

Investigation of a TiO₂ photocatalyst immobilized with poly(vinyl alcohol)

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Abstract

Immobilization of TiO₂ photocatalyst was realized with application of poly(vinyl alcohol) (PVA). However, these PVA-based foils were too instable to be used for photocatalytic water cleaning. Their stability could be significantly enhanced by a thermal treatment, but this procedure generated various water-soluble derivatives such as aldehydes, ketones, and aromatic species. Photocatalytic pre-treatment of the foils proved to be suitable to remove these products from the surface of the composite. After three subsequent pre-treating cycles of irradiation and rinsing, the PVA-TiO₂ foil became applicable for photocatalytic degradation of Triton X-100, a widely used non-ionic detergent. The composite catalyst kept its stability and efficiency even after some cycles of re-usage, while its surface underwent a perceptible, although quantitatively negligible degradation.

Keywords: TiO₂ based photocatalysis, immobilization, thermal decomposition of PVA, organic pollutant, TritonX-100

1. Introduction

The continuously increasing number of environmentally risky chemicals strongly demands the developments of new procedures which can be successfully deployed against a wide range of man-made contaminants.

Heterogeneous photocatalysis as one of the advanced oxidation processes (AOPs) satisfies this requirement. TiO_2 is a widely used photoactive semiconductor for this purpose, mostly in suspension form. One of the main drawbacks of this method is that the phase separation after the water treatment is very difficult and expensive. This problem can be eliminated if the catalyst is immobilized. But, unfortunately, this method is not free of disadvantages. Immobilization decreases the active surface area of the catalyst, diminishing its efficiency [1].

The TiO_2 -covered surfaces, which may be used in practical applications, should meet the following important requirements:

- Strong interaction between the surface and the catalyst to get the desired stability.
- The coated support should not change the activity of the catalyst.
- A large surface area is essential to ensure a high efficiency of degradation via easy adsorption of the pollutants.
- A long-term use requires the durability of immobilization.
- The applied carrier must withstand the photocatalytic processes, as well as the long-term radiation [2].

Among the first, *Tennakone et al.* used polymer surface for fixing titanium dioxide in 1995 [3]. A catalyst film was taken up to the polyethylene backing by a simple thermal treatment. Later, a number of other polymers were used for this purpose in other laboratories, e.g. polyethylene sheets [4], PVC [5], polyethylene terephthalate bottle [2], and poly(vinyl alcohol) [6–11]. Usually a physical contact is formed between the polymer and the catalyst [2,4], but in some cases they are chemically bound [6]. The advantage of the polymeric fixation is that a large proportion of the materials is chemically inert and mechanically stable, commercially available and inexpensive, most of them have a high resistance to UV radiation [2].

Recently, several research teams used titanium dioxide immobilized with poly(vinyl alcohol) for photocatalytic applications. *Habiba et al.* (2016) created chitosan/PVA/Na-titanate/ TiO_2 composite with solution casting method and used it for the photodegradation of two dyes [12]. The Na-titanate improved the water-resistance but decreased the crystallinity of chitosan. The removal efficiencies were 100% and 99% in the case of methyl orange and congo red, respectively.

Adb El-Rehim et al. (2012) fixed TiO₂ at the surface of PVA micro gel and used for the degradation of methyl orange dye [13]. *Xiuyun et al. (2015)* investigated the photocatalytic activity (in the visible range) of a PVA-TiO₂ composite film produced by a sol-gel method [10].

Lei et al. (2012) immobilized P25 TiO₂ with poly(vinyl alcohol) by a casting technique with thermal treatment [6]. The composite catalyst prepared was a white thin film. They used this composite for the decomposition of methyl orange. The TiO₂ loss was only 1.1% after the 25th usage. We have tried to reproduce this method. In our case, the thermal treatment changed the color of the PVA support to dark brown. This was not mentioned in the referred study [6], however, *Song et al. (2014)* [14] reported about the browning during the thermal treatment, and the effect was explained by the rearrangement of the polymer structure. The color gradually faded during the irradiation, while the total organic carbon content (TOC) in the solution significantly increased. The degradation of the methyl orange model compound was only followed by UV-vis spectroscopy [6], so the dissolved materials (from the polymer) in the solution phase were not detected. The aim of our work was to investigate the changes taking place during the thermal treatment and the effects of them on the stability and efficiency of the composite photocatalyst. Triton X-100, one of the most widely used non-ionic detergents, was chosen as a model substrate to be degraded in this system. This 4-(1,1,3,3-tetramethylbutyl)phenyl polyethoxylate (with an average ethoxylate number of $n \approx 9.5$) can hardly be degraded by biological treatments [15–19]. In a recent study, we have thoroughly examined the TiO₂-based photocatalytic degradation of this tensid under various circumstances in aqueous suspension [20]. The results of that work contributing to the elucidation of the degradation mechanism could serve as a reliable basis for an investigation of the immobilized photocatalyst.

2. Materials and methods

2.1. Materials

For our experiments, commercially available chemicals were used without further purification. The titanium dioxide catalyst used was Degussa P25 (70% anatase, 30% rutile; Evonik-Degussa GmbH). The concentration of TiO₂ was 1.5 g dm⁻³ in the case of suspensions. Triton X-100 (C₁₄H₂₂O(C₂H₄O)_{9.5}, Alfa Aesar) was chosen as a model compound to be degraded. For preparation of foils, high-molecular-weight distributed poly(vinyl alcohol) was

applied ($M=146000-186000 \text{ g mol}^{-1}$, hydrolysis degree: 99+%, Aldrich). Double distilled water was purified with a Milli-Q system before using it as solvent in this study.

2.2. Immobilization

Based on the work of *Lei et al. (2012)*, 0.3 g TiO_2 powder was suspended into 10 cm^3 distilled water, then, after sonication, 0.2 g PVA was mixed into this suspension [6]. The suspension containing 60% TiO_2 was stirred at 90°C for 1 hour, then at 60°C for two additional hours, while a dense viscous solution was obtained, which was poured into a 7-cm diameter Petri dish, and dried at room temperature. A thermal treatment was applied to enhance the stability of the foil prepared; it was heated at 140°C for 2 hours under argon. The average weight of the composite catalyst with 40% PVA content was 0.47 g, while the weight of the pure PVA foil was 0.19 g. Notably, the amount of TiO_2 (0.3 g) immobilized in PVA was equal to that contained in 200 cm^3 of suspension (see Section 2.1), for the comparability of the applications of this photocatalyst in these (two different) forms.

2.3. Photoreactor

For stability and photodegradation studies, the volume of the liquid phase was 200 cm^3 . The catalyst film was placed on a perforated glass platform (foil holder) standing on a glass frit, through which compressed air was bubbled from a gas bottle at a flow rate of 10 $\text{dm}^3 \text{ h}^{-1}$, ensuring a constant oxygen concentration. The reaction mixture containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ Triton X-100 was circulated with a magnetic stirrer. Fig. S1 displays the schematic diagram of the reactor. It was irradiated from above with an Oriel LCS-100 solar simulator resulting in a 72- mW/cm^2 light intensity on the surface of the reaction mixture. Its emission spectrum is shown by Fig. S2.

2.4. Analytical Procedures

The absorption spectral changes of the reaction mixtures were followed with a Scinco S3100 spectrophotometer. The TOC of the solution phase was followed by application of a Thermo Electron Corporation TOC TN 1200 apparatus.

In the study of the TiO_2 dissolution from the composite, the concentration of titanium in the aqueous phase was determined with an inductively coupled plasma-atomic emission spectrometer ICP-AES (OPTIMA DV2000 Perkin-Elmer) at 334.94 nm. The analytical measuring curve was obtained by using acidic samples (0.1 M HNO_3) containing titanium ions (0.1–10 mgdm^{-3}). High purity argon (99.99%) was used for the measurements with flow rates

of $15 \text{ dm}^3\text{min}^{-1}$ (plasma), $0.8 \text{ dm}^3\text{min}^{-1}$ (nebulizer) and $0.2 \text{ dm}^3\text{min}^{-1}$ (shearing gas), respectively. The output power of the generator was adjusted to be 1500 W.

The degradation of Triton X-100 was monitored by UHPLC described in our previous work [20]. The decrease of the overall concentration of this detergent was followed by this method. Also the adsorptions of Triton X-100 on pure PVA foil and PVA-TiO₂ composite were determined by this technique. In either case, according to our measurements, the adsorption did not exceed 2 % after a 2-hour equilibration period. These results suggested that the adsorption did not significantly influence the analysis of the photoinduced degradation of this surfactant.

During the stability studies, the compounds dissolved in the liquid phase were determined by GC-MS method, applying two different ways of sample preparation. One half of a sample was directly injected after evaporation and dissolution with methylene chloride-methanol 1:1 mixture, while the other half was injected after silylation (at 80 °C, 1 hour) with BSTFA reagent (BSTFA+ TMCS: 99:1) and pyridine (100-100 µl). The separation was carried out on an Agilent 6890N gas chromatograph with an Agilent DB 5-ms UI column (30 m × 0.25 mm × 250 µm). The carrier gas was high purity He with 1 ml min^{-1} flow rate. The temperature of the injector was 270°C, ~1 µl sample was injected to the column with splitless mode. The initial temperature of the column was 60°C and held it at this temperature for 2 minutes, after that with 10°C/minutes rate heated to 300°C and kept for 5 minutes. The total runtime of a measurement was 31 minutes. The temperature of Aux was 280°C. As a detector, an Agilent 5973 N-type electron ionization (EI) mass spectrometer was used in scan mode ($m/z = 33\text{--}550$, 3.14 scans/sec). The solvent delay was 4.5 minutes. The conditions applied for the analysis of Triton X-100 and its degradation products were described earlier [20]. In the present study p-terphenyl was used as internal standard.

