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PHOTOCATALYTIC TREATMENT OF TEXTILE INDUSTRIAL WASTEWATER

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ABSTRACT

The main target of this project is to investigate experimentally the removal the dyestuff from dyeing textile industrial wastewater by photosensitization process, for its reuse in the same industry or for domestic purpose and/ or irrigation. In the present work, the photocatalytic decolorization of two collected samples of real and one prepared simulated textile industrial wastewater was examined under artificial source of irradiation using titanium dioxide and zinc oxide. The effects of various operational parameters such as catalyst mass, type of catalyst, type of reactor, type of dye, dye concentration, and temperature were also investigated.

Photolysis and photocatalytic treatments were carried out over a suspension of titanium dioxide or zinc oxide under artificial irradiation. The progress of treatment stages was followed spectrophotometrically at different wavelengths. Under optimal conditions, the extent of decolorization was about 100 % after different periods of time ranging from 20 to 100 minutes. The decolorization percentages differ with the difference in type of dye used in textile industry. The results indicate clearly that titanium dioxide and zinc oxide could be used successfully in photocatalytic treatments of textile industrial wastewater. However, the order of their activity is -

$$\text{ZnO} > \text{TiO}_2\ (\text{Anatase}) > \text{TiO}_2\ (\text{Rutile})$$

Incubations of colored industrial wastewater without light and without catalyst was also performed to demonstrate that decolorization of the dye requires the presence of both ; light and catalyst.

Key words: Photocatalytic treatments, Industrial wastewater, Titanium dioxide, Zinc oxide, Decolorization efficiency.

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INTRODUCTION

Photosensitization process occurs as a result of initial absorption of radiation by colored molecules in wastewater, which will act as photosensitizer.

The band gap of TiO_2 and ZnO is slightly more than 3.0 eV and that means a very small part in the solar radiation could be suitable for the excitation of electrons from the valence band to the conduction band (the ultraviolet part only). However, the existence of colored compounds in the wastewater guarantees the utilization of visible light by photosensitization process. Photosensitization is based on the utilization of longer wavelength than that in UV region, in the existence of a suitable conductor to degrade the organic compounds to CO_2, H_2O and mineral acid. This process is very interesting in Arab homeland due to the more availability of solar energy. The advantage of this technique is to avoid the production of other colored contaminants.

Semiconductors are used to degrade organic pollutants in water to less harmful inorganic material[1]. Numerous studies have been 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 times and it has become a subject of major public health concern and scientific interest.

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

In our previous studies[4-9], we have reported that titanium dioxide and zinc oxide have good photocatalytic properties and both catalysts are nominated to be promising substrates for photodegradation of water pollutants as they show the appropriate activity in the range of solar radiation.

Recent studies have focused on the most important photocatalytic applications of titanium dioxide and zinc oxide. Xiaobo and Samuel[10] reviewed, recently, the wide applications of titanium dioxide. These applications include the photodegradation of various pollutants[11 -15] killing bacteria[16] and killing tumor cell in cancer treatments[17-18].

In recent years, there is a substantial interest in decolorization of industrial wastewater, especially textile wastewater. Textile industry generates large quantities of wastewater and also regarded as very toxic due to the difficulty of its disrobement by physical, chemical, and microbiological methods[19]. 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 and water intensive[20], i.e. these type of industries produce 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 requires less quality of water. This is considered to be very excellent means for saving huge amounts of water, especially, in the countries, which are suffering with water deficiency.

Numerous studies focused on decolorization of industrial wastewater using different methods of treatments; however, most of these methods have difficulty in practical uses. In recent studies, different systems were used, such as, ozonation[21-22], H_2O_2/UV[23-25], photocatalysis[26-27], photo-Fenton[28-29], electrocoagulation[30], sonolysis[31], gamma–radiolysis,(32) biological[33-34] and combined anaerobic–photocatalytic treatment[35].

The aim of the present project is to investigate photocatalytic decolorization of real and simulated textile wastewater using TiO_2, and ZnO as photocatalysts irradiated with artificial radiations at different conditions.

