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EFFECTS OF CONCENTRATION AND UV RADIATION WAVELENGHTS ON PHOTOLYTIC AND PHOTOCATALYTIC DEGRADATION OF AZO DYES AQUEOUS SOLUTIONS BY SOL-GEL TiO_2 FILMS

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The photocatalytic and photolytic degradation of anionic azo dyes Methyl Orange and Congo Red dye aqueous solutions was investigated in glass reactors with/without TiO_2 films that were irradiated with UV light. Two nanostructured sol-gel TiO_2 films were prepared by means of the dip-coating technique with and without of polyethylene glycol (PEG) as a structure-directing agent. Experiments were carried out by varying the concentration of dyes, TiO_2 films and sources of UV radiation. The concentrations of dyes were 0.0125 mmol L^{-1}, 0.025 mmol L^{-1} and 0.05 mmol L^{-1}; the wavelengths of the incident ultraviolet light were predominantly 254 (UV-C) and 365 nm (UV-A). In the presence of TiO_2 film UV-C radiation showed higher degradation efficiency for both dyes than UV-A radiation. Also, UV-C radiation without TiO_2 photocatalyst was capable of degrading both dyes, while UV-A radiation alone did not show a potential for dyes degradation. Higher photoactivity showed TiO_2 film with addition of PEG.

Key words: UV radiation, TiO_2 film, Congo red dye, Methyl Orange dye, photocatalysis, photolysis.

Utjecaj koncentracije i valnih duljina UV zračenja na fotolitičku i fotokatalitičku razgradnju vodenih otopina azo bojila uz korištenje sol-gel TiO_2 filmova. Fotokatalitička i fotolitička razgradnja vodenih otopina anionskih azo bojila metiloranža i kongo crvene istraživane su u staklenim reaktorima s TiO_2 filmovima i bez TiO_2 filmova koji su ozračeni UV zračenjem. Dva nanostrukturirana sol-gel TiO_2 filma dobivena su pomoću tehnike uranjanja, s dodatkom i bez dodatka polietilen glikola (PEG) kao sredstva za oblikovanje strukture. Pokusi su izvedeni kombiniranjem različitih koncentracija bojila, TiO_2 filmova i izvora UV zračenja. Koncentracije bojila bile su 0,0125 mmol L^{-1}, 0,025 mmol L^{-1} i 0,05 mmol L^{-1}; valne duljine ulaznog ultraljubičastog zračenja bile su uglavnom 254 (UV-C) i 365 nm (UV-A). U prisutnosti TiO_2 filma UV-C zračenje pokazuje višu učinkovitost razgradnje za oba bojila od UV-A zračenja. Također, UV-C zračenje bez TiO_2 fotokatalizatora pokretalo je razgradnju oba bojila, dok samo UV-A zračenje ne pokazuje potencijal za razgradnju bojila. Višu fotoaktivnost pokazao je TiO_2 film s dodatkom PEG-a.

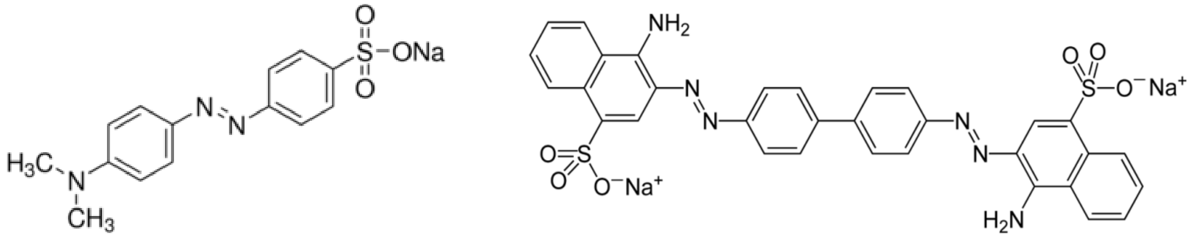
Ključne riječi: UV zračenje, TiO_2 film, bojilo kongo crvena, bojilo metiloranž, fotokataliza, fotoliza.

