



Effect of titanium dioxide and gadolinium dopants on photocatalytic behavior for acriflavine dye

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ABSTRACT

Herein, we report the experimental methodology to optimize the operational parameters of the photocatalytic degradation of acriflavine dye using TiO₂ and Gd³⁺ as dopant. A series of Gd³⁺ doped TiO₂ nanoparticles were synthesized via hydrothermal route and characterized using various techniques like FT-IR, UV, XRD, FESEM and EDS. It is observed that synthesized particles are in the range of 25–30 nm with spherical shape in nature. TiO₂ has rutile phase and the average particle size was estimated from Scherrer's equation. Energy bandgap was estimated using Tauc's plot. The photodegradation was carried out under UV light in pseudofirst order condition. To understand the kinetics, four experimental parameters were chosen as independent variables like percentage of dopant, initial concentration of dye, dosage of catalyst and pH of reaction medium. The degradation efficiency of 92% was observed for 0.5% Gd doped TiO₂ at catalyst dosage of 0.3 g/dm³, pH 10 and dye concentration of 3 × 10⁻⁶ mol/dm³. It is observed that, the photocatalytic activity of TiO₂ can be increased by using gadolinium as dopant only in optimum concentration. Further, this photocatalyst can be employed to degrade other organic pollutants.

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1. Introduction

Water is the most essential component for the existence of life on earth. Water resources are continuously being exploited due to rapid industrialization from mid of the last century. Many organic pollutants persist in water and have been detected in the range from ng/L to mg/L,¹ but it has made adverse effect on environment. Sensitive receptors such as phytoplankton, zooplankton, including human beings and animals are facing life threatening problems² over the last decade due to gradual change in aquatic environment and interaction with food chain. Water resources are polluted due to organic contaminants which are discharged by manufacturing industries, pharma industries, fertilizer industries, chemical industries, textile and dyeing industries.³ Further, the municipal waste-water, runoff from agricultural procedures and chemical spills also contribute towards contamination of water resources. Organic contaminants persist in water and enter in

biological food chain which affects human health and entire ecosystem. In recent years, environmentalists and scientists have raised serious concern over growing deterioration in quality of water. Today's challenge is to get clean water which should be free from color, odor, contaminants and pollutants.

Acriflavine [AFN] is used as an antiseptic since the World War. It was synthesized by a German medical researcher, Dr. Paul Ehrlich and various researchers used it as antibacterial agent.⁴ Acriflavine hydrochloride is soluble in water and generally employed to treat fungal infections of aquarium fish. It is also used in biochemistry due to its fluorescent property. Despite its medicinal importance, acriflavine is also known for its harmful effects on human beings such as skin irritation, eye irritation, breathing problems.⁵ Acriflavine is also found to be toxic to aquatic plants. It also imparts fluorescent color to water which is required to be removed to meet the ideal characteristics of clean water.

In recent years, TiO₂ has emerged as a promising heterogeneous catalyst among numerous semiconductors and attracted researchers for having versatile properties like chemical stability, non-toxicity towards environment and cost effectiveness.⁶ The

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holes and electrons generated upon photoexcitation have better oxidizing and reducing properties, respectively. It has band gap between 3.0 and 3.2 eV⁶ which requires UV light within 415 nm for excitation. Several attempts have been made to enhance photocatalytic activity^{7,8} via doping with inner transitional elements like La³⁺, Eu³⁺, Nd³⁺, Gd³⁺, Pr³⁺.⁹ The lanthanides are preferred to enhance the photocatalytic activity¹⁰ of TiO₂ because they have vacant f-orbitals¹¹ which are capable to make complex efficiently with functional groups of organic compounds such as aldehydes, ketones, alcohols, amines, thiols, etc.¹² The complex forming ability of lanthanides makes dye molecules to adsorb on TiO₂ surface to larger extent which facilitates photodegradation.¹² The higher the adsorption dye molecules on the surface of TiO₂ matrix, the higher the efficiency of photodegradation would be.¹³ Intrigued by the above observations, herein, we report the low cost heterogeneous photocatalyst, Gd doped TiO₂ for degradation of acriflavine.¹⁴ Further, we have studied the effect of various parameters such as dye concentration, doses of photocatalyst and pH of solution on the rate of photodegradation.

2. Experimental

2.1. Chemicals and reagents

Titanium (IV) butoxide [Ti(OBu)₄ or Ti(OC₄H₉)₄] was purchased from Alfa Aesar chemicals, India. Nitric acid was purchased from Nice Chemicals, India. Acriflavine hydrochloride and gadolinium(III) nitrate were purchased from Sigma Aldrich. The pH of solution was maintained using buffer solutions, and analytical grade chemicals were used to maintain required pH. Acetate and phosphate buffer were used to maintain acidic medium (pH 4.0 to 5.0) and neutral medium (6.5–8.5), respectively. Basic medium (pH 9.0 to 10.0)¹⁵ was maintained using borate buffer solution. All solutions used in experiments were prepared using milli pore water.