EXPERIMENTAL

Different types of photocatalytic reactors were experimented in this work. Fig. 1 shows the photograph of the more effective reactor and close to the real applications. The reactor consisted of a graduated 400 cm^3 Pyrex glass beaker and a magnetic stirring set up. The radiation source was a Philips 125W/542 high pressure mercury lamp (Holland). The lamp was positioned perpendicularly above the beaker.

The mercury lamp was allowed to warm up for 3 minutes to ensure a stable light intensity before commencing a reaction. TiO_2 P-25 anatase was purchased from Degussa, TiO_2 rutile was obtained from Fluka and zinc oxide with 99.5% purity was supplied by Carlo ERBA.

In all experiments, the required amount of the catalyst was suspended in 100 cm^3 of industrial wastewater using a magnetic stirrer. At predetermined times; 1.5 cm^3 of reaction mixture was collected and centrifuged (4,000 rpm, 15 minutes) in an 800B centrifuge. The supernatant was carefully removed by a syringe with a long pliable needle and centrifuged again at same speed and for the same period of time. This second centrifugation was found necessary to remove fine particles of ZnO or TiO_2. After the second centrifugation, the absorbance at certain wavelengths of the supernatants was determined using ultraviolet-visible spectrophotometer, type UV-1650PC, Shimadzu and visible spectrophotometer type v-1000, T-ChromoTech.

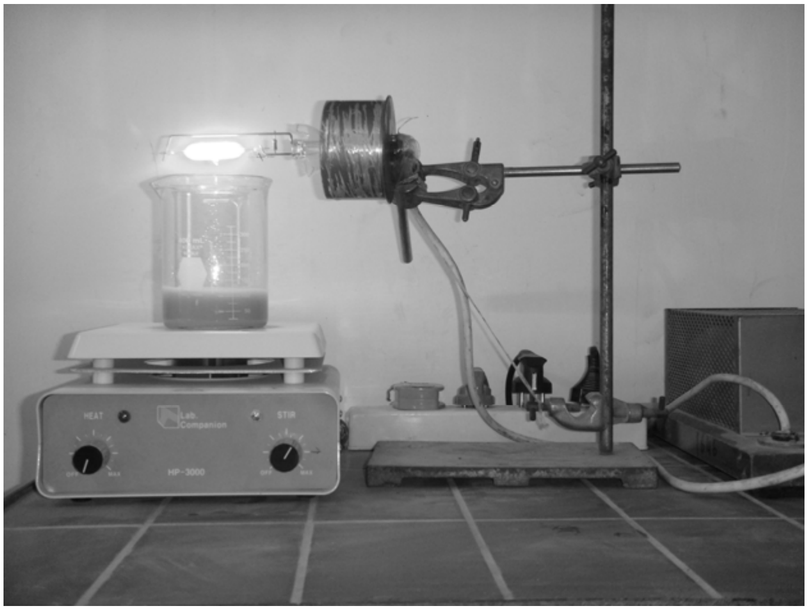

Fig. 1: Photocatalytic reactor

Decolorization efficiency (DE) was calculated from a mathematical equation adapted from measurements of decolorization used before[36,37].

$$DE = \frac{(\text{Absorbance})_o - (\text{Absorbance})_t}{(\text{Absorbance})_o} \times 100 \qquad \ldots(1)$$

Where $(\text{Absorbance})_0$ is the absorbance before irradiation and $(\text{Absorbance})_t$ is the absorbance at time t. To check the validity of the previous equation for used textile industrial wastewater, the photodegradation percentage of the dye was followed, spectrophotometrically, by a comparison of the absorbance, at specified interval of times, with a calibration curve accomplished by measuring the absorbance, at known wavelengths, with different concentrations of the dye solution.

A set of experiments has been carried out to determine the optimum conditions, which led to high decolorization efficiency (DE). These experiments include the sufficient weight of catalyst, the concentration of dye, temperature, light, and type of photocatalytic reactor.

RESULTS AND DISCUSSION

Effect of catalyst mass

Photocatalytic decolorization of real textile industrial wastewater using different masses of anatase or rutile or zinc oxide and mercury lamp as a source of irradiation was studied in an open atmosphere at 298.15 K**.** Rate of decolorization was obtained from the slopes of linear reaction progress. Figs. 2 and 3 show that weight of 175 mg of anatase is sufficient for the maximum rate of decolorization.

