PHOTOCATALYTIC DEGRADATION OF TWO AZO-DYES IN SINGLE AND BINARY MIXTURE BY La MODIFIED TiO₂

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ABSTRACT

In this work photodegradation of single and binary mixture of two azo dyes - Reactive Black 5 (RB5) and Congo Red (CR) was studied in La-TiO₂ suspension under UV irradiation. Lanthanum modified TiO₂ photocatalyst was prepared by nonhydrolytic sol-gel method. Effect of various parameters such as initial pH, catalyst dose, and initial dye concentration were studied in order to propose the optimum conditions for maximal decoloration efficiency. It was observed that photodegradation of both dyes in binary solution was to a lesser extent than those in single solution under comparable conditions. After 60 min UV irradiation with 0.67 mg/ml of La-TiO₂ catalyst, complete removal of single 20 mg/l RB5 and 14 mg/l CR was obtained, but only 88 % and 67 % of binary 20 mg/l RB5 and 14 mg/l CR was removed, respectively. This could be attributed to the competitive adsorption of the dyes.

Keywords: La-TiO₂ catalyst, photocatalytic degradation, Reactive Black 5, Congo Red.

INTRODUCTION

Wastewaters originated from textile industry contain various organic pollutants and can be considerable source of environmental pollution [1 - 5]. Most of the textile dye effluents are toxic, potentially carcinogenic and impart their colors to water sources, thus damaging aquatic flora and fauna. The organic dyes color is very intensive and their presence in water is highly visible even at very low concentrations. This effect is undesirable because the color hinders the sunlight access to aquatic pools and reduces the photosynthetic action within the ecosystem [1 - 8]. There has been considerable interest in the removal of color from the wastewaters.

Among the textile dyes, the azo dyes constitute the largest and the most important class of commercial dyes. Those dyes make up to 70 % of all textile dyestuffs produced [1, 9]. Azo dyes are known to be resistant to fading and largely non-biodegradable under aerobic conditions [9, 10]. Traditional wastewater treatment methods such as flocculation, adsorption, filtration and biological degradation have been extensively used, but these technologies only transfer the pollutant from one phase to another, thus causing secondary pollution and are usually ineffective [9 - 11]. Therefore, increasing attention to developing new methods for organic dyes degradation is observed in recent years.

There has been considerable interest during the last three decades in the application of heterogeneous photocatalytic oxidation processes involving irradiation of semiconductor particles for the degradation of various types of pollutants [1 - 9]. These processes are based on the generation of hydroxyl radicals, which are highly reactive and nonselective oxidants toward organic compounds [12]. Photocatalysis has many significant advantages in terms of the pollutants decomposition, owing to its low energy consumption, high oxidizing ability, mild reaction conditions and little secondary pollution [13]. Among the semiconductors, TiO₂ is the most widely used because of its high photocatalytic activity,
nontoxicity and high stability [6]. Titanium dioxide is generally considered to be the best photocatalyst and has the ability to detoxify water from a number of organic pollutants [6]. Many studies deal with photocatalytic decolorization of textile dyes with TiO$_2$ [1 - 17], but there are very limited studies on degradation of dye mixtures [11, 18 - 20]. Usually textile dye effluents contain mixture of organic pollutants and the simultaneous decomposition of multi-component solutions is a very complex problem. This study continues our previous research on synthesis, characterization and properties of modified nanosized TiO$_2$ powders by nonhydrolytic sol-gel method [21 - 23]. The main focus of these papers was the phase formation, short range order and optical properties of pure and doped TiO$_2$ powders.

In this work photodegradation of single and binary mixture of two azo dyes - Reactive Black 5 (RB5) and Congo Red (CR) was studied in La-TiO$_2$ suspension under UV irradiation. TiO$_2$ has been doped with La in order to improve its photocatalytic activity and was prepared by nonhydrolytic sol-gel method. The degradation of single and binary mixtures of dye solutions were studied at different reaction conditions.

EXPERIMENTAL

Sample preparation and characterization
La-doped TiO$_2$ nanopowders (6 nm) were prepared by non-hydrolytic reaction from titanium(IV) chloride, benzyl alcohol and lanthanum(III) nitrate. The full procedure is described in a previous work [24]. The phase transformations and structure of synthesized La-TiO$_2$ powdered samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance X-ray apparatus).

Photocatalytic degradation experiments
The photocatalytic degradation of dyes by La-TiO$_2$ nanopowders was studied in La-TiO$_2$ suspension under UV irradiation. The effect of various experimental parameters, such as: initial pH, initial concentration of dye and dose of catalyst was determined by varying one of the parameters, while keeping others constant.

Initially, titanium sample was added to the dye solution to form suspension. Prior to irradiation, the suspension was magnetically stirred for 30 min in dark to reach an adsorption-desorption equilibrium. A black light blue lamp (Sylvania BLB 50 Hz 8W T5) was used as UV radiation source with a peak of 365 nm. The UV light lamp was fixed at 10 cm above the treated solution. Additional blank experiments were performed with dye solutions without catalysts in order to estimate the possibility for direct photolysis of the dyes. All photocatalytic tests were performed at magnetic stirring (400 rpm) and room temperature of 25°C. At a certain time intervals aliquot samples were taken out from the test solutions, centrifuged for 15 min at 5500 rpm and filtered to remove the catalyst particles.

The photocatalytic degradation was monitored by measuring the absorbances of clear aliquots by a Jenway 6505 UV-Vis spectrophotometer at the characteristic wavelengths of the dyes – 500 nm for CR and 600 nm for RB5. The percentage decoloration ($D\%$) was calculated as follows:

$$D\% = \frac{C_o - C_t}{C_o} \times 100,$$

where $C_o$ is the initial concentration and $C_t$ is the concentration at illumination time $t$.

