Journal of Photochemistry and Photobiology A: Chemistry 150 (2002) 195–205

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Silylation and sulfonation of structured supported catalysts active in the decoloration of azo-dyes under visible light

T. Yuranova [a], L. Garamszegi [b], Jan-Anders Manson [b], M. Bensimon [c], J. Kiwi [a,*]

[a] Laboratory of Photonics and Interfaces, Institute of Molecular Chemistry and Biology, Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland
[b] Laboratory of Polymer and Composites Technology (LTC), Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland
[c] Department of Civil Engineering, Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland

Received 15 March 2002; accepted 20 March 2002

Abstract

Structured silica woven fabrics have been derivatized with functional groups able to anchor by exchange of Fe^{3+}-ions and TiO_2 showing a stable performance during the visible light induced decoloration of the Orange II azo-dye. The kinetics and efficiency of the decoloration mediated by the catalytic loaded silica fabrics with Fe^{3+}-ions were seen to be much higher than found with homogeneous Fenton reagents (Fe^{3+}/H_2O_2) with the equivalent Fe^{3+} content. The same was observed for derivatized membranes where TiO_2 has been anchored as the active catalyst surface species. In the case of the silica Fe^{3+}-ions loaded fabrics, the decoloration was studied as a function of the amount of H_2O_2 oxidant added in solution, the intensity of the applied visible light and the concentration of the initial Orange II. In the case of the silica-TiO_2 fabrics the decoloration kinetics was observed to be a function of the O_2 present in solution. In the case of the derivatized Fe^{3+} and TiO_2 loaded silica fabrics, the decoloration process presented three common features: (a) the decoloration process was observed only in the presence of light pointing to a photo-induced process in both cases, (b) the decoloration was also observed to be truly catalytical following repetitive cycles for Orange II, and finally (c) the decoloration processes were limited by the mass transfer kinetics taking place at the surface of both derivatized fabric catalyst and proceeded with about the same kinetics in both cases. The numerical values for the diffusion distance of the radicals species $OH^{\bullet}$ and $HO_2^{\bullet}$ as well as the decrease in the concentration of radicals away from the silica fabric during the photodegradation of Orange II is estimated by the Smoluchowski diffusion equation.

Keywords: Silylation and Sulfonation of structured surfaces; Photo-assisted immobilized Fenton processes; Immobilized TiO_2 mediated processes; Orange II azo-dye

---

1. Introduction

Suitable H_2O_2 decomposition kinetics with meaningful yields of $OH^{\bullet}$-radicals were recently attained in photo-assisted Fenton reaction [1,2]. Fe-sludge disposal and/or regeneration after the Fenton reactions poses a serious problem during Fenton photo-assisted processes in homogeneous media. Large volumes of contaminated waters to be treated imply the use of important amounts of chemicals and manpower to separate the Fe^{3+}-sludge at the end of the process and prepare the Fe^{3+}-ions for reuse. Only at concentrations above 40 mg/l, the Fe^{3+}-ions attain the necessary level to decompose with an acceptable kinetics the H_2O_2 during oxidative Fenton processes involving Advanced Oxidation Technologies [3]. But EEC regulations only allow 2 ppm of Fe-ions in drinking water [4].

In order to overcome this problem, we undertook the present study where we immobilize Fe^{3+} on derivatized silica fabrics. These new materials will be applied as immobilized photocatalysts for the decoloration of non-biodegradable azo-dye Orange II as a model compound. This study is targeted on the preparation of new materials that could be used over many cycles without the loss of activity.

Orange II is found commonly in the effluents of the textile industry and has been degraded by novel methods suggested in our laboratory [5,6]. During the last few years, we have examined other membrane supports for anchoring Fe^{3+}-ions like Nafion [7] and Nafion/SiO_2 [8]. Nafion is in general too expensive for widespread use although it does not corrode in the presence of $OH^{\bullet}$ and $HO_2^{\bullet}$ produced during the Fenton treatment and the anchoring of the Fe^{3+}-ions on the Nafion sulfonic groups is stable due to the excess electrostatic charge and it does not allow the Fe^{3+}-ions to leach out during the abatement process. Alginate complexes have also been used as Fenton immobilized photo-catalysts

---

* Corresponding author. Tel.: +41-21-693-3621; fax: +41-21-693-4111.
E-mail address: john.kiwi@epfl.ch (J. Kiwi).

1010-6030/02/$ – see front matter
PII: S1010-6030(02)00138-7

to degrade Orange II [9]. More recently, modified polyethylene copolymers were derivatized with maleic anhydride creating suitable carboxylic anchoring groups on their surface for Fe^{3+}-ions and/or TiO_2 semiconductor particles [10]. When TiO_2 is anchored on a suitable support like the latter polyethylene copolymer, no H_2O_2 is needed as an oxidant like in Fenton processes, since the O_2 available in the solution is sufficient for these purposes due to the semiconductor behavior of the titania under band gap irradiation producing surface $OH^{\bullet}/HO_2{}^{\bullet}$ and peroxides [2,3].

During this study, the catalyst performance will be shown to depend on the suitable combination of: (a) the catalytic site, either Fe^{3+} or TiO_2 anchored on the derivatized silica surface; (b) the oxidant leading to the most effective decoloration; and (c) the light intensity of the visible light source used. Both O_2 and H_2O_2 have been used as oxidants for the reactions. In the case of the silica-Fe^{3+}, H_2O_2 is used as an oxidant, whereas, in the case of the silica-TiO_2, O_2 was able to carry out the oxidation of the model compound Orange II.

2. Experimental section

2.1. Materials

Reagents benzyl-trichlorosilane ($C_7H_7Cl_3Si$) and 3-mercapto-propyltriethoxysilane ($C_9H_{22}O_3SSi$) were used as received from ABCR (ABCR GmbH and Co., Postfach 210135, Karlsruhe 76151, Germany). Chemicals like α,α′-azo-*iso*-butyronitrile ($C_8H_{12}N_4$), benzene (C_6H_6), triethylamine ($C_6H_{15}N$), Orange II ($C_{16}H_{11}N_2NaO_4S$), dichloro-methane (CH_2Cl_2) and ethanol were products from Fluka AG (Buchs, Switzerland) and used without further purification. Styrene (C_8H_8) was purified before use by vacuum distillation. De-ionized water was employed throughout this work.

