

Influence of operational parameters on eliminating azo dyes from wastewater by advanced oxidation technology

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Abstract: In this research the effect of various parameters on the TiO₂/UV photocatalytic degradation of benzidien yellow (Y12) in aqueous heterogeneous suspensions have been studied. Parameters such as pH, amount of photocatalyst, presence of various inorganic ions and solvents as a main operational parameters selected and their influence on degradation efficiency have been investigated. The experiments showed that TiO₂ and UV light had a negligible effect when they were used on their own. Investigation of the ZnO/UV system indicated that ZnO can be used as an alternative catalyst to TiO₂. A semi-log plot of dye concentration versus time showed to be linear, which suggested a first order reaction for the TiO₂/UV system .

Keywords: Photocatalyst; Benziden yellow (dye); Advance oxidation technology

Introduction

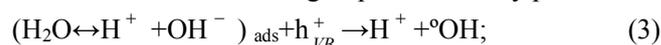
One of the most important of organic pollutions in wastewater are dyes. Fifteen percent of the total world production of dyes is lost during the dyeing process and is released as textile effluents¹. Presence of dyes in waste stream is a dramatic source of pollution. These pollutants do not decompose rapidly through natural processes². Azo dyes constitute the largest class of dyes used in industry and are resistant to aerobic degradation³. The azo linkage is reduced to aromatic amines under anaerobic conditions that are colorless and can be toxic and potentially carcinogenic⁴⁻⁶. The conventional methods for eliminating organic compounds, such as dyes, include physical, biological and chemical methods⁷⁻¹⁰. Numerous works have been carried out to improve the recovery of water purification systems. One of the latest methods that is recently used is Advanced Oxidation Technology for the treatment of organic pollutions. This method appears to be effective in that it can convert organic pollutions into biodegradable molecules or mineralization into CO₂ and other inorganic¹¹⁻¹⁶. It appears that TiO₂/UV system is applied more than other photocatalyst system in Advanced Oxidation Technology¹⁶. This is because TiO₂ is very effective, relatively inexpensive, easily available and chemically stable photocatalyst. The mechanisms of the degradation of organic pollutions are given as follows:
absorption of efficient photons ($h\nu \geq E_G = 3.2 \text{ eV}$) by titana:



—oxygen ionosorption



—neutralization of OH⁻ groups into °OH by photoholes



—oxidation of the organic reactant via successive attacks by °OH radicals



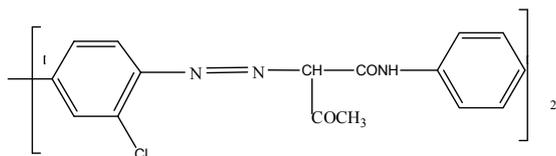
—or by direct reaction with holes



In this study, the influence of various parameters such as TiO₂/UV, pH, amount of TiO₂ particles, solvents and various inorganic salts on photocatalytic degradation of an azo dye (Y12) have been investigated. Degradation efficiency of Y12 by ZnO/UV system was compared with that of TiO₂/UV system. The rate of degradation and color removal versus irradiation time have also been reported.

Experimental

Materials. The material (Y12) which its molecular formula is given below was from Merck:



Titanium dioxide of analytical reagent was from Merck ($\geq 99\%$). Powder solution of dye (1000 mg/L) was prepared with distilled water and further diluted in the experiment. All the other chemicals used in this study were of analytical reagent grade. NaNO_3 , NaCl , $\text{Na}_2\text{S}_2\text{O}_3$, SnCl_4 salts and solvents such as, t-Butylalcohol, n-Butanol, 2-Propanol, Acetonitrile and n-hexane were also from Merck.

Apparatuses. A UV-Vis spectrophotometer (BIO-TEK922 model), pHmeter (Horiba-f12) sensitivity of ± 0.02 , centrifuge (KoKusan H-108N), Batch photoreactor of 150 ml in volume with an UV lamp (sunlamp, ultraviolet radiation, Philips 40 W) were used.