INTRODUCTION

In this paper, the photocatalytic and photolytic colour removal of the aqueous solution of anionic azo dyes Methyl Orange (MO) and Congo Red (CR) has been investigated.

Azo dyes that are the subject of this research, are the substances containing one or more azo groups (-N = N-) as a chromophore group. According to the number of azo groups in the molecular structure, azo dyes are divided into monoazo, diazo, triazo and polyazo dyes, [1]. Azo dyes are the most common group of commercial dyes and have the widest range of applications in the textile industry, the paper industry, leather, plastics etc. Most of them are used for coloring material from the both aqueous and non-aqueous media [2-4]. Wastewater containing dyes may be carcinogenic, mutagenic and toxic [5-6]. Therefore, the removal of synthetic dyes with azo aromatic groups from wastewater streams is very important for environmental protection. One of the adequate processes for degradation and removal of dyes from wastewaters is photocatalytic oxidation using TiO_2 as a photocatalyist [7-8]. In this study, the immobilized photocatalyst thin films were used for the photocatalytic degradation process. Therefore, sol-gel TiO_2 films were prepared with and without the addition of polyethylene glycol (PEG) as an organic/polymer additive to the initial sol (colloidal solution). The films were deposited on the borosilicate glass reactors using the sol-gel dip-coating method and were characterized on the same way already described elsewhere [9]. Since it was expected that rougher photocatalytic films, with larger active surface area, can have higher photoactivity it was necessary to follow the roughness of the films with and without addition of PEG.

Aqueous solutions of MO and CR dyes were chosen as model solutions. MO is a commonly used water-soluble azo dye. Its production and use as a pH indicator and as a dye for textiles may result in its release into the environment through various waste streams. MO dye in water is highly visible, even at very low concentrations and therewith can have adverse effects on photosynthesis, [4]. CR is used in medicine (as a biological stain) and as an indicator since it turns from red-brown in a basic medium to blue in an acidic one. It is also used to dye textiles and it could also be used as a gamma-ray dosimeter since its coloration decays with the intensity of radiation, [10]. Due to the sulfonic groups, both dyes are well-soluble in water. The molecular structures of these dyes are shown in Figure 1.



A B

Figure 1. The molecular structures of the azo dyes: A - Methyl Orange, B - Congo Red, [11]
Slika 1. Struktura molekula azo bojila: A - metiloranž, B - kongo crvena, [11]

The main goal of this study was to check the activity of the TiO_2 films within different concentrations of dyes and with the use of different UV lamps (with predominant radiation wavelengths of 365 and 254 nm).

EXPERIMENTAL DETAILS

Preparation and characterization of sol-gel TiO_2 films

Three borosilicate glass cylinders were used as the photoreactors (200 mm in height and 30 mm in diameter). Two of them were deposited with different TiO_2 films and only one of them was left without TiO_2 film. Cleaning and preparation of the glass substrates were described elsewhere [9]. Titanium (IV) isopropoxide ($Ti(C_3H_7O)_4$)-TIP, i-propanol (C_3H_7OH)-PROH, acetylacetone ($CH_3(CO)CH_2(CO)CH_3$)-AA, nitric acid (HNO_3)-NA and polyethylene-glycol (PEG) ($HO(C_2H_4O)nH$, Mr = 5000–7000) were used as a Ti precursor, as a solvent, as a chelating agent, as a catalyst and as an organic/polymer additive, respectively. All chemicals were of analytical grade.

For two different TiO_2 films two different starting sols (colloidal solutions) were prepared: sol A – without PEG addition and sol B – with addition of 2 g of PEG to the same starting mixture as in case of sol A. Further procedure of films production strictly followed the procedure described elsewhere [9].

The roughness of the TiO_2 film samples were determined by using a Multimode AFM with a Nanoscope IIIa controller (Veeco Instruments), under ambient conditions in air. Results were presented as R_a, R_q and Z_{max} values.

For the determination of crystal structure of the TiO_2 films Micro-Raman analyses were performed using a Bruker SENTERRA Dispersive Raman spectrometer equipped with an Olympus microscope.

