Trends in Photochemistry & Photobiology
Vol. 14, 2012

Original Communication

Removal of indigo carmine by immobilized TiO_2 heterogeneous photocatalytic oxidation in a batch photoreactor

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ABSTRACT

Aqueous solutions of indigo carmine, a hazardous dye, are photodegraded under ultraviolet light using TiO_2 coated non-woven fibres as photocatalyst. The process has been carried out at different pH values, concentrations of the dye, and effects of the electron acceptor H_2O_2. It is found that the photocatalytic degradation process follows first-order reaction kinetics. In addition, the degradation efficiency (%) increased with decrease in pH, which implies that the pH is a very important parameter in dye adsorption. In order to evaluate the effect of the electron acceptor, the effect of H_2O_2 on the oxidation process is also monitored and it is found that generation of hydroxyl radicals and retardation of electron-hole recombination takes place. The used immobilized TiO_2 photocatalyst can be recovered and reused with no decline in the photodegradation efficiency. It was observed that photocatalytic oxidation by TiO_2 is an economic and faster mode of removing indigo carmine from aqueous solution.

KEYWORDS: titanium dioxide, immobilization, dye, photocatalytic oxidation

1. INTRODUCTION

Wastewater containing the dyes is usually toxic, resistant to biodegradation, persistent in the environment, and difficult to be treated by general methods. Applications of semiconducting catalysts for environmental protection and remediation have attracted much attention in recent years. Heterogeneous photocatalysis using semiconducting materials is efficient and broadly used for environmental applications such as air purification, water disinfection, hazardous water remediation, and water purification [1-3]. Amongst the various semiconductor photocatalysts, TiO_2 has been considered as one of the most promising photocatalysts due to its stability, non-toxicity, low cost, and high efficiency in the photocatalysis process [4]. However, a disadvantage of the use of TiO_2 powder form as a photocatalyst in large scale processes is the difficulty in separating it from reaction systems, which precludes the recovery and reuse of the catalyst [5]. In order to avoid the use of TiO_2 powder, which entails later separation from the water, various researchers began to work on ways of immobilizing TiO_2 particles, for example in thin film form [6].

In our work, we reported the TiO_2 coated non-woven fibres as photocatalyst and their photocatalytic activity in the degradation of indigo carmine which is an anionic dye usually used in the textile, food, and cosmetics industries. Indigo carmine is regarded as a highly toxic dye that may lead to tumours at the site of application, cause skin or eye irritation, and permanent injury to cornea and conjunctiva, and can be fatal if consumed [7-9].

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The degradation of indigo carmine dye was investigated by using photocatalyst TiO_2 coated non-woven fibres. All experiments were done in order to assess the kinetics of degradation of the dye. The effect of various parameters such as pH of dye solution, initial concentration and addition of oxidant H_2O_2 were carried out. The possibility of recycling the photocatalyst was also evaluated.

2. MATERIALS AND METHODS

2.1. Materials

The immobilized photocatalyst used in this study consists in PC500 titania by Millennium inorganic chemicals (anatase: > 99%, specific surface area 350-400 m^2/g, crystallites mean size = 5-10 nm). Titania PC500 was coated on non-woven fibres (natural and synthetic fibres 254 µm of thickness) using an inorganic binder. The binder was an aqueous dispersion of colloidal SiO_2. A specific surface area extender (zeolite, 2000 m^2/g) was used to increase adsorption properties of the photocatalyst.

Indigo carmine ($C_{16}H_8N_2Na_2O_8S_2$, MW = 466.35 g/mol) was purchased from Labosi (colour index No. 73015) and used as received without further purification. Solutions were prepared by dissolving requisite quantity of the dye in distilled water. The pH was adjusted to a given value in the range 3-10 by addition of HCl (1N) or NaOH (1N) and was measured using a Schott titroline pH-meter. The H_2O_2 solution (30%) was obtained from Merck.

2.2. Photocatalytic reactor

Photocatalytic experiments were carried out in a cylindrical batch reactor of 500 ml in volume, 8 cm in diameter and 12 cm in working height. The water jacket has a diameter of 5 cm, contains a UV lamp, and permits water circulation (Fig. 1). The photocatalytic reactor was covered inside with (11 cm x 25 cm) of the photocatalyst and was exposed to a luminous source (an HPK 125W Philips ultraviolet lamp with a wavelength maximum of 365 nm), placed in axial position inside the water jacket. The reactor was stirred continuously at a low setting, 100 rpm, by a magnetic stirrer.