Procedure. For investigating the photocatalytic degradation of Y12, a solution containing known concentration of dye (15 ppm) and TiO_2 was prepared and it was allowed to equilibrate for 10 minutes in darkness, then 100 ml of the prepared suspension was transferred to a 150 ml Pyrex reactor. Having adjusted the suspension pH values at the desired level, diluted NaOH and H_2SO_4 were prepared by pH meter. Then, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained to keep the suspension homogenous. The aliquots of 5 ml were collected at regular time intervals and the suspension was sampled after an appropriate interval time. The initial time was taken as $t = 0$, after which the dye was mixed with catalyst for 10 minutes without the presence of UV. The samples were then taken at 10 minutes time intervals with the presence of UV light and centrifuged for 15 minutes at 4500 rpm. The concentration of dye in each degraded sample was determined by a spectrophotometer at $\lambda_{\text{max}} = 403 \text{ nm}$. The percentage degradation was calculated by the following equation:

$$\text{Degradation (\%)} = (C_0 - C/C_0) \times 100\%$$

where C_0 is the initial dye concentration, and C is the dye concentration after the treatments in terms of ppm.

Results and discussion

Effect of UV irradiation and TiO_2 particles on degradations of dye sample:

The effects of UV irradiation time and TiO_2 particles individually and also together on photodegradation of Y12 are shown in Fig 1. It can be seen from Fig 1, in the presence of both TiO_2 and UV light, 60% degradation of the dye was observed with irradiation time of 1.5 h. Whereas, no degradation was observed for the same experiment in the absence of TiO_2 , and also when the UV lamp switched off and the reaction was allowed in the darkness.

Effect of pH on photocatalytic degradations of dye sample: The pH value is one of the important factors

influencing the rate of degradation of organic compounds in the photocatalytic process. It is also an important operational variable in actual wastewater treatment. The data given in Fig 2 demonstrates the photodegradation of Y12 at different pH values from 2 to 11, which shows that the optimum value obtained in the acidic solution (pH=2, $X=100\%$). According to the zero point of charge of TiO_2 , its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution. As carbonyl groups of the dye have negative (δ^-) and positive (δ^+) charged groups in its structure, the acidic solution favours adsorption of dye onto the photocatalyst surface. Thus, this increased the photodegradation efficiency as shown in Fig 2. Measurements of the pH solutions after irradiation time of 60 mins are given in Table 1.

As can be observed from Table 1, changes of pH values may be due to the decomposition of dye structure and generation of organic and inorganic acidic anions, such as NO_3^- and ClO^- . From the results obtained in Table 1, the pH=2 was taken as optimum pH value and used for other experiments.

Effect of the amount of photocatalyst on photocatalytic degradation of dye sample:

The effect of the amount of TiO_2 on Y12 are shown in Fig 3. As can be seen from Fig 3, the photodegradation efficiency initially increases with increasing amount of photocatalyst and reaches an optimum value of photocatalyst at 2000 ppm and then decreases. Thus the most effective decomposition of Y12 was observed at 2000 ppm of TiO_2 . The reason for this is due to the fact that when all dye molecules are adsorbed on TiO_2 , the addition of higher quantities of TiO_2 seems to have no effect on the degradation efficiency. Another reason may be due to the increased opacity of the suspension, as a result of excess TiO_2 particles.

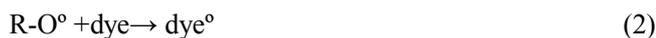
Effect of various solvents on photocatalytic degradation of dye sample:

In order to investigate the influence of various solvents, 2 ml of selected solvents were added to the dye solutions and then experiments were carried out at optimum condition of pH=2 and at $\text{TiO}_2=2000 \text{ ppm}$. The decomposition value (%) of dye samples in presence of various solvents are shown in Fig 4 to 8. As can be seen from Fig 4 to 8, all the solvents used have inhibited the photocatalytic degradation of Y12. The decreasing orders of the solvents in the degradation efficiency are as follows:

t-Butyle alcohol > n-Butanol > 2-Propanol > acetonitrile > n-Hexane

Alcohols are commonly used to quench hydroxyl radicals. This is because hydroxyl radicals play a major role in photocatalytic oxidation as shown in Eq 1 and Eq 2, respectively.





Oxidation potential of $R-O^\circ$ is less than $^\circ\text{OH}$ and this is thought to be due to the spatial hindrance effect of alcohol. As R group become smaller, reaction shown in Eq 2 can take place easier. As t-Butyl alcohol has a higher spatial hindrance effect compared with other alcohols, therefore, has a higher restricted effect on the photo-oxidation of Y12, and in despite of 60 minutes irradiation of UV light negligible decomposition of Y12 was observed. With addition of solvents such as acetonitrile and n-hexane which compete with dye molecules for trapping the hydroxyl radicals is shown to

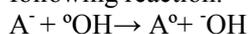
have reduced the degradation efficiency of dye samples as shown in Fig 7 and Fig 8, respectively.