A Bruker SENTERRA Raman microscope was also used to analyse the samples. The laser source was a green semiconductor-laser of 532 nm with a maximum power of 10 mW. For the microscope, a 20x objective was applied. The Raman signal was collected with a thermoelectrically cooled charge-coupled device (CCD) detector and recorded for typically 20 scans. A typical integration time for recording the Raman spectra was 10 s on the average. The spectral resolution was 4 cm^{-1} .

The FT-IR spectra were measured on a BRUKER Vertex 70 type spectrometer with a Bruker Platinum ATR adapter without sample preparation. The spectra were recorded at a resolution of 2 cm^{-1} with a room temperature DTGS detector (512 scans were co-added).

The morphology of the composite catalysts produced was analysed with a Philips XL30 scanning electron microscope (SEM) equipped with an EDR 288 energy dispersive X-ray analyser.

3. Results and Discussion

Photoinduced degradation of the model compound was studied in 2×10^{-4} M solutions under various conditions (see Fig. S3). The reaction mixture was irradiated for 6 hours in each experiment, using solar simulator. Triton X-100 was decomposed to a small extent in the absence of catalyst, i.e. in direct photolysis; its concentration decreased by 33% during a 6-hour irradiation. A decrease of 62% was observed in the presence of TiO_2 embedded in PVA foil, while in the case of suspended photocatalyst 90% degradation was reached, after the same irradiation periods. The TOC of the solution decreased by 17% with suspended TiO_2 , while it increased by 12% in the presence of immobilized catalyst. The latter result suggested that organic compounds were dissolved from the foil, i.e. it was not stable; instead, it was degraded upon irradiation. Our aim in this work was to elucidate this phenomenon and to improve the stability of the composite foil.

For this purpose, foils of two different compositions, i.e. pure PVA and 40:60 (w/w%) PVA- TiO_2 composite, were synthesized, and their stabilities were investigated under our experimental conditions. Both types of them were tested without thermal treatment and also after heating them at 140°C for 2 hours. After these two possibilities of preparation, the foils were rinsed in distilled water for 8 hours in the reactor described in Section 2.3. These rinsing actions were carried out both in dark and combined with irradiation. The decrease in the mass of the solid phase, the change in the composition of the foils and that of the rinsing solution were studied.

The pure PVA foil was transparent and colorless, while the one containing catalyst was white. During the thermal treatment both turned to brown. Such a color change was not mentioned by either *Lei et al. (2012)* or *Ren et al. (2015)* [6,21] while *Song et al. (2014)* observed this phenomenon but without any discussion of its reasons [14].

3.1. Change of mass

The masses of the foils were measured before and after rinsing, the change of mass was given in percentage compared to the original mass of the foil (before rinsing). The values obtained under various conditions are shown in Fig. 1. The highest mass reductions were observed in the case of pure PVA foils; 33% after an 8-hour rinsing in the dark, while 41.8% upon irradiation with solar simulator. Notably, the temperature of the solution increased during the irradiation, from 23°C to 31°C, which ought to be taken into consideration at the evaluation of the results. PVA is water-soluble and its solubility is enhanced upon increasing temperature, which could contribute to the higher mass reduction in the irradiated system. However, in the case of the thermally treated foils (H-PVA) the mass reductions after the soaking became small and similar; 1.8% in the dark and 2.2% under irradiation (Fig. 1). These results indicated that the thermal treatment dramatically enhanced the stability of the polymer foil, and the temperature increase during the irradiation did not significantly affect it. Since one could expect that some loss of mass of the foils occurred during their thermal treatment, they were weighed before and after this procedure (still before rinsing). An average loss of 4.65 ± 0.07 % was obtained from four samples of starting mass of about 0.47 g. This indicated that a slight part of the polymer evaporated, due to the formation low-weight, volatile compounds during the treatment.

Comparing the mass reductions of the catalyst-containing foils to those of the pure PVA foils (obtained under the same experimental conditions), a considerable difference can be observed. These results suggest that the connection between the semiconductor particles and the polymer chains, i.e. crosslinking [6], improves the stability of foils in water. An 8-hour soaking caused only 5.3% mass reduction, which is about one sixth of that observed for the pure PVA. Upon irradiation, the initial mass decreased by 12.9 %, which was somewhat higher than the doubled value obtained in dark. This increase can be attributed to both the temperature elevation (enhancing the solubility of PVA) and the photoactivity of titanium dioxide causing some degradation of PVA. The stability of TiO₂-containing foils was further increased by thermal treatment, due to the higher degree of crosslinking. Accordingly, soaking in dark caused only a very slight decrease (0.33%), while after irradiation 3.4% mass reduction was observed. The latter value, however, still exceeded that of the pure PVA (also heated, 2.2%) as a consequence of the photocatalyzed degradation of the foil.

In order to check if any loss of the catalyst from the composite occurred during both rinsing (without or after thermal/photo-treatments) and irradiations, TiO₂ concentration of the liquid phase was measured by ICP after these operations. No trace of this catalyst was detected in any case. These results were in accordance with the UV-Vis spectra of the corresponding samples as Fig. S4 indicates. While the spectrum of the TiO₂ suspension displays a characteristic maximum at about 330 nm, even at lower concentration, those of the liquid phase after the first and the second pre-treatment are featured by a shoulder at a much shorter wavelength (at ca. 270 nm). The previous spectra are in accordance with earlier published ones regarding TiO₂ suspension [22], nanocrystalline film [23], and PVA-TiO₂ thin layer [9].

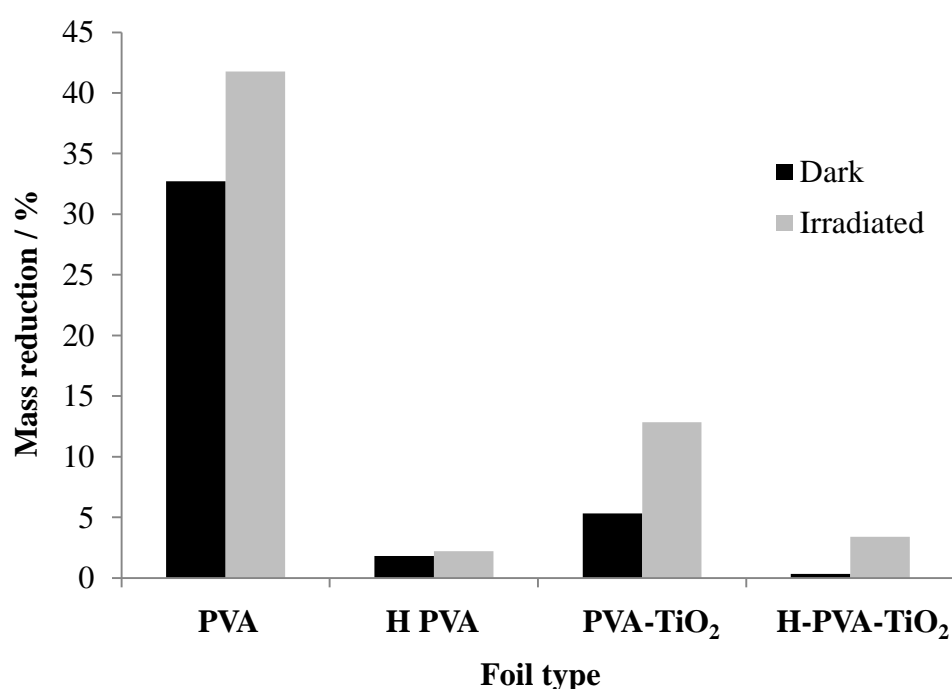


Fig. 1. Changes in the mass of various foils after 8-hour soaking in dark and upon irradiation.

3.2. Change of TOC

In our experimental series, not only the changes in the mass of the foils, but also the TOC values of the solution phase were measured. Fig. 2 shows the time dependence of the TOC values of the solution phase soaking various foils during 8-hour irradiations. These functions are in good accordance with the data of mass reduction (Fig. 1). The stability of the non-treated foils (PVA, PVA-TiO₂) is rather low; PVA was dissolved during soaking, increasing the TOC of the solution phase. The presence of titanium dioxide in the foil increased its stability; the

change in the TOC value was considerably lower than in the case of pure PVA. However, even the non-treated PVA-TiO₂ foil proved to be too instable to be applicable in photocatalytic water cleaning procedures. The thermal treatment significantly increased the stability of the foils studied; the TOC values of the solution phase did not exceed 50 mg dm⁻³ after an 8-hour soaking for both H-PVA and H-PVA-TiO₂. While temperature elevation increases the solubility in both cases, photocatalytic degradation enhances the TOC value only with H-PVA-TiO₂ as manifested in the slight difference between the corresponding plots.