2.2. Preparation of structured silica woven fabrics

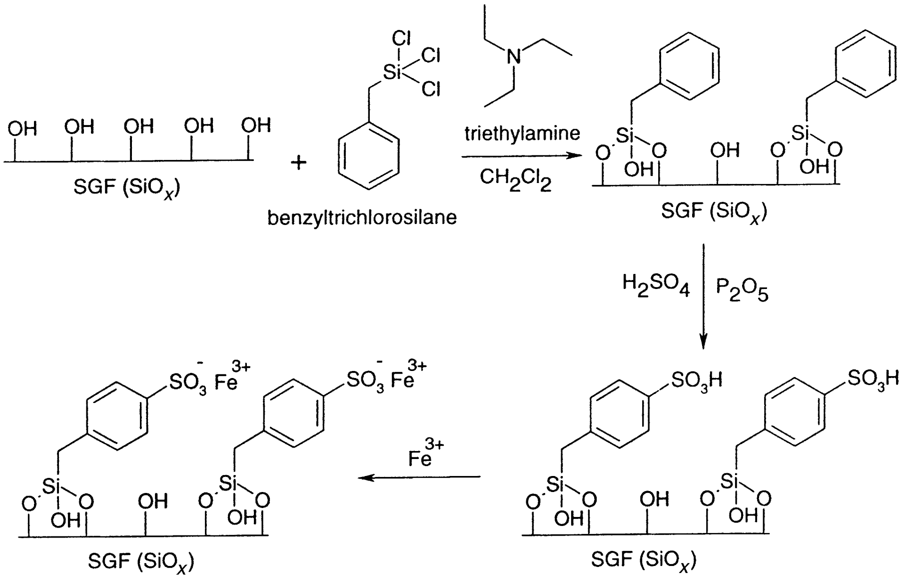
The E-type glass woven fibers with 2 m^2/g were obtained from Vetrotex, S.A. (France). The non-silica components of the glass were leached out of the latter material at 25 °C in HCl (1.0 N) for about 40 min by a procedure previously reported [11,12]. The sample was then rinsed in water and dried in air. The surface area of the modified fabrics was ~20 m^2/g, since the acidic pre-treatment creates a porous structure on the silica fibers [11,12].

2.3. Functionalization by silylation of the silica woven fabrics

In the first step, the material was organofunctionalized using benzyl trichlorosilane as noted later by method A [13,14]. Or, alternatively this organo-functionalization was carried out with mercaptopropyl-triethoxysilane and is denoted later as method B. Only then sulfonation was carried out on each of these materials.

2.3.1. Method A

The silica woven fabric was heated at 200 °C for 2 h in order to remove adsorbed water. Subsequently, the fabric was silylated using benzyl-trichlorosilane. In a typical preparation, a piece of the fabric material (200 cm^2) was immersed into 400 ml of dichloro-methane. To this solution, 10 ml of triethylamine and 10 ml of benzyl-trichlorosilane



Scheme 1.

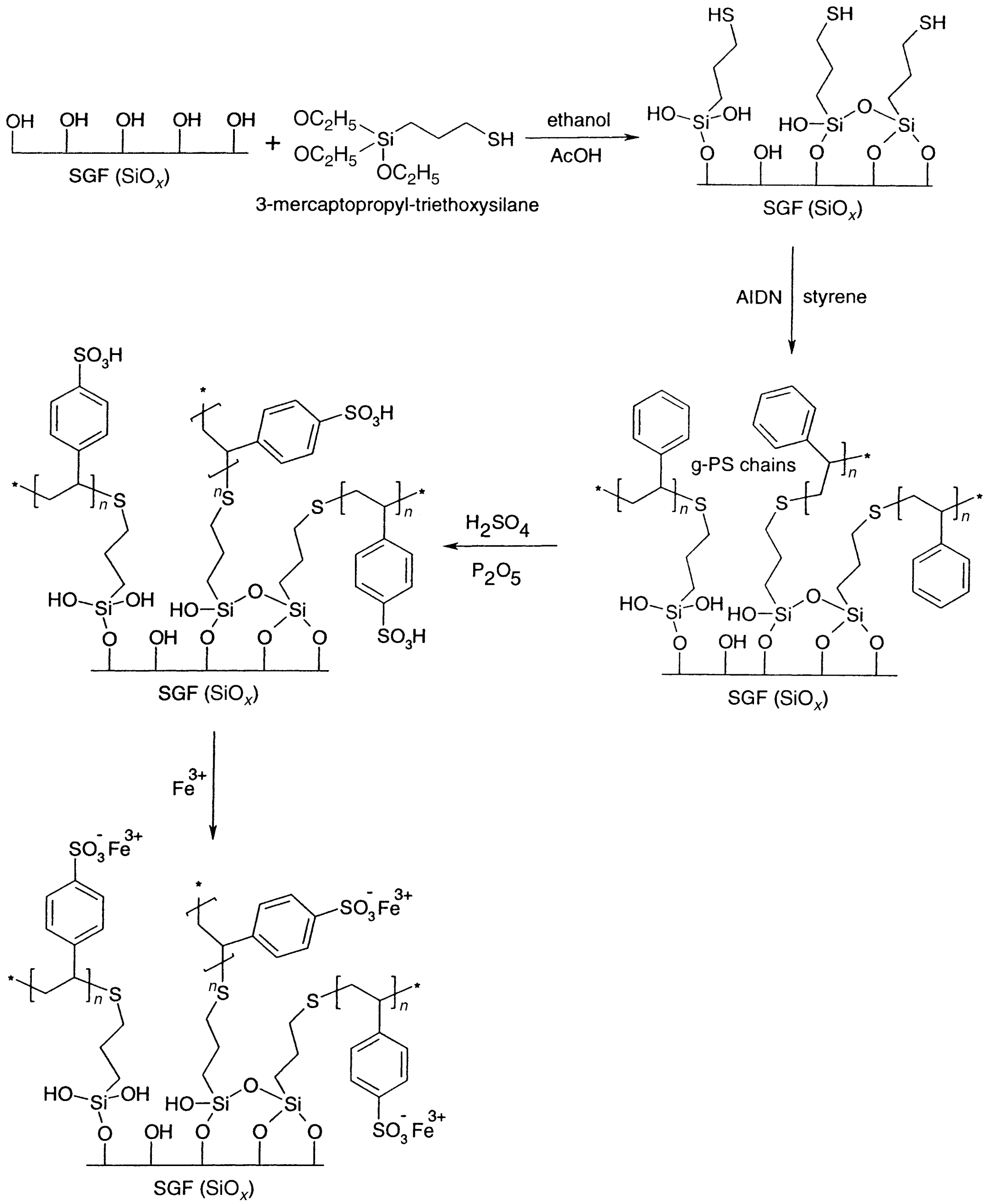
were added under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h. The final material was washed with CH_2Cl_2 and dried in air. The synthetic route is as shown in Scheme 1.

2.3.2. Method B

First, the silica surface was silylated using mercapto-propyltriethoxysilane [15]. On the next step, grafting polymerization of styrene on the modified silica surface was performed.

