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ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
Vol. 5, No.2, pp.219-223, April 2008

Photocatalytic Degradation of Textile Dyeing Wastewater Using Titanium Dioxide and Zinc Oxide

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Received 23 July 2007; Accepted 22 September 2007

Abstract: Photodegradation of a real textile dyeing wastewater taken from Hilla textile factory in Babylon Governorate, Iraq have been investigated. Photocatalytic degradation was carried out over suspensions of titanium dioxide or zinc oxide under ultraviolet irradiation. Photodegradation percentage was followed spectrophometrically by the measurements of absorbance at λmax equal to 380 nm. The rate of photodegradation increased linearly with time of irradiation when titanium dioxide or zinc oxide was used. A maximum color removal of 96% was achieved after irradiation time of 2.5 hours when titanium dioxide used at 303K and 82% color reduction was observed when zinc oxide used for the same period and at the same temperature. The effect of temperature on the efficiency of photodegradation of dyestuff was also studied. The activation energy of photodegradation was calculated and found to be equal to 21 ± 1 kJ mol^{-1} on titanium dioxide and 24 ± 1 kJ mol^{-1} on zinc oxide.

Keywords: Photocatalytic degradation, Titanium dioxide, Zinc oxide, UV light, Wastewater treatment, Textile industry

Introduction

Semiconductors are used to degrade organic pollutants in water to less harmful inorganic material[1]. There have been numerous studies carried out across the globe focusing on the decolorization of textile wastewater. The importance of these types of research is being increasingly in the recent and has become a subject of major public health concern and scientific interest.

Grzechulska and Morawski[2] were considered that the removal of color from wastewaters is often more important than the removal of other organic colorless chemicals. Decolorization of effluent from textile dyeing and finishing industry was regarded important because of aesthetic and environmental concerns[3].

Hussein *et al*[4] reported that titanium dioxide and zinc oxide have good photocatalytic properties nominated both catalysts to be promising substrates for photodegradation of water pollutants and show the appropriate activity in the range of solar radiation.

Recent studies focused on the most important photocatalytic applications of titanium dioxide and zinc oxide. Xiaobo Chen and Samuel S. Mao reviewed, recently, the wide applications of titanium dioxide[5]. These applications include the photodegradation of various pollutants[6-10] killing bacteria[11] and killing tumor cell in cancer treatments[12-13].

The overall benefits of the decolorization of textile industrial wastewater may include very interesting subject, saving a huge amount of water, because textile industries are regarded as chemical intensive and water intensive[14], *i.e.* these type of industry is more pollutants and consumes a huge amount of water. The treated water may be recycled in the same factory or reused in other applications such as other industries or agriculture that require a less quality water. This is considered to be very excellent means for saving huge amounts of water, especially, in the countries which are suffered with water deficiency

The present work reports an investigation of photocatalytic decolorization of real textile wastewater of Hilla Textile Factory (Iraq), using TiO_2, and ZnO as photocatalysts with irradiation with UV-light at adifferent temperatures.

Experimental

In this study titanium dioxide powder (anatase) form and zinc oxide (Dentam) were used as supplied. These chemicals are supplied by (BDH) with a purity of 99.99%. In all experiments 150 mg of titanium dioxide or zinc oxide is suspended in 30 cm^3 of the real textile dyeing wastewater which is placed in a photoreaction cell .The real textile wastewater was filtered to remove suspended particles the solution in the cell is kept homogeneous by stirring with magnetic stirrer. The cell contains side arms for passing air and for water circulation around the cell in order to keep temperature of the reaction at a desired value.

The cell is fitted with ultraviolet radiation from a low pressure mercury lamp, type TQ150Z2 supplied by Karl Kolb Company**.** A schematic representation of the reactor is shown in Figure 1, which was used in our previous works[15-16].

