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Degradation and toxicity reduction of textile wastewater using immobilized titania nanophotocatalysis

Niyaz Mohammad Mahmoodi [a,*], Mokhtar Arami [b]

[a] Department of Environmental Research, Institute for Colorants, Paint and Coatings, Tehran 1668814811, Iran
[b] Textile Engineering Department, Amirkabir University of Technology, Tehran, Iran

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ABSTRACT

The feasibility and performance of photocatalytic degradation and toxicity reduction of textile dye (Acid Blue 25) have been studied at pilot scale in an immobilized titania nanoparticle photocatalytic reactor. UV–Vis, Ion Chromatography (IC) and chemical oxygen demand (COD) analyses were employed to obtain the details of the photocatalytic dye degradation. The effects of operational parameters such as H_2O_2, pH and dye concentration on the photocatalytic degradation of Acid Blue 25 were investigated. The aliphatic carboxylic acid intermediates and inorganic anions generated during the dye degradation process were analyzed. *Daphnia magna* bioassay has been used to test the progress of toxicity during the treatment process. Total disappearance of dye was attained. During the photocatalytic treatment process, the residual acute toxicity was reduced. The results showed that immobilized titania nanophotocatalysis capable to degradation and toxicity reduction of acid dye textile wastewater.

1. Introduction

The textile dyeing industry consumes large quantities of water at its different steps of dyeing and finishing, among other processes. The non-biodegradable nature of dyes and their stability toward light and oxidizing agents complicate the selection of a suitable method for their removal. Moreover, toxicity bioassays have demonstrated that most of them are toxic [1–6].

Daphnia magna is often used for the assessment of acute and chronic toxicity in wastewater [7]. Many European countries conduct their routine, acute as well long-term toxicity tests with *D. magna*, because of its easy growth, maintenance, relatively simple test procedure and reproducibility, as well as high sensitivity towards industrial pollutants and industrial wastewater [8].

The traditional techniques for dye removal from wastewater are the use of biological, adsorption and coagulation. Each method has its advantages and disadvantages. For example, due to the large degree of aromatics present in dye molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for decolorization and degradation. Adsorption is non-destructive, since it just transfers dyes from water to another phase, thus causing secondary pollution. Consequently, regeneration of the adsorbent materials and post-treatment of solid-wastes, which are expensive operations, are needed. Coagulation, using alums, ferric salts, or limes is also a low-cost process. However, it suffers from the disposal of the waste [9–19].

Over the last two decades, photocatalysis using titanium dioxide nanoparticle has been shown to be potentially advantageous and useful for the degradation of wastewater pollutants. Several advantages of this process are: (1) complete mineralization of organic pollutants to CO_2, water and mineral acids, (2) no waste-solids disposal problem, and (3) only mild temperature and pressure conditions are necessary. Also, titanium dioxide is (1) photoactive, (2) biologically and chemically inert, and (3) non-toxic [18–21].

Photocatalysis using titanium dioxide nanoparticle involves two kinds of reaction system, suspension and immobilized systems. In large scale applications, the use of suspensions requires the separation and recycling of the catalyst particles from the treated wastewater prior to the discharge and can be a time-consuming expensive process. In addition, the depth of penetration of UV light is limited because of strong absorptions by catalyst particles [22,23]. Above problems can be avoided by immobilization of photocatalyst over suitable supports. Although, the use of immobilized TiO_2 decreased the reaction rate due to the low surface area of catalyst available for reaction.

Considering the above-indicated facts, in the present research, the degradation of a textile dye, Acid Blue 25 (AB 25), was studied using immobilized titania nanophotocatalysis. This dye was selected as a representative pollutant due to its chemical structure (anthraquinone dye), wide application range and recalcitrant nature. Although many experimental works have been conducted

* Corresponding author. Tel.: +98 021 22956126; fax: +98 021 22947537.
E-mail address: mahmoodi@icrc.ac.ir (N.M. Mahmoodi).

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to assess the toxicity reduction of dyes using suspended titania photocatalysis [24–29], little research has been done to reduce the toxicity using immobilized titania photocatalysis from the textile wastewater [30]. The major purpose of applying the immobilized titania nanophotocatalysis for the degradation of the textile dye at pilot scale was to reduce its acute toxicity on *D. magna* which has been used to monitor toxicity diminution of different pollutants including textile industry wastewater by advanced oxidation processes [31] to non-detectable levels.

2. Experimental

AB 25 was purchased from CIBA. The descriptions of AB 25 and its chemical structure are shown in Table 1 and Fig. 1, respectively. Other chemicals were Analar grade from Merck. Titanium dioxide nanoparticle (commercial TiO_2 Degussa P25) was utilized as a photocatalyst. Its main physical data are as follows: average primary particle size 30 nm, purity above 97% and with 80:20 anatase to rutile.

Experiments were done in a batch mode immersion rectangular immobilized TiO_2 nanoparticle photocatalytic reactor made of Pyrex glass. The radiation source was two UV–C lamps (15 W, Philips) which were protected by quartz tubes. The photocatalyst (TiO_2) powder was immobilized by a UV resistant polymer in the inner surface of the reactor. Inner surfaces of reactor walls were cleaned with acetone and distilled water to remove any organic or inorganic material attached to or adsorbed on the surface and dried in the air. A pre-measured mass of TiO_2 were attached on the inner surfaces of reactor walls using a thin layer of a UV resistant polymer. Immediately after preparation, the inner surface reactor wall – polymer – TiO_2 system was placed in the room temperature (25 °C) for at least 60 h for complete drying of the polymer [1].

