Photocatalytic degradation of a textile azo dye, Sirius Gelb GC on TiO_2 or Ag-TiO_2 particles in the absence and presence of UV irradiation: the effects of some inorganic anions on the photocatalysis

A. Özkan, M.H. Özkan, R. Gürkan*, M. Akçay, M. Sökmen

Department of Chemistry, Faculty of Science and Arts, University of Cumhuriyet, Sivas 58140, Turkey

Abstract

The aqueous phase photocatalytic degradation of Sirius Gelb GC used in the textile industry, was investigated. In order to optimize the working pH, three different dye solutions were prepared at pH 3.5; 7.0 and 11.0. One hundred cubic centimeter portions of the solution were irradiated with a low pressure UV lamb in the absence and presence of catalysts TiO_2 or Ag loaded-TiO_2. In all conditions, the samples withdrawn from the reactor were centrifuged and separated from the catalyst and degradation percentages were calculated from the measurement of the residual dye concentrations, spectrophotometrically. The optimum pH, which provides the best degradation ratio was found to be 3.5 for the dye. At the same pH, it was found that silver loaded catalyst is more effective than neat TiO_2 catalyst. The silver loading dramatically reduced the irradiation time from 20 min to 8 min for Sirius Gelb GC. However, the catalytical behavior of the both the catalysts was also investigated in heavy salt media such as simulated wastewater and in a river fluent. Pooled standard deviation (S_{pooled}) of the repeated measurements in all conditions is 0.615 for $N = 47$ and 38 degrees of freedom. Confidence limit of the method is 98.8 ± 0.2 in 95% confidence level.
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1. Introduction

Since TiO_2 is an effective, easily available, relatively inexpensive and chemically stable photocatalyst, numerous applications of this technique has arisen in the literature and some important reviews were published [1–7]. The latest review appeared in this field considered the recent applications especially usage in cancer treatment [8].

Heterogeneous photocatalysis is a process in which the illumination of an oxide semi-conductor, usually anatase or rutil, produces photo-excited electrons (e^-) and positive charged holes (h^+). The photo-excitation of the semi-conductor particles by UV light changes the energy state of the electrons from the valence band of the solid to the conduction band. The complete degradation of many organic pollutants is provided by one of the mechanistic ways as follows:
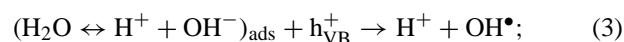
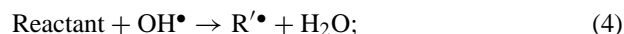- absorption of efficient photons ($h\nu \geq E_G = 3.2\,eV$) by titania

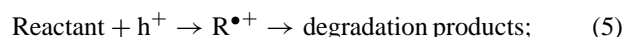$$TiO_2 + h\nu \rightarrow e_{CB}^- + h_{VB}^+; \quad (1)$$

- oxygen ionosorption

$$(O_2)_{ads} + e_{CB}^- \rightarrow O_2^{\bullet-}; \quad (2)$$
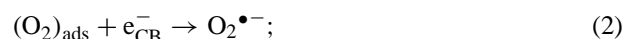
- neutralization of OH^- groups into $OH^\bullet$ radical by photo-holes

$$(H_2O \leftrightarrow H^+ + OH^-)_{ads} + h_{VB}^+ \rightarrow H^+ + OH^\bullet; \quad (3)$$

- oxidation of the organic reactant via successive attacks by $OH^\bullet$ radicals

$$Reactant + OH^\bullet \rightarrow R'^\bullet + H_2O; \quad (4)$$

- or by direct reaction with holes

$$Reactant + h^+ \rightarrow R^{\bullet+} \rightarrow degradation\ products; \quad (5)$$

Azo dyes constitute the largest class of dyes used in industry. In the textile industry, it is estimated that 10–15% of the dye is lost during the dyeing process and released as effluent. Azo dyes are resistant to aerobic degradation. However, under anaerobic conditions, the azo linkage is reduced

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* Corresponding author. Tel.: +90-3462191010; fax: +90-3462191186.
E-mail address: rgurkan@cumhuriyet.edu.tr (R. Gürkan).

to generate aromatic amines that are colorless but can also be toxic and potentially carcinogenic.