Mercaptopropyl functionalization of the dried silica woven fabrics were carried out by immersing these fabrics into a mixture of 150 ml of ethanol (95%) and 3 g of mercapto-propyltriethoxysilane for 30 min at 25 °C. Then, samples were rinsed three times with ethanol and subsequently dried at 110 °C for 30 min.

The grafting polymerization was carried out by immersing the silica derivatized woven fabric into the 0.25 M solution of styrene in benzene in the presence of azo-*iso*-butyronitrile (1%) used as initiator of grafting process [16]. The reaction mixture kept at 60 °C for 10 h and the material obtained was washed with benzene and dried in air. This synthetic route is as shown in Scheme 2.



Scheme 2.

2.4. *Sulfonation of derivatized silica woven fabrics*

The sulfonation of the samples A and B described in the preceding paragraphs were carried out by immersion of these samples into a mixture of 20 ml of H_2SO_4 (95%) and 37 g of P_2O_5 at 40 °C for 1 h. Samples were washed with water and dried in air.

2.5. *Loading by Fe^{3+} and TiO_2 of the derivatized silica woven fabrics*

The sulfo-derivatized silica woven fabrics were loaded with Fe^{3+}-ions by ion-exchange from $FeCl_3$ (0.5 M) aqueous solution by a procedure reported previously. To exchange TiO_2 on the sulfo-derivatized silica, the fabric was dipped in an aqueous suspension containing 5 g/l TiO_2 (Degussa P-25). The suspension was sonicated for 30 min prior to use. Together with the silica fabrics and the titania suspension, it is heated to 75 °C for 1 h. The fabric was dried at 100 °C and washed with water to remove the loosely attached particles of TiO_2 [10].

2.6. *Irradiation of Orange II azo-dye by visible light irradiation*

The photochemical reactors consisted of cylindrical Pyrex flasks of 80 ml containing 70 ml of the solution. Irradiation of the model organic compound Orange II with light of the appropriate intensity was carried out and the decoloration observed for the different runs reported in Figs. 1–6 was monitored by a Hewlett-Packard 8452 diode-array spectrophotometer at the maximum of the Orange II absorbance ($\lambda = 486$ nm). The derivatized and catalytically loaded silica woven fabric strips of 48 cm^2 were placed immediately behind the wall of the reaction vessel.

The irradiation of samples was carried out in the visible region in the cavity of a Hanau Suntest solar simulator air-cooled at 45 °C. The Suntest lamp had a wavelength distribution with about 7% of the photons between 290 and 400 nm. The profile of the photons emitted between $\lambda = 400$–800 nm followed the solar spectrum. The Suntest solar simulator was tuned to light intensities of 50, 90 and 130 mW/cm^2. The radiant flux was monitored by a power meter of LSI Corporation (Yellow Springs, CO, USA).

2.7. *Analyses of Fe^{3+}, Ti^{4+} and H_2O_2 during irradiation experiments*

The detection of Fe^{3+}-ions in solution was carried out by complexation with thiocyanate and for the determination of Fe^{2+}-ions ferrozine was used [17]. Spectrophotometric analyses in solution was carried out with a Hewlett-Packard 8452 diode-array spectrophotometer.

For determination of the Ti^{4+}-ion in irradiated solution, the method of high resolution inductively coupled plasma spectrometry (ICPS) was used. The samples were acidified with nitric acid and diluted in ultrapure water. The ion-beam

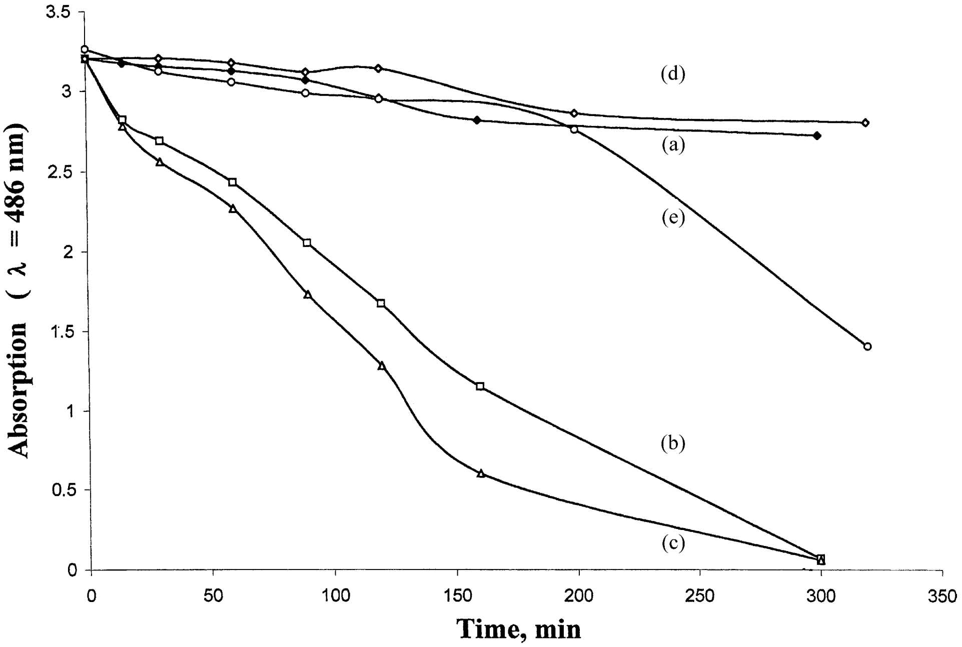


Fig. 1. Decoloration of Orange II (0.2 mM) under Suntest light irradiation (90 mW/cm^2) at pH 6.6 in the presence of H_2O_2 (10 mM) as a function of time: (a) sample A (Fe^{3+}) dark; (b) sample A (Fe^{3+}) light; (c) sample B (Fe^{3+}) light; (d) homogeneous solution Fe^{3+} (0.5 mg/l); (e) homogeneous solution Fe^{3+} (2 mg/l) light.

