Photocatalytic decolourization of basic green dye by pure and Fe, Co doped TiO$_2$ under daylight illumination

R. Lakshmi Narayana$^a$, Manickam Matheswaran$^a$, Azrina Abd Aziz$^b$, Pichiah Saravanan$^{b,*}$

$^a$ Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli-620015, Tamilnadu, India
$^b$ Water Research Center, Department of Civil Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

Abstract

In the present study, a pure TiO$_2$ photocatalyst, Fe and Co doped photocatalyst was prepared via sol-gel method. The prepared photocatalysts were tested for its photocatalytic activity by decolorizing a basic dye namely malachite green dye under sunlight. The prepared photocatalysts were characterized with X-ray diffraction, scanning electron microscope and UV-Visible spectroscopy. From the decolorizing study, it was observed that Fe-doped TiO$_2$ shown highest photocatalytic activity among the other two with 98% in 3 h. The Kinetics of dye decolorization was rationalized by a modified Langmuir–Hinshelwood model. The overall rate constants ($k'$) for dye decolorization was observed in the order of 0.8 h$^{-1}$ for Fe-doped 0.67 h$^{-1}$ for Co-doped and 0.31 h$^{-1}$ for pure TiO$_2$.

1. Introduction

In recent years advanced oxidation processes (AOPs) have been developed to meet the increasing need of an effective wastewater treatment. Among advanced oxidation processes (AOPs), photocatalysis is the prominent method. In this process a photocatalyst generates powerful oxidizing hydroxyl radicals which completely destroy the pollutants in waste water. The semiconductor photocatalyst TiO$_2$ has a wide band gap i.e., 3.2 eV and hence successfully used as a photocatalyst for the treatment of organic and dye pollutants [1–4]. The photo bleaching of some dyes could be achieved by solar light irradiation using TiO$_2$ as a photocatalyst [5]. A good potential exists for the use of highly concentrated sunlight in order to overcome such limitation. Doping TiO$_2$ with metals ions like Fe, Sb, Co, etc., can extends the absorption spectrum to infrared radiation i.e., to visible light spectrum (400 nm -800 nm), where the day light source is limited [9]. Similarly Cobalt (Co) also seems to improve photodegradation slightly or selectively for some organic compounds as found by Di Paola et al., 2002[13] Amadelli et al., 2008 also studied the photodegradation of 4-chlorophenol and Bisphenol A to assess the photocatalytic activity of the Co-TiO$_2$ and TiO$_2$ and show that the activity of the former is higher, both under UV and visible light irradiation, depending on the degree of doping [10].

Hence in the present study of pure, Fe and Co- doped photocatalyst was prepared and studied for its photocatalytic activity. The prepared doped photocatalysts physical characteristics were examined and finally photo catalytic activity was evaluated and compared with pure TiO$_2$ by adopting malachite green dye as model pollutant under daylight illumination.

2. Materials and Methods

2.1. Chemicals

Malachite green dye C.I basic green 4 (C$_{23}$H$_{25}$ClN$_{2}$, Purity is ≥96.0%) , precursors for preparation of doped TiO$_2$ and pure TiO$_2$
2.2. Preparation of doped and pure TiO2 catalyst

Doped and pure TiO2 samples were prepared by a simplest sol-gel technique. 40 mL ethanol and 10 mL butyl tetratitanate were mixed as precursor in the process of TiO2 formation. 25 mL glacial acetic acid was introduced to perform acetate reaction at room temperature with constant stirring in air, the process was exothermic. Subsequently, 60 mL solution containing Fe(NO3)3·9H2O, according to the required iron dopant amount 0.05%, (mass fraction), was slowly dropped into the mixture with constant stirring. After half an hour, 0.07 g PEG-4000 was added to the above solution. Afterward, 1.2 mL of 96% concentrated nitric acid as hydrolysis catalyst was added to the solution to control pH at 1.0, at this time the mixture was transparent. The mixture was oscillated by supersonic wave at 40 °C for 15 min, where the transparent mixture was formed. The gel was frozen and dried at 50 °C for 2 h and the xerogel was obtained from Merck Germany and SD Fine-Chemicals, India and used with out further modification.

2.3. Experimental setup

Photo catalytic experiments with the prepared catalyst were carried out in a batch reactor (Glass beaker) of 1 L capacity with a working volume of 500 mL. The reactor is a simple glass beaker, operated with continuous stirring using a magnetic stirrer in presence of daylight as a light source. The experiments were carried until completion decolourization was achieved in good sunny day with a maximum temperature of 37 °C. The experiments were carried until completed decolourization was achieved in good sunny day with a maximum temperature of 37 °C (between 10:00 AM to 1:00 PM). The intensity of sunlight was in the range between 32,000–130,000 lux. Two different metal ion doped TiO2 catalysts were used to assess the performance. The catalyst loading was varied from 0.05 g to 1 g/500 mL with an initial dye concentration of 100 mg/L. The dye solution had an initial pH of the pure TiO2 consists of a mixture of anatase and rutile phases in the weight ratio of 80:20; while the pure TiO2 nanoparticles displayed almost the anatase crystal phase only.