2.3. Analysis

Indigo carmine was analyzed on a UV-VIS spectrophotometer (Techcomp 2300 series).

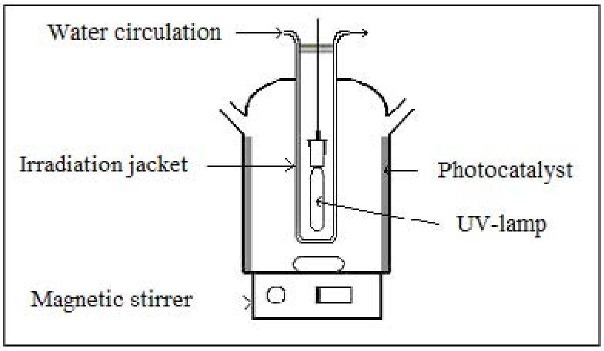

Fig. 1. Schematic diagram of the photoreactor.

The wavelength of the maximum of absorption (λ_{max}) was 610 nm. The dye aqueous solutions were filtered by Millipore membrane filter type 0.45 µm and the determined absorption was converted to a concentration through the standard-curve method of dye.

3. RESULTS AND DISCUSSION

3.1. Effect of substrate concentration

The effect of indigo carmine concentrations has been investigated at 4 mg/l, 8 mg/l, 12 mg/l, 16 mg/l and 20 mg/l. The experimental data could be analyzed to assume-first order kinetic (for the first few minutes of irradiation) as shown in Fig. 2.

It was found that on increasing the dye concentration the degradation efficiencies of dye decreases. Hence, the photooxidation process will work faster at a low concentration of pollutants. These results are in agreement with previous reports [10-12] that photodegradation of textile dye decreased with increasing concentrations.

At high concentrations of dye, the deeper coloured solution would be less transparent to UV light and the dye molecules may absorb a significant amount of UV light causing less light to reach the photocatalyst and thus reducing the OH° radical formation. Since an increasing in the initial concentration caused to increased in the adsorption of indigo carmine molecules on the surface of the catalyst, which lead to reduce in the OH° radical generation, because very low active site available as free on the surface of catalyst.

On the other hand, considering Beer Lambert law, as the initial dye concentration increases, the path

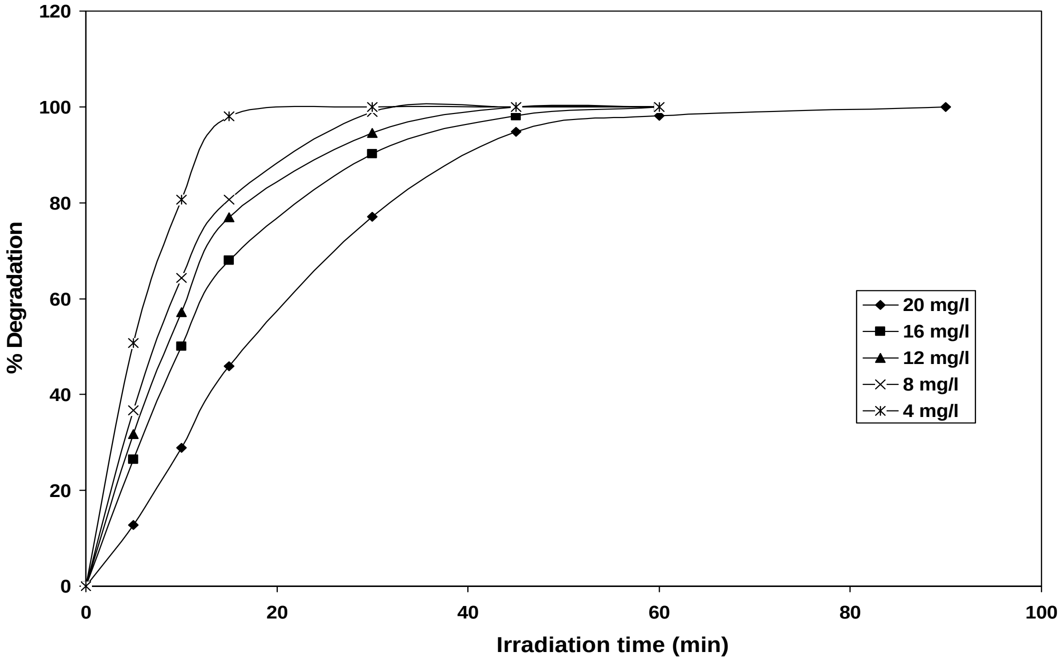

Fig. 2. Effect of the initial indigo carmine concentration on photodegradation efficiency.

length of photons entering the solution decreases, which result in lower photons absorption on catalyst particle, and consequently lower photocatalytic reaction rates [13].