Effect of inorganic salts on photocatalytic degradation of dye sample: The effect of inorganic salts (by spiking the 300mg/L from the selected salts) into the dye solutions on the photocatalytic degradation were also investigated. The degradation percentages as a function of irradiation time are shown in Fig 9 to Fig 12.

As can be seen from Fig 9 the presence of $\text{Na}_2\text{S}_2\text{O}_3$ showed no change in the initial dye concentration. It is known that $\text{Na}_2\text{S}_2\text{O}_3$ is used as a reductive material in water purification processes. This may therefore confirm the assumption that all of $^\circ\text{OH}$ generated were consumed for the oxidation of $\text{Na}_2\text{S}_2\text{O}_3$.

The effect of SnCl_4 salt on the degradation of dye sample is shown in Fig 10. The photocatalytic decolorization rate significantly decreased in the presence of SnCl_4 . Sn^{4+} affected the photocatalytic oxidation of the organics by trapping electrons which may have trapped the holes and this may explain the decreasing of the e^-/h^+ recombination rate. Thus, resulted in a higher generation of $^\circ\text{OH}$, and, therefore leading to the retardation of the reaction.

As can be seen in Fig 11 and Fig 12 the effect of TiO_2/UV system decreased in the presence of NaCl . and NaNO_3 Salt, respectively. This is because these anions (NO_3^- and Cl^-) compete with $^\circ\text{OH}$ as shown in the following reaction:



After fluorine with oxidation potential of 3.03 V, hydroxyl radical is the strongest oxidative species with oxidation potential of 2.80 V. Since the potential of A° is less than that of $^\circ\text{OH}$, therefore, this is thought to have led to the reduction of degradation efficiency of the dye sample.

Effect of ZnO on photocatalytic degradation of Y12: The effect of ZnO on the Y12 removal was studied and the results obtained are shown in Fig 13. It is observed that the rate of decolorization of the dye's solutions increased in the presence of ZnO as a photocatalyst. These results showed that ZnO can be used as an alternative catalyst to TiO_2 . It should be noted that ZnO

at acidic pH (less than 4) is ionized and loses its photocatalytic property and cannot be used in the acidic conditions. Thus, for this reason the ZnO is used less than TiO_2 in waste-water purification.

Kinetics of photocatalytic degradation of Y12: The plot of Ln dye versus irradiation time for Y12 is observed to be linear suggesting that the photodegradation reaction obeys the first order kinetics reaction as shown in Fig 14. Rate constant obtained from the slope of the curve in the neutral pH value is $K_{ap} = 9.4 \times 10^{-3} \text{ min}^{-1}$.

Conclusions

1. The results obtained showed that TiO_2/UV system could be efficiently used to degrade the Y12.
2. Photodegradation efficiency of dye was negligible when photolysis was carried out in the absence of TiO_2 and UV light.
3. The results indicated that the degree of degradation of Y12 was obviously affected by pH value and the amount of TiO_2 . The optimum amount of photocatalyst was 2000 ppm, at dye concentration of 15 ppm.
4. It was concluded that hydroxyl radicals were the main reactive species. It should be noted that among the alcohols, t-butyl alcohol had the most inhibitive effect. This may be due to the spatial hindrance effect of the t-butyl alcohol.
5. It was observed that addition of some salts retarded the photodegradation efficiency of the dye samples.
6. It was noted that using the ZnO as a photocatalyst it increased the rate of degradation.
7. The plot of Ln dye versus irradiation time for Y12 was linear which showed that the photodegradation reaction obeys the first order kinetics reaction with rate constant $K_{ap} = 9.4 \times 10^{-3} \text{ min}^{-1}$.

Table 1. The changes of pH solutions after 60 minutes of irradiation time.

