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Short communication

Decolourising textile wastewater with modified titania: the effects of inorganic anions on the photocatalysis

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Abstract

In this study, the environment of the TiO_2 photocatalyst modified with silver was investigated. The photocatalytic degradation of textile dye Astrazone Orange G was carried out in the presence and absence of common inorganic salts to determine the effect of the anionic species. It was shown that degradation of dyes in the first 20 min in the presence of anions exhibited different behaviour. While the catalytic activity of TiO_2 was significantly retarded in the presence of common inorganic anions it was not affected or was promoted in many cases with Ag-loaded TiO_2. In TiO_2/UV system positive charged holes (h^+) might be scavenged by the negatively charged anions and the adsorption of dyes on the surface of TiO_2 was significantly inhibited. However, this inhibition effect was not observed with modified titania and possible mechanism was thought to be the trapping of the conductive band electrons by silver islands producing more positively charged holes as well as the reduction of the band gap energy. Additionally, the adsorption of the dye on the Ag–TiO_2 catalyst surface was significantly increased in the presence of anions and this might be responsible for another promoting effect. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalytic oxidation; Silver-loaded TiO_2; Anions; Textile dyes

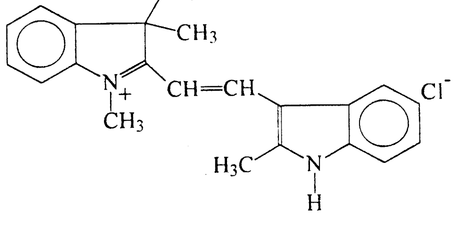
1. Introduction

Since the 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 excellent reviews were published [1–7]. The latest review appeared in this field considered the recent applications especially usage in the cancer treatment [8].

Heterogeneous photocatalysis is a process in which the illumination of an oxide semi-conductor, usually anatase or rutile, 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 formation of active species was previously discussed in details [1]. The effects of salt water on the photocatalytic oxidation products of liquid 3-octanol and 3-octanon [9] and influences of solution matrix on the phtocatalytic removal of humic acid [10] were studied before. It was also pointed out that cationic dyes, e.g. Rodamine B, was adsorbed poorly on the TiO_2 surface and additional surface modification is required [11]. Since the TiO_2 surface is positively charged, the question is how presence of anionic species effects the catalyst's behaviour and how it will be effected in the case of silver-loaded TiO_2.

The present study was undertaken to examine the effect of common inorganic salts that present in the real world samples. Therefore, aqueous Astrazone Orange (an acidic cationic dye) samples, which molecule formulation is given below, containing following inorganic salts were prepared and TiO_2/UV and Ag–TiO_2/UV processes were carried out: NO_3^-, Cl^-, CO_3^{2-}, HPO_4^{2-}, $C_2O_4^{2-}$, SO_3^{2-}, SO_4^{2-}, acetate and citrate. Decomposition and colour removal rates versus illumination time were determined and the possible effects of anions were evaluated.



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2. Materials and methods

Anatase form of TiO_2 (99.9% TiO_2 Aldrich, specific surface area 9.35 $m^2\,g^{-1}$) was used in all experiments. $NaNO_3$, NaCl, Na_2CO_3, Na_2HPO_4, $Na_2C_2O_4$, Na_2SO_3, Na_2SO_4, NaOAc and NaCit. (Merck) were used as purchased. A 100 cm^3 of aqueous dye solutions (20 ppm, Aldrich) containing 250 ppm corresponding salt were prepared in distilled water and 0.2 g TiO_2 or Ag–TiO_2 added solution were illuminated with a Osram-Ultra Vitalüx 300 W low pressure Hg lamb (5.8 W output 254 nm) with continuous stirring. A 2 cm^3 of suspensions were withdrawn at 2 min intervals and heterogenous portions were immediately centrifuged to separate the catalyst and residual dye concentrations after

