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Research Article

PHOTO CATALYTIC DEGRADATION OF CATIONIC DYE BY MGO DOPED TIO$_2$ NANO PARTICLES UNDER UV IRRADIATION

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ABSTRACT

Metal oxide nanoparticles plays an important role in water treatment. Ultra fine 5%, 10% and 15% MgO doped TiO_2 nanoparticles have been synthesized by Sol-gel method. Synthesized nano particles were characterized by XRD, SEM, FT-IR analysis. Degradation experiments were conducted with the variable such Photocatalyst dosage (10-100mg), Initial ion concentration(2-10ppm) and pH (3, 6, 9) with Irradiation time(0-100). The optimal conditions for the degradation of cationic MB were 80 Min, 6 ppm of dye concentration, acidic pH 6 and 40mg/L of catalyst dosage.

Keywords: MgO doped TiO_2, Nano Catalyst, Photo Degradation, Cationic Dye, Methylene Blue.

1. INTRODUCTION

The polluted environment and energy shortage are two utmost complications faced by this generation; providentially these two issues are inter-linked. Even though shortage of energy is essential issue, we are in hectic condition to rectify the environmental pollution especially on polluted water bodies, because water plays a vital role in day to day life. Dyes are the major source of water pollution. The discharged water from industries such as dyeing, tanneries, paper, textile, petroleum and chemical industries polluted the water bodies [1-2]. Now a days almost 10,000 types of dyes and pigments are generally utilized by all types of industries and over $7x10^5$ tons of synthetic dyes are polluting all over the world. [3-5]. The effluent of dyes are highly toxic in nature as it contains high suspended solid, COD, along with some types of heavy metals like Cr, Cu, Cd, Zn, Ni and Pb. About 80% of the dyes only stick with the cloth, remaining amount of dyes are drained out,when drained out part of dyes are mingled with water bodies, it just affects the quality of water, some of the dyes makes carcinogenic, mutagenic or terogenic disorders in man. The people who worked in dyeing sectors may be affected by triple primary cancers involving kidney, urinary bladder and liver also [6-12]. Among the many harmful dyes, Methylene blue is one of the most common toxic dye which is used in many industrial sectors. Even though it is used as a safe drug, it makes toxicity in higher amount of dosages; it may cause hyperbilirubinemia, meth-Hemoglobin formation, respiratory diseases, pulmonary edema, Bluish discoloration of tracheal secretions and urine [13]. Due to the less availability of fresh water and to save the environmental health we should clean off the dye related environmental problems. There are many types of modern techniques are available to degrade or rectify the toxicity of dyes. Several waste water treatment technologies have been developed for the removal and degrading of organic contaminants, there are physical methods such as adsorption [14,15], Reverse Osmosis [16], Ultra-filtration [17], Ion Exchange [18] etc. Chemical methods such as Ozonation, Chlorination [19], Aerobic and anaerobic treatments [20] are also used. But the main disadvantage of these removal methods is non converting the pollutants as eco-friendly products, moreover the end products of the above methods should be treated for further complete degradation. Photocatalysis is an emerging technology for the complete mineralization of hazardous organic chemicals to water, CO_2 and simple mineral acid. Generally nano catalyst is enhanced by irradiation of light. When the light is illuminated, surface of the metal electrons absorb it and gets excited. The photocatalyst should be non-toxic, inexpensive and highly photoactive [21-23]. Among the photocatalysts, TiO_2 has been

extensively used for many environmental and energy related applications due to its efficient photoactivity, high stability, low cost and eco friendly nature. The wide band energy gap 3.2eV and fast recombination nature of TiO_2 suppresses the photocatlytic activity. To overcome the limitations, doping of metals, metal oxides and non metals are introduced, it enhances the photocatalytic activity of TiO_2 photocatalyst [24-25]. Many of the transition metals like Fe [26], ZnO [27], Cu, Ni [28], Cd [29], Mn [30] etc. were previously reported. Recently, studies have demonstrated the good degrading nature of MgO/TiO_2 on various organic dyes [40]. Hence the main aim of this study was to prepare MgO doped TiO_2 through sol-gel method, then the effect of initial ion concentration, catalyst loading, pH with irradiation time on the degradation of Cationic Methylene Blue (MB) degraded under UV- irradiation was also studied.