The conventional treatment methods for eliminating dyes from the waste stream include flocculation with lime, activated charcoal adsorption, and bio-treatment. Lime treatment and charcoal adsorption generate large amount or solid wastes, which require costly disposal and regeneration methods. Bio-treatment processes rely on indigenous soil microorganisms to degrade dye compounds. Since the synthetic dyes are resistant to aerobic biodegradation, this process is likely to be insufficient. Thus, there is a need for developing treatment technologies that are more effective in eliminating dyes from the waste stream at its source.

The formation of active species was previously discussed in details [1]. The effects of salty water on the photocatalytic oxidation products of liquid 3-octanol and 3-octanon [9] and influences of solution matrix on the photocatalytic removal of humic acid [10] were studied before. It was also pointed out that cationic dyes as Rhodamine B, was adsorbed poorly on TiO_2 surface and additional surface modification is required [11].

Since TiO_2 surface is positively charged, the question is how the presence of anionic species affect the catalyst's behavior and how it will be affected in the case of Ag loaded-TiO_2.

In this study, photocatalytic degradation of a textile azo dye, Sirius Gelb GC on TiO_2 or Ag-TiO_2 particles in the absence and presence of UV light was investigated. Also, the present study was undertaken to examine the effect of common counter-anions as Cl^-, NO_3^-, SO_4^{2-}, CH_3COO^-, $C_2O_4^{2-}$, CO_3^{2-}, SO_3^{2-}, HPO_4^{2-} and citrate that present in the real samples. Degradation and color removal rates versus irradiation time were determined and the possible effects of the anions were evaluated.

2. Materials and methods

2.1. Materials

Sirius Gelb GC, the molecular formula of which is given below, was purchased from Bayer Firm (Germany) and used without further purification.
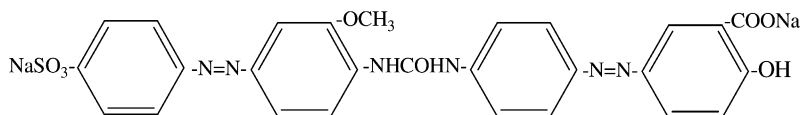
Titanium dioxide of analytical reagent grade was supplied by Aldrich firm (99.9% (w/w) TiO_2, in anatase form with a specific surface area of $9.35\,m^2\,g^{-1}$ as catalyst). Stock solution of the dye ($1000\,mg\,l^{-1}$) was prepared with de-ionized water, and further diluted to various concentrations in the experiment. The initial pHs of working samples of $20\,mg\,l^{-1}$ were adjusted to 3.5, 7.0 and 11.0 by addition of 1.00 M H_2SO_4 or 1.00 M NaOH solution and by controlling with

a pH meter (Jenway 3010 mark) operating at a measurement sensitivity of ±0.02. All the other chemicals used in this study were of analytical reagent grade. $NaNO_3$, NaCl, Na_2SO_4, $Na_2C_2O_4$, Na_2CO_3, Na_2HPO_4, Na_2SO_3, NaOAc and Na-citrate (Merck) salts were used as purchased.

2.2. Analysis

The sample solution of 100 ml was irradiated with a low pressure Hg lamb of 300 W (Osra-Ultra Vitalüx with 5.8 W output at 254 nm). The aliquots of 10 ml were collected at regular time intervals (0(initial), 2, 4, 6, 8, 10, 20, 30 and 60 min) and separated from the TiO_2 or Ag-TiO_2 catalyst by centrifuging 10 min at 4500 rpm (Hetich Universal Mark). The concentration of the dye in the supernatant was determined using UV-Vis spectrophotometer (UV-160 A Shimadzu model spectrophotometer) at 394 nm.

2.3. Experimental procedures

One hundred cubic centimeter of aqueous dye solutions ($20\,mg\,l^{-1}$, Aldrich), previously adjusted to a fixed pH value containing $250\,mg\,l^{-1}$ corresponding salt, were prepared in distilled water and 0.2 g TiO_2 or Ag loaded-TiO_2 added solution were irradiated with continuous stirring. Two cubic centimeter of aliquots were withdrawn at predetermined periods and were immediately centrifuged to separate the catalyst, and residual dye concentrations were determined spectrophotometrically by measuring the absorption maximum of Sirius Gelb GC at 394 nm.

