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Comparative photocatalytic studies of degradation of a cationic and an anionic dye

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Abstract

Photocatalytic degradation of Methylene Blue, a cationic dye and Procion Red, an anionic dye, has been examined in TiO_2 dispersions under visible light (λ 400–580 nm). Adsorption is a prerequisite for the TiO_2 assisted photodegradation and the extent of degradation has been discussed in terms of the Langmuir–Hinshelwood model. Like most semiconductors the photocatalytic nature of TiO_2 is pH dependent because of its amphoteric nature. It has been found that pH ~ 9.5 and pH ~ 3.22 were suitable for Methylene Blue and Procion Red, respectively. The degradation pathway of Procion Red was found to be somewhat different from Methylene Blue.

Keywords: Cationic and anionic dyes; Photo-irradiation; Adsorption isotherm

1. Introduction

Much attention has been directed at investigating degradation of organic pollutants mediated by TiO_2 particles in aqueous dispersion under UV–light irradiation. Mechanistically, it is now commonly accepted that the photocatalyst TiO_2 is first excited by UV light and subsequently initiates the photodegradation process. However, artificial UV light and TiO_2 particles tend to be somewhat expensive and the UV component in sunlight reaching the earth surface and available to excite TiO_2 is relatively small (ca. 3–5%). Therefore, our efforts have been focused on exploring means to utilize the sunlight and artificial inexpensive UV or visible light sources and degrading agents for treating polluted water.

Organic pollutants like dyestuffs have the ability to absorb visible light. The electron transfer process from dye to semiconductor, especially TiO_2 has been found to be very effective. The visible light mechanism suggests that the light excites the dyestuff [3–5].

$$D + h\nu \rightarrow D^* \tag{1}$$

$$D^* + TiO_2 \rightarrow D^+ + TiO_2(e) \tag{2}$$

$$TiO_2(e) + O_2 \rightarrow TiO_2 + O_2^{\bullet -} \tag{3}$$

$$O_2^{\bullet -} + 2H_2O \rightarrow H_2O_2 + e \tag{4}$$

$$H_2O_2 + e \rightarrow {}^{\bullet}OH + OH^- \tag{5}$$

$$D^{\bullet +} + O_2(\text{or } O_2^{\bullet -} \text{ or } {}^{\bullet}OH) \rightarrow \text{Degraded products} \tag{6}$$

The excited dye (D*) injects an electron to the conduction band of TiO_2 where it is scavenged by O_2 to form active oxygen radicals. These active radicals drive the photodegradation or mineralization of organic compounds. However, only light of wavelengths below 400 nm can be absorbed by TiO_2 particles (e.g.,

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3.2 eV ≅ 388 nm) [1–9]. The photodegradation mechanism in the presence of light $\lambda < 400$ nm is somewhat different. In this process, TiO_2 absorbs light ($\lambda < 400$ nm) to generate e^-/h^+ pair. The ejected photosensitized electron generates radicals ($O_2^{\bullet -}$, $^{\bullet}OH$) followed by degradation of dyestuff in the system. In this process degradation is faster than that of visible light [1–9]. Serpone and coworkers have studied the photocatalytic kinetics of an anionic dye Eosin [1]. Recently we reported degradation of Malachite Green in the homogeneous and heterogeneous media [2,14]. In this report Methylene Blue (MB), a cationic dye and Procion Red (PR), an anionic dye, have been studied to observe comparative kinetic degradation as an example of wastewater pollutants in different industries. pH of the medium is one of the important factors for the degradation because of the amphoteric nature of most semiconductors. The effect of pH on degradation has also been discussed on the basis of the experimental results.

2. Experimental

2.1. Materials

TiO_2 photocatalyst (P25, 90% anatase, specific surface area 50 $m^2\,g^{-1}$) used was supplied by Degussa. Methylene Blue (MB), Procion Red (PR), etc. were of laboratory reagent grade and were used without further purification. Double distilled and deionized water was used throughout the study.

2.2. Photoreactor and light source

A mercury lamp, visible light source (400–580 nm) (PASCO Scientific), was used for photolysis. The lamp was positioned 10 cm apart from a cylindrical pyrex vessel which was surrounded by circulating water jacket to control the temperature.

2.3. Photolysis of solution

An aqueous TiO_2 suspension was prepared by dissolving 25 mg with 25 ml distilled water in a 50 ml volumetric flask. Procion Red or Methylene Blue solution was added to the volumetric flask such that the final concentration of dye solution becomes the desired concentration. The pH was adjusted with HCl or NaOH as required. The solution was then stirred for 30 min by magnetic stirrer for adsorption–desorption equilibrium to be reached. The extent of equilibrium adsorption was estimated from the decrease in solution concentration. Subsequently, the dispersion was irradiated under air-equilibrated conditions. A 3 ml aliquot was taken at various intervals then it was filtered through a filter paper prior to analysis. Variations in the concentration of dyes in each degraded solution were monitored by UV–visible spectrophotometer (Shimadzu 160 A, absorption at λ_{max} 512 nm for PR and 664 nm for MB). All the experiments were done at 30 °C.

