

Photocatalytic degradation of reactive dye RED-3BA in aqueous TiO₂ suspension under UV-visible light

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ABSTRACT. The photo-catalytic degradation efficiency of several commercial titania powders (Degussa P-25 and Ishihara Sangyo ST-01) and of TiO₂ supported on diatomite were investigated in the degradation of a reactive dye (RED-3BA) under UV-Visible light. The observed rate constant for Degussa P-25 was found to be higher than that achieved by using Ishihara Sangyo ST-01 ($k_{\text{obs}} = 3.3 \times 10^{-2} \text{ min}^{-1}$ for Degussa P-25 and $4 \times 10^{-4} \text{ min}^{-1}$ for Ishihara Sangyo ST-01). This could be related to the amount of basic hydroxyl groups on the surface of TiO₂ particles as shown in the IR spectra. TiO₂ Degussa P-25 supported on diatomite was prepared by dip-coating method. The photo-catalytic activity of supported TiO₂ was twice smaller than TiO₂ Degussa P-25 ($k_{\text{p-25}} = 3.3 \times 10^{-2} \text{ min}^{-1}$; $k_{\text{p25/diatomite}} = 1.6 \times 10^{-2} \text{ min}^{-1}$). The higher surface areas of ST-01 and the TiO₂/diatomite could not lead to a higher degradation rate and to a higher degree of mineralization but TiO₂/diatomite could be separated more promptly and more easily from the solution. The effect of pH was investigated in the range 4–9. Acidic (pH = 4) *medium* was found to favor the adsorption and degradation rate with P-25 particles.

1. INTRODUCTION

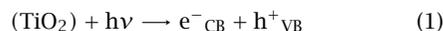
Industrial textile processes generally use many chemicals such as surfactants, chelating agents, pH regulators and different kinds of dyes. These chemicals are always present in wastewaters at different concentrations. Among dyes, reactive azo dyes are commonly used in textile industry in *Ho Chi Minh City* (they represent 50% of the dyeing staff). Dye pollutants in wastewaters are the principal source of environmental aqueous contamination. They need to be removed from wastewaters by different methods. Photocatalysis has been successfully used to oxidize many organic pollutants [1–8] and particularly to decolorize and mineralize dyes [9–14].

The release of colored wastewaters in the ecosystem is a dramatic source of aesthetic pollution, eutrophication, and perturbations in aquatic life. As international environmental standards are becoming more stringent (ISO 14001, October 1996), technological systems for the removal of organic pollutants, such as dyes have been recently developed. Physical methods, such as adsorption, biological methods (biodegradation), and chemical methods (chlorination, ozonation) are the most frequently used.

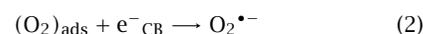
Among the new oxidation methods or “Advanced Oxidation Processes” (AOP), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralization of many organic pollutants [1–14], according to the following

proposed processes:

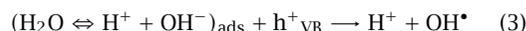
- absorption of efficient photons by titania ($h\nu \geq E_G = 3.2 \text{ eV}$)



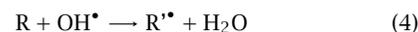
- oxygen ionosorption



- neutralization of OH⁻ groups into OH[•] by photoholes



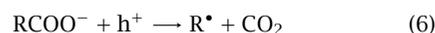
- oxidation of the organic reactant via successive attacks by OH[•] radicals



- or by direct reaction with holes



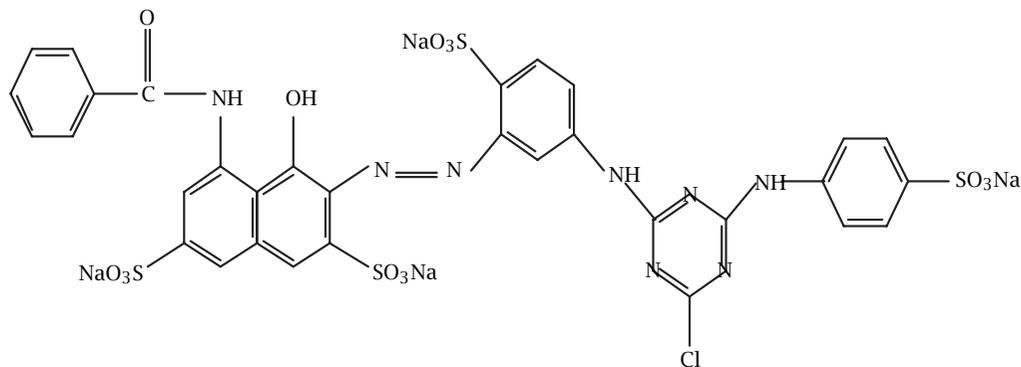
As an example of the last process (5), holes can react directly with carboxylic acids generating CO₂ according to the so-called photo-Kolbe reaction:



