



# Synthesis and Characterization of Titania Pillared Montmorillonite Clay and Study of Its Photocatalytic Activity

<sup>1</sup>Pankaj Kr. Ghosh, <sup>2</sup>Atul Prasad Sikdar, <sup>3</sup>Dhanju Mani Pathak, <sup>4</sup>Jatindra Nath Ganguli

<sup>1</sup>Assistant Professor, <sup>2</sup>Associate Professor, <sup>3</sup>Assistant Professor, <sup>4</sup>Retired Professor

<sup>1</sup>Department of Chemistry

<sup>1</sup>Mangaldai College, Mangaldai, Darrang-784125, Assam, India

## Abstract:

In this study, the high-surface-area Titania pillared Montmorillonite clay was prepared from the source montmorillonite clay by exchanging the interlayer ions (e.g. Na, Ca, etc.). The pillared clay was characterized by XRD, SEM and FT-IR. The photocatalytic activity was studied in the Rhodamine B.

*Index Terms* : Na-montmorillonite clay,  $K_2TiF_6$ , decomposition, Rhodamine B.

## I. INTRODUCTION :

Dyes and pigments are coloured compounds used extensively in the textile, paper, paint, pharmaceutical, dyeing and many other industries. It is estimated that 10 – 15% of the dyestuff is discharged as effluent during the dyeing processes [1]. Discharging large amounts of dyes into water resources, accompanied by organics, bleaches, and salts, can affect the physical and chemical properties of fresh water [2]. Once these dyes enter the water systems through industrial effluent, it becomes difficult to prevent fauna and flora from severe water pollution. Also sunlight penetrates less in coloured polluted water, thereby affecting the biochemical oxygen demand (BOD). The removal of dyes is stringent due to their toxic effect on micro-organisms [3].

The pollutant molecules from water and environment can be removed by photocatalytic degradation. Among some photocatalysts,  $TiO_2$  is the most popular material due to its high band gap energy (3.2 eV) and less toxicity [4-6]. Degradation of hazardous substances by  $TiO_2$  refers to redox reactions generated from absorption of photons by  $TiO_2$  that leads photoexcitation: the formation of electron – positive hole pairs [5]. A continuous process under available photon source such as UV light from sunlight make it markedly effective for destroying toxic organic molecules in wastewater treatment [6]. However, the use of  $TiO_2$  in bulk form suffers from some practical problems, such as catalyst agglomeration, difficult to recovery and its minimum adsorptivity related to its low surface area affecting to reduce the photocatalytic efficiency. These problems can be solved, in part, if  $TiO_2$  is immobilized on the inert supported materials without loss of activity. Thus, various kinds of supports like silica, alumina, activated carbon, zeolite and clay [7-10] are most widely used to immobilize the catalysts. Among these, the most promising materials are clay and clay based matrix as they are chemically inert, resistant to deterioration and commercially available in larger quantities [11-13]. Clays, such as Montmorillonite, rectorite or kaolinite are mostly used in wastewater decontamination. They have large surface area, high cation exchange

capacity and can adsorb the organic substances on their external surfaces or within their inter-laminar spaces. The titania pillared clay shows high adsorption ability [14-15].

## II. EXPERIMENTAL SECTION :

The materials used are Rhodamine B GR dye and Potassium Hexafluoro Titanate ( $K_2TiF_6$ ) were procured from LOBA Chemie. In this study, we have used the Montmorillonite clay from Source Clay, Mineral Repository, crook country, Wyoming U. S. A. Swy-2.

### II.1. SYNTHESIS OF THE CATALYST :

The preparation of Titania pillared clay involves three steps. In the first step, a Titania sol was prepared. From the Titania sol Titania pillared clay was prepared in the second step and finally the product was calcined in the third step.

#### a) **Preparation of Titania Sol:**

A 0.2 M  $K_2TiF_6$  solution was prepared in 500 mL distilled water. The solution was hydrolyzed by the slow addition of ammonium hydroxide ( $NH_4OH$ ) solution under constant stirring at room temperature until the reaction mixture attained a  $p^H$  of 7.5. The precipitate obtained was separated by filtration and washed with distilled water. The precipitate was further dispersed in 1 L of hot distilled water and peptized by the addition of 10%  $HNO_3$  solution to get the Titania sol at around a  $p^H$  of 1.6.

#### b) **Preparation of Titania Pillared Montmorillonite Clay :**

The  $<2 \mu m$  fraction of the Montmorillonite clay was separated using standard sedimentation process. The purified clay was converted into Na-Mont by the standard method.