2.2. Instruments employed for experiments and characterization

- (1) Kinetic study: The degradation kinetics was followed using an Analytika Jena Specord 200 plus UV-Visible spectrophotometer.
- (2) Degradation study: A mercury lamp (Philips, TUV 10 W, E_{max} = 254 nm) mounted in lab made cabinet was used for degradation study. The light intensity falling on reaction mixture was 5 mW/cm²
- (3) Band gap measurement: The Analytika Jena, Specord 200 plus UV-Visible spectrophotometer with Win Aspect Software was used for absorption and band gap measurements.
- (4) Functional group identification: An FT-IR spectrophotometer (Nicolet 6700, USIC, Karnataka University Dhrwad) was used for functional group confirmation. The sample was analyzed between 4000 and 400 cm⁻¹ in KBr pellet at resolution of 2 cm⁻¹.
- (5) Detection of crystal structure and particle size: An X-ray diffractometer (XRD, Cu Source, λ = 0.15 nm, Rigaku pro analytical, Manipal Institute of Technology, Manipal) was used to detect crystal structure and particle size. The samples were analyzed by scanning at the rate of 0.02(°)/s in the range between 20° and 80°.
- (6) Surface morphology and elemental composition: A field emission scanning electron microscope (FESEM) was used to study the surface morphology. The elemental composition was ascertained by an energy dispersive detector (EDS), DST-PURSE Laboratory, Mangalore University, Mangalore.

- (7) pH measurement: The pH of solution was measured using a Systronics pH meter.

2.3. Hydrothermal synthesis of TiO₂ and Gd-TiO₂

Titanium(IV) butoxide was used as precursor for the synthesis of TiO₂ nanoparticles by hydrothermal method. A mixture of 15 mL water and 15 mL concentrated nitric acid were taken in a 100 mL beaker. 0.6 mL of titanium(IV) butoxide solution was added dropwise with constant stirring and the mixture was stirred for 1 h. The clear solution was transferred into a Teflon lined stainless steel autoclave, the autoclave was tightly sealed and placed in a hot air oven at 180 °C for 3 h.¹⁶ Then, the autoclave was cooled to ambient temperature. The reaction mixture was centrifuged to obtain a fine powder. The product was washed repeatedly with milli pore water and ethanol. Later it was dried in the hot air oven at 100 °C for 1 h.

The TiO₂ was doped using Gd for which gadolinium nitrate was used in mole ratio of 0.2%, 0.3%, 0.5% and 1.0% to TiO₂. The dopant was dissolved in mixture of 15 mL water and 15 mL concentrated HNO₃ and rest of the procedure is the same as mentioned above.

2.4. Photodegradation study

In order to study the photocatalytic degradation of acriflavine, a known concentration of acriflavine solution was taken in a 100 mL beaker. The pH of solution was maintained using buffer solution and 0.3 g/dm³ of TiO₂ nanoparticles was added as photocatalyst. The solution was kept in dark for 2 h to achieve adsorption equilibrium between substrate and photocatalyst. After that, the beaker was placed under 10 W UV- lamp (Philips) mounted in lab made UV irradiation cabinet. During the illumination, the solution was stirred continuously with the help of magnetic stirrer. The decrease in concentration of acriflavine was monitored by measuring the decrease in absorbance at 262 nm using a UV-visible spectrophotometer. For every 15 min, the analyte was taken out for the measurement of absorbance at 262 nm. Before the measurement, the solution was centrifuged for 10 min at 5000 r/min to remove any turbidity. All kinetic data were evaluated using Microsoft Excel 2010 program.

3. Results and discussion

3.1. Characterization of TiO₂ and Gd-TiO₂

Samples were subjected to X-ray diffraction studies to ascertain the crystal structure and particle size. The XRD patterns were obtained by using Cu source at wavelength of 0.15 nm and scanning at the rate of 0.02(°)/s in the range between 20° to 80°.

The XRD pattern for pure TiO₂ is shown in Fig. 1(a), the observed Bragg reflection peaks at 2θ and corresponding reflection planes are 27.392° (110), 35.087° (101), 39.126° (200), 41.230° (111), 43.970° (210), 54.275° (211), 56.528° (220), 62.823° (002), 68.921° (301), 69.841° (112) and 82.217° (321). The 2θ values obtained in XRD pattern were compared with data sheet No. 89–0552 of Standard Joint Committee on Powder Diffraction Standards (JCPDS). It exhibits that the pure TiO₂ is having rutile phase with tetragonal structure. The XRD pattern of pure TiO₂ shows sharp, broad and strong peaks, which indicates TiO₂ formed is crystalline in nature.

