VISIBLE LIGHT MEDIATED DEGRADATION STUDIES OF METHYLENE BLUE BY NANO TiO_2 SYNTHESIZED BY *AZARDICA INDICA* LEAF EXTRACT

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Abstract

The goal of present study was to use biosynthesized nano TiO_2 as possible alternative for colored waste water treatment. TiO_2 nano particles are synthesized by green route using Titanium Isopropoxide precursor and Azardica Indica (neem) leaf extract. The green synthesized nano TiO_2 were characterized by Scanning Electron Microscopy, X-ray diffraction, and Particle size distribution. Feasibility of synthesized nano TiO_2 was tested for degradation Methylene blue dye in presence of visible light by biosynthesized nano TiO_2. Batch experiments were conducted where in methylene blue solution, synthesized TiO_2 are allowed to degrade in presence of visible light under continuous magnetic stirring condition. The concentration of the samples after degradation at different time intervals was tested. The factors affecting degrading kinetics such as The effect of amount of TiO_2, irradiation time, pH were also studied.

Keywords: *Photocatalysis, Methylene Blue, TiO_2, Advanced Oxidation Process, Pollutants.*

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1. INTRODUCTION

Industrial wastewater treatment, management and its disposal are the most explored area by the researchers due to the large number of chemical compounds present in industrial effluent which in turn are major concern for public health and the environment (Statinakis S 2008). The Dyes are the essential and toxic components used by mankind and hence are major contributors of industrial effluents which are coming from manufacturing industries. Dyes pose threat to the environment due to the potential carcinogenic properties of the chemicals existing in dye of (Zubair Alam M et al. 2010). The dyeing industry effluent in general is chemically more stable, highly toxic and has more chemical oxygen demand stability (Mondal K et al. 2014).The other adverse effects of dyeing effluent are they absorb oxygen from water and block the penetration of sunlight and thereby creating threat to aquatic life (Karthik V et al. 2008). Hence removal of dye from waste water becomes inevitable.

The conventional biological, physical or chemical treatment methods have some drawbacks. For example, biological treatment even though being cheap and simple is not as efficient because the synthetic dyes cannot be degraded by aerobic biodegradation. Physical methods are effective but have high post operation costs. Chemical methods result in harmful byproducts (Spagni A et al. 2010; Koprivanac N et al. 2009; Mahmoodi NM et al. 2009; Akyol A et al. 2004; Baldrian P et al. 2006). Photocatalytic degradation is categorized under the group of Advanced Oxidation Processes (AOPs) has become more popular as it can address many of the drawbacks of conventional physical, biological and chemical treatment methods. Nanosized TiO_2 photocatalysts has gained importance in the field of research community by virtue of its biocompatibility, the stability of its chemical structure, non-toxicity, strong oxidizing power and low cost. (Gupta VK et al. 2012; Hu A et al. 2013; Chen X and Mao SS 2007; Ahmed MA 2013; Ahmed MA et al. 2013). It has high efficiency, low energy consumption and is environmentally safe. Promising results are published on the degradation of dyes such as Methyl orange, Naphthol blue Black, Congo red and Indiago caramine Dye by nano TiO_2. (Rashed M N et al. 2007;Gao et al. 2000; Wahi et al. 2005;Subramani et al. 2007). Methylene blue is one among the common dyes found in dyeing industry effluent few researchers are worked on methylene blue degradation by nano TiO_2. Anatase TiO_2 synthesized by titanium isopropoxide precursor by sol-gel method and used in the degradation of methylene blue (Ling et al. 2004). Anatase phase TiO_2 sol prepared by tetrabutyl titanate precursor was also tried (Yao et al. 2010). TiO_2 film of 80% anatase and 20% rutile was prepared through wet chemical method was used for methylene blue degradation (Rosu et al. 2009). Nanocrystalline TiO_2 synthesized by hydrothermal treatment using titanium isopropoxide was used to degrade methylene Blue (Tayade et al. 2007). There is no much research reported on degradation of methylene blue by green route synthesized nano TiO_2. In the present work an effort is made for photocatalytic degradation of methylene blue by biosynthesized anatase phase nano TiO_2

2. MATERIALS AND METHODS

Analytical grade Titanium Isopropoxide and Ethanol were procured from Spectrochem Pvt. Ltd. Mumbai, India for synthesis of nano TiO_2. The good conditioned leaves of neem were procured from RVCE campus, Bangalore, Karnataka, India. Methylene Blue Dye was obtained from S. D. Fine Chemicals, Bangalore

2.1 Bio Synthesis of Nano TiO_2

The healthy leaves of *Azardica Indica* were cleaned with water till they become dust free and are dried at room temperature for two weeks. Fine powder of neem leaves was obtained by subsequent grinding and sieving of dried leaves. Three grams of the leaf powder and 50mL of ethanol were placed in soxhlet apparatus under reflux condition for extraction of phyto components present in leaves for 5 hrs. The temperature was maintained at 50°C. Extract was obtained by filtering the extraction mixture by Whatmann No.1 filter paper.

