## Photocatalytic Degradation of Bleaching Some Organic Dyes with TiO<sub>2</sub> under direct Sun Light

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#### ABSTRACT

The photocatalytic degradation of some dyes in aqueous solutions has been investigated under solar radiation as energy source in the presence of TiO<sub>2</sub>. A dye solution containing  $1 \times 10^{-5}$  M was completely degraded within 150 min. The effect of initial dye concentration, pH, light intensity and TiO<sub>2</sub> mass were investigated and the optimized conditions for maximum amount of degradation were determined. Experiments were performed at the range of temperature (33-40) °C, The combined effect of pH and catalyst concentration was greater. The intensity of the solar light was measured using digital lux meter. The higher removal efficiency was obtained for Azor C dye (88 %).

#### **1- Introduction**

Dyes are an important class of aquatic pollutants and are becoming a major source of environmental contamination and the release of this colored a major problem for the industry <sup>(1-2)</sup>. TiO<sub>2</sub> photocatalysis has been the most effective as well as technologic for the application in pollutant industrial effluents. A large number of chemical pollutants have been shown that are susceptible of being oxidized through heterogeneous photocatalytic processes <sup>(3-4)</sup>. Other investigations have been carried out under UV radiation, since TiO<sub>2</sub> photocatalysts show relatively high activity and chemical stability under UV light and absorbs only small portion of solar spectrum UV which reaching the surface of earth, Therefore only (4–5) % of the solar energy reaching the surface of the earth could in principle be utilized as direct and diffused components when  $TiO_2$  is used as a photocatalyst <sup>(5-6)</sup>. Many researches suggested that the potential exists for the use of highly concentrated sunlight in the removal of dyes from wastewater <sup>(7-10)</sup>. When the energy of the photon is equal or greater than the energy of the band gap of  $TiO_2$ , The photocatalytic process consists of the excitation of the titanium dioxide by light wavelength corresponds to h < 400nm. The photonic excitation leaves behind an empty unfilled valence band, and thus creating the electron- hole pair(e<sup>-</sup> - h<sup>+</sup>). The series of chain oxidative reductive reactions that occur at the photon activated surface was widely postulated the mechanism of the electron hole pair formation as follows <sup>(11-13)</sup>:

According to above equations,  $h^+_{VB}$  may combine with H<sub>2</sub>O or <sup>-</sup>OH to produce the hydroxyl radical ('OH), being a very strong oxidizing agent (standard redox potential +2.8V) can oxidize most of dyes and  $e_{CB}^-$  can be picked up by oxygen to generate a superoxide radical <sup>(14-15)</sup>. The aim of this study was to investigate the photocatalyst degradation reaction of 6 dyes using TiO<sub>2</sub> as catalyst. Different process variables – temperature, initial pH, solar light intensity and catalyst concentration were evaluated in direct sun light. All photocatalytic experiments were carried out under similar conditions on sunny days between 10:30 a.m. to 01:00 p.m. in May (2012) in the range of temperature (33-40) °C.

#### 2- Materials and Methods

#### 2-1- Materials and Instrument

 $TiO_2$  used in the experiment were kindly supplied by Degussa P-25 (Germany). The dyes were obtained from Aldrich that's shown in Table(1) and the structure formula of dyes shown in Figure(1)<sup>(16)</sup>. Solutions were prepared by dissolving requisite amount of the dye in double distilled water. The pH of the solutions was adjusted using  $H_2SO_4$  or NaOH then measured using pH meter 211,HANNA instruments. The Temperature was adjusted by using regulator water bath WB 710M (Optima) . TiO<sub>2</sub> suspensions were Centrifuged of by using Centrifuge CORP Triup International , Italy instruments. the absorption was measured by using spectrophotometer (Shimadzu UV-Visible 1650 spectrophotometer).

