

Synthetic polymer delivery system. Sustained release of persulfate during the photo-oxidation of an azo-dye

M.R. Dhananjeyan, E. Fine, J. Kiwi*

Laboratory of Photonics and Interfaces, Department of Chemistry, Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland

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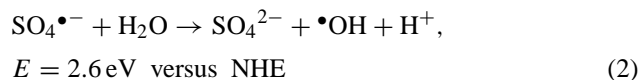
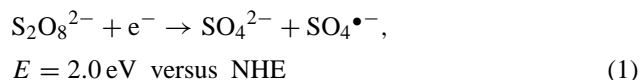
Abstract

A synthetic delivery system based on the copolymer ethylene vinyl-acetate (from now on EVA-polymer) and the carrier, bovine serum albumin (from now on BSA) were prepared by polymer dissolution in the presence of persulfate. This system acted as a long-term polymer release device, cleaning aqueous solutions containing Orange II under visible light irradiation. The polymer and the carrier used were found to be inert and the observed oxidation was only due to persulfate. As expected, the higher initial loadings of persulfate deliver a higher amount of oxidant, leading to a faster photo-degradation of Orange II. The decoloration of Orange II by persulfate only occurred under visible light irradiation suggesting a dye sensitized process. The persulfate release during the reaction was sufficient to decolorate amounts of Orange II, usually found in large water bodies (~50 mg C/l). Disks of EVA-persulfate were used in conjunction with light increasing the release performance of the synthetic delivery system. The addition of BSA can be selective in order to regulate the release of persulfate in the delivery system. The synthetic polymer delivery system was reused over many cycles, since, the polymer delivery system could be retrieved after each cycle. The repetitive use of the persulfate based disks have implications for the long-term detoxification of contaminated water, opening the way for new applications that are not possible by simple addition of persulfate-ions in homogeneous solutions. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Azo-dye; Orange II; Persulfate-ions; Industrial pollutants; Polymer delivery; Sustained release of oxidants

1. Introduction

Persulfate has been used as an oxidant in the field of Advanced Oxidation Technologies (AOTs) during the last decade in processes that occur in the presence of TiO₂ to abate a variety of toxic and industrial pollutants [1–3]. These processes involve degradation of the pollutant in the minute to hour range in the dark, or activated by UV–VIS light in suspensions, loaded with different types of titania. The persulfate added during the degradation acts by: (a) scavenging conduction band electrons preventing the wasteful electron-hole recombination and (b) forming oxidized species such as SO₄^{•-} and •OH as shown below:



* Corresponding author. Tel.: +41-21-693-3621; fax: +41-21-693-3637.
E-mail address: john.kiwi@epfl.ch (J. Kiwi).

in competition with



The persulfate has a high oxidation potential as seen in Eq. (1), but the reaction proceeds with a slow kinetics and is irreversible. The reason for this slow kinetics is that, it is very difficult for the persulfate-ion to accommodate an extra electron on the shell structure and not being able to form S₂O₈³⁻ as shown below in Eq. (4):



Sulfate radical-anion as shown in Eq. (2) are formed by photolytic or thermal oxidation of the persulfate radical (see Eq. (1)), oxidizing water to •OH-radicals [4,5]. Such a mechanism has been invoked during the last few years during the abatement of 4-chlorophenol [6] and pentachlorophenol [7] mediated by titania suspensions using persulfate as the oxidant under UV-light irradiation. In the absence of illumination, the degradation of these pollutants was seen to be extremely slow. Titania-persulfate catalysts mediated the photocatalytic degradation of dichloroacetic and acetic acids at a high kinetic rate [8]. The oxidative mechanism of

persulfate-ion when reacting with dimethyl-formamide has been recently reported [9].

