PHOTOCATALYTIC DEGRADATION OF METAMITRON (HERBICIDE) IN AQUEOUS SOLUTION USING ANATASE TiO$_2$

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ABSTRACT

In this study photocatalytic degradation of herbicide, metamitron has been studied using photocatalyst, anatase TiO$_2$. Anatase TiO$_2$ was synthesized by the hydrolysis route using dilute sulphuric acid as an oxidizing agent and ammonia solution for precipitation. The catalyst prepared was characterized by XRD and SEM analysis. Effect of various process parameters such as pH, initial concentration of metamitron, catalyst loading etc has been studied in order to obtain the optimal conditions for maximum degradation of metamitron. The optimal pH is found to be 3 and the optimal initial metamitron concentration was 25ppm with catalyst loading of 100mg/L. The rate of degradation of metamitron in various processes such as only UV, only TiO$_2$, UV+ TiO$_2$ followed first order kinetics. The extent of degradation achieved was analyzed using UV- VIS Spectrophotometer.

Keywords: Metamitron, Herbicide, Photocatalyst, Tio$_2$, Kinetics

I. INTRODUCTION

In the past few decades pollution of drinking water by organic compounds has increased tremendously. The pollutants enter into the water system through various sources such as agricultural runoffs and industrial effluents and chemical spills. In the recent times a lot of attention has been given to the protection of environment by industrial effluents and other hazardous wastes. [1-3]

The organic compounds present in the water sources indicates that a significant amount of compounds are non biodegradable and have the ability to persist in the environment for long periods and hence pose a threat to the aquatic and mammalian life.[4, 5]

Pesticides have become an inseparable part of the agriculture and industrial scenario in the recent times. Generally pesticide is a chemical compound that is used to inhibit, kill or retard the growth of pests. Pesticides are broadly categorized as insecticides, herbicides, fungicides and bactericides [5]. Chemical industries and pesticides comprise of a major component of wastewater. These wastewaters contain toxic and non biodegradable components that are difficult to remove even after conventional treatment. Due to poor management of waste this water is discharged into the large water bodies from where it enters the human food chain. Hence the human population is exposed to the pesticides and it has adverse and prolonged effects on the human body. [6, 7]

Among them, some compounds are derived from the structure of 4-amino-1, 2, 4-triazin-5 (4H)-one. Substances of this class, such as metribuzin and metamitron, are used worldwide as herbicides. They are chemically stable and can penetrate slowly through the soil and cause long-term contamination of underground resources of drinking water. [2]

Due to these reasons it has become imperative to find alternative treatments for the removal of these harmful pesticides compounds from wastewater before its discharge. [6]

A lot of techniques are being used in the treatment of wastewater such as coagulation, advanced oxidation processes, filtration, biological treatment, ozonation etc. [8] In recent times the advanced oxidation process is considered as an attractive alternate along with conventional techniques for the removal of toxic components from water and wastewater. Advanced oxidation process (AOPs) essentially makes use of variety of oxidants, ultraviolet irradiations and different catalysts to generate hydroxyl ions (OH•). The hydroxide ions are immensely reactive with an oxidation potential of 2.8 V. These hydroxyl ions oxidize the organic pollutant in the wastewater and further mineralize it to carbon dioxide, inorganic mineral ions and water. A lot of studies have shown the efficiency of AOPs in degradation of organic pollutants (pesticides) in water. The AOPs include a variety of techniques some of them are H_2O_2 treatment, Fenton, homogeneous Photo Fenton, photocatalysis etc. [6, 7, 9]