The Titania sol as prepared in the first step was then added to the previously prepared 1% suspension of the Na-Mont clay. The solution was stirred at 343 K for 24 h with a magnetic stirrer. After stirring, the solution was kept overnight without any disturbance, filtered and washed with distilled water and dried at 383 K.

#### c) **Calcination :**

The dried product was calcined at 773 K for 5 h in a Muffle Furnace to get the Titania pillared clay and stored in a desiccator.

### II.2. PHOTOCATALYTIC ACTIVITY OF THE CATALYST IN THE AQUEOUS PHASE DEGRADATION OF RHODAMINE-B :

Rhodamine B was selected as the target compound for the photo activity of Titania pillared Montmorillonite clay under UV light. An immersion well photochemical reactor (HEBER) made of Pyrex glass was used in this study. Aqueous dispersion of the catalyst was prepared by addition of a given weight (0.2 g) of catalyst to about 100 mL of aqueous solution of the dye ( $10^{-5}$  M) and sonicated for 5 min. The dispersion is then put into the Pyrex vessel of the photoreactor along with an additional amount of dye solution ( $10^{-5}$  M) just enough to fill the vessel. Prior to the illumination, the solutions were purged with air for 15 min to ensure the equilibrium among the catalyst, Rhodamine B and oxygen. The dispersions were kept under constant stirring by air bubbling with the help of air pump during irradiation. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. Irradiations were carried out using a 25 W, 254 nm medium pressure lamp. IR radiation and short wavelength UV radiation were eliminated by a water circulating Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation for analysis. The degradation of Rhodamine B was monitored by measuring the absorbance on HITACHI U320 at 554 nm. The rate of decomposition of the dye can thus be determined from the absorption vs. time plots. Photocatalytic degradation of Rhodamine B is a pseudo-first order reaction, and its kinetics according to Langmuir-Hinshelwood kinetic model can be expressed as follows:

$$\ln(C_0/C_t) = kt$$

where  $C_0$  is the initial concentration,  $C_t$  is the concentration of the dye after t min reaction, k is the rate constant.

**III. RESULTS AND DISCUSSION :****III.1. CHARACTERIZATION OF THE TITANIA PILLARED MONTMORILLONITE CLAY :**

The Titania pillared clay was identified by XRD measurement substantiated by IR spectroscopy, SEM.

**III.1.1. POWDER XRD STUDY :**

The XRD pattern of the Titania pillared clay is shown in the Fig.1 and the details of XRD values are recorded in Table-1. There is an absence of (001) diffraction which may be due to lack of sufficiently ordered and oriented silicate layer structure [16, 17]. But the pillaring does not effect on (020) and (006) reflection of the Montmorillonite clay. The presence of titania appeared from the reflections corresponding to the anatase phase which was identified by comparing with the standard report as given in table-2 [18,19].