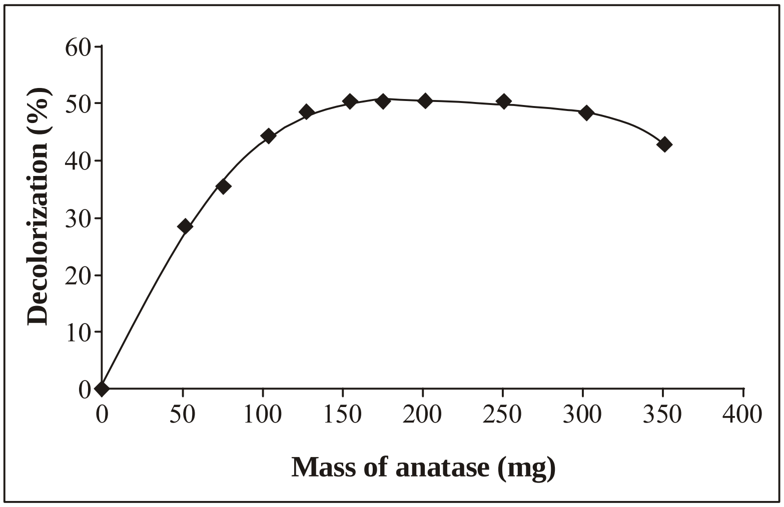

Fig. 2: Effect of mass of anatase on decolorization % of real textile industrial wastewater

The effect of ZnO masses on photocatalytic degradation of real and simulated textile industrial wastewater was also studied. The results indicated that the optimum mass, which was needed for maximum decolorization efficiency was independent on type of wastewater or time of irradiation or type of irradiation source. Fig. 4 shows the effect of mass of ZnO on decolorization % of simulated textile industrial wastewater after 10 and 20 minutes of irradiation. The results indicate that 350 mg of ZnO is sufficient for the maximum rate of decolorization.

The results of the effect of titanium dioxide (anatase and rutile) and zinc oxide masses on the photocatalytic decolorization of real and prepared simulated textile dyeing wastewater show that the decolorization efficiency increases with increase in masses of catalysts and it become constant at a certain mass and then started to decrease with increasing the mass of catalyst further. The increasing catalytic activity with increase in masses of catalyst was explained due to increasing availability of photocatalysts sites[38] and the decrease of catalytic activity after the plateau region is related to increasing of light scattering due to the excess of catalyst.

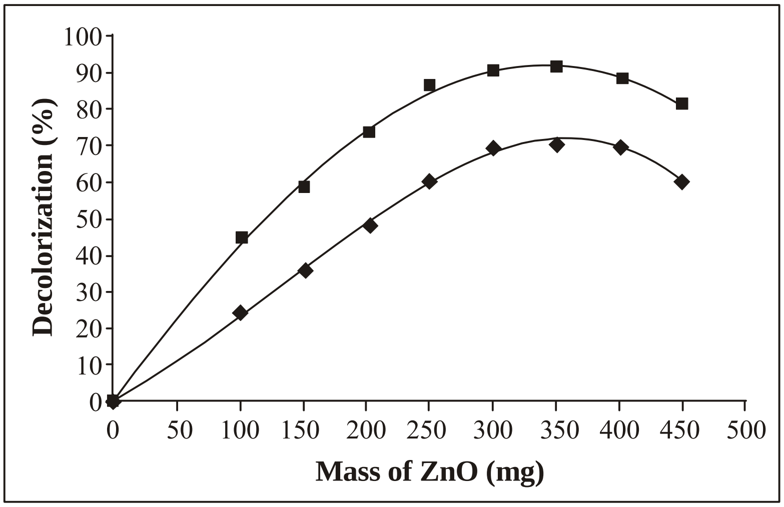

Fig. 3: Mass effect of ZnO on decolorization of simulated textile industrial wastewater

Effect of type of catalyst

Decolorization percentage of real textile industrial wastewater on rutile, anatase, and zinc oxide for 60 minutes at 298.15 K showed that the activity of different catalysts fell in the sequence.

$$ZnO > TiO_2 \text{ (Anatase)} > TiO_2 \text{ (Rutile)}$$

Fig. 4 shows that zinc oxide was three times more active than that of rutile and two times than that of anatase. However, the amount of zinc oxide required reaching the optimum activity is two times than that for titanium dioxide (anatase or rutile).

