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ORIGINAL ARTICLE

Photocatalytic degradation of an azo reactive dye, Reactive Yellow 84, in water using an industrial titanium dioxide coated media

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Abstract The photocatalytic degradation of an azo reactive dye, Reactive Yellow 84 (RY84), in aqueous solutions using industrial titanium dioxide coated non-woven paper was studied. The experiments were carried out to investigate the factors that influence the dye photocatalytic degradation, such as adsorption, initial concentration of dye, temperature, and solution pH. The experimental results show that adsorption is an important parameter controlling the apparent kinetics constant of degradation. The photocatalytic degradation rate was favored by a high concentration of solution in respect to Langmuir–Hinshelwood model. The degradation was enhanced by the temperature and was favored in acidic pH range.

1. Introduction

Wastewater from fabric dyeing industry is a considerable source of environmental contamination. The effluent from the dyeing and finishing processes is characterized by a low biodegradability (Liakou et al., 1997). In recent years, reactive dyes have been most commonly used due to their advantages such as better dyeing processing conditions and bright colors. Moreover, the use of reactive dyes is rapidly growing due to the increased use of cellulosic fibers.

Generally reactive dyes contain functional groups such as azo, anthraquinone, phthalocyanine, formazin, and oxazine as chromophore. Among the reactive dyes, approximately 66% are azo dyes (Cooper, 1995). The reactive site of the dyes reacts with functional group on fiber under influence of heat and alkali. One of the major factors determining the release of a dye into environment is its degree of fixation on the fiber. Reactive dye is hydrolyzed to some extent during application

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processes; some of reactive dyestuff is inactivated by a competing hydrolysis reaction.

Consequently, the release of reactive dyes into dyebath effluent is exacerbated by their relatively low fixation (50–90%) to cellulosic fibers, compared with other dyes such as acid, basic, disperse and direct dye (Cooper, 1995; Reife and Freeman, 1996). Reactive dyes in dyeing wastewater have been identified as recalcitrant compounds since they contain high alkalinity, high concentration of organic materials and strong color in comparison with other dyes. Unless coloring materials are properly removed, dye wastewater significantly affects photosynthetic activity in aquatic life due to reduce light penetration (Kouba and Zhuang, 1994).

Heterogeneous photocatalysis is an efficient technique to destroy organic pollutants in water (Schiavello and M., 1987; Ollis and Al-Ekabi, 1993; Herrmann et al., 1998; Herrmann, 1999; Zhang et al., 2001; Farre et al., 1127; Pereza and Penuelab, 2006). This technique is based upon the use of UV-irradiated semiconductors (generally TiO_2 under the form of anatase). When TiO_2 is irradiated with photons whose energy is equal to or higher than its band gap energy (E_G = 3.2 eV) i.e. with λ = 390 nm, electron–hole pairs are created. In aqueous system, holes react with H_2O or OH^- adsorbed at the surface of the semiconductor to produce $OH^{\cdot}$ radicals which are the most oxidizing species in this process. On the other hand, electrons are trapped at surface sites and removed by reactions with adsorbed molecular O_2 to form superoxide anion radical $O_2^{\cdot -}$ (or $HO_2^{\cdot}$ at lower pH) (Vulliet et al., 2003).

For the degradation process two methods are favored, suspended photocatalyst in aqueous media, and immobilized on support materials. In view of practical engineering, the immobilized photocatalyst should be preferred, to avoid downstream treatment (particle–fluid separation and/or photocatalyst recycling) (Pozzo et al., 2000). This has led to a major attempt to immobilize the photocatalyst on support including ceramic (Sunada and Heller, 1998), glass fiber (Shifu, 1996), glass, quartz and stainless steel (Fernandez and Lassaletta, 1995), activated carbon (Takeda et al., 1998) and others. However, these efforts have not produced materials which meet all demands of photocatalytic activity.

In this work, the photocatalytic degradation of an azo reactive dye (Reactive Yellow 84) was investigated using a new photocatalytic material, which consists on TiO_2 supported on natural and synthetic non-woven fibers. The factors that influence the dye photocatalytic removal were carried out.

