# Photocatalytic Degradation of Arsenazo as a Model Compound

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## Abstract

Titanium dioxide ($TiO_2$)Was used as photocatalyst for the detoxification of water containing arsenazo dye(AD) which was degraded under UV radiation source. No degradation It was found that for the arsenazo dye in the dark place in the presence of $TiO_2$.Saveral experiments were performed to optimize the experimental parameters by employing medium pressure mercury lamp (MPML 125W).Firstly ,it has been found that best $TiO_2$ mass was 60 mg which gave the highest rate of degradation. The temperature in the range (283-303) K was studied to evaluate the activation energy of degradation which was 21.0612 KJ/mole .The effect of PH has been studied over the range (4,6,8,and 9) . It has been found that the  highest degradation rate was at PH=4.

$TiO_2$

(          125)

$TiO_2$

.                                                                  60 mg

/          21.062

.PH=4                    PH

## Introdoction

Water resources are limitted in developing countries and there is great need to recycle water and to reuse it in agriculture and industry[1]. Solar energy is aboundaut in most developing countries. Solar energy intensity is quite suitable and can be used as a source for the photocatalytic detoxification of polluted water[2]. This process may prove to be economically and technologically feasible[1-3] for water treatment and detoxification of water.Photocatalysis has received growing interest over the last few years[4] .

Titanium dioxide ($TiO_2$) is generally considered to be the best photocatalyst and has the ability to detoxification water from a number of organic pollutant[5] . Anatase ($TiO_2$) has a wide band gap, Eg=3.2 eV [6] thus only  light below 400 nm is absorbed and capable to forming ($e^-$ /$h^+$ ) pair[7] which recombine in competition with separation to yield a conduction band

electron and valance band hole in less then 30 ps[8] . The presence of oxygen is very essential for the trapping of photo electrons to reduce recombination pocess, which occurs between ($e^-_{cb}$ /$h^+_{vb}$ ) pair[9], $TiO_2$ acts as short circuited photoelectrochemical cells and directly oxidize absorbed electron donors or reduce adsorbed electron excerptors by electron and hole transfer at two positions on $TiO_2$ surface.

Photo catalysis is potential technology for the destruction of organic contaminants in water such as aromatic compounds, which present a potential hazard to the environment. Oxidation of organic compounds in aqueous solution is achieved by the reactive hydroxyl radical (OH). Using photocatalysis has mineralized different compounds, among them hydrocarbons[8] ,phenols[10] , chlorophenols[11-12] .

The aim of the present work is to explore the possibility of using solar radiation for the detoxification of different pollutant. Arsenazo dye (AD) (Figure 1) was used as a model compound because it was possible to use UV- visible spectroscopy to monitor the degradation under different conditions such as ($TiO_2$) concentration, different temperature, and PH of the solution.
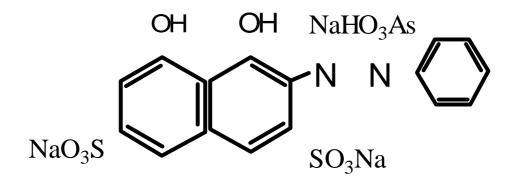


**Figure (1) : Structural Formula of arsenazo I .**

## Experimental
### *Chemicals:*

All chemicals were used without further purification. Arsenazo dye was supplied by BDH , Titanium dioxide (P-25) was supplied by Degussa . Double distilled water was used in all experiments.

### *Instruments:*

Medium pressure mercury lamp (MPML) type OSRAM (125 W) was used as source of irradiation.

photo cell with quartz window was used as vessel and medium pressure mercury lamp (type Osram 125 watt) was used and fit controlling the temperature was adjusted by circulating thermo state was used. Cintra-5 UV Visible spectrophotometer was used to determination the undegarded dye in the λ max (497 nm). The temperature was adjusted dye regulator thermostat (Desaga Frigostat) . The PH of suspension was controlled by using PH meter (Radiometer Copenhagen).

### *Photodegradation Experiments:*

All photodegradation experiments were carried out by irradiating the aqueous suspension of dye by visible light emitted from LPML in the reaction vessel (25 $cm^3$) fitted with quartz window (2 $cm^2$) with continuous stirring of suspension and bubbling of oxygen by using a compressor . The suspensions were irradiated for 75 min. A small quantity (0.5 ml) of suspension was taken and

centrefuged and filtrated to remove $TiO_2$ .

To detect the optimum conditions of photodegradation process , the effect of $TiO_2$ quantity (10-90 mg/25 cm$^3$), dye concentration (2 x 10$^{-2}$ -2 x 10$^{-5}$ M ) , Temperature (283-303 K) , and PH(4,6,8,9) were performed.

Some of experiments were done in the dark in presence of $TiO_2$ for comparison with photodegradation process.

## Result and Discussion

Arsenazo (AD) was chosen as a model compound. This is red in the aqueous solution. The UV-visible spectrum show two maxima wave length.