Ag loaded-TiO_2 containing 1% (w/w) silver was prepared by following the method described elsewhere [12]. Initially, a 9.2 ml volume of $AgNO_3$ solution (1.00 M) was added 10 ml volume of a 1% (w/v) Na_2CO_3 solution. The aqueous suspension was dried at room temperature and then baked for 6 h at 400 °C (surface area, $8.49\,m^2\,g^{-1}$). Its pH was adjusted to 3.5; 7.0 and 11.0 with 1.00 M H_2SO_4 and 1.00 M NaOH, respectively.

The statistical tests were also carried out to determine significance of the difference of the two methods. Mean values and standard deviations of the three replicates after 5–10 min irradiation were determined, corresponding pooled standard deviation was calculated for nine groups of experiment (that is pH optimization, TiO_2, TiO_2/UV, Ag-TiO_2/UV replicates). Then, the calculated experimental values were compared with the corresponding critical value of it. Additionally, the synthetic samples were prepared by spiking the known concentrations of phenol, chromium and sulfite (on the condition that their concentrations are 0.12 mg phenol/l, 0.27 mg Cr^{3+}/l and 0.09 mg $SO_3^{2-}\,l^{-1}$ in final volume) into

the dye samples of $20\,mg\,l^{-1}$, which its initial pH was previously adjusted to 3.5. The dye solutions of $20\,mg\,l^{-1}$ were prepared in river water (Kızılırmak, Sivas). pH of solutions were constantly 7.33. The color intensity of dyes remained without degradation in solutions and was measured as absorbance. The dye concentrations remained without degradation were established by using the calibration curve method. The percentage degradation were calculated by using the equation given below:

$$\text{Degradation}\,(\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (6)$$

in which C_0 is the initial dye concentration, C the dye concentration after the treatments as concentration unit, $mg\,l^{-1}$. The dye adsorbed on catalyst surface without any interaction with UV rays were described as the initial corresponding absorptions ($t = 0$, the approximate 30 s time interval which the dye was mixed with catalyst.). The percentage initial adsorption were calculated by using the equation given below:

$$\text{Initial adsorption}\,(\%) = \frac{C_0 - C'}{C_0} \times 100 \qquad (7)$$

in which C' is the dye concentration remained without adsorption on catalyst surface as concentration unit, $mg\,l^{-1}$.

3. Results and discussion

The concentration characteristic of dye effluents are generally affected from pH and anion variations. The pH, which gives rise to modification of the physical properties (including charge) of molecules with ionisable functional groups, plays an important role in the adsorption and oxidation of the dye on TiO_2 or Ag loaded-TiO_2. Therefore, both pH and counter-anions were chosen as the main factors in the present study. All of the dye concentration variation were followed via a calibration curve set up in the concentration range of 0–$20\,mg\,l^{-1}$. The calibration equation is $A - 0.0006 + 0.03446xC_{dye}$ with correlation coefficient of 0.9999 (r) where A is the absorbance of dye at 394 nm, C_{dye} the concentration of dye with the concentration unit as $mg\,l^{-1}$.

3.1. Effect of pH on the photocatalytic degradation of the dye sample

The experimental data of pH effect studies are given in Figs. 1–3, separately. Each of the points shown in all figures represent the mean of three replicates. As seen in Fig. 1, the maximum decomposition rate (97%) was reached (at 8 min) in Ag-TiO_2/UV system whereas it was reached to this yield in the first 20 min in TiO_2/UV system. In TiO_2 system alone, 58% of the dye was adsorbed as soon as the sample interacts with TiO_2 particles and no variation was observed during the 60 min. A similar behavior was also observed in the UV system alone.
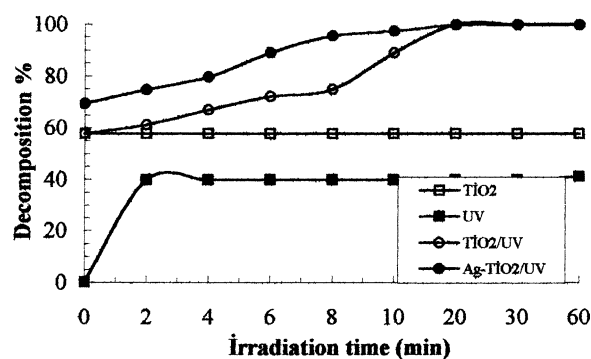