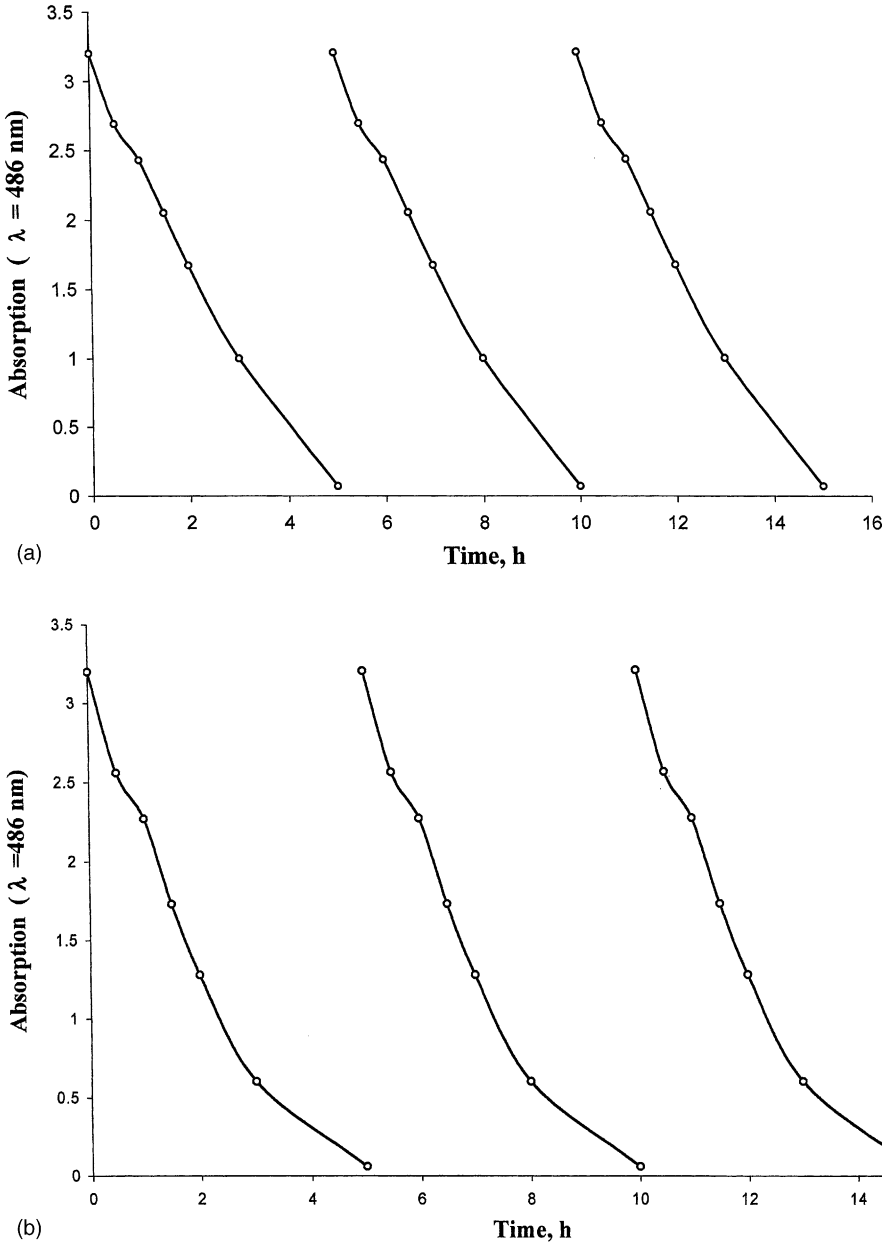


Fig. 2. (a) Repetitive photocatalytic decoloration of Orange II (0.2 mM) under Suntest light irradiation (90 mW/cm^2) at pH 6.6 in the presence of H_2O_2 (10 mM) and sample A (Fe $^{3+}$); (b) the same as shown in Fig. 2(a) but using sample B (Fe^{3+}).

in the plasma of the instrument (Micromass, UK) was directed through the sampling interface and then accelerated into the mass analyzer. The collector assembly consisted of a dual-detector system provided with a Faraday cup for high-beam current coupled with an electron-multiplier amplifier for the low-intensity signals. To overcome the overlap interference problems, measurements were referred to a mass resolution of 3500. The peroxide concentration in the solution was followed by Merkoquant® paper at levels between 0.5 and 25 mg/l of H_2O_2 in aqueous solution.

3. Results and discussion

3.1. *Homogeneous photo-assisted Fenton processes versus heterogeneous photo- assisted Fenton immobilized processes decoloration of Orange II*

Fig. 1 shows the decoloration of Orange II solutions under visible light irradiation. Trace (a) shows that the fabric derivatized sample A in the dark does not induce any decoloration of Orange II solutions within 2 h. Control experiments using silica fabric alone in the dark and under light