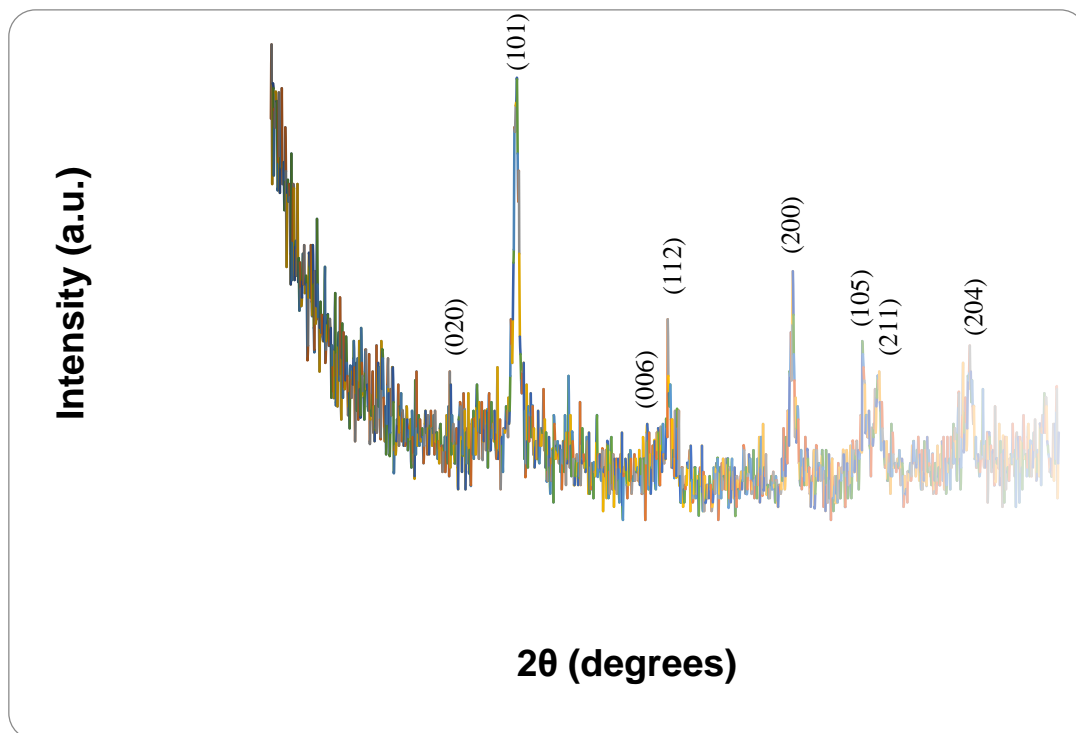


Fig.1 : XRD of Titania Pillared Clay

Table-1: The d-spacing of Titania pillared Montmorillonite clay

Angle (2θ) in degree	d-value (Å)	Plane (hkl)
19.85	4.478	020
25.30	3.516	101
36.2	2.478	006
37.75	2.380	112
48.05	1.891	200
53.80	1.719	105
55.20	1.662	211
62.65	1.481	204

Table-2 : The standard  $2\theta$  values of pure anatase Titania

Angle ( $2\theta$ ) in degree	Plane (hkl)
25.25	101
38.00	112
47.95	200
53.95	105
55.10	211
63.00	204

### III.1.2. FT – IR STUDY :

The IR spectra of the titania pillared montmorillonite clay is shown in the Fig.2. The bands at around  $3500\text{ cm}^{-1}$ , in the  $-\text{OH}$  stretching region are attributed to silanol groups ( $3700\text{ cm}^{-1}$ ) of the external layer and a broader band due to  $\text{Al}_2\text{OH}$  group ( $3650\text{ cm}^{-1}$ ) of the octahedral layer [20]. The band at  $1631\text{ cm}^{-1}$  is due to HOH bending vibration. The band at  $922\text{ cm}^{-1}$  is attributed to the vibration of  $\text{Si} - \text{O} - \text{Ti}$  [21]. The bands at  $524\text{ cm}^{-1}$  and  $466\text{ cm}^{-1}$  is associated with the  $\text{Si} - \text{O}$  bending vibration [22].

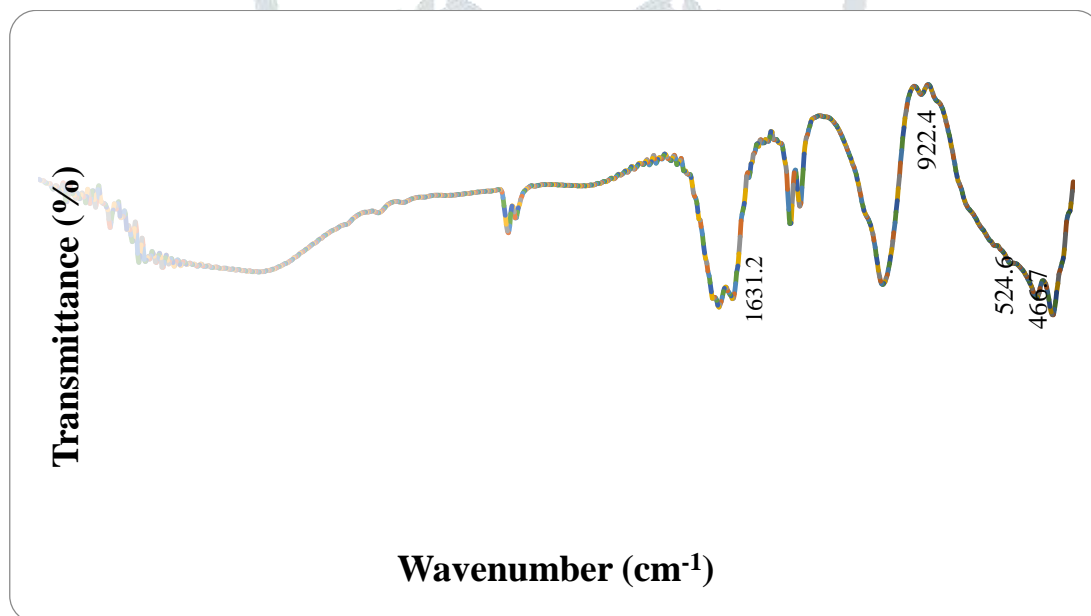


Fig.2 : IR Spectra of Titania Pillared Montmorillonite Clay

### III.1.3. SCANNING ELECTRON MICROSCOPE (SEM) STUDY :

The SEM image of the titania pillared Montmorillonite clay is shown in the Fig.3. The titania pillared clay shows the formation of disordered structure. In the image of titania pillared clay, the larger platelets and layer structure of clay can hardly be observed. There are a lot of small aggregates.