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A general list of various families of organic pollutants which can be treated by photocatalysis has been



Scheme 1. Developed formula of Reactive Red 3BA (Cibacron Brilliant Red 3BA).

compiled by Blake [8]. In most cases, the degradation is conducted for dissolved compounds in water with UV-illuminated TiO_2 powder.

Kamat et al. [15] reported that the dyes adsorbed at the TiO_2 surface undergo degradation upon photo-excitation with visible light and only the molecules at monolayer or submono-layer coverage underwent photo-degradation. The kinetics of the destruction of organic compounds on the TiO_2 surface follow the Langmuir-Hinshelwood mechanism [3]. The use of slurries in wastewater treatment has some disadvantages: the separation of fine particles is slow and penetration of light is limited because of strong absorptions by TiO_2 and dissolved organic species. These problems can be minimized by supporting TiO_2 on various materials such as glass plates, fiberglass, silica beads, zeolites, activated carbons, and diatomite. Many techniques have been developed to obtain advanced material based on TiO_2 .

In the present work, we focus on the degradation of reactive dyes, to compare the photocatalytic efficiency of some TiO_2 powders with supported TiO_2 in the decolorization and mineralization of dyes. The oxidation of reactive Red-3BA is carried out in aqueous suspensions of industrial TiO_2 Degussa (P-25, TiO_2 ST-01) and of TiO_2 /supported on diatomite, irradiated by UV-visible light.

The decrease of Red-3BA concentration during degradation can be monitored by the absorption intensity at various time intervals and the total organic carbon (TOC) is measured. The kinetics of photo-oxidation is determined on the basis of experimental results.

2. EXPERIMENTAL

2.1. Materials. TiO_2 samples of industrial origin were supplied (i) by Degussa (Germany) (titania P-25; anatase $\approx 80\%$; Rutile $\approx 20\%$; BET surface area = $50\text{ m}^2/\text{g}$, mean particle size $\approx 30\text{ nm}$) and (ii) Ishihara Sangyo (Japan) (ST-01, anatase $\approx 83\%$, BET surface area = $138\text{ m}^2/\text{g}$, particle size $\approx 7\text{ nm}$). Degussa P-25 has been deposited on diatomite. The commercial

diatomite has a BET surface area equal to $197\text{ m}^2/\text{g}$. The weight percentage of deposited titania P-25 was equal to 8.8%. Therefore, since titania alone was used at 0.100 g/L , diatomite-supported titania was used at 1.150 g/L to work with the same amount of titania to obtain reliable comparable data.

The sample of reactive dye Red-3BA was purchased from Cibacron and used without further purification. Its developed formula is given in Scheme 1.

2.2. Photo-reactor and light source. The experiments were carried out in a photocatalytic reactor identical to that described in ref. [16]. A 150 W halogen lamp (OSRAM HLX) was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket to cool the lamp. The halogen lamp has a spectral emission ranging from 360 nm to 830 nm.

2.3. Procedures and analyses. An aqueous solution of Red 3BA ($V = 150\text{ ml}$) at a definite concentration of 50 mg/l and TiO_2 powder (100 mg/l) was magnetically stirred in the vessel during 30 min in the dark to obtain the equilibrium of adsorption of the dye under air atmosphere. The solution was subsequently irradiated by the halogen lamp.

Slurry samples were withdrawn at various intervals, and then filtered using Millipore filters (Blue grade) to remove the TiO_2 particles before analysis. The variations of the concentration of dyes were monitored with a UV-VIS spectrometer (Model Jasco-V 530 (Japan)) at $\lambda_{\text{max}} = 519\text{ nm}$.

- The total organic carbon (TOC) was determined with a TOC analyzer (Model ANATOC II, (Australia)).

- The pH was adjusted with HClO_4 or NaOH as required.

