

# Experimental Studies of Photocatalytic Degradation of Rhodamine B by Doped Titania under Solar Light Radiation

P. Buella Nesa Kumari<sup>1</sup>, G. Allen Gnana Raj<sup>2</sup>

Department of Chemistry and Research Centre, Scott Christian College, (Autonomous), Nagercoil, Tamilnadu, India

**Abstract:** *The photocatalytic degradation of aqueous solutions of rhodamine B in doped titania suspensions have been investigated with the use of sunlight as energy source. Semiconductor photocatalysis is an resourceful method for the chemical consumption of energy from sunlight. It is based on the surface trapping of light-generated charges which induce interfacial electron-transfer reactions with a great variety of substrates. A visible-light-active photocatalyst was prepared through carbon doping by using dextrose as carbon source. Preparation was performed by a sol-gel method at 400° C and named as 1C-TiO<sub>2</sub>. The effects of catalyst loading, dye concentration, pH and component on the phase composition and photocatalytic activity were investigated. The results demonstrated that carbon atoms are exist in the structure of titania and led to the response to visible light. The resulting photocatalyst was characterized by XRD, SEM, EDX. The decrease in concentration of rhodamine B was monitored by UV-Visible spectroscopy. The characterizations found that the photocatalyst possessed a high surface area and a crystalline size is about 10 nm. On the degradation of rhodamine B in water under visible light irradiation [ $\lambda = 554$  nm]. The photocatalytic activity increased with decrease in concentration of catalyst and increase in light intensity and alkaline pH.*

**Keywords:** Photocatalysis, titanium dioxide, degradation, rhodamine B

## 1. Introduction

In present situation chemical and biological pollution treatment is one of the foremost concerns of the mankind. All the conventional water and air pollution treatment systems are costly and energy concentrated. Many researchers have been trying to develop new efficient photocatalysts for pollution treatment after the invention of photocatalysis by Fujishima and Honda [1-6]. Photocatalytic degradation by semiconductors is a new and effective technique for the removal of pollutants from water [7-9]. The semiconductor photocatalyst TiO<sub>2</sub> has a wide band gap i.e. 3.2 eV and hence successfully used as a photocatalyst for the treatment of organic and dye pollutants [10-13]. The photo bleaching of some dyes could be achieved by solar light irradiation using TiO<sub>2</sub> as a photocatalyst [14]. In most of the catalytic applications, high surface area and optimum pore size are needed for interaction with active sites and diffusion of reactive species [15]. A suitable method to enhance the photocatalytic ability of titania including introduction of impurities to increase the visible light responsiveness. Pure titania is doped with different metals like Cu, Zn, Cr, Fe [16-19] and non metals including N, S, C [20-22] have been reported. Doping with metal and doping nonmetal were the most feasible methods for improving the photocatalytic performance of titania. When the electron hole pairs migrate from the inside of the photocatalyst to the surface, the doping metal atoms can suppress the recombination of photo-induced electron-hole pairs so as to increase the photo quantum efficiency [6,9]. On the other hand the doping non metal atoms can be incorporated into the lattice structure of titania, decrease the band gap and give rise to the response to the visible light [23-26].

The objective of the current work is to prepare carbon doped titania in anatase phase and to study the effectiveness of the catalyst in photodegradation of rhodamine B in aqueous

media. In this paper the carbon doped titania photocatalyst was prepared and was characterized by XRD, SEM, EDX. The degradation of rhodamine B under visible light illumination was used to evaluate the photocatalytic properties.

## 2. Methodology

### 2.1 Preparation of 1C-TiO<sub>2</sub> by Sol-gel method

1C-TiO<sub>2</sub> photocatalyst was prepared by sol-gel method, the benefits derived from preparing 1C-TiO<sub>2</sub> by sol-gel method which include synthesis of nanosized crystallized powder of high purity at relatively low temperature, possibility of stoichiometry controlling process. TTIP as the precursor of titanium and dextrose as the source of carbon. 12.00 g of TTIP liquid was mixed with 5 cm<sup>3</sup> of absolute ethanol unit, the homogeneous solution was given. Dextrose solution is added drop by drop into TTIP under constant stirring, white precipitate was given immediately. Solution with white precipitate was stirred 30 minutes and stand 18 hrs for aging. After aging white solid was filtered and calcined at 400° C for two hours and named as 1C-TiO<sub>2</sub>.

