International Journal of Recent Research and Review, Vol. VII, Issue 3, September 2014
ISSN 2277 – 8322

UV Light Induced Photocatalytic Degradation of Malachite Green on TiO_2 Nanoparticles

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Abstract **- This study involves synthesis of TiO_2 nanophotocatalyst and its role in degradation of Malachite Green dye. Nanocrystalline TiO_2 was synthesized by Sol-Gel route using titanium tetraisopropoxide as a metal precursor. The catalyst was characterized by X-ray diffraction (XRD), Transmission Electron Microoscopy (TEM), Fourier-transform infrared spectroscopy (FT-IR). TiO_2 was found to be of anatase phase.TEM images showed Cuboidal shape of TiO_2 nanoparticles. FTIR reveals the functional groups present in the synthesized TiO_2 nanoparticles. The photodegradation of malachite green (MG), a cationic triphenylmethane dye, is examined both under different dye concentration and amounts of TiO_2. The spectrophotometric technique was used to obtain a better understanding on the TiO2-assisted photodegradation of the MG dye with UV irradiation. After 15W UV-365 nm irradiation for 1 hr, catalysis 99.9% of MG was degraded with addition of 20mg TiO_2 to solutions containing 40 mg L−1 of the MG dye. The photo-degradation mechanism of Malachite Green is ecofriendly and cost effective process for removal of hazardous dyes.**

Keywords**- Photo reduction, titanium oxide, textile effluent.**

I INTRODUCTION

In the past decade, TiO_2-mediated photocatalysis has been successfully used to degrade pollutants [1-2]. TiO_2 is broadly used as a photocatalyst because of its non-toxicity and photochemical stability [3]. The initial step in the TiO_2- mediated photocatalysis degradation is proposed to involve the generation of a (e−/h+) pair leading to the formation of hydroxyl radicals (•OH), superoxide radical anions (O2•−), and hydroperoxyl radicals (•OOH), and these radicals are the oxidizing species in the photocatalytic oxidation processes. The efficiency of the dye degradation depends on the concentration of the oxygen molecules, which either scavenge the conduction band electrons (ecb−) or prevent the recombination of (e−/h+). The electron in the conduction band can be picked up by the adsorbed dye molecules, leading to the formation of dye radical anions and the degradation of the dye [4].

The chemical structure of this MG dye is shown in Fig. 1. It is an extensively used biocide in the global aquaculture industry, and is highly effective against important protozoal and fungal infections [5-6]. Essentially, it works as an ectoparasiticide and has been used to control skin flukes and gill flukes. It is not only used in aqua industries but also used as a food coloring agent, food additive, medical disinfectant, and anthelminthic as well as a dye in the silk, wool, jute, leather, cotton, paper, and acrylic industries [7]. However, malachite green has now become a highly controversial compound due to the risks it poses to the consumers of treated fish [8], including its effects on the immune system and reproductive system and its genotoxic and carcinogenic properties [9]. Though the use of this dye has been banned in several countries and is not approved by US Food and Drug Administration, it is still being used in many parts of the world due to its low cost, ready availability, and efficacy. A considerable amount of research is being devoted to the wide spectrum of biological effects on different animals and on mankind. The US Food and Drug Administration have nominated MG as a priority chemical for carcinogenicity testing. There is concern about the fate of MG and its reduced form, leucomalachite green in aquatic and terrestrial ecosystems. They occur as contaminants and pose potential human health hazards [10].

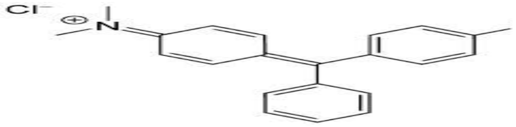

Fig. 1: Chemical structure of Malachite Green

Present study focuses on synthesis and characterization of TiO_2 nanoparticles and its role in photocatalytic dye degradation of Malachite Green dye.

II. MATERIALS AND METHODS

Titanium tetraisopropoxide (97%), acetic acid (99.7%) and Malachite Green, were purchased from Hi-media and Merck, INDIA.

A. TiO_2 nanoparticles synthesis

The catalyst was prepared by a modified sol-gel route [11]. 12 m titanium isopropoxide was added to 23 mL of acetic acid with continuous stirring. After that, 72 mL water was added to the mixture drop by drop with vigorous stirring. The solution was kept stirring for 6 h until achieving a clear transparent sol. Dried at 100℃, after that it was calcined at 600^o C for 2 hrs. The photocatalytic activities were determined by using degradation reaction. [12].