2. MATERIAL AND METHODS

2.1. Synthesis of MgO doped TiO_2 nano particles by Sol-gel method

Titanium tetra-n-butoxide [$Ti(O\text{-}Bu)_4$], Magnesium nitrate purchased from E-Merck (German) AR analytical grade, were used as titanium and magnesium sources for preparing MgO doped TiO_2 photocatalyst. All other chemicals and reagents were of Merck (India) analytical grade.

Initially 21 ml of titanium tetra-butoxide was dissolved in 80ml of isopropyl alcohol and the obtained solution was stirred vigorously. Then 2ml of water and 0.5 ml of acetic acid 50% were added to another 80 ml of acetic acid solution. Later on solution was slowly added to the [Ti $(O\text{-}Bu)_4$] isopropyl alcohol solution under vigorous stirring. When the resulting mixture turned into sol, the magnesium nitrate solution (5, 10, 15 wt %) was added drop-wise. The resulting transparent colloidal suspension was stirred for more than 2 hours and aged at 25°C until the gel was formed. Again the gel was dried at 70°C in vacuum pressure of 600psi and then ground. The resulting powder was calcined at 400°C for 2 hours in 50°C increments for every half an hour until reaching 400°C. After calcinations, the furnace was cooled for 3 hours. The calcined powder was smashed using pestle and mortar [31].

2.2. Characterization of Mg doped TiO_2

The synthesized Mg doped TiO_2 were characterized using different techniques to know obtained properties. The Powder-XRD (Hitachi, Model S-4000, Japan) was used to identify the crystalline structure and particle size with Bragg's angle ranging from 10-70 with a speed of 3 /per minute using nickel-filtered Cu Ka radiation source and obtained results were ratified by comparing JCPDS file. The structural elucidation and functional groups were identified by FT-IR (JASCO-460 PLUS, JAPAN). Morphology and microstructures of Mg doped TiO_2 nanoparticles were identified by Scanning Electron Microscope (SEM) (Hitachi, Model S-4000, Japan).

2.3. Photocatalytic activity Experiment

The photocatalytic degradation of dye by synthesized photocatalyst was effectuated under UV-Visible light irradiation. The degradation process was observed using UV-Visible light irradiation at $\lambda_{max} > 464$ nm as a photon energy source using 250 Watt xenon light. For all experiments, a small amount of catalyst was suspended in 100 ml of dye solution in a conical flask. The conical flask was encased by aluminum foil then stored in dark for 60 minutes for photo adsorption. The set up was irradiated with visible light source from fixed lamp in the middle of the system and 12 cm above the surface of the solution. To observe the changes in concentration, dye solution (5 mL) were taken for every 30 minutes and centrifuged followed by measuring the absorbance of the clean solution by UV-Vis spectrometer. The concentration of dye was directly proportional to absorbance according to Beer-Lambert law, so the degradation efficiency of dye was calculated by formula [32].

Degradation efficiency = $C_0 - C / C_0 \times 100$

Co -concentration before degradation, C - concentration after degradation

3. RESULTS AND DISCUSSION

3.1. XRD image of MgO doped TiO_2

The XRD patterns of MgO doped TiO_2 nano composites are illustrated in Fig 1. The grain size of the MgO doped TiO_2 were calculated with the scherrer formula by the full width at half maximum of the (101) Diffraction peak of TiO_2 after subtraction of the equipment broadening [33]. The diffraction peaks in the patterns of the samples are all contributed by the anatase phase and no other impurities phase can be detected. The corresponding hkl values for the peak intensity of MgO doped TiO_2 are (101), (103), (112), (105), (211), (204), (424), (521), (215) and it was well matched with JCPDS CARD No 78-2486. The estimated powder grain size of MgO doped TiO_2 powders were 42.46nm and for MgO (5%, 10%, 15%) TiO_2 were 89.0nm, 95.4 nm and 85.3nm.

Due to the smaller size of the nanoparticles crude sample was taken for further studies for better photodegradation.