Preparation of CR and MO dyes aqueous solutions

The CR dye ($C_{32}H_{22}N_6Na_2O_6S_2$, molar mass: 696.665 g mole^{-1}) was supplied by ACROS, as a high purity biological stain. The MO dye ($C_{14}H_{14}N_3NaO_3S$, molar mass: 327.33 g mole^{-1}) was supplied by Sigma-Aldrich, as ACS grade. Both dyes were used as the model compounds in aqueous solution, without further purification.

All solutions used in the experiments were prepared using ultrapure water (0.055 μS/cm of electrical conductivity) treated by GenPure system (TKA, Germany).

Photocatalytic experiments

All experiments were carried out in 0.11 L borosilicate glass cylinders as the reactors:

(A) Reactor A (R-A), with a sol-gel TiO_2 film A, without the addition of PEG,

(B) Reactor B (R-B), with a sol-gel TiO_2 film B, with the addition of PEG and

(C) Reactor 0 (R-0), a borosilicate glass cylinder without coating.

Two UV-radiation lamps were used: model Pen-Ray CPQ 7427, with λ_{max} = 365 nm (UV-A) and model Pen Ray 90-0004-07 with λ_{max} = 254 nm (UV-C), both lamps are manufactured by UVP. The removal/ degradation of the dyes was investigated with different concentrations of MO and CR dyes – 0.0125, 0.025 and 0.05 mmol L^{-1}, with continuous purging with air (O_2) to the solution, using three different conditions, as in [13]:

(a) under UV illumination in the absence of TiO_2 film (photolysis),

(b) “in the dark” (without UV radiation) with TiO_2 film (adsorption), and

(c) under UV illumination in the presence of TiO_2 film (photocatalysis).

The samples were taken from the reactor, shown in Figure 2, for analysis at certain reaction intervals (15, 30, 45, 60, 90 and 120 min) and the remaining dye concentration was analyzed by an UV-Vis spectrophotometer (Perkin Elmer, model Lambda 25) using a 1 cm quartz cell.

As a measure of the mineralization process of organic matter degradation, inorganic anions and cations evolution was followed. Inorganic anions (NO_3^-, NO_2^-, SO_4^{2-}), were quantified by a Dionex ion chromatograph (USA), model ICS 2000 using a AS15 column (Dionex). Inorganic cations (NH_4^+) , were quantified by a Dionex ion chromatograph (USA), model ICS 1500 using a CS 16 column (Dionex). Mobile phases were 38 mmol L^{-1} KOH for the determination of anions and 30 mmol L^{-1} methanesulfonic acid for the ammonium ion determination.

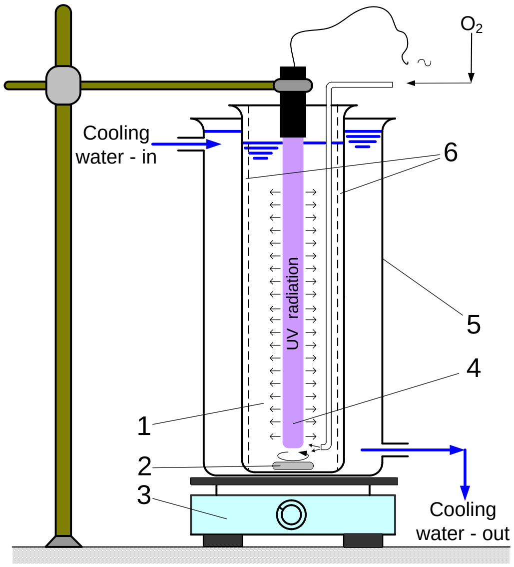


Figure 2. Scheme of the photoreactor system: 1 – reactor with a solution of the dye, 2 – PTFE magnetic stir bar, 3 – magnetic stirrer, 4 – UV-A or UV-C lamp, 5 – thermostatic bath, 6 – TiO_2 film

Slika 2. Shema fotoreaktorskog sustava: 1 – reaktor s otopinom bojila, 2 – PTFE magnetski mješač, 3 – magnetska miješalica, 4 – UV-A ili UV-C svjetiljka, 5 – termostatirajuća kupelj, 6 – TiO_2 film

The reaction temperature, 25.0 ± 0.1 °C, was controlled by the circulation of cooling water around the reactor with thermostatic circulation bath, E-100, Lauda. For each experimental condition, repetition tests were done to ensure reproducibility.

