COMPARISON BETWEEN SOLAR AND ARTIFICIAL PHOTOCATALYTIC DEGRADATION OF TEXTILE INDUSTRIAL WASTEWATER

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Abstract

In this study the photocatalytic degradation of industrial wastewater was investigated by using TiO_2 and ZnO photocatalysts. Heterogeneous photocatalytic processes applied under natural weathering conditions, in the presence of solar radiation show a promising degradation capability. The complete removal of color could be achieved in a relatively short time of about 20 minutes, when ZnO was used and about 100 minutes when TiO_2 was used under solar irradiation. However, in the presence of artificial UV-light, complete decolorization of textile industrial wastewater was obtained after less than one hour of irradiation when ZnO was used and in less than two hours, when TiO_2 was used at the same temperature.

The results indicate that the degree of photocatalytic degradation of textile industrial wastewater was obviously affected by different parameters. These parameters include catalyst mass, type of catalyst, type of reactor, type of dye, dye concentration, and temperature.

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 the climatic conditions of most countries.

1. Introduction

Treatments of industrial wastewater, especially textile wastewater will provide huge amount of water to face water scarcity around the World. Moreover the reliable treatments of wastewater will reduce contamination of soils, surface and ground water, and as a result public health will be protected. Textile wastewaters are strongly colored and contain high amounts of organic matter depending on forms of dyes and auxiliary chemicals (Meric et al, 2004; Muruganandham and Swaminathan, 2004).

Titanium dioxide and zinc oxide are widely and economically available. These semiconductors can be excited with light of a wavelength in the range of the solar spectrum ($\lambda > 310$ nm). Using of solar irradiation is very attractive technology from the economical point of view.

We have investigated previously, prolifically, the decolorization, photodegradation, and phytoremediation of many water soluble toxic compounds in real and simulated industrial wastewater. 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 % (Alkhateeb et al. 2005, 2007; Hussein et al 2008; Al-Zahra et al. 2007; Attia et al. 2008; Hussein and Al-Khateeb 2007; Hussein and Abid-Abass, 2010a, 2010b, Hussein et al. 2010a, 2010b, 2010c).

The aim of the present paper is to investigate photocatalytic decolorization of real and simulated textile wastewater using TiO_2, and ZnO as photocatalysts with irradiation with solar and artificial radiation at different conditions.

2. Experimental

Experiments were carried out during December, 2008 till July 2009. Solar irradiation 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 illuminations was accomplished in a 300 cm^3 glass container containing 100 cm^3 of the industrial wastewater solution. The sunlight radiation was collected using converging lens with a focal length of 14 cm. Artificial irradiation experiments are performed in a homemade reactor. The reactor consists of graduated 400 cm^3 Pyrex glass beaker and a magnetic stirring setup. 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 purchased from Degussa, TiO_2 rutile was obtained from Fluka and Zinc oxide with 99.5% purity, supplied by Carlo ERBA.

In all experiments, the required amount of the catalyst, titanium dioxide (anatase or rutile) or zinc oxide was suspended in 100cm^3 of industrial wastewater using a magnetic stirrer. At predetermined times; 1.5cm^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, Shimadza and visible spectrophotometer type v-1000, T-ChromoTech.

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.

3. Results and Discussions

3.1. Photocatalytic decolorization of real textile industrial wastewater at different conditions

Figure 1 shows the change in photocatalytic decolorization efficiency (P.D.E) of real textile industrial wastewater in the present and absent of catalyst and in the present and absent of solar or artificial irradiation.