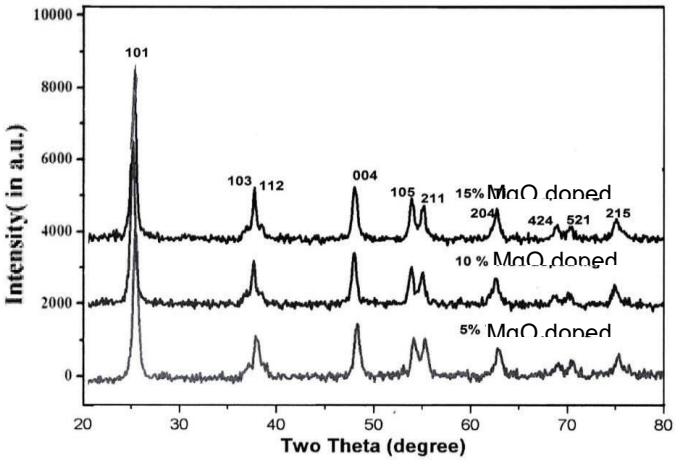

Fig. 1: XRD patterns of MgO doped TiO_2

3.2. Scanning Electron Microscope(Sem)

The SEM image of MgO doped TiO_2 was used to explain the external morphology, chemical composition and orientation of materials. Spherical shaped MgO doped TiO_2 nanopaticles slightly agglomerated which is clearly shown in Fig. 2(a-c), this spherical morphology creating high surface area and porosity and it enhances the photocatalytic degradation. The uniformity indicates the doping of MgO on TiO_2 lattice [34].

3.3. FT-IR studied of MgO doped TiO_2

FT-IR spectra of MgO doped TiO_2 nano powder is shown in Fig. 3. FT-IR spectra of MgO doped TiO_2 indicates the narrow stretching vibration of O-H from hydroxyl and O-H bending vibration at 3406.42cm^{-1} and 3226.11cm^{-1}. The presence of peak at 2849.30cm^{-1} indicates the presence of Symmetric stretching vibration. A characteristic band presence with strong and wide absorption at below 1000cm^{-1} indicates the formation of Mg-O-TiO_2 lattice. The stretching band corresponding to the magnesium in lattice structure (Ti-Mg-O-Ti) can be detected by 1382$cm^{-1.}$ From the FT-IR results we can confirm the presence of Mg/MgO as doping in TiO_2 crystal lattice.

3.4. Effect of initial ion concentration of MB dye

The effect of initial concentration of cationic MB aqueous solution on the photocatalytic degradation efficacy was studied under UV irradiation. The concentration of dye solution varied from 2-10ppm. The percentage of degradation is 74.14, 74.61, 75.32, 66.66 and 66.21% which is shown in Fig. 4. The amount of photodegration was gradually increased upto 6ppm, the solution was very transparent and clear in low concentration (from 2-6ppm) of dye, so the photons are easily entering to the dye solution and reacts directly with dye solution and give maximum photo degradation. While increasing the concentration of dye gives more active sites which shielded the dye molecules and generates the $OH^{\bullet}$ radicals on catalyst's surface so it restricts the entry of photons which reduces the degradation quantity automatically [34-36]. The reduction of excitation of (e-) from valence band to conduction band also retards the photo degradation [37]. The maximum photodegradation *i.e.* 75.32 % was attained at 6ppm of dye concentration, so that it was considered as optimum level and prescribed for further studies.

