Photocatalytic degradation of some toxic analytical reagents with TiO₂

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ABSTRACT. Photodegradation processes of two azo dyes at TiO₂/H₂O interface under visible and ultraviolet light irradiation are investigated with different experimental techniques (absorption and fluorescence spectroscopy as well as total organic carbon analysis). Measuring their fluorescence spectra monitored the generation of some degradation intermediates. The photodegradation rate depends on dye structure and pH of the dispersion. The rate was found to be enhanced by increasing dissolved oxygen concentrations in the medium. The mechanism of the photodegradation process under uv-visible light illumination involves an electron excitation into the conduction band of the TiO₂ semiconductor leading to the generation of very active oxygenated species that attack the dye molecules leading to photodegradation.

1. INTRODUCTION

The increased pollution of water and air by industrial wastes demands the application of new and clean purification technology [1]. Azo dyes represent a large class of industrial effluents that stand for an increasing environmental danger [2]. Photocatalytic degradation of azo dyes in presence of TiO₂ has been investigated by several authors [3–11]. Large quantities of these dyes are manufactured annually worldwide and are used in a variety of applications as textiles, paper, foodstuffs, and cosmetics and also as reagents in analytical determination of heavy metals. Therefore, there should be continuous efforts on the development of photocatalytic degradation of this class of toxic materials.

In this contribution we report on the photocatalytic degradation of two azo compounds which are used as reagents for spectrophotometric determination of lanthanides. Our aim is to get information about their photostability by light stress testing using UV-visible light that dominates intense region in the solar spectrum. The factors that affect the efficiency of the photocatalytic degradation *e.g.*, pH, molecular structure are examined and discussed on the bases of electron/hole pair generation leading to redox processes. The degradation mechanism and the splitting of the molecular moieties leading to the formation of molecular intermediates will be discussed.

2. MATERIALS AND METHODS

Compounds under investigation are obtained from Fluka (pure grade) and are used as received. The TiO₂ fine powder heated to about 600 °C for one hour before use (Degussa P25) is used. The irradiation source was a 75 W Xenon arc lamp (PTI-LPS-220 Photon Technology International) operated at 70 W. The light intensity were measured using ferrioxalate actinometry and found to be 0.12 mEinsteins/min. Illumination of the dye solution in presence of TiO₂ with visible light (above 435 nm) reveals the importance of UV-light in the pho-

todegradation process using TiO₂ and rolled out the electron injection mechanism from the CT state of the free dye molecule. The buffer KCl/HCl of pH 2.5 and borax buffer of pH 9.2 are used.

The photochemical reactor is a cylindrical double-walled quartz cell, 50 mm diameter and 50 mm path length, with inlet and outlet for cooling by water to maintain the temperature at 25 °C ± 0.2. The illumination surface area was 15 cm². Appropriate weight of TiO₂ powder is added to buffered aqueous solutions of the compounds and stirred magnetically in air equilibrated solution. Sample solutions are withdrawn for analysis and centrifuged to separate TiO₂ particles. The absorption spectra were recorded using Helios α Unicam spectrophotometer. Fluorescence measurements were done using RF-5301 PC SHIMADZU spectrofluorophotometer. Total organic carbon, TOC, measurements are obtained using IONICS model 1555 B carbon analyser. Approximate PPP-SCF-CI-MO quantum chemical computations are performed using QCPE program no. QCMP054, Indiana University, using standard parameters. Qualitative results are obtained for a simplified molecular structure by neglecting the AsO₃H₂ groups.

The formation of substituted naphthalene moieties (fragments of *m/e* larger than 280) as intermediates was confirmed by gas mass chromatography. (GCQ, Finnigan MAT, capillary column Rtx-5MS 30 meter, 0.25 mmID, 0.25 μmdf “measured at the central lab of Ain Shams University”).

3. RESULTS AND DISCUSSION

The absorption spectra of the two compounds in different pH media are shown in Figures 1 and 2 for arsenazo III and chlorophosphonazo III, respectively. These dyes absorb strongly over UV and visible regions of the spectrum. The absorption spectrum of each of the compounds studied shows intense band around 550 nm characterising the charge migration over the whole molecule during light absorption (CT-transition). In the UV region, local absorption band at about 314 nm is observed and is attributed to $\pi - \pi^*$ transition of the substituted naphthalene moiety. The results are in agreement with the theoretical results obtained by applying PPP-SCF-CF-MO method.

Figure 1. Absorption spectra of arsenazo III in different pH media.

Figure 2. Absorption spectra of chlorophosphonazo III in different pH media.

This assignment is based on the analysis of the calculated contribution of different centres of molecules in the molecular orbitals (Configuration Interactions) involved in the transitions. Furthermore, the spectra of these compounds show the expected bathochromic shift of the CT-band with pH.