Effect of dye concentration

Fig. 5 shows UV-Visible spectra of decolorization of real textile industrial wastewater after 60 minutes of irradiation for different initial dye concentrations on anatase at 298 K with the initial real dye concentrations (25 % - 100 %). The results indicate that decrease in dye concentration decreases the time of decolorization also. Fig. 6 shows UV-Visible spectra of decolorized real textile industrial wastewater after 60 minutes of irradiation for different initial dye concentrations (25 % - 100 %) on anatase at 298 K.

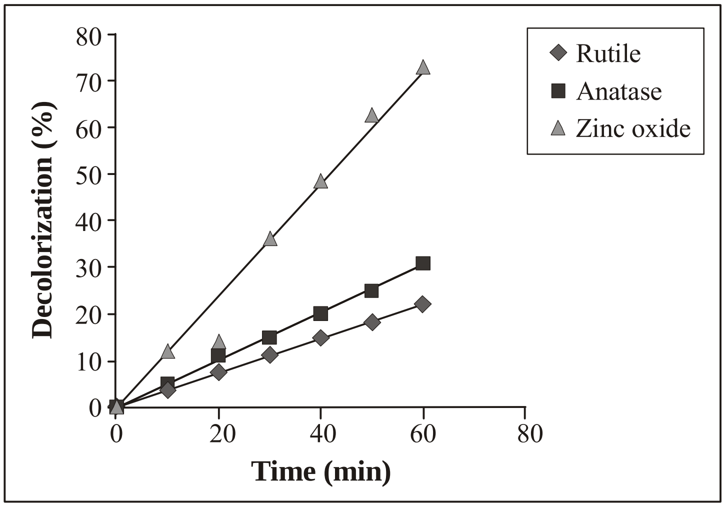

Fig. 4: Decolorization percentage of real textile industrial on wastewater on different catalysts

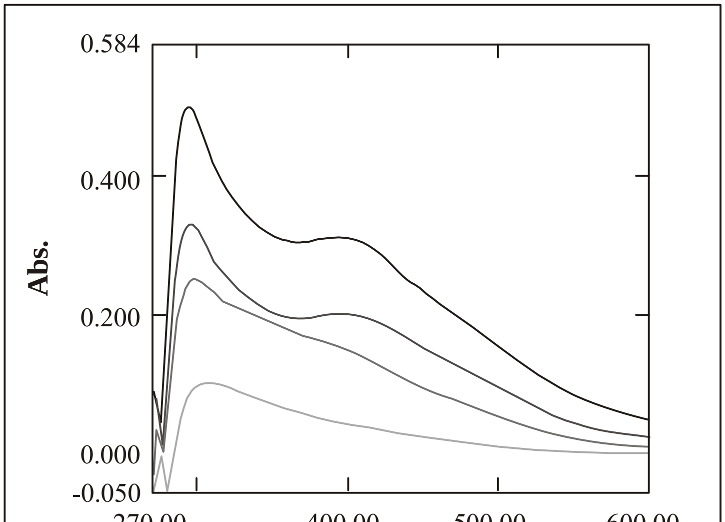

Fig. 5: UV-Visible spectra of decolorization of real textile industrial wastewater after 60 minutes of irradiation for different initial dye concentrations on anatase at 298 K

This behavior could be explained due to complete coverage of catalyst active sites by dye ions, when the concentration of real textile industrial wastewater is less than 25 % of the original concentration[39]. The more concentrated dye may also cause light screening so the light intensity will be reduced. This could be explained by the results shown in Fig. 6, where the decolorization percentage decreased linearly with increase in dye concentration.