The reasons to choose persulfate as oxidant in the polymer delivery system are fourfold: (a) the relatively low solubility of $K_2S_2O_8$ in aqueous systems, allowing slow release of the persulfate into the system, (b) the high amounts of sulfate allowed in industrial or drinking water (50–250 mg/l) which makes the starting reagent persulfate an attractive and suitable oxidant in the abatement of organic industrial compounds in aqueous solutions [10], (c) the rapidly expanding use of encapsulation technology for many environmental purposes [11]. The approach presented here using polymeric delivery systems activated by light irradiation may open new ways for the use of oxidants over long-term in dye abatement processes and (d) until now, the efforts in the advanced oxidation technology field (AOTs) has been directed towards the rapid destruction of industrial pollutants. Little effort has been made to develop materials that release slowly the oxidant in aqueous solutions to clean pollutants within prolonged time periods. The light activated investigation of this last type of reactions is, therefore, warranted.

The destruction of non-biodegradable toxic dyes, like azo-dyes comprising 15% of the world dye production, is a growing problem with regards to their decoloration/degradation. This study focus on the oxidation of dye concentrations typically found in large water bodies continuing work, reported recently by our laboratory [12–13].

In this study, we have chosen the ethylene-vinylacetate (EVA-polymer Ocusert[®]) as a matrix of a polymer release system having a low molecular weight ($MW < 600$).

2. Experimental section

2.1. Materials

The ethylene vinyl acetate copolymer (ELVAX 40 W) was received from DuPont Willmington, DE, USA. Tri-distilled water was used in all experiments. The EVA-polymer is used in the treatment of glaucoma [14], diabetes [15] and as an immunology carrier [16], due to its adequate bio-compatibility and release kinetics. The inert protein carrier bovine serum albumin (BSA MW 69 000) allows the persulfate to escape from the EVA-polymer matrix, was obtained from Fluka AG Buchs (Switzerland). Peroxydisulfate of potassium $K_2S_2O_8$ (from now on persulfate), ethylene chloride NaCl, acids and bases and Orange II were from Fluka AG Buchs (Switzerland) and used as received.

2.2. Preparation of polymer release matrices

EVA-polymer was dissolved in methylene chloride at a concentration of 10% weight to volume. Persulfate was added to this solution that contained either BSA protein powder or NaCl. The BSA or NaCl act as a filler that dissolves out of the matrix when it is placed in an aqueous

solution. This forms interconnecting pores in the non-degradable polymer matrix, allowing the active agent to be released into the environment. The solution was poured into a mold. Solid polymer disk matrices were formed when the solvent volatilized off at ambient conditions [16–19]. The implantation of this type of system has been experimented with, to release therapeutic drugs over extended periods of time. This entailed the local delivery of the drugs to the target site replacing repetitive large dosing by systematic injection or oral administration. The polymer is bio-compatible and fabrication technique is not detrimental to the activity of the loaded reagents. In addition, the shape of the matrix and the percent loading of the contents can be altered in order to manipulate the release kinetics. A set of six different samples were fabricated to determine the influence of initial loading and carrier substance on the kinetics of the decoloration of Orange II. These samples consisted of (1) 100% EVA polymer, (2) 76% EVA polymer/ 24%, (3) 95% EVA polymer/5% persulfate, (4) 99% EVA polymer/ 1% persulfate (5) 76% EVA polymer/19% BSA/5% persulfate, (6) 76% EVA polymer/24% BSA, (7) 76% EVA polymer/ 24% NaCl and (8) 76% EVA polymer/ 19% NaCl/ 5% persulfate. Amounts are in weight percent and typically 0.76 g of EVA was used for each 1 g disk.