Recently a lot of study has been done in the field of degradation of organic compounds using AOPs. S. Malato [7] et al studied the photocatalytic degradation of water-soluble pesticides (diuron, imidacloprid, formetanate and methomyl) using solar UV light by photo-Fenton process and TiO_2 catalyst. It was found that photo-Fenton process was more efficient in degradation of compounds as well as mineralization than TiO_2. Ioannis K. Konstantinou et al [10] carried out light induced degradation of herbicide compounds molinate and propanil under simulated solar irradiation in aqueous suspension of TiO_2 and found out complete disappearance of herbicide in less than an hour. Alexander Gora et al [11] carried out the degradation of various herbicide compounds such as simazine, propazine and isopruton over irradiated TiO_2 suspensions in single and multicomponent systems. A direct comparison of the binding constants of the herbicides observed under dark adsorption and under PCO shows that the degradation of isoproturon, simazine and propazine mixtures follows a surface or near-surface reaction according to a competitive L–H mechanism. Biljana Abramovic et al [1] compared the degradation of Picloram using TiO_2 Wackherr and TiO_2 Degussa P25 to observe that the Wackherr TiO_2 showed improved degradation of Picloram than P25 TiO_2 when high catalyst loading and high substrate concentrations were used.

Different types of semiconductors have been studied as efficient photocatalysts for the oxidation of organic compounds. Amongst these TiO_2 is the most popular semiconductor because of its innumerous advantages over other catalysts such as non toxicity, cheaply available, stability towards photocorrosion. [7, 12]

Photocatalytic reaction occurring at the surface of TiO_2 has attracted a lot of attention owing to its practical applications in cleaning of environment. Due to its superhydrophilicity and strong oxidation properties it can also be used as an antibacterial agent. The reactivity and chemical stability of TiO_2 is high under UV light ($\lambda <$ 387nm). Its energy exceeds the band gap of 3.3 eV in the anatase crystalline phase. [6, 12, 13]

The primary step in the process involves the generation of conduction band electrons and valence band holes by the illumination of the TiO_2 with light energy greater than the band gap energy. Some of the electrons and holes migrate to the surface of the particle before recombination occurs. Oxidation occurs if the photogenerated holes

react with adsorbed organic molecules whose oxidation potentials are less positive than the valence band edge. The results of many studies are consistent with the oxidation proceeding via hydroxyl and other oxygen containing radicals formed in reactions between the positive holes and hydroxyl groups or water adsorbed at the titania surface. These radicals are powerful oxidizing agents capable of attacking a wide variety of organic molecules. [9]

Titanium dioxide can prepared using varied processes; sol gel, chemical vapor decomposition, hydrothermal, hydrolysis etc. [14]. Titanium dioxide occurs in three crystalline forms: rutile anatase and brookite. [15]Amongst these the anatase form has shown higher photocatalytic activity [16]. With respect to anatase TiO_2, Malinger et al [17] synthesized crystalline nanoparticles of TiO_2 via continuous hydrothermal method. The size of the catalyst was in the range of 7-13 nm. Also Chi-Hwan Han et al [18] prepared nanocrystalline TiO_2 using sol gel combustion hybrid method with acetylene black as fuel.

In our study we have synthesized TiO_2 catalyst using precipitation route. The prepared catalyst is compared with the commercial catalyst Degussa P25 to study the degradation of herbicide metamitron in presence of UV light. Also the various optimal conditions necessary to obtain the maximum degradation of compound are also studied.

II. EXPERIMENTAL

2.1: Synthesis of catalyst

Materials: Titanium tetrachloride ($TiCl_4$), sulphuric acid (H_2SO_4, 98%), ammonium hydroxide (NH_3, H_2O) were obtained from Thomas Bakers, Mumbai. The reaction was carried out in magnetic stirrer provided with heating plate. Distilled water was used for the preparation of catalyst throughout. Ice bath was used for maintaining cooling temperature.

Method: TiO_2 was prepared using hydrolysis of acid followed by precipitation.

15 ml of 10% dilute sulphuric acid solution was prepared in distilled water. The solution was kept in ice bath so that the temperature is maintained at 0^0C with magnetic stirring. Maintaining the stirring 1ml of $TiCl_4$ was added to the solution slowly. Fumes preferably of HCl were given out. After the addition of $TiCl_4$ the stirring was continued for one hour. After that the temperature of the solution was increased to 65^0C. The heat was removed consequently and the solution was kept to attain room temperature. After attaining room temperature ammonia solution was added drop wise to the solution till pH 7 is attained. The precipitate formed was allowed to stay overnight. The formed TiO_2 nanocrystals were then washed with water and acetone alternately and then dried in oven at 60^0C for 12 hours.