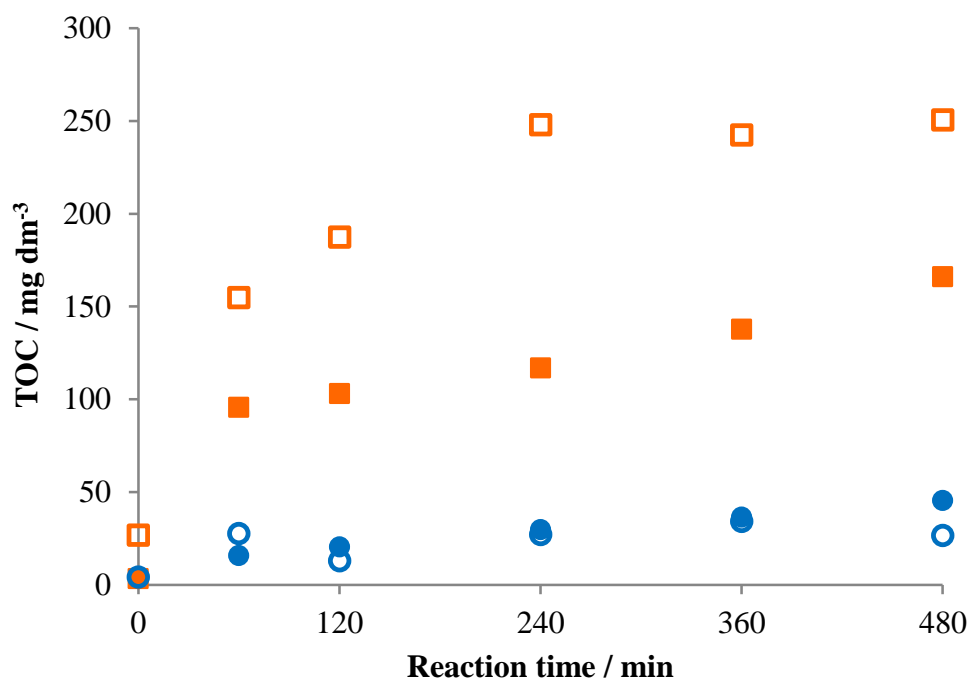


Fig. 2. The change of TOC of the solution phase during the soaking of various foils under irradiation

□ PVA ■ PVA-TiO₂ ○ H-PVA ● H-PVA-TiO₂

3.3. Spectral changes

The processes taking place during the irradiations were also followed by monitoring the absorption spectra of the solution phases (Fig. 3).

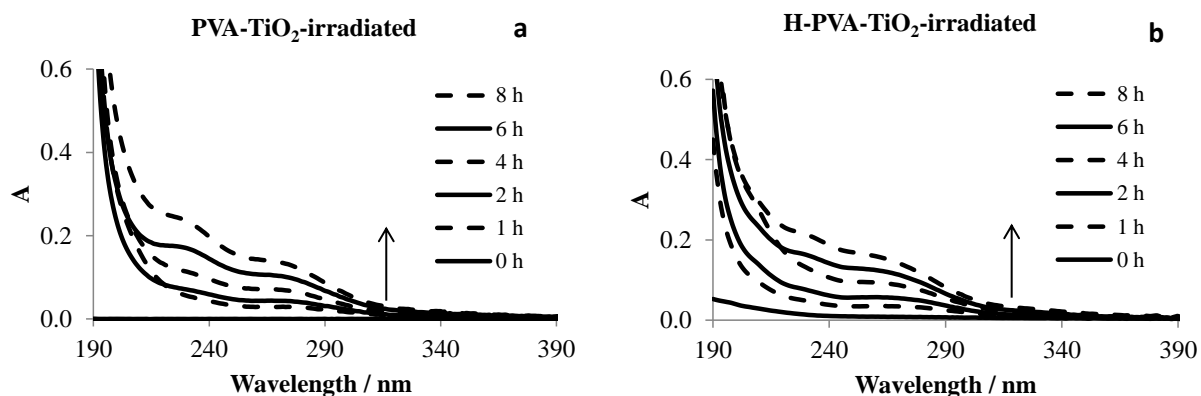


Fig. 3. Absorption spectra

The light absorption of the **non**-treated foils (PVA, PVA-TiO₂) gradually increased during **the** soaking in dark. The characteristics of these absorption spectra well agrees with those obtained by dilution of poly(vinyl alcohol), i.e., PVA was dissolved out of the foils, decreasing their mass and increasing the TOC of the solution phase. Upon irradiation of the solution phase obtained by soaking PVA-TiO₂ foil, the absorption spectrum significantly changed. The absorbance gradually increased (Fig. 3/a). These spectral changes confirmed our assumption that the dissolved polymer transformed in heterogeneous photocatalytic processes, i.e. the spectra obtained involve the absorption of both the dissolved polymer and its degradation products.

In the case of the brown, thermally treated foils, their soaking in dark caused negligible dissolution, i.e. no perceptible spectral change, in accordance with mass reduction results (Fig. 1).

Upon irradiation of the thermally treated foils, the absorbance gradually increased (Fig. 3/b). The spectral changes were the result of several parallel processes. On one hand, PVA and its products formed in the thermal treatment were dissolved from the foil, on the other hand, all these compounds transformed already on the surface of the foil and **also** in the solution phase in heterogeneous photocatalytic processes. The spectral changes of the solution phase in the irradiated systems containing PVA-TiO₂ or H-PVA-TiO₂ are of very similar features. In both cases, the characteristic bands appearing the 230-260 nm range suggest the formation of aromatic products. It was confirmed by GC-MS analyses, detecting various aromatic compounds, such as acetophenone, benzaldehyde and 2-hydroxybenzaldehyde, in the solution phase. These aromatic compounds could be produced from the reactive unsaturated moieties formed in scission of the polymeric chains and dehydroxylation. During the thermal treatment,

cracking of PVA can take place, giving various products as shown later. Upon irradiation of untreated TiO₂-containing foils, aromatic compounds can be formed from PVA in reactions initialized by hydroxyl radicals. These products can undergo further hydroxylation during the degradation. Such a phenomenon was observed by *Zheng et al.*, studying the thermal dissociation of a PVA-SiO₂ composite [24]. In the dissociation products 15.1% benzenoid derivatives were determined by pyrolysis-GC-MS method.

3.4. Raman and infrared spectra

A comparison of the Raman spectrum of the initial PVA foil (Fig. 4) to those of the surface of the thermally treated, brown foil (Fig. 4/a) and of the ether solution in which the surface was soaked (Fig. 4/b) indicates that during the thermal treatment under argon atmosphere the polymer underwent dehydroxylation and cracking processes.

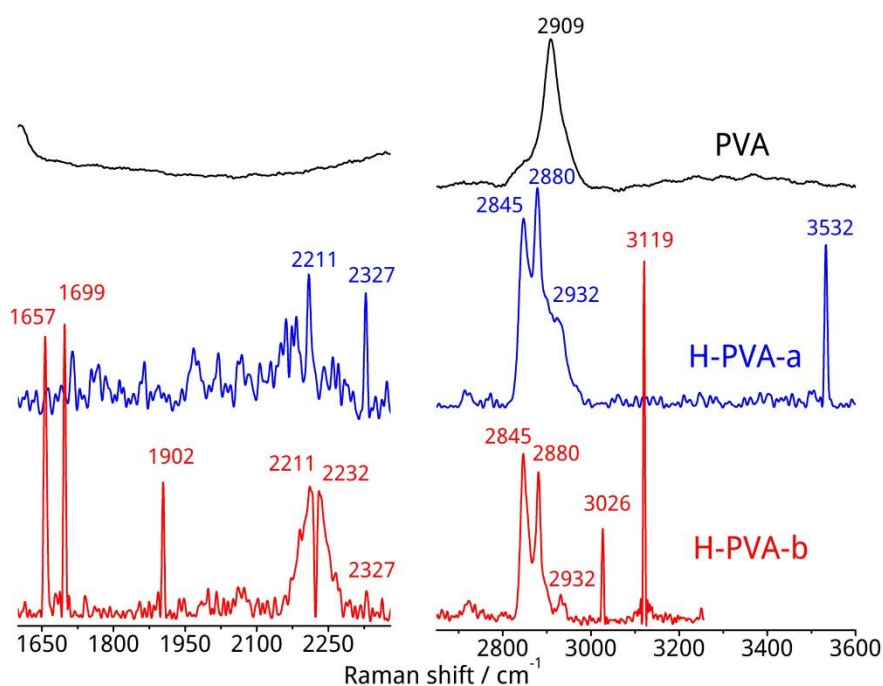


Fig. 4. Raman spectra of PVA, H-PVA surface (a) and ether solution in which the surface of H-PVA was soaked (b).

The band at 2909 cm⁻¹ in the spectrum of the initial PVA, characteristic of aliphatic hydrocarbons, split up and shifted toward the lower frequencies. This change may be attributed to the decrease of tension originating from the lack of HO-groups. Detachment of a hydroxyl group can lead to the formation of double bonds isolated by water elimination and of vinyl groups as indicated by the band of the asymmetric CH₂ valence vibration of the vinyl group at 3119 cm⁻¹. Elimination of two hydroxyl groups may result in the formation of -C=C- double

bonds in the hydrocarbon chain ($1657, 1699 \text{ cm}^{-1}$), in allene position $-\text{C}=\text{C}=\text{C}-$ (1902 cm^{-1}), isolated triple bonds (2211 cm^{-1}) as well as conjugated triple bonds (2327 cm^{-1}). Detachment of three HO-groups may produce conjugated bond systems, ring structures, even benzene rings (3026 cm^{-1}) [25,26]. Fig. 5 summarizes the possible transformations of PVA during the thermal treatment.

