

Studies on Nano-Engineered TiO₂ Photo Catalyst for Effective Degradation of Dye

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Abstract.

All Heterogeneous photo catalysis employing efficient photo-catalyst is the advanced dye degradation technology for the purification of textile effluent. The present work focuses on Congo red dye degradation employing synthesized Ag doped TiO₂ nanoparticles as photocatalyst which is characterized using SEM, XRD and FTIR. Studies are conducted to study the effect of various parameters such as initial dye concentration, catalyst loading and pH of solution. Ag Doped TiO₂ photocatalyst improve the efficacy of TiO₂ by reducing high band gap and electron hole recombination of TiO₂. The reaction kinetics is analyzed and the process is found to follow pseudo first order kinetics.

Keywords: Congo red dye; Photocatalytic degradation; photocatalyst; Ag doped TiO₂ nanoparticles.

1. Introduction

Human race has exploited the available water resources without considering its adverse impact on the environment, resulting in water pollution. The textile industry stands out to be the prominent source of water pollution as the discharge of dyes to the water source causes pollution mainly due to the composition of dyes and harmful substances obtained as by-products when the dye undergo various chemical reactions. According to several tests it is found that the dyes emitted from the textile industry are toxic mutagenic and genotoxic, further the experiments conducted on animals have shown that the dyes possessing azo bonds are carcinogenic resulting in tumours of urinary bladder and liver. [1, 2]. Many methods of dye degradation are available mainly classified as - physical, chemical and biological methods. [3, 4, 5]. Often a single method is either not feasible or economical thus there is a scope of development of the highly efficient and cost effective treatment process. [6,7] Heterogeneous photocatalysis employing TiO₂ which is one of the AOPs is preferred over all other methods as it results in complete mineralisation and also the catalyst used is easily available cost effective and highly efficient in dye degradation[8, 9]. The semiconductor composites namely CdS, TiO₂, Fe₂O₃, ZnS and ZnO etc. used for photo catalysis along with UV or

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visible light source. When the catalyst is subjected to irradiation with the light whose energy is more than the band gap energy of the photocatalyst the electrons present in valence band are excited to reach conduction band creating hole in the valence band. The pair of electron and hole thus formed either interacts with other molecules independently or recombines with each other. The holes present in the valence band has the ability to oxidize water to hydroxide ensuing subsequent formation of hydroxyl radicals similarly the electrons present in conduction band produces super oxide radicals the intermediates thus produced react with the complex molecules of dye which get adsorbed on the catalyst surface hence facilitating dye degradation process [10]. The major drawback in the photo catalysis is recombination of electron and hole pairs that significantly reduces the activity of photocatalysis. Recent research in the field of photocatalysis focuses on reduction of electron-hole recombination by adding doping metal ions into the TiO_2 lattice which facilitates to extend the light absorption to the visible range [11, 12, 13, 14, 15]. The most preferred metals for doping are noble metals namely platinum, gold, silver and palladium with platinum showing the highest efficacy [16, 17, 18]. Though the photocatalytic activity is well enhanced with the addition of Pt the metal silver has found wide application owing to the economic feasibility and ease of preparation [16]. Also silver poses a special behaviour of adsorption of oxygen thus facilitating the charge transfer to O_2 which is found to increase the reaction rate [19, 20, 21]. The investigation on photocatalytic degradation employing Ag doped TiO_2 nanoparticles found profound enrichment in photocatalytic activity using both UV and Visible light irradiations. Due to the fact that nano sized silver on TiO_2 surface increases the electrons accumulation and facilitates charge separation thus showing better efficiency than pure TiO_2 [10, 22]. Thus the combination of two nonmaterial's (Ag and TiO_2) is found to enhance the optical and catalytic properties of the photocatalyst [23]. In the present work Congo red dye degradation using silver (Ag) doped TiO_2 nanoparticles is studied under batch mode using sunlight. The objectives of the present work are synthesize and characterization of nano particles (photocatalyst) and to study degradation of the azo dye under sunlight, the various parameters effecting the process such as pH of solution, dye to catalyst ratio, initial dye concentration. The present work also focuses on the study of the degradation Kinetics in presence of visible light under batch mode.