The obtained catalyst was calcined in a muffle furnace for two hours at 400^0C.

2.2: Photocatalytic experiments:

Materials: Metamitron was obtained from Gharda Chemicals, Mumbai as a free sample. The pH of the solution was adjusted using H_2SO_4 and NaOH for acidic and basic side respectively.

Method: The photocatalytic experiments were performed in a quartz glass reactor with (27cm ×7cm, internal diameter with volume capacity of 250ml). The reactor was provided with a jacket to supply cooling water essentially to maintain the temperature of the reaction mixture. The source for irradiation was UV lamps. Water

was used for cooling and the temperature was maintained at 20-25^{0}C. The agitation required for the reaction was provided by magnetic stirrers at the base of the reactor. 250ml solution of the mother solution prepared was used for the experiments. The pH was adjusted using H_2SO_4 and NaOH for the acidic and basic side respectively and it was measured using pH meter.

Analysis: Samples were removed at different times of irradiation, centrifuged in Remi RC 800 centrifuge for 5 min and the supernatant solution was removed from the top whilst the TiO_2 settled at the bottom. The sample was then analyzed by UV-Vis Spectrophotometer with λmax at 301nm (maximum wavelength for Metamitron). The UV-Vis Spectrophotometer is Perkin Elmer.

III. RESULTS AND DISCUSSION

3.1: Characterization of synthesized anatase TiO_2

The phase identification was achieved by X Ray Diffractometer. The XRD pattern of TiO_2 and is shown in Fig.1. The peaks of anatase phase of TiO_2 are seen evidently in the pattern, namely (101), (004), (200), (211), (204), (220), and (215) at 2θ values of ca. 25.38, 37.82, 48.18, 54.4, 62.92, 69.92, 74.9 respectively.
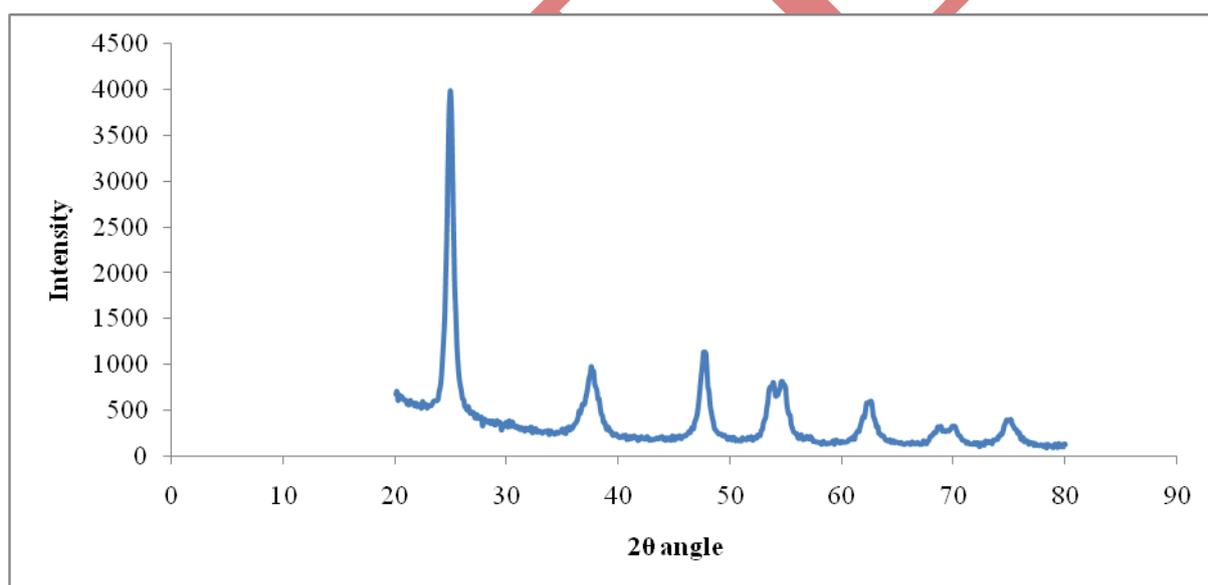
Figure 1: XRD pattern of synthesized anatase TiO_2 calcined at 400^{0}C.