RESULTS AND DISCUSSION

XRD pattern of La-doped TiO$_2$ is shown in Fig. 1. It is seen that anatase (TiO$_2$) (JCPDS 78-2486) is a dominating crystalline phase detected by XRD. No peaks of rutile were observed. Moreover, lanthanum was not observed in the patterns, as well. Obviously, modification by lanthanum cannot enhance a phase transformation of anatase to rutile. In our previous investigations, it was

![Fig. 1. XRD pattern of La-doped TiO$_2$.](image-url)
established that Fe and N co-doping enhanced rutile crystallization which appeared at lower temperatures (500°C) [25]. Average particle sizes of the as-synthesized La-doped TiO$_2$ samples calculated from diffraction line broadening using Scherrer equation is about 6 nm. For comparison, the particle size of pure TiO$_2$ obtained by nonhydrolytic sol-gel method is ~20 nm and these results are published elsewhere [22]. Probably, this is due to the nature of used precursors, experimental conditions as well as to applied non-hydrolytic sol-gel synthesis method [21 - 25].

**Study of absorption spectra**

The absorption spectra of aqueous solutions of CR (14 mg/l), RB5 (20 mg/l) and the same concentration of their mixture show that the $\lambda_{\text{max}}$ and maximum absorbance values do not change (Fig. 2). Two distinct pics are observed for CR and RB5 and therefore the degradation of these dyes in the mixture was studied separately at their corresponding $\lambda_{\text{max}}$ values of 500 nm for CR and 600 nm for RB5.

**Effect of initial pH**

pH value is one of the most important factors influencing the rate of degradation of organic compounds in the photocatalytic process. To study the effect of pH on decoloration efficiency under UV light, all experiments were carried out at various pH values and constant initial dye concentrations (14 mg/l CR, 20 mg/l RB5) and La-TiO$_2$ catalyst loading (0.67 mg/ml) (Figs. 3 and 4). The initial pH of the dye solutions was varied from 3.9 to 9.8 by adding the required volume of 1 mol solution of HCl or NaOH.

It has been observed that for both dyes the decoloration efficiency exhibits maximum at their natural pH values, without any correction – pH 6.1 for CR and pH 6.9 for RB5. Therefore the subsequent experiments were performed without addition of any acid or base to the reaction mixture.

**Effect of photocatalyst concentration**

Modification of TiO$_2$ by doping with rare metals is a promising approach for the improvement of its photocatalytic performance. Due to their larger radii lanthanide ions can be distributed mainly on the surface of TiO$_2$. It is expected that the organic pollutants will concentrate at the semiconductor surface, which can lead to the enhancement of photoactivity [24]. In our previous study we found that the addition of small amounts of La to TiO$_2$ was favorable for the photocatalytic activity under UV irradiation [24].

The effect of the amount of La-TiO$_2$ on decoloration of CR and RB5, respectively, at the dye original pH was studied as shown in Figs. 5 and 6. The photodegradation of both dyes increases with an increase in the amount of photocatalyst, reaches the higher value of catalyst amount (1 mg/ml) and then decreases. The reason of this observation can be explained by the fact that with the increase of catalyst dosage the total active surface area also increases. When all dye molecules are adsorbed on the catalyst surface, the addition of higher quantities of La-TiO$_2$ would have no effect on the degradation efficiency. Another cause for this is an increase in turbidity of the suspension, as a
result of excess of photocatalyst particles [26].

Higher dose of photocatalyst may not be useful both in view of aggregation as well as reduced penetration of UV light. For both dyes the most effective decomposition was observed with 0.67 mg/ml photocatalyst and this concentration was used for further studies.

Effect of the initial dye concentration in single and binary dye solutions

In order to investigate degradation of the each dye in binary solutions, the degradation studies were done by varying the initial concentrations of the studied dyes at their original pH. Keeping all other experimental parameters constant, the concentration of dyes was changed from 7 to 30 mg/l. It was observed that the photocatalytic bleaching decreases with increase in the concentration of dyes above 14 mg/l CR and 20 mg/l RB5, respectively (Figs. 7 and 8).

As the initial concentration of dye increases, the requirement of catalyst surface needed for degradation also increases [27]. Besides, high concentrations of dye impart darker color to the solution and it may act as a filter to the light reaching the surface of photocatalyst.

Photocatalytic bleaching of CR and RB5 dyes in single and binary mixtures

After 60-min UV irradiation with 0.67 mg/ml of La-TiO₂ catalyst, complete removal of single 20 mg/l RB5 and 14 mg/l CR was obtained, but only 88 % and 67 % of binary 20 mg/l RB5 and 14 mg/l CR was removed, respectively (Figs. 9 and 10). This could be attributed to the competitive adsorption of the dyes.

Improved degradation efficiency 93 % of RB5 and 82 % of CR in binary mixture of 20 mg/l RB5 and 14 mg/l CR was achieved by increasing the catalyst concentration (Fig. 11) due to increased total active surface area.
CONCLUSIONS

The photocatalytic degradation of two azo dyes, CR and RB5, was studied at different experimental conditions for single and binary dye solutions. Effects of various parameters such as pH values, initial dye concentration and photocatalyst dose were studied in order to propose the optimal conditions for maximum degradation of studied organic pollutants. The photodegradation of both dyes increases with an increase in the amount of photocatalyst up to an optimum concentration of 0.67 mg/ml and then decreases. The rate of photocatalytic bleaching decreases with increase in the concentration of dyes above 14 mg/l CR and 20 mg/l RB5, respectively. Improved degradation efficiency of RB5 and CR in binary mixture was achieved by increasing the catalyst concentration from 0.67 mg/ml to 1.33 mg/ml.

REFERENCES