2. Materials and Methodology

2.1 Chemicals Used.

Congo red 17 dye was procured by Sigma-Aldrich (India). Titanium tetra isopropoxide (TTIP) Sigma-Aldrich (India) was used as precursor. 2-Propanol, nitric acid (HNO_3), ammonium hydroxide (NH_4OH), silver nitrate (AgNO_3) and hydrochloric acid (HCl) all are of GR grade procured from Merck. Sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) procured from Merck was used for maintaining required pH. Distilled water is employed throughout the experiments.

2.2 Synthesis of silver doped TiO_2 by sol gel (Ag doped – SG TiO_2) method.

Sol gel method of synthesis was adopted to synthesize silver doped TiO_2 nanoparticles. Ag doped TiO_2 using sol gel method is prepared according to the procedure proposed by Sobana et al [24]. 10 mL of titanium alkoxide was introduced to the solution containing 40 mL of 2-propanol. This solution was added drop by drop into a solution containing water (10 mL) and 2-propanol (10 mL). The solution pH is maintained at pH 3 using HCl or NH_4OH . Ag is employed as the metal-ion precursor; the required amount of Ag is added to the above mixture in order to obtain the required doping. The solution is stirred for 1 hour until yellowish transparent gel is formed. The gel was dried at 105°C till the solutions transforms into yellow crystals followed by calcination at 450°C for 3h.

2.3 Experimental methods

Experimental setup consists of the 250 mL beaker placed on the magnetic stirrer subjected to sunlight

irradiation. Appropriate concentration of dye solution in water (100ml of solution volume) which has specific quantity of Ag doped TiO₂ nano particles are employed in all experiments. Aqueous dye solutions are magnetically stirred. There is no external air supplied to the reaction mixture. 5mL of samples is withdrawn at regular interval of time. The samples are subjected to centrifugation for five minutes followed by measuring the absorbance at 497 nm for Congo red dye using a UV spectrophotometer and then the corresponding concentration of dye is obtained. Further the degradation percentage is analyzed using the equation

$$\% \text{ degradation} = \frac{(\text{initial dye concentration} - \text{dye concentration at specific time})}{\text{initial dye concentration}} \times 100 \quad (1)$$

3. Results and discussion

3.1 Control run

100 ppm of dye solution is kept in the sunlight without any catalyst and it is found that there is no degradation of the dye after 4 hours of exposure to sunlight. The 100mg of Ag doped TiO₂ catalyst is put in the 100 ppm dye solution under dark and there was no degradation of the dye. This is in good agreement with the fact that the degradation process occurred only in the presence of both catalyst and sunlight which plays a vital role in the photocatalytic degradation process.

3.2 Characterization of Optimized Photo catalyst using SEM, XRD and FTIR

The SEM image of 0.1 wt% Ag doped TiO₂ photocatalyst (magnification of 10000X and 50000X) is shown in the Figure 1. The image shows agglomeration of particles. The particles are found to be spherical in shape. The bright surface indicates Ag on the surface of TiO₂ ensuring the doping of the silver metal on TiO₂.

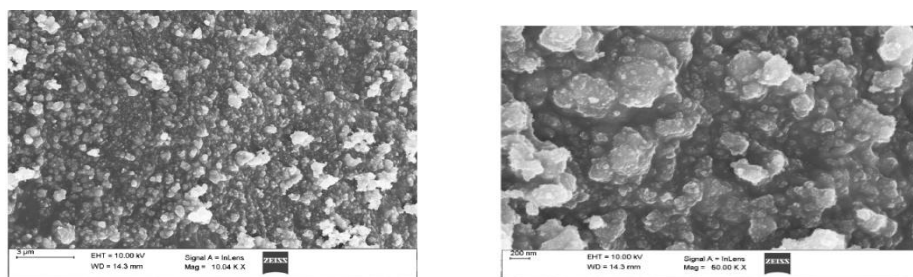


Figure 1. (a) SEM image of Ag doped TiO₂ (10000X magnification); (b) SEM image of Ag doped TiO₂ (50000X magnification).