The SEM images of the catalyst prepared are shown in Fig.2. Scanning electron microscopic image is used to observe the cross-sectional morphology of the catalyst.
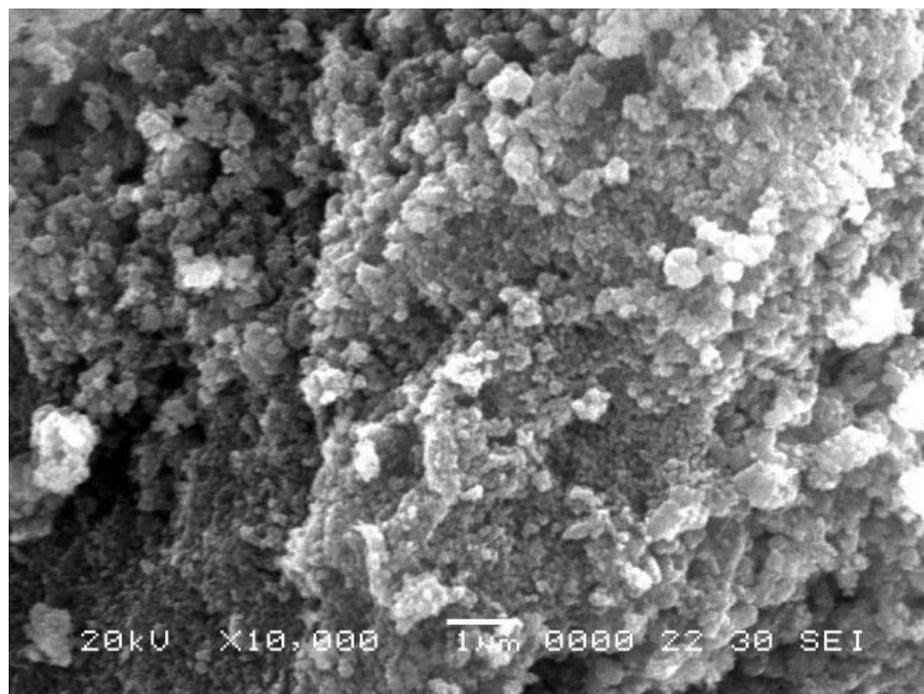
Figure 2: SEM image of synthesized anatase TiO$_2$ calcined at 400^{0}C.

The photocatalytic activity of TiO$_2$ in studied in the degradation of herbicide compound Metamitron in UV light.

3.2. Photocatalytic activity of anatase TiO$_2$

The photocatalytic activity of prepared catalyst is studied using various reaction conditions. The various experiments are carries out using only TiO$_2$, only UV, UV+ TiO$_2$ and UV + P25. It was observed that in experiment consisting of only TiO$_2$, the extent of degradation achieved is very low (5.75%). With the only UV experiment the rate of degradation achieved was substantial. But with the photocatalytic experiments i.e. using prepared catalyst and commercial catalyst, enhanced degradation rate was achieved. It has been observed that the degradation achieved using prepared catalyst and Degussa P25 is comparable. The Table. 1 summarizes the values of k (rate constant) and R^2 (linear coefficient value) for the various processes and the percentage of degradation in each process which depicts that the data approached first order kinetics. The kinetic plot of the various experiments is shown in Fig.3.

Table 1: Kinetics study of the degradation rate of metamitron for different conditions with pH maintained at 3 for all the experiments and initial concentration of metamitron is maintained at 25 ppm.