2.3. Photoreactor and irradiation procedures

The irradiation vessels used were 60 ml cylindrical Pyrex flasks (cut-off $\lambda \approx 290$ nm) each containing 40 ml of reagent solution. The Suntest solar simulator had an intensity of 80 mW/cm^2 ($\sim 1.6 \text{ photons/s cm}^2$) within the wavelength range of 290–800 nm. The short wavelength UV radiation from the Suntest solar simulator ($\lambda < 310$ nm) was prevented from reaching the samples by the Pyrex wall of the reaction vessels. The radiant flux reaching the solutions in the photolysis vessels (60 ml Pyrex) was set at $50\text{--}80 \text{ mW/cm}^2$. The Suntest lamp had a wavelength (λ) distribution with about 7% of the emitted photons between 290 and 400 nm. The profile of the photons emitted between $\lambda = 400$ nm up to $\lambda = 800$ nm followed closely the solar spectrum. The radiant flux in mW/cm^2 was measured with a power meter of LSI Corp. Yellow Springs, CO, USA.

2.4. Analysis of the irradiated solutions

Spectrophotometric analyses of the Orange II solutions were performed by a Hewlett–Packard 8452 diode array spectrophotometer at the maximum of the Orange II absorbance wavelength ($\lambda = 486$ nm). The total organic carbon (TOC) was monitored via a Shimadzu 500 instrument equipped with an ASI automatic sample injector. Persulfate-ion was analyzed via a Dionex D-100 ion-liquid chromatograph (ICL) provided for with an Ion-Pac IA/44 column and a mobile phase consisting of Na_2CO_3 and $NaHCO_3$.

2.5. Scanning electron microscopy (SEM)

SEM was carried out by means of Philips 300 S instrument. The limit of resolution of such an instrument is 4 Å. Results are presented in Fig. 8.

3. Results and discussion

3.1. Decoloration of Orange II under visible light irradiation mediated by EVA-polymers

Fig. 1 presents the experimental results for the decoloration of Orange II in the presence of EVA-polymer and EVA-polymer-persulfate (24%). The determining influence of light irradiation is seen when comparing the kinetics observed for the runs under light and in the dark. Decoloration only occurs in the presence of persulfate under light irradiation. Fig. 1 also shows decoloration kinetics of Orange II in the presence of persulfate in homogenous solution in an amount equivalent to the persulfate in the EVA-polymer-persulfate (24%) matrix (37 mg/40 ml). This is due to persulfate near the surface of the polymer matrix released rapidly into the solution. At later time, persulfate leaves the matrix at a slower rate because, it has a longer distance to travel from the interior of the matrix before it exits. In addition, the concentration of Orange II might be low enough, making possible that persulfate in concentrations of 37 mg/40 ml could easily oxidize the azo-dye in solution.

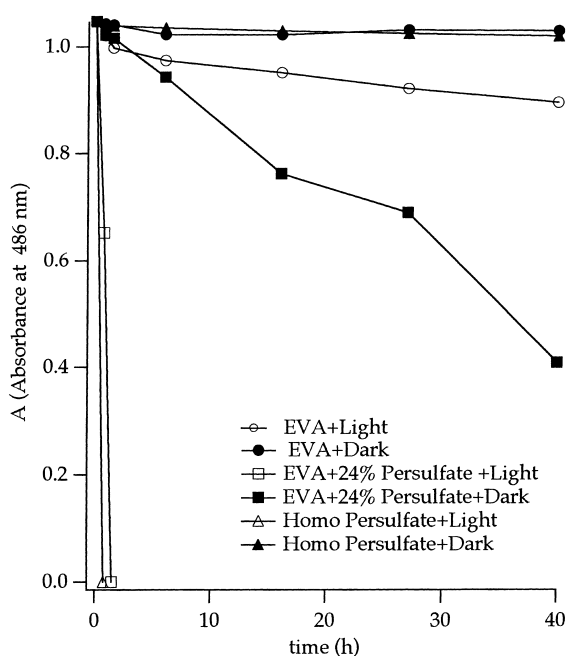


Fig. 1. Decoloration of Orange II (0.05 mM) in aqueous solution with an initial pH 5.5. Suntest light irradiation (80 mW/cm²). The EVA (76%)-polymer-persulfate (24%) and EVA (100%) were added into the irradiation vessels in the amount of 0.25 g/40 ml in each case. The full points refer to runs in the dark and the open points refer to light activated runs.