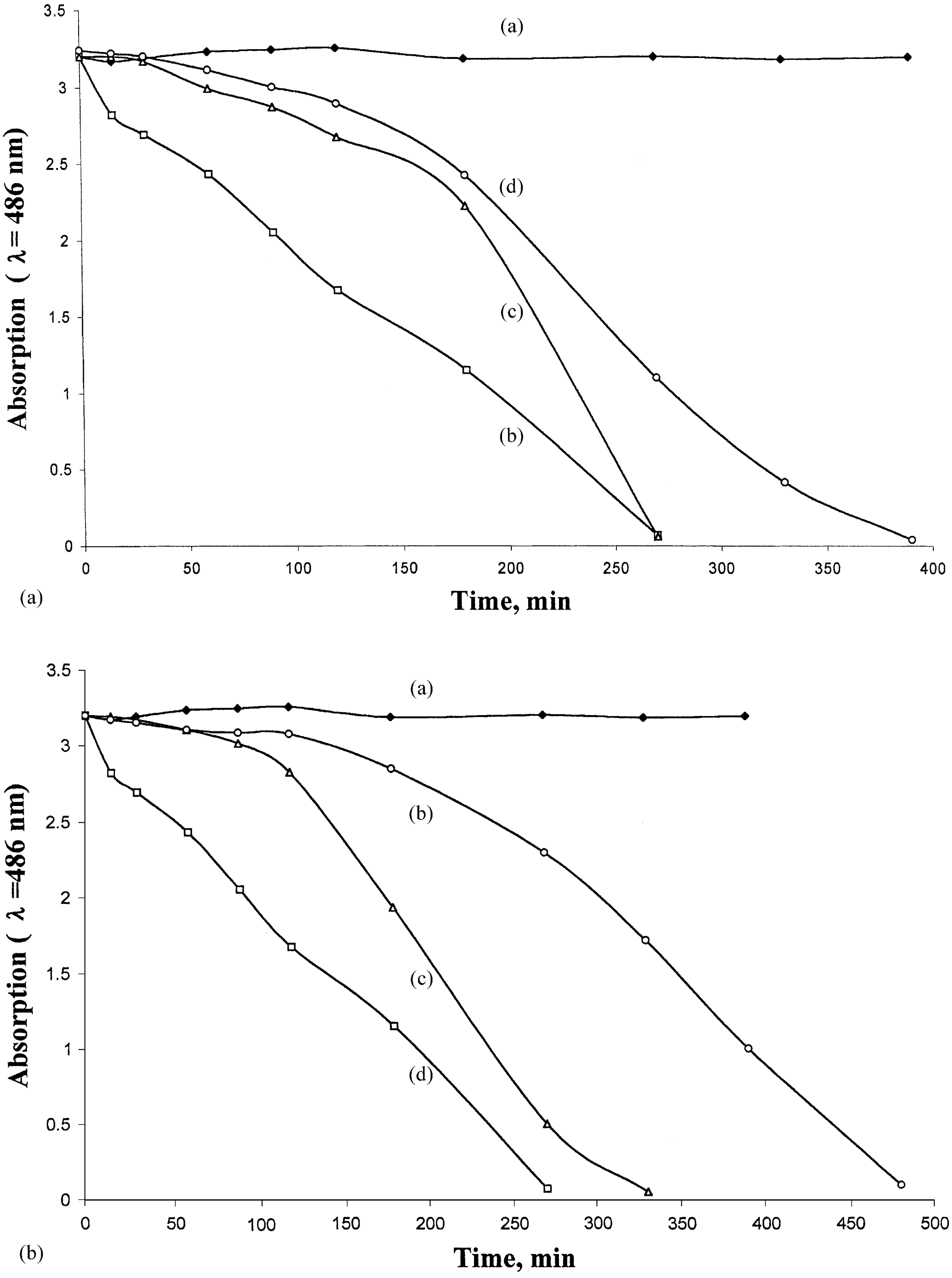


Fig. 3. (a) Photocatalytic decoloration of Orange II (0.2 mM) by sample A under Suntest light irradiation (90 mW/cm^2) at pH 6.6 in the presence of sample A (Fe^{3+}): (a) H_2O_2 (20 mM) dark, (b) H_2O_2 (10 mM) light, (c) H_2O_2 (14 mM) light, (d) H_2O_2 (20 mM) light; (b) the same as in Fig. 3(a) but using the sample B.

did not induce any measurable dye decoloration in solution. Trace (b) shows that sample A induces full decoloration within 2 h under visible light irradiation. The maximum peak of Orange II at $\lambda = 486$ nm was followed in each case. The complete decrease in the coloration within 2 h was also attained using sample B under light as shown in trace (c). Trace (d) shows that if 0.5 mg/l of Fe^{3+}-ions are added in solution along with H_2O_2 (10 mM), the homogeneous Fenton decoloration of Orange II did not proceed. The 0.5 mg/l Fe^{3+} in solution is equivalent to the Fe^{3+} concentration found after 2 h using sample A. Trace (e) show homogeneous Fenton photo-assisted processes carried out with 2 mg/l Fe^{3+}-ions added in solution corresponding to the Fe^{3+} level after 2 h irradiation using sample B as a photocatalyst. The level of iron in the solution was determined by thiocyanate solution as noted in the experimental part which was able to detect Fe^{3+}-ions in solution down to ~0.10 mg/l.

The decomposition of the intermediates adsorbed on the silica woven fabric seems to play an important role in the decoloration process. This observation in conjunction with

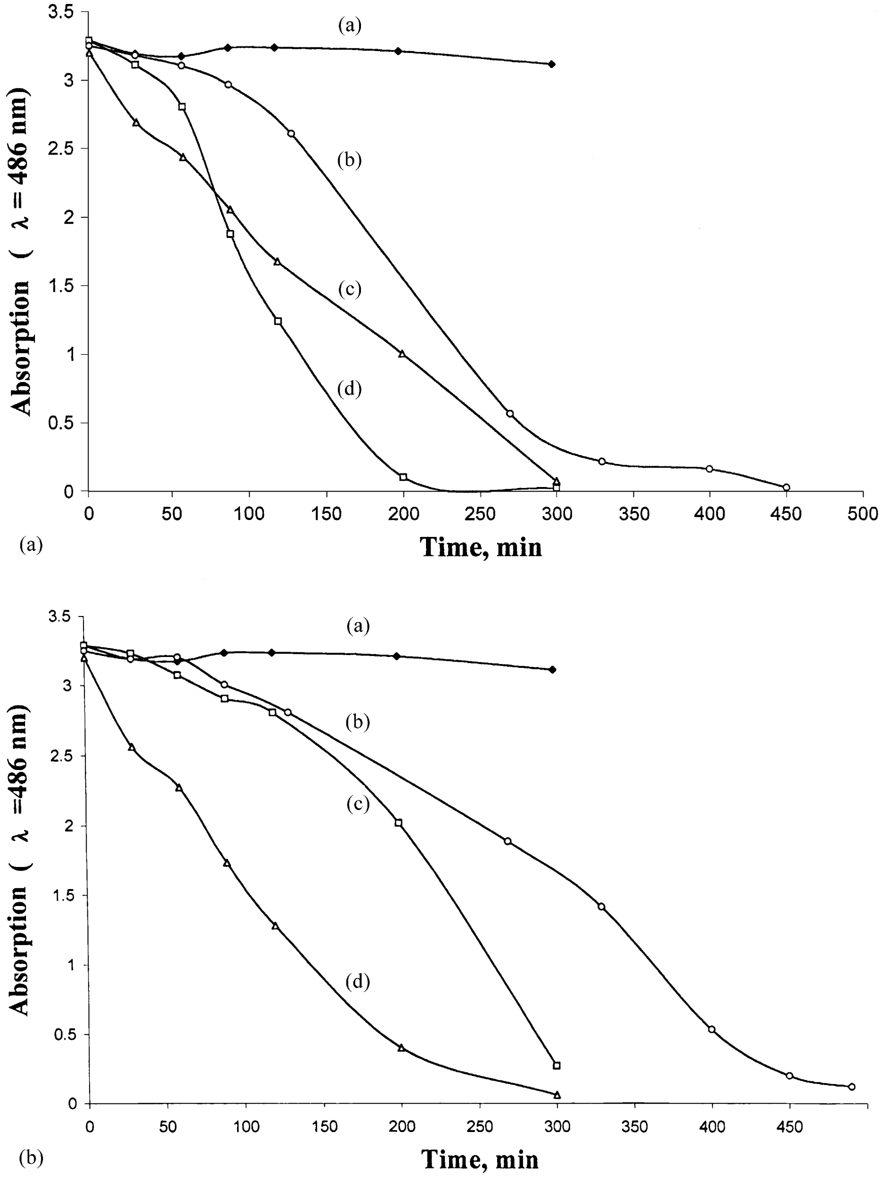


Fig. 4. (a) Photocatalytic decoloration of Orange II (0.2 mM) under Suntest light irradiation at pH 6.6 in the presence of H_2O_2 (10 mM) mediated by sample A (Fe^{3+}): (a) reaction in the dark, (b) Suntest light irradiation of 50 mW/cm^2, (c) Suntest light irradiation of 90 mW/cm^2 and (d) Suntest light irradiation of 130 mW/cm^2; (b) the same as in Fig. 4(a) but using sample B (Fe^{3+}).

the effect of the oxidative radicals originating from the Fe^{3+}/H_2O_2 or on the TiO_2 anchored on the surface of the silica fabrics under light irradiation.