3.2. Effect of pH

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and the size of aggregates it forms.

The decomposition of indigo carmine was studied in the pH range between 3 and 10 (Fig. 3). This figure shows that the efficiency of the photocatalytic processes strongly depends on the pH of the reaction solution. The efficiency decreasing as the pH values increased in the order: (pH) 3 > 4 > 7 > 8 > 10.

Generally, for a charged surface containing TiO_2 particles, a significant dependence of the photocatalytic efficiency on the pH value is observed, since the overall surface charge and hence the adsorptive properties of TiO_2 particles depend strongly on the solution pH [14, 15]. It is known that the metal oxide particles in water exhibit amphoteric behaviour and readily reacts with dye by a mechanism which can be described by the following equations:

$$TiOH + H^+ \longrightarrow TiOH_2^+ \quad (1)$$

$$TiOH + OH^- \longrightarrow TiO^- + H_2O \quad (2)$$

The charge of TiO_2 depends on the solution pH. The pH at the point of zero charge (pH_{PZC}) for TiO_2 has been reported to be in the range 6.25-6.90 [1]. Thus, the TiO_2 surface is positively charged in acidic media ($pH < pH_{PZC}$), and negatively charged under alkaline conditions ($pH > pH_{PZC}$).

It was observed that increasing pH of the solution resulted in decreasing of the photocatalytic degradation efficiency of indigo carmine. Since the dye has sulfonate groups in its structure, which are negatively charged, the acidic solution favours adsorption of the dye onto TiO_2 surface. Thus, degradation efficiency increased. It is expected that at a pH below pH_{PZC}, the surface of photocatalyst acquires a positive charge, indicated by (1), and hence attracts the negatively charged indigo carmine dye skeleton resulting in a large number of dye molecules being attracted (or adsorbed) onto the sheet surface. As the dye concentration at the surface increases the photodegradation activity also increases, as

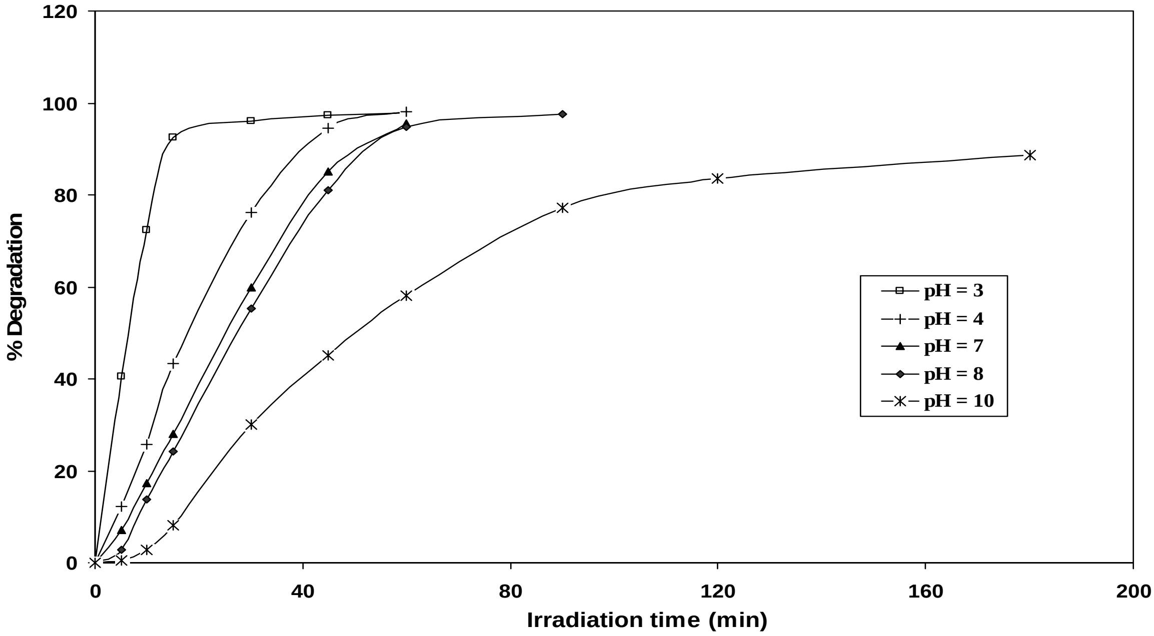

Fig. 3. Effect of pH on the photodegradation efficiency of indigo carmine dye.