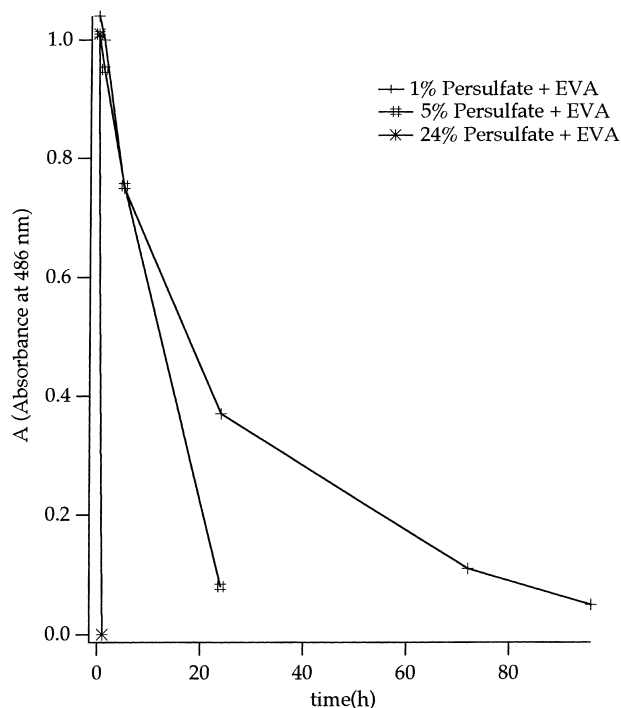


Fig. 2. Decoloration of Orange II (0.05 mM) as a function of irradiation time under the same conditions used in Fig. 1. The three concentrations of persulfate in the EVA-polymer are noted in the captions.

The decoloration of Orange II solution as a function of the persulfate content of the EVA-polymer is presented in Fig. 2. The rate of decoloration (disappearance of Orange II) increases as the content of persulfate loading was increased. The decrease in absorbance can be directly correlated to the release kinetics of the persulfate from the matrix and is a function of percent loading. This could be ascribed to the ability of the porous matrix to release persulfate at a zero-order release rate, as has been reported previously for other synthetic delivery systems [14]. The rate of Orange II oxidation is seen to decrease with time for the EVA-polymer with persulfate loadings of 5 and 1%. This is probably due to two factors (a) an initial rapid release of the near surface persulfate into the solution as the reaction progresses, because it has a longer distance to travel from the interior of the matrix before it exits, and (b) as the degradation reaction of the Orange II proceeds, the solution accumulates long lived difficult to oxidize intermediates.

Fig. 3 shows the decrease of the total organic carbon (TOC) of a solution of Orange II under Suntest light in the presence of EVA-polymer-persulfate. The TOC (mg C/l) is seen to go from 43 to ~5 mg C/l after 50 h irradiation. A higher concentration of Orange II is used for the experimental runs reported in Fig. 3, compared to the concentrations used in Figs. 1 and 2, since only in this way it is possible to report TOC measurements with acceptable precision. The initial increase in the TOC values observed at the beginning of the reaction involves the appearance of