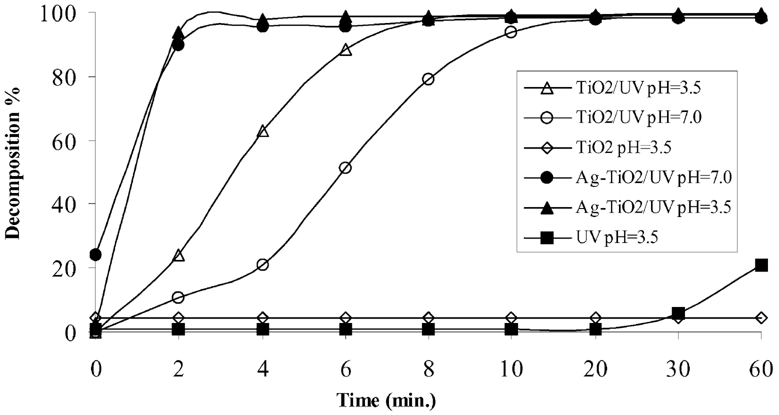

Fig. 1. The residual Astrazone Orange G concentration by illumination time for several systems.

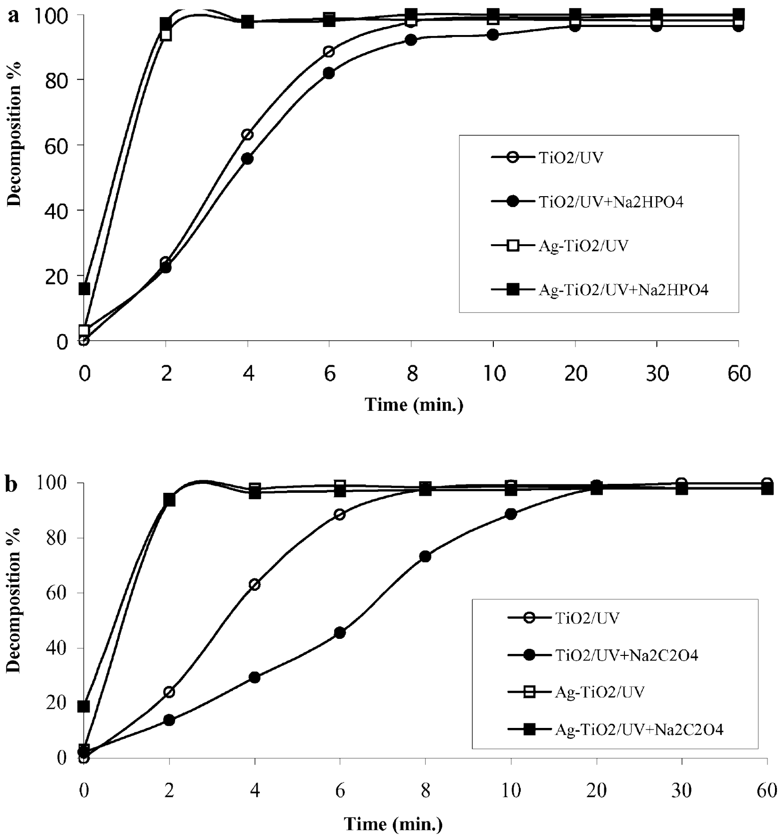

Fig. 2. The degradation percentage of Astrazone Orange G by illumination time in the presence of 250 ppm. (a) Na_2HPO_4 at pH = 3.5 (for Na_2HPO_4, $t_{\mathrm{experimental}} = 5.7 > t_{\mathrm{critic}} = 2.78$ ($N = 4$ and $p = 0.05$) with TiO_2/UV; $t_{\mathrm{experimental}} = 0.8 < t_{\mathrm{critic}} = 2.78$ ($N = 4$ and $p = 0.05$) with Ag–TiO_2/UV). (b) $Na_2C_2O_4$ at pH = 3.5 (for $Na_2C_2O_4$, $t_{\mathrm{experimental}} = 20.8 > t_{\mathrm{critic}} = 2.78$ ($N = 4$ and $p = 0.05$) with TiO_2/UV; $t_{\mathrm{experimental}} = 0.5 < t_{\mathrm{critic}} = 2.78$ ($N = 4$ and $p = 0.05$) with Ag–TiO_2/UV).

illumination were determined spectrophotometrically by measuring the absorption maximum of Astrazone Orange at 484 nm.

