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Photocatalytic Decolorization of Industrial Wastewater Under Natural Weathering Conditions

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Industrial wastewater released fromthe Spinning and Textile Factory in Sanaa was photodecolorized by using a suspension of titanium dioxide or zinc oxide, as a catalyst, under natural weathering conditions. The photocatalytic decolorization of the dyes was studied under different conditions, such as type of catalyst and the pH. The decolorization rates of the dyes have been found to be strongly affected by the mentioned parameters. These were obtained by the values of λ_{max} at 206 and 620 nm at certain intervals of time. The results showed that zinc oxide was more active than titanium dioxide when the concentration of the catalyst was 1.6 g L^{-1}. The rate of decolorization of industrial wastewater was found to be higher in basic medium. A radical mechanism for photocatalytic degradation with ultraviolet light and a photosensitized degradation with visible light are proposed.

Key Words: Industrial wastewater, Photocatalytic decolorization, Weathering conditions.

INTRODUCTION

It is well known that textile factories are using a huge amount of different types of dyes. Dyes are regarded as serious hazardous compounds causing serious diseases such as cancer, hormone deficiency and bronchitis[1]. Very small amounts of dyes, *i.e.*, below 1 ppm, cause a clear visible colour in wastewater and the removal of coloured compounds was regarded to be more important than removal of colourless chemicals[2].

The removal of these types of pollutants has become a more interesting project during the past two decades and many attempts have been made to develop different methods for the treatment of industrial wastewater.

Throughout industrial processes, about 15% of synthetic azo-dyes, as an example, were lost in industrial wastewater. This percentage represents a high environmental consequent pollutants because of their widespread use in textile factories, which are distributed throughout the world and their potential to form toxic aromatic amines[3]. Therefore, the removal of coloured dyes from industrial wastewater in textile industries by different methods could play a great role in the treatment of industrial wastewater.

Heterogeneous photocatalysis is one of the most important methods which is widely used in the photodegradation process of textile industrial wastewater[4–7]. This method is based on the activation of a semiconductor, especially TiO_2 or ZnO, which are widely used in the existence of solar or artificial light. The mechanism of photodegradation in aquatic media is based on the excitation of one electron from the valence band of the semiconductor to the conduction band, leaving a positive hole which oxidizes the OH^- of adsorbed water on the surface of the catalyst, whereas a reduction of oxygen to form O_2^- on conduction band[8] takes place. The formation of OH^- and O_2^- leads to the formation of different types of free radicals leading to complete mineralization of the dye to CO_2 and H_2O.

Titanium dioxide and zinc oxide have been widely used as heterogeneous photocatalysts for the treatment of coloured industrial wastewater in textile industry[8–14]. However, anatase is regarded better because it is cheap, non-toxic and can be activated by solar energy[15].

The present work aims to study the photocatalytic oxidation of industrial wastewater, formed after the dying process in the spinning and textile factory, located in Sanaa, Yemen, using naked TiO_2 or ZnO. The work includes also the effects of several parameters such as the pH and type of catalyst. Moreover, the project aims to utilize solar energy to get rid of water pollutants and recycling the treated water for the use of the same factory or in any other field.

EXPERIMENTAL

Titanium dioxide powder (BDH) and zinc oxide powder (Dentam) were utilized as supplied. All chemicals were obtained from BDH of the highest purity (*ca.* 99.99%).