2. Materials and methods

2.1. Materials

The immobilized photocatalyst used in this study was developed by Ahlstrom firm (France). It consists a non-woven natural and synthetic fibers (254 µm of thickness) coated with a mixture of TiO_2 (PC500 by Millennium inorganic chemicals), SiO_2 (EP1069950B1 European patent) and zeolite (UOP, 2000 m^2/g). The surface load of the photocatalyst was 18 g/m^2 of PC500, 20 g/m^2 of SiO_2 and 2 g/m^2 of zeolite.

The Reactive Yellow 84 was obtained from a textile firm as a commercial available dye formulation designed as Suncion Yellow H-E4R. The chemical structure of RY84 is given in Fig. 1.

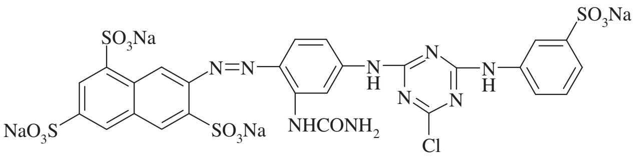

Figure 1 Chemical structure of Reactive Yellow 84.

Solutions were prepared by dissolving small quantity of the dye without further purification in distilled water. The pH was adjusted to a given value in the range 2–10 by adding of HCl (1 N) or NaOH (1 N) (analytical grades) and was measured using a Schott titroline (TE96) pH-meter.

2.2. Photocatalytic reactor

Photocatalytic experiments were carried out using a cylindrical batch reactor opened at air, 8 cm in diameter and 12 cm in working height (Fig. 2). The water jacket has a diameter of 5 cm contains the UV-lamp and permit the water circulation. The photoreactor was recovered inside with (11 × 25 cm) of the photocatalyst and was exposed to a luminous source composed of a HPK 125 W Philips UV-lamp (the wavelength maximum of the light source was 365 nm) placed in axial position inside the water jacket. The reactor was maintained in low continuous stirring (100 rpm) by means of a magnetic stirrer.

2.3. Procedure and analysis

The adsorption/photocatalytic degradation experiments were carried out by loading 500 ml of the dye solutions in the photocatalytic reactor. The effect of initial concentration was obtained with different initial dye concentrations (4–20 mg/l) at 25 °C and initial pH. The effect of temperature was investigated by studying the photocatalytic degradation at different solution temperatures (20–40 °C) with an initial solution concentration of 12 mg/l. The effect of pH was carried out by varying the initial pH of aqueous solution from 2 to 10, with an initial concentration of 12 mg/l at T = 25 °C.

The irradiation of the solutions was done after 1 h of previous adsorption in the dark (kinetics of adsorption shows that only 30 min are sufficient to establish equilibrium).The adsorbed quantity was calculated by measuring the concentration of the solution before and after adsorption using the following equation:

$$q_{\text{ads}} = (C_0 - C_e)/S \tag{1}$$

where q_{ads} (mg/m^2) is the amounts of RY84 adsorbed per unit surface of the photocatalyst at adsorption equilibrium, C_0 (mg/l) is the initial RY84 concentration, C_e (mg/l) is the RY84 concentration at equilibrium and S (m^2/l) is the ratio between the surface of the photocatalyst and the volume of the aqueous solution.

2.4. Analyses

The RY84 aqueous solutions were filtered by Millipore membrane filter type 0.45 µm HA, and the concentrations were determined from UV–Vis absorbance characteristic with the calibration curve method. A Jenway 6405 UV/Visible

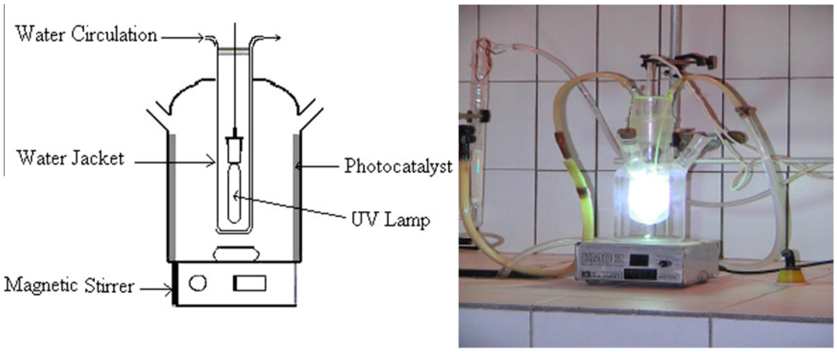

Figure 2 Schematic diagram and photograph of the photocatalytic reactor.

spectrophotometer was used. The wavelength of the maximum of absorption ($\lambda_{\max}$) was 226 nm.