Initial Ph (t = 0)	11	10	6.3	5	2
Decomposition % at (t= 60)	73.44	61.02	28.68	93.54	100
Final pH(t= 60)	7	8.5	6.0	2.5	1.6

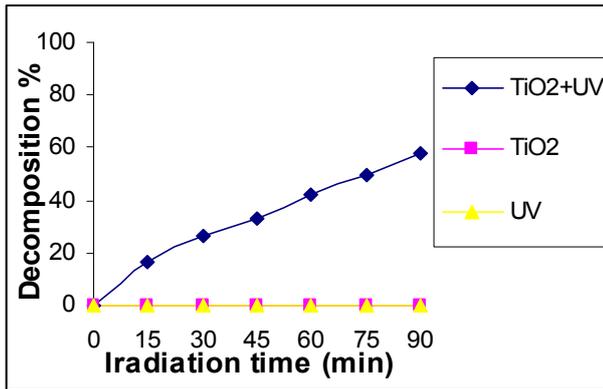


Figure 1. The changes of decomposition value (%) of dye sample versus irradiation time at neutral pH in presence of 2000 ppm of TiO₂.

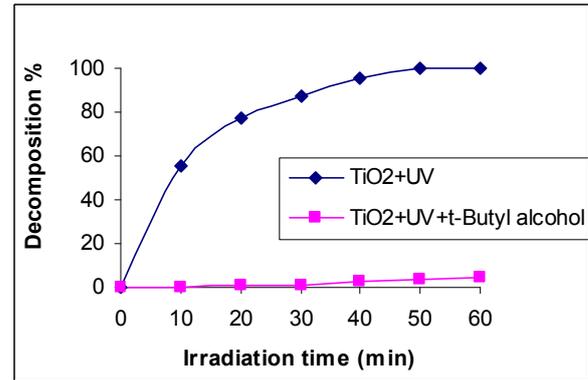


Figure 4. The changes of decomposition value (%) of dye sample versus irradiation time in presence of t-Butyl alcohol

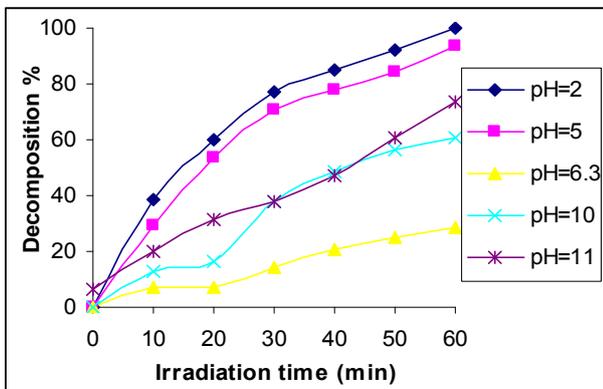


Figure 2. The changes of decomposition value (%) of dye sample versus irradiation time at various pH values in presence of 2000 ppm TiO₂.

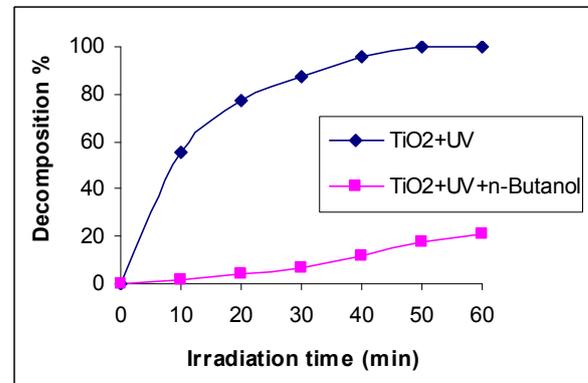


Figure 5. The changes of decomposition value (%) of dye sample versus irradiation time in presence of n-butanol.

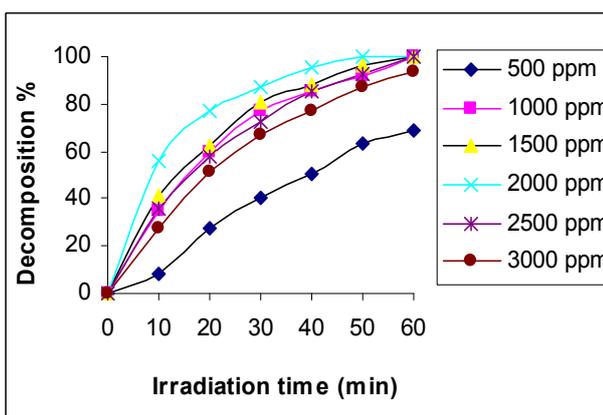


Figure 3. The changes of decomposition value (%) of dye sample versus irradiation time at pH = 2 in presence of various amount of TiO₂.