Fig. 1(b) represents XRD pattern for Gd doped TiO₂, the observed Bragg's reflection peaks at 2θ and corresponding reflection planes are 27.331°(110), 35.833° (101), 39.037° (200), 40.982° (111), 43.870° (210), 54.023° (211), 56.395° (220), 62.213° (002), 63.779°

(310), 68.642° (301), 69.234° (112), 81.898° (321) and 83.861° (400). The 2θ values obtained in XRD pattern were compared with data No. 89–6975 of JCPDS which confirms that Gd doped TiO_2 is having rutile phase and tetragonal structure. The average particle size was calculated using Scherrer's equation.¹⁷ The estimated values for TiO_2 and Gd doped TiO_2 are 20.89 and 13.12 nm, respectively. The width of diffraction peak increases after doping with Gadolinium,¹⁸ which may be due to decrease in grain size. According to Scherrer's equation, the width of diffraction peaks is inversely proportional to crystal size. Hence after doping, the particle size reduces due to which increase in width of diffraction peak is observed.¹⁹ Further, is not anticipated Gd^{3+} to enter in crystal lattice of TiO_2 , because the ionic radius of Gd^{3+} (0.094 nm) is greater than the Ti^{4+} (0.068 nm).²⁰ Hence Gd^{3+} ions, rather deposit on the surface and grain boundaries of TiO_2 matrix. The intensity of diffraction peaks increases with increase in concentration of dopant atoms. Generally, the peak intensities are being affected by electron density, when dopant concentration increases the electron density increases due to large size of Gd^{3+} ions. Thus, doping with more number of Gd^{3+} ions incorporates more number of scattering centers which enhances the peak intensity.²⁰

FESEM was employed to study the surface morphology of pure TiO_2 and Gd doped TiO_2 . The FESEM images of pure TiO_2 and Gd-doped TiO_2 are shown in Fig. 2(a,b) and (c,d), respectively which reveals the average particle size of pure TiO_2 is about 30 nm, whereas average particle size of Gd doped TiO_2 nanoparticles is 25 nm. Particles of both pure and Gd doped TiO_2 are spherical in shape. The decrease in particle size is observed with doping, perhaps due to restriction in crystal growth imposed by Gd^{3+} owing to its adsorption on active sites of TiO_2 matrix.¹² The EDX spectrum of pure TiO_2 represents the peaks corresponding to Ti and O. Similarly, the EDX spectrum of Gd doped TiO_2 represents presence of Gd, Ti and O. Trace amount of residual carbon is also found in both the samples (Available as supplementary data).

The UV-visible spectral analysis was carried out from 300 to 600 nm. The UV-visible spectra of both pure TiO_2 and Gd doped TiO_2 are shown in Fig. 3 which reveals that pure TiO_2 shows the maximum absorption at 344 nm and gadolinium doped TiO_2 shows the maximum absorption at 317 nm. The absorption maximum is shifted to lower wavelength which indicates the presence of gadolinium in TiO_2 matrix. For the estimation of band gap of TiO_2 and Gd- TiO_2 Tauc's plot was plotted and is shown in Fig. 4. The estimated band gap for TiO_2 and Gd- TiO_2 is 3.06 and 3.54 eV, respectively.¹⁷ As the particle size decreases, the grain size decreases and less number of atomic orbitals overlap and discrete electronic bands are formed, due to which the bandwidth reduces. This increases band gap and absorption band shifts

towards shorter wavelength.¹⁹ The UV absorption band of pure Gd_2O_3 nanoparticles is around 278 nm, whereas TiO_2 is at 344 nm. Gd^{3+} does not enter into the crystal lattice of TiO_2 but deposits on the surface of TiO_2 matrix. Hence, absorption takes place in shorter wavelength.²¹

The FT-IR spectra of pure TiO_2 and Gd doped TiO_2 are shown in Fig. 5. The pure TiO_2 shows strong and broad absorption band around 650 cm^{-1} corresponding to Ti–O–Ti stretching. Whereas, broad peak found at 3400 cm^{-1} is ascribed to OH stretching frequency of water molecule associated with TiO_2 matrix. Further, a medium absorption band at 1650 cm^{-1} is observed due to bending vibration of Ti–O. While, Gd doped TiO_2 shows strong and broad Gd–O stretching frequency at 600 cm^{-1} . But there is increase in intensity of absorption band which is due to presence of Gd^{3+} ions along with TiO_2 . Since, stretching frequency of Gd–O and Ti–O–Ti more or less falls in the same range with slight disparity. Consequently, the intensity of broad band ranging between 650 to 550 cm^{-1} is more in case of Gd doped TiO_2 compared with pure TiO_2 .¹⁷