Synthesis of titanium dioxide was done in Erlenmeyer flask where in 0.4Molar titanium tetraisoproxide is reacted with ethanolic Azardica Indica leaf extract under stirring at 50°C for 4 hours. The reactions mixture was centrifuged for 15 minutes at 10000 rpm. The separated particles were ethanol washed and were again centrifuged for 10 minutes at 5000 rpm. The product obtained after centrifugation is dried, grinded and calcined for about 3 hours at 500°C in muffle furnace. [Shilpa et. al.,2014). The calcined titanium dioxide powder was characterized by SEM and XRD and are further used as catalyst for degradation of Methylene Blue.

2.2 Characterization of the Photocatalyst

The synthesized TiO_2 was characterized by XRD, SEM and particle size analyzer. SEM images were captured on a JEOL JSM 6390. Powder X-ray diffraction patterns are obtained by a Panlytical X Pert PRO Diffractometer with Kα radiation (λ = 1.5406 Å). The particle size distribution was determined by Zetatrac NPA-152 Microtrac. Histograms, from the nanotrac analyzer.

2.3 Photocatalytic Experiments

The photocatalytic degradation of 10ppm methylene Blue was studied in a batch reactor with a magnetic stirrer in presence of visible light and Synthesized Titanium dioxide powder (Catalyst) for specified time interval. The solution was withdrawn at different intervals and centrifuged. Concentrations of the solution was found at various times of intervals by Systronics UV-VIS spectrophotometer and tabulated. The percentage of degradation was calculated by measuring changes in absorbance and thus the concentration at different time intervals given by Eq.(1)

$$\%\text{Degradation} = \frac{(\text{Initial Conc.} - \text{Final Conc.})}{\text{Initial Conc}} \text{ X } 100 \quad (1)$$

The catalyst loading affects the kinetics of the photocatalytic degradation. Hence the dyes were degraded at various catalyst loadings and tested for their efficiency.

The catalyst loading affects the kinetics of the photocatalytic degradation. To study this the loading of the catalysts were varied from 25mg to 100mg. The amounts of catalyst used were 25, 50, 75 and 100mg of catalyst.

The effect of exposure time on the rate of photocatalytic dye degradation was studied after selecting the optimum dosage of the photocatalyst. The irradiation time was varied from 5 to 240 minutes with intervals of 30 minutes. 100 ml of the dye solution containing optimum amounts of the photocatalyst was exposed to visible light at room temperature. After every 30 minutes, a small aliquot of the sample was withdrawn, centrifuged and the concentration of the sample as reported.

To study the role of pH photocatalyst reaction is conducted at pH of 5,7,9,10,11 and 13 for 100 ml of 10 ppm methylene blue dye solution.

3. RESULTS AND DISCUSSION

3.1 Characterization of the Photocatalyst

The SEM images shown in Figure 1 reveal that synthesized particles are agglomerates of nearly spherical particles. The average size of particle was from 18 to 22nm.

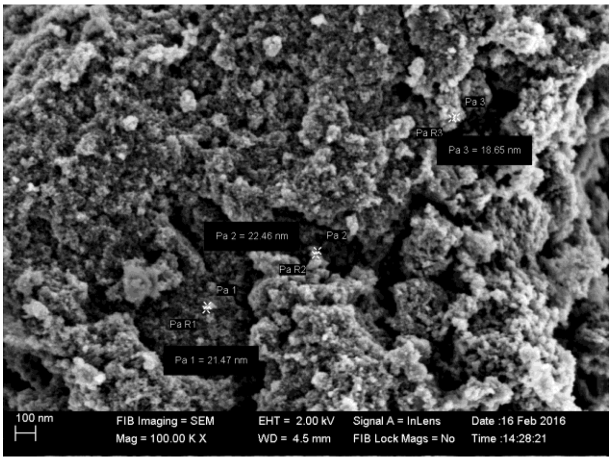

Fig 1. SEM micrographs of synthesized TiO2 nanoparticle

The XRD graph shows major peaks at 2θ values of 25.06°, 37.78°, 48.12°, 54.46°and 62.48° in plot shown in Figure 2. The peaks match with literature values of JCPDS Data, Ref. code-00-021-1272 which corresponds to anatase phase of Titanium dioxide particles. The average size of the particles was calculated using Debye-Scherrer’s formula Eq.(2):

$$\mathbf{d} = \frac{\mathbf{k} * \boldsymbol{\lambda}}{\mathbf{FWHM} * \cos(\boldsymbol{\theta})} \quad (2)$$