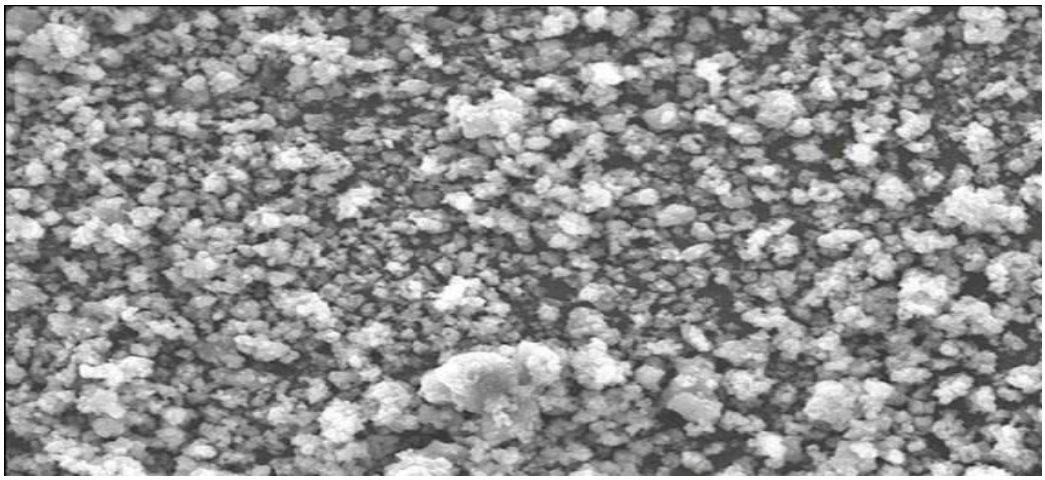

Fig. 2a: 5% MgO doped TiO_2

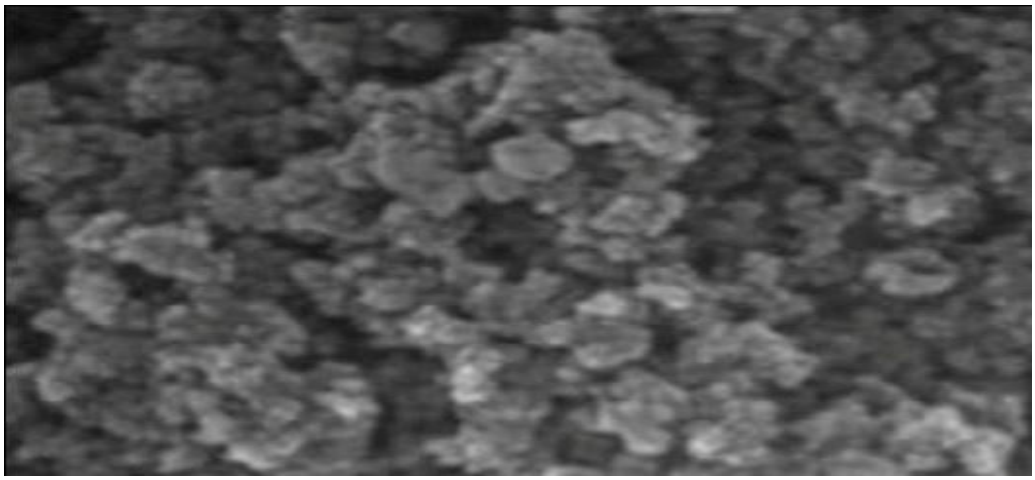

Fig. 2b: 10% MgO doped TiO_2

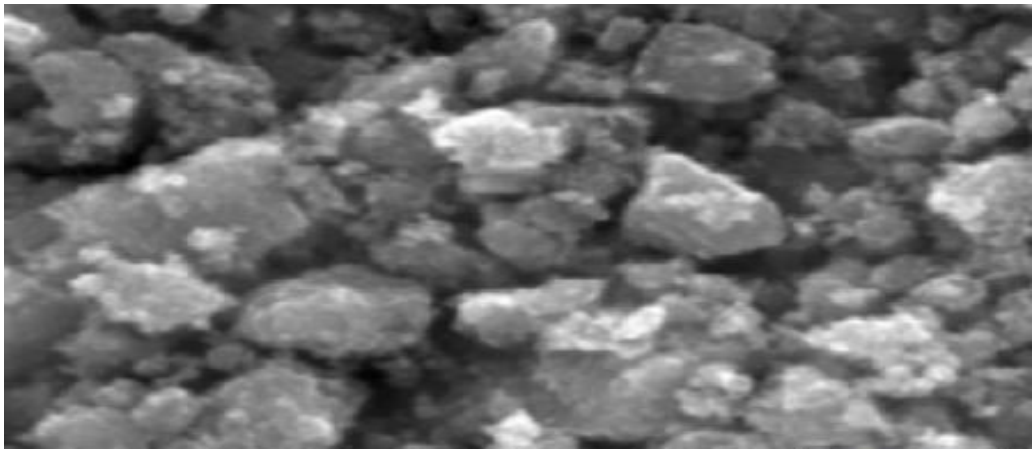

Fig. 2c: 15% MgO doped TiO_2

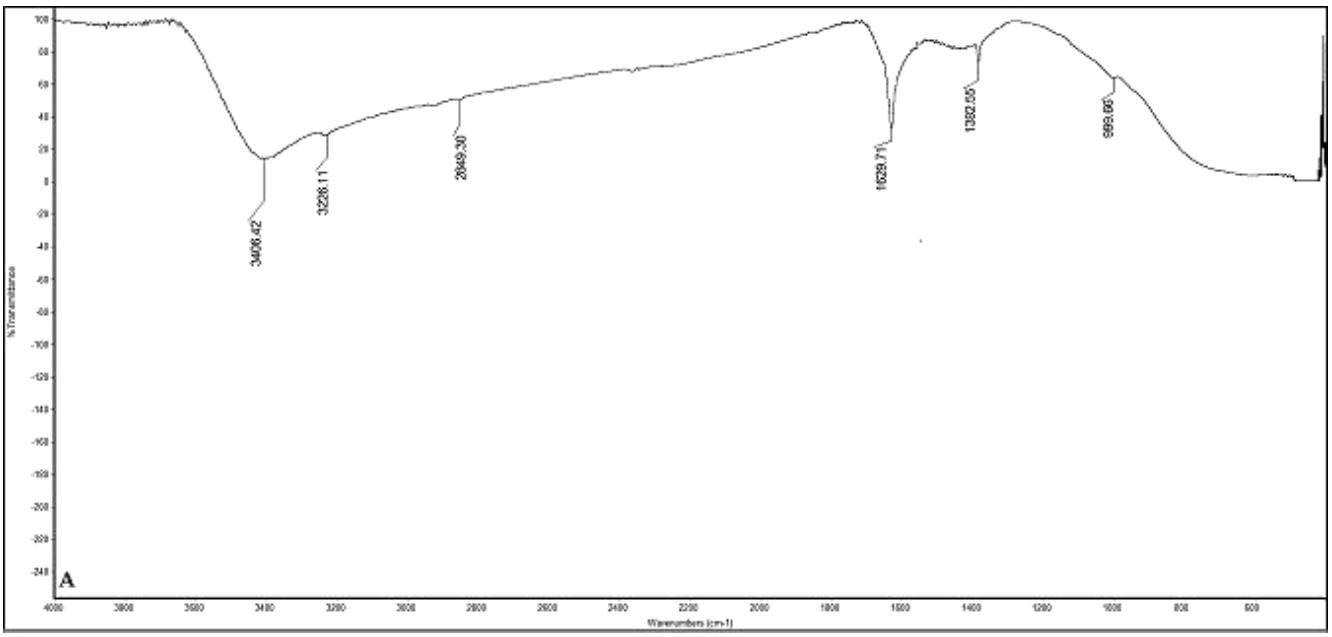

Fig. 3: FT-IR images of MgO doped TiO_2

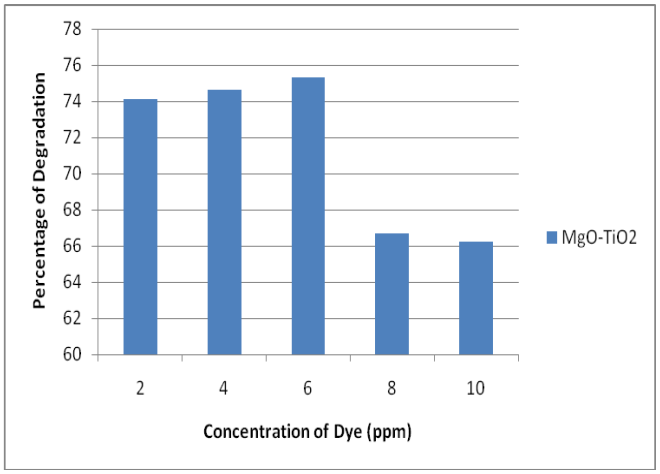

Fig. 4: Effect of Dye Concentration (ppm)

3.5. Effect of Catalyst loading on Methylene Blue dye degradation

The photodegradation of Methylene Blue is studied by Varying the amount of photocatalyst from 10-100 mg. The Photocatalytic degradation is increasing with increased amount of photocatalyst, up to 40 mg, after that the degradation was decreased gradually. The elevation of degradation rate at lower amount of photo-catalytic dosage can be attributed to the increased the number of available number reaction sites which for Methylene Blue dye adsorption or photo adsorption leads to higher number of hydroxyl radicals. At 40 mg of photocatalyst shows a better degradation of 81.80% and it is considered as optimum level of photo degradation. Beyond the optimum level, the inimical effects of higher dosage of catalyst are observed. Higher concentration of photocatalyst suppresses the pene-tration of UV light as well as the photo adsorption of Methylene Blue dye on the available surface of the catalyst. Further more gradual increase of photocatalyst concentration, the opacity in the slurry and light scattering by the particles prevent the efficient light harvesting, which results in less illuminated reactive sites on the surface of the photocatalyst. Particle agglomeration of photocatalyst is also reason for die down of photocatalytic degradation [38, 39] which is shown in Fig. 5.