RESULTS AND DISCUSSION

Characterization of sol-gel TiO_2 films

After the detailed characterization process, described in [9, 12] can be concluded that two different used TiO_2 films after the calcination process consist only of anatase crystal form of TiO_2. Besides, surface roughness analysis using the AFM analysis was provided. The values of roughness parameters (R_a, R_q and Z_{max}) of both films were determined.

The values of roughness parameters (R_a, R_q and Z_{max}) of both investigated films are:

- for the film A (2.06, 2.61, 32.7 nm) and
- for the film B (4.38, 6.20, 50.0 nm).

The R_a values of the TiO_2 films are similar to those (2–4 nm) reported in the literature, indicating good homogeneity of the TiO_2 particles on the surface, [14-15]. The addition of PEG to the TiO_2 film starting solution (Film B) significantly increased roughness parameters.

Adsorption process

Influence of adsorption process in removal of dyes from the solution to the reactor walls was observed without the UV irradiation, i.e. in the reactors covered with alum foil. The adsorption rate, observed as the absorbance decrease at 466 nm (for MO) and at 498 nm (for CR), was less than 1.0 % after 120 min of stirring the solutions of dyes. Practically, the degree of adsorption of dyes on the surface of the reactors' walls was negligible in the overall color removal process.

Degradation processes during photolysis and photocatalytic oxidation

To determine the adsorption rate of the dyes from the solution to the reactor walls and photolytic and photocatalytic degradation of MO and CR in aqueous solutions, the changes of three initial concentrations of dyes (0.0125 mmol L^{-1}, 0.025 mmol L^{-1} and 0.050 mmol L^{-1}) were followed. It was also determined the dependence of degradation on the type of the three different reactor walls (R-0, R-A and R-B), at a temperature of 25.0 °C and with the application of UV-A and UV-C radiation.

For all solutions starting and ending pH values have been measured, without continuous monitoring and adjusting of the initial pH. Starting pH values for dye solutions of 0.0125 mmol L^{-1}, 0.025 mmol L^{-1} and 0.050 mmol L^{-1} for MO dye were 6.8, 6.6 and 6.3 and for CR dye 5.8, 5.7 and 5.5, respectively. Ending pH values were, depending on the rate of degradation process, always lower or equal to the starting pH (only in the case when the degradation was not observed), usually between 3.8 and 5.2.

UV-Vis spectra of starting solutions of MO and CR dyes are shown in Figure 3. The CR dye absorbs more in UV region (200-400 nm) than MO dye.

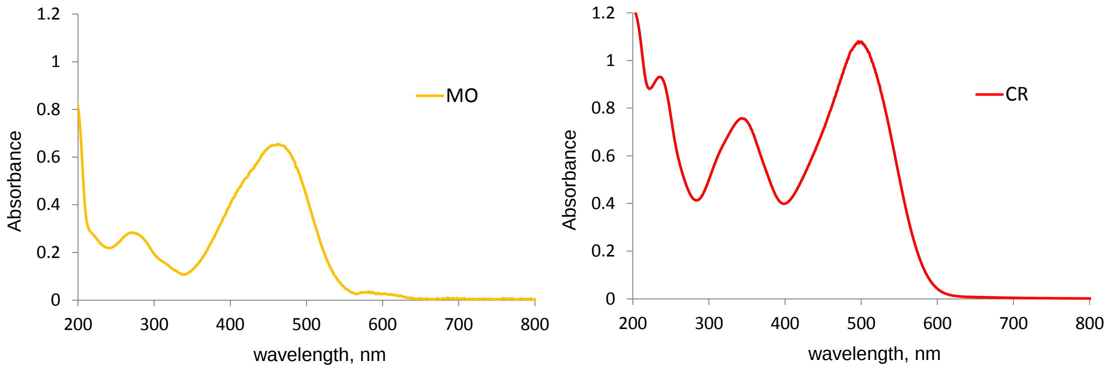


Figure 3. UV–Vis spectra of starting solutions of MO and CR dyes (c_0 = 0.025 mmol L^{-1})
Slika 3. UV–Vis spektar početnih otopina bojila MO i CR (c_0 = 0,025 mmol L^{-1})

As in Figure 4 can be seen, for both UV lamps, in reactors with TiO_2 film and with UV-C radiation, total decolorization of the both MO and CR dyes was reached in 60 minutes. With UV-A radiation even after 120 minutes of the degradation process total decolorization was not reached both for MO and CR dyes. This situation is expected due to the fact that UV-C radiation, with smaller wavelengths than UV-A radiation, possesses higher energy content.