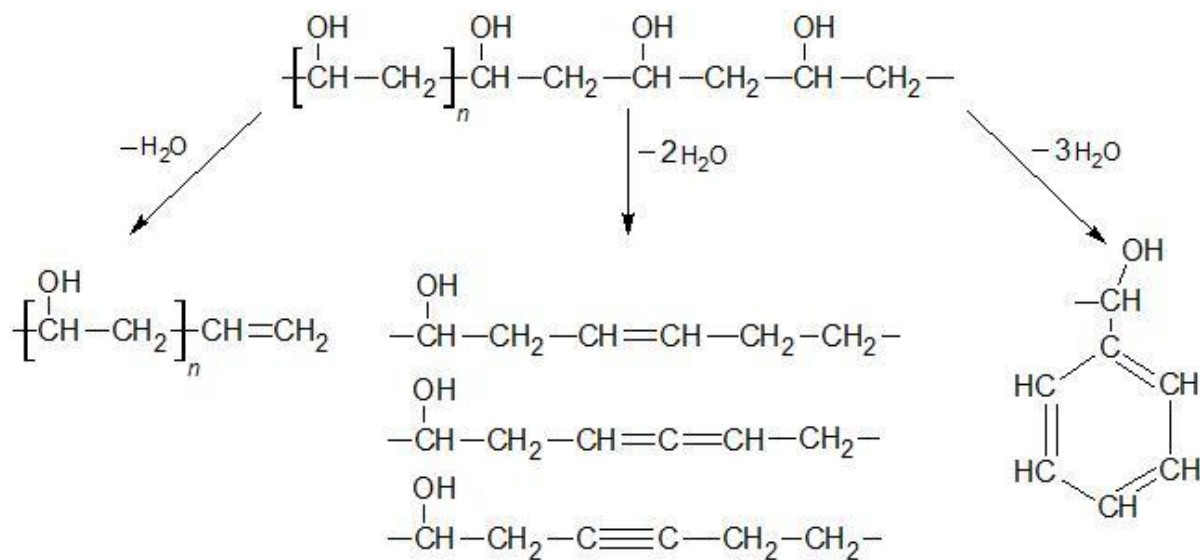


Fig. 5. Possible transformations of PVA during the thermal treatment.

The Raman spectrum of the composite and those of its constituents are shown in Fig. 6. The previous one displays bands assigned to the vibrations of aliphatic C-H bonds characteristic of PVA around 2900 cm^{-1} . In the spectrum of TiO_2 , the typical bands can be found in the $400\text{-}700 \text{ cm}^{-1}$ range. In the Raman spectrum of the **non**-treated catalyst (PVA- TiO_2) the specific bands of both constituents appear with their original characteristics. No significant change or shift of them could be observed.

The thermal treatment significantly changed the Raman spectrum of the catalyst-containing foil (H-PVA- TiO_2 in Fig. 6). Although the three peaks characteristic of TiO_2 are still apparent, the fine structure typical for the spectrum of PVA in the $900\text{-}1700 \text{ cm}^{-1}$ range [25] disappeared. Instead, new peaks appeared at higher wavenumbers, indicating the formation of products generated by the thermal treatment. The bond systems identified in this spectrum are similar to those observed in the case of the pure PVA foil; the shifts of the typical bands are the consequences of the presence of TiO_2 . The presence $-\text{C}=\text{C}-$ bonds in the sample are indicated

by the 1522 cm^{-1} band, which appears in the case of conjugation with polyene or vinyl moieties. The band assigned to $\text{-C}\equiv\text{C-}$ bonds, which belong to the most Raman active groups, clearly appear in this spectrum, similarly to that of the thermally treated PVA.

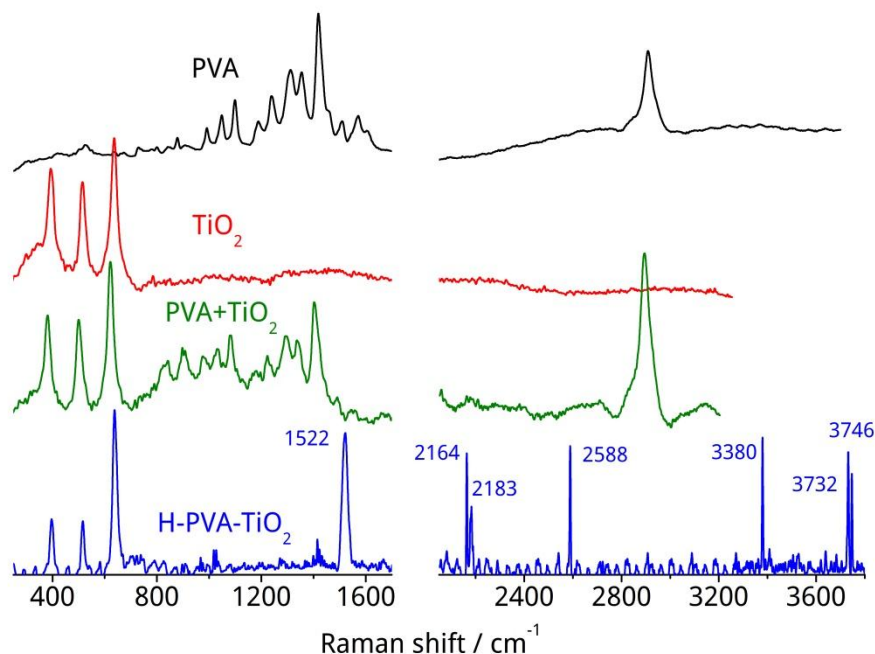


Fig. 6. Raman spectra of the composite catalyst and its constituents.

The corresponding vibrational bands of H-PVA-TiO₂ can be seen at frequencies lower than 2200 cm^{-1} . This phenomenon suggests that these triple bonds are located at the end of a chain in a conjugated system. This is confirmed by the appearance of the C-H vibration of a vinyl group at 3380 cm^{-1} . The 2588 cm^{-1} band suggests the presence of a hydroxyl group in intramolecular hydrogen bond or a triple bond in a strongly conjugated system. Such a big shift (compared to 2200 cm^{-1}), in the case of a triple bond, can only occur in an extremely strong unsaturated, conjugated bond system, while a compound able to form intramolecular hydrogen bond has already been identified (as 2-hydroxybenzaldehyde) in this system by GC-MS.

The bands at 3700 cm^{-1} can be assigned to isolated HO-groups in a rather apolar environment, i.e., without any partner suitable to the formation of hydrogen bond. This is not surprising because dehydroxylation generally produces a **nonpolar** C-H system. In such an environment, the bands of HO-groups belonging only to isolated CH or CH₂ moieties may shift so much.

It is clearly seen, on the basis of the analytical results discussed in the previous sections, that the PVA foil was degraded during the thermal treatment, no matter if it contained TiO₂ or not; organic compounds of similar structures formed in this process.

No change was observed upon irradiation of the PVA foil, however, in the case of the PVA-TiO₂ composite the IR spectrum of the solid phase indicates significant chemical transformations (Fig. S5). These spectral changes suggest dehydroxylation, formation of oxidized products and double-bond systems. The explanation of these spectra is involved in the supplementary material.

In the solution phases of the thermally treated samples (H-PVA and H-PVA-TiO₂), the changes were very similar to those observed for the solid samples in the range of the C-H vibrational bands (Fig. 7): shifts toward the lower frequencies (2924 and 2855 cm⁻¹). Additionally, the C-H deformation bands (1300-1460 cm⁻¹) and the H-O deformation bands (1000-1100 cm⁻¹) have also significantly changed compared to the corresponding bands in the spectrum of the initial PVA. In the range above 3000 cm⁻¹, the bands belonging to aromatic systems cannot be observed, being masked by those of the HO-groups. However, their existence cannot be excluded because the GC-MS analysis indicated the formation of aromatic compounds such as phenol, various aromatic aldehydes (e.g., cinnamaldehyde), ketones, and their hydroxylated derivatives. Also in the case of H-PVA and H-PVA-TiO₂, diffuse bands assigned to carbonyl (1700-1747 cm⁻¹) and -C=C- (1500-1650 cm⁻¹) bonds can be seen in the IR spectra. The intensity for the vibrations of the more weakly bound carbonyl groups (in aldehydes) is much higher in the spectrum of H-PVA than in that of H-PVA-TiO₂.