3. Results and discussions

The absorption spectra of aqueous solutions of MB ($C_0 = 1 \times 10^{-5}$ M) and PR ($C_0 = 1 \times 10^{-4}$ M) were recorded following irradiation with visible radiation (λ, 400–580 nm). The absorption peaks corresponding to the dye solutions were diminished and finally disappeared under photolysis, indicating the degradation of MB and PR. No new bands appeared in the UV–visible regions, especially absorption bands of any aromatic moieties and other similar intermediates.

After analyzing the end products, for both dyes pH was found to decrease and the presence of ${SO_4}^{-2}$, Cl^- and ${NO_3}^-$ ions and evolution of CO_2 were marked which indicates the complete mineralization of both dyes. Thus it can be inferred that both MB and PR molecules split into different inorganic materials as in Eq. (7).

$$\mathrm{PR/MB} \rightarrow H^+ + SO_4^{2-} + Cl^- + NO_3^- + CO_2 \qquad (7)$$

Fig. 1 shows that adsorption of MB on TiO_2 surface and corresponding photodegradation is largely maximum at higher pH (pH ~ 9.5) and in the case of PR most adsorption and photodegradation occurs at lower pH (pH ~ 3.22) as shown in Fig. 2. This might be because of amphoteric behavior of the TiO_2 semiconductor. The potential at zero charge of TiO_2 surface is at $pH_{pzc} = 6.80$ [6]. TiO_2 surface is thus positively charged in acidic pH (pH < 6.8) and negatively charged

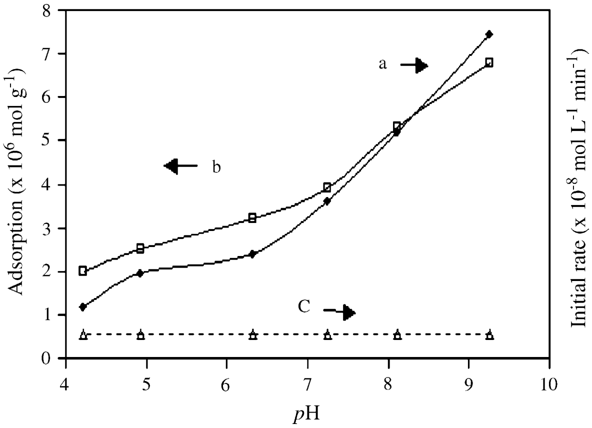

Fig. 1. Influence of pH on the degradation kinetics of MB (10×10^{-6} M, 50 ml); (a) initial degradation rate of MB with TiO_2(25 mg); (b) adsorption of MB on the TiO_2(25 mg) surface; (C) initial degradation rate of MB without TiO_2.

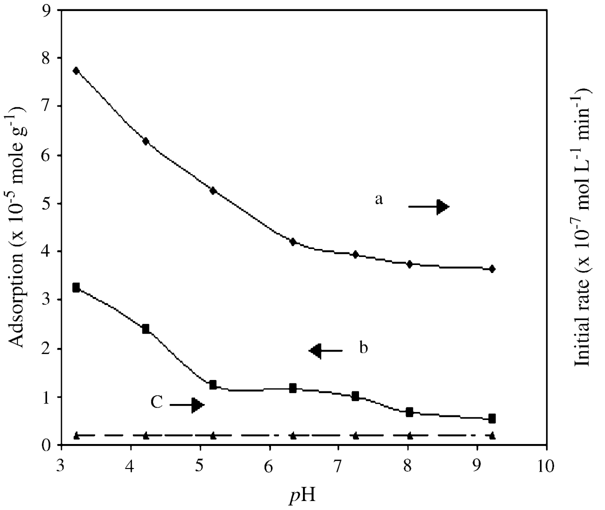

Fig. 2. Influence of pH on the degradation kinetics of PR (10×10^{-5} M, 50 ml); (a) initial degradation rate of PR with TiO_2 (25 mg); (b) adsorption of PR on the TiO_2 (25 mg) surface; (C) initial degradation rate of PR without TiO_2.

in alkaline pH (pH > 6.8). At higher pH electrostatic interactions between the negative TiO_2 surface and MB cations lead to strong absorption and enhancing degradation rate. In the acidic pH (pH < 6.8) there was a poor adsorption, because the TiO_2 surface and MB are both positively charged in the acidic media. Therefore, decrease in pH causes decrease in degradation rate.