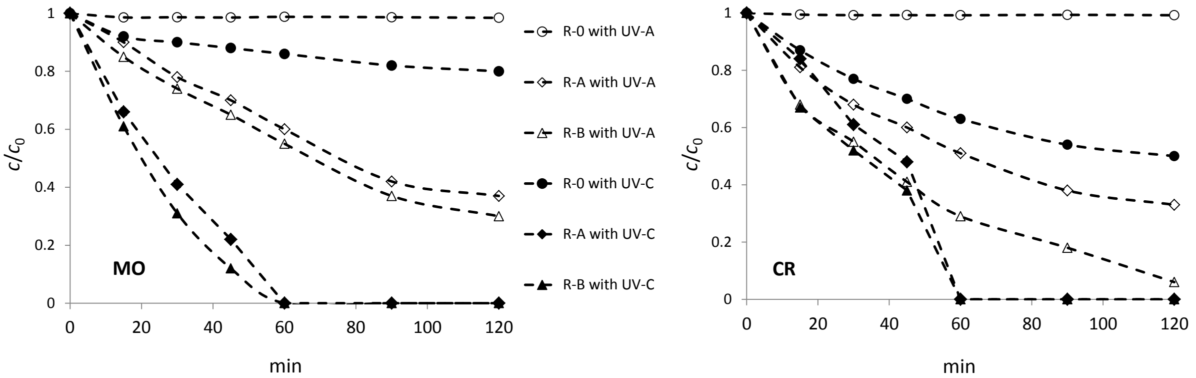


Figure 4. Degradation process of the MO and CR dye during 120 min in three different reactors under UV-C and UV-A radiation (c_0 = 0.0125 mmol/L, 25.0 °C)
Slika 4. Proces razgradnje MO i CR bojila tijekom 120 minuta u tri različita reaktora pri UV-C i UV-A zračenju, (c_0 = 0,0125 mmol/L, 25,0 °C)

Figure 5 shows the degradation of the dyes with higher concentration, where the total decolorization was reached for both dyes slower - in 120 minutes for the combination - TiO_2 film and UV-C radiation.

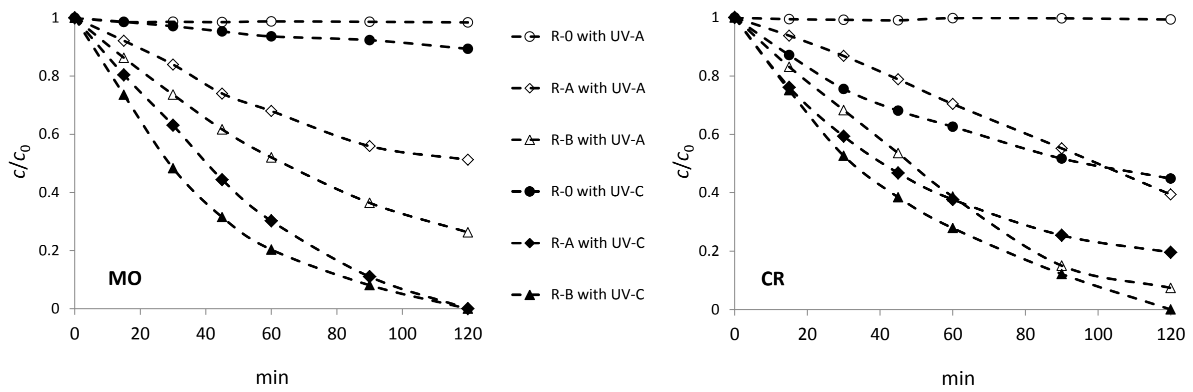


Figure 5. Degradation process of the MO and CR dye during 120 min in three different reactors under UV-C and UV-A radiation (c_0 = 0.025 mmol/L, 25.0 °C)
Slika 5. Proces razgradnje MO i CR bojila tijekom 120 minuta u tri različita reaktora pri UV-C i UV-A zračenju, (c_0 = 0,025 mmol/L, 25,0 °C)

In third case, Figure 6, the total decolorization was not reached for both dyes in 120 minutes regardless of the reactor type or lamp type.

