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SOLAR PHOTOLYSIS AND PHOTOCATALYTIC TREATMENT OF TEXTILE INDUSTRIAL WASTEWATER

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ABSTRACT

The objective of this research was to investigate experimentally the removal the dyestuff from dyeing textile industrial wastewater by photosensitization process, for reusing it in the same industry or for domestic purpose and/ or irrigation. In this study, the photocatalytic decolorization of two collected samples of real and one prepared simulated textile industrial wastewater using titanium dioxide and zinc oxide were examined under natural weathering conditions. The effect of various operational parameters such as catalyst mass, type of catalyst, type of reactor, type of dye, dye concentration, and temperature were investigated.

Photolysis and photocatalytic treatments were carried out over a suspension of titanium dioxide or zinc oxide under solar irradiation. The progress of treatment stages was followed spectrophotometrically at different wavelength. Under optimal conditions, the extent of decolorization was 100% after different periods of time ranging from 10 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 efficiently in photocatalytic treatments of textile industrial wastewater. However, the activity fell in the sequence:

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

Decolorization of real and simulated textile industrial wastewater without light and without catalyst was performed to demonstrate that decolorization of the dye depends on the presence of light and catalyst, both.

Key words: Solar photolysis, Photocatalytic reactions, Industrial wastewater, Titanium dioxide, Zinc oxide, Decolorization efficiency.

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INTRODUCTION

Water shortage in many developing countries is being recognized as one of the most serious political and social issues at present. Arab world will face this problem in a very near future. However, the availability of sunlight in this area could become the key of solving this problem. The direct solar radiation in the Arab homeland is ranging between 4.1-6.7 KWH/day. Quite a large amount of water could be saved by recycling industrial wastewater by applying photosensitization process. Textile industries, which are dispersed widely in Arab world used a huge amount of water. Moreover, the textile dyes were considered as major environmental pollutants and where, about 15% of the dyes are lost in the dyeing process and released in the industrial wastewater[1,2].

Different physical, chemical and biological as well as the various combinations of pre-treatment and post-treatment techniques have been developed over the last two decades for industrial wastewaters treatment in order to meet the ever-increasing requirements of human beings. However, the photocatalytic degradation processes are gaining importance in this area, since these processes result in complete mineralization with operation at natural conditions of temperature and pressure. The large bang gap of titanium dioxide and zinc oxide (~ 3.2 eV) put a limitation of using these semiconductors in photocatalytic degradation under natural weathering conditions. Only 4-6% of the overall solar intensity could be useful in such photodegradation processes. However, the existence of dye on the surface of catalyst reduces the energy required for excitation and then increases the efficiency of the excitation process by extending its absorption in the visible region of the spectrum.

Muruganandham and Swaminathan[3] studied the photocatalytic degradation of dyes on titanium dioxide under solar irradiation. Photocatalytic degradation of textile dye, using ZnO as the catalyst was also carried out under sunlight illumination and it was found that in addition to removing the color from the dye solution, the COD of the solution was also reduced. They explained that the reduction of COD was related to the mineralization of the produced fragments.

We have investigated previously, prolifically, the decolorization, photodegradation, and phytoremediation of many water soluble toxic compounds in industrial wastewater obtained from some factories in the Arab homeland. The treated wastewaters could be recycled in the same industry or reused in another industry or for agricultural fields. The efficiency of these methods of treatments are between 70-95 %[4-10].

The aim of this work is to investigate photocatalytic decolorization of real and simulated textile wastewater using TiO_2 and ZnO as photocatalysts with irradiation with

solar radiations at different conditions.

EXPERIMENTAL

Experiments were carried out during December, 2008 till July 2009. All experiments have been performed at the floor of Chemistry Department building in College of Science, Babylon University, in an open atmosphere between 11.00 a.m.-1.00 p.m. Sunlight illumination was accomplished in a 300 cm^3 glass container containing 100 cm^3 of the industrial wastewater solution as shown in Figure 1. The sunlight radiations were collected using converging lens with a focal length of 14 cm. In all experiments, a certain amount of the catalyst, titanium dioxide (anatase or rutile) or zinc oxide, was suspended in industrial wastewater solution using a magnetic stirrer.

At predetermined times; 2 cm^3 samples of the reaction mixture were withdrawn using a syringe with a long pliable needle 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 the 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.