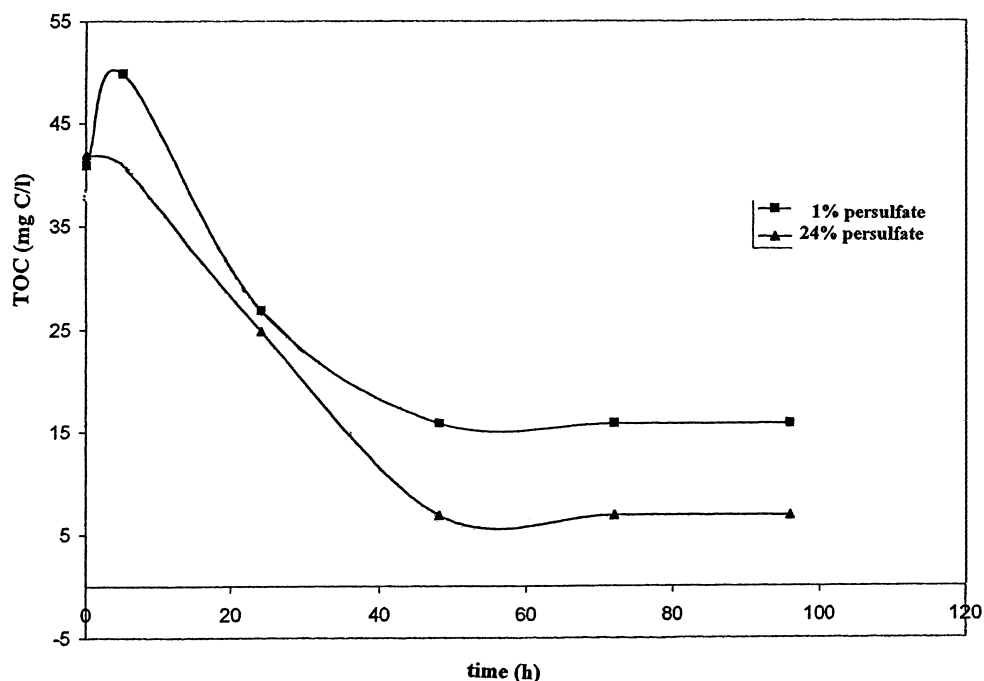
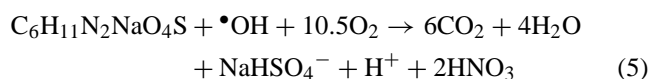


Fig. 3. Decrease in TOC for a solution Orange II (2.5 mM) as a function of time at the initial pH 5.5 under Suntest irradiation. EVA-polymer matrices loaded with 1 and 24% persulfate.

C-containing intermediates due to the $\bullet\text{OH}$ radical generated in Eq. (2). These radicals will react with the polymer moiety before mineralization and sets in at later reaction stages during Orange II mineralization. Both, the decrease in absorbance (Fig. 2) and the decrease in TOC (Fig. 3) of Orange II indicate that Orange II is the compound being decolorized and mineralized by the EVA-polymer-persulfate matrix with the approximate stoichiometry



where the $\bullet\text{OH}$ radicals available to the solution are generated as shown above in Eq. (2).

Fig. 4 shows Orange II decoloration when EVA-polymer-NaCl is present. The EVA(76%)-polymer-NaCl (24%) in the dark and under light is seen in Fig. 4 to lead almost no decoloration of Orange II. Orange II disappearance under light irradiation mediated by EVA(76%)-polymer-NaCl (19%)-persulfate (5%) is seen to proceed within ~ 3 h. This is faster than the time span reported in Fig. 2 for the runs using EVA(76%)-polymer-persulfate (24%), since the persulfate content of the catalyst used in Fig. 1 was higher. Control experiments with homogeneous solutions containing 7.7 mg/40 ml of persulfate — the equivalent amount of the persulfate of EVA(76%)-polymer-NaCl-persulfate (5%) — lead to Orange II decoloration in ~ 2 h. This time is longer than decoloration time of Orange II reported in Fig. 1 for homogeneous solutions since a higher amount of persulfate was added in respect to Fig. 1.

3.2. Decoloration of Orange II on EVA-polymer-BSA-persulfate moieties

Fig. 5 presents, the results of runs in which the synthetic polymer delivery system consisting of EVA-polymer