### 2.2 Photodegradation of rhodamine B

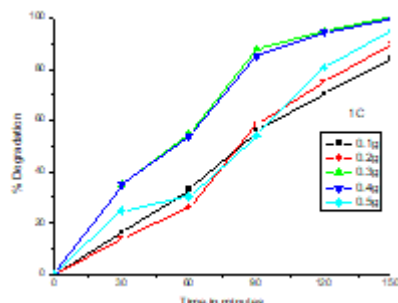
The photodegradation of rhodamine B was examined by sunlight of intensity 800 X100 Lux. The experiment was performed with 100 mL of water containing 10<sup>-4</sup> M rhodamine B and 0.1g of 1C-TiO<sub>2</sub> respectively. The described intensity allowed to pass through the reaction mixture and the progress of the degradation of rhodamine B was monitored every 30 minutes by UV – Visible spectroscopy. The extent of decomposition can be measured using UV – Vis spectrometer at a wavelength of 554 nm, which corresponds to the absorption maximum of rhodamine B. At the same time 100 mL of water with 10<sup>-4</sup> M

rhodamine B was tested and monitored by UV – Vis spectroscopy to investigate if degradation also occurs in the absence of the photocatalyst.

### 3. Results

#### 3.1 Effect of Catalyst Load

(Fig.1) shows the influence of catalyst concentration on photocatalytic degradation rhodamine B at  $10^{-4}$  M solution and 0.1g/100 mL 1C-TiO<sub>2</sub>

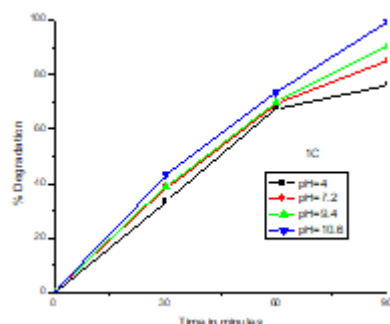


**Figure 1:** Effect of catalyst concentration on % degradation using 1C-TiO<sub>2</sub>

The effects of catalyst loading on photocatalytic degradation of dyes in wastewaters have been studied [27]. Results show that the the initial rates were found to be directly proportional to catalyst concentration. Further observed that there is a limit of catalyst concentration that must be used for the photodegradation of rhodamine B, above which the rate of photocatalysis will even decrease. This is in agreement with recent reports [28]. Here the percent degradation of 1C-TiO<sub>2</sub> is increase maximum amount of 0.3g/100 ml. This indicated that the active site provided for the adsorption of substrate on the catalyst surface is limited to catalyst amount of 0.3g/100 ml. The increase in the degradation efficiency of the dye is due to an increase in the active sites available on the catalyst surface for the reaction, which in turn increases the rate of radical formation. The reduction in the degradation when the catalyst amount is increased ie beyond 0.3g/100 ml is due to light scattering and reduction in light penetration through the solution and also the deactivation of activated molecules by collision with ground state molecules.

#### 3.2 Effect of pH

(Fig.2) shows the influence of pH on photocatalytic degradation rhodamine B at  $10^{-4}$  M solution and 0.1g/100 mL 1C-TiO<sub>2</sub>

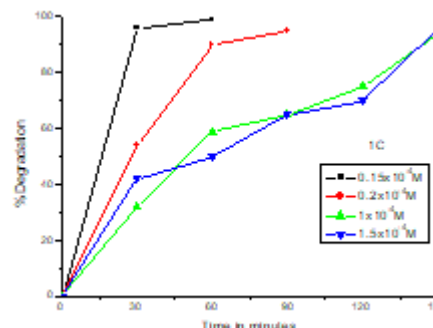


**Figure 2:** Effect of pH on % degradation using 1C-TiO<sub>2</sub>

It is evident from the graph fig 2 that as the pH of dye solution changes from acidic to alkaline; the percentage of degradation is increasing. In the alkaline solution at pH 9.4 the % of degradation is 90.7% likewise, at pH 10.6 the % degradation is 99.52%. But when the pH is decreased from 10.6 to 4 the degradation was decreased upto 76%. So the maximum degradation has been found at pH 10.6 after 90 min of exposure.