2.4. Analytical Methods

2.4.1. X-ray diffraction studies

The XRD spectra were obtained with Rigaku Ultima III. From the obtained XRD peaks the crystallite size of the catalysts was determined by applying Scherrer’s formula (14). The formula is given below:

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

Where D = Crystalline size (nm); \( \lambda \) = X-ray wavelength (1.5406 A°); \( \theta \) = Contour peak angle (radian) and \( \beta \) = Width of the obtained peak (radian).

2.4.2. SEM Analysis

Morphology of the prepared photocatalysts was examined by SEM, samples was dried and coated with gold film in a sputter coater, and finally, the morphology was recorded in LEO 1430VP SEM instrument at a magnification of 4350 at 15 KV.

2.4.3. UV-Visible Spectrophotometer

The prepared catalyst is dissolved in distilled water and analyzed for UV-Visible absorbance spectrum on a Jasco V-570 UV-Visible spectrophotometer (USA) with a quartz cell (10 mm path length), and their spectral properties were examined. The dye samples were collected at a regular interval, filtered (Whatman No.1) and the residual malachite green dye concentration was determined spectrophotometrically by monitoring absorbance at \( \lambda_{max} \) of 613 nm.

3. Results and Discussion

3.1. XRD analysis

Fig. 1 shows the reliance of the phase transformation of pure and Fe and Co doped TiO2 calcined at 500 °C. The transition from amorphous state to anatase is observed for pure TiO2 from Fe and Co doped TiO2. It is evident that the phase transition from anatase to rutile is caused by structural iron and cobalt doping, the substitution of titanium ions by iron and cobalt ions in the titanium dioxide structural framework. From the obtained peak the average nanocrystallite size was measured according to Debye-Sherrer formula as given in Eq. (1). In comparison with the pure TiO2 (control Sample) the doped showed a better size i.e., in the order of 12.6 nm for Fe–TiO2, 12.8 nm for Co-doped TiO2 and 17 nm for the pure TiO2. Qing et al., 2003 prepared Fe doped TiO2 via sol-gel method and obtained a catalyst with particle size of 63.5 nm [8]. Similarly Chen et al., 2008 prepared Fe doped TiO2 via sol-gel method and obtained a catalyst with particle size of 25.47 nm [9]. Though they obtained a particle size less than that of pure TiO2, their doped catalyst showed a larger particle size than the present study. The pure TiO2 consists of a mixture of anatase and rutile phases in the weight ratio of 80:20; while the doped TiO2 nanoparticles displayed almost the anatase crystal phase only, which is generally considered more photo reactive. The presence of Fe and Co is also in the TiO2 framework is also confirmed from the obtained pattern. Moreover the XRD spectra of samples with Fe and Co doped showed peaks due to anatase and rutile, which is expected. Since the pure TiO2 used is well known to be a mixture of the two polymorphs. There is an evident change in neither anatase/rutile phase distribution due to Fe and Co doping, which results in obtaining very good band gap to utilize the visible light.

Please cite this article as: R.L. Narayana, et al., Photocatalytic decolourization of basic green dye by pure and Fe, Co doped TiO2 under daylight illumination, Desalination (2010), doi:10.1016/j.desal.2010.11.007
3.2. SEM Micrographs

Fig. 2 shows the SEM pictures of the prepared catalyst along with the pure one. From the figure it is evident that the growth of particle is restrained by Fe and Co-doping. This is of significantly important not only for the design of surface properties and surface area, but also for tuning the electronic structure i.e., to make the visible light spectrum more active for the better photocatalytic activity.

3.3. UV - Visible Spectrometer Analysis

The UV-Vis absorption spectra pattern of pure, Fe doped and Co doped TiO₂ absorption spectrum was shown in the Fig. 3. The spectrum was obtained by scanning in the range of 300 - 800 nm. The absorption edge of Fe-doped TiO₂ has a red shift and the sample also has a stronger absorption than the pure TiO₂ in the visible region. Since Fe doped TiO₂ can absorb light in a wider range of wavelength and utilize more light energy than pure TiO₂, a higher photo catalytic activity should be expected for Fe-doped TiO₂ than the Co doped.