observed at pH 3. At a pH above pH_{PZC}, electrostatic repulsion between the negative charge at the surface of photocatalyst, as shown in (2), and anionic dye skeleton retards the accumulation of dye molecules at the surface resulting in decrease of the photodegradation activity. For basic pH, the small of degradation efficiency could be attributed to a slight increase in OH° radicals whose formation is favoured by the presence of hydroxyl ions OH^-.

3.3. Effect of addition of H_2O_2

The addition of an oxidant into a semiconductor has been proven to enhance the photodegradation rate of a variety of organic pollutants [16-18]. In our study the addition of hydrogen peroxide (H_2O_2) was evaluated. The result as shown in Fig. 4, indicate that the hydrogen peroxide had accelerated the photocatalytic degradation rate (r_o) of indigo carmine. The photocatalytic oxidation of indigo carmine increased when hydrogen peroxide concentration increased from 0 to 5 $.10^{-4}$ mol/l. This could be due to the increase in the OH°, where working to prevent electron-hole recombination, as in following equations.

$$H_2O_2 + e^- \longrightarrow OH^- + OH° \quad (3)$$

$$H_2O_2 + O_2 \longrightarrow OH^- + OH° + O_2 \quad (4)$$

Moreover increasing of hydrogen peroxide concentration more than 5.10^{-4} mol/l decreased the rate of photocatalytic degradation that could be due to by scavenging effect.

$$H_2O_2 + OH° \longrightarrow H_2O + HO_2° \quad (5)$$

$$HO_2° + OH° \longrightarrow H_2O + O_2 \quad (6)$$

The rate of photocatalytic degradation was decreased at higher concentration of H_2O_2, this negative effect of H_2O_2 at higher concentration may occur due to inhibition of OH°, because at high concentration of H_2O_2, the amount of OH° formed on the surface was increased quickly and hence the annihilation OH° + OH° → H_2O_2 rate which consider faster than the degradation rate of indigo carmine.

Therefore an optimal concentration must be designated in order to achieve the best results. According to previous authors this concentration depends on the H_2O_2/contaminanat molar ratio [19, 20].

3.4. Photocatalyst reuse

The possibility of catalyst recovery and reuse in photocatalytic processes has received considerable attention since it can contribute significantly to

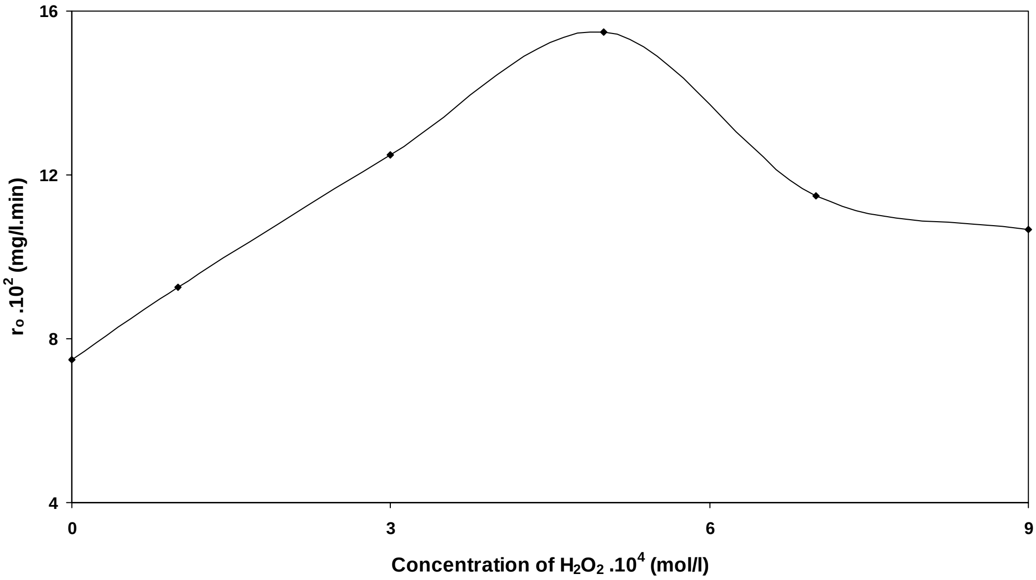

Fig. 4. Evaluation of photocatalytic degradation rate according to different H_2O_2 concentrations.