Sr. No.	Process	Value of rate constant k (min^{-1})	R^2	% Degradation
1	TiO$_2$ only	0.0001	0.955	5.75
2	UV only	0.005	0.953	41.37
3	UV+ TiO$_2$	0.005	0.956	45.7
4	UV+ P25	0.005	0.994	46.93
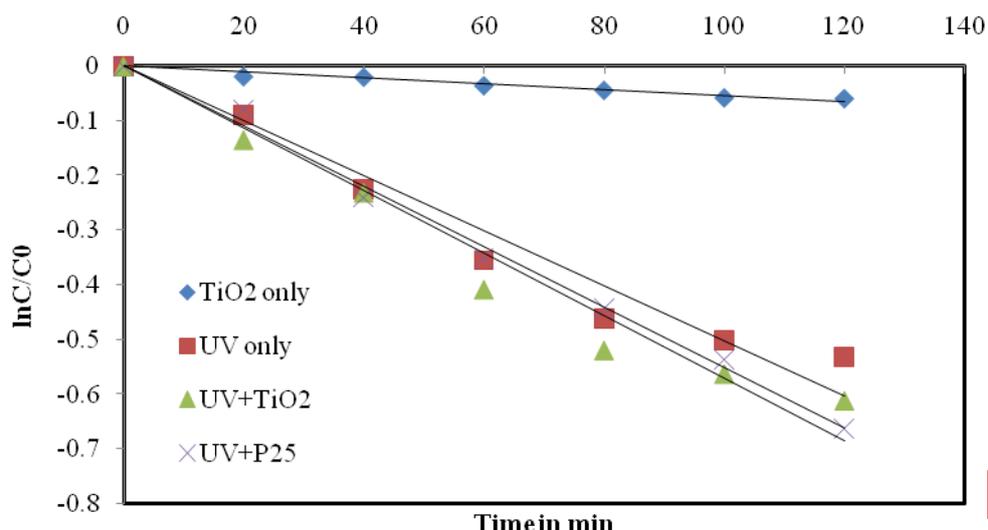
Figure 3: Kinetic plot for the rate of degradation of metamitron for various process conditions. (Subjected to pH- 3, initial concentration of metamitron- 100mg/L)

3.3. Effect of operational parameters:

The photocatalytic process generally depends on the generation and reaction of highly reactive species i.e. the OH• radical. A lot of factors affect the efficiency of the process. We studied the effect of initial concentration of metamitron, catalyst loading and pH variation.

3.3.1. Effect of initial concentration of metamitron:

The effect of initial concentration of metamitron was studied in the range from 10ppm to 40ppm on the rate of degradation. The rate of degradation is depicted in Fig.4 where the pH of the solution and the catalyst concentration were kept constant while the concentration of metamitron was changed.

Table. 2 shows the kinetic study for the degradation rate at different concentrations of metamitron. It was observed that the degradation was achieved maximum at 25ppm. The parameters of pH and catalyst concentration were maintained at 3 and 100mg/L respectively.

Under the relevant experimental conditions, the reactions followed a first order kinetics (as the linear correlation coefficients were in the range 0.956- 0.989).

Table 2: Kinetics study for the effect of change in initial concentration of metamitron with other parameters at optimal conditions. (pH- 3, catalyst concentration- 100mg/L)

Sr No.	Initial concentration of metamitron in ppm	Value of rate constant k (min^{-1})	R^2	% Degradation
1	10	0.004	0.975	41.48
2	20	0.004	0.979	43.51
3	25	0.005	0.956	45.70
4	40	0.004	0.989	42.23
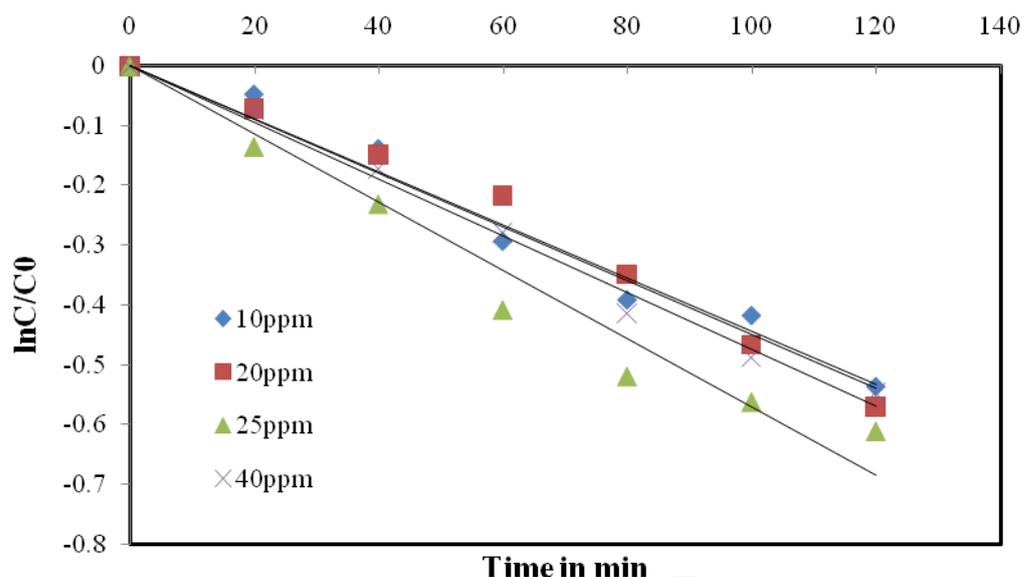
Figure 4: The effect of change in initial concentration of metamitron on its degradation. The pH is maintained at 3 and the catalyst concentration is 100mg/L.