#### 3.3 Effect of dye concentration

(Fig.3) shows the influence of dye concentration on photocatalytic degradation rhodamine B of 0.1g/100 mL 1C-TiO<sub>2</sub>

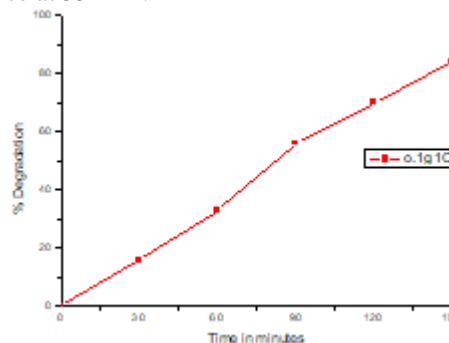


**Figure 3:** Effect of initial dye concentration on % degradation using 1C-TiO<sub>2</sub>

The effect of rhodamine B dye concentration on the degradation was studied by varying concentration. If the dye concentration is  $0.15 \times 10^{-4}$  M the degradation efficiency was found to be increased because the dye concentration decreased, more and more active sites are available for the reaction, the solution becomes less colored and the path length of photons entering the solution increase and more number of photons reach the catalyst surface and the generation of hydroxyl and superoxide radical is increased.

#### 3.4 Effect of time

A 100 ml of  $10^{-4}$  molar aqueous solution of rhodamine B with catalyst amount of 0.1 g was used for this study. Before irradiation the system was magnetically stirred for 30 minutes under dark to establish the adsorption desorption equilibrium between the catalytic surface and the dye. After irradiation of sunlight, around 10ml of the suspension was pipetted out from the solution at an interval of 30 minutes. The pipetted sample was filtered and measured its absorbance at 554 nm.

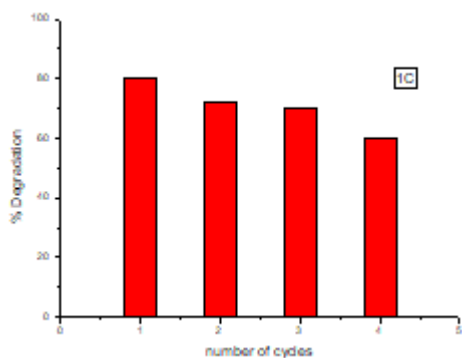


**Figure 4:** Effect of time on % degradation using 1C-TiO<sub>2</sub>

The photocatalytic percent degradation of rhodamine against the irradiation time is shown in (Fig.4). Results show that the 1C-TiO<sub>2</sub> gives a linear relationship with the increase of time. When time increases more and more light energy falls on the catalyst surfaces which increases the formation of photo excited species and enhances the photocatalytic activity.

### 3.5 Recycling of catalyst

To evaluate activity of the catalyst for photocatalytic degradation, recycling studies are conducted over 1C-TiO<sub>2</sub> using 0.1g/100 mL catalyst and the results are provided in (Fig.5)

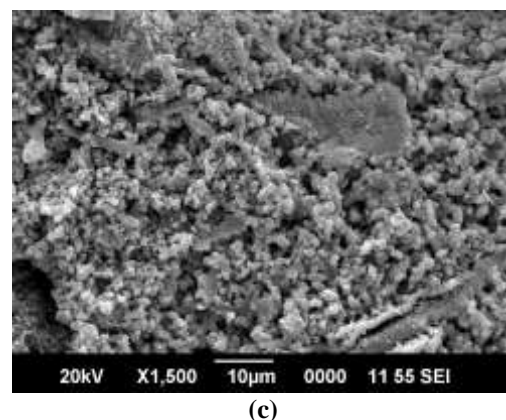
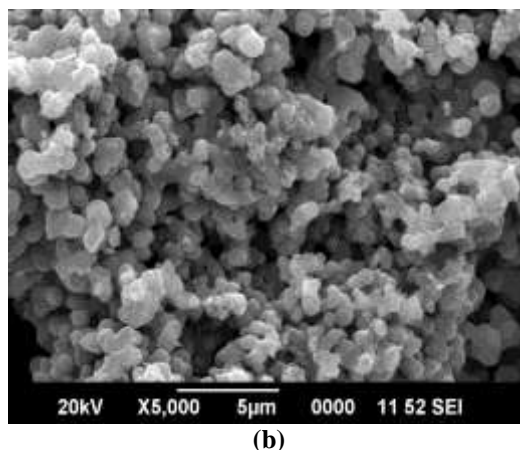
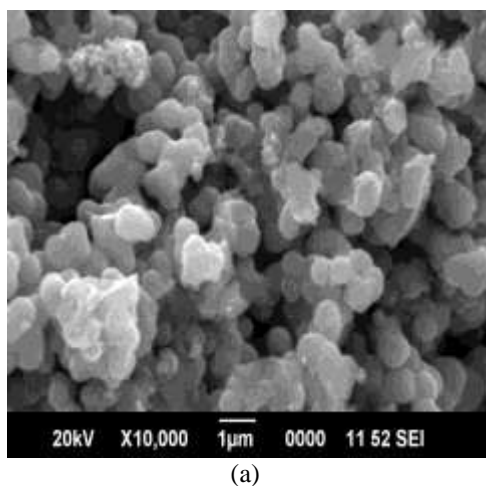