Photocatalytic degradation processes were carried out using 7 L solutions containing specified concentration of dye. The initial dye concentration was 50 mg/L. The degradation processes were performed at 298 K. The pH of real acid dye dyeing wastewater is acidic but varying between 3.5 and 6. Hence, the photocatalytic degradation of AB 25 was performed at natural pH (5.6). Samples were withdrawn from sample point at certain time intervals and analyzed for degradation and toxicity reduction. H_2SO_4 and NaOH were used to pH adjustment of dye solutions.

Decolorization of dye solutions was checked by measuring the absorbance of dye solutions at 603 nm at different time intervals by UV–Vis CECIL 2021 spectrophotometer. The dearomatization was monitored by UV absorption at 280 nm [32].

Ion Chromatograph (METROHM 761 Compact IC) was used to assay the appearance and quantity of formate, acetate, oxalate, SO_4^- and NO_3^- ions formed during the degradation and mineralization of AB 25 using a METROSEP anion dual two, flow 0.8 ml/min, 2 mM $NaHCO_3$/1.3 mM Na_2CO_3 as eluent, temperature 20 °C, pressure 3.4 MPa and conductivity detector.

The COD tests were carried out according to close reflux, colorimetric method [33] using a DR/2500 spectrophotometer (Hach, USA) and COD reactor (Hach, USA).

Acute toxicity of the colored wastewater was determined using *D. magna* neonates as the test species in accordance with standard methods [33]. In the first step of toxicity analyses, the samples were prepared for the test procedure. The remaining hydrogen peroxide after photocatalytic degradation was removed with an excess of sodium sulphite and any remaining sulphite was removed by bubbling O_2 [34]. The pH of the raw and treated samples was adjusted to the required value. The test animals were grown with a 16 h light/8 h dark light cycle using 1000-lux fluorescent lamps. Toxicity tests were done using ten young *daphnids* in 50 mL test beakers at pH 8.0, providing a minimum of 6 mg/L dissolved oxygen and a constant temperature of 20 °C. The LC_{50} values (lethal concentration causing 50% death) of the dye samples was calculated by interpolation of the log (percent dye wastewater dilution) versus percent death, that were established using the experimental data obtained form the acute toxicity tests [32].

3. Results and discussions

Fig. 2 shows the C/C_0 of AB 25 versus irradiation time for the various H_2O_2 concentrations. As it is clear from Fig. 2, decreasing the dye concentration obeys linear pattern towards the elapse of irradiation time for different H_2O_2 concentrations. This means that the zero order kinetics relative to dye is operative. The decolorization rate constants (k) and correlation coefficients (R^2) of AB 25 for the various H_2O_2 concentrations was shown in Table 2.

As seen in Fig. 2 and Table 2, the decolorization rate increased when H_2O_2 concentration changed from 0 to optimal concentration (600 mg/L). There were not appreciable changes at decolorization rate when the concentration of H_2O_2 further increased. Generally, the degradation rate of dye increases as the H_2O_2 concentration increases until an optimal H_2O_2 concentration is achieved. However,

Table 1
The properties of AB 25

Parameter	AB 25
Commercial name	Erio Blue GRL
C.I. number	62055
C.I. name	Acid Blue 25
Class	Acid anthraquinone dye
Color	Blue

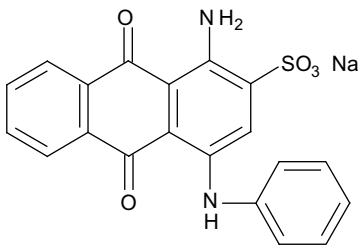

Fig. 1. The chemical structure of Acid Blue 25.

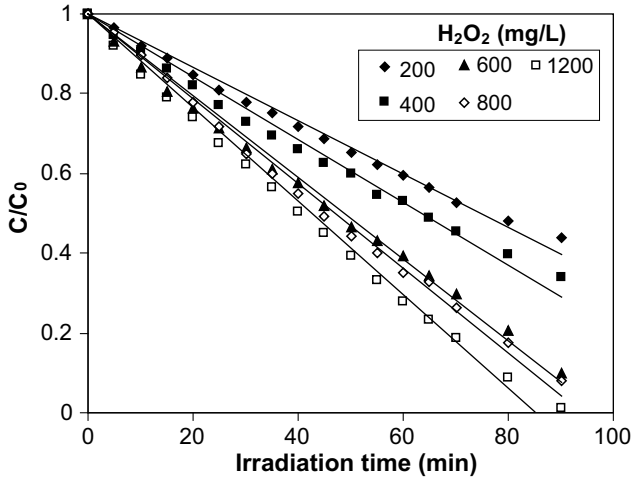

Fig. 2. Photocatalytic decolorization of AB 25 with different concentrations of hydrogen peroxide at different time intervals of irradiation (Dye 50 mg/L and pH 5.6).