In absence of TiO_2 particles, no significant degradation was observed. This means that the photodegradation of dye molecules assisted by TiO_2 particles occurs as soon as dye molecules are adsorbed on TiO_2 surface. The degradation of organic molecules is caused by $^{\bullet}OH$ (or$^{\bullet}OOH$) radicals. The lifetime of $^{\bullet}OH/^{\bullet}OOH$ radicals is too short to move far from TiO_2 surface, therefore it is likely that degradation occurs on TiO_2 surface or within few monolayers around the TiO_2 surface. Because of TiO_2 surface above pH ~ 6.8 is negatively charged therefore, repulsive force dominates between negative TiO_2 surface and PR anions i.e. poor adsorption of PR molecules in the basic pH causes poor degradation of PR molecules.

In absence of light no degradation occurs. The oxidation potential of excited dye is usually more negative than the potential of the conduction band of TiO_2[7–9]. When dye molecule is absorbed on the surface of TiO_2 and excited by visible light, it can eject electron to the conduction band of colloidal TiO_2 and these electrons are responsible for radical generation [12,13].

Since the photodegradation of dye occurs predominantly on TiO_2 surface, the adsorption of dye molecules from aqueous solution particularly on to TiO_2 surface is very important. The extent of adsorption of dye at various concentrations was measured by monitoring its concentration in blank solution after the adsorption–desorption equilibrium had been reached. The photodegradation kinetics of many organic compounds is often modeled using simple Langmuir–Hinshelwood equation which expresses the relation between rate (ν) as function of concentration [8,9]:

$$1/\nu = 1/kK[\mathrm{D}] + 1/k \tag{8}$$

where k is the apparent rate constant for the process and K is adsorption coefficient under irradiation conditions. Examining degradation rate of dyes at different initial concentrations, photodegradation kinetics under UV light irradiation were assessed. A good linear relationship between ν^{-1} and $[\mathrm{D}]^{-1}$ indicates that degradation kinetics of both dyes follow L-H model. The adsorption constant K determined from Eq. (8) and adsorption coefficient K' Langmuir equation (9) in the dark have been listed in Table 1.

$$[\mathrm{D}]_e/(x/m) = [\mathrm{D}]_e/K' + 1/k_1K' \tag{9}$$

where $[\mathrm{D}]_e$ is equilibrium concentration and x/m is the amount of dye adsorbed per gram of TiO_2, k_1 is adsorption constant and K' is adsorption coefficient. The difference between K and K' was caused by photodesorption and/or photo-adsorption of substrate molecules on the TiO_2 surface. Similar results also have been reported by other researchers [1,10,11].

The degradation kinetics of both dyes were found to follow first order integrated rate equation (10).

$$\ln[\mathrm{D}]_t = -kt + \ln[\mathrm{D}]_0 \tag{10}$$

where $[\mathrm{D}]_t$ = dye concentration at different time intervals and k is the rate constant. Under irradiation condition half-lives of MB and PR were 66.0 min (at pH 9.5) and 311.0 min (at pH 3.22), respectively. In this study the degradation pattern of MB and PR was found to be somewhat different. Fig. 3 shows that MB concentration decreases gradually causing degradation and on the other hand PR concentration increases until 6 min then decrease in concentration starts. This might be because of MB forming monolayer that is suitable for quicker degradation ($t_{1/2}$ = 66 min) and in case of PR, it might form several multilayers. Initially the multilayers undergo desorption under irradiation with the visible light source. When the multilayers (after 6 min) are removed, the perfect monolayer only then came into degradation.

Table 1
Adsorption coefficient of MB and PR

Dye	K (l mol^{-1})	K'(l mol^{-1})
MB	1.96×10^5	2.70×10^5
PR	0.9×10^5	1.10×10^5

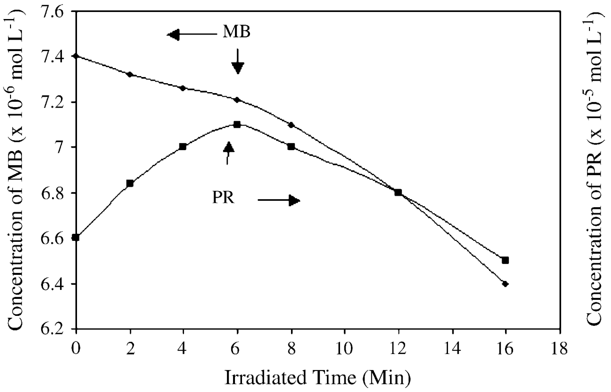

Fig. 3. A comparative view of concentration change of MB and PR due to degradation on photolysis in first 20 min. $[MB]_0 = 10 \times 10^{-6}$ M (pH = 9.5), $[PR]_0 = 10 \times 10^{-5}$ M, (pH = 3.22), TiO_2, 25 mg in 50 ml. (B) MB and (C) PR.

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