The Ag-loaded titanium dioxide containing 1% (w/w) silver was prepared by following the method described elsewhere [12]. Initially, 9.2 cm^3 of $AgNO_3$ solution (0.1 M) was added to a TiO_2 slurry containing 10 g of TiO_2 followed by ca. 10 cm^3 of a 1% (w/w) Na_2CO_3 solution. The aqueous suspension was dried at room temperature and then baked for 6 h at 600 °C (surface area 8.49 $m^2\,g^{-1}$). The pH was adjusted to 3.5 and 7.0 with 1 M H_2SO_4 and NaOH, respectively. pH measurements were made using Jenway 3010 pH meter.

Significance tests were also carried out to determine whether two methods give results differ significantly or not. Mean value and standard deviation of the three replicates after 5–10 min illumination was determined, corresponding pooled estimate of standard deviation was calculated. Following this, calculated experimental t-values were compared with the tabulated critical value of t.

3. Results and discussion

A series of experiments involving the degradation of Astrazone Orange G was carried out in the presence of TiO_2 with or without UV illumination and the same procedure was repeated with Ag-loaded TiO_2 at different pHs. The findings are given in Fig. 1 and each data points shown in all figures represent the mean of three replicates. Control experiments show that Astrazone Orange dye is not degraded with the TiO_2 suspension in the dark or UV light in the absence of the TiO_2 particles for 30 min period.

The photo-degradation process is highly pH-dependent and the process exhibits different behaviour with the chemical character of the dye. Therefore, the process was repeated at pH 3.5 and 7.0. As a result of its chemical structure, the dye undergoes massive degradation at higher pH.

According to these results, the mean values are 21.1 ± 1.5 at pH 7.0 and 63.1 ± 1.9 at pH 3.5 for TiO_2/UV system (after 4 min illumination). Degradation values (%) were found 95.6 ± 1.3 at pH 7.0 and 97.7 ± 1.5 at pH 3.5 for Ag-loaded TiO_2/UV system. Pooled standard deviation is 1.71 and $t_{\text{experimental}} = 24.79$ at pH 3.5. Since the $t_{\text{experimental}}$ greater than tabulated t_{critic} value (2.78) for $N = 4$ and $p = 0.05$, the two methods differ significantly and silver-loading significantly increases the degradation rates. Although the degradation rate was significantly affected with neat titania but in the case of silver-loaded catalyst system at pH 3.5.

The effect of the environment on the degradation process was investigated with the same manner. The degradation percentage as a function of illumination time have been determined and given in Figs. 2–4 for both catalyst systems in the presence of salts.

