 8 (b).



(a) (b)

Fig. 8. Rate of degradation of pyrazine (a) using gold and silver photodeposited TiO_2 (0.5 wt 5% both) (b) using different gold nanoparticles-TiO_2 composites.

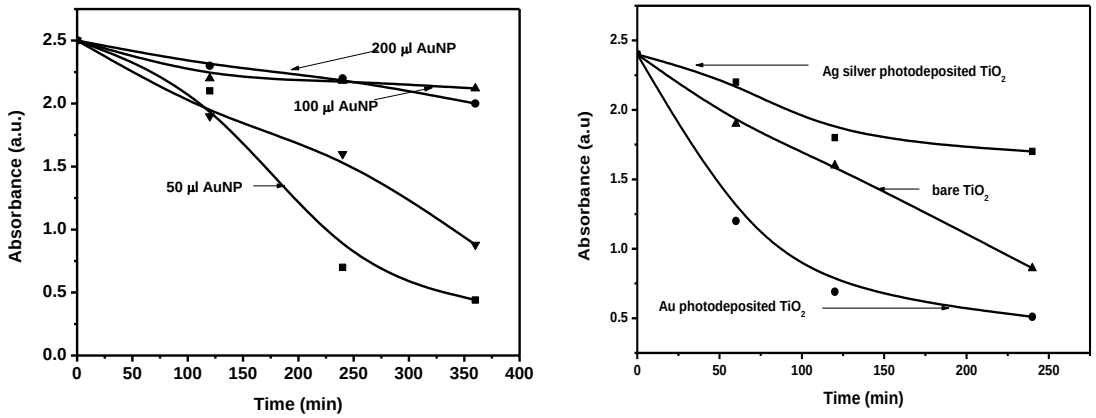
5.3 Pyridazine : Degradation results for pyridazine aqueous solution for bare TiO_2 are shown in fig 9 (a)



(a) (b)

Fig. 9. UV-Vis spectra of pyridazine solution degraded (a) with bare TiO_2 (b) 1 wt % Fe^{+2} –TiO_2 .

For 1 wt % Fe^{+2}-TiO_2 the rate of degradation rate is shown in figure 9 (b) which is slower as compared to bare TiO_2 .



(a) (b)

Fig. 10. Rate of degradation of pyridazine with (a) different amount of gold nanoparticles (b) with gold and silver photodeposited TiO_2 (0.5 wt % each).

Figure 10 shows the degradation of behavior of pyridazine aqueous solution with different amount of gold nanoparticles addition. Also the pyridazine solution was degraded using silver and gold photodeposited TiO_2 (0.5 wt %). The pyridazine degraded more with gold photodeposited TiO_2 compared with Ag deposition as seen in fig 10 (b) above.

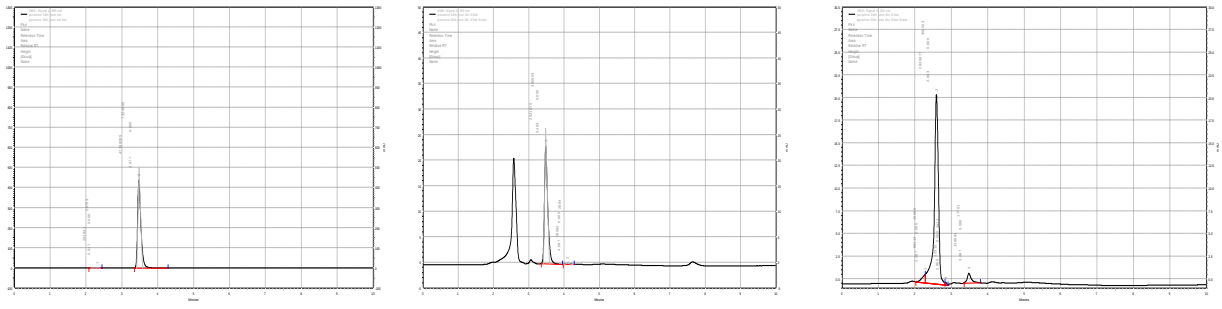
5.4 HPLC analysis: The rate of degradation of three heterocycles (Pyridine ,Pyrazine and Pyridazine) was studied using HPLC analysis. The following table shows the chromatogram data obtained for pyridine degradation at various time