3.2. Effect of concentration of dye on photodegradation

To study the effect of variation of dye concentration on photocatalysis, the concentration of dye was varied from 3×10^{-6} to $20 \times 10^{-6}\text{ mol/dm}^3$ and remaining parameters such as pH and dosage of catalyst were maintained constant. Table 1 and Fig. 6 represent effect of dye concentration on photodegradation. We observed decrease in rate constant (k_{obs}) with increase in concentration of dye. This can be explained on fact that, initially as the concentration is low, adequate number of dye molecules acquire active sites on surface of TiO_2 and electrons of photocatalyst get excited from valence band to conduction band creating holes. These holes will react with water molecules, which results in generation of hydroxyl ($\cdot\text{OH}$) free radicals, which are responsible for degradation of dye molecules that are adsorbed on surface of photocatalyst and also the molecules which are near to surface of catalyst.²² But, when the concentration of dye increases, more number of dye molecules absorb UV light due to which screening effect for photocatalyst occurs. Consequently, photocatalyst may not receive desired intensity of UV light required for the excitation. Hence, the rate of generation of $\cdot\text{OH}$ free radical decreases and accordingly the rate of degradation decreases.²³

3.3. Effect of catalyst on photodegradation

In view to understand the effect of dosage of catalyst, the photodegradation was carried out by varying catalyst from 0.1 to 1 g/

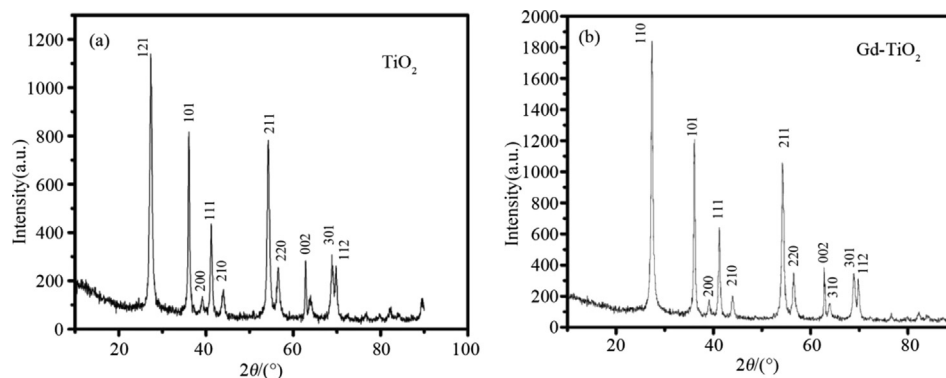


Fig. 1. XRD patterns for pure TiO_2 (a) and Gd doped TiO_2 (b).

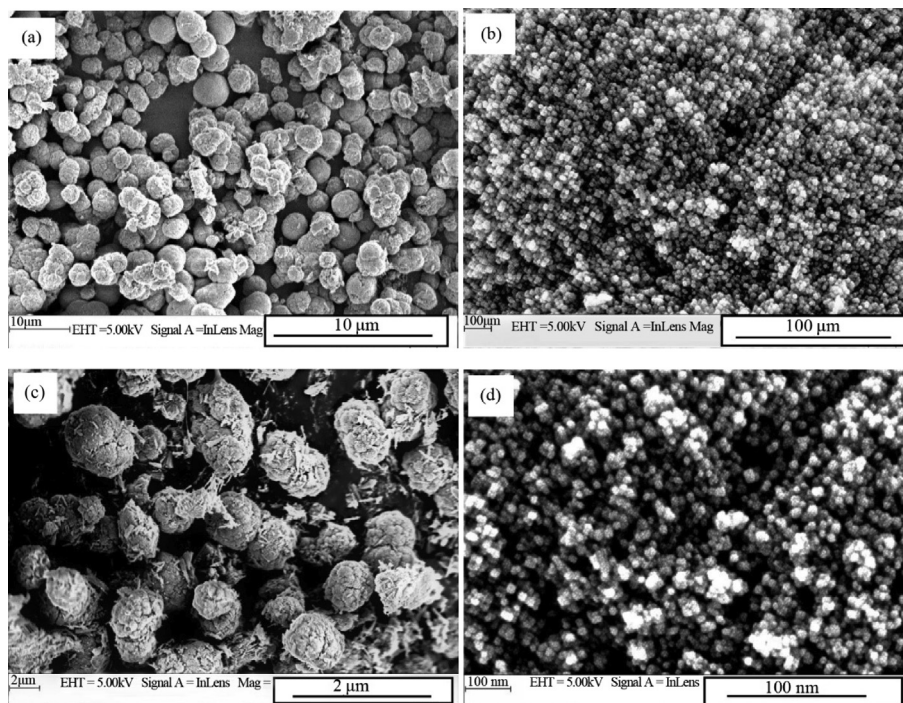


Fig. 2. FESEM images of pure TiO₂ at 10 μm (a) and 100 nm (b) and Gd doped TiO₂ at 2 μm (c) and 100 nm (d).