3.2. Photocatalytic nature of the decoloration mediated by samples A and B

The photocatalytic nature of the Orange II decoloration process under visible light is shown for sample A in Fig. 2a and for sample B in Fig. 2b. After each cycle, the membranes are washed thoroughly with water and Orange II and H_2O_2 was added to make the final oxidant concentration 10 mM. The pH at the end of each run was observed to decrease from 6.6 by 2 pH units for samples A and B in Fig. 2a and b. This drop in pH will be helpful when suggesting a reaction mechanism for Orange II decoloration in the section of Fig. 5a and 5b below.

3.3. Effect of the oxidant concentration and intensity of applied light on the decoloration of Orange II mediated by samples A and B

Fig. 3a presents the decoloration of Orange II in the presence of sample A in the dark and under light irradiation as a function of the time of reaction. The decoloration is noticed not to proceed in the dark (trace (a)) but to proceed under light irradiation (trace (b)) when H_2O_2 (10 mM) is added to the solution. If the concentration of H_2O_2 is progressively

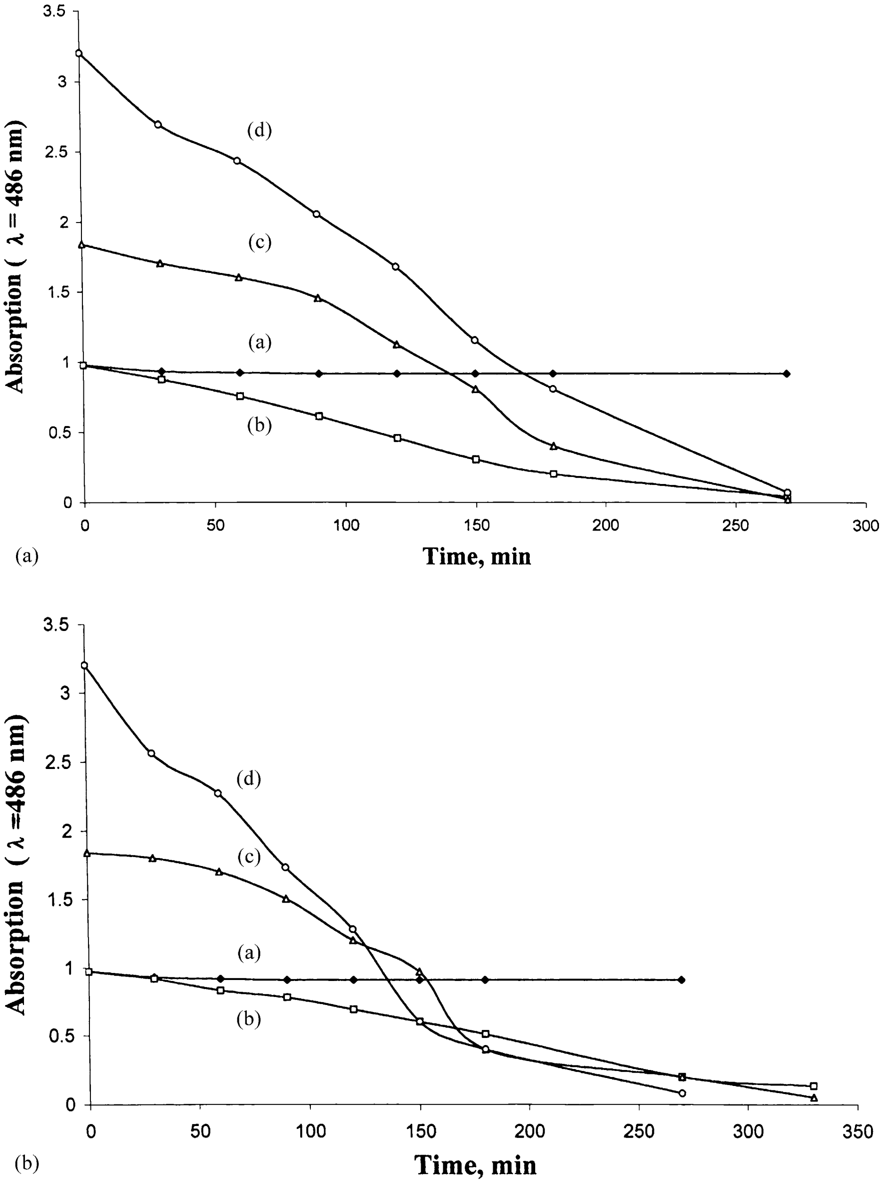


Fig. 5. (a) Photocatalytic decoloration of Orange II under Suntest light irradiation (90 mW/cm^2) with H_2O_2 (10 mM) mediated by sample A (Fe^{3+}) at the Orange II concentrations: (a) 0.05 mM dark reaction, (b) 0.05 mM light, (c) 0.1 mM light, (d) 0.2 mM light; (b) similar as in Fig. 5(a) but using sample B (Fe^{3+}) as photocatalyst.

increased as shown by traces (c) and (d) to 14 and 20 mM the decoloration is seen to proceed less favorably. This is due to the fact that in Fenton reactions the excess H_2O_2 hinders the propagation step acting as an $OH^{\bullet}$ radical scavenger:

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2{}^{-\bullet} \qquad (1)$$

The same trend for the decoloration of Orange II as a function of the H_2O_2 concentration added in solution is reported in Fig. 4b when sample B was used as the Fe-supported heterogeneous catalyst during the decoloration of Orange II.