3.3.2. Effect of catalyst concentration:

The loading range of catalyst was varied from 50mg/L to 300mg/L to examine the effect of change in concentration of catalyst on the degradation of metamitron as shown in Fig.5.

The information summarized in Table. 3 implies that with increase in the concentration of catalyst the rate of degradation initially increased but after a critical point, the degradation began to decrease, which was the optimal concentration of TiO_2 that is needed for maximum efficiency. With initially increase in the amount of catalyst, the degradation increased due to the increase in available surface (active sites) for reaction. But with further increase in the catalyst amount the surface of the catalyst gets clogged due to agglomeration, hence causing a decrease in the number of active sites and consequently the rate of degradation. Dusan Mijin et al [2] carried out the degradation of metamitron using suspensions of ZnO and observed that complete disappearance of metamitron was observed using high catalyst loading (about 2g/L) in about 4 hours.

The experimental results showed that the procedure follows a first order kinetics as the linear correlation coefficient is in the range 0.943- 0.965.

Table 3: Kinetic study to determine the effect of change in catalyst loading on the rate of degradation of metamitron. (pH-3, initial concentration of metamitron- 25 ppm)

Sr No.	Catalyst loading mg/L	Value of rate constant k (min^{-1})	R^2	% Degradation
1	50	0.005	0.965	44.37
2	100	0.005	0.956	45.70
3	200	0.004	0.943	36.25
4	300	0.003	0.951	25.68
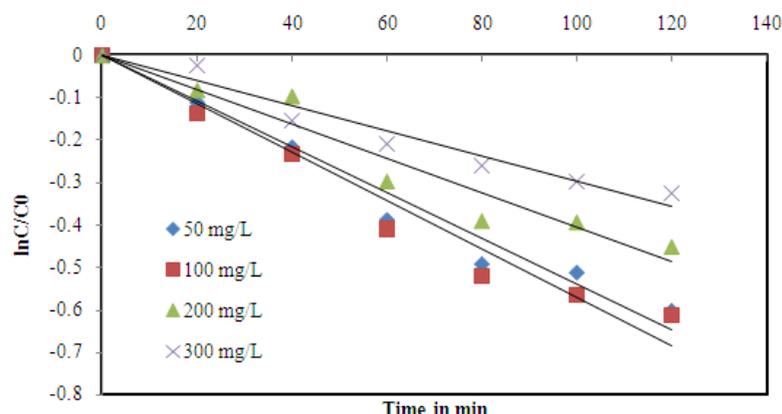
Figure 5: Effect of catalyst loading on the rate of degradation of metamitron at pH 3 maintained throughout with 25ppm initial concentration of metamitron solution.

3.3.3. Effect of pH:

It has been observed that the pH has an influence on the photodegradation of certain organic compounds. As shown in Fig.6; the pH values 3, 4, 7 and natural were studied to find the optimum pH for the higher efficiency of degradation of metamitron with catalyst concentration of 100mg/L. The optimal value of pH is obtained at 3. Kinga A. Malinger et al [17] synthesized anatase nanoparticle TiO_2 of controlled size in the range 7-13nm by precipitation of $TiCl_4$ using NaOH at pH 3. The pH was adjusted prior to the photocatalytic reaction by addition of H_2SO_4 and NaOH for acidic and basic pH respectively.