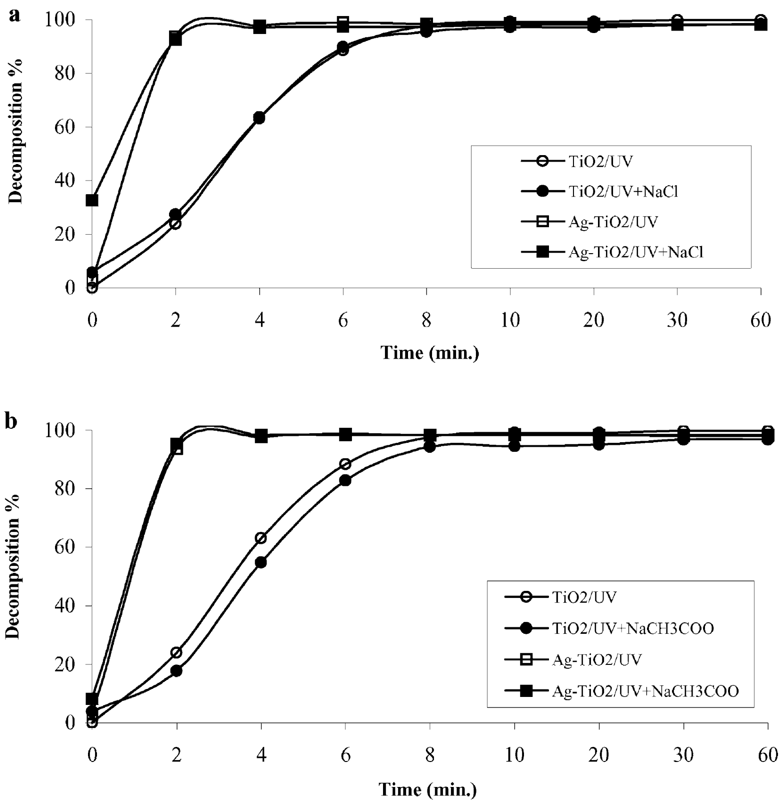

Fig. 3. The degradation percentage of Astrazone Orange G by illumination time in the presence of 250 ppm: (a) NaCl and (b) NaOAc at pH = 3.5.

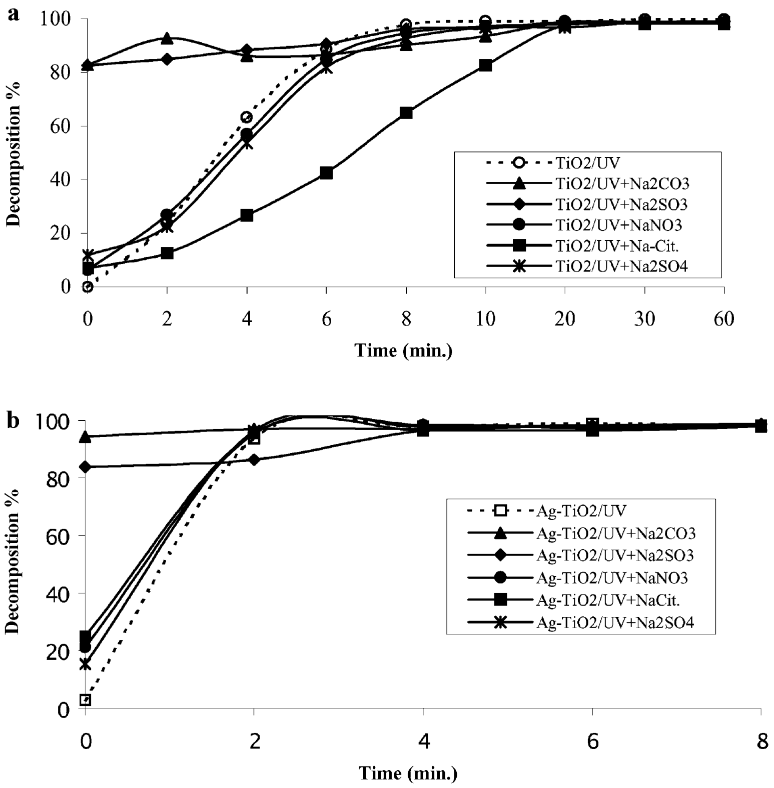

Fig. 4. The degradation percentage of Astrazone Orange G by illumination time in the presence of 250 ppm: Na_2CO_3, Na_2SO_3, $NaNO_3$, NaCit. and Na_2SO_4 at pH = 3.5. (a) $TiO_2/UV + salt$, (b) Ag–$TiO_2/UV + salt$ (first 8 min).

As can be seen from the above figures, the effectiveness of TiO_2/UV system was significantly decreased in the presence of inorganic anions. Since the surface modification with anions might increase the absorption of Astrazone Orange (a cationic dye) on TiO_2, increasing colour removal rates might be expected. While the adsorption of Astrazone Orange on TiO_2 was promoted in the presence of all salts, the photo-decomposition was retarded with $HPO_4{}^{2-}$, $C_2O_4{}^{2-}$, OAc^-, $SO_4{}^{2-}$, $NO_3{}^-$, and Cit.$^-$ and the presence of NaCl had little effect on it.