Fig. 4a and b show the samples A and B mediated decoloration of Orange II as a function of the intensity of the applied visible light. In both the cases, trace (a) presents the results for a dark run. No decoloration was observed in this case. Traces (b)–(d) present the favorable effect of light irradiation as reported during the last decade. The increased photonic flux has been reported accelerate the kinetics of Fenton processes due to: the kinetically faster regeneration of Fe^{2+}-ion in the Haber–Weiss cycle with concomitant increase in $OH^{\bullet}$ production [1–3]

$$Fe(III)(OH) + h\nu \rightarrow Fe(II) + OH^{\bullet} \qquad (2)$$

or, alternatively accelerate the recycling of the iron-complexes due to the photolysis of the polydentate species containing carboxylate ligand leading in a later stage to substrate mineralization [18] as follows:

$$[R\text{–}COO^{-} \cdots Fe^{3+}] + h\nu \rightarrow [R^{-}]^{\bullet} + CO_2 + Fe^{2+} \qquad (3)$$

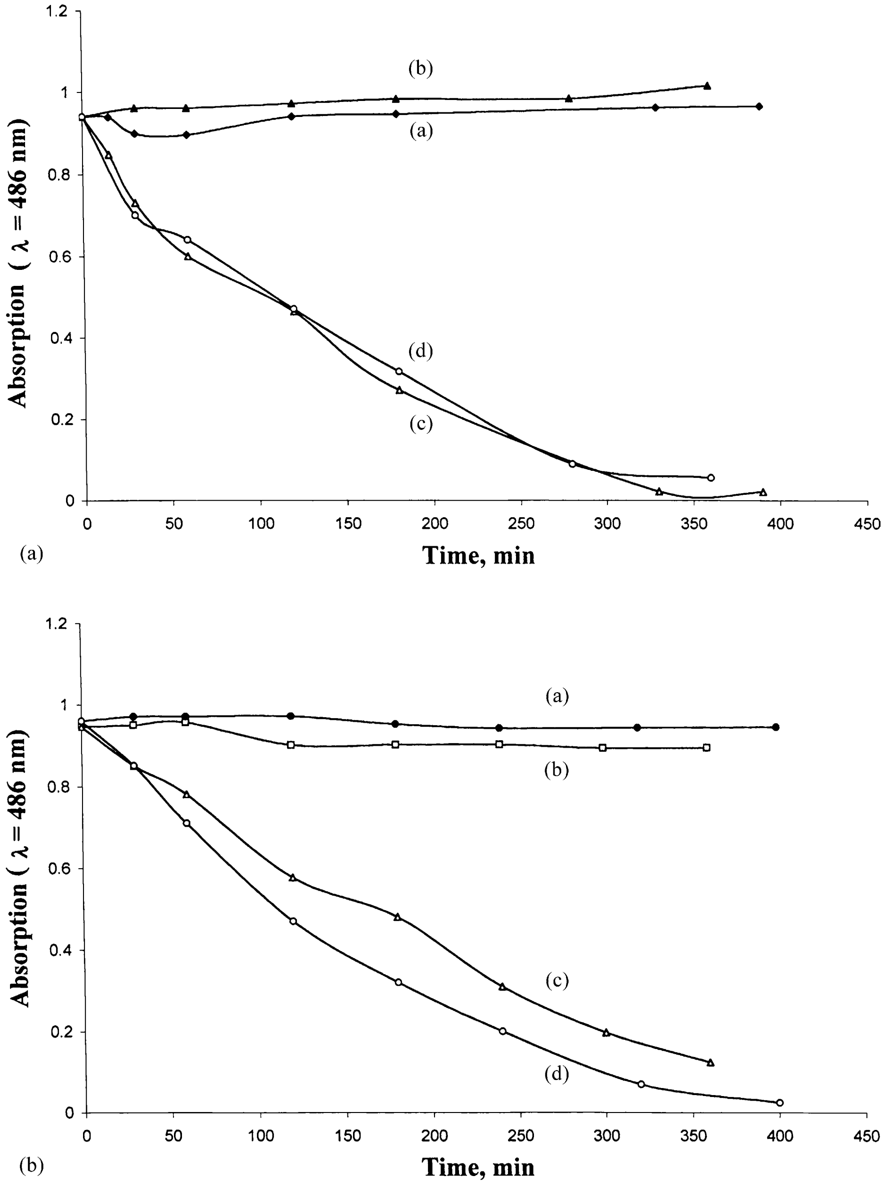


Fig. 6. (a) Photocatalytic decoloration of Orange II (0.05 mM) mediated by sample A (TiO_2) under Suntest light irradiation (90 mW/cm^2) at pH 5.2 in the presence of O_2: (a) 1 atm, dark; (b) 2 atm, light; (c) 1 atm, light; (d) 2 atm, light; (b) photocatalytic decoloration of Orange II (0.05 mM) mediated by sample B (TiO_2) under Suntest light irradiation (90 mW/cm^2) at pH 5.2 in the presence of O_2: (a) 2 atm, dark; (b) 1 atm, light without membrane; (c) 1 atm, light; (d) 2 atm, light.

3.4. Effect of the concentration of Orange II on the decoloration kinetics mediated by samples A and B

Fig. 5a presents the results of the photocatalytic decoloration of three different concentrations of Orange II mediated by sample A. Similar results are presented in Fig. 5b for decoloration reactions mediated by sample B. It is readily seen in Fig. 5a and b that the time for full decoloration is about the same when different concentrations of Orange II are used catalyzing the decoloration with samples A or B. This points out that we are not in the presence of a diffusion controlled process but to a decoloration process that is controlled by mass transfer at the catalyst surface.

The steeper decline in the optical absorption at higher concentrations of Orange II is due to the difference in the Orange II concentration existing in the diffusion layer between the bulk solution and the fabric interface. If $k \approx 10^7$ to $10^5\,M^{-1}\,s^{-1}$ for the reaction rate between the radical $HO_2^{\bullet}$ and the solution is Orange II (0.2 mM), then the lifetime of the reaction pair is $1/\tau = k_{HO_2}$ [OrangeII] $= 2 \times 10^2\,s^{-1}$. The Smoluschowski relation:

$$x^2 \approx D\tau \qquad (4)$$

with $D \approx 5 \times 10^{-6}\,cm^2\,s^{-1}$ and $\tau \approx 0.5 \times 10^{-2}$ s estimates a value of the $HO_2^{\bullet}$ radical, a diffusion distance of $x \approx 1.2 \times 10^{-4}$ cm. Supposing that the concentration of radicals

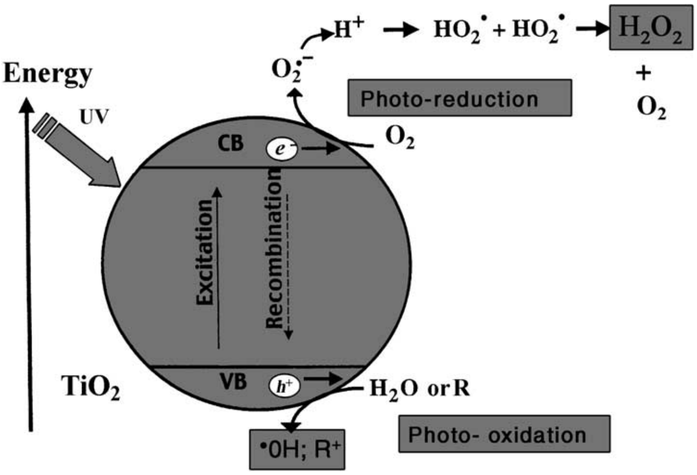


Fig. 7. Schematic of the light induced reactions on the TiO_2 surface in the presence of O_2.

away from the sample A follows a smooth function, the decrease in the concentration of $HO_2^{\bullet}$ radicals when moving away from the silica woven fabric can be estimated from the relation:

$$\frac{d[HO_2^{\bullet}]}{dt} = k[c][HO_2^{\bullet}] \qquad (5)$$

Substituting the numerical values in Eq. (5) with: ($c \approx 10^{-12}$ M), Orange II ($c = 0.2$ mM) and the diffusion controlled rate in aqueous solution of $k \approx 6 \times 10^{9}\,M^{-1}\,s^{-1}$, then $d[HO_2^{\bullet}]/dt$ is $1.2 \times 10^{-6}\,M\,s^{-1}$.