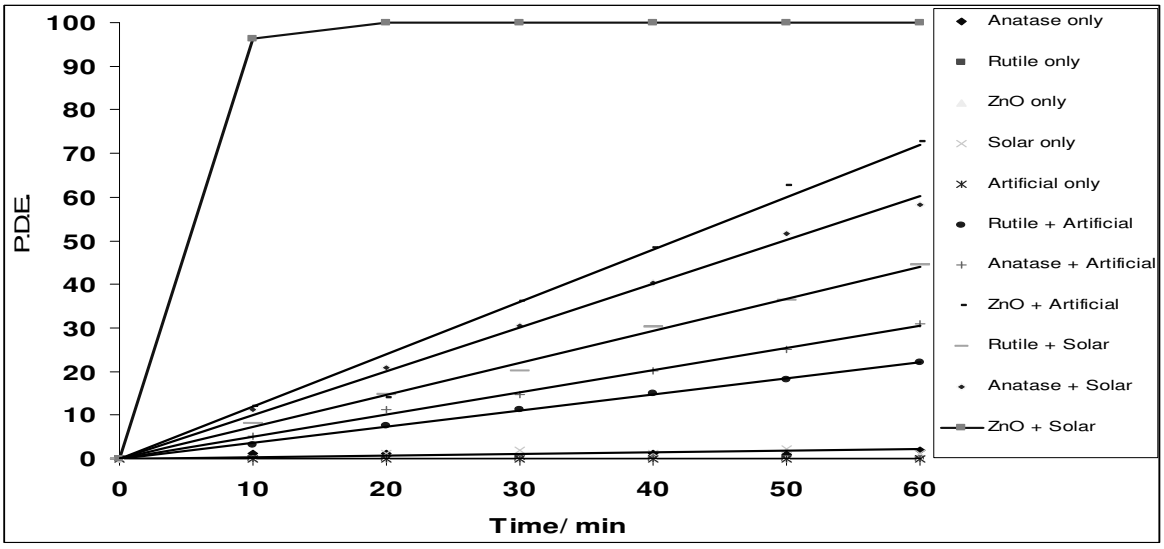


Fig. 1: Effect of types of catalyst and irradiation on photocatalytic decolorization of real industrial wastewater

The results indicate that the activity of different catalysts fell in the sequence:

ZnO (solar) > ZnO (artificial) > Anatase (solar) > Rutile (solar) > Anatase (artificial) > Rutile (artificial) >>

No catalyst= No solar or artificial irradiation = 0

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

Results indicate that ZnO in the existence of solar irradiation is most active. Sakthivel et al (2003) explained the higher activity of ZnO due to absorption of large fraction of the solar spectrum and absorption of more light quanta by ZnO than TiO_2.

All types of catalysts used in this research showed higher photocatalytic activity under sunlight irradiation. This may be due to high light intensity of solar radiation in IRAQ. Neppolian et al (2002) reported that solar energy may emerge as a viable method for textile wastewater treatment because of its eco-friendliness and cost effective where 96% of textile industrial wastewater was photodegradated during April–June; peak summer period of the year in Chennai, India. However, Akbal (2005) concluded that the photocatalytic decolorization rate of methylene blue and methyl orange with UV light irradiation was higher than that with solar light irradiation.

3.2. Effect of catalyst mass

Figure 1 shows that 175mg of anatase is sufficient for maximum rate of decolorization when mercury lamp was used for irradiation. Moreover the same mass was found also sufficient when the reaction vessel was illuminated with solar irradiation. These observations proved that the optimum mass to achieve maximum decolorization percentage is independent on type of irradiation source and solar irradiation in this system is more efficient than 125w/542 high pressure mercury lamp.

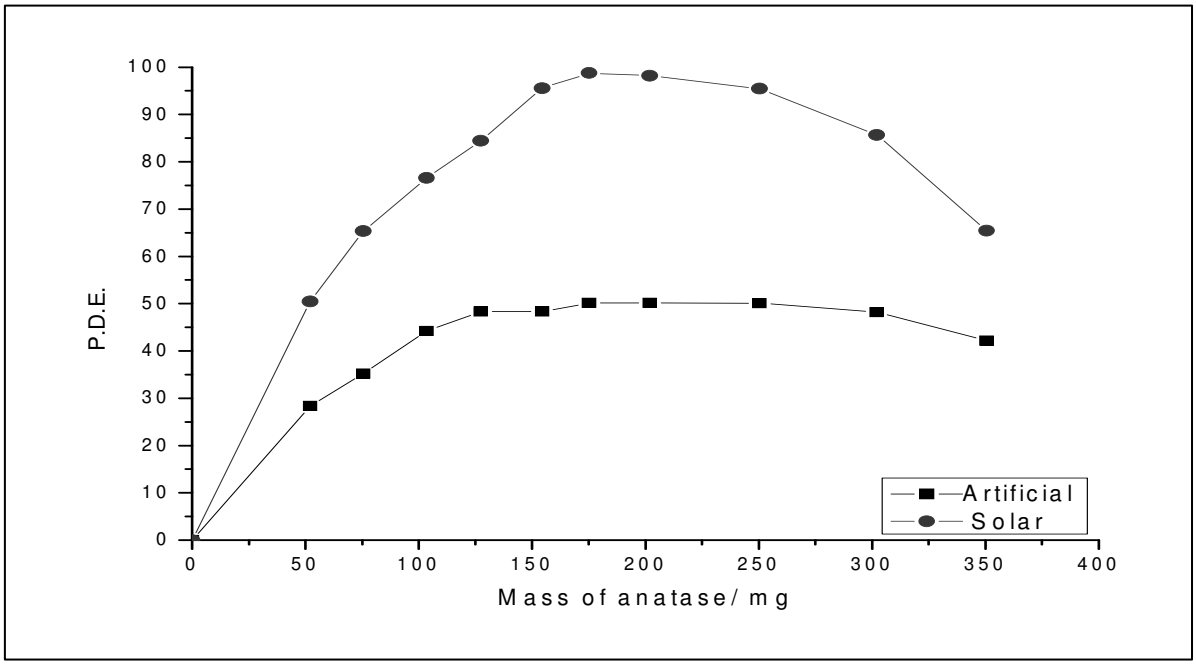
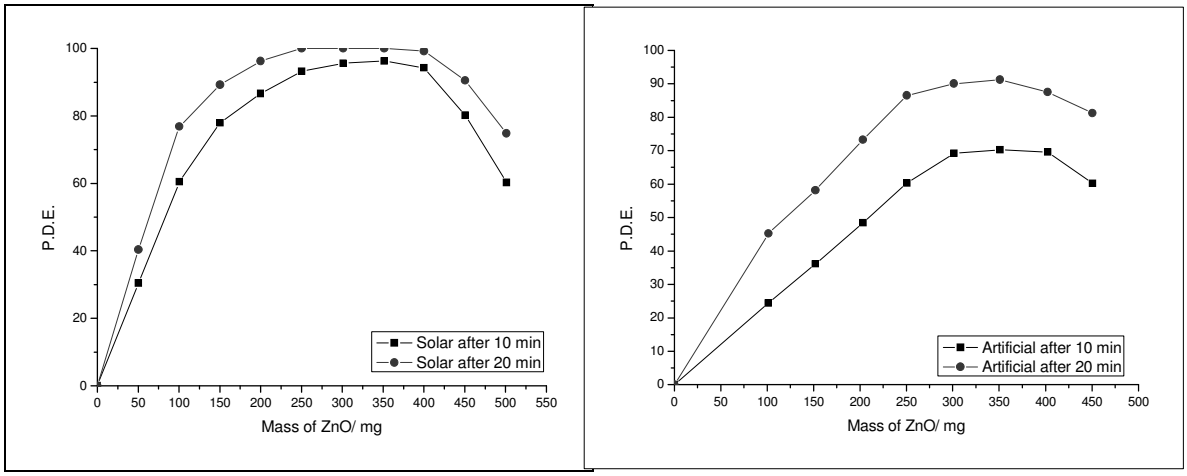