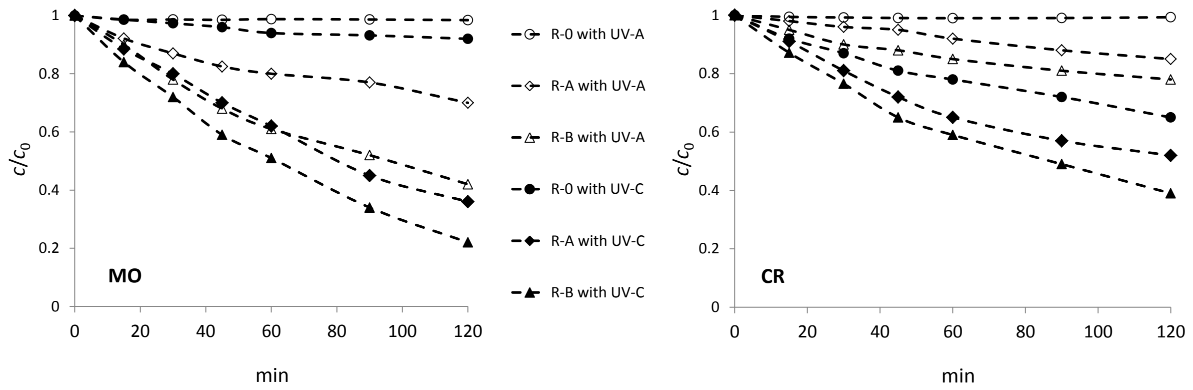


Figure 6. Degradation process of the MO and CR dye during 120 min in three different reactors under UV-C and UV-A radiation (c_0 = 0.050 mmol L^{-1}, 25.0 °C)
Slika 6. Proces razgradnje MO i CR bojila tijekom 120 minuta u tri različita reaktora pri UV-C i UV-A zračenju, (c_0 = 0,050 mmol/L, 25,0 °C)

For the presence of both the sol-gel TiO_2 film and UV-A irradiation, the decolorization process was progressing proportionally for both dyes with the irradiation time. For the UV-C radiation, decolorization process takes place also in reactor R-0 (without TiO_2) due to the process of photolysis. Besides, UV-C radiation in combination with TiO_2 films causes two effects – (*i*) photolysis of the dyes in direct contact of the photons with the dye molecules, and (*ii*) photocatalytic oxidation of the dyes when some of the photons of the UV-C radiation (transmitted light through the dye solution) reach the TiO_2 surface. Obtained results show also that the addition of PEG to the initial sol improves the photocatalytic activity of the TiO_2 film B. This higher decolorization rate for both dyes solution was the most likely the result of greater photocatalytic area, i.e. higher roughness of the film.

From the Figures 4-6 it can be seen that MO dye solutions were faster degraded than CR dye solutions. This can be explained by the effect of “wasted light”, [16], i.e. radiation from the lamps is mostly just absorbed by the dyes’ molecules and only small portion undergo degradation reactions as a consequence of radiation absorption.

In Figure 7 influences of dyes concentration and also the UV radiation range on decolorization efficiency is shown. As expected, decolorization efficiency decrease with increase of concentration of dyes, [17-19].