Fig. 1. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time at pH 3.5.
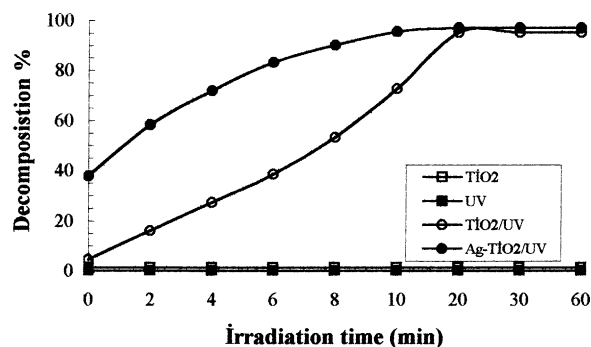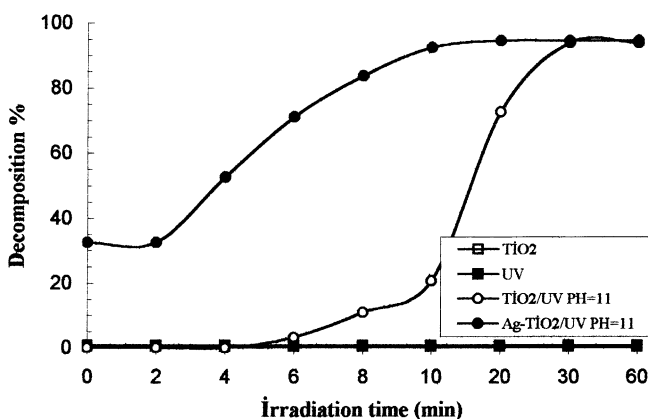

Fig. 2. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time at pH 7.0.

In this situation, when the dye sample interacted with UV rays in the first 2 min, 40% of the dye was degraded and remained invariably during the 60 min.

As seen in Fig. 2, the maximum decomposition rate (95%) was reached (at 10 min) in Ag-TiO_2/UV system whereas it was reached to this yield in 20 min in TiO_2/UV system. Neither TiO_2 system nor UV system gave rise to any color removal at pH 7.0. As seen in Fig. 3, the maximum decomposition rate (92%) was reached (at 10 min) in Ag-TiO_2/UV system whereas it was reached to this yield in 30 min in

Fig. 3. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time at pH 11.0.
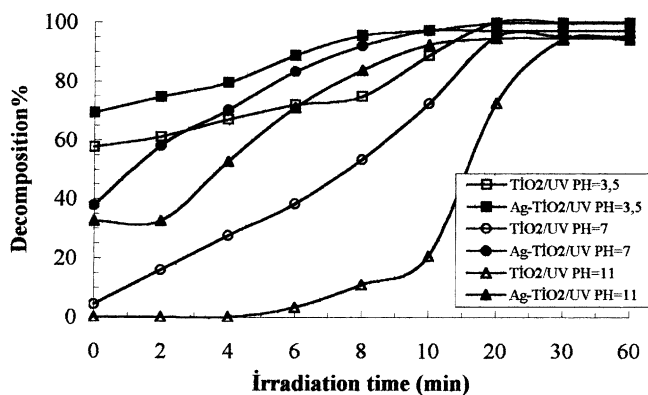
Fig. 4. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time pH 3.5, 7.0 and 11.0 in TiO_2/UV and Ag-TiO_2/UV systems.

Fig. 6. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time in Na_2SO_4 salt media at pH 3.5 in TiO_2/UV and Ag-TiO_2/UV systems.

TiO_2/UV system. Both TiO_2 system alone and UV system alone didn't give rise to any color removal at pH 11.0. Additionally, the percentage degradation rates (%) of the dye with irradiation time are simultaneously given for three different pH values in Fig. 4.