In Fig. 5a and b, the pH of the solution decreased within the decoloration period from 6.6 by about 2 pH units. This corresponds to an increase of a factor of 100 in the H^+ concentration in the solution. This is due to the production of sulfuric acid as a reaction product during the mineralization of Orange II.

Reaction (6) can be suggested as the main pathway for radical production leading to Orange II decoloration:

$$\text{functionalized-SiO}_2/\text{Fe}^{3+} + H_2O_2 \rightarrow \text{functionalized-SiO}_2/\text{Fe}^{2+} + HO_2^{\bullet} + H^+ \qquad (6)$$

rather than reaction (7):

$$\text{functionalized-SiO}_2/\text{Fe}^{2+} + H_2O_2 \rightarrow \text{functionalized-SiO}_2/\text{Fe}^{3+} + OH^{\bullet} + OH^- \qquad (7)$$

3.5. *Decoloration of Orange II on derivatized silica woven fabrics exchanged with TiO_2*

Fig. 6a shows the decoloration of Orange II silica fabrics samples A (TiO_2) exchanged with TiO_2. The beneficial effect of the light irradiation and the O_2 dissolved in the aqueous solution is readily seen from inspection of Fig. 6a. The same combined effect of light and O_2 is shown for the decoloration of Orange II mediated by sample B (TiO_2) in Fig. 6b. The effect of an increased oxygen concentration on the decoloration of Orange II is more noticeable in Fig. 6b with respect to Fig. 6a. The H_2O_2 available in solution due to the formation and consumption of H_2O_2 at the TiO_2 surface has been reported to be of the order of 0.5–1.0 mg/l. The formation of H_2O_2 proceeds due to the capture of conduction band electrons by the dissolved oxygen [2,3,10] and, therefore, there was no need to add H_2O_2 as the oxidant in solution. Work on a variety of oxidative peroxytitanate species adsorbed on the titania surface have been reported in the literature [19,20]. The scheme for the reaction taking place in the presence of silica fabrics derivatized and exchanged with TiO_2 under light irradiation is as shown in Fig. 7.

4. Conclusions

An innovative synthetic route has been presented to anchor Fe-ions and TiO_2 particles on silica woven chemically inert fabrics having an adequate surface area. The decoloration of Orange II taken as model azo-dye was seen to proceed photocatalytically over many repetitive cycles in the presence of H_2O_2 (silica derivatized Fe^{3+}) or using O_2 as oxidant in the case of silica derivatized TiO_2 woven fabrics. The decomposition of Orange II mediated by anchored Fe^{3+}-ions on the silica fabrics proceeded more favorably than in Fenton homogeneous photo-assisted solutions with an equivalent amount of Fe^{3+}-ions due to the adsorption of intermediates on the heterogeneous catalyst. The IR signals to follow the decomposition intermediate on the catalyst fibers were too weak to render meaningful data about the nature of these intermediates during Orange II decoloration. The decoloration of Orange II was possible on the silica woven fabrics starting from pH 6.6. This is 2 units of pH higher than on Fe^{3+}-ions immobilized on Nafion membranes as reported some time ago [7]. The kinetics of Orange II decoloration was mass transfer controlled at the surface of the derivatized silica fabrics used in this study. The observed kinetics was similar for the new synthetic materials presented indicating that the chelate complexes with Fe^{3+}-ions and TiO_2 may not be very different.

Acknowledgements

The financial support of KTI/CTI TOP NANO 21 (Bern, Switzerland) under Grant no. 5320.1 TNS is appreciated.

References

[1] G. Ruppert, R. Bauer, G. Heisler, J. Photochem. Photobiol. Part A. Chem. 73 (1993) 75.
[2] M. Halmann, Photodegradation of Water Pollutants, CRC Press, Boca Raton, FL, 1996.
[3] F. Ollis, H. Al-Ekabi, Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.
[4] EEC List of Council Directives 76/4647, European Economic Community, Brussels.
[5] V. Nadtochenko, J. Kiwi, Faraday Trans. 93 (1997) 2373.
[6] L. Lucarelli, V. Nadtochenko, J. Kiwi, Langmuir 16 (2000) 1102.
[7] J. Fernandez, J. Bandara, A. Lopez, Ph. Buffat, J. Kiwi, Langmuir 15 (1999) 185.
[8] M. Dhananjeyan, J. Kiwi, P. Albers, O. Enea, Helv. Chim. Acta 84 (2001) 3433.
[9] J. Fernandez, M. Dhananjeyan, J. Kiwi, Y. Senuma, J. Hilborn, J. Phys. Chem. B 104 (2000) 5298.
[10] M. Dhananjeyan, E. Mielczarski, K. Thampi, Ph. Buffat, M. Bensimon, A. Kulik, J. Mielczarski, J. Kiwi, J. Phys. Chem. B 34 (2001) 321.
[11] L. Kiwi-Minsker, I. Yuranov, B. Siebenhaar, A. Renken, Catal. Today 54 (1999) 39.
[12] L. Kiwi-Minsker, I. Yuranov, E. Slavinskaia, V. Zaikovskii, A. Renken, Catal. Today 59 (2000) 61.
[13] M. Harmer, Q. Sun, M. Michalczyk, Z. Yang, Chem. Comm. (1997) 1803.
[14] D. Margolese, J. Melero, S. Christiansen, G. Stucky, Chem. Mater. 12 (2000) 2448.
[15] Y. Mori, Th. Pinnavaia, Chem. Mater. 13 (2001) 2173.
[16] Y. Tran, P. Auroy, J. Am. Chem. Soc. 123 (2001) 3644.
[17] A. Gibbs, Ch. Anal. Chem. 48 (1976) 1976.
[18] V. Nadtochenko, A. Lopez, J. Kiwi, 34 (2000) 2162.
[19] J. Kiwi, M. Grätzel, J. Molec. Catal. 39 (1987) 63.
[20] G. Munuera, A. Gonzales-Elipe, J. Espinos, J. Chem. Soc., Faraday Trans. 1 85 (1989) 1279.