It can be seen from Table. 4 that the reactions followed first order kinetics where the linear coefficient value ranges from 0.930- 0.986.

The pH of the solution when on acidic side showed higher degradation and the rate of degradation decreased with increase in pH and was negligible on the basic side. With direct photolysis the degradation was found higher on the basic side. In the neutral form the adsorption on the surface was not affected hence there was a slight increase in the rate of degradation at natural pH.

Table 4: Kinetic study of the degradation of metamitron for the effect of change in pH (with initial concentration of metamitron 25ppm and the catalyst concentration at 100mg/L).

Sr. No.	pH	Value of rate constant k, (min^{-1})	R^2	% Degradation
1	3	0.005	0.956	45.7
2	4	0.002	0.942	27.3
3	5	0.002	0.986	22.71
4	7	0.001	0.930	17.13
5	Natural	0.001	0.949	25.56
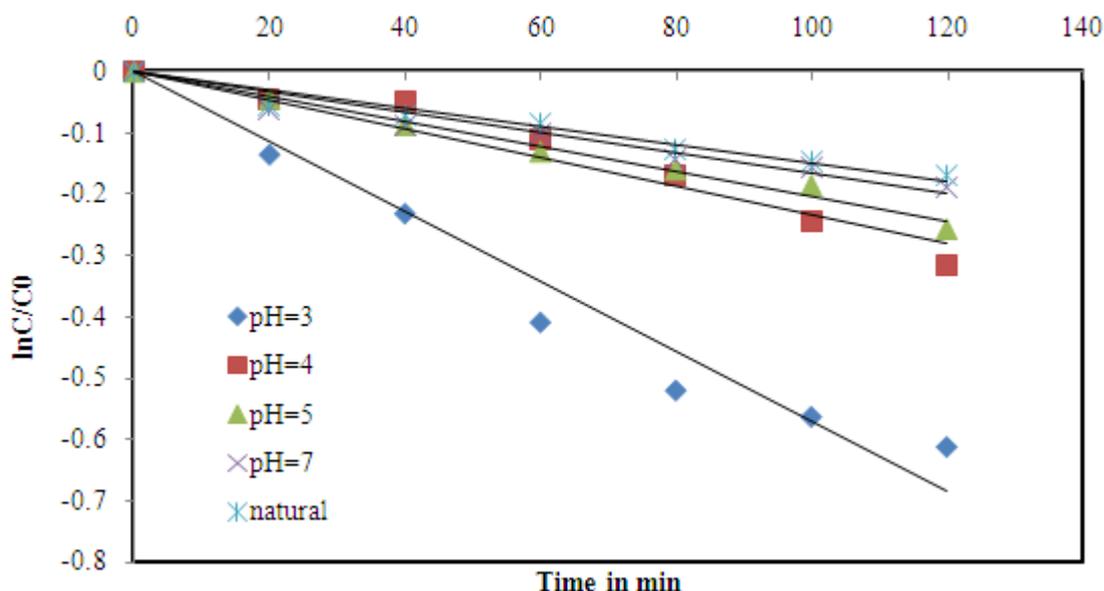
Figure 6: Effect of pH on the degradation of metamitron with catalyst loading of 100mg/L and initial concentration of metamitron of 25ppm.

IV.   CONCLUSION

The photocatalytic degradation of metamitron was studied using anatase TiO_2 and UV light source. It has been observed that the anatase TiO_2 can be used successful for the effective degradation of metamitron. The performance of synthesized anatase TiO_2 was comparable to commercial catalyst Degussa P25, since the extent of degradation of metamitron was obtained to be 45.7% using prepared anatase TiO_2 and 46.93% using commercial Degussa P25. The study of operational parameters indicated that the initial concentration of metamitron, catalyst concentration and pH variation have an impact on the rate of degradation. The optimal value of initial concentration was 25ppm for catalyst concentration of 100mg/L. The optimal pH value for the degradation was found to be 3.

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