Pooled standard deviation (S_{pooled}) is 1.56 and $t_{experimental}$ = 20.13 at optimum pH value (that is 3.5). Since the $t_{experimental}$ is greater than tabulated $t_{critical}$ value (2.78) for $N = 4$ and $P = 0.05$, two methods differ significantly and silver-loading significantly increases the degradation rates. Although the degradation rate was significantly affected with neat titania; in case of Ag-loaded catalyst system the degradation rate was more efficient at pH 3.5. Therefore, a value of 3.5 was considered as optimum degradation pH. Salt environment and simulated/synthetic waste water environment studies were also made at pH 3.5.

3.2. Photocatalytic degradation of the dye at pH 3.5 in the salt environment

The salt media being $250 \, mg \, l^{-1}$, the final anion concentration were prepared and their photocatalytic degradation
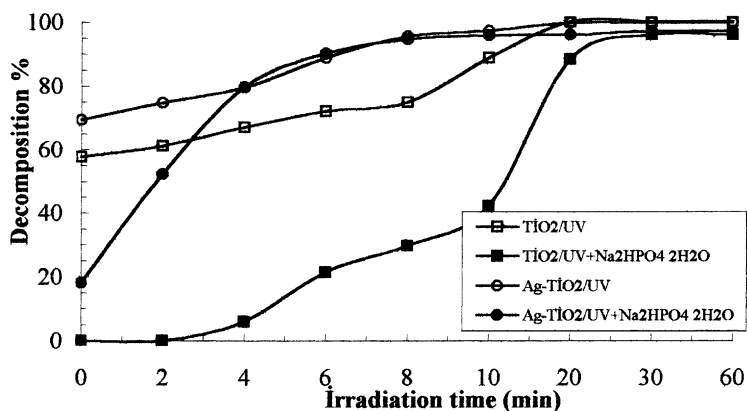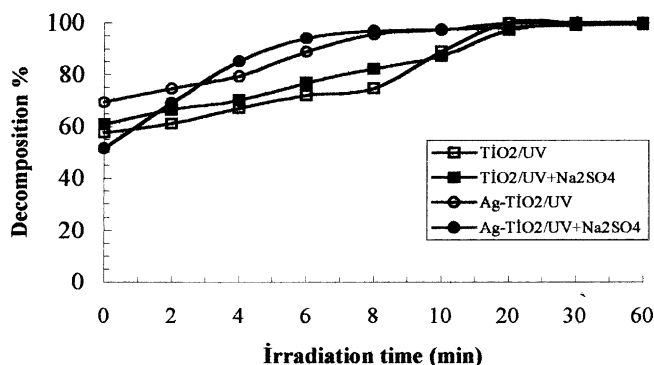

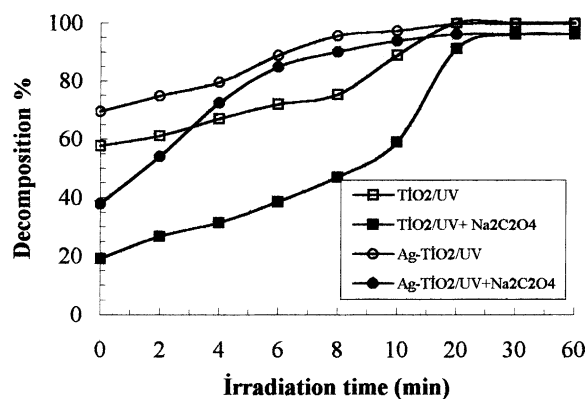Fig. 7. The change of decomposition on value (%) of Sirius Gelb GC sample with irradiation time in $Na_2C_2O_4$ salt media at pH 3.5 in TiO_2/UV and Ag-TiO_2/UV systems.

were examined by spiking the Na-salts of the anions into the dye solutions of $20 \, mg \, l^{-1}$, previously adjusted to pH 3.5. The salt effect on the degradation process was investigated with the same way. The degradation percentages as a function of irradiation time were determined and given in Figs. 5–13 for both catalyst systems in the presence of salts.
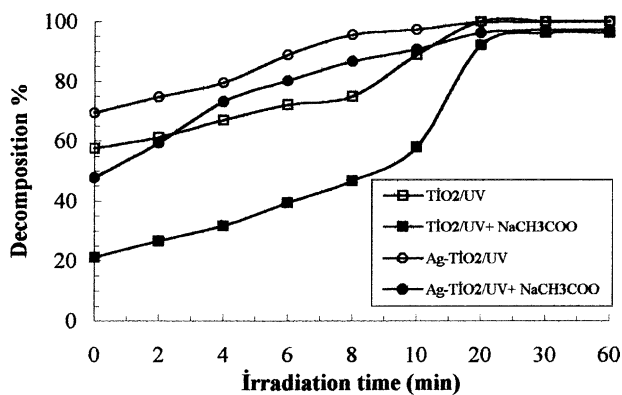

Fig. 5. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time in $Na_2HPO_4 \cdot 2H_2O$ salt media at pH 3.5 in TiO_2/UV and Ag-TiO_2/UV systems.