- The IR spectra of the catalysts were recorded with an IR spectrometer (Model Bruker Vector -22) (Germany). The samples were prepared by mixing 5 mg of titania powder (Degussa P-25 or ST-01) with 500 mg KBr before compression into pellets. To evaluate the moisture of the sample, the samples have been dried at 110°C under vacuum for 4 h before recording IR spectra.

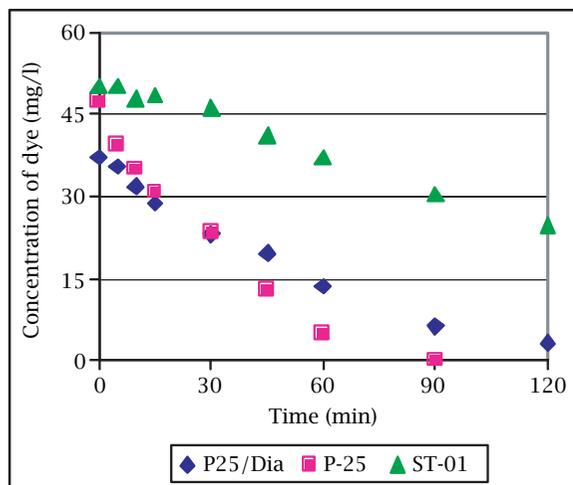


Figure 1. Decrease of dye concentration vs. irradiation time on different catalysts. Initial dye concentration: 50 mg/l; amount of TiO_2 = 100 mg/l, pH of the solution = 6.8.

3. RESULTS AND DISCUSSION

3.1. Degradation of Red-3BA in TiO_2 slurries.

The primary control experiments were carried out in different conditions: (i) in the absence of TiO_2 powder under irradiation; (ii) with TiO_2 slurry in the dark and (iii) with TiO_2 powder irradiated with UV-visible light.

Preliminary experiments showed that Red-3BA is photostable in absence of TiO_2 and not decomposed in the dark in presence of TiO_2 ruling out existing of any dark reaction such as hydrolysis. However, it was significantly degraded by TiO_2 slurries under UV-irradiation. This clearly means that the degradation observed is typically a photocatalytic reaction. The decrease in dye concentrations versus time of irradiation ($t \leq 2$ h) are presented in Figure 1.

The comparison between the noticed photocatalytic efficiencies of Degussa P-25 and of ST-01 titania samples showed that Degussa P-25 is more active than ST-01. IR investigation of the TiO_2 particles showed a band in the $3750\text{--}2600\text{ cm}^{-1}$ region with a maximum at about 3418 cm^{-1} and a band at 1636 cm^{-1} (Figure 2). The band at 3418 cm^{-1} can be ascribed to basic hydroxyl groups OH^- , whereas the band at 1636 cm^{-1} corresponds to adsorbed molecular water [17]. It has to be mentioned that the IR recorded spectra are identical before and after drying, indicating that the peaks are related to strongly bound species.

These results indicate that surfaces of both samples are fully hydrated and hydroxylated. However, for titania ST-01 both bands at 3418 cm^{-1} and 1636 cm^{-1} are much larger than for Degussa P-25. This means that the amount of hydroxyl groups OH at the surface of ST-01 are more numerous than on P-25 particles. Since the samples prepared for IR spectroscopy have

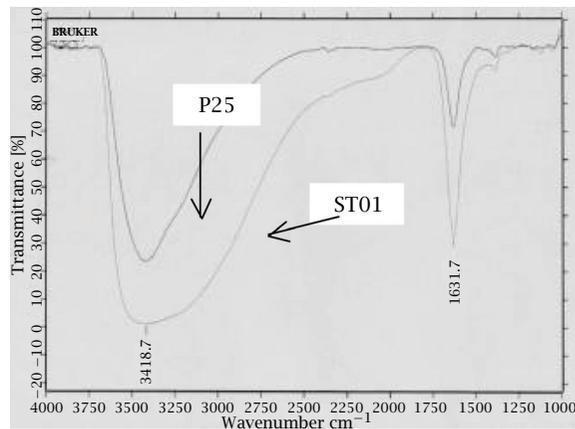


Figure 2. IR spectra of ST-01 and P-25 photocatalysts.