The phase confirmations regarding the doped catalysts and particle size analysis are carried out using XRD instrument. Figure 2 shows XRD pattern, All observed peaks are in good agreement with the standard data (JCPDS data card- 83-2243) confirming the formation of single phased anatase TiO₂. A shift towards right indicates that doping is taken place in the TiO₂ molecules. The silver deposition on TiO₂ lattice is further confirmed by the peak at $2\theta = 38.1^\circ$ which is the characteristic of Ag metal [25].

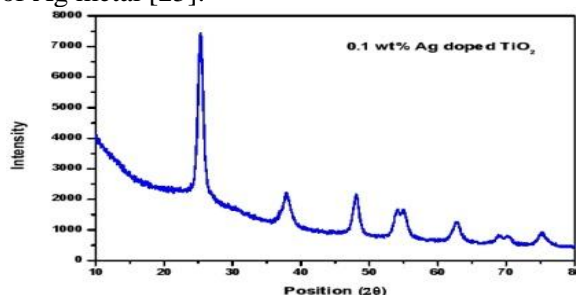


Figure 2. XRD Pattern for 0.1 wt% Ag doped TiO₂.

From the Figure 1 the 2θ diffraction angles at the range of 10° and 80° shows five dominant peaks at 25.38° , 38.38° , 48.45° , 55.02° and 62.53° which are associated with distinct diffraction planes attributed to anatase phase of TiO₂. Peak at 69.19° is associated with distinct diffraction planes attributed to rutile phase of TiO₂. The observation shows that the TiO₂ is mainly anatase with minimum amount of rutile. The Scherrer's equation $D = \frac{k\lambda}{\beta \cos \theta}$ (2) is used to calculate the

average particle size of TiO₂ photocatalyst D which is expressed in nm and are presented in Table 1. In the above equation, $k = 0.89$ (shape factor) which is a constant, λ (Cu K α) represents the X-ray radiation wavelength 0.154 nm, β represents full width at half maximum and θ represents the half diffraction angle [26, 6]. Average crystallite size is found to be 14.1 nm thus, the obtained crystallite size indicates that the crystallite size is in nano range. The XRD pattern of the photocatalyst do not show considerable change in size of the crystal with the addition of silver particles more over the patterns of XRD of Ag doped TiO₂ and pure TiO₂ is very much similar with no additional diffraction peaks formed by silver thus emphasizing the fact that dopant are located on crystal surface. The presence of silver showed no significant effect on the size of crystal showing similar XRD patterns for silver doped TiO₂ and pure TiO₂. The absence of diffraction peaks by virtue of silver doping shows that dopant silver is arranged on the crystal surface [6].

Table 1. XRD analyzing to obtain crystallite size

No.	Peak Position (2θ)	β - value	Crystallite size (nm)
1	25.299	0.591	13.8
2	37.833	0.514	16.3
3	48.064	0.821	10.6
4	53.972	0.514	17.3
5	62.967	0.744	12.5

The presences of functional groups like metallic bonding, hydroxyl ions are analyzed under FTIR. Figure 3 shows FTIR Pattern of TiO₂ in broad band at $3600 - 3200 \text{ cm}^{-1}$ which correspond to hydroxyl stretching, this could be due to adsorbed water molecules and broad band at $600 - 400 \text{ cm}^{-1}$ corresponds to metal – oxide stretching which confirms the metal oxide formation. Silver used in the doped TiO₂ catalyst did not result in any significant change in the FTIR spectrum. The observations obtained are in good agreement with respect to the literature [27]