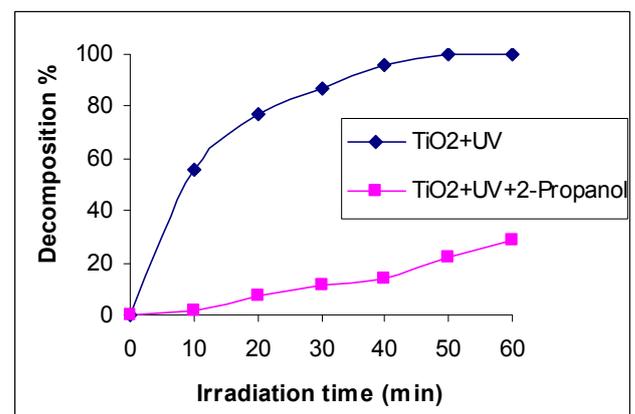


Figure 6. The changes of decomposition value (%) of dye sample versus irradiation time in presence of 2-propanol.

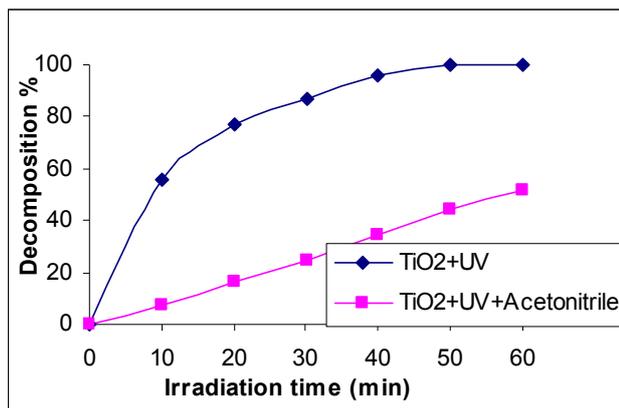


Figure 7. The changes of decomposition value (%) of dye sample versus irradiation time in presence of acetonitrile.

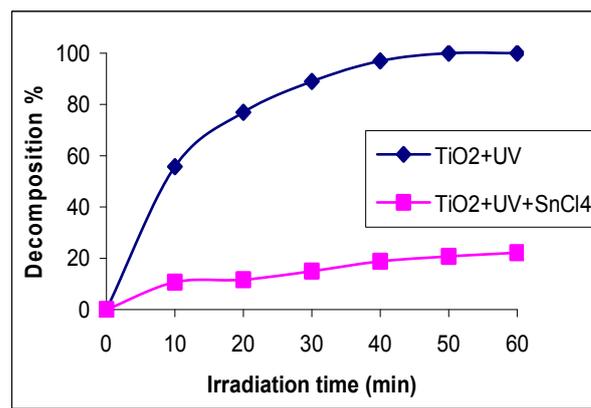


Figure 10. The changes of decomposition value (%) of dye sample versus irradiation time in presence of SnCl₄.

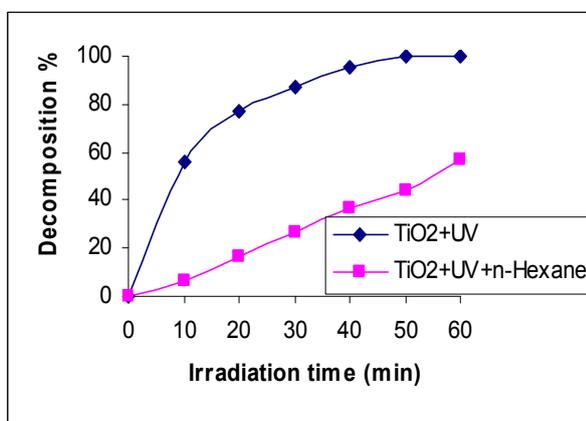


Figure 8. The changes of decomposition value (%) of dye sample versus irradiation time in presence of n-Hexane.

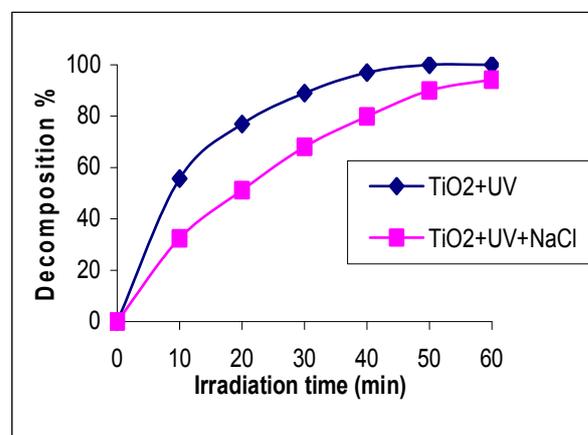


Figure 11. The changes of decomposition value (%) of dye sample versus irradiation time in presence of NaCl.