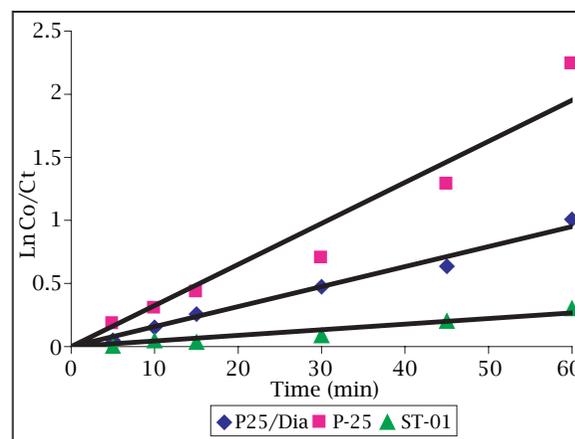


Figure 3. First order linear plots $\text{Ln}(C_0/C) = f(t)$ for the three different photocatalysts.

the same amount of titania (5 mg in 500 mg KBr), the higher amount of OH groups has to be related to its higher surface area (138 vs. $50\text{ m}^2/\text{g}$).

Red-3BA is a reactive dye with some sulfonate groups in its molecule to ensure a better solubility. In aqueous solution, it behaves as a poly-anionic species, the adsorption of which is more difficult on the surface with more numerous basic hydroxyl groups because of electrostatic repulsion. This behavior can explain the better activity of P-25 compared with that of ST-01.

The degradation of dyes in aqueous suspension of TiO_2 follows a pseudo-first order kinetics [3, 9–14]. Presently, the apparent rate constants k can be calculated from the slope of linear transform $\text{Ln } C_0/C = f(t)$ given in the semilog plot of the concentration of dyes versus time in Figure 3.

The obtained data of the apparent first order rate constants (Table 1) indicate that the activity of TiO_2 Degussa P-25 is 8 times higher than that of ST-01. In addition, Degussa P-25 supported on diatomite has a rate

Table 1. Apparent first order rate constants of the reaction with different catalysts.

Catalysts	$k_{app}(\text{min})^{-1}$	Ratio of k_{p25}/k_i
ST-01	0.0044	8.2
P-25	0.0325	1
P-25/diatomite	0.0159	2

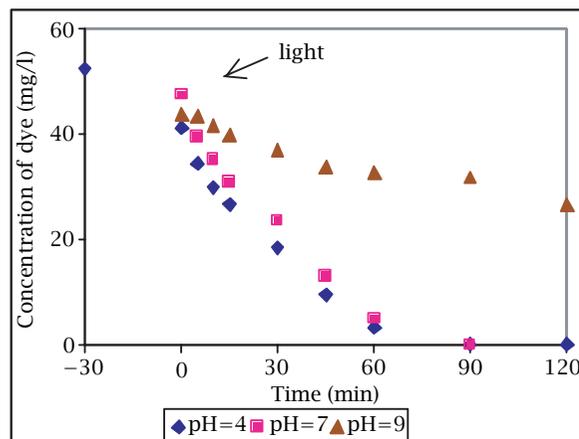


Figure 4. Influence of pH on the photocatalytic efficiency of TiO_2 P-25 catalyst.

constant twice smaller than that of TiO_2 in suspension. These results could be explained if one considers that for immobilized TiO_2 , only a part of TiO_2 is illuminated, whereas the other part is in contact with the support.

Despite its higher surface area, TiO_2 ST-01 has a lower photocatalytic activity in the degradation of Red 3BA than that of TiO_2 (Degussa P-25). In case of TiO_2 Degussa P-25 immobilized on diatomite, the support has a high surface area ($197 \text{ m}^2/\text{g}$) and its ability to uptake titania is not reflected in any increase in its photocatalytic efficiency. This leads to the suggestion that the surface area of the support and the titania particle size have no direct relationship with catalyst activity.

The TOC measurements after 2 hours of UV-irradiation showed that the mineralization conversion is about 30% for TiO_2 P-25 and 10% for TiO_2 ST-01. TOC continued to decrease for a longer irradiation time. This means that probable intermediate substances such as peroxides, aldehydes, and carboxylic acids might be appeared and disappeared for photocatalytic treatment longer than 2 hours of irradiation.

3.2. Effect of pH. An important parameter of the reaction is the pH of the solution, since it influences the surface charge of the photocatalyst. The TiO_2 surface is positively charged in acidic media, whereas it is negatively charged under alkaline conditions [6].