3. Results and discussion

3.1. Effect of initial concentration on adsorption/photocatalytic degradation

3.1.1. Kinetics analyses

The kinetics curves of adsorption/photocatalytic degradation of RY84 at different initial concentrations are represented in Fig. 3. It is evident that the degradation rate depends on the initial concentration of the dye. Since the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react at or near the location where they are formed. A high dye concentration logically enhances the probability of collision between organic mater and oxidizing species, leading to an increase in the discoloration rate.

The kinetics of the photocatalytic degradation rate of most organic compounds is described by pseudo-first order kinetics:

$$\ln\left(\frac{C_0}{C}\right) = k_{\mathrm{ap}}t \tag{2}$$

The plot of $\ln(C_0/C)$ versus t with different initial concentration of RY84 is shown in Fig. 4. The figure shows that the photocatalytic degradation follows perfectly the pseudo-first order kinetic with respect to RY84 concentrations.

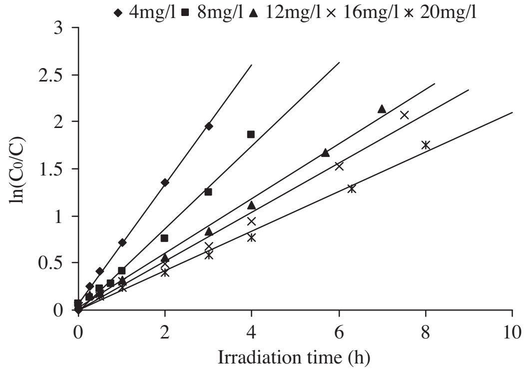

Figure 4 Plot of $\ln(C_0/C)$ versus irradiation time.

3.1.2. Effect of initial concentration on the adsorption

Sorption of the dye is an important parameter in determining photocatalytic degradation rate. The adsorbed dye on the surface of the semiconductor particles acts as an electron donor, injecting electrons from its excited state to the conduction band of the semiconductor under UV irradiation.

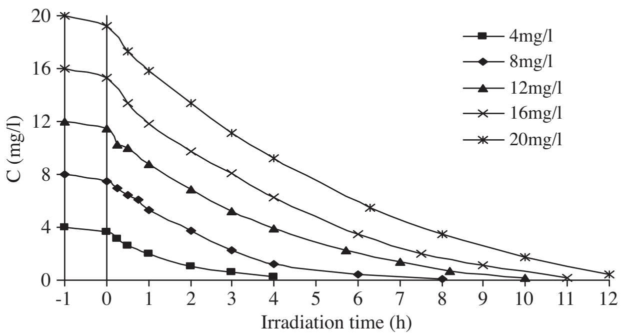

Figure 3 Variation of RY84 concentration versus irradiation time for different initial concentrations.

Adsorption tests in dark were carried out in order to evaluate the equilibrium constants of the adsorption of the dye on the photocatalyst surface. Fig. 5 shows an isotherm of L-shape according to the classification of Giles et al. Giles et al. (1974). The L-shape of the isotherm means that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent surface sites.

The experimental data was fitted to the Langmuir equation (Eq. (3)) to describe the adsorption of RY84 on the surface of the photocatalyst:

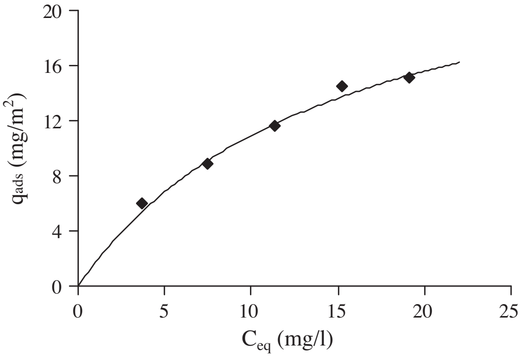

Figure 5 Adsorption isotherm of RY84 on the photocatalyst.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k \cdot q_m} \times \frac{1}{C_e} \tag{3}$$

where q_m (mg/m^2) is the maximal amount of the dye adsorbed per unit surface of the photocatalyst, q_e (mg/m^2) the amount of the dye adsorbed per unit surface of the photocatalyst at the equilibrium, K (l/mg) Langmuir equilibrium constant and C_e (mg/l) the concentration of the dye in aqueous solution at the equilibrium.