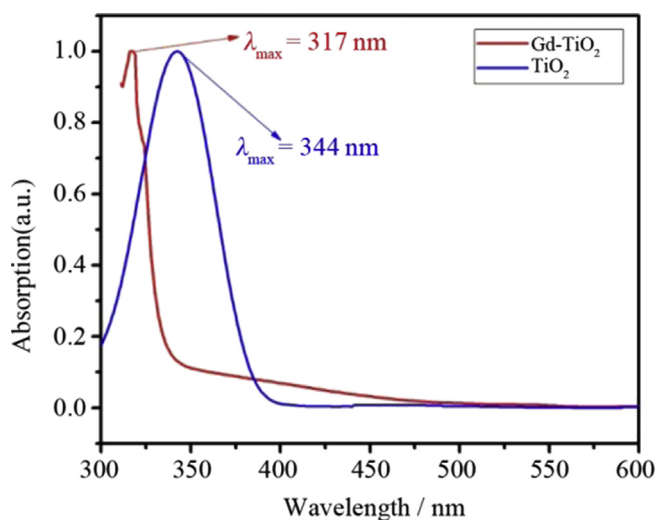


Fig. 3. UV-visible spectra of pure TiO₂ and Gd doped TiO₂.

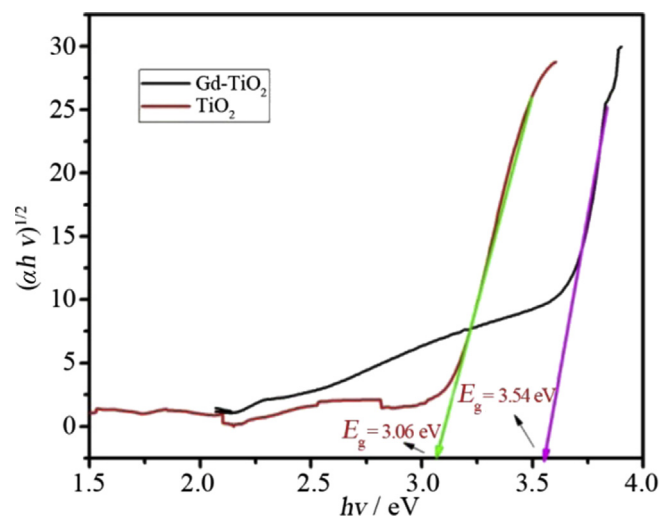


Fig. 4. Tauc's plot.

dm³ and other parameters such as concentration and pH were maintained as 3×10^{-6} dm³ and 7, respectively. Table 1 and Fig. 7 present effect of dosage of photocatalyst on photodegradation. The rate constant (k_{obs}) increased as the dosage of photo catalyzed was increased from 0.1 to 0.3 g/dm³, but thereafter the rate constant started decreasing from 0.4 to 1 g/dm³ and the rate of photodegradation was very low at dosage of 1 g/dm³.

This observation indicates that, the photocatalytic activity is the maximum at certain optimized condition that is 0.3 g/dm³. As the dosage of photocatalyst increases, dye molecules get more active sites for adsorption due to increase in surface area of photocatalyst.¹⁵ However, as the dosage exceeds certain limiting value, the degradation decreases because turbidity in solution does not allow enough light to reach the catalyst which is essential for

excitation. Therefore, there is a decreasing trend in rate of degradation.²²

3.4. Effect of pH on photodegradation

The pH of solution plays a very crucial role in governing the photocatalytic activity of any heterogeneous catalyst.²⁴ The pH of solution affects the adsorption of dye molecules by altering the surface-charge properties of TiO₂. The surface charge of TiO₂ mainly depends on pH of solution. TiO₂ has point of zero charge at pH 6.8,²⁵ when the pH of solution falls below 6.8 or in acidic solution, the surface of TiO₂ acquires positive charge and it attracts anions. On other hand,⁶ when pH increases more than 6.8 or in

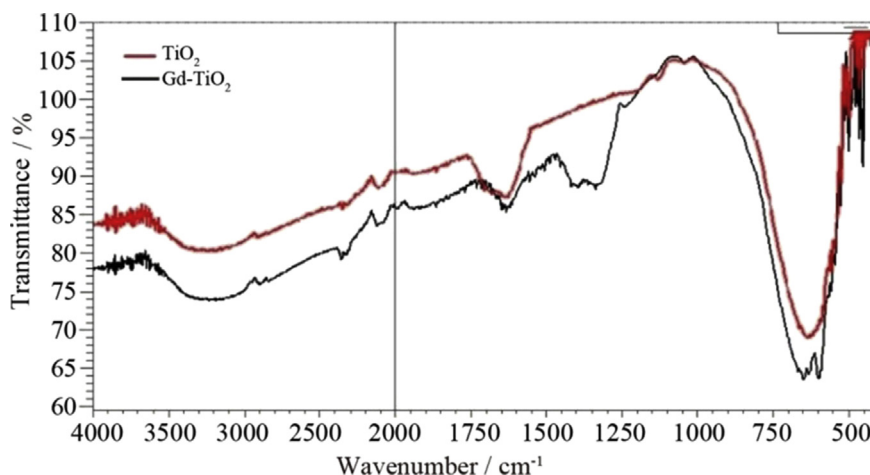


Fig. 5. FT-IR Spectra of pure TiO₂ and Gd-TiO₂.