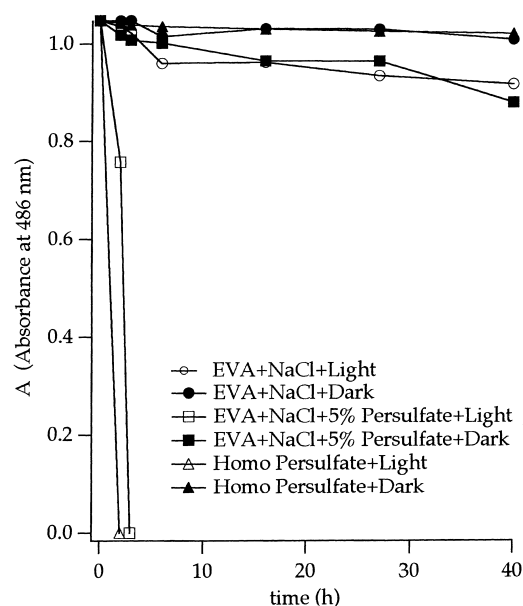


Fig. 4. Decoloration of an Orange II (0.05 mM) solution with initial pH 5.5 in the presence of EVA-polymer-NaCl and EVA-polymer NaCl-persulfate disk under light irradiation and in dark reactions. Open points correspond to runs under light and full points correspond to runs in the dark. For other experimental details see text.

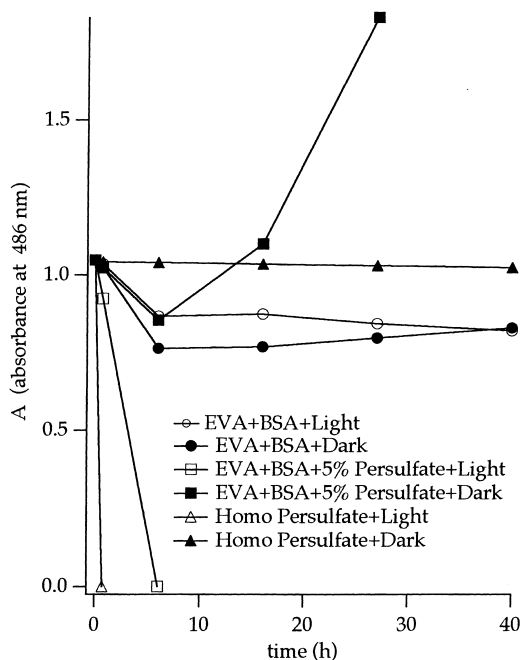


Fig. 5. Decoloration of Orange II as a function of time at pH 5.5 under Suntest light irradiation for EVA (76%)-polymer-BSA (24%) and EVA (76%)-polymer-BSA (19%)-persulfate (5%). The full points refer to runs in the dark and the open points refer to light activated runs. For further experimental details see text.

(76%)-BSA(19%)-persulfate (5%) act as photocatalyst abating Orange II in aqueous solution. Fig. 5 shows that dark control experiments lead to a negligible decrease in the optical absorption of Orange II. If persulfate is added to a homogeneous solution in an amount equivalent to the content of the polymer (10 mg/40 ml) Orange II does not decolor in the dark, but under light irradiation the decoloration takes place within 1 h as shown previously in Fig. 4.

The EVA-polymer (76%)-BSA(19%)-persulfate (5%) in the dark shows an increase in Orange II absorbance after a decrease up to 6 h. The observed increase in optical density probably due to the formation of long-lived intermediates in solution having an increased absorbance at $\lambda = 486$ nm [20]. The BSA, when entering into the aqueous solution may form complexes with persulfate adding to the optical absorption of the system. In the dark, radicals generated in the solution may also lead to the formation of colored non-degradable intermediates that preclude further decoloration of the solution.