Fig. 2: Mass effect of TiO_2 (anatase) on photocatalytic decolorization efficiency of real textile industrial wastewater for different times of irradiation under solar and artificial radiation

The same observations were noted when ZnO was used as photocatalyst. However the optimum mass to achieve maximum P.D.E is 350mg. These results are shown in figure 2.



A **B**

Fig. 3: Mass effect of ZnO on photocatalytic decolorization efficiency of real textile industrial wastewater for different times of irradiation under solar irradiation (A) and artificial radiation (B)

Mass of catalyst is regarded as the major parameter affecting the photocatalytic degradation efficiency (Dong et al. 2010). The results plotted in figures 2 and 3 shows that the photocatalytic degradation efficiency of real industrial wastewater increases linearly with the increasing in catalysts mass at the first stages. This behavior may be due to an increase in the amount of active site on surface of photocatalyst particles and as a result, the number of dye molecule that adsorbed on the surface of photocatalyst will be increased and that will lead to an increase in the density of particles in the area of illumination (Kim and Lee, 2010). However, after reaching maximum photocatalytic degradation rate, addition of excess amount of catalysts has no effect on photocatalytic rate, so a plateau region was observed. After the plateau region is achieved, the activity of photocatalytic decolorization decrease with increase of catalyst concentration for titanium dioxide and zinc oxide. This behavior is more likely due to Light scattering by catalyst particles at higher concentration which leads to decrease in the passage of irradiation through the sample leading to poor light utilization (Gaya et al., 2010; Kavitha and Palanisamy, 2011). Deactivation of activated photocatalyst molecules colliding ground state molecules with increasing the load of photocatalyst may be also cause reduction in photocatalyst activity (Kim and Lee, 2010). High concentration of loading catalyst also decreases the number of surface active sites (Thakur et al., 2010).

3.3. Effect of Temperature

Reaction was followed at four different temperatures in the range 293.15- 315.15 K using 175 mg of anatase under solar radiation. The results in table 1 indicate that the P.D.E of real textile industrial wastewater increases with increasing of temperature.

Table 1: Effect of temperature on photocatalytic decolorization efficiency of real textile industrial wastewater on TiO_2 and solar radiation

Temperature / K Time/ min	293.15	298.15	304.15	310.15
0	0	0	0	0
10	9.11	11.23	12.43	14.22
20	18.23	20.88	23.54	26.44
30	26.66	30.43	34.05	39.76
40	36.55	40.22	46.12	55.45
50	45.65	51.65	58.54	70.34
60	55.24	58.34	65.45	78.85

Reaction was also followed at four different temperatures in the range 290.15- 319.15 K using mercury lamp and 350mg of zinc oxide. The results are listed in table 2. The results indicate that P.D.E of real textile industrial wastewater increases with increasing of temperature. However it is clear that temperature is the less active parameter in the photocatalytic decolorization of real textile industrial wastewater.