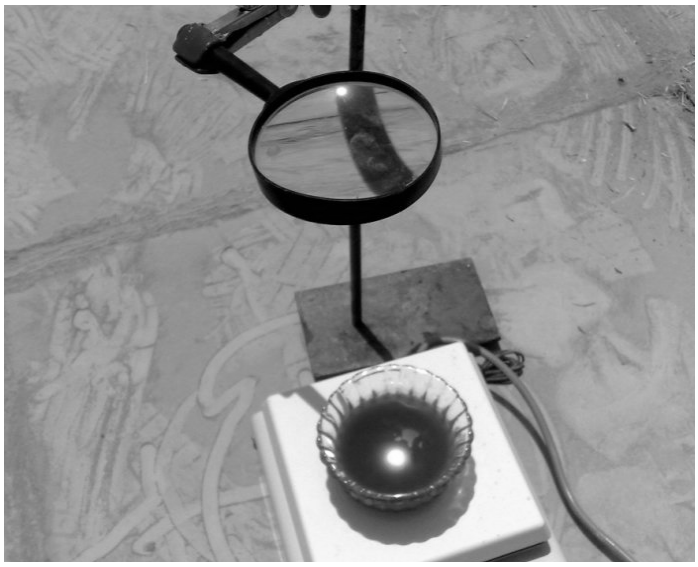

Fig. 1: Solar reactor

The photodegradation percentage of the dye was followed spectrophotometrically by a comparison of the absorbance, at specified interval times, with a calibration curve accomplished by measuring the absorbance, at known wavelengths, with different concentrations of the dye solution. Figure 2 shows UV-Visible spectra of different concentrations of real textile industrial wastewater.

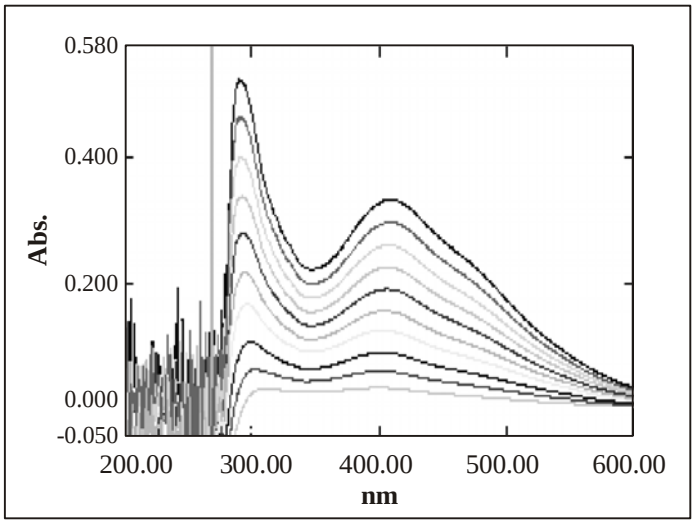

Fig. 2: UV-Visible spectra of different concentrations of real textile industrial wastewater

A set of experiments were also performed in the absence or presence of the semiconductor in the presence and absence of sunlight**.**

Titanium dioxide 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.

Decolorization efficiency (DE) was calculated from a mathematical equation adapted from measurements of decolorization used as reported earlier.[11,12]

$$DE = \frac{(Absorbance)_0 - (Absorbance)_t}{(Absorbance)_0} \times 100$$

Where $(Absorbance)_0$ is the absorbance before irradiation and $(Absorbance)_t$ is the absorbance at time t. To check the validity of the previous equation for use in case of textile industrial waste water, the photodegradation percentage of the dye was followed spectrophotometrically, by a comparison of the absorbance, at specified interval 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 maximum decolorization efficiency (DE). These experiments include the sufficient weight of catalyst, the concentration of dye, temperature, light, and type of catalyst.

RESULTS AND DISCUSSION

The effect of catalyst mass

Photocatalytic decolorization of real textile industrial wastewater using different masses of TiO_2 (rutile and anatase) varying from 0 to 350 mg was studied in an open atmosphere. The results are plotted in Figure 3.

