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Factors influencing the photocatalytic degradation of Rhodamine B by TiO_2-coated non-woven paper

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Abstract

The photocatalytic degradation of Rhodamine B (RhB) has been investigated in aqueous solutions using TiO_2-coated non-woven paper as photocatalyst. The experiments were carried out to investigate the factors that influence the RhB photocatalytic degradation, such as adsorption, initial concentration of dye solution, temperature, and some inorganic species commonly present in real wastewaters such as Cl^-, NO_3^-, SO_4^{2-}, CH_3COO^- and HPO_4^{2-}. The experimental results show that adsorption is an important parameter in controlling the apparent kinetic order of the degradation. The photocatalytic reaction is favoured by a high concentration in respect to Langmuir–Hinshelwood model. The photodegradation was temperature-dependent with a high degradation rate at high temperature. The presence of the Cl^-, CH_3COO^- and HPO_4^{2-} ions leads to the reduction of the effectiveness of the photodegradation. However, the presence of SO_4^{2-} increases the rate of the degradation.

Keywords: Photocatalytic degradation; Rhodamine B; TiO_2; Non-woven paper; Inorganic salts

1. Introduction

Heterogeneous photocatalysis is an efficient technique to destroy organic pollutants in water [1–8]. This technique is based upon the use of UV-irradiated semiconductors (generally titania). When TiO_2 is irradiated with photons whose energy is equal to or greater than its band gap energy ($E_G = 3.2$ eV) i.e., with $\lambda = 390$ 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 $OH^\bullet$ 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 $O_2^{\bullet -}$ (or $HO_2^\bullet$ at lower pH) [9].

For the degradation process tow methods are favoured, 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) [10]. This has led to a major attempt to immobilize the photocatalyst on support including ceramic [11], glass fibre [12], glass, quartz and stainless steel [13], activated carbon [14], non-woven paper [15] and others. However, these efforts have not produced materials which meet all demands of photocatalytic activity.

The Rhodamine B is one of the most common xanthenes dyes for textile industry, it is famous for its good stability as dye laser materials, and it is also used as biological stain. The Rhodamine B is highly soluble in water and organic solvent, and its colour is fluorescent bluish-red. This compound is now banned from use in foods and cosmetics because it has been found to be potentially toxic and carcinogenic. So the photodegradation of RhB is important with regard to the purification of dye effluents.

Recent articles have shown that Rhodamine B can be destroyed in aqueous suspension using TiO_2 [16], TiO_2-coated silica [17] and TiO_2-coated silicone sealant [18]. In this work, the influence, on the photocatalytic degradation of Rhodamine B by immobilized TiO_2 on non-woven paper, of various parameters such as the initial RhB concentration, the previous adsorption in the dark, the temperature and some organic anions commonly present in real wastewaters was studied.

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2. Experimental

2.1. Materials

The immobilized photocatalyst used in this study was a commercial titania photocatalyst from Ahlstrom firm (France), it consists of PC500 Titania by Millennium inorganic chemicals (anatase: >99%, specific surface area 350–400 $m^2\,g^{-1}$, crystallites mean size = 5–10 nm). Titania PC500 was coated on non-woven paper (natural and synthetic fibres 254 μm of thickness) using an inorganic binder. The binder was an aqueous dispersion of colloidal SiO_2 (EP1069950B1 European patent). A specific surface area extender (zeolite UOP, 2000 $m^2\,g^{-1}$) was used to increase adsorption properties of the photocatalyst. The physical and chemical properties of the photocatalyst are shown in Table 1.

The Rhodamine B (purity, 99%) was purchased from Exciton (USA) and used as received. It consists on green crystals or reddish-violet powder, its molecular formula is $C_{24}H_{31}ClN_2O_3$ (molecular weight: 479.02). The Rhodamine B structure is given in Fig. 1. All the other reagents used in this study were analytical grade. NaOAc (Rhône-Poulenc), Na_2HPO_4 (BDH Chemicals), Na_2SO_4 (Labosi), NaCl and $NaNO_3$ (Merck) salts were used as purchased.