The UV-Visible for (AD) in distilled water show two absorption maxima (Figure 2). The first band observed at 361 nm while the second band at 497nm. The second band at 497nm was used to monitor the photo catalysis on the degradation of (AD) to study the optimum condition and the effect of different parameters on the degradation of (AD) under the UV radiation the following experiments were used degradation decay follow a first order kinetics from the slops of 1m(concentration vs. time).

### Effect of solar Radiation without TiO2 :

The reaction vessel was exposed to the UV radiation without $TiO_2$ for 3hr . It was noticed that AD is quite stable under solar condition. This means that light ,$O_2$,and $TiO_2$ are very essential for photocatalytic degradation of arsenazo dye[13] .

### TiO$_2$ Concentration Optimization:

As expected for photocatalytic reaction , the rate of photocatalytic degradation of Arsenazo dye has been increased with the amount of catalyst due to complete absorption of the incident light potentially absorbable by $TiO_2$.

Figure (3) shows such behavior, maximum value of rate has been obtained at 60 mg of $TiO_2$ for 25cm$^3$ of the solution so that this quantity was chosen to study the effect of other parameters. Using low weight of $TiO_2$produce direct proportional between weight of $TiO_2$ and photocatalytic degradation and this observation can be explained that the number of $TiO_2$ particles are a few as compared with the number of incident photons, so that the rate of degradation has been increased with increasing $TiO_2$ particles, but when the weight of $TiO_2$ more than 60 mg /25 ml , particles form inner filter [14] which absorb high portion of incident light as well as scatters parts of light.
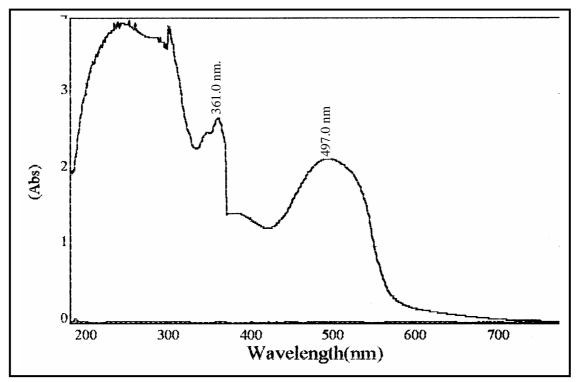
**Figure (2) : Spectroscopic absorption spectrum of arsenazo dye dissolved in distilled water**

**Table (1): Rates of arsenazo dye degradation over different weights of TiO$_2$ at 283 K .**

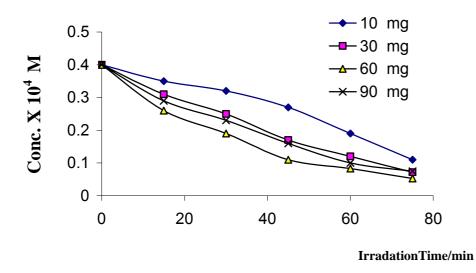| Weight of TiO$_2$\mg | Rat of degradation x 10$^6$\ mol.L$^{-1}$S$^{-1}$ |
|:---:|:---:|
| 10 | 3.6 |
| 30 | 3.9 |
| 60 | 4.2 |
| 90 | 3.8 |



**Figure (3): photocatalytic degradation of (AD) with different weight of TiO$_2$**

## *Effect of PH:*

The PH of the solutions which include 60mg $TiO_2$ and affixed concentration of (AD) were varied. The experiments were performed at the same time, the best degradation was obtained with PH=4.

Most of photocatalytic reactions are perfomed in aqueous solution. The PH of the solution effects on the particle size, the surface charge , and the band edge positions of the TiO2 due to it's amphoteric character . When the PH solution is around 7 the surface of $TiO_2$ is uncharged. While in acidic media .The particle surface is positively charged , in alkaline media , the surface charge is negative[15] according to the following equations:-

$$TiOH_2^+ \longleftrightarrow TiOH + H^+$$
$$TiOH \longleftrightarrow TiO^- + H^+$$

Positive charge of $TiO_2$ surface enhanced adsorption of an ionic and polar substrates so that the initial photocatalytic rate was increased with increasing PH solution.

Figure(4) shows that the effect of PH on the degradation of the pollutants is variable and controversial . Where the photocatalytic degradation rate has been decreased with increasing PH . This means that the acidic medium was more suitable for the photocatalytic degradation of (AD) .
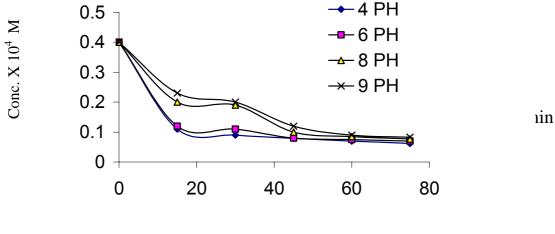
## *Effect of Temperature and Determination of Activation Energy:*

A series of experiment have been done over range of temperatures (283-303) K. Their experiments were carried out under illumination with light of 366 radiations from mercury lamp. The results are show in Table (3) and plotted in Figure (5) .The linear dependence of rate reaction on temperature variations was found in this work .The increased rate of reaction with increasing in the temperature may be attributed to the effect of temperature on the adsorption and desorption processes on the surface of $TiO_2$[16] .