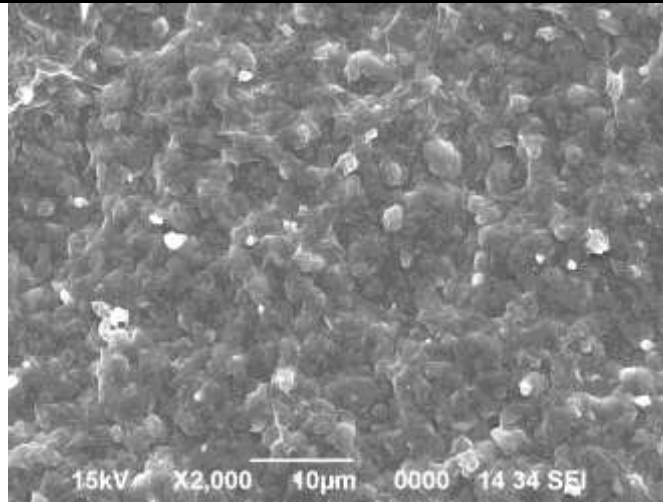


Fig. 3 : SEM image of Titania Pillared Montmorillonite Clay

### III.2. PHOTOCATALYTIC ACTIVITY STUDY :

The photocatalytic activity of the catalyst was then evaluated by measuring the absorbance ( $C_t$ ) of Rhodamine B using UV-visible spectrum at 554 nm during every 10 min interval. With the assumption that Beer's law was obeyed, the graph of absorbance against t is equivalent to the graph of concentration against t and the latter was plotted as shown in Fig.4. The rate of degradation of the chromospheres of the dye thus determined from the concentration vs. time plot.

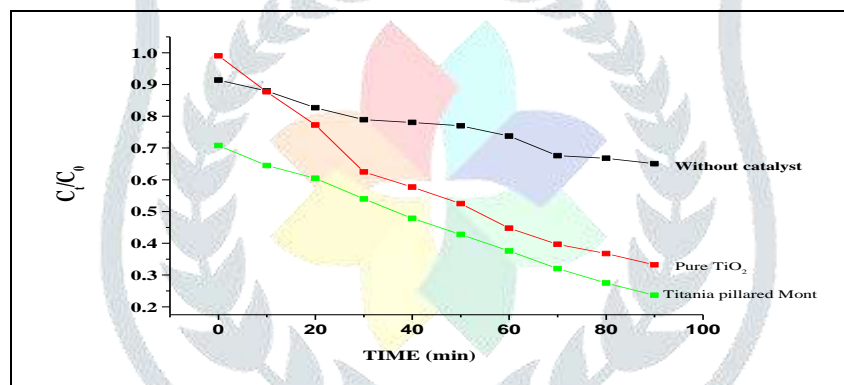
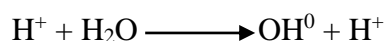
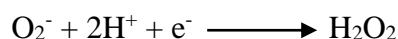
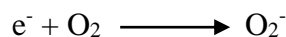
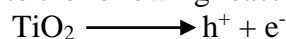


Fig.4 : Photochemical decomposition of Rhodamine B

Titania pillared Montmorillonite clay showed higher photocatalytic activities than that of pure  $TiO_2$ . The high photocatalytic activity of Titania pillared Montmorillonite clay can be explained by the band gap as well as the co-ordination of Ti ions. It is commonly accepted that a larger band gap corresponds to powerful redox ability [23]. The oxidative degradation of Rhodamine B by  $TiO_2$  is believed to be initiated by OH radicals. In presence of  $O_2$ , the OH radicals are formed according to the following reactions [24].



Further the mesoporous nature of the material result in the increase of surface area. More the surface area more will be production of hydroxyl radicals and hence more will be photocatalytic decomposition. These combined effects make the substrate adsorption stronger. It is clear from Fig.4 that Titania pillared Montmorillonite clay with higher surface area and smaller particle size, photocatalytic activity was better.