B. Characterization of synthesized nanoparticles

The crystal structure was determined by Powder XRD (Phillips X'pert MPD system, Holland) using CuKa radiation (λ=1.5405 A^o) in a 2y range of 5–601 at a scan speed of 0.11 s^{-1}, maintaining applied voltage at 40kV and current at 40mA. XRD patterns were compared with the standard anatase diffractograms [13].The shape and sizes of the particles were obtained through Transmission Electron Microscope (TEM) using a model Philips Tecnai 20, Holland with an accelerating voltage of 100kV. For TEM measurements, the samples were placed on carbon coated copper grids. The chemical composition of the synthesized material was evaluated using FT-IR spectrophotometer (SPECTRUM GX, Perkin- Elmer). The spectrum is recorded in the range of wave-number 400–4,000 cm-1[14].

C. Photocatalytic experiment

Photocatalytic study was revealed in series of flasks containing dye and nanoparticles. The effect of dose of catalyst on various concentration of dye solution was investigated. Isotherms were run by taking selected different concentrations (10ppm, 20ppm, 30ppm, 40ppm) of malachite green and determined using a UV-visible spectrometer. Catalysts containing tubes were placed on UV- radiation lamp. Four 15 W low pressure mercury UV tubes (Spectronics) emitting near UV radiation with a peak at 365 nm were used. The residual dye concentration in each solution was measured spectrophotometrically at the corresponding λ_{max} (615nm). Dye containing tube without nanoparticles was also placed on UV to show that though during UV irradiation, direct photolysis of dyes could occur, mineralization of dyes only takes place in the presence of a photocatalyst [15] and the extent of removal of the dye, in terms of the values of percentage removal has been calculated using the following formula:

Percentage Removal (%R) = 100*(Ci-Cf)/Cf ----------------- (1)

Where, Ci= initial concentration of dye (ppm); Cf = final concentration of dye (ppm) at given time.

III RESULT AND DISCUSSION

A. Crystallinity and crystallite size

Catalyst's structure and crystal phase has high influence on its photocatalytic activity. The crystal structure and crystal phase characterization of pure TiO_2 was investigated. The XRD patterns of samples are shown in Fig. 2. Anatase form was detected in synthesized TiO_2 nanoparticles. All the peaks in the XRD patterns can be indexed as anatase phases of TiO_2 and the diffraction data were compatible with JCPDS files # 21-1272 [16]. Only Anatase TiO_2 was detected and no Rutile phase can be found in the sample [17]. Crystallite size was obtained by Debye-Scherrer's formula given by equation at diffraction peak 2□ =25.28^o (101)

$$D=K\lambda/ (\beta\cos\theta)$$

where D is the crystal size; λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα; K is usually taken as 0.89; and β is the line width at half-maximum height. The relatively wide width of the peaks indicates small crystallite size, which was estimated to be approximately 24 nm using Scherrer's equation from the XRD peak broadening analysis at (1 0 1) [18]. The crystallite size was in the range of 20–30 nm, which is known to be optimum for high catalytic activity.