Presence of anions except for $CO_3{}^{2-}$ and $SO_3{}^{2-}$ inhibited the rate of colour removal in the first 10–20 min of illumination. But 90–95% colour removal was still achieved after 20 min illumination whether anionic species present or not.

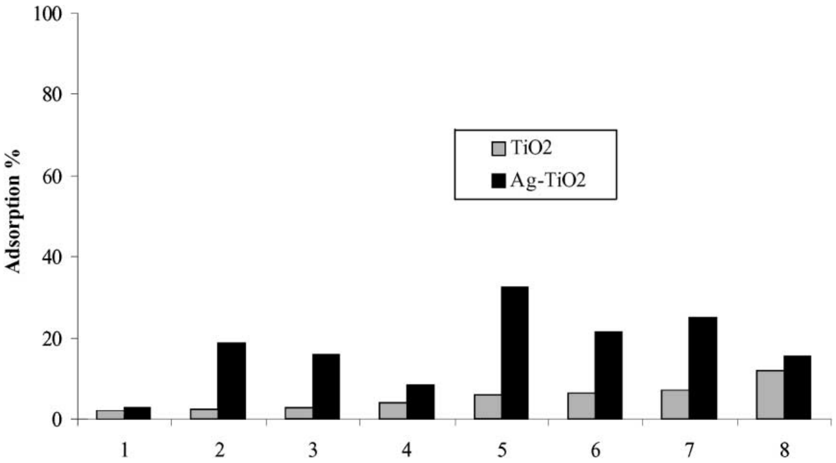

Fig. 5. Initial absorption percentage of Astrazone Orange on TiO_2 and Ag–TiO_2 at pH 3.5. (1) TiO_2 or Ag–TiO_2, (2) $Na_2C_2O_4$, (3) Na_2HPO_4, (4) NaOAc, (5) NaCl, (6) $NaNO_3$, (7) NaCit., (8) Na_2SO_4.

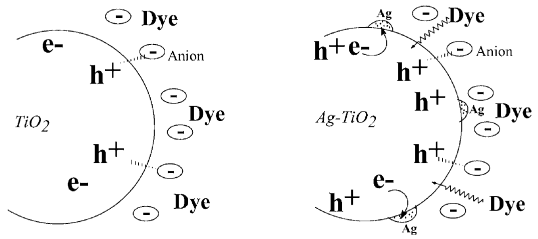

Fig. 6. Scavenging of positive holes by negative-charged anions.

Massive degradation of the dye itself was observed with the solution containing only CO_3^{2-} or SO_3^{2-} anion and characteristic peak at 484 nm disappeared soon after the addition of these anions.

Adsorption of Astrazone Orange on silver-loaded TiO_2 was also significantly increased in the presence of the anionic species. Adsorption behaviour of both catalysts in an anion containing media is given in Fig. 5.

Inhibition effects of anions except for CO_3^{2-} and SO_3^{2-} can be explained as the reaction of the positive holes (h^+) formed on the TiO_2 with anions and those anions behaved like h^+ scavengers resulting prolonged colour removal in 10–20 min illumination. Probably, the adsorbed anions compete with dye for the photo-oxidising species on the surface and preventing the photocatalytic degradation of Astrazone Orange by oxidative species like hydroxyl radicals (Fig. 6).

Formation of inorganic radical anions under these circumstances were also reported in the literature [9,10] and possible mechanism was proposed as following:

$$Cl^- + h^+ \rightarrow Cl^\bullet, \quad NO_3^- + h^+ \rightarrow NO_3^\bullet$$

Although, the reactivity of these radicals with chromophic groups of Astrazone Orange may be considered, the observed effect is still thought to be the strong adsorption of the anions on Ag–TiO_2 surface. Photocatalytic oxidation of dyes over modified TiO_2 is a promising method for decolourising of textile wastewaters. Catalyst modification with silver-loading enables the catalyst more effective and shortening of the illumination 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 inorganic anions with TiO_2/UV, it was promoted or had no effect with Ag–TiO_2/UV system.

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