**IV. CONCLUSION :**

The Titania pillared Montmorillonite clay can be synthesized by a simple hydrothermal method involving  $K_2TiF_6$ , ammonium hydroxide ( $NH_4OH$ ) and Na-Montmorillonite clay. Pillaring by Montmorillonite stabilizes the titania in the anatase phase and Lewis acid sites were developed. Pillaring by Montmorillonite also caused a mark change in the  $TiO_2$  particle size as well as surface area thereby increasing photocatalytic activity. Photocatalytic activity of titania pillared Montmorillonite clay is much more than that of unpillared titania due to higher surface area.

**REFERENCES :**

- [1] B. Zohra, K. Aicha, S. Fatima, B. Nourredine, D. Zoubir, *Chem. Engg. J.*, **2008**, 136, 295.
- [2] E. Erdem, N. Karapinar, R. Donat, *J. Colloid Sci.*, **2004**, 280, 309.
- [3] Q.H. Hu, S.Z. Quao, J. Haghseresht, M.A. Wilson, G.Q. Lu, *Ind. Eng. Chem. Res.*, **2006**, 45, 733.
- [4] G. Liu, X. Li, J. Zhao, S. Horikoshi, H. Hidaka, *J. Mol. Catal. A : Chem.*, **2000**, 153, 221.
- [5] A. L. Linsebigler, G. Lu, J. T. Yates Jr., *Chem. Rev.*, **1995**, 95, 735.
- [6] K. Rajeshwar, M.E. Osugi, W. Chanmenee, C.R. Chenthamarakshan, M.V.B. Zanoni, P. Kajitvichyanukul, R.K. Ayera, *J. Photochem. Photobiol. C : Photochem. Rev.*, **2008**, 9, 15.
- [7] K. Shimizu, T. Kaneko, T. Fujishima, T. Kodama, H. Yoshida, Y. Kitayama, *Appl. Catal. A : Gen.*, **2002**, 225, 185.
- [8] M.S. Vohra, K. Tanaka, *Water Res.*, **2003**, 37, 3992.
- [9] E.P. Reddy, L. Davydov, P. Smirniotis, *Appl. Catal. B*, **2003**, 42, 1.
- [10] C.H. Ao, S.C. Lee, J.C. Yu, *J. Photochem. Photobiol. A*, **2003**, 156, 171.
- [11] P. Aranda, R. Kun, M.A.M. Luengo, S. Letaïef, I. Dékány, E.R. Hitzky, *Chem. Mater.*, **2008**, 20, 84.
- [12] E. Dvininov, R. Pode, L. Cochechi, P. Barvinschi, V. Nica, *Journal of Hazardous Materials*, **2009**, 167, 1050.
- [13] L. Bouna, B. Rhouta, M. Amjoud, F. Maury, M.C. Lafont, A. Jada, F. Senocq, L. Daoudi, *Appl. Clay Sci.*, **2011**, 52, 301.
- [14] J. Sterte, *Clays Clay Miner.*, **1986**, 34, 658.
- [15] M.A. Vicente, M.A.B. Munoz, R. Torenzo, L.M. Gandia, A. Gil, *Clays Clay Miner.*, **2001**, 36, 125.
- [16] P. Yuan, X. Yin, H. He, D. Yang, L. Wang, J. Zhu, *Microporous and Mesoporous Materials*, **2006**, 93, 240.
- [17] N. Jagatap, V. Ramaswamy, *Applied Clay Science*, **2006**, 33, 89.
- [18] H.G. Yang, C.H. Sun, S.Z. Qiao, J. Zou, G. Liu, S.C. Smith, H.M. Cheng, G.Q. Lu, *Nature*, **2008**, 453, 638.
- [19] O.K. Mahadwad, P.A. Parikh, R.V. Jasra, C. Patil, *Bull. Mater. Sci.*, **2011**, 34, 551.
- [20] S. Bodoardo, F. Figueras, E. Garrone, *J. Catal.*, **1994**, 147, 223.
- [21] L. Liu, X. Li, S. Zuo, Y. Yu, *Appl. Clay Sci.*, **2007**, 37, 275.
- [22] X. Xu, Y. Pan, X. Cui, Z. Suo, *Journal of Natural Gas Chemistry*, **2004**, 13, 4, 204.
- [23] J. Lin, J.C. Yu, D. Lo, S.K. Lam, *J. Catal.*, **1999**, 183, 368.
- [24] H. Yamashita, M. Honda, M. Harada, Y. Ichihashi, M. Anpo, T. Hirao, N. Itoh, N. Iwamoto. *J. Phys. Chem. B*, **1998**, 102, 10707.