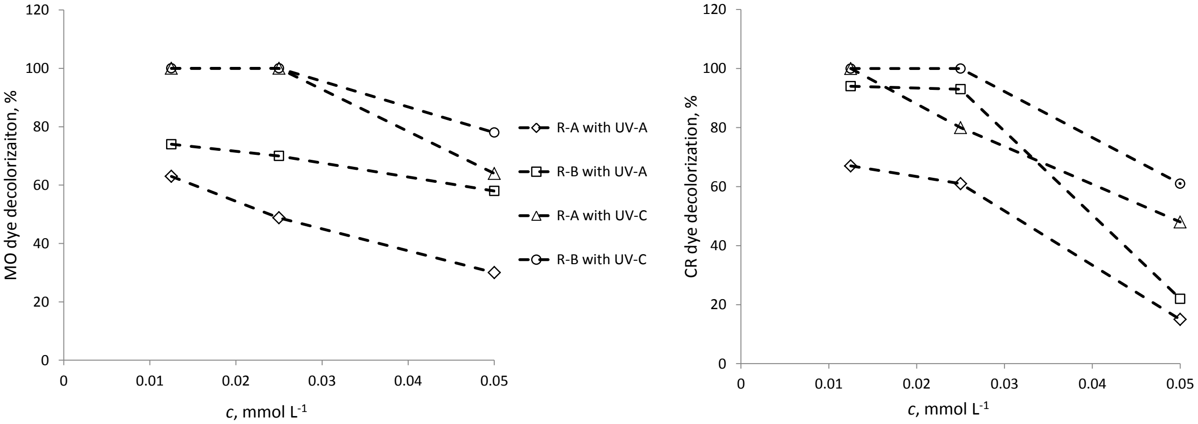


Figure 7. Effect of dyes concentration on the decolorization efficiency for MO and CR dyes (reaction time 120 min, 20 °C)

Slika 7. Učinak koncentracije bojila na učinkovitost obezbojenja za bojila MO i CR (reakcijsko vrijeme 120 min, 20 °C)

The best decolorization efficiency has shown photocatalytic process with film B and with UV-C radiation for both dyes. In this process there is actually a synergy between photolysis (which is noticeable in the case of UV-C radiation, Figures 4-6) and photocatalysis with UV-C radiation and TiO_2 film. Dyes decolorization efficiency decreases with increase in concentration for both dyes. It is assumed that with increasing concentration of dyes the number of $HO^{\bullet}$ radicals on the catalyst surface were reduced because the active sites of the catalyst are covered with the dyes molecules. However, there is another possible reason for these results - again the effect of “wasted light”, mentioned above, can be used for the explanation: at high concentration of dyes part of UV radiation from the UV lamps can be absorbed by the molecules of dyes before it reaches the surface of TiO_2, which will lead to a reduction in the catalytic activity of the photocatalytic film.

Mineralization of the dyes’ solutions

Mineralization process of the dyes’ solutions implies the appearance of inorganic ions, like sulfate, nitrate, nitrite, ammonium, etc., [20-22]. Their appearance during the process of the dyes degradation is shown in Figures 8 and 9.

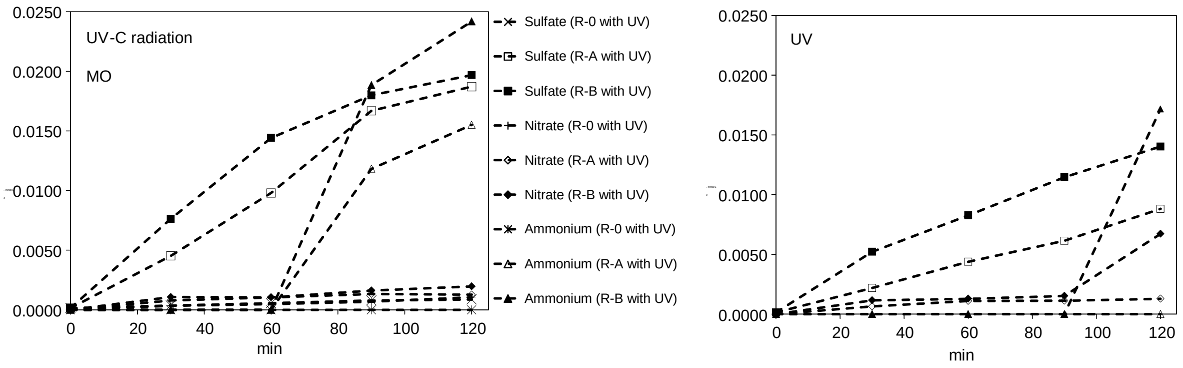


Figure 8. Sulfate, nitrate and ammonium ions appearance during the UV irradiation experiment with MO dye solutions (25.0 °C, c_0=0.025 mmol L^{-1})

Slika 8. Nastanak sulfatnih, nitratnih i amonijevih iona tijekom UV ozračenja otopine bojila metiloranž (25,0 °C, c_0=0,025 mmol L^{-1}).