**Figure 5:** Efficiency on the recycling of 1C-TiO<sub>2</sub> catalyst

The first cycle the degradation is 80 %. After the completion of the first cycle, the catalyst is removed, dried and is reused as such for the second cycle, a slight decrease in the degradation is observed compared to the first cycle i.e; 72 %. When the same catalyst is reused without calcinations for the third and fourth cycles the degradation % of rhodamine B is 70% and 60% respectively.

### 3.6 SEM Analysis

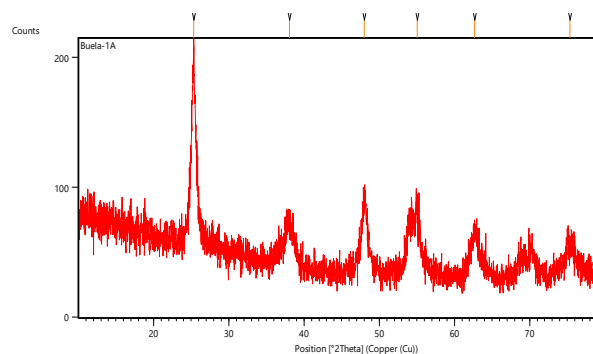
(Fig.6) shows SEM image of the typical sample 1C-TiO<sub>2</sub>. The as-prepared 1C-TiO<sub>2</sub> has the small particle size and a good dispersion. A good dispersion imparts not only for the surface properties but also improve the electronic structure i.e to make the visible light spectrum more active for the better photocatalytic activity.



**Figure 6:** SEM images of 1C-TiO<sub>2</sub> (a) at 1µm (b) at 5µm (c) at 10µm

### 3.7 XRD analysis

The XRD pattern of synthesized 1C-TiO<sub>2</sub> photocatalysts is shown in (Fig.7)



**Figure 7:** XRD patterns of 1C-TiO<sub>2</sub>

From the XRD patterns, the average crystalline size of 1C-TiO<sub>2</sub> found to be 10 nm using Debye-Scherrer equation. The 1C-TiO<sub>2</sub> sample can be assigned to pure anatase TiO<sub>2</sub> with reflection peaks in (101), (112), (200), (211), (204) and (215) crystal planes.

### 3.8 EDAX analysis

(Fig.8) shows a typical EDX spectrum of the as formed 1C-TiO<sub>2</sub> sample. The spectrum indicates Titanium and Oxygen as the major elements in the photocatalyst and also confirms the presence of dopant Carbon(6.55Atom%) in TiO<sub>2</sub>.

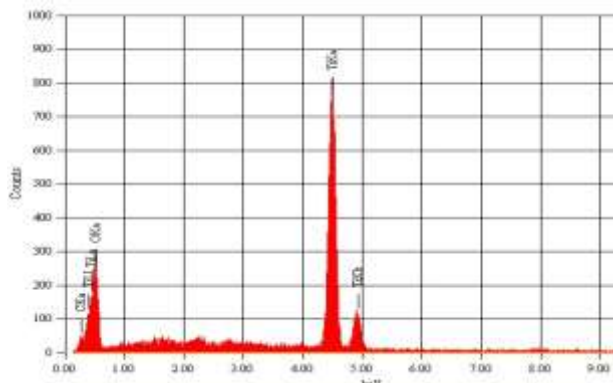


Figure 8: EDAX diagram of 1C-TiO<sub>2</sub>

Table 1: Composition of 1C-TiO<sub>2</sub>

Element	keV	Mass %	Atom %	K
C K	0.277	2.13	6.55	1.7199
O K	0.525	11.63	26.87	0.6543
TiK	4.508	86.24	66.57	1
Total		100	100	

### 3.9 Photodegradation of rhodamine B

Several authors have studied the degradation of different dyes by the photocatalytic treatment and reported that the decolourisation due to complete mineralization of dye was observed in UV-visible spectrophotometer.