The ordinate at the origin is equal to the reciprocal of q_m, whereas K can be calculated from the slope ($1/q_\mathrm{m}$ K). From the data obtained, the maximal adsorption quantity and the Langmuir adsorption constant are, respectively, 27.40 mg/m^2 and 0.066 l/mg.

3.1.3. *Effect of initial concentration on the photocatalytic degradation rate*

The effect of initial RY84 concentration on the initial rate of degradation is shown in Fig. 6. The figure indicates that the rate of discoloration increases with increasing initial concentration of RY84 which correspond to Langmuir–Hinshelwood model according to the following equation:

$$r_0 \;=\; k_{\mathrm{ap}} C_0 \;= \frac{k_c K\, C_0}{1 \;+\; K\, C_0} \tag{4}$$

where r_0 (mg/l h) is the initial rate of the photocatalytic degradation, k_ap (1/h) is the apparent rate constant and k_c a constant depending on the other factors influencing the process.

A linear expression can be conventionally obtained by plotting the reciprocal initial rate constant versus initial concentration:

$$\frac{1}{k_{\mathrm{ap}}} \;=\; \frac{1}{k_c} \quad C_0 \;+\; \frac{1}{k_c\, K} \tag{5}$$

The plot of $1/k_\mathrm{ap}$ versus C_0 as shown in the insert in Fig. 6 gives linear relationship between $1/k_\mathrm{ap}$ and C_0. From the values of the slope ($1/k_c$) and the intercept ($1/k_cK$), k_c and K values for the photocatalytic degradation of RY84 were found to be, respectively, 4.18 mg/l h and 0.32 l/mg.

3.2. *Effect of temperature*

Generally, photocatalysis is not a temperature dependent. However, an increase in temperature can affect the amount of adsorption and helped the reaction to complete more efficiently with e^{-}_h^{+} recombination (Daneshvar et al., 2004). Fig. 7 shows the effect of temperature on the adsorption/photocatalytic degradation of RY84. The figure indicates that adsorption is not affected by temperature. However, the rate of the photocatalytic degradation is temperature dependent and is favored with the increase of solution temperature.

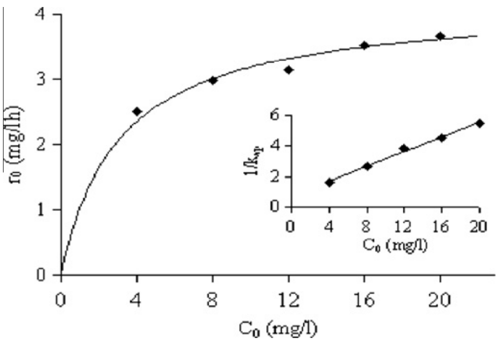

Figure 6 Effect of initial RY84 concentration on the initial rate of degradation. In the insert: Reciprocal of apparent constant rate of degradation versus initial concentration.

The apparent activation energy (Ea) has been calculated from the Arrhenius equation:

$$k_{\mathrm{ap}} = A \exp\left[-\left(\frac{\mathrm{Ea}}{RT}\right)\right] \tag{6}$$

where A is a temperature independent factor (1/h^1), Ea is the apparent activation energy of the photocatalytic degradation (J/mol), R is the gas constant (8.31 J/K mol) and T is the solution temperature.

The linear transform ln (k_ap) = $f(1/T)$, which is shown in Fig. 8, gives a straight line whose slope is equal to $-\mathrm{Ea}/R$, from the data obtained, the apparent activation energy equals to 32.95 kJ/mol.

3.3. *Effect of pH*

Fig. 9 shows the variation of the amount of RY84 adsorbed on the photocatalyst as function of pH at 25 °C. The figure indicates that the amount of dye adsorbed is higher in acidic medium and decrease with increasing initial pH. This result may be due to the influence of the solution pH on both the surface state of TiO_2 and the ionization state of ionisable organic molecule of the dye.