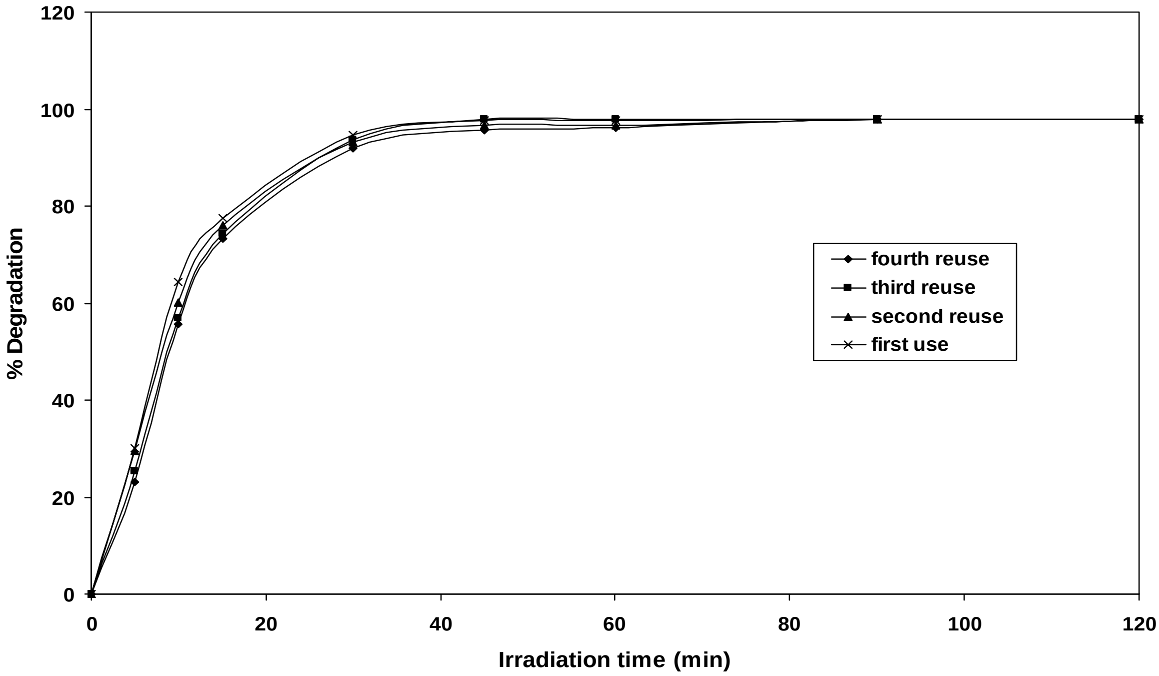

Fig. 5. Effect of reused photocatalyst on the degradation of indigo carmine.

lowering the operational cost of the process, which is an important parameter in the applicability of photocatalysis as a method for wastewater purification [14, 21]. In order to evaluate reused photocatalyst efficiency, a series of experiments were performed (used for 4 times). The used catalyst was washed with distilled water three times and dried at room temperature during 24 h. All of the studies of indigo carmine degradation were performed using the same photoreactor and UV source. As can be seen from Fig. 5, the used catalyst showed no loss in activity.

CONCLUSIONS

The conclusions drawn from this study can be summarized as follows:

- The degradation efficiency (%) of indigo carmine by using TiO_2 photocatalyst depends strongly on concentration of this dye.
- The photocatalytic disappearance of indigo carmine by UV-irradiated TiO_2 found follow first order kinetics.
- The pH influences both the photocatalyst surface and dye chemical structure.
- In an acidic environment, the dye is degraded faster than in basic environment.
- Addition of H_2O_2 is very important to increase the rate of photocatalytic degradation.
- The used immobilized TiO_2 did not show any loss in activity.
- Immobilization of TiO_2 is an easy method to resolve the problems of suspended photocatalyst powder such as filtration and recovery of fine particles.
- This technique, considered as an adequate process, may be valuable for the treatment of large-scale textile wastewater and reuse of treated water.

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