No	Name of dye(Molecular formula)	λ max (nm)
1	Azor A (C <sub>14</sub> H <sub>14</sub> ClN <sub>3</sub> S)	632 nm
2	Azor B (C <sub>15</sub> H <sub>16</sub> ClN <sub>3</sub> S)	646 nm
3	Azor C (C <sub>13</sub> H <sub>12</sub> ClN <sub>3</sub> S)	611.5 nm
4	Rhodamine 6G (C <sub>28</sub> H <sub>31</sub> ClN <sub>2</sub> O <sub>3</sub> )	526.5 nm
5	Rhodamine B (C <sub>28</sub> H <sub>31</sub> ClN <sub>2</sub> O <sub>3</sub> )	554 nm
6	Alizarin Red S (C <sub>14</sub> H <sub>7</sub> NaO <sub>7</sub> S)	512 nm

Table (1) : Molecular formula and absorption maxima of dyes.



Azor B

Azor A

Azor C



Fig (1): Structures formula of dyes.

#### 2-2- Solar light intensity measurements

The intensity of solar light was measured using Digital Lux meter (model no. LX1010B) at time intervals of between 10:30 a.m. and 01:00 p.m. in 20 May 2012 .The average light intensity over the duration of each experiment is presented in Figure (2).



Figure (2): The average light intensity over the duration of each experimental in presence of 0.5 gm/L of TiO<sub>2</sub> and [Dye]= $1.0 \times 10^{-5}$ M.

### 2-3- Experimental Procedure

Aqueous TiO<sub>2</sub> suspensions were prepared by adding 0.5 gm of TiO<sub>2</sub> powder to 1L of aqueous dye solution initial experiments were conducted using different concentrations and choose  $1X10^{-5}$  M to focus as a perfect concentration of all dyes. Then all solutions were placed in petridishes and directly exposed to natural sun light for 150 min at temperature range (33-40) °C in May 2012. At each time step, one petridish was

wrapped with aluminum foil, and waited until all irradiations were finished, then samples were taken and pH was determination by used pH-meter .In the same time the absorption was measured by using spectrophotometer after removal the TiO<sub>2</sub> particles by centrifugation and filtration then recording the results and absorbance at  $\lambda$ max which determine advance, also the intensity of solar light was recorded by using a Digital Lux Meter for different times.

#### **3-Results and Discussion**

#### **3-1-** Photolysis Experiment

The degradation of the dyes was performed by using sunlight (in sunny day) using titanium dioxide as the photocatalyst. This technique seems to be effective since complete degradation is achieved within 150 min under the experimental conditions used. The degradation performance of the process was assessed in terms of degradation efficiencies defined as shown in equation as follow:

Where  $Abs_0$  and  $Abs_t$  are the initial and remaining dye concentrations at given time (t) respectively.

Figure (3) shows the ratio between the Abs<sub>t</sub>/Abs<sub>0</sub> and irradiation time that supports this conclusion, In comparison of photobleaching rate of dyes indifferent families according to Table(1) the photobleaching rate of dyes can be ordered as such thiazine dyes is faster degradation than Xanthene dyes. In Figure (4) it was observed that higher removal efficiency is of following trend: for Azor C <sup>\*</sup>Azor B <sup>\*</sup> Azor A <sup>\*</sup> Rhodamin 6G <sup>\*</sup> Rhodamin B <sup>\*</sup> Alizarin Red S. During the bleaching process, hydroxyl radicals attack dye molecule starting with oxidation of the hydroxyl groups, and eventually ending with cleavage of the dye molecules. This result suggests a photobleaching system using visible light might be useful for the treatment of dye

contaminated wastewater. Similar conclusions were reached in other studies <sup>(17-18)</sup>. The results reveal that photocatalytic degradation may be a useful technique in the removal of dyes in aqueous solutions.



Figure (3): Kinetic of photobleaching degradation of dyes under direct solar light in presence of 0.5 gm/L of TiO<sub>2</sub> and  $[Dye]=1.0 \times 10^{-5} M$ .



Figure (4): The removal efficiency % of photobleaching degradation of dyes under direct solar light,

in presence of 0.5 gm/L of TiO<sub>2</sub> and [Dye] = $1.0 \times 10^{-5}$ M.