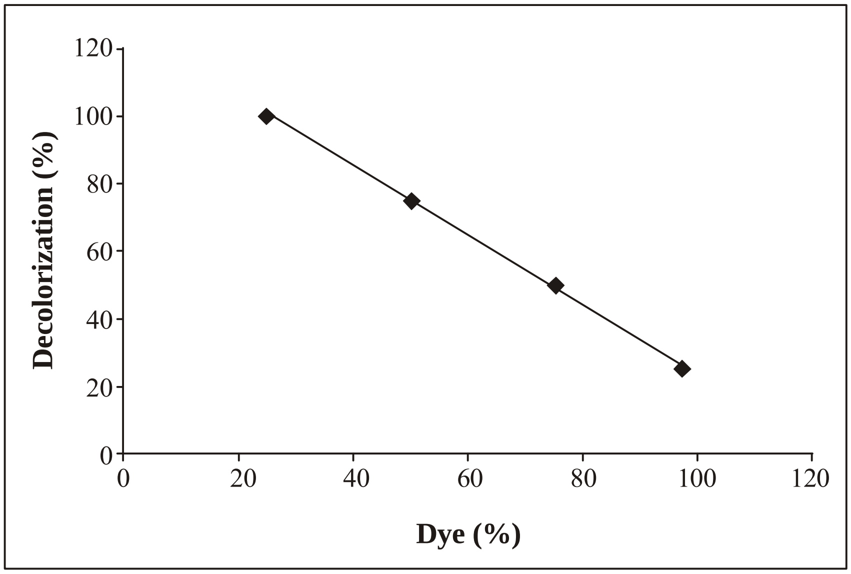

Fig. 6: The change of decolorization percentage of real textile industrial wastewater and initial dye concentrations on anatase at 298 K.

Effect of temperature

Reaction was followed at different temperatures in the range 290.15- 319.15 K using mercury lamp and 175 mg of anatase or rutile and 350 mg of zinc oxide. The results indicate that the decolorization of real textile industrial wastewater with time increases with increasing temperature for all types of catalysts. Fig. 7 shows the changes of rate of decolorization of real textile wastewater with time at four different temperatures in the range 290.15- 319.15 K using mercury lamp and 350 mg of zinc oxide.

The results show that higher temperature is significantly helpful to diminish the color of textile industrial wastewater. Complete decolorization of real textile industrial wastewater was obtained after 50 minutes of irradiation with mercury lamp using 350 mg of ZnO at 319.15 K. However, the decolorization efficiency was 52.3 % at the same condition, when the temperature was reduced to 290.15 K. Similar results were obtained in our previous work[8], when anatase was used as a photocatalyst.

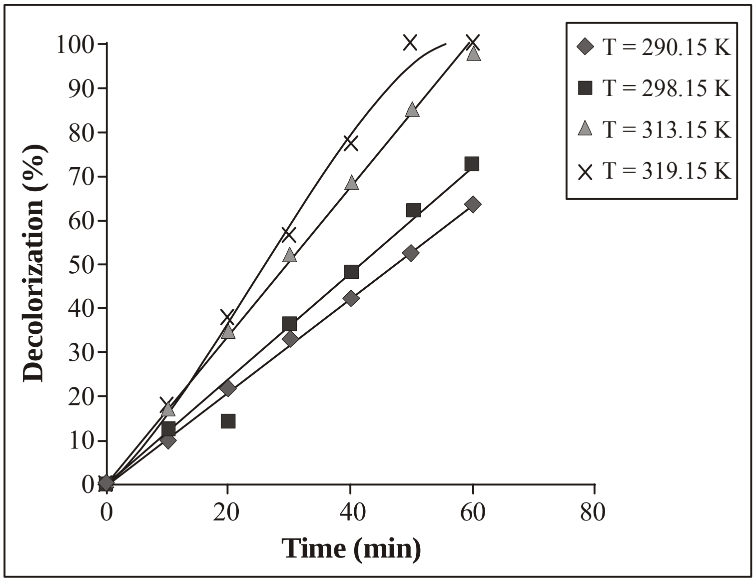

Fig. 7: Effect of temperature on decolorization efficiency

CONCLUSIONS

(i) The existence of catalyst and lights are essential for photocatalytic degradation of colored dyes.

(ii) Dye concentration, catalyst concentration, and temperature have a considerable effect on decolorization efficiency (DE) (%).

(iii) Complete decolorization of textile industrial wastewater could be obtained, after less than one hour of irradiation at 320 K, when 3.5 g L^{-1} ZnO was used and in less than 1.5 hours, when 1.75 g L^{-1} of anatase was used at the same temperature.

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