2.2. Photocatalytic reactor

Experiments were carried out using a cylindrical batch reactor opened at air, 8 cm in diameter and 12 cm in working height, the water jacket has a diameter of 5 cm contain the UV-lamp and permits the water circulation (Fig. 2). The photoreactor was recovered inside with (11 cm × 25 cm) of the photocatalyst and was exposed to a luminous source composed of a HPK Philips UV-lamp (125 W), placed in axial position inside the water jacket. The reactor was initially loaded with 500 mL of RhB aqueous solution and maintained in low continuous stirring (100 rpm) by means of a magnetic stirrer.

2.3. Procedure and analysis

The adsorption experiments were carried out by immersing 11 cm^2 of the photocatalyst in 20 mL of RhB solutions during

Table 1
Chemical and physical properties of the Ahlstrom photocatalyst (Ref: 1048)

Composition	
PC500	18 $g\,m^{-2}$
SiO_2	20 $g\,m^{-2}$
UOP200	2 $g\,m^{-2}$
Physical properties	
Mass per unit area	75 $g\,m^{-2}$
Thickness	254 μm
Air permeability	2570 $L\,m^{-2}\,s^{-1}$
Tensile strength MD	1100 $N\,m^{-1}$
CD	500 $N\,m^{-1}$
Elongation MD	3%
CD	5%
Water drop	2 s

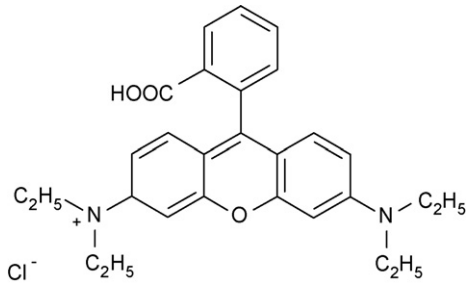

Fig. 1. Molecular structure of Rhodamine B.

1 h, the adsorption isotherms were obtained by different initial concentration (4–20 mg L^{-1}) at 25 °C, and the effect of temperature was obtained by varying temperature from 25 to 40 °C with an initial concentration of 12 mg L^{-1}. The quantity adsorbed was calculated by measuring the concentration of the solution before and after adsorption using the following equation:

$$q_e = \frac{(C_0 - C_e)}{S} \quad (1)$$

where q_e (mg m^{-2}) is the amounts of RhB adsorbed per unit surface of the photocatalyst at adsorption equilibrium, C_0 (mg L^{-1}) is the initial RhB concentration, C_e (mg L^{-1}) is the RhB concentration at equilibrium and S ($m^2\,L^{-1}$) is the ratio between the surface of the photocatalyst and the volume of the aqueous solution.

The photocatalytic degradation experiments were carried out by loading 500 mL of RhB solutions in the photocatalytic reactor. The effect of initial concentration was obtained with different initial concentrations (4–20 mg L^{-1}) at 25 °C. The effect of temperature was obtained by studying the photocatalytic degradation at different solution temperatures (25–40 °C) with an initial solution concentration of 12 mg L^{-1}. For the effect of the inorganic anions, the mass of each salts equivalent to 200 mg L^{-1} of each anion was added to the initial solution of the dye. All solutions were irradiated after 1 h of previous adsorption.

The RhB 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 spectrophotometer was used. The maximum adsorption wavelength (λ_{max}) was 554 nm. The concentrations were calculated taking

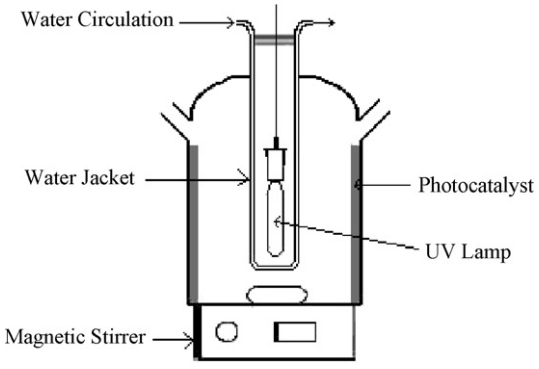

Fig. 2. Schematic diagram of the photocatalytic reactor.