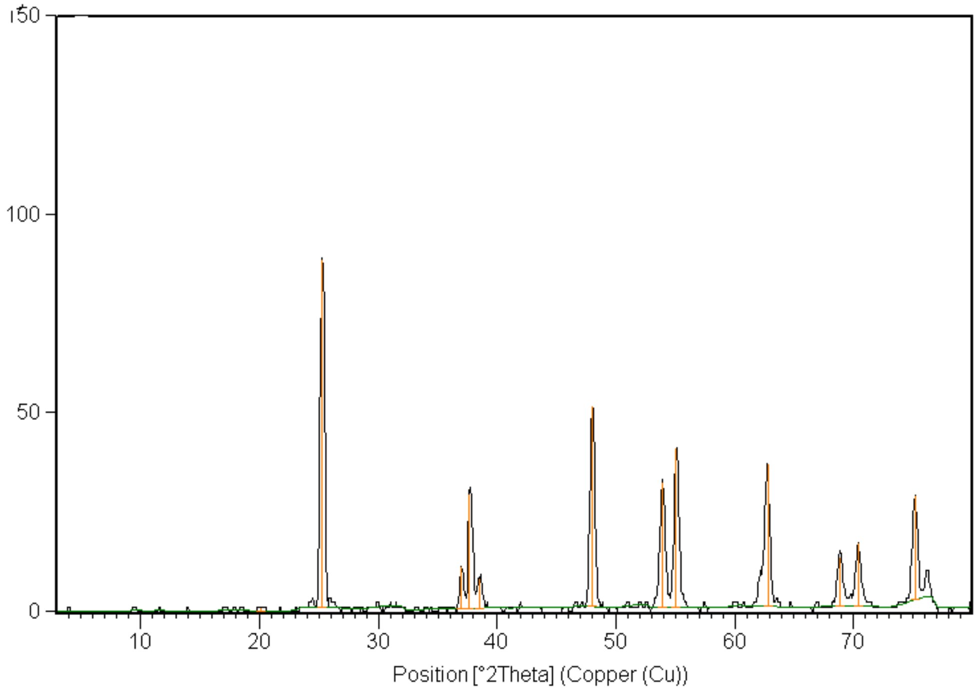

Fig. 2 XRD powder pattern of synthesized TiO_2 by Sol-Gel

B. *Functional Group analysis of TiO_2 nanoparticles*

Fourier transform infrared (FTIR) spectrum of synthesized anatase TiO_2 nanoparticles is shown in Fig. 3. Strong band in the range of 700–500 cm-1 confirms the presence of TiO_2. The absorption in the range from 3,5000 to 2,500 cm-1 was related to the presence of O–H stretching vibration. The absorption band at 1,637 cm-1 shows presence of O–H bending which is probably due to reabsorption of water from the atmosphere has occurred [19].

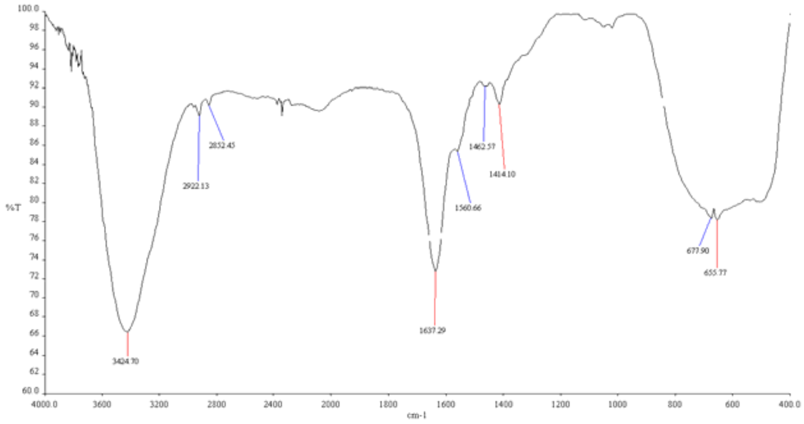

Fig. 3: FTIR spectra of synthesized TiO_2

C. Structural characteristics of TiO_2 nanoparticles

Confirmation of nanosize formation for synthesized titanate was carried out by TEM study and showed the uniformity of particles size ranging from 20 -30 nm (Fig 4). Small percentage of the total particles exhibit a diameter size bigger than 30 nm. The crystallites had sets of clearly resolved lattice fringes giving evidence that the TiO_2 material was highly crystalline [20].