Fig. 8. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time in CH_3COONa salt media at pH 3.5 in TiO_2/UV and Ag-TiO_2/UV systems.
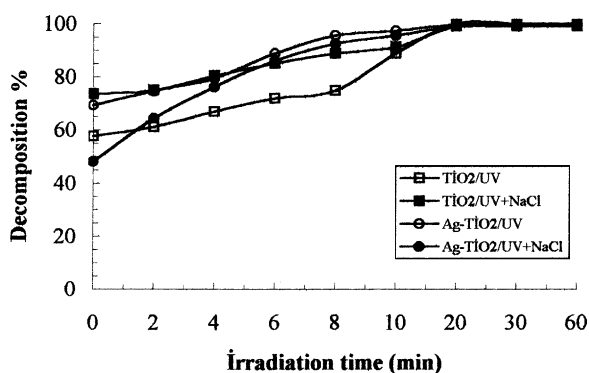

Fig. 11. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time in Na_2SO_3 salt media at pH 3.5 in TiO_2/UV and Ag-TiO_2/UV systems.

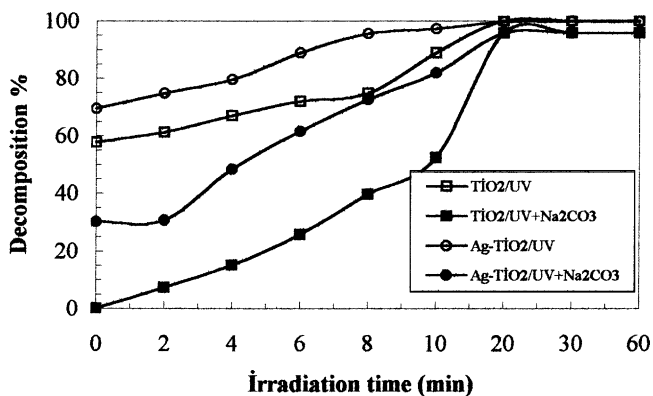Fig. 9. The change of decomposition value (%) of Sinus Gelb GC sample with irradiation time in NaCl salt media at pH 3.5 in TiO_2/UV and Ag-TiO_2/UV systems.
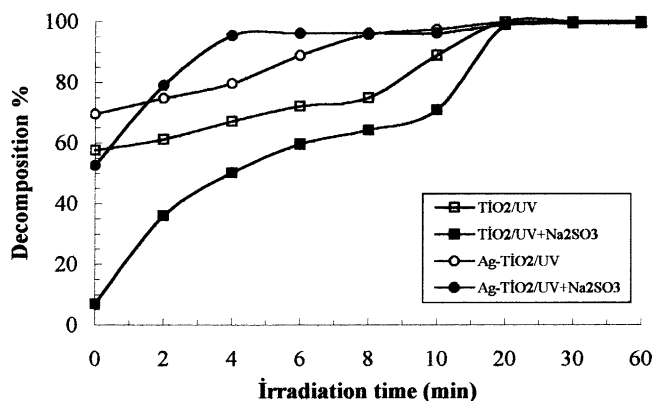

Fig. 12. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time in $NaNO_3$ salt media at pH 3.5 in TiO_2/UV and Ag-TiO_2/UV systems.