	Retention time	Area%	Height %
Authentic pyridine sol	8.74	100	100
1hr degraded sample	6.427 8.753	17.73 78.77	20.49 73.02
2hr degrade sample	6.403 8.737	17.73 5.18	53.02 5.85

Table 1: Raw HPLC data for the degradation of pyridine using TiO_2 .

It can be seen from HPLC analysis that concentration (100 %) of pyridine (retentime time, R_t 8.73 min) solution gradually decreases (78.77 and 5.18) with increasing (1-2 h) irradiation time.

Pyrazine analysis: For HPLC analysis of pyrazine chromatograms of aqueous solution of pyrazine and its degradation samples with Fe^{+2} –TiO_2 (0.5 wt %) at different time intervals were analyzed (1h, 2h and 4h). From the chromatograms, the peak area/height of pyrazine (retention time 3.47 min) gradually reduces with time and a new peak appears with retention time of 2.5 min whose height % goes on increasing (29, 45.9 and 90.53) with the gradual increase in the time intervals and pyrazine peak completely vanishes at 4 h irradiation. This new peak can be of 2-hydroxypyrazine.



(a) (b) (c)

Fig 12: HPLC chromatogram of pyrazine degardation sample with Fe^{+2} (0.5 wt %) (a) authentic solution (b)1 hour (c) 2 hour (d) 4 hour degraded samples.

For authentic sample and for the intermediate formed with time, the retention values and their corresponding area % and height % are given in table 2.

	Retention time	Area %	Height %
Authentic pyrazine sample	3.47	99.84	99.93
1 hr degraded sample	3.48 2.557	66.29 33.56	70.9 29
2hr degraded sample	3.48 2.57	45.19 50.98	52.02 45.97
4hr degraded sample	3.48 2.58	4.52 92.18	4.57 90.53

Table 2. Area % and height % for pyrazine degradation using 1 wt % Fe^{+2} - TiO_2.

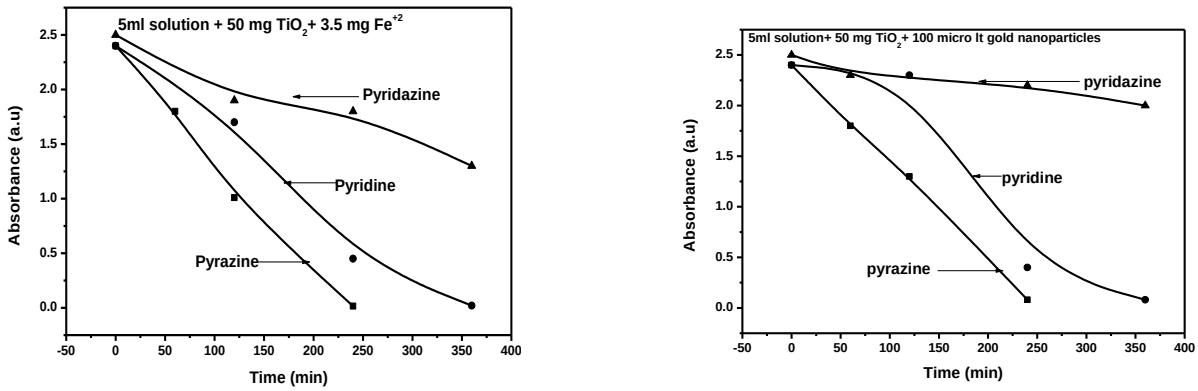
Pyridazine chromatogram: HPLC analysis of pyridazine degradation was done using 1 wt % Fe^{+2}-TiO_2. For pyridazine degradation, not much intermediates were formed. Only a peak with retention time 3.02 and with 14.08 height % appears after time interval of 4 hours. Degradation rate is slow compared with pyridine and pyrazine.