3.4. Photo decolorization studies in presence of day light source

Fig. 4 illustrates the effect of percentage decolorization of malachite green dye at two different amount of catalyst loading of Fe-doped TiO₂. The colour removal percentage is higher (98%) for catalyst dosage of 0.1 g than 0.05 g catalyst loading (64%). Similar observation was reported by Qing et al., 2004, where Fe-doped TiO₂ showed higher photocatalytic efficiency than the pure TiO₂ in the treatment of paper mill wastewater [9]. Fig. 5 illustrates the effect of percentage decolorization of malachite green dye at two different catalyst dosage of Co-doped TiO₂. A maximum degradation of 86% was achieved at higher for catalyst dosage of 0.1 g, while 0.05 g loading results in 53%. Though Co doped the photocatalyst showed a comparably lower photo activity than the Fe doped catalyst, they both exhibited an excellent performance in removal of malachite green dye than the pure one with better utilization of visible light. In all cases the solution pH after decolorization was in the range of between 7.3 – 7.5.

It is widely reported in the literature that anatase and rutile pair (pair of polymorphs) can effectively reduce the recombination of photogenerated charge carriers to enhance the photocatalytic activity [15]. The band gap in the rutile phase is responsible for visible light excitation. In the present study the decolorization experiment with Fe doped catalyst showed a good prospective, which indicates that the rutile phase, had a very good band gap. Such similar effect was also observed in Co doped catalyst also. Where else in the pure catalyst the anatase phase plays a major role in decolorization, hence poor decolorization efficiency was achieved. It was reported that the conduction band edge of rutile usually lies below 0.2 eV compared to the conduction band edge of anatase. Due to this the photogenerated electron from conduction band of rutile gets transferred to trapping sites of anatase phase in presence of sunlight. Such effect could be considered as antenna effect by rutile phase. Subsequent transfer of electrons to

![Fig. 2. SEM Micrographs (A) control TiO₂, (B) Fe-doped TiO₂ and (C) Co-doped TiO₂.](image)

![Fig. 3. UV-Vis absorption spectra pattern of prepared photo catalyst.](image)

![Fig. 4. Effect of Fe-TiO₂ on dye degradation under day light (Initial concentration of Malachite green dye = 100 mg/L).](image)

Please cite this article as: R.L. Narayana, et al., Photocatalytic decolourization of basic green dye by pure and Fe, Co doped TiO₂ under daylight illumination, Desalination (2010), doi:10.1016/j.desal.2010.11.007
3.5. Kinetics of decolourisation

The kinetics of malachite green dye decolourisation was also studied and its fit is illustrated in Fig. 6 by plotting the logarithm of the normalized dye concentration against irradiation time. An almost good linear relationship with the correlation coefficient R2>0.98 was observed, indicating that the decolourization reactions followed the first-order kinetics. A modified Langmuir–Hinshelwood (L–H) was adopted to rationalize the dye degradation kinetics [18]. The equation is given below:

\[
\frac{dC}{dt} = k_r K_e C \left(1 + K_e C\right)
\]

Where C being the dye concentration, kr the apparent reaction rate constant, and Ke the apparent equilibrium constant for the adsorption of the dye on the catalyst surface. The integrated form of Eq. (2) is given in below

\[
t = \frac{1}{K_r K_e} \ln \left(\frac{C_0}{C}\right) + \frac{1}{k_r} (C_0 - C)
\]

The above equation could be also expressed as follow:

\[
\ln \left(\frac{C_0}{C}\right) = k_r K_e t = k t
\]

provided when the concentration of the dye is sufficiently low (in present work the concentration is low when compared to the dying wastewater). It was observed by solving the above equation graphically the overall rate constants (k) for dye degradation are in the following order: Fe-doped (0.8 h⁻¹), Co-doped (0.67 h⁻¹) and pure TiO₂ (0.31 h⁻¹). The obtained kinetic parameter clearly indicates the photo catalytic activity of doped TiO₂ in presence of the day light. Fe-doped TiO₂ had faster dye degradation of 2.5 times than the pure one.

4. Conclusions

The photo decolourization effect of Fe and Co-doped photocatalyst on a dye was studied in comparison with the pure TiO₂. The Fe-doped showed a photocatalyst showed an excellent performance in degrading malachite green dye under daylight over the Co-doped photocatalyst. The reaction kinetics followed an apparent first-order reaction and was rationalized by a Langmuir–Hinshelwood type mechanism. The prepared doped photocatalyst also showed it superiority in the grain size too. Overall, doped TiO₂ photocatalysts revealed its potential for rapid degradation of recalcitrant compounds, such as malachite green dye, in wastewater using visible light.

Acknowledgement

The corresponding author is grateful to University of Malaya Research Grand (RG091/10US) for their financial support.

References


Please cite this article as: R.L. Narayana, et al., Photocatalytic decolourization of basic green dye by pure and Fe, Co doped TiO$_2$ under daylight illumination, Desalination (2010), doi:10.1016/j.desal.2010.11.007