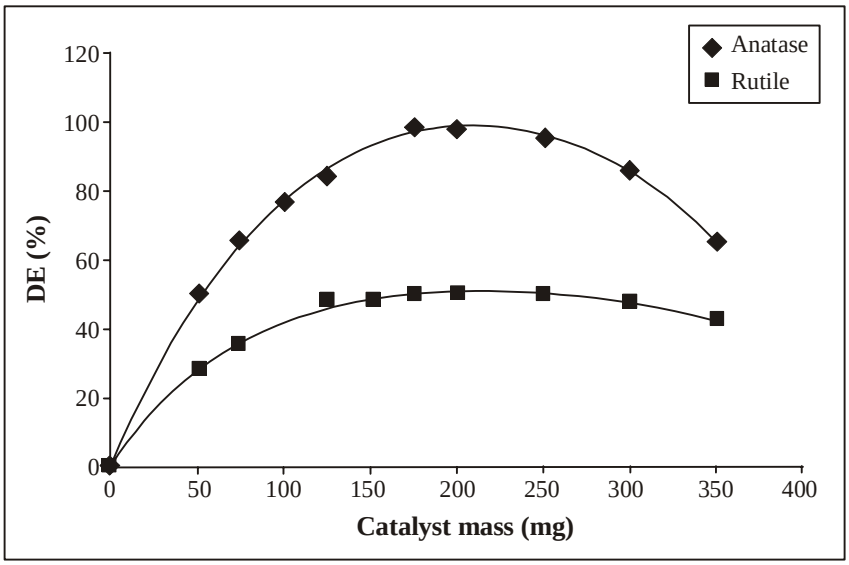

Fig. 3: Effect of TiO_2 mass on DE (%) of real textile industrial wastewater

These effect of catalyst mass on decolorization efficiency (DE) % of real textile industrial wastewater has also been investigated by employing different masses of ZnO varying from 0 to 450 mg under natural weathering conditions for 10 and 20 minutes of irradiation and the results are plotted in Figure 4.

The results in both these cases indicate that the decolorization efficiency increases with increase in catalysts mass and then it becomes constant. It is clear from consideration of the catalyst concentrations at which the activity plateau were achieved that the mass effect

does not depend upon the type of dye and source of irradiation. Moreover, plateau regions were achieved and then the activity of decolorization decreased with increasing catalyst concentration, for all types of catalysts used in this project. This behavior is more likely to arise from variation in the intensity of radiation entering the reaction vessel and how the catalyst utilizes that radiation. Light scattering by catalyst particles at higher concentration lead to decrease in the passage of irradiation through the sample leading to poor light utilization[13]. These results are in good agreement with our previous findings[8] and with those reported before[14,15]. Zhao and Zhang[16] found that the rate of degradation on ZnO increased with increasing ZnO dosage and explained that the reaching to maximum dosage was related to the entirely absorption of incident photons and the maximum dosage was changed with the change in light intensity.

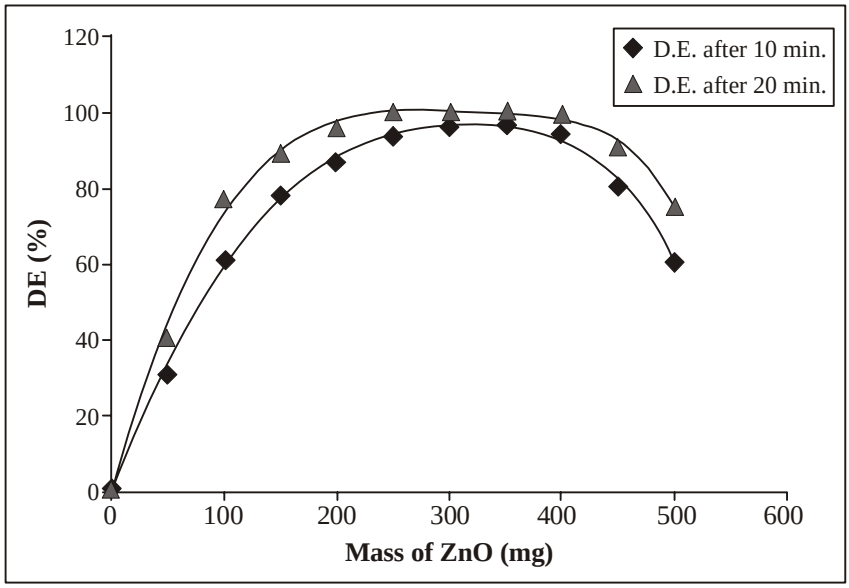

Fig. 4: Mass effect of ZnO on DE (%) of real textile industrial wastewater for different times of irradiation

The effect of type of catalyst and solar radiation

Decolorization efficiency of real textile industrial wastewater in the present and absent of catalyst and in the present and absent of solar radiation was also invistigated. The results indicate that the activity of different catalysts fell in the sequence:

ZnO > TiO_2 (Anatase) > TiO_2 (Rutile) > in the absent of catalyst = in the absent of solar radiation = 0

The results are plotted in Figure 5.