As can be seen from the figures, the effectiveness of TiO_2/UV system was significantly decreased in the presence of HPO_4^{2-}, $C_2O_4^{2-}$, CH_3COO^-, CO_3^{2-}, SO_3^{2-} and citrate ions whereas its effectiveness increased partly in the presence of NO_3^-, Cl^-, SO_4^{2-} ions. The photocatalytic degradation was also increased with NO_3^-, Cl^-, SO_4^{2-}

ions in the first 20 min of irradiation while the adsorption of the dye on TiO_2 particles was promoted in the presence of these anions. The photocatalytic degradation was retarded with HPO_4^{2-}, $C_2O_4^{2-}$, CH_3COO^-, CO_3^{2-}, SO_3^{2-} and citrate ions while the adsorption of the dye on TiO_2
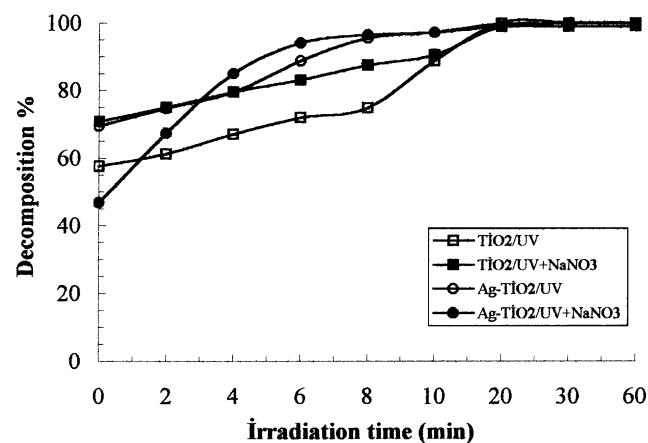

Fig. 10. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time in Na_2CO_3 salt media at pH 3.5 in TiO_2/UV and Ag-TiO_2/UV systems.
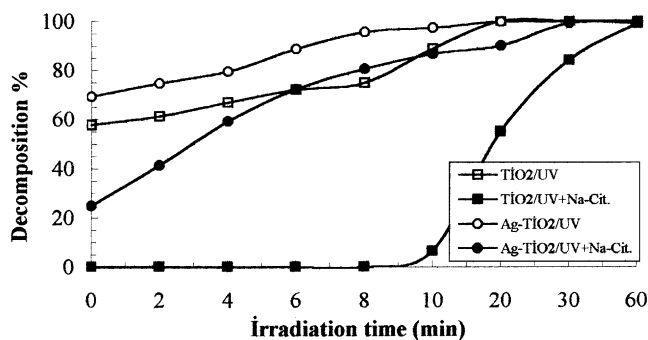

Fig. 13. The change of decomposition value (%) of Sirius Gelb GC sample with irradiation time in Na-citrate salt media at pH 3.5 in TiO_2/UV and Ag-TiO_2/UV systems.

particles was slown down in the presence of these anions. Presence of anions except for NO_3^-, Cl^-, SO_4^{2-} inhibited the rate of color removal in the first 10–20 min irradiation. But 95–99% of color removal was still achieved after 20 min irradiation whether anionic species present or not. The effectiveness of Ag-TiO$_2$/UV system was partly decreased in the presence of $C_2O_4^{2-}$, CH_3COO^-, Cl^-, CO_3^{2-} and citrate ions.

In case of HPO_4^{2-}, SO_4^{2-}, SO_3^{2-} and NO_3^- ions, the Ag-TiO$_2$/UV system showed different behaviors. While the adsorption of the dye on Ag loaded-TiO$_2$ was greatly decreased in the presence of all anions, the photocatalytic degradation (%) was retarded with $C_2O_4^{2-}$, CH_3COO^-, Cl^-, CO_3^{2-}, citrate ions and the presence of HPO_4^{2-}, SO_4^{2-}, SO_3^{2-}, NO_3^- ions had different effects on it.

3.3. Photocatalytic degradation of stimulated sample spiked with the dye at pH 3.5

The stimulated sample was prepared at the solutions with final concentration of phenol, Cr^{3+} and SO_3^{2-} ion of 0.12, 0.27 and 0.09 mg l^{-1}, respectively and dye concentration of 20 mg l^{-1} at pH 3.5. The photocatalytic degradation curves are given in Fig. 14. In TiO$_2$/UV system, the initial adsorption of the dye sample was increased from 58 to 70%. In Ag-TiO$_2$/UV system, with these interfering matrix components, its initial adsorption was decreased from 70 to 59%. Additionally, for 99% decomposition it was observed that the decomposition time increased from 8 min to 20 min. In TiO$_2$/UV system, any variation in this time was not observed while the decomposition time is 20 min without any interfering species when phenol, Cr^{3+} and SO_3^{2-} ions were added to it.