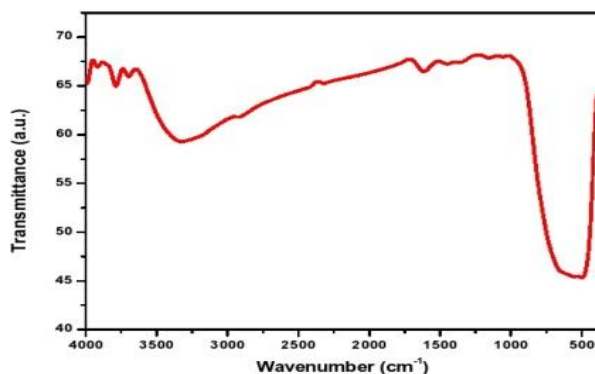


Figure 3. FTIR Pattern shows Formation of metal oxide bond.

3.3 Studies on Dopant concentration

The studies on amount of dopant for the photocatalytic Congo red dye degradation using Ag doped TiO_2 photocatalyst were investigated. Ag is introduced into the parent TiO_2 in the ratios 0.05, 0.1, 0.2, 0.5 wt% respectively to analyze the optimum dopant concentration for the dye degradation process. Following experimental conditions were used: 10 ppm of 100ml initial dye, degradation time of 90 minutes. Catalyst loading of 10 mg. Figure 4 represents the effect of dopant concentration on degradation of Congo red dye analysed by varying the amount of dopant concentration. The dopant concentration of 0.1 wt% gave 100% degradation in 80 minutes; more than 90% of degradation was obtained in 1 hour. The dopant concentration of 0.2wt% gave 94 % of degradation in 80 minutes where as the catalyst without dopant gave only 59% degradation in 80 minutes. 0.1 wt % showed highest degradation than 0.2 wt %. 0.5 wt% showed relatively less degradation in comparison to 0.1wt% and 0.2 wt%. 0.05 Wt% showed much lesser degradation and 0 wt% or no dopant gave the least degradation. 0.1 wt% of Ag added to TiO_2 gave the best degradation hence the photocatalytic Congo red dye degradation is done employing 0.1wt% of Ag doped to TiO_2 nano particles.

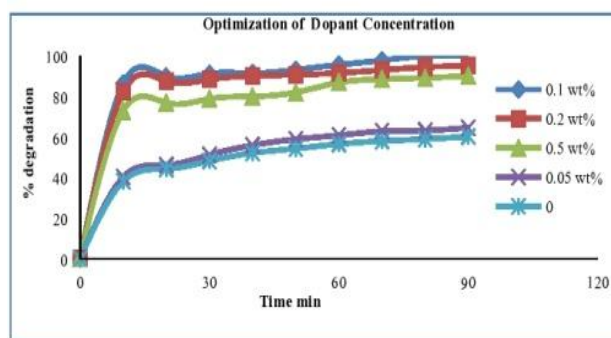


Figure 4. Effect of dopant concentration on the dye degradation (10 mg of catalyst, initial dye concentration 10ppm).

The noble metal silver facilitates the movement of electrons away from the surface of TiO_2 thus preventing the electrons and holes recombination and also increasing the activity of the photocatalyst in the visible range. Further the presence of silver has the ability to trap electrons resulting in most effective transfer of electrons to the donors and electrons acceptors adsorbed on top of the catalyst surface. Superoxide anion and hydroxyl radicals are originated by reduction of oxygen by electrons and oxidation of hydroxide ions by the holes respectively. These intermediates play a significant role in the dye degradation thus addition of silver increases the activity of the photocatalytic process [25, 6, 7, 10]. The reduction in the activity of photocatalysis with increase in the amount of dopant beyond 0.1 wt % can be due to the fact that the metal deposits might cover

the TiO_2 hindering the light penetration thus decreasing the number of electrons and holes production and excess metal deposit might occupy the active sites of TiO_2 reducing its activity [6]