#### **3-2-** Photolysis of TiO<sub>2</sub>

From the results and effect of  $TiO_2$  determined on the degradation of all dyes from aqueous solutions can be seen that different amounts of photocatalyst. The effect of  $TiO_2$  loading on percentage degradation of the dyes has been examined by varying its amount from 0.1 to 1.0 gm/L of the dye solution [Dye] =1.0 X 10<sup>-5</sup> M, the results are presented in figure (5). Complete photobleaching requires 150 min in solar irradiation of dyes. The percentage degradation increases rapidly with the increase in the amounts of semiconductor for all dyes can be attributed to the fact that a larger amount of photons are adsorbed, thus accelerating the process. When all the solution molecules are adsorbed on TiO<sub>2</sub>, The photogenerated electrons could reduce the dyes or react with electron acceptors such as O<sup>•</sup><sub>2</sub><sup>-</sup> adsorbed on the Ti<sup>+3</sup>, surface or dissolved in water, reducing it to superoxide radical anion. The photogenerated holes can oxidize the dye

molecule to form positive spice or react with <sup>-</sup>OH and H<sub>2</sub>O oxidizing them into hydroxyl radicals<sup>(19-20)</sup>. The results are reported in Fig (6), this results is similar to the study was carried out by <sup>(21-22)</sup>. At the semiconductor surface causing the degradation of dyes according to (1-3) equations, the mineral photocatalysis with end-products as follows:





Figure (5): Kinetic of photobleaching degradation of dyes under direct solar light in presence of different concentration of  $TiO_2$  and  $[Dye]=1.0 \times 10^{-5} M$ .



Figure (6): The removal efficiency % of photobleaching of  $[dye] = 1.0 \times 10^{-5} \text{ M}$  under direct solar light at different concentration of TiO<sub>2</sub>.

#### 3-3- Effect of pH

In Figure (7) the results are reported the effect of pH on the rate of photobleaching of dyes in the different range of pH. Degradation removal efficiency is evidenced to be affected by pH photocatalytic degradation in presence of 0.5 gm/L of TiO<sub>2</sub> and solar light all this experiment could be achieved at the range of temperature (33-40) °C. Incomplete degradation at different pH can yield diverse intermediates. Photocatalyzed intermediates seem to have slightly different functional groups, also can due the bleaching degradation to generations of •OH radicals, which are produced from the interaction of •OH and hole (h+) of the semiconductor these •OH oxidize the dyes molecules in their forms <sup>(23)</sup>. The ionization state of the surface according to the following reactions:

 $TiOH + H^{+} \leftrightarrow TiOH_{2} \qquad \dots \dots \dots (8)$  $TiOH + ^{-}OH \leftrightarrow TiO^{-} + H_{2}O \qquad \dots \dots \dots (9)$ 

pH plays an important influence the adsorption of dye molecules on the  $TiO_2$  surfaces an important step for the photodegradation have already reviewed that acid-

base properties of the metal oxide surfaces can have important considerable <sup>(24)</sup>. The point of zero charge of the TiO<sub>2</sub> is at pH 6.8 Thus, the TiO<sub>2</sub> surface is positively charged in acidic media (pH<6.8), where as it is negatively charged under alkaline conditions (pH> 6.8) <sup>(25)</sup>. At pH<6 a strong adsorption of the dyes on the TiO<sub>2</sub>. At pH>6.8, dyes molecules are negatively charged in alkaline media, their adsorption is also expected to be affected by an increase in the density of TiO<sub>2</sub> groups on the semiconductor surface.



Figure (7): The effect of pH on removal efficiency % of photobleaching of [dye] = 1.0X10<sup>-5</sup> M under direct solar light , 0.5 g/L of TiO<sub>2</sub>.