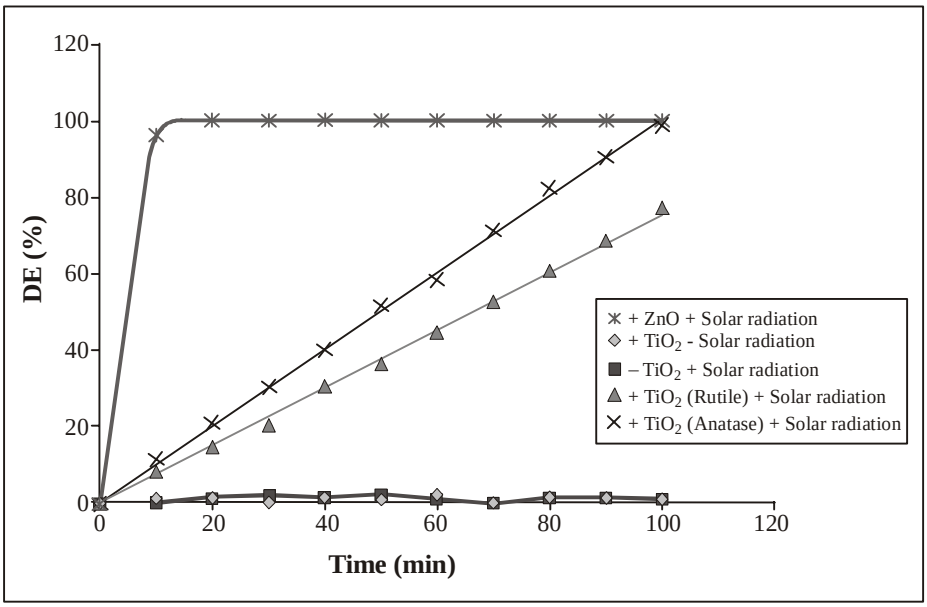

Fig. 5: Photocatalytic decolorization of real textile industrial wastewater at different conditions

These results also indicate that there was no dark reaction. Incubations of colored industrial wastewater without solar radiation and/or without catalyst was performed to demonstrate that decolorization of the dye was dependent on the presence of both; light and catalyst.

Effect of time of irradiation

The rate of decolorization was found to increase significantly with time of irradiation. Under optimal conditions, the extent of decolorization was about 100% after different periods of time ranging from 10 to 100 minutes under solar irradiation depending on type of catalyst.

It was noticed that the decolorization percentage reached 100% after less than 20 minutes of irradiation in the presence of ZnO. However, a complete decolorization needs more than 80 minutes in the case of using anatase as shown in Figure 6.

These results are in a good agreement with our previous findings[17]. It is believed that reduction of original color to colorless form is irreversible in nature and the

photocatalytic degradation processes followed the pseudo first-order kinetics according to the Langmuir–Hinshelwood model.

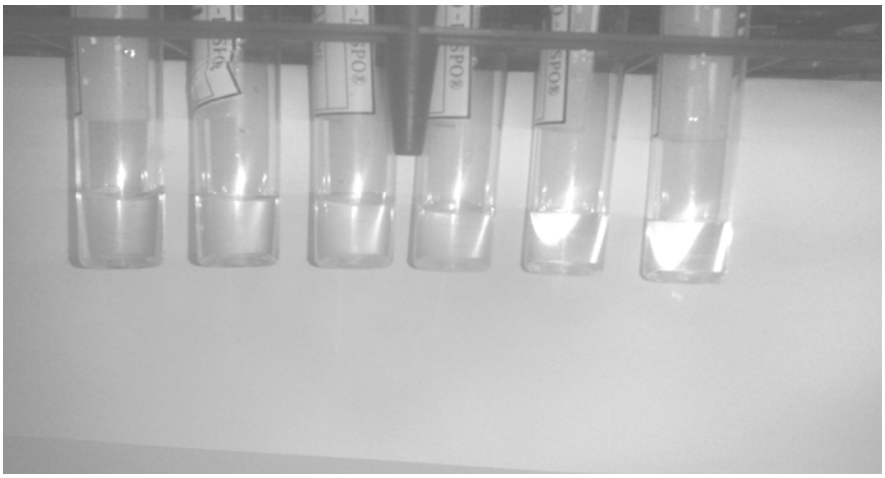

Fig. 6: Changes of real textile industrial wastewater color with time using anatase and solar radiation

Effect of dye concentration

The results in Table 1 show the changing of rate of decolorization of real textile industrial wastewater on 175 mg of anatase at 298 K with the initial direct dye concentrations (25 %-100 %) at different times. The results indicate that decrease in dye concentration decreases the time of decolorization.