Table 1
Effect of variation of [AFN], dosage of photo-catalyst and pH on rate constant.

| [AFN] | Dosage of photo-catalyst g/dm ³ | pH | Rate constant k_{obs} (s ⁻¹) |
|---------------------|--|----|--|
| 3×10^{-6} | 0.3 | 7 | 0.74×10^{-2} |
| 5×10^{-6} | 0.3 | 7 | 0.44×10^{-2} |
| 7×10^{-6} | 0.3 | 7 | 0.42×10^{-2} |
| 10×10^{-6} | 0.3 | 7 | 0.33×10^{-2} |
| 3×10^{-6} | 0.1 | 7 | 0.42×10^{-2} |
| 3×10^{-6} | 0.2 | 7 | 0.69×10^{-2} |
| 3×10^{-6} | 0.3 | 7 | 0.47×10^{-2} |
| 3×10^{-6} | 0.4 | 7 | 0.29×10^{-2} |
| 3×10^{-6} | 0.5 | 7 | 0.43×10^{-2} |
| 3×10^{-6} | 1.0 | 7 | 0.66×10^{-2} |
| 3×10^{-6} | 0.3 | 4 | 0.60×10^{-2} |
| 3×10^{-6} | 0.3 | 5 | 0.66×10^{-2} |
| 3×10^{-6} | 0.3 | 7 | 0.74×10^{-2} |
| 3×10^{-6} | 0.3 | 9 | 1.23×10^{-2} |
| 3×10^{-6} | 0.3 | 10 | 1.44×10^{-2} |

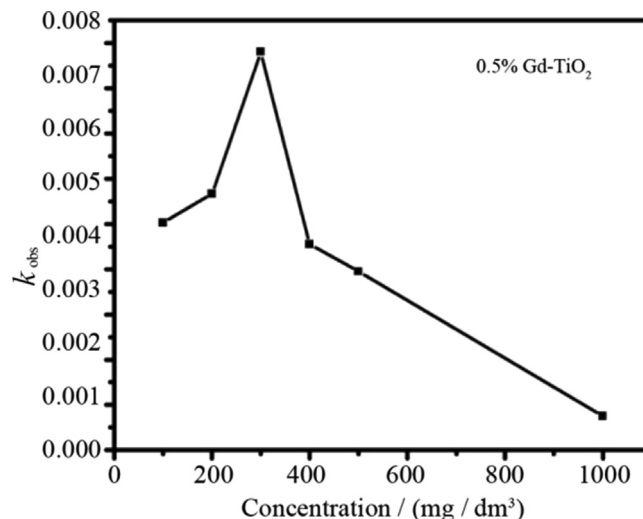


Fig. 7. Effect of photo-catalyst dosage on rate of photo-degradation.

parameters were maintained constant. Table 1 and Fig. 8 present effect of pH on photodegradation. The rate of degradation increased with increase in pH of solution. The rate of degradation was low at pH 4 and high at pH 10. Such trend may be due to more electrostatic force of attraction between cationic dye molecules and TiOH₂⁺ which is an active species in alkaline condition.²⁶ But in acidic condition, surface of photocatalyst acquires positive charge and hence the electrostatic repulsion between TiO⁻ and cationic dye molecules does not favor adsorption on surface of photocatalyst.²⁷ Hence the rate of photodegradation decreases. Further, in alkaline condition the rate of formation of hydroxyl radicals is more which favors photodegradation.

3.5. Mechanism of photodegradation and assessment of photocatalytic efficiency

The photodegradation of acriflavine was studied in various conditions viz., UV, UV/TiO₂, UV/0.2% Gd-TiO₂, UV/0.3% Gd-TiO₂, 0.5% Gd-TiO₂, UV/1.0% Gd-TiO₂ and other parameters were kept constant: [AFN] = 3×10^{-6} , [photocatalyst] = 0.3 g/dm³ and pH = 7. Variation of [AFN], dosage of photocatalyst and pH on rate constant values are tabulated in Table 1.