3.4 The effect of pH on the degradation of dye (Congo red dye)

The effect of pH on the photocatalytic Congo red degradation using sunlight irradiation in batch reactor using Ag doped TiO_2 nanoparticles was investigated. The 100 ml of 10 ppm initial dye concentration, reaction time of 3 hour and 10 mg of catalyst was used. Figure 5 represents the effect of pH on Congo red degradation. In the presence of hydrochloric acid at pH 3, highest degradation is observed in very short span of time. At neutral pH, that is, without presence of any external agents, complete degradation is observed in 4 hours. At higher pH, the degradation of Congo red is not appreciable; In fact, it is very low compared to neutral pH. pH 3 is found to be optimum, where complete degradation is taking place in short time. Thus the Congo red dye degradation rate is enhanced with decrease in pH.

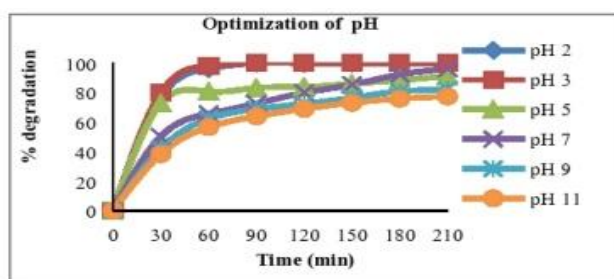


Figure 5. Effect of pH on Congo red dye degradation (10 mg of Ag doped catalyst, 10ppm initial dye concentration).

The influence of pH on the photocatalytic dye degradation is well understood by the concept point of zero charge (pzc). For TiO_2 6.2 is found to be pzc. In the media with pH less than 6.2 the TiO_2 surface becomes positively charged and in the solution with pH more than 6.2 it is negatively charged. The good degradation under low pH is because of the electrostatic attraction of the catalyst present in acidic reaction mixture which increases photocatalytic degradation process whereas the negatively charged TiO_2 surface and the negatively charged molecules of dye in the higher pH solution are subjected to columbic repulsion which hinders the photocatalytic activity. The other reason for very good photocatalytic activity at pH3 may be due to the fact that acidic media facilitates the production of active species i.e hydroxyl radicals in the presence of light unlike alkaline media in which such radical species are scavenged reducing the activity of the photocatalyst [28].

3.5 The studies on catalyst loading on Congo red dye degradation

The efficacy of Ag doped TiO_2 was investigated for the dye (Congo red) degradation employing sunlight irradiation in batch reactor. Effect of catalyst loading was investigated using 100 mg/L of initial dye concentration, pH maintained at 3, irradiation time of 3 hour. Catalyst loading was varied from 10 mg to 250 mg. Figure 6 present the effect of photo catalyst loading on degradation of Congo red dye. Degradation rate tend to escalate with the increase in amount of catalyst. With 100 mg and 200 mg of catalyst around 100% degradation occurred in 3 hour; with 100 mg of catalyst 95% degradation occurred in 2.5 hour. When the catalyst loading was further increased to 200 mg almost 100% degradation occurred in 3 hours almost similar degradation pattern is observed with that of 100 mg of catalyst whereas further increase in the catalyst dosage resulted in decrease of the photocatalytic activity showing 92% degradation in 3 hours comparatively lesser than that of 100 mg of catalyst. So 100 mg catalyst in 100 ml is found to be optimum catalyst loading for 100 mg/100mL dye thus the optimum dye to catalyst ratio is 1:1 for Congo red dye under sunlight light irradiation. The decolourisation of the photocatalytic process with progress of time is as shown in Figure 7. It is

observed that the increase in photocatalyst loading leads to availability of more number of catalytic sites for adsorption further increase in the dosage results in saturation and very high dosage results in increased turbidity of the suspension hindering the light penetration due to shielding effect thus reducing the efficiency of the process. Also high loading of TiO_2 might form agglomerated particles with small active surface which results in decreased catalytic activity [6, 28]