(Fig.9) shows the absorption spectra of rhodamine B dye during the reaction time. The primary absorption peaks of the original dye solution are at 554 nm.

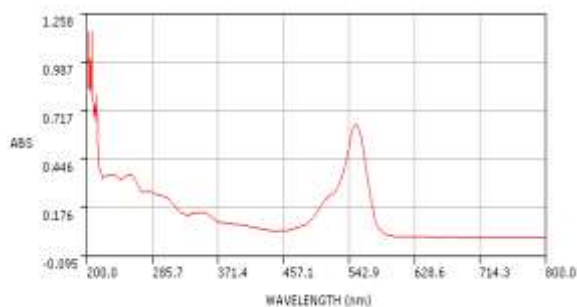


Figure 9: UV-visible absorption spectra of rhodamine B dye

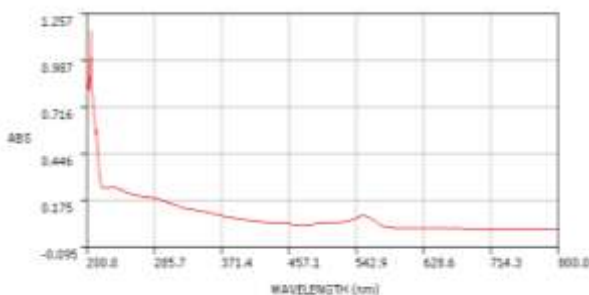


Figure 10: UV-visible absorption spectra of degraded rhodamine B dye

(Fig.10) represents the absorption spectra of degraded rhodamine B dye with 1C-TiO<sub>2</sub>. As the reaction proceeds, the peak at 554 nm disappears gradually, indicates that the main chromophore in rhodamine B gets cleaved with 1C-TiO<sub>2</sub>.

### 4. Conclusion

The sol-gel synthesised carbon doped nanocrystalline titania powder 1C-TiO<sub>2</sub> was employed as a catalyst for the decomposition of rhodamine B dye. It was found that the dye is completely decomposed on irradiation in the presence of the 1C-TiO<sub>2</sub> catalyst at alkaline pH under solar light irradiation. The complete decolourization of the dye was followed by UV-visible spectrophotometry. As formed 1C-TiO<sub>2</sub> exhibit better photocatalytic activity. From the SEM-EDX, UV-Vis results, it was confirmed that the assimilation of carbon in TiO<sub>2</sub> decreases the grain size and hence increases the photocatalytic degradation of rhodamine B under visible light irradiation. Increase in time, minimum catalyst amount (0.3g/100mL), lower dye concentration (0.15x10<sup>-4</sup>M), alkaline media (pH=10.6) are the factors which enhance the photocatalytic activity. Overall, 1C-TiO<sub>2</sub> photocatalyst possesses the highest visible light absorption and fast degradation of rhodamine b in aqueous media using visible light.

### References

- [1] Fujishima, A and Honda, K, Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238: 37–38, 1972.
- [2] Norman, S Allen, Michele Edge, Gonzalo Sandoval, Jo Verran, John Stratton and Julie Maltby, Photocatalytic coatings for environmental applications. *Photochemistry and Photobiology*, 81(2): 279-290, 2005.
- [3] Ren, J Wang, W Sun, S Zhang, L and Chang, J, Enhanced photocatalytic activity of Bi<sub>2</sub>WO<sub>6</sub> loaded with Ag nanoparticles under visible light irradiation. *Applied Catalysis B: Environmental*, 92: 50–55, 2009.
- [4] Fengna, C Xudong, Y and Qiong, W, Photocatalytic oxidation of Escherichia coli, Aspergillusniger, and formaldehyde under different ultraviolet irradiation conditions, *Environmental Science and Technology*. 43: 4606–4611, 2009.
- [5] Akhavan, O and Azimirad, R Photocatalytic property of Fe<sub>2</sub>O<sub>3</sub> nanograin chains coated by TiO<sub>2</sub> nanolayer in visible light irradiation, *Applied Catalysis A: General*. 369 : 77–82, 2009.
- [6] Ranjith G. Nair, Jetendra K. Roy, Samdarshi, S K and Mukherjee, A K , Mixed phase V doped titania shows high photoactivity for disinfection of Escherichia coli and detoxification of phenol, *Solar Energy Materials & Solar Cells*. 2012; 105 : 103–108.
- [7] Ali Mahyar, Mohammad Ali Behnajady and Naser Modirshahla, Enhanced Photocatalytic Degradation of C.I. Basic Violet 2 Using TiO<sub>2</sub>-SiO<sub>2</sub> Composite Nanoparticles, *Photochemistry and Photobiology*. 87: 795-801, 2011.
- [8] Shivaraju H P, Removal of Organic Pollutants in the Municipal Sewage Water by TiO<sub>2</sub> based Heterogeneous Photocatalysis, *Int.J. Environ. Sci.* 1(5): 911-923, 2011.
- [9] Narayanappa Madhusudhana, Kambalagere Yogendra and Kittappa M Mahadevan, Photocatalytic Degradation of Violet GL2B Azo dye by using Calcium Aluminate Nanoparticle in presence of solar light, *Research Journal of Chemical Sciences*. 2012; 2(5) : 72-77.