3.4. Photocatalytic degradation of river water solution of the dye

The dye sample was prepared with river water having pH 7.33 (Kızılırmak River, Sivas) instead of distilled water. In-
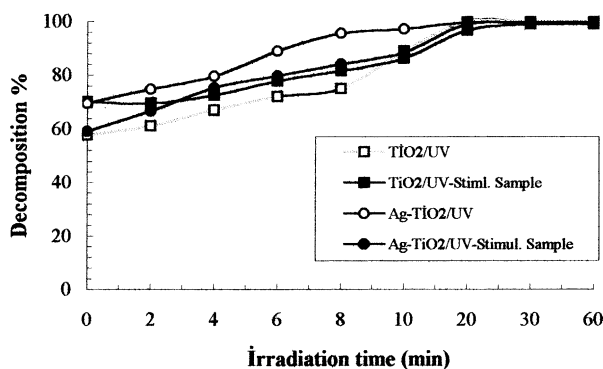

Fig. 14. The change of decomposition Value (%) of Sirius Gelb GC sample with irradiation time in synthetic waste water media at pH 3.5 in TiO$_2$/UV and Ag-TiO$_2$/UV systems.
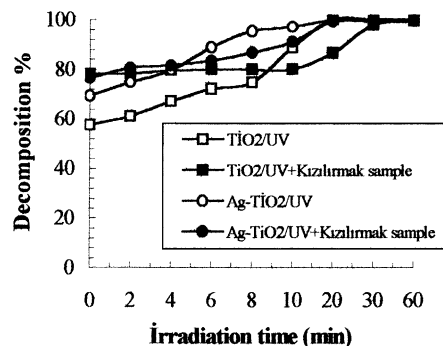

Fig. 15. The change of decomposition value (%) of Sirius Gelb CC sample, previously prepared with river water (Kızılırmak Sivas) having pH 7.33 with irradiation time in TiO$_2$/UV and Ag-TiO$_2$/UV systems.

tentionally, the pH of the dye sample wasn't adjusted to 3.5. The photocatalytic decomposition curves of the dye with time are given in Fig. 15. When it was compared with the initial adsorption of the dye sample having pH 3.5, the initial adsorption of the river water solution increased from 58% to 78% in TiO$_2$/UV system while its corresponding value increased from 70 to 76% in Ag-TiO$_2$/UV system, respectively.

In case of the dye sample prepared with river water, 99% of the dye sample was degraded in 20 min in Ag-TiO$_2$/UV system while it was degraded in 30 min in TiO$_2$/UV system.

In case of the dye sample prepared with distilled water at pH 3.5, 98% of the dye was degraded in 8 min in Ag-TiO$_2$/UV system while 99% of the dye was degraded in 20 min in TiO$_2$/UV system.

4. Conclusions

Photocatalytic oxidation of textile dyes in example Sirius Gelb GC over TiO$_2$ or modified TiO$_2$ is a promising method for color disappearance of textile wastewater.

Catalyst modification with Ag-loading enables the catalyst more effective and hence shortening of the irradiation period can be more valuable procedure than neat titania on the economical point of view. Although the oxidation rates were retarded in the presence of some inorganic anions with TiO$_2$/UV, it was promoted or had no clear effect with Ag-TiO$_2$/UV system. Why Ag-TiO$_2$ catalyst is influenced less than TiO$_2$ catalyst is because of the fact that holes on TiO$_2$ semi-conductor surface are filled with anions. However, these holes on Ag-TiO$_2$ catalyst are much more and are not observed a clear influence in which the holes are filled with anions.

The photocatalytic degradation of the dyes by Ag loaded-TiO$_2$ is rather advantageous according to other oxidation processes:

(i) The complete decomposition is achieved in a very short time.

 (ii) There is necessary to more little energy.
(iii) Catalyst system can be reused.
(iv) The used catalyst system isn't too much influenced from salt environment, waste water environment and natural conditions.

Therefore, this method can be easily and efficiently applied to the removal of industrial waste waters, drinking waters, contaminated underground waters, air and soil pollutants.

Acknowledgements

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