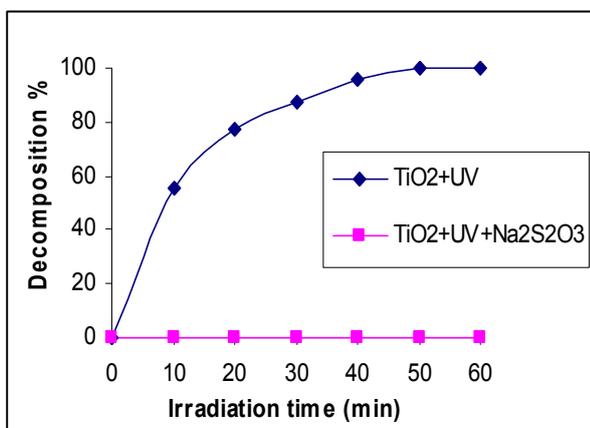


Figure 9. The changes of decomposition value (%) of dye sample versus irradiation time in presence of Na₂S₂O₃.

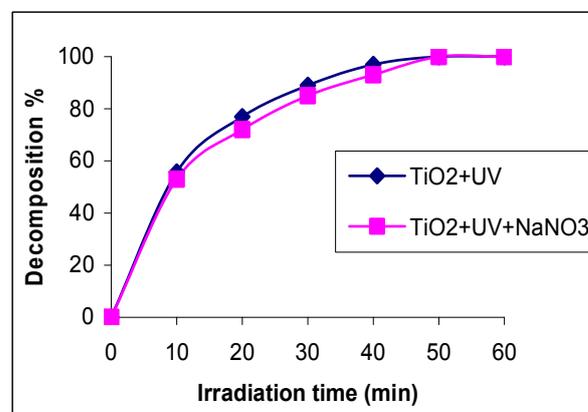


Figure 12. The changes of decomposition value (%) of dye sample versus irradiation time in presence of NaNO₃.

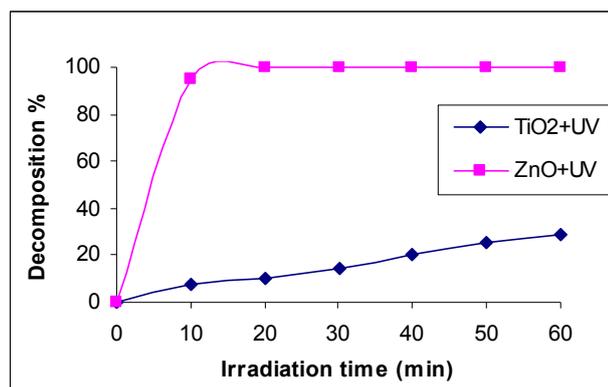


Figure 13. The changes of decomposition value (%) of dye sample versus irradiation time in presence of 1000 ppm of ZnO and TiO₂ at neutral pH.

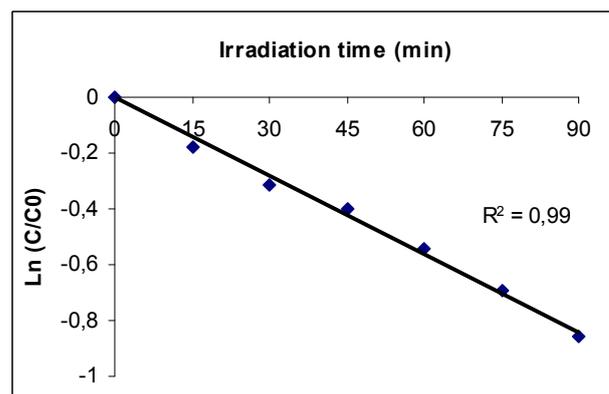


Figure 14. Relationship between [Y12] versus irradiation time on photocatalytic degradation of Y12. [Y12]₀=15 ppm, TiO₂=1000 ppm, and at neutral pH.

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