3.6. Effect of pH and Irradiation Time on photodegradation of Methylene Blue

In a heterogeneous photocatalysis, reaction always takes place on the surface of the photocatalyst. The surface property of the semiconductor photocatalyst plays a markable role. In this study, the influence of solution pH was examined in the range from pH 3-9, as shown in Fig. 6 by increasing the pH from 3-6 the rate of degradation was highly enhanced, but further increasing the pH, the rate of photodegradation was declined slightly. This is due to electrostatic interaction between negative surface and cationic dye loading to the strong photo adsorption on the metal oxide support. From the observed study pH6 suspension was selected as optimum pH for dye degradation which shows the high degradation percentage of 75.98%.

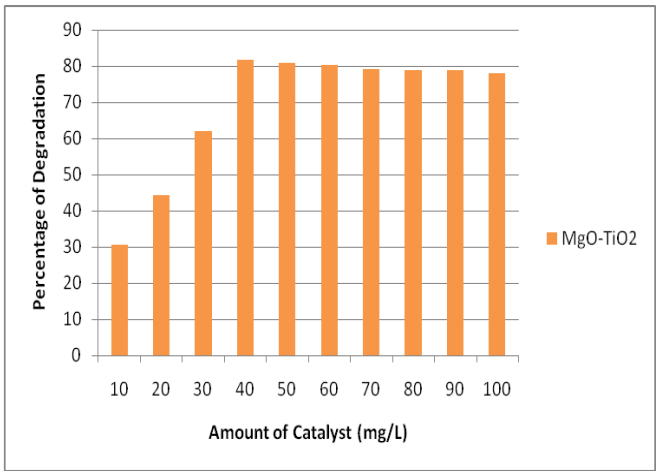

Fig. 5: Effect of Catalyst Dosage on Methylene Blue dye degradation

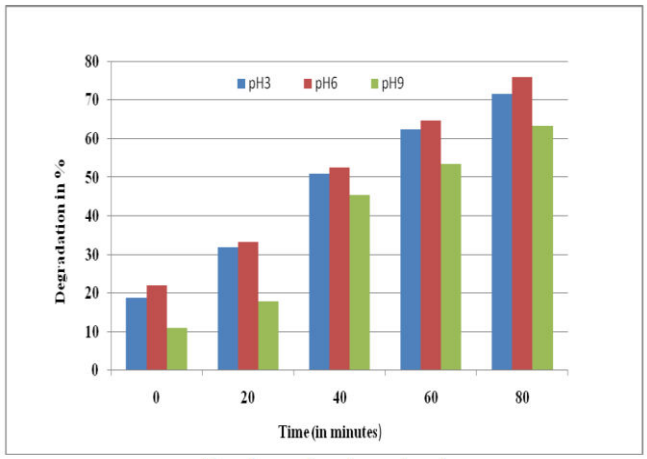

Fig. 6: Effect of pH on degradation of MB dye

Generally the degradation is depending upon the surface charge of the photocatalyst. MB is a cationic dye; exists in positive charge when it is dissolved in water. The surfaces of the particles are adversely charged when the pH of solution is higher than the zero point charge. The opposite charges between suspension and surface of the

catalyst enhanced the degradation of MB [40]. The number of photo generated electrons and holes that reach the surface of the particles determine the effectiveness of the dye degradation. A higher pH value could provide a higher concentration of hydroxyl ions they can react with photo generated holes to form $OH^{\bullet}$ and eventually enhances the degradation. In lower range of acidic pH or neutral pH medium, the degradation efficiency was decreased because it does not provide sufficient hydroxyl group to form $OH^{\bullet}$ [41]. Increasing the time of UV irradiation increases the degradation, in prolonged UV irradiation the high concentrated dye molecules scatters the light source it leads decrease in degradation.

4. CONCLUSION

In this study, removal of MB dye are performed using MgO doped TiO_2 photocatalyst synthesized by Sol-gel method. The MgO doped TiO_2 nanoparticles was found to have a high degradation efficacy. To analyze the degrading nature of the synthesized nanometal oxides, the effect of various parameters on the rate of degradation were also examined. Under the optimum conditions (Catalyst loading 40 mg/L, initial ion concen-tration-6 ppm, Irradiation time -80 minutes, acidic pH 6) MgO doped TiO_2 gives maximum degradation.

5. REFERENCES

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