Under light irradiation, the EVA-polymer(76%)-BSA (19%)-persulfate (5%) decolorated Orange II within ~6 h in a faster process than when EVA-polymer (76%)-persulfate (24%) was used in Fig. 1. The BSA with its interconnecting structure is therefore, seen to be beneficial for the longer term release of persulfate in the EVA(76%)-polymer-persulfate (5%) moiety [14,17,19]. This shows that the BSA can be added in a way to alter selectively the release time of persulfate into the aqueous solution. At this point, it is interesting to comment on the release of persulfate from

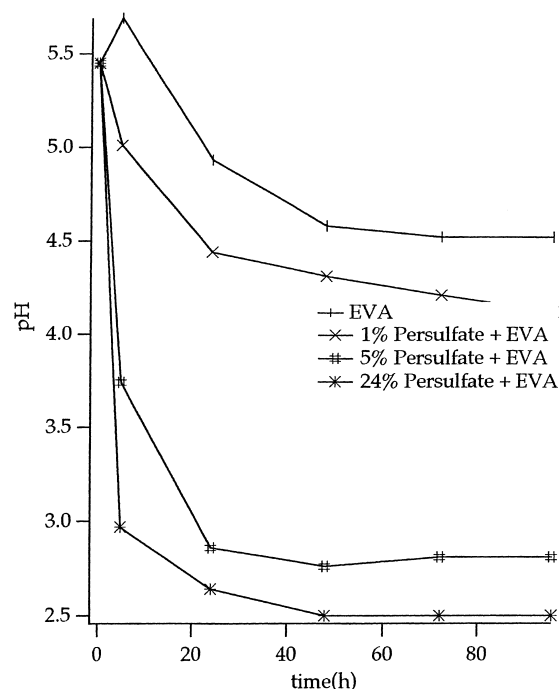


Fig. 6. Variation of the pH during the decoloration of Orange II (0.05 mM) under Suntest light in the presence of EVA and EVA-polymer with 1, 5 and 24% persulfate.

the EVA polymer, EVA + NaCl and EVA + BSA with 5% persulfate. In the case of the EVA polymer alone, it takes 22 h to decolor Orange II. When EVA + NaCl was used, the decoloration of Orange II needed 3 h. The salt

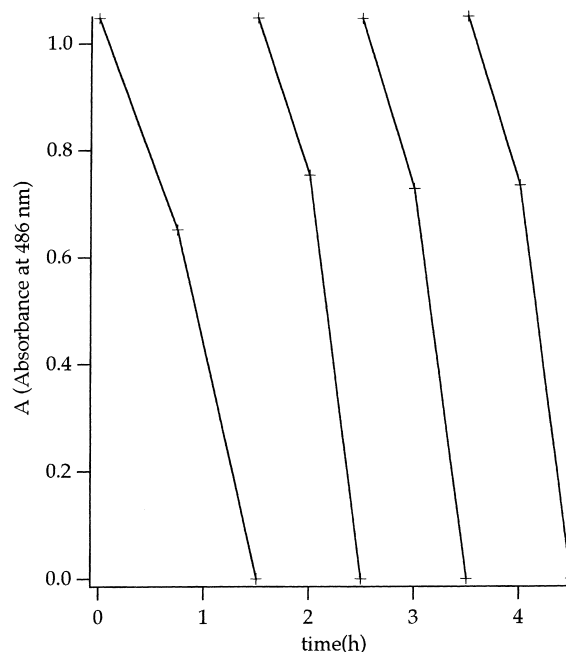


Fig. 7. Decoloration of Orange II (0.05 mM) at pH 5.5 mediated by EVA (76%)-polymer-persulfate (24%) under Suntest light. The kinetics of Orange II decoloration is shown for four repetitive catalytic cycles using the synthetic polymer disks.

is released quickly into the aqueous systems and seems to lead to very fast release of persulfate into the solution. For the EVA-BSA- 5%-persulfate system, the decoloration was observed within 6 h, due to carrier dissolving, the matrix in this time period when placed in the aqueous system.