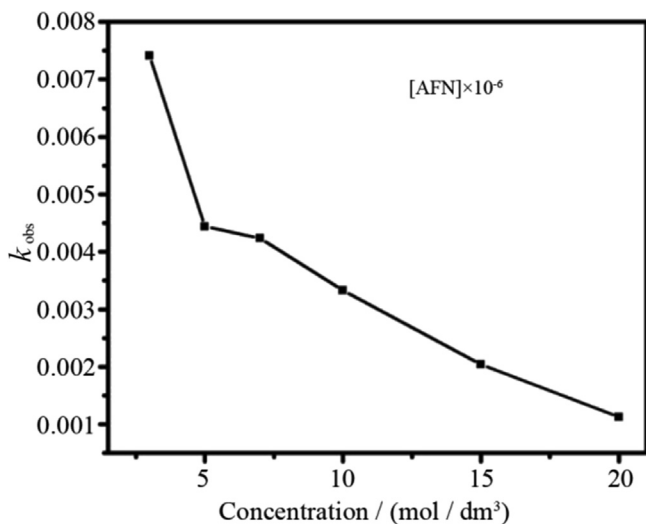


Fig. 6. Effect of variation of dye concentration on rate of photo-degradation.

alkaline solution, the surface of TiO₂ acquires negative charge and it attracts cations.

To study the effect of pH on rate of photocatalytic degradation, the pH of solution was varied from 4 to 10 and remaining

The photo degradation efficiency for various percentage of dopant in TiO₂ is shown in Fig. 9(a). The degradation of acriflavine using only UV light can be neglected, because only 13% degradation was achieved in 120 min. The percentage of dopant showed substantial effect on photocatalytic activity of TiO₂. The degradation efficiency increased with increase in percentage of dopant up to 0.5% that is 92%, whereas for 1.0% Gd-TiO₂, the degradation efficiency was reduced to 63%. Such behavior might be due to change in surface area to volume ratio of nanoparticles. As dopant concentration increases, the particle size increases, due to which the surface area decreases and hence degradation efficiency decreases.¹⁹ Moreover, Gd³⁺ does not enter into TiO₂ matrix rather it deposits on the surface. The increase in concentration of dopant above the optimum value might cover the surface of TiO₂ due to which TiO₂ matrix will not receive adequate amount of UV light required for excitation. The excess of Gd dopant reduces the photocatalytic capacity of TiO₂, possibly due to excess of vacancy generated which act as recombination center instead electron scavenger.¹⁹

The maximum degradation efficiency of 92% was by 0.5% Gd-TiO₂ compared with bare TiO₂ which showed only 54% in 120 min. Among different Gd-TiO₂, the decreasing order of degradation efficiency was found to be 0.5% Gd-TiO₂, 92% > 0.3% Gd-TiO₂, 84% > 0.2% Gd-TiO₂, 76% > 1.0% Gd-TiO₂, 63% > TiO₂, 54% > UV, 13%. Since 0.5% Gd-TiO₂ showed the maximum efficiency, further all studies were carried out using 0.5% Gd-TiO₂. Hence it was observed that, photocatalytic activity of TiO₂ can be enhanced only by using

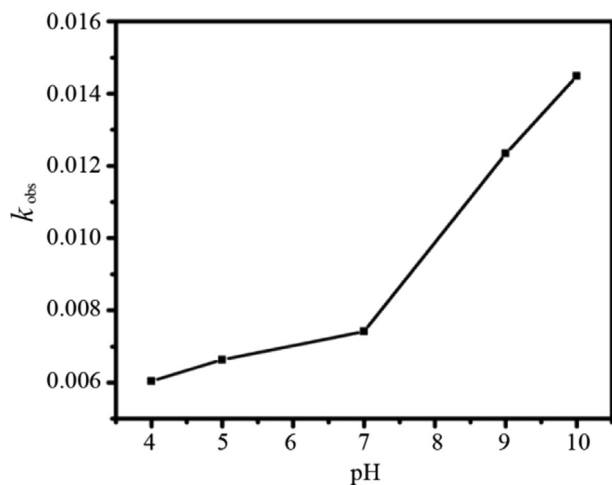
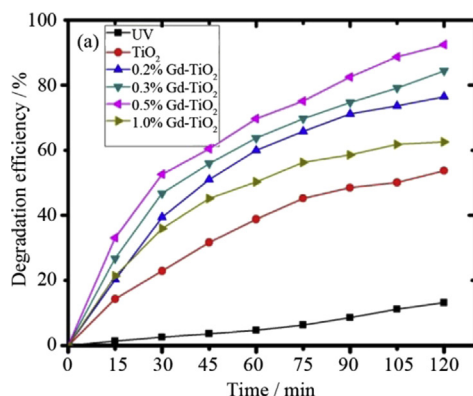
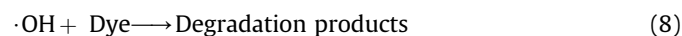
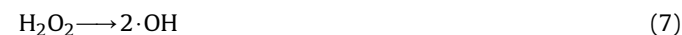
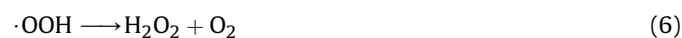
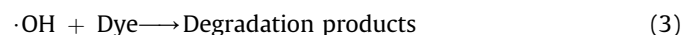


Fig. 8. Effect of pH on rate of photo-degradation.



optimum concentration of Gd. The degradation of acriflavine by 0.5% Gd doped TiO₂ is shown in Fig. 9(b).