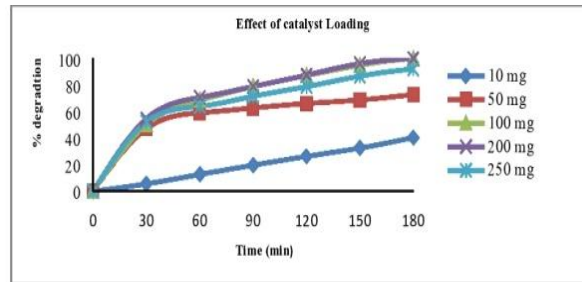


Figure 6. Effect of catalyst loading on the dye degradation (pH 3, Ag doped TiO_2 catalyst, initial dye concentration 100ppm).

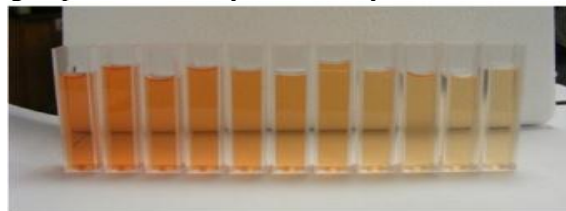


Figure 7. Congo red dye samples at regular intervals of time as it undergoes advanced oxidation

3.6 Effect of initial concentration of dye on Congo red degradation

The effect of the parameter initial dye concentration was investigated using 100 mg of catalyst, pH was maintained at 3, irradiation time of 3 hours, Figure 8 represent the effect of initial concentration on the degradation of the dye. The photocatalytic degradation gradually declined as the initial dye concentration was increased. Approximately 100% dye degradation of 50 ppm dye was observed in 2 hours. But it took 3 hours with 100ppm dye. Only 51% dye was degraded in 4 hours with 300 ppm dye solution. The rate of photocatalysis decreased as the dye concentration increased because the number of dye molecules tend to increase with increase in dye concentration, with fixed count of active sites on the catalyst the dye molecules has to compete for the active sites thus reducing the degradation rate. High initial concentration of dye also hinders light penetration along the radial direction in the reactor, hence lowering the rate of degradation.

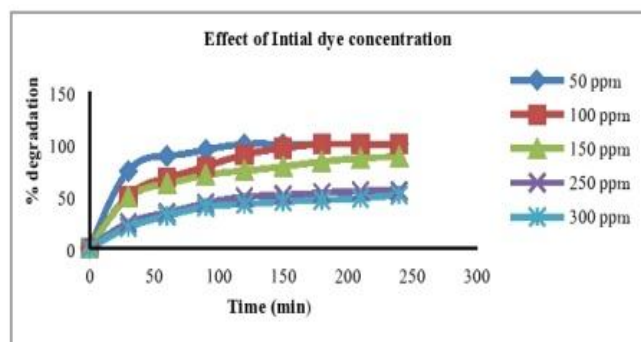


Figure 8. Effect of initial dye concentration on Congo Red dye degradation (pH 3, 100 mg/100ml of Ag doped TiO_2 catalyst).

The results obtained shows that the dye degradation process decreased concentration of dye increased for the specific amount of catalyst used. The increase in dye concentration hinders the light penetration which further affects the formation of hydroxyl and superoxide radicals thus reducing the degradation process. [25, 28]

3.7 Chemical Kinetics

The relation between dye degradation reaction rate and the dye concentration in the presence of irradiation is well described by kinetic model proposed by Langmuir Hinshelwood.

$$\text{Rate}(\text{ppm} / \text{min}) = -\frac{dC_o}{dt} = \frac{kKC_o}{1 + KC_o} \quad (3)$$

KC_o in the above expression (3) is neglected as the value of KC_o is very small. Integrating the equation with respect to time yields pseudo first order kinetic equation

$$\ln [C_o/C] = kK * t = k_{app} * t \quad (4)$$

in the above equations (4) C_o represents initial dye concentration (ppm), The dye concentration at specific time is represented by $C(\text{ppm})$, t being the reaction time, k is the rate constant of the reaction (min^{-1}) and K represents the adsorption co efficient of reactant molecules on the surface of the photocatalyst(l/mg). [16, 25].