The results obtained (Figures 4, 5, and 6) indicated that at $\text{pH} = 4$, electrostatic interactions between the positive TiO_2 surface and the anionic form of the dye

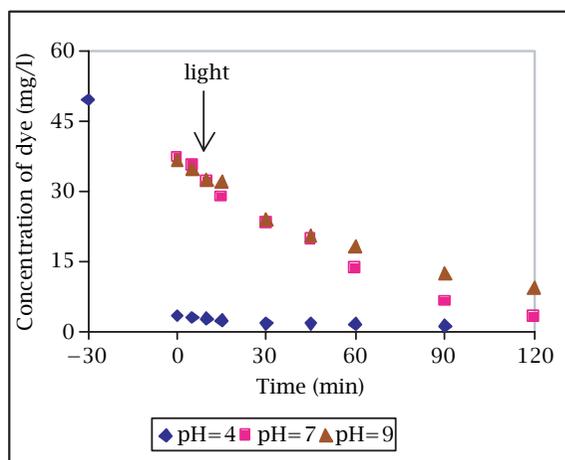


Figure 5. Influence of pH on the photocatalytic efficiency with TiO_2 P-25/Diatomite catalyst.

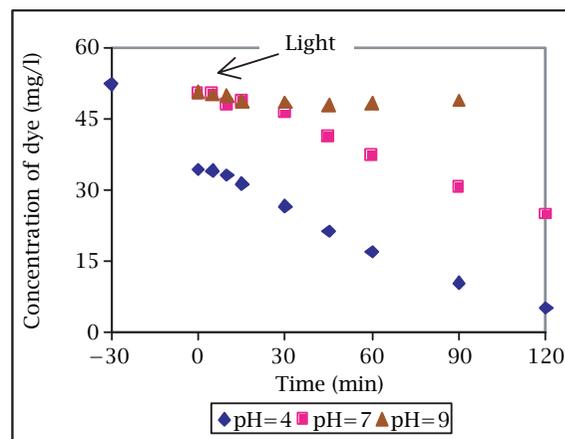


Figure 6. Influence of pH on the photocatalytic efficiency with TiO_2 ST-01 catalyst.

leads to a strong adsorption of the dye and to a relatively high initial rate. A confirmation of this statement could be established from the pK_a of the dye. Unfortunately, it could not be found neither in handbooks nor in the characteristics given by the producer. However, by analogy with other sulfonated dyes already studied in LACE [9–14], this assumption could be admitted.

Increasing the pH of the solution above 4 results in decreasing the adsorption and the value of the initial rate constant. As indicated in previous studies [3, 18–20], photodegradation process occurs at the surface.

The absorption of photons ($\lambda > 400 \text{ nm}$) by the adsorbed dye molecules induces electron injection into the conduction band of the TiO_2 particles. The injected electrons are then scavenged by preadsorbed oxygen to form adsorbed oxygen radical $\text{O}_2^{\bullet-}$. The transfer of an electron from the dye to titania on which it is trapped

as $O_2^{\bullet-}$ induces the decolorization of the dye. However, the number of molecules of dyes decolorized is equal to the number of electrons transferred to titania and trapped by adsorbed oxygen molecules as $O_2^{\bullet-}$. This is a stoichiometric reaction but not a catalytic reaction. This has been clearly demonstrated for Indigo Carmine either by reducing oxygen pressure, by purging, or by introducing a much higher initial concentration of the dye. A careful Total Organic Carbon (TOC) analysis indicated that TOC remained constant [10]. This confirms that visible light can participate to a (partial) stoichiometric decolorization but not to a catalytic degradation of the dye.

In alkaline media, both TiO_2 surface and dye Red 3BA are negatively charged. Consequently, the adsorption decreases and the photocatalytic efficiency is diminished.

4. CONCLUSIONS

Reactive Red-3BA dye can be degraded by TiO_2 suspension under UV-Visible light. The photo-catalytic activity of TiO_2 particles is related to the amount of basic hydroxyl groups on the surfaces and to the adsorption properties.

The specific surface area and the size of particles had a little effect on the photocatalytic activities of the photocatalysts in the conditions presently used in this case.

Diatomite-supported TiO_2 (1.50 g/L), with the same amount of titania was found less active than pure powder TiO_2 . This can be due to the titania-support interface inaccessible either to the photons and more probably to the reactants. However, this sample could be separated from the solution much more easily, only after some minutes of sedimentation, which was accelerated by the presence of the support. Therefore, it can be suggested that, from the chemical engineering point of view, a less active sample could be preferentially chosen for an easier use.

Acidic medium (pH = 4) was found to favor both adsorption and the consequent degradation rate.

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