- [10] Mills, A and LeHunte, S, An overview of semiconductor photocatalysis, Journal of Photochemistry and photobiology A : chemistry.1997; 108 : 1-35.
- [11] M.Muruganandham, N.Sobanaa, M.Swaminathan, Solar assisted photocatalytic and photochemical degradation of reactive black 5, journal of hazardous materials. 137: 1371-1376, 2006.
- [12] Forgacs, E Cserhati, T and Oros, G, Removal of synthetic dyes from wastewaters: a review, Environment International. 30: 953-971, 2004.
- [13] Liu, W Che, S Zhao, W and Zhang, S, Study on the photocatalytic degradation of trichlorfon in suspension of titanium dioxide, Desalination. 249: 1288-1293, 2009.
- [14] Mills, J and Wang, J, Photobleaching of methylene blue sensitized by TiO<sub>2</sub>: an ambiguous system, Journal of photochemistry and photobiology A: chemistry. 127 : 123-13, 1999.
- [15] Tsai, C C and Teng, H, Chem..Mater, 16 : 4352-4358, 2004.
- [16] Li, H Duan, X Liu, G and Li, L, Mater.Res.Bull. 43:1971-1981, 2008.
- [17] Xu, J C Lu, M Guo, X Y and Li, H L, J.Mol.Catal.A:Chem. 226: 123-127, 2005
- [18] Zhzng, S Chen, Y Yu, Y Wu, H Wang, Zhu, B Huang, W and Wu, S, J.Nanopart.Res.10: 871-875, 2008.
- [19] Deng, L Wang, S Liu, D Zhu, B Huang, W and Zhang, S Catal.Lett.129:513-518, 2009.
- [20] Geng, J Yang, D Zhu, J Chen, D and Jiasng, J, Mater.Res.Bull. 44 : 146-150, 2009.
- [21] Chen, X Zhang, X Su, Y and Lei, L, Appl.Surf.Sci. 254: 6693-6696, 2008.
- [22] Sun, H Bai, B Cheng, Y jin, W Xu, N Ind.Eng.chem.Res.45: 4971-4976, 2006.
- [23] Asahi, R Morikawa, T Ohwaki, T Aoki, K Taje, Y Visible-light photocatalysis in nitrogen-doped titanium oxides, Science. 293 : 269-271, 2001.
- [24] Khan, S U M Shahry, M A and Ingler W B , Efficient Photochemical water splitting by a chemically modified n-TiO<sub>2</sub>, Jr., Science. 297 : 2243-2245, 2002.
- [25] Ohno, T Akiyoshi, M Umebayashi, T Asai, K Mitsui, T and Matsumura, M, Preparation of S-doped TiO<sub>2</sub> photocatalysts and their photocatalytic activities under visible light.265 : 115-121, 2004.
- [26] Lin, L Lin, W Xie, J I Zha, Y X Zhao, B Y and Xie, Y C , Phocatalytic properties of phosphor-doped titania nanoparticles, Appl.Catal.B-Environ. 52-58: 2007
- [27] Yu, H Zheng, X Yin, Z Tao, F Fang, B and Hou, K, Preparation of nitrogen-doped TiO<sub>2</sub> nanoparticle catalyst and its catalytic activity under visible light, Chin. J.Chem. Eng. 15(6) :802-807, 2007.
- [28] Saquiba, M Tariqa, M A Faisala, M and Muneer, M, Photocatalytic degradation of two selected dye derivatives in aqueous suspensions of titanium dioxide, Desalination.219 : 301-311, 2008.