When ultra-violet light falls on the surface of photocatalyst, photons having energy equal to or greater than the band gap of semiconductor are absorbed by the electrons. These electrons are excited to conduction band and equal number of holes are created in valence band as shown in Eq. (1). Holes (h_{vb}^+) generated in valence band react with water molecules on the surface of photocatalyst which results in formation of hydroxyl free radicals ($\cdot OH$) as given in Eq. (2). These hydroxyl free radicals degrade dye molecules which are adsorbed on the surface and vicinity of photocatalyst.²⁸ On the other hand, the electrons (e_{cb}^-) in conduction band react with dissolved oxygen to produce superoxide ions²⁰ which helps in avoiding electron–hole recombination as shown in Eq. (4). Superoxide ion ($O_2^{\cdot -}$) reacts with H^+ ions to form hydroperoxy radical ($\cdot OOH$), which turns into hydrogen peroxide and dissociates in subsequent step to form hydroxyl free radicals ($\cdot OH$). These hydroxyl free radicals take part in dye degradation.⁶



There was enhancement in photocatalytic activity on doping with gadolinium. The enhanced photocatalytic activity is perhaps due to decrease in particle size and increase in surface area.¹¹ Since, gadolinium belongs to inner transitional elements which are known to form complex with various organic compounds.⁶ The organic compounds generally being Lewis bases, such as amines, aldehydes, alcohols, acids and thiols interact with the half-filled f-orbitals of gadolinium ions through their functional groups and molecules of substrate concentrate on the surface of Gd-TiO₂ matrix. The higher the accumulation of substrate molecules on the surface of photocatalyst, the higher the photocatalytic degradation

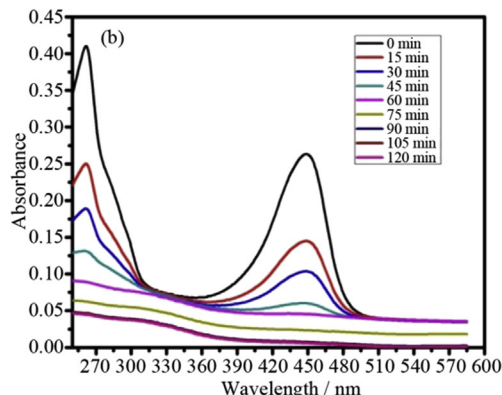
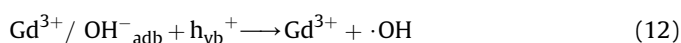


Fig. 9. %Degradation efficiency by various treatment methods with respect to time (a) and degradation of AFN by 0.5% Gd-TiO₂ with time (b).

would be. Such consequences lead to enhancement in the photocatalytic activity.¹¹ Further, gadolinium ions have half-filled f-orbitals, due to which it can prevent potential recombination of electron–hole pairs by acting as scavenger for electrons of conduction band. Gd³⁺ ions are stable due to half-filled orbitals, but stability gets destroyed when Gd³⁺ ion traps electron from conduction band to form Gd²⁺ (Eq. (9)). The Gd²⁺ ion tries to return to stable Gd³⁺ state by transferring an electron to oxygen molecule, it leads to formation of superoxide ion (Eq. (10)) which contributes towards photodegradation.²⁹



On other hand, Gd³⁺ ions also act as scavenger for holes through indirect pathway.²⁹ When TiO₂ is doped with gadolinium ions, there is a charge imbalance which is compensated by adsorbing more number of OH⁻ ions (Eq. (11)) on the surface of photocatalyst. The holes generated during photoexcitation react with adsorbed OH⁻ ions which lead to formation of hydroxyl radicals³⁰ (Eq. (12)).



This conclusion can also be fortified due to high photocatalytic degradation which is observed at pH 10.

4. Conclusions

Eco friendly hydrothermal route was used for the synthesis of TiO₂ and Gd doped TiO₂ nanoparticles. It was confirmed by various characterization techniques. Acriflavin was degraded under UV light using TiO₂ and Gd doped TiO₂ nanoparticles. Among various percentages of Gd doped TiO₂, the maximum efficiency is found for 0.5% Gd doped TiO₂. The degradation efficiency increases only up to the optimum percentage of dopant. The photocatalytic activity of TiO₂ is enhanced by Gd due to its complex forming ability with dye molecules. Gd is found to be reliable dopant to enhance the photocatalytic activity of TiO₂. We also further analyzed the effect of various parameters on the photocatalytic dye degradations. Following results were obtained.

- (1) The maximum photocatalytic activity is observed for the dye concentration [AFN] = 3 × 10⁻⁶ mol/dm³
- (2) The photocatalytic activity is observed the maximum at certain optimized catalyst dosage of 0.3 g/dm³
- (3) The photo-catalytic activity goes on increasing as pH value is increased, the maximum is observed at pH 10.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jre.2019.09.006>.

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