Where
d = average size of the particles, in metres.

k = a constant which usually ranges from 0.85 to 1. The optimum value is 0.89.
λ = is the wavelength used for analysis, for Cu it is 1.541 Å

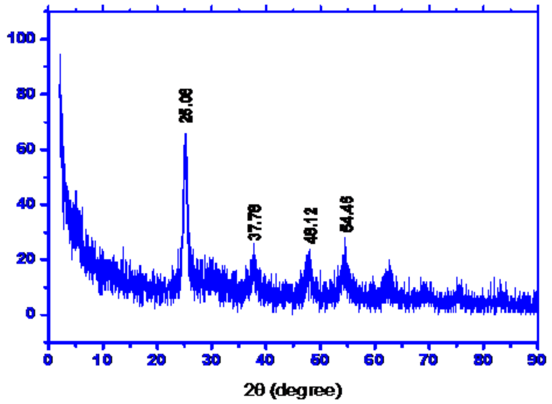

Fig 2. XRD peaks of synthesized TiO_2

The average size of the synthesized TiO_2 particles was found to be 20nm.

Particle size distribution was obtained by zeta potential particle size analyser which show majority of particles are within 100nm

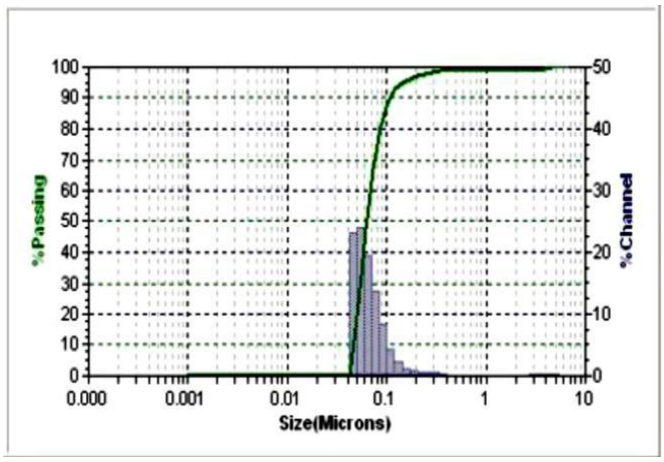

Fig 3: Particle size distribution of synthesized TiO2 nano particles

3.2 Photocatalytic Degradation

The photocatalytic degradation of 10 ppm Methylene Blue was conducted in presence of visible light and the effect of various parameters such as effect of catalyst loading, pH etc. were studied.

3.3 Effect of Irradiation Time on Degradation of Dyes

Time taken for maximum degradation of the dye was around 200-240 minutes of irradiation. Beyond 240 minutes, the degradation was found to be negligible (Figure 4). From the results obtained it can be concluded that the photocatalytic approach promotes the decline of chromophore peaks in the dye molecule in 240 minutes.

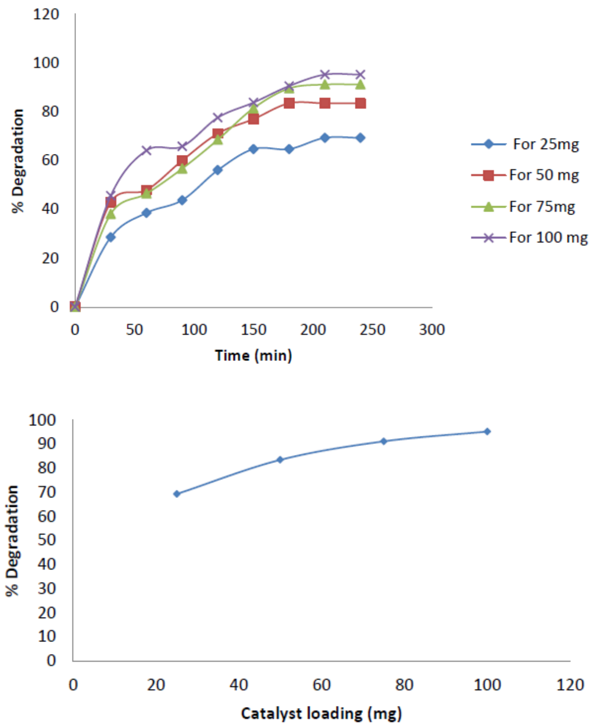

Fig . 4 Effect of TiO_2 loading on degradation of Methylene Blue

3.4 Role of pH in Degradation of Dyes

Degrdation of dye is low at acidic pH. Increase in pH results in increased degradation upto pH 10 (Figure 5) as the acid reacts with TiO_2 catalyst, and forms respective salts due to decomposition. Beyond 10 pH degradation decreases and reaches least at pH 13. As pH becomes acidic, the. At basic pH after certain pH level the Titanium hydroxide is formed due to reaction between hydroxide ions and TiO_2.