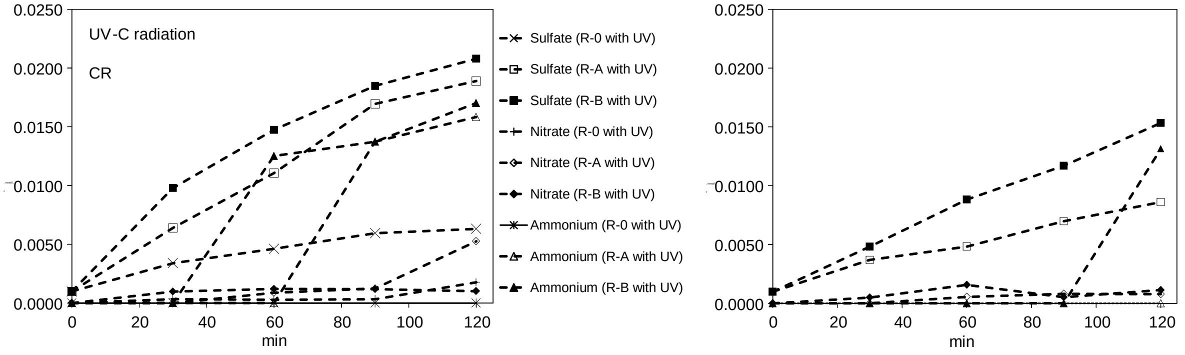


Figure 9. Sulfate, nitrate and ammonium ions appearance during the UV irradiation experiments with CR dye solutions (25.0 °C, c_0=0.025 mmol L^{-1})

Slika 9. Nastanak sulfatnih, nitratnih i amonijevih iona tijekom UV ozračenja otopine bojila kongo crvena (2,0 °C, c_0=0,025 mmol L^{-1})

Higher content of some ions corresponds to the higher level of degradation of the starting dye substance. As can be seen in Figure 8 and 9, on parallel comparison for all the dyes and UV ranges for concentration of 0.025 mmol L^{-1}, it is evident that the application of UV-C radiation generated higher concentration of ions, what is expected due to the fact the UV-C radiation is richer in energy than the UV-A radiation.

CONCLUSION

From the present study the following can be concluded:

- total decolorization of the low-concentration (0.0125 mmol L^{-1}) MO and CR dyes solutions was reached in 60 minutes for both UV-A and UV-C lamps in the laboratory scale reactor. However, for high-concentration MO and CR dyes solutions (0.05 mmol L^{-1}) decolorization was not reached even in 120 minutes of the reaction time.

- roughness parameters of the photocatalytic TiO_2 film with the addition of PEG in its initial sol are higher than the film without the PEG addition. Additionally, higher roughness parameters of the TiO_2 film resulted with the increase of its photoactivity during photocatalytic degradation of MO and CR dyes both with UV-C and UV-A radiation, i.e. addition of PEG into the starting sol enhanced photocatalytic properties of the TiO_2 film.
- UV-A radiation alone is not sufficient to degrade MO or CR dye. However, the use of the UV-A/TiO_2 process showed degradation potential of the dyes solutions, although UV-A/TiO_2 process seems to be less efficient than the UV-C/TiO_2 process. When only UV-C radiation was used, the degradation was measurable.
- Adsorption process of the dyes on the TiO_2 films was negligible.
- Mineralization process of the dyes' solutions, observable as the appearance of inorganic ions, like sulfate, nitrate, nitrite, ammonium, the application of UV-C radiation generated higher concentration of ions confirming the fact that photocatalytic degradation of dyes solutions was faster when UV-C radiation was used.

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