Chun et al. (2000) and Hu et al. (2003) have suggested that the isoelectric point of TiO_2 decreases from 6.5 to pH 3 when

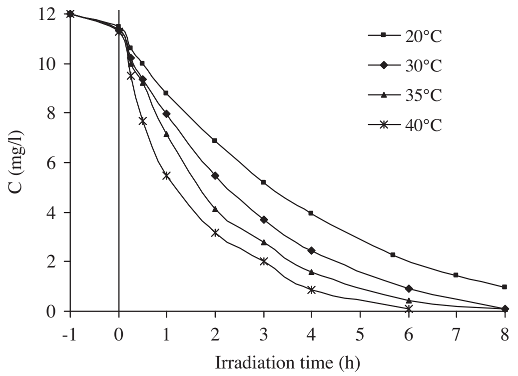

Figure 7 Effect of temperature on the adsorption/photocatalytic degradation of RY84.

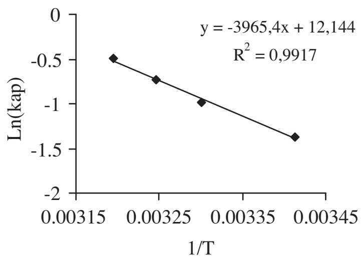

Figure 8 Plot of ln (k_ap) versus $1/T$.

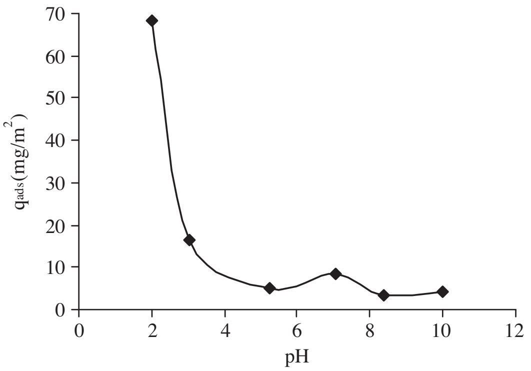

Figure 9 Variation of RY84 amount adsorbed on the photocatalyst as function of pH.

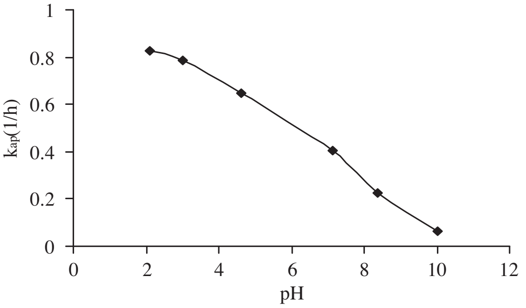

Figure 10 Effect of the pH on the pseudo-first order constant.

the TiO_2 is supported on SiO_2. As a consequence, the $TiOH_2^+$ group is predominant when pH solution is < 3 in the case of TiO_2/SiO_2 photocatalyst. Moreover, the dye is a weak acid. It dissociates less towards an acid pH and is found consequently in neutral electrical form $\varphi\text{-}SO_3H$.

From Fig. 9, it can be seen that the amount of RY84 adsorbed on the photocatalyst material decreases for a pH higher than three, in correlation with the decrease of the amount of $TiOH_2^+$. It appears, therefore, that $TiOH_2^+$ could be responsible for the dye adsorption on the photocatalyst surface, suggesting that electrostatic attraction leads to the observed adsorption. On the opposite, the adsorption at basic pH is prevented by repulsive electrostatic forces existing between $\varphi\text{-}SO_3^-$ and TiO^- which are considered predominant species in this range of pH.

Fig. 10 shows results obtained for the apparent rate constant of the photocatalytic degradation with varying the initial pH of aqueous solution. The high adsorption of the dye on the photocatalyst material leads to a fast decrease of the dye concentration in acid pH zone. These results suggest that the influence of the initial pH of the solution on kinetics of photocatalysis is due to the amount of the dye adsorbed on TiO_2. This hypothesis agrees with a reaction occurring at the surface of TiO_2 and not in the solution, close to the surface.

4. Conclusion

The results of this study have shown that the degradation of Reactive Yellow 84 was successfully carried out using TiO_2 coated on paper fibers. A correlation between the adsorption of the dye onto photocatalyst material and the rate of degradation has been studied. It has been found that, the photocatalytic degradation can be explained in terms of Langmuir–Hinshelwood kinetic model. The maximum dye adsorption and photocatalytic degradation was higher for pH < 3. The rate of the photocatalytic degradation was sensitive to the solution temperature with activation energy of 32.95 kJ/mol. The use of TiO_2 coated on Ahlstrom non-woven fibers is an efficient photocatalyst to degrade textile dye avoiding the tedious filtration step.

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