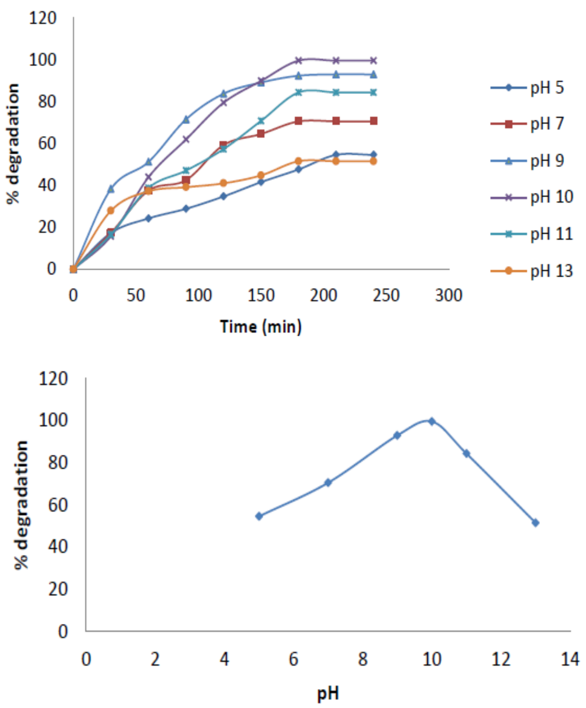

Fig 5 Role of pH on the degradation of Methylene Blue

3.5 Kinetic Studies

The kinetic data obtained was best fit using Modified Langmuir-Hinshelwood's model. (Fig no.6). This model explains that the photo catalytic degradation follows pseudo first order reaction. The model

Is represented by the Eq.(3)

$$Rate\ of\ Reaction - \frac{dc}{dt} = \frac{kr\ ke\ C}{1 + KeC} \qquad (3)$$

Eq.(3) is solved by integrating the differential equation resulting in Eq.(4)

$$t = \frac{1}{kr\ ke} ln \frac{CO}{C} + \frac{1}{kr}(Co - C) \qquad (4)$$

second term on the right hand side of Eq.(4) are the concentrations of the dyes can be neglected as they are in ppm level. This will reduce the Eq. (4) to Eq. (5).

$$t = \frac{1}{krKe} ln \frac{Co}{C} \qquad (5)$$

Eq.(6) is obtained from Rearranging Eq.(5)

$$\ln \frac{Co}{C} = t\ kr\ ke \qquad (6)$$

Eq.(7) was obtained by Substituting $kr\,ke = k'$ in Eq. (6)
We get,

$$ln \frac{Co}{C} = tk' \qquad (7)$$

Slope of line obtained by plotting time vs ln (Co/C) is overall rate constant k' (Figure 6). From the plot it can be inferred that the degradation of methylene Blue is pseudo first order reaction and best fit by Langmuir-Hinshelwood model of kinetics with rate constant of $6.11 \times 10^{-3} min^{-1}$

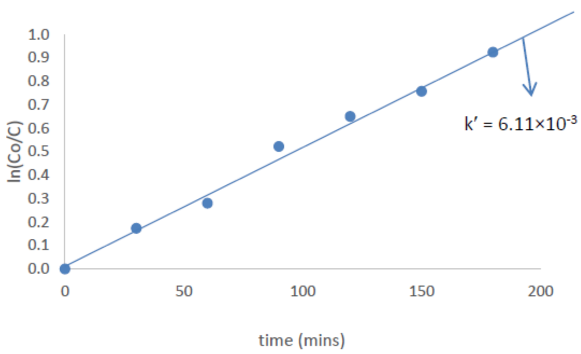

Fig 6 Kinetics of degradation of Methylene Blue

4. CONCLUSION

Nano TiO_2 was synthesized by green method mediated by neem leaf extract. The formation of nano TiO_2 was confirmed by characterization techniques. The synthesized TiO_2 was quite efficient in photodegradation of Methylene Blue. Degradation rate increase with increase on TiO2 till it reaches saturation. The degradation is better at a pH of 10. The kinetic data was best fit by Langmuir Hinsehel wood modified equation with a overall rate constant of the degradation of 6.11×10^{-3} min^{-1}.

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