Table 1: Change of decolorization percentage with dye concentration on anatase

Dye Conc. (%) / Time (min.)	100	75	50	25
0	0.00	0.00	0.00	0.00
10	11.23	23.25	30.65	44.65
20	20.88	41.34	60.28	88.44
30	30.43	62.22	91.55	100
40	40.22	81.57	100.00	100.00
50	51.65	98.78	100.00	100.00

The inverse proportionality of decolorization efficiency with the initial dye concentration was found independent on the type of catalyst.These results are in good agreement with those reported before[18,19]. A decrease in decolorization efficiency with increase in dye concentration is due to the fixed amount of the dye adsorbed on the semiconductor. The reaction system exhibits the same dependence on the amount of dye. The formed intermediates during the reaction course start a competition with the dye molecules for the surface active sites of catalyst leading to the decrease in the degradation rate. Rashed and El-Amin[18] attributed this behavior due to the reduction of generation of hydroxyl radicals on the catalyst surface since the active sites are covered by excess dye ions.

Effect of temperature

Reaction was followed at five different temperatures in the range 293.15- 315.15 K using 175 mg of anatase under solar radiation. The results as shown in Figure 7 indicate that the decolorization of real textile industrial wastewater with time increases with increasing temperature.

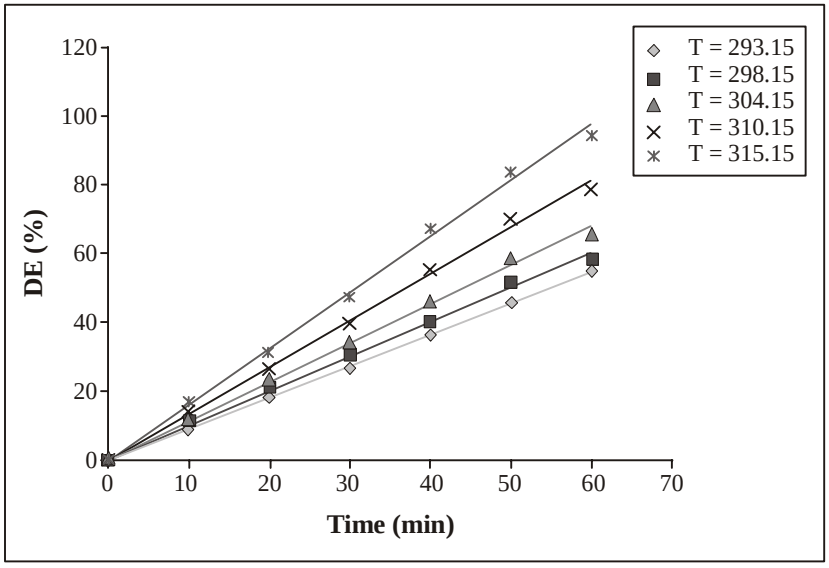

Fig. 7: Change of DE (%) of real textile industrial wastewater with time at different temperatures

The results also indicate that the decolorization of real textile industrial wastewater with time increases with increasing temperature, when solar radiation was used in the presence of rutile and zinc oxide. In a recent study, Khamnang and Sarnthina[19] reported

that rhodamine B decolorization increased with increasing temperature until it reached its maximum at 308.15 K. This observation may be related to thermal decomposition of the enzyme, which used in the study. Other researchers[20] found that increase in temperature from 298.15 to 373.15 K reduced the decolorization efficiency. However, other studies reported that the temperature did not significantly affect the decolorization of textile dyes[21,22]. These dissimilarities may be related to type of techniques used in decolorization.

CONCLUSIONS

(i) Solar photocatalytic treatment has proved as an efficient technique for decolorization of industrial wastewater through a photocatalytic process and the transformation is practically complete in a reasonable irradiation time.

(ii) Results presented in this project indicated that visible light / ZnO and visible light/TiO_2 systems could be efficiently used for photodegradation of textile industrial wastewater. The results indicate that the degree of photodegradation of textile industrial wastewater was obviously affected by different parameters. The complete removal of color could be achieved in a relatively short time of about 20 minutes, when ZnO was used under solar irradiation.

(iii) In Iraq, intense sunlight is available throughout the year and hence, it could be effectively used for photocatalytic degradation of pollutants in industrial wastewater.

(iv) The results of this research clearly demonstrate the importance of choosing the optimum degradation parameters to obtain a high photocatalytic decolorization rate, which is essential for any practical application of photocatalytic oxidation processes using different photocatalysts.

(v) The procedure used in this research can be used as an efficient technology for solar photocatalytic degradation of the colored wastewater discharged from the textile industry under Iraqi climatic conditions.

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