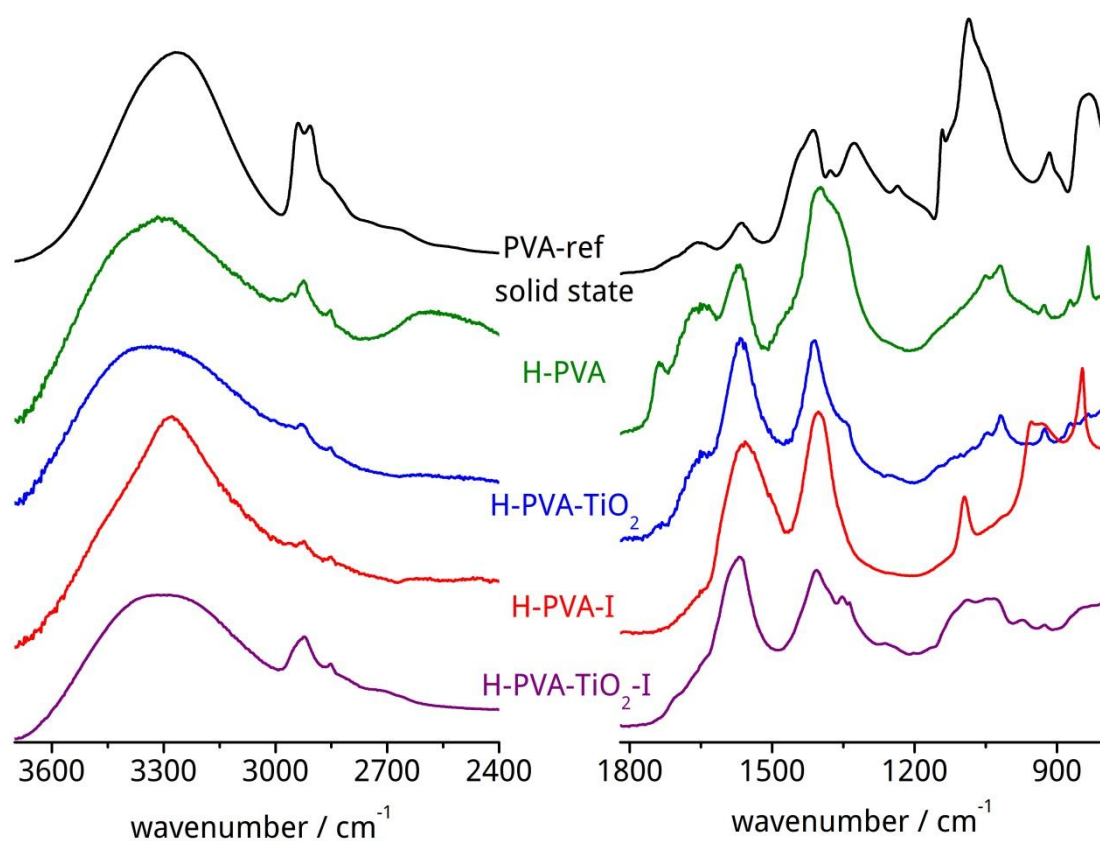


Fig. 7. IR spectra of solutions soaking various foils along with that of solid PVA as reference.

Comparing the IR spectrum of H-PVA kept in dark to that of the irradiated one (H-PVA-I), it can be observed that the bands characteristic of the oxidized products almost totally disappeared upon irradiation. In the range of the diffuse H-O valence vibrational bands, a wide but distinct peak rises at 3287 cm^{-1} , besides, only one H-O deformation band became significant at 1096 cm^{-1} . These results suggest that the thermal products dissolved were further degraded upon UV irradiation, even in the absence of TiO_2 . These observations are in good accordance with the results of the GC-MS analysis, on the basis of which mostly stearic acid and its derivatives with several double bonds (such as 9,12-octadecadienoic acid(Z,Z) and 9-octadecanoic acid) were detected in the sample kept in dark. Stearic acid was also found in the irradiated sample, but various carboxylic acids of shorter hydrocarbon chain (e.g. myristic or tetradecanoic acid, capric acid, and malic acid) were also detected, due to further degradation.

Also in the case of the thermally treated and irradiated composite (H-PVA- TiO_2 -I) degradation was promoted by UV excitation; its spectrum significantly deviates from that of the corresponding sample kept in dark. It is more complex than that of H-PVA-I, due to the

numerous degradation products formed in the TiO₂-based photocatalysis. Almost all bands became wider; this phenomenon is especially conspicuous in the ranges of the C-H valence and deformation vibrations, the carbonyl vibrations, and the H-O deformations. Summarizing our observations above, the degradation products of H-PVA decomposed further under UV irradiation, even without TiO₂, but more types of oxidized products formed in the TiO₂-containing samples, due to the photocatalytic processes.

3.5. Pre-treatment

The thermally treated composite catalyst cannot be directly used for photocatalytic purposes because the PVA support is also degraded upon irradiation, increasing the TOC of the solution to be cleaned. Our aim with the pre-treatment was the mineralization of the products of the thermal cracking. The foils were soaked to „clean” before their usage as photocatalysts. After the first 8-hour irradiation, the TOC of the solution phase was 50 mg dm⁻³. Then the experiment was repeated with pure distilled water; the TOC of the solution phase was much lower (21.6 mg dm⁻³), while the brown color of the foil gradually faded. According to our expectation, a further, significant decrease in the TOC change was observed during the third irradiation (Fig. S6). These results clearly indicate that the thermally treated foils have to be cleaned by irradiation pre-treatments to remove the pollutants formed in the cracking processes.

3.6. Study of re-usage

After three pre-treating irradiations (see Section 3.5), the activities of our immobilized catalysts were tested by a threefold usage. In each cycle, 200 cm³ solution of Triton X-100 was irradiated. After each cycle, the foils were soaked with distilled water without drying. The 6-hour irradiations were carried out with the solar simulator. Fig. S6 shows the actual concentration of the surfactant during each irradiation; 58% degradation was achieved in the first cycle, 65% in the second, and 56.5% in the third one. The photoactivity of the foils did not significantly change (decrease) between these cycles. The TOC of the solution phase decreased during the irradiations; by 20.5 % in the first cycle, 20.9% in the second, and 20.7% in the third one. Notably, the decrease of TOC is much less than the value expected on the basis of the change in the substrate concentration. The main reason for this deviation is that the mineralization of this detergent takes place via cleavage producing intermediates. The formation of larger intermediates hardly contribute to the TOC decrease; only their further degradation (mineralization) can significantly diminish its value. Accordingly, the TOC decrease at an early stage of irradiations can be attributed to the prompt CO₂ (or carbonate)

formation from an end or edge of the starting molecules or the initially generated intermediates. GC-MS analyses of the liquid samples confirmed this explanation (see Figs. S7-S12 and the corresponding text in the Supplementary). The temporal changes of the relative concentrations could be monitored for both the components of Triton X-100 and some characteristic intermediates formed from them. Notably, GC-MS analyses did not detect any intermediates which might derive from the PVA support, indicating that three pre-treating cycles of irradiation and rinsing proved to be enough for a sufficient removal of the derivatives formed during the thermal treatment.

The structure of the foils was investigated by SEM. The surface of the thermally treated (i.e. heated) but still not applied foil is rather smooth; the TiO₂ aggregates are manifested as brighter (light grey) parts in the dark background (Fig. S13). **It does not seem to be quite uniform, which is the consequence of the inhomogeneous aggregation of the catalyst particles, due to the lack of a dispersing agent during the formation of the composite.** It can also be seen that the TiO₂ aggregates are close to the surface at one place, while they are located deeper, covered by the polymer at another place. During several subsequent applications the surface structure of the foil became cavernous **and** labyrinthine, **increasing its area.** The surface of the used foil seems to consist of only catalyst particles; the polymer layer on the surface exposed to light must have degraded. The polymer foils could be successfully applied for the photocatalytic degradation of the model compound in **three subsequent** cycles. The degradation of the surface layer of the polymer cannot be seen with naked eye, it became rigid after desiccation.

4. Conclusion

Heterogeneous photocatalysis is a widely used method for degradation of organic pollutants. Generally, suspensions of the photocatalyst **are** applied in these procedures, at the end of which the semiconductor particles have to be separated from the treated solution. This step can be eliminated by immobilization of the catalyst, which was realized with poly(vinyl alcohol) in this work. **Despite the favourable effect of the immobilized TiO₂ on the crosslinking of the polymer, the stability of the PVA support was too low for a practical use, due to its still considerable water-solubility. The stability of the PVA-based foils could be significantly enhanced by a thermal treatment. Before a photocatalytic application, however, the water-soluble products of the heating process had to be removed from the surface of the PVA-TiO₂ composite foil. Three cycles of irradiation and rinsing proved to be sufficient for this purpose.**

The composite foil pre-treated in this way could be applied for the photocatalytic degradation of a widely used non-ionic detergent, Triton X-100. The efficiency of this mineralization remained constant during three subsequent cycles, while the surface of the polymeric foils underwent a perceptible, but quantitatively negligible photocatalytic degradation. The efficiency of this PVA-TiO₂ composite foil was significantly lower than that of the suspension of the catalyst, due to the reduced reaction surface. Since only a minor part of the emission spectrum of our light source (similarly to that of Sun) can excite TiO₂, further work is in progress to extend the action spectrum of this photocatalyst by modification of its structure, compensating the effect of the reduced reaction surface.

Acknowledgment

The authors wish to express their deepest and sincerest recognition of Prof. András Dombi a key figure in the topic of photocatalytic materials for the degradation of contaminants of environmental concern.

The financial supports of the National Research, Development and Innovation Office (OTKA K101141) and Széchenyi 2020 under the GINOP-2.3.2-15-2016-00016 are acknowledged. The competent help by Mr. Ádám Tóth and Dr. András Hoffer in the GC-MS measurements is also appreciated.