Table 2: Effect of temperature on photocatalytic decolorization efficiency of real textile industrial wastewater on ZnO and artificial radiation

Temperature / K Time/ min	290.15	298.15	313.15	319.15
0	0	0	0	0
10	10.22	12	17.25	18.22
20	21.4	14.12	35.25	38.04
30	32.8	36.22	52.33	56.22
40	42.44	48.35	68.88	77.25
50	52.3	62.55	85.25	100
60	63.55	72.85	97.88	100

It is well known that the most desirable system for complete mineralization of a wide range of organic substrates that which operates under natural weathering conditions without producing of harmful byproducts (Kansal et al. 2007). Photocatalytic treatments and especially with solar irradiation offer that because they are mostly proceeds under natural weathering conditions. Adsorption of reactants on the surface of catalysts is a spontaneous exothermic phenomenon so it is enhanced by reduction of temperature (Malato et al 2003).

3.4. Effect of Initial Dye Concentration:

The results in figure 4 show the changing of rate of decolorization of real textile industrial wastewater on 175mg of anatase by using solar and artificial irradiation at 298.15K with the initial direct dye concentrations (25%-100%) at different times. The results indicate that decreasing of dye concentration decreases the time of decolorization.

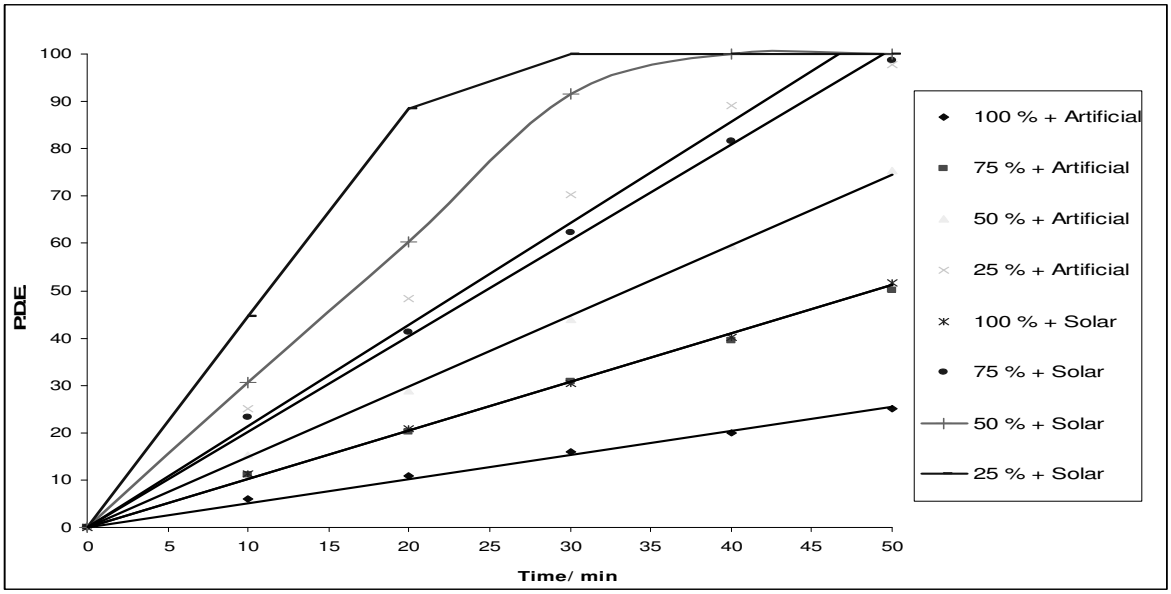


Fig. 4: Effect of initial dye on photocatalytic decolorization of real textile industrial wastewater on TiO_2 (anatase) and solar radiation

This behavior related to decreasing of the path length of photons entering the solution as the initial concentration of dye increases and as a result the number of photon absorbed by the catalyst decreases.

This behavior related to decreasing of the path length of photons entering the solution as the initial concentration of dye increases and as a result the number of photon reached to the catalyst surface decreases (Davis et al. 1994, Rideh et al. 1997 Murugesan and Sakthivel 2002 and Nam et al. 2002).

4. Conclusions

1- The existence of catalyst and lights are essential for photocatalytic degradation of colored dyes.

2- Solar photocatalytic treatment is an efficient technique for decolorization of industrial wastewater through a photocatalytic process and the transformation is practically complete in a reasonable irradiation time.

3- 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.

4- 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 natural weathering conditions.

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