Arrhenius plots shown in Figure (6). The Activation energy has been calculated from the effect of different temperature on the rate of reaction. The manner in which activation energy for (AD) degradation over TiO2 is 21.062 $kJ.mol^{-1}$, so that this energy was independent on the reaction condition led to suggest that , it was the energy required to promote photoelectrons from the photo catalyst to be trapped at surface by adsorbed oxygen molecules[17] .

**Table (2): Rates of arsenazo dye degradation in the rang of PH (4-9) by using 60 mg $TiO_2$ at 283 K .**

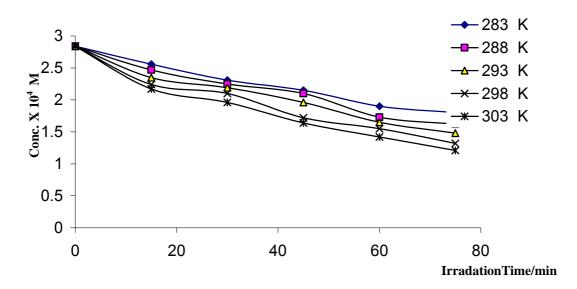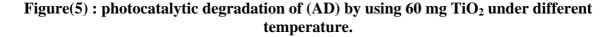| PH | Rat of degradation x $10^6$ \mol.$L^{-1}S^{-1}$ |
|----|-------------------------------------------------|
| 4  | 3.15 |
| 7  | 2.81 |
| 8  | 2.62 |
| 9  | 2.34 |

**Figure(4) : photocatalytic degradation of (AD) under different PH by using 60 mg TiO$_2$ at 298 K .**

**Table (3): Rates of arsenazo degradation by using 60 mg TiO$_2$ in the rang of temperature (283-303)K.**

| T/K | Rat of degradation x 10$^6$\ mol.L$^{-1}$Sec$^{-1}$ |
|---|---|
| 283 | 4.1 |
| 288 | 4.3 |
| 293 | 4.9 |
| 298 | 5.2 |
| 303 | 5.5 |



**Figure(5) : photocatalytic degradation of (AD) by using 60 mg TiO$_2$ under different temperature.**

$$Slope = -1.1 \times 10^3$$
$$Slope = -E_{a/} 19.1475$$
$$E_a = 21.062 \times 10^3 \ J. \ mol^{-1}$$
$$E_a = 21.062 \ kJ.mol^{-1}$$

[Figure: Log rate (mol.L⁻¹.s⁻¹) vs 1/T × 10³ K⁻¹ plot with data points and a straight line fit]
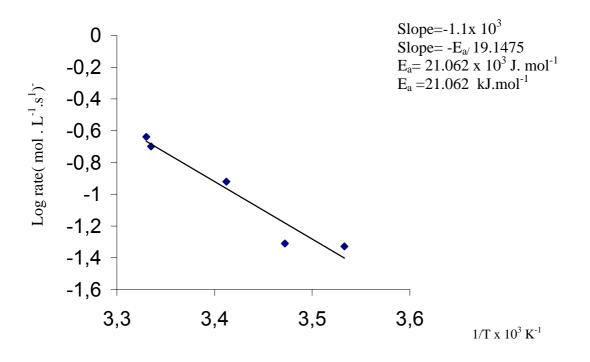
**Figure (6) : Temperature dependence for the photocatalytic degradation of arsenazo over 60 mg TiO$_2$**

## Conclusions

TiO$_2$ was used as photocatalyst for the detoxification of (AD) which was used as a model compound one can conclude the following.The presence of light and TiO$_2$were very necessary in photocatalytic degradation of (AD) .The ideal weight of The presence of light and TiO$_2$, which gave an optimum efficiency for (AD)degradation is 60 mg/25 ml. The photo degradation has been increased with the amount of catalyst due to complete absorption of the incident light potentially absorbable by TiO$_2$, while using more than 60 mg of TiO$_2$ reduces the rate of photodegradation, due to the formation of inner filter which absorbs high portions of incident light and scatters other part .

The PH of the solution effect on the rate degradation. the rate of photocatalytic degradation was increased with decreased PH solution because the surface of TiO$_2$become positive charge in acidic media and this positive charge was enhanced adsorption of ionic and polar substrates.

The rate of photocatalytic degradation of (AD) has been increased with increasing temperature, because increase in temperature leads to enhance adsorption and desorption processes which occur on the surface of TiO$_2$.

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