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Supplementary

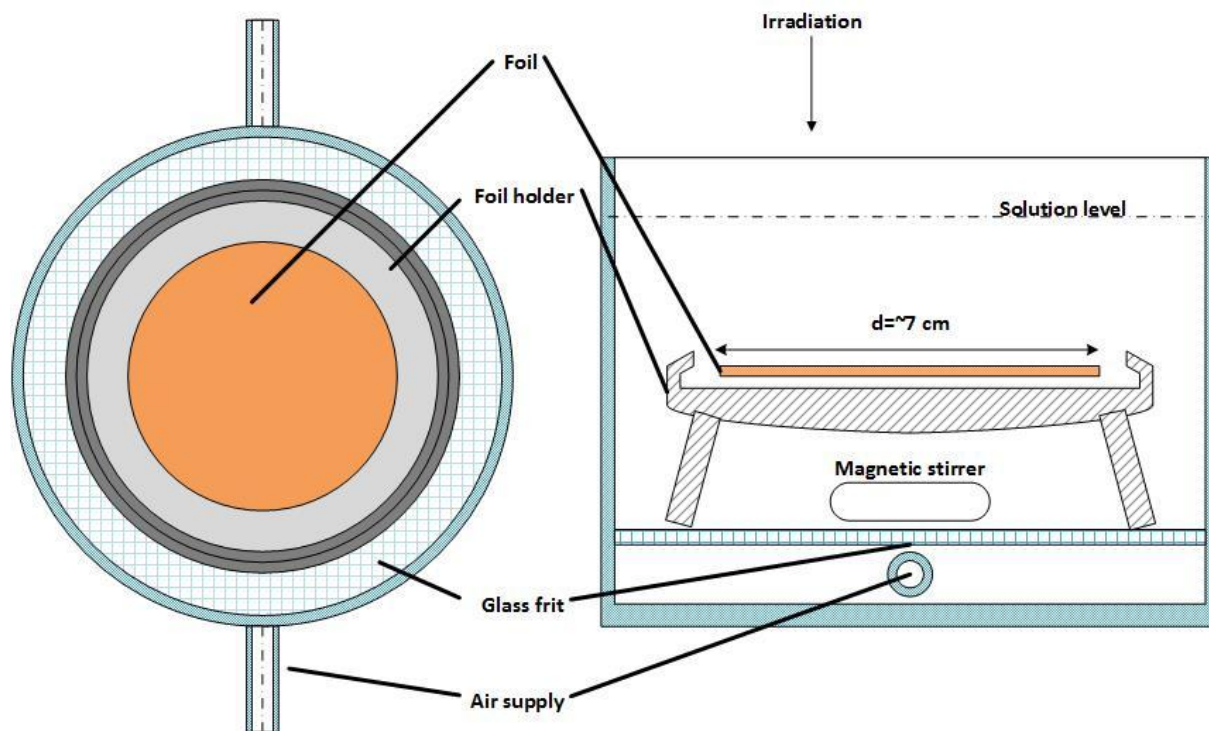


Fig. S2. Schematic diagram of the reactor applied.

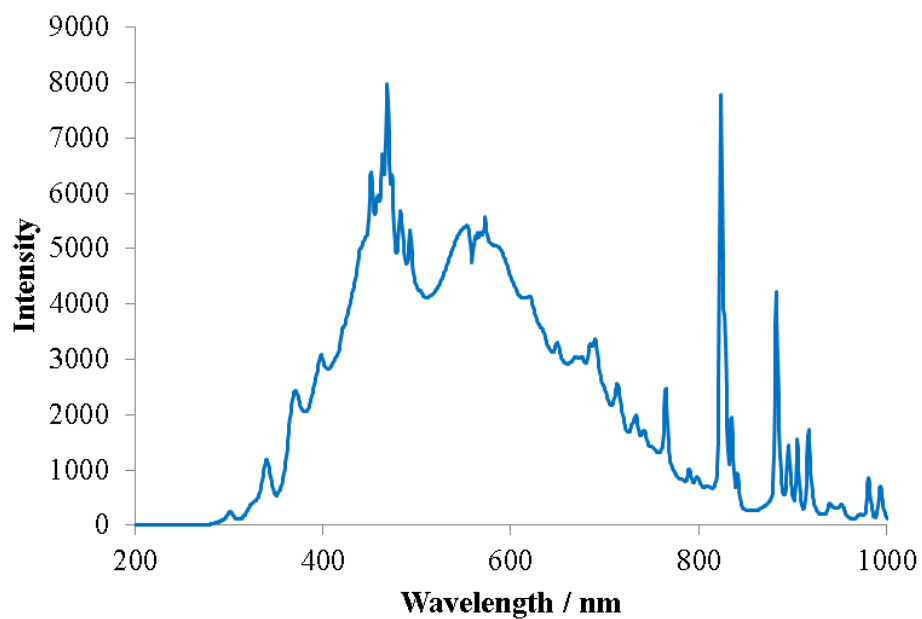


Fig. S2. Emission spectrum of the solar simulator applied.

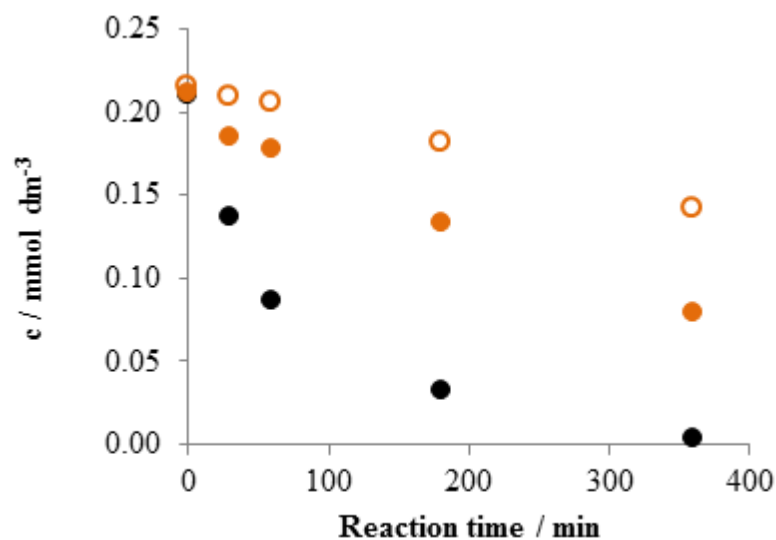


Fig. S3. Degradation of Triton X-100 under various conditions:

○ Irradiation ● PVA-TiO₂-Irradiation ● TiO₂ suspension-Irradiation

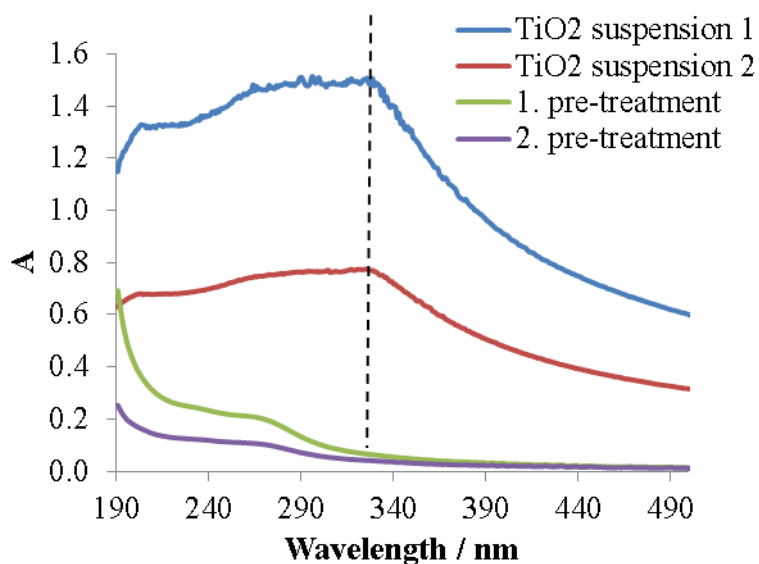


Fig. S4. Absorption spectra of TiO₂ suspensions (a) 0.05 g dm⁻³, (b) 0.033 g dm⁻³, and the aqueous phase after first (c) and the second (d) pre-treatment of the composite foil.