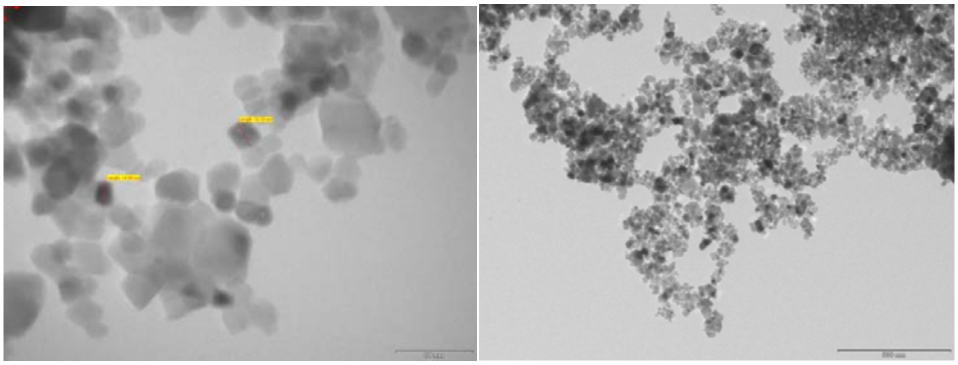

Fig. 4 TEM image of synthesized TiO_2 nanoparticles

D. Decolorization efficiency of UV/TiO_2 photocatalysis process

Photocatalytic properties of samples were examined by degradation of MG dye solution under UV light irradiation at room temperature. In order to identify possible losses of malachite green in the system, control experiments were preformed without catalyst. Four dye concentrations- 10ppm, 20ppm, 30ppm, 40ppm were irradiated with different catalytic doses of 5mg, 10mg, 15mg and 20mg. At 20mg catalyst, MG dye was found to be completely decolourised within 60 minutes.. The dye degradation increases with increasing catalytic dose (figures 5).

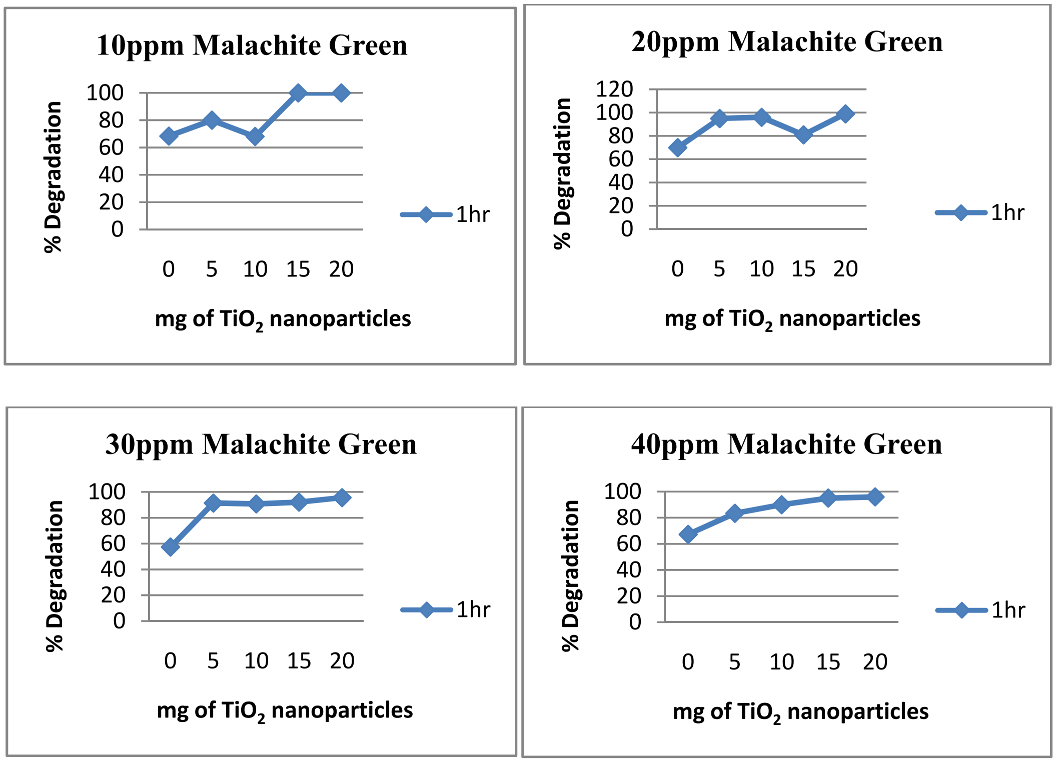

Fig.5 Degradation of Malachite Green by TiO_2 nanoparticles

IV CONCLUSION

In this study, a easy, simple and reproductive method was followed for the synthesis of TiO_2 and its photocatalytic activity on Malachite Green was carried out. The physical and chemical characterization of nanocatalyst was done by TEM , XRD and FT-IR which comply with that of standard values. The ultraviolet (UV) light irradiation of the dye by using nanoanatase TiO_2 as a catalyst has yielded absolute decolouration for a catalyst loading of 20mg.

V ACKNOWLEDGEMENT

The authors would like to thank Sophisticated Instrumentation Centre for Advanced Research and Testing (SICART),Vallabh Vidyanagar,Gujarat, for TEM , XRD and FT-IR analysis of samples.

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