Experiments were conducted in April and May 2004, over a continuous 45 days period. All experiments were done at the floor of the Chemistry Department building in IBB University, in an open atmosphere between 11.00 a.m. and 1.00 p.m. Sunlight illumination was carried out in a 400 mL beaker containing 100 mL of industrial wastewater, which was used as collected from the factory. The sunlight radiation was collected using converging lens with a focal length of 5 cm. In all experiments, 400 mg of the catalyst, anatase or zinc oxide, was suspended using a magnetic stirrer in the coloured wastewater. During the irradiation of the reaction mixture, 2 mL samples of the reaction mixture were, periodically, withdrawn using a syringe with a long pliable needle. These were centrifuged to separate the solid catalyst. In each case, 1 mL of the supernatant was drawn and diluted to 50 mL to measure the absorbance at 206 and 620 nm, using ultraviolet-visible spectrophotometer, type UV 2100, supplied by Unico Company. The percentage of photodegradation of the dye was followed spectrophotometrically by comparing the absorbance at known intervals of time with a calibration curve conducted by measuring the absorbance at known wavelengths with different concentrations of the coloured industrial wastewater, which was collected from the spinning and textile factory located in Sanaa, Yemen.

RESULTS AND DISCUSSIONS

A number of experiments were accomplished to determine the best conditions necessary for the degradation of the maximum amount of the dye existing in the wastewater. The photodegradation process was followed by measuring the absorbance. It was found that the existence of the semiconductor and sunlight are essential to the reaction carried out, whereas no degradation was observed in the absence of the catalyst.

Fig. 1 shows that ZnO is more active than TiO_2. This result is in good agreement with previous findings[14]. Moreover, Kamat and Vinodgopal[16] reported that, although the emission spectra of degassed samples of TiO_2 and ZnO exhibited emission maxima around 500 nm, the relative quantum yield on ZnO particles was twice that on TiO_2.

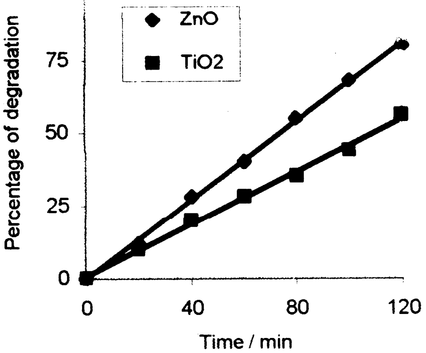

Fig. 1. Photocatalytic degradation of coloured industrial wastewater on TiO_2 and ZnO under natural weathering conditions

Concerning the effect of pH upon the photodegradation process, the rate of degradation increased by 1.86% when the pH was increased from 5.41 to 10.24. The pH of the collected industrial wastewater was 5.41. This phenomenon could be explained according to the findings of Munuera *et al.*[17] The authors detected that the adsorbed molecular water and the most acidic hydroxyl groups on the surface of titanium dioxide, which are removed at lower temperatures (infrared bands at 3680 and 3620 cm^{-1}), did not greatly influence the photoactivity of titanium dioxide. However, the removal of the most basic OH groups (infrared band at 3730 cm^{-1}) at temperature higher than 537 K resulted in the decay of photoactivity. So the interaction of exitons with basic OH^- groups was considered as an important step in photoadsorption:

$$OH^- \text{ (basic)} + h - e \text{ } (Ti^{+3}O^-, \text{exiton}) \longrightarrow {}^{\cdot}OH + e^- \text{ (free)} \qquad (1)$$

The mechanism for photocatalytic degradation and photosensitized degradation of dyes

Because only light below 356 nm is absorbed and capable of transferring an electron from the valence band to the conduction band of TiO_2 or ZnO, only 5% of solar energy reaching the earth surface could be used in the photocatalytic reaction on TiO_2 or ZnO (their band gap *ca.* 3.2 eV). However, sensitization of

TiO_2 was found to increase significantly the photocatalytic activity[14, 18–21] of TiO_2 in the existence of solar radiation. Fig. 2 shows a schematic diagram for photocatalytic degradation which is created by the small portion of ultraviolet light in solar radiation (A), while (B) shows the photosensitized degradation.