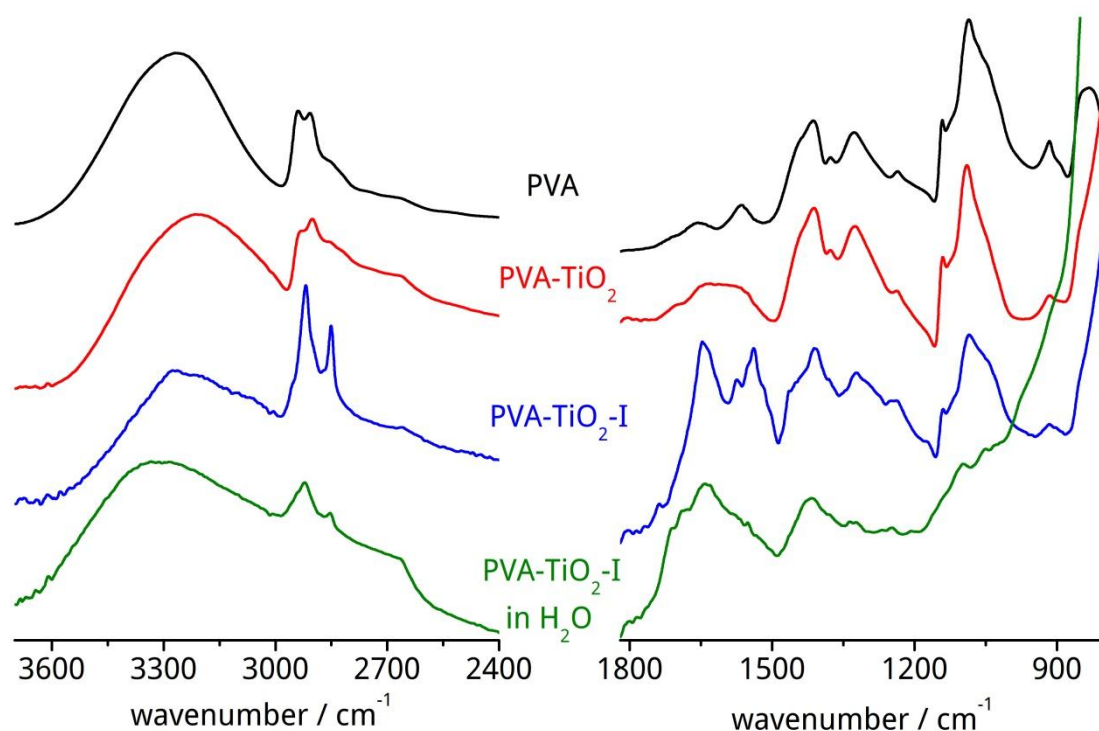


Fig. S5. Infrared spectra of the foil surfaces.

The bands assigned to the C-H valence vibrations (2944 and 2906 cm^{-1}) shifted toward lower frequencies (2922 and 2850 cm^{-1}), which can be attributed to the consequence of dehydroxylation. This suggestion is confirmed by the change of the bands assigned to the C-H deformation modes (1445 and 1413 cm^{-1}) as well as the band appearing at 1650 cm^{-1} , which can be assigned to the deformation of water molecules as inclusions. In this frequency range, there is a wide shoulder of the 1650 cm^{-1} band, which may be attributed to the valence vibration of the -C=C- bonds formed. Besides, high-intensity bands appeared at 1578 and 1540 cm^{-1} , which can be assigned to conjugated -C=C- bonds or aromatic systems. The C-H valence vibrational bands of the aromatic vibrations cannot be identified in the IR spectra because the valence vibration of the HO-groups can mask them. Beside dehydroxylation, also some bands can be observed which can be related to oxidized (C=O) products such as aldehyde (1741 cm^{-1}), ketone and carboxylate derivatives (shoulder at 1700 cm^{-1}). Similar changes can be observed in the IR spectrum of the solid composite irradiated by UV light, although the spectrum is much more diffuse. The 1741 cm^{-1} band is less dominant, instead, the carbonyl vibrations at 1716 cm^{-1} became more characteristic. Additionally, the intensity of the H-O deformation bands in the $1050\text{-}1100\text{ cm}^{-1}$ range considerably decreased.

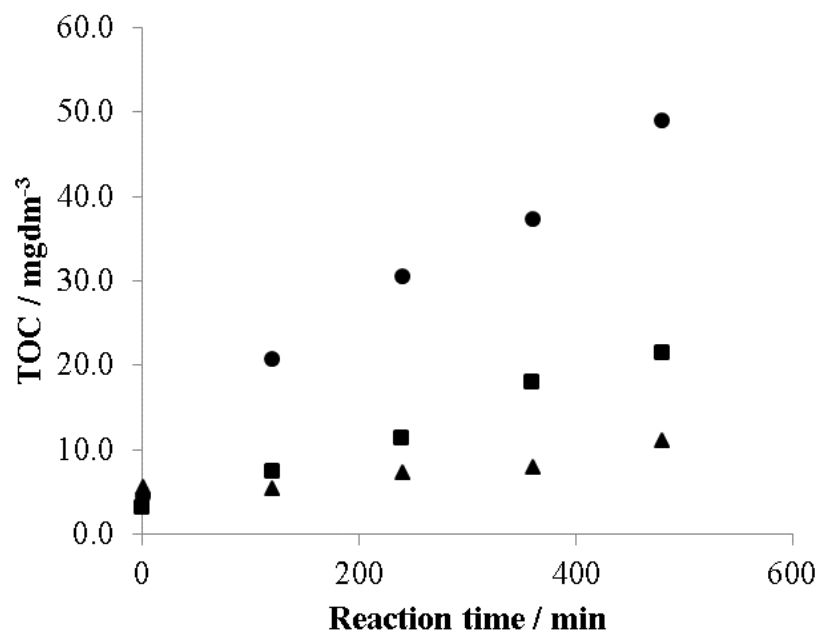


Fig. S6. Organic carbon content of the liquid phase during pre-treatments of the PVA-TiO₂ foil.

● 1st irradiation ■ 2nd irradiation ▲ 3rd irradiation

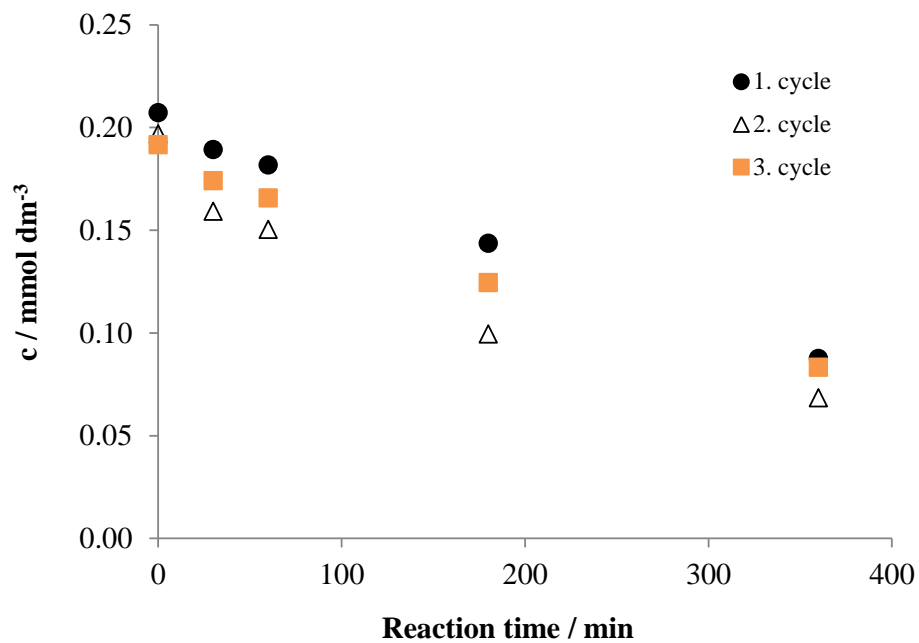


Fig. S7. Degradation of the model compound in 3 cycles.

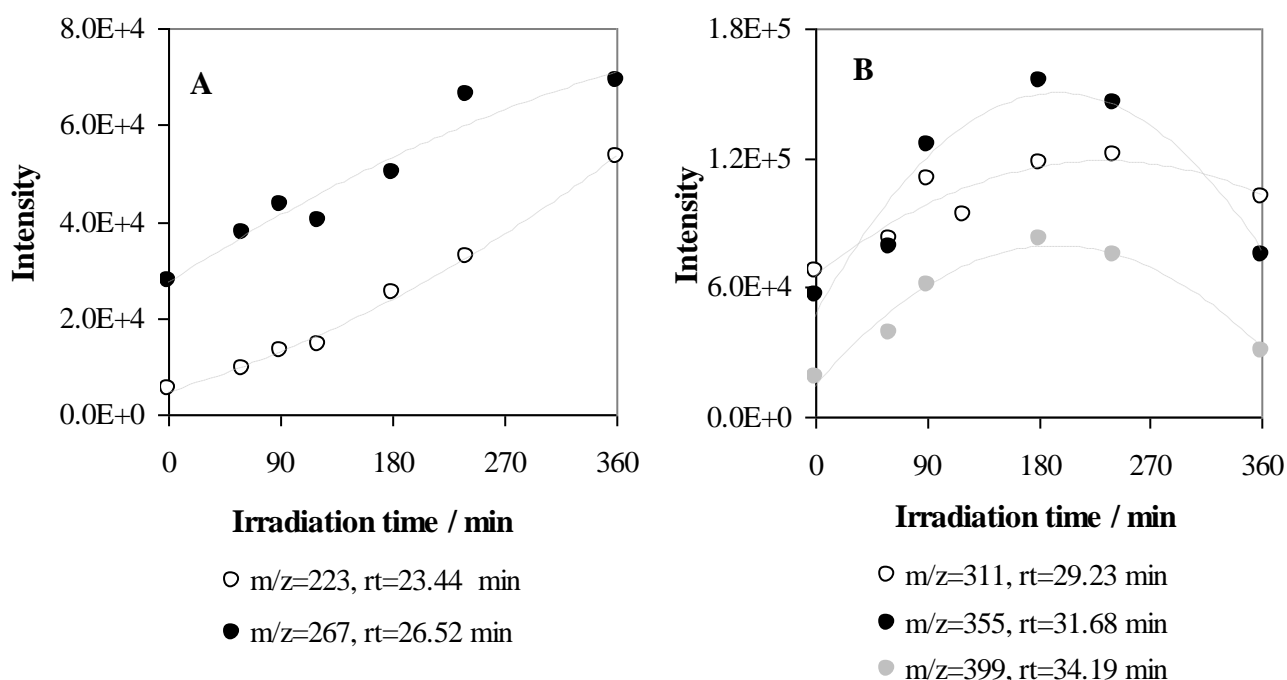


Fig. S8. Intensity vs. irradiation time plots for the most abundant fragment ion of the starting components of Triton X-100 with molecular weight of 294 ($m/z = 223$), 338 ($m/z = 267$) (A), 382 ($m/z = 311$), 426 ($m/z = 355$), 470 ($m/z = 399$) (B) in the photocatalysis of the system containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ Triton X-100 and PVA-TiO₂ foil.