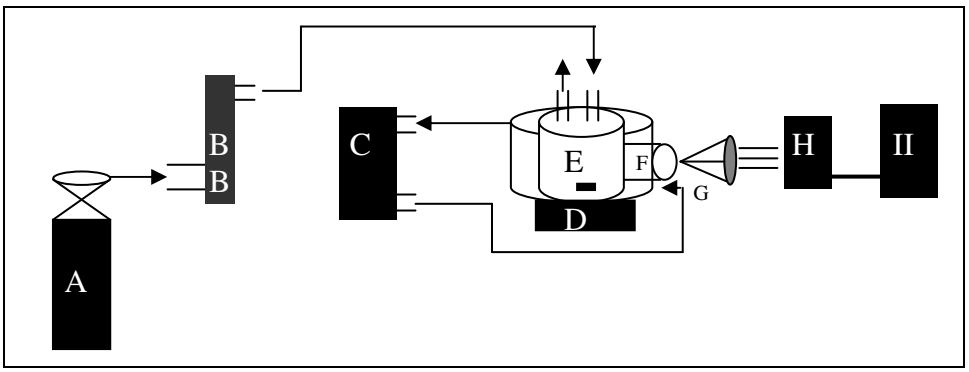

Figure 1. Schematic diagram of the experimental apparatus for photocatalytic reaction. (A) gas container, (B) gas flow meter, (C) circulating water thermostat (D) magnetic stirrer (E) quartz cell, (G) lenses, (H) low pressure mercury lamp, (I) power supply unit**.**

Periodically 2 cm^3 of irradiated samples were withdrawn by microsyringe and centrifuged to separate the solid catalyst and the absorbance of the supernatant liquid is

measured at λ=380 nm using UV-Visible Spectrophotometer (Cintra 5-GBC-Astrural.). The absorbance at a given time was compared with a calibration curve. The calibrating plot was obtained by using a known percentage of colored real textile wastewater.

Results and Discussions

Wastewater from the dyeing process was effectively decolorized using titanium dioxide or zinc oxide. Under optimal conditions, the extent of decolorization was achieved about 96 % by using TiO_2 and 82 % by using ZnO at 303K. Figure 2 shows that photodecolorization of real textile industrial wastewater is directly proportional with the time of irradiation TiO_2 was found more active than ZnO. This finding is in contrast with our previous work[4]. This disagreement may be related to the type of TiO_2 used in the two works. Moreover, in this work U.V. radiation was used, while solar radiation was used in the previous work.

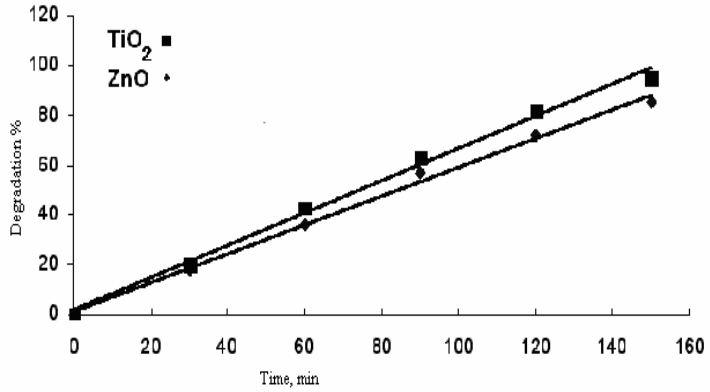

Figure 2. Photocatalytic degaradation of textile industrial wastewater on titanium oxide and zinc oxide at 303K

Figure 3 shows a schematic representation for photo catalytic degradation of dye by U.V. radiation and/ or visible radiation. The diagram indicated that there are two different pathways followed in photodecolorization processes. In the first pathway, where U.V irradiation is used in the photocatalytic reaction, electrons in the semiconductor are excited from the valence band to the conduction band leaving positive holes in the valance band. The electrons in the conduction band react with the adsorbed oxygen molecules to form O_2^- species, while the positive holes react with the adrsobed hydroxyl ions to form hydroxyl radicals. These processes could be represented in the following equations.

$$TiO_2 \text{ or } ZnO + h\nu \ (\text{ energy} \geq 3.2 \text{ e v }) \rightarrow e^- + h^+ \quad (1)$$

$$e^- + O_{2\,(ads)} \rightarrow {}^{\cdot}O_2^-{}_{(ads)} \quad (2)$$

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

The highly reactive hydroxyl radicals oxidize the dye molecules as follows:

$$OH + \text{dye} \longrightarrow \text{degradation} \quad (4)$$

In the second pathway where a solar radiation is used a photosensitization process occurs. In this process, the sensitizer (the dye) absorbs radiation in the visible range to yield an excited state of the sensitizer. The dye radicals inject electrons to the conduction band of the TiO_2 or ZnO and convert to $dye^{\cdot +}$. The electron transfer from the excited dye molecule to the conduction band of TiO_2 usually is too fast (in the range of tens of femtoseconds)[17,18]. The formed species oxidize the dye molecules, as follows:

$$\text{dye} + \text{visible light} \longrightarrow \text{dye}^{\cdot} \quad (5)$$

$$\text{dye} + \text{semiconductor} \longrightarrow \text{dye}^{\cdot+} + \text{e-}\ (\text{to C.B.}) \quad (6)$$