#### **3-4-** Effect of Intensity light

Figure (8) shown the effect of light intensity on photobleaching of  $[dye] = 1.0 \times 10^{-5}$  M and 0.5 g/L of TiO<sub>2</sub>. The maximum color removal occurred at maximum solar light intensity 8.6 mW/cm<sup>2</sup>. It may be explained on the basis that as the light intensity was increased, the number of photons striking per unit area also increased, resulting into a higher rate of degradation. Further increase in the intensity beyond the maximum limits

result in decrease in the rate of reaction. It may be probably due to thermal side reactions <sup>(21-26)</sup>.



Figure (8): Kinetic of photobleaching degradation with light intensity in presence of solar light,

0.5 gm/L of TiO<sub>2</sub> and [Dye]=1.0 X10<sup>-5</sup>M.



Figure (9): Effect of light intensity with removal efficiency of photobleaching degradation of dyes under direct solar light in presence of 0.5 gm/L of TiO<sub>2</sub> and [Dye] = $1.0 \times 10^{-5}$ M.

### **3-4-** Effect of Temperature

The effect of temperature is shown in Figure (10). When working at a low temperature, the desorption of the products formed limits the reaction because it is slower than the degradation on the surface and the adsorption of the reactants. On the other hand, Figure (11) show the effect of temperature on the kinetic of removal of photobleaching dyes, at high temperature charged chemical species may be recombined and adsorption of dye intermediates may be inhibited on catalyst, the limiting stage becomes the adsorption of the dye on the TiO<sub>2</sub> <sup>(27-29)</sup>. Solar irradiation consisting UV-A (315 to 400 nm; 3.10- 3.94 e.V) and UV-B (280 to 315 nm; 3.94-4.43 eV) provide sufficient photons for the activation of TiO<sub>2</sub> catalyst. UV-C (100 to 280 nm) is absorbed by earth's atmosphere and does not reach to earth surface however <sup>(12)</sup>.



Figure (10): Effect of temperature on Removal Efficiency of photobleaching under direct solar light ,  $[dye]=1.0 \times 10^{-5} \text{ M}$  and 0.5 g/L of TiO<sub>2</sub>.



Figure (11): Effect of temperature on kinetic of removal of photobleaching under direct solar light [dye]=1.0 X10<sup>-5</sup> M and 0.5 g/L of TiO<sub>2</sub>.

#### 4. Conclusions

This paper reported has showed that the dyes can be degraded by solar light irradiation, Solar energy has been proved more efficiency for removal the dyes. The best removal for Azor A was 88%. The degradation reaction was proved to be the photocatalytic process in nature, evidenced by the dependence of catalyst light intensity and several control experiments. The photocatalysts  $TiO_2$  have a potential to completely oxidize a variety of organic compounds, thus, all dyes can be degraded photo catalytically by using  $TiO_2$  as solar light photocatalyst. the catalyst amount has positive impact on the photodegradation rate.

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# التجزئة الضوئية المحفزة لبعض الأصباغ العضوية باستعمال ثاني اوكسيد التيتانيوم تحت ضوء الشمس المباشر حسن عباس حبيب - بتول صالح حسين - أزل شاكر

#### : الخلاصة

تحققت التجزئة الضوئية المحفزة لبعض الأصباغ في المحاليل المائية تحت أشعة الشمس كمصدر للطاقة وبوجود ثاني اوكسيد التيتانيوم TiO<sub>2</sub> . تم استعمال تركيز مقداره 1×10<sup>-5</sup> مو لاري لجميع الأصباغ المستخدمة في الدر اسة وتمت التجزئة خلال زمن مقداره 150 دقيقة . تم در اسة تأثير تركيز الصبغة و الدالة الحامضية PH وشدة الضوء وتأثير تركيز ثاني اوكسيد التيتانيوم . و الشروط الحركية لتحديد اكبر كمية للتجزئة . أنجزت التجارب عند مدى من الحرارة يتر اوح مابين (33-40) درجة مئوية . وكان اتحاد تأثير الدالة الحامضية مع العامل المحفز ثاني اوكسيد التيتانيوم هو الأكبر تأثير . فيست شدة أشعة ضوء الشمس باستعمال جهاز (