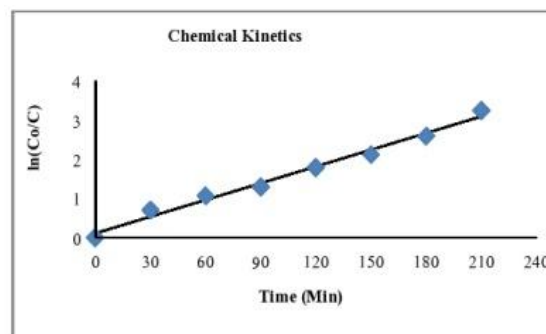


Figure 9. Kinetic curves showing Pseudo First order kinetics.

The kinetic data obtained on the Congo red dye degradation with Ag^+ doped TiO_2 is observed to follow pseudo first order kinetics and confirmed by the linear transform,

($\ln(C_o/C) = k_{app} * t$) (5) [29, 30] as shown in Figure 9. The rate constants at maximum wave length= 590 nm (for Congo red) are found to be $k_{app}=0.014 \text{ min}^{-1}$, $R^2=0.98$. The linear regression value is found to be higher than 0.9 emphasizing the fact that the model is in agreement with the experimental data.

3.8 Reusability

At the end of each trial for an optimized time of 4 hours, the degradation observed during the reuse of catalyst is shown in Table 2.

Table 2. Reuse of Photo catalyst for different trials of 100ppm Congo red dye degradation.

Trials	% degradation
First Trial	98%
Second Trial	94%
Third Trial	88%

The number of times the photo catalyst could be reused was investigated to analyze the economic feasibility of the photocatalytic degradation process. The catalyst already used once could be used again with 94% efficacy. The regeneration process is carried out using a simple process in which the

catalyst was allowed to settle down in degraded dye solution for 12 hours followed by decantation of the supernatant. The photo catalyst was subjected to washing using distilled water followed by drying and the catalyst thus regenerated was used for further application in dye degradation process with fresh dye solution [20]. The catalyst can be reused for the third time with 88% efficiency. There is reduction in the photocatalysis when reused catalyst is used which is due to the conversion of Ag^+ ions to Ag^0 during the process and also complete regeneration is not possible due to the agglomeration of catalyst with the degraded dye. This factor gives the maximum number of times the photo catalyst can be used for the degradation process for best cost effective degradation.

4. Conclusions

The photocatalysis process using Ag doped TiO_2 catalyst is found to be very effective and economical technique for degradation of Congo red dye. The Ag doped TiO_2 nanoparticles synthesized was subjected to characterization using SEM, XRD and FTIR. The SEM images showed the spherical catalyst with doping of Ag on the surface of TiO_2 . The presence of silver and anatase phase of TiO_2 was confirmed from XRD analysis. The FTIR analysis confirmed the formation of metal-oxide. The catalyst doping of the catalyst with silver metal enabled the catalyst to show high efficacy under sunlight. The optimum amount of dopant used in efficient Congo red dye degradation process was found to be 0.1 wt% of Ag. The optimum amount of catalyst essential for the effective dye degradation of 100 ppm Congo red dye using photo catalytic degradation process was found to be 100 mg/100 mL of catalyst. The degradation is highly effective under acidic conditions. The kinetic study of the degradation process with Ag^+ doped TiO_2 is observed to follow pseudo first order kinetics. Regeneration and reuse of catalyst is performed and found that the catalyst can be reused for 3 times with negligible change in photocatalytic activity, thus the Ag doped TiO_2 nanoparticles is found to be cost effective and highly efficient photocatalyst.

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