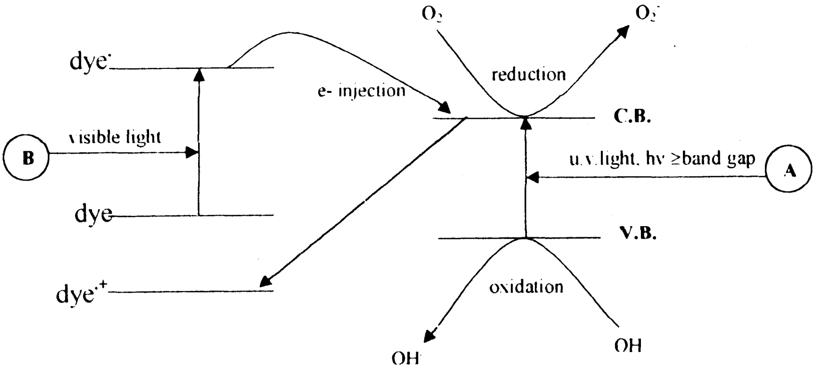

Fig. 2. Schematic diagram for photocatalytic degradation of dye: (A) photocatalytic degradation by UV light, (B) photosensitized degradation by visible light

In process (A), the photocatalytic degradation of the dye could follow the following mechanism:

$$\text{Semiconductor} + h\nu \ (\text{energy} \geq \text{energy gap}) \longrightarrow e^- + h^+ \qquad (2)$$

Bickley *et al.*[22] reported that photoholes are trapped at surface hydroxyl groups $OH_{(S)}$ and photoelectrons are trapped by molecular oxygen:

$$h^+ + OH^-_{(S)} \longrightarrow {}^{\cdot}OH_{(S)} \qquad (3)$$

$$e^- + O_{2\,(ads)} \longrightarrow {}^{\cdot}O^-_{2\,(ads)} \qquad (4)$$

Horikoshi and co-workers[23] suggested the formation of the hydroxyl radicals on the surface of the catalyst by the reaction of oxygen, water and hydroxide ion. Moreover, peroxyl radicals could also be formed by the protonation of superoxide radical anions:

$${}^{\cdot}O_2^- + H^+ \longrightarrow HOO^{\cdot} \qquad (5)$$

The ${}^{\cdot}OH_{(S)}$ radical is primarily responsible for the photocatalytic oxidation and O_2^- could react with H_2O molecule[24] to form $HOO^{\cdot}$ as follows:

$${}^{\cdot}OH_{(S)} + \text{dye} \longrightarrow \text{degradation} \qquad (6)$$

$$O^-_{2\,(ads)} + H_2O \longrightarrow OH^-_{(S)} + HOO^{\cdot} \qquad (7)$$

H_2O_2 could be formed by the combination of two ${}^{\cdot}OH_{(S)}$[25]:

$${}^{\cdot}OH_{(S)} + {}^{\cdot}OH_{(S)} \longrightarrow H_2O_2 \qquad (8)$$

Both, hydroxyl and peroxyl radicals could be shared in photodegradation process of dye molecules as follows:

$${}^{\cdot}OH \text{ or } HOO^{\cdot} + \text{dye} \longrightarrow \text{photodegradation} \qquad (9)$$

In the process indicated in (B), in the systematic diagram shown in Fig. 2, dye molecules, which are adsorbed on the surface of TiO_2 form a photosensitized catalyst, which in turn, can be excited by the visible light to achieve the ability of degradation of other dyes molecules, as follows:

$$\text{dye} + h\nu \text{ (visible light)} \longrightarrow \text{dye} \tag{10}$$

$$\text{dye}^{\cdot} + \text{semiconductor} \longrightarrow \text{dye}^{\cdot+} + e^{-} \text{ (to C.B.)} \tag{11}$$

$$O_2 + e^{-} \longrightarrow {}^{\cdot}O_2^{-} \tag{12}$$

$$^{\cdot}O_2^{-} + H_2O \longrightarrow HOO^{\cdot} \tag{13}$$

$$HOO^{\cdot} + \text{dye} \longrightarrow \text{photodegradation} \tag{14}$$

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