The effect of illumination time on the absorption spectra of aqueous solution (pH = 6) of arsenazo III in presence of TiO_2 suspension (0.5 g/L) is shown in Figure 3. Initially rapid disappearance of the visible band concomitant with slight increase in the absorption of the 314 nm band points to the generation of substi-

tuted naphthalene moiety as a main product of the first degradation step. After about 90 minutes of irradiation, the 314 nm absorption band starts to respond to the photolysis process leading to complete mineralization. Similar behaviour is observed for chlorophosphonazo III. These observations prompted us to follow up selectively the generation of substituted naphthalene moiety by monitoring its characteristic fluorescence.

Figure 3. Photocatalytic degradation of aerated aqueous solution of arsenazo III in 0.5 g/L TiO_2 colloidal suspension. The spectra were recorded after different illumination intervals.

The monitored fluorescence intensity at 430 nm (which is characteristic for naphthalene derivatives) is increasing by time of illumination until a point is reached at which it starts to decrease (Figures 4 and 5). This observation led us to the conclusion that the degradation is a stepwise process and specific. In other words, bond cleavage starts at the azo group bridge first forming both substituted naphthalene and benzene fragments. Then a fast degradation of both moieties to complete mineralization was occurred.

Figure 4. Change of the fluorescence spectra of the intermediate substituted naphthalene moiety generated by illumination of the chlorophosphonazo III at different times. The spectra were recorded at different illumination times following up the formation (—) and destruction (···) of the naphthalene fragment. (Similar results were obtained in case of arsenazo III).

Figure 5. The change of the fluorescence intensity at $\lambda_f = 430 \text{ nm}$ as a function of illumination time for chlorophosphonazo III in different pH media. (Similar results were obtained in case of arsenazo III).

Figure 6 shows the dependence of the concentration of arsenazo III on the illumination time at different pH values. Similar plot was obtained for chlorophosphonazo III. The rate at different pH of photodegradation of the studied compounds are summarised in Table 1. It was found that the determined rate of the photodegradation is weakly dependent on the pH between 2.5 and 9.2 in agreement with previous results obtained for some other systems [12–14].

Figure 6. The effect of time of illumination on the concentration of arsenazo III in different pH media. (Similar results were obtained in case of chlorophosphonazo III).

Table 1. Overall rate constants ($\times 10^2 \text{ min}^{-1} \pm 0.2$) for the complete degradation of the aqueous suspension of the reagents studied with TiO_2 .

(Values given between brackets for the formal quantum efficiency (FQE) calculated by $(\text{FQE} = \text{rate of reaction} / \text{incident light intensity})$ [15] in case of polychromatic light source).

pH	As III	CP III
2.5	2.8 [0.23]	2.2 [0.18]
6.0	2.2 [0.18]	1.9 [0.16]
9.2	1.8 [0.15]	3.1 [0.26]

To confirm the complete degradation of the studied compounds, total organic carbon (TOC) changes were followed. The results obtained from TOC analysis (Figure 7) confirm the stepwise mechanism mentioned above and are in agreement with the conclusion drawn from the fluorescence measurements (Figure 8).

Figure 7. Photodegradation of a solution of chlorophosphonazo III at pH = 6.0 as a function of illumination time followed by TOC technique. (Similar results were obtained in case of arsenazo III).

Figure 8. Change of TOC and fluorescence intensity (I_f at $\lambda_f = 430 \text{ nm}$) as a function of the illumination time for chlorophosphonazo III in acidic medium at pH = 2.5. (a) Generation of naphthalene moiety. (b) Mineralization (destruction) of naphthalene moiety.

During photodegradation process no noticeable change was observed in the pH of the buffered solutions (pH = 2.5 and 9.2) of the interaction system. However, in neutral medium the pH value of the solution was dropped from pH = 7.0 to 4.5 and to 4.0 in case of arsenazo III and chlorophosphonazo III, respectively, indicating the generation of oxoacids of S due to the mineralization process.

The above results point to the applicability of the current explanation of the applied mechanism of photocatalytic degradation [16, 17]. Active oxygen and its different free radicals generated at $\text{TiO}_2/\text{H}_2\text{O}$ interface

by the interaction of light with TiO_2 particles are responsible for the degradation of the molecules under investigations. As a further support to this suggestion, a saturated oxygen suspension of TiO_2 containing the dye molecule was subjected to light illumination. A remarkable enhancement of the rate of degradation was observed (Figure 9).

Figure 9. The effect of light (uv-visible or visible only) and oxygen concentration on the rate of photocatalytic degradation of arsenazo III in neutral suspension. Use of uv-visible light and oxygen saturated suspension (■), UV-visible light source and air equilibrated suspension (○). Visible light source and air equilibrated suspension (△) or oxygen saturated suspension (●).

4. CONCLUSION

Analytical reagents under study were found to be stable and resist stress light effect in media of different pH value as shown by the relatively low value of the formal quantum efficiency for the degradation process. The most important feature of the photocatalytic degradation of such a class of compounds is the degradation of a molecule leading to the generation of different fragments that initially contains naphthalene derivatives before complete mineralization has taken place. Specifically, using of the fluorescence technique could follow up the formation/destruction of the substituted naphthalene moiety as an intermediate in the photocatalytic process. It is interesting to notice that the experimental results obtained by different experimental techniques are consistence with each other (TOC and luminescence measurements).

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