3.3. The variation of pH during the decoloration of Orange II mediated by EVA-polymer-persulfate moieties

Fig. 6 shows, the pH variation as a function of time during the decoloration of Orange II starting at the natural pH 5.5. For the EVA-polymer alone, the pH variation is seen to be about half a pH unit towards more acidic values during the course of the experiment. When EVA-polymer moieties are used, having different amounts of persulfate, the pH variation becomes more significant as the concentration of the oxidizing anion goes up. A higher concentration of

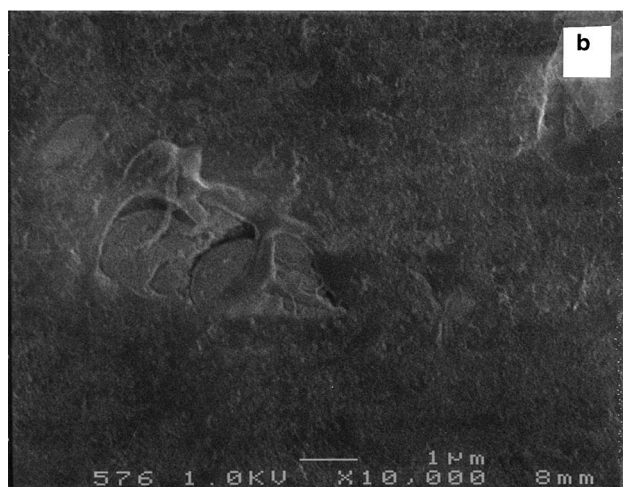
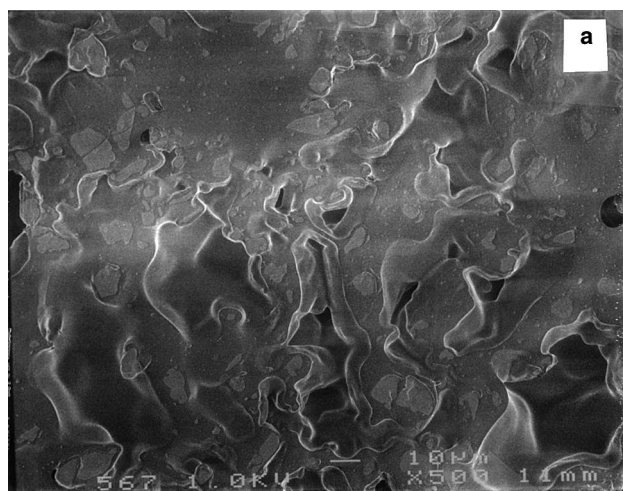


Fig. 8. Scanning electron microscopy (SEM) of the EVA(76%)-polymer-persulfate (24%) moiety before Orange II decoloration and after four catalytic cycle abatement cycles. The experimental conditions used were as in Fig. 7.

persulfate leads to an increased amount of HNO_3 , H^+ and NaHSO_4 , as stated above in Eq. (5).

3.4. Catalytic nature of the Orange II photo-decoloration through EVA(76%)-polymer-persulfate(24%) moiety

Fig. 7 shows, the catalytic nature of the decoloration of Orange II mediated by EVA(76%)-polymer-persulfate (24%) under Suntest irradiation. At the end of each cycle, the disk of the polymeric moiety is washed three times with water and Orange II is added in the amount necessary to make the solution 0.05 M. Then, the next irradiation cycle is started. The results show that the polymer delivery system can be retrieved and used again over many cycles.

Fig. 8 shows, the scanning electron microscopy (SEM) of the EVA-polymer (76%)-persulfate (24%) before the first cycle and after the fourth cycle. In Fig. 8a white contours of diverse shape due to the upper layer persulfate are clearly noticed. They are not visible in Fig. 8b. This confirms that the persulfate close to the surface layer participates during the abatement cycles of Orange II under light irradiation as shown in Fig. 7.

4. Conclusions

In this paper, the Orange II decoloration under light is reported due to the persulfate release into the aqueous solution from the synthetic polymer system EVA + BSA + persulfate. Close to zero-order decoloration kinetics was observed under certain conditions of polymer composition. The details of the sustained release of persulfate at different oxidant concentrations are reported. The synthetic polymer delivery system can be reused over many cycles, showing the catalytic nature of the decoloration reaction. It seems necessary to characterize better the structure of the materials used for future environmental applications.

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