The formed $dye^{\cdot+}$ radical ions acts react with dye molecules in the same way of the reaction of hydroxyl radicals.

$$\text{dye}^{\cdot+} + \text{dye} \rightarrow \text{degradation} \quad (7)$$

Reaction was followed at different temperatures, in the range 293–303 K. The activation energy of 21 ± 1 kJ mol^{-1} for photodegradation of textile industrial wastewater on titanium dioxide and of 24 ± 1 kJ mol^{-1} on zinc oxide were calculated from Figure 4 .

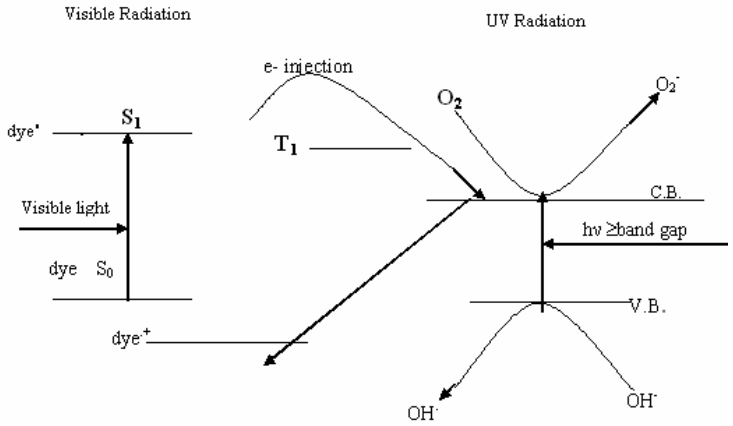

Figure 3. Schematic diagram for photocatalytic degradation of dye by U.V. radiation and/ or visible radiation

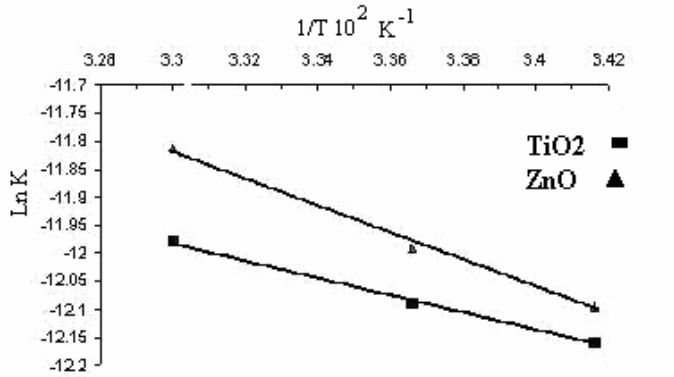

Figure 4. Temperature dependence for the photocatalytic degradation of textile industrial wastewater on titanium dioxide and zinc oxide.

The activation energy for the photocatalytic degradation of textile industrial wastewater on titanium dioxide is similar to our previous findings[16,19,20] for photocatalytic oxidation of different types of alcohols on anatase and metallized anatase. The single value of activation energy (21±1 kJ mol^{-1}) could be related to that the calculated activation energy of photooxidation of different species o titanium oxide is associated with the transport of photoelectron through the catalyst to the adsorbed oxygen on the surface. However, different values of activation energies were obtained for titanium dioxide and zinc oxide for the same

reactions. In this case the rate controlling process is associated with surface steps and accordingly, a different type of sensitization gives a different reaction rate[21].

Conclusions

1. Titainum dioxide and zinc oxide could be used powerfully in photocatalytic degredation of textile industrial wastewater, where the extent of decolorization was achieved about 96 % by using TiO_2 and 82 % by using ZnO at 303K after 2.5 hours of irradiations.
2. Different values of activation energies were obtained for titanium dioxide and zinc oxide for the same reactions (21 ± 1 kJ mol^{-1} for titanium dioxide and of 24 ± 1 kJ mol^{-1} for zinc oxide). This difference is related to the rate controlling process, which is associated with surface steps and accordingly, a different type of sensitization gives a different reaction rate

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