	Retention time	Area %	Height %
Authentic sample	3.213	100	100
4h degraded sample	3.087 3.22	12.16 87.84	14.08 85.92

Table 3: Area % and height % for pyridazine degradation using 1 wt % Fe^{+2}-TiO_2 .

5.5 Comparative study of three heterocyclic compounds

The results for three heterocycles were discussed in above section. Now for studying the effect of number and position of nitrogen atoms present in six membered heterocyclic compounds and their comparative rate of degradation graph are plotted. From the graphs shown in fig 13, it is quite clear that degradation is achieved faster in pyrazine than for pyridine and slowest in case of pyridazine. For 1 wt % Fe^{+2}-TiO_2 and Au nanoparticles added TiO_2, the results are shown in figure 14 (a,b), which clearly shows the degradation trend for pyrazine, pyridine and pyridazine. The graphs showed that the rate of degradation of pyridazine is always least among the three compounds studied.



(a) (b)

Fig.13. Comparative degradation rate of three heterocyclic compounds by (a) 1 wt % of Fe^{+2}-TiO_2 (b) 100 µl gold nanoparticles –TiO_2 composite

It is evident that pyrazine was degraded very first in all the cases, then comes pyridine but its degradation rate is almost comparable to pyrazine and then comes pyridazine. Pyrazine> pyridine > pyridazine. This trend can be explained on the basis of resonance energy. It is generally accepted that for a simple aromatic system a high degree of stabilization is mainly due the fact that at least two of the possible valence-bond structures are indistinguishable, as that are for benzene. Amongst the six membered, aromatic heterocyclic ring systems with one or several nitrogen atoms in the ring, pyridine has identical structure. From the diazines, 1,4-isomer i.e pyrazine has analogous structure. The resonance energies for pyridine, pyrazine and pyridazine are 24.2 Kcal/mol, 8.1 kcal/mol and 12.3 Kcal/mol respectively. So the trend obtained for degradation are explained on the basis of resonance energy and it also depends upon the number of identical Kekules-stucture obtained for the aromatic compound. On substituting –CH= group with –N= the resonance energy decreases as much as 16 Kcal/mol, so the aromatic compounds with two nitrogen atoms have lesser resonance energy as compared to single nitrogen containing aromatic compound. So pyrazine gets degraded before pyridine. For pyridazine, the Kekules structures are not identical, so it is less energetically favored and has higher energy than pyrazine and degraded at slower rate as compared to pyrazine. Also due to different number and position of N atoms, the extent of rate of hydroxylation is different which leads to different rate of degradation.

Conclusion

We have done the above study of photocatalytic degradation of heterocyclic compounds and from the results discussed above, it is observed that the position and number of nitrogen atoms present in the six membered heterocyclic compounds effects the rate of degradation of six membered heterocyclic compounds. Rate of degradation is faster in case of pyrazine, then follows pyridine and pyridazine.

Pyrazine > Pyridine > Pyridazine

The reason for faster rate for pyrazine and the above sequence of degradation rate is combined effect of resonance energy and number of identical Kekule-structures which can be assumed. On degradation these compounds get mineralized to nitrate and ammonium ions. With gold loaded TiO_2 the rate is faster than bare TiO_2 which in turn is faster than iron loaded TiO_2 and other metals co-catalysts are not so effective compared with bare TiO_2 The primary step in the degradation of these compounds is the hydroxylation, the extent of which depends upon the ring structure of the compound leading to the different rates of degradation. The degradation intermediates were analyzed by HPLC. Many intermediates at various time intervals are observed although we have not identifed them. If we know all the intermediates formed than we can have an idea about the mechanism of degradation process of these heterocyclic compounds.

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