Fig. S8/A shows the starting components of Triton X-100 with ethoxylate number (n) of 2 and 3, i.e., with molecular weight of 294 and 338, respectively. The concentrations of these components increased during the 6-hour irradiation. However, the concentrations of the components with $n = 4, 5$, and 6 (Fig. S8/B), i.e., with molecular weight of 382, 426, and 470, respectively, increased in the first irradiation period of 3 hours, then gradually decayed. These tendencies clearly indicate that in the 6-hour photocatalysis the degradation of the starting components of Triton X-100 with $n > 3$ resulted in the continuous increase of the concentrations of the components with $n = 2$ and 3. The initial increase of the concentrations of the components with $n = 4, 5$, and 6 was the consequence of the degradation of bigger components (with $n > 6$).

Fig. S9 clearly indicates that cleavage of the alkylphenyl part of the starting components of Triton X-100 took place from the beginning of the irradiation period. As complementary intermediates originated from such a cleavage, ethylene glycol and dioxolane derivatives could also be detected. These intermediates unambiguously formed from the ethoxy chain of the starting components, and their concentration, after an induction period due to the fragmentation steps, monotonously (moreover, accelerating) increased during the applied irradiation time (Fig. S10).

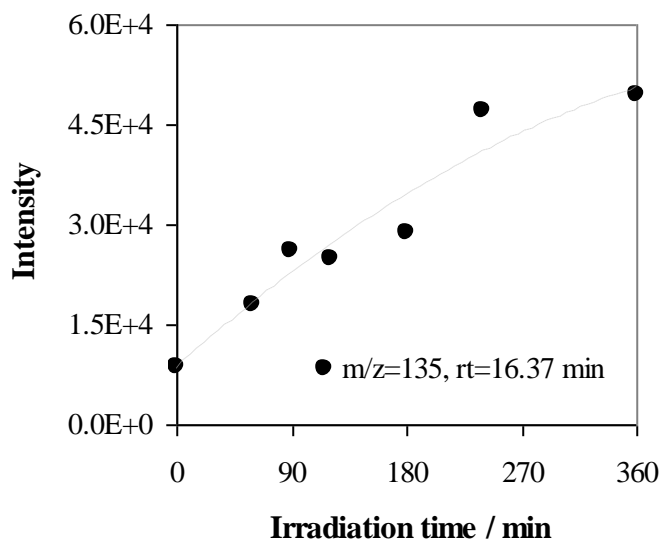


Fig. S9. Intensity vs. irradiation time plots for the most abundant fragment ion of an intermediate with molecular weight of 206 ($m/z = 135$) in the photocatalysis of the system containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ Triton X-100 and PVA-TiO₂ foil. The structure of this intermediate could be unambiguously identified as 4-(1,1,3,3-tetramethylbutyl)phenol, i.e., the alkylphenyl (= octylphenyl) part of the starting components of Triton X-100.

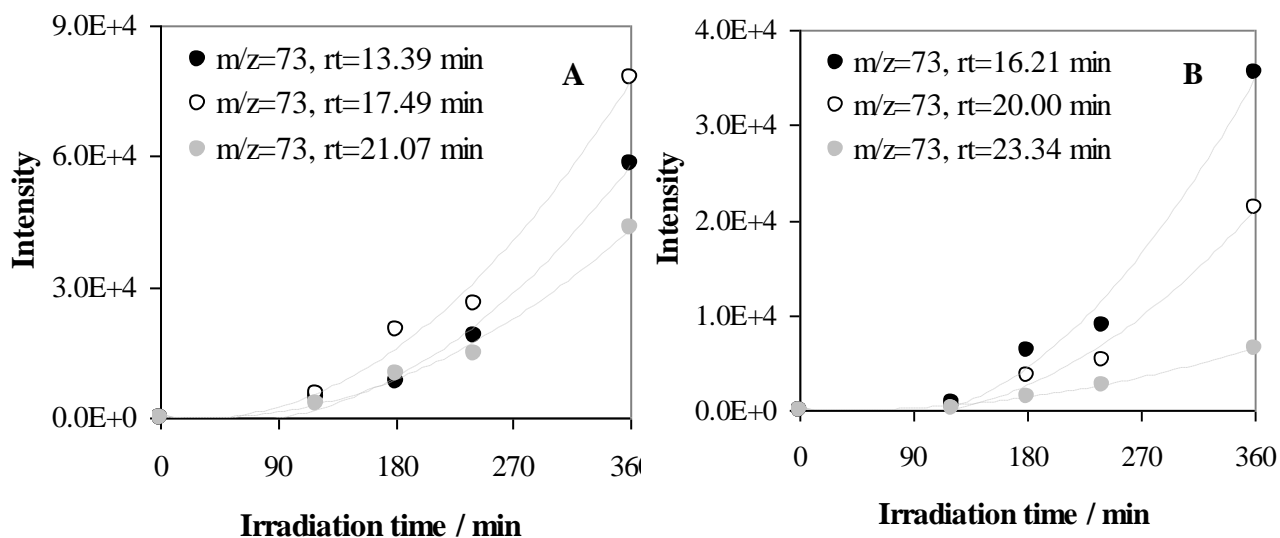
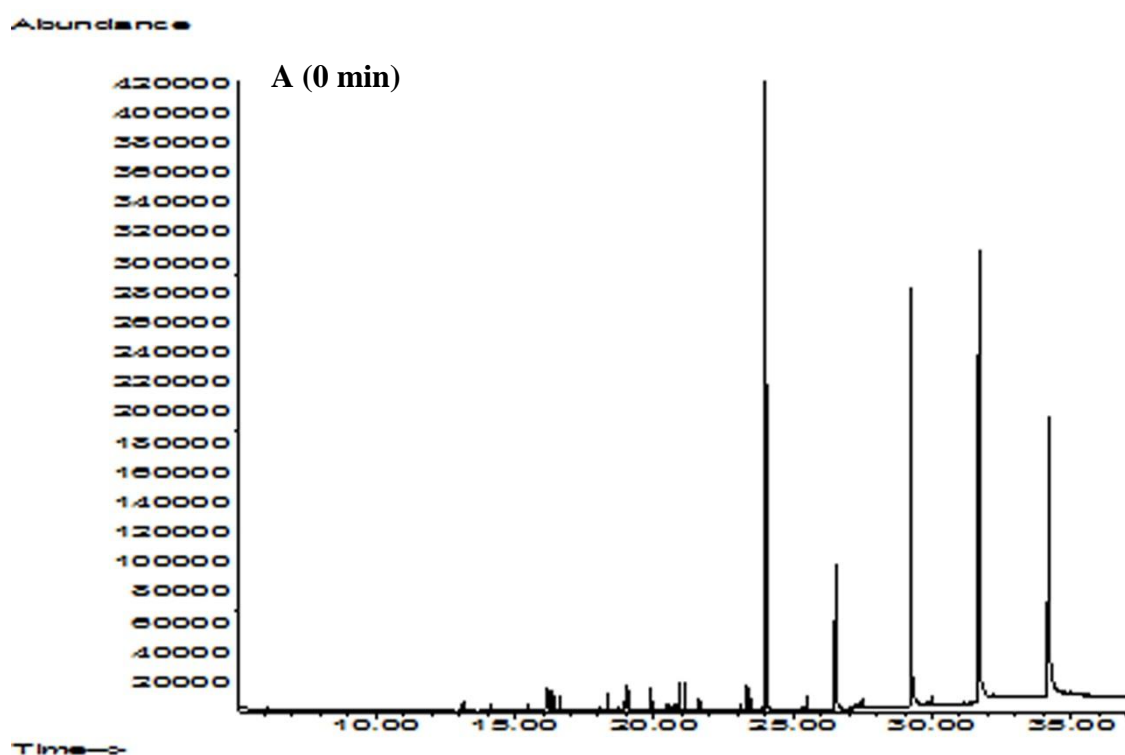


Fig. S10. Intensity vs. irradiation time plots for the most abundant fragment ion ($m/z=73$) of characteristic intermediates with different retention times (rt=13.39 min, 17.49 min, 21.07 min) (A) and (rt=16.21 min, 20.00 min, 23.34 min) (B). The structure of these intermediates could be unambiguously identified as dioxolane compounds (A) and as ethylene glycol compounds (B), which were clearly derived from the ethoxy chain of the starting molecules via fragmentation.

The concentration changes of both the starting components of Triton X-100 and the characteristic intermediates are in accordance with our earlier observations with a similar system applying suspended catalyst (see ref 20). But in the present work, due to the slower degradation processes (also as a consequence of the different light source; solar simulator instead of a UVA immersed tube), the decrease of the concentrations of some starting components and the intermediates detected could not be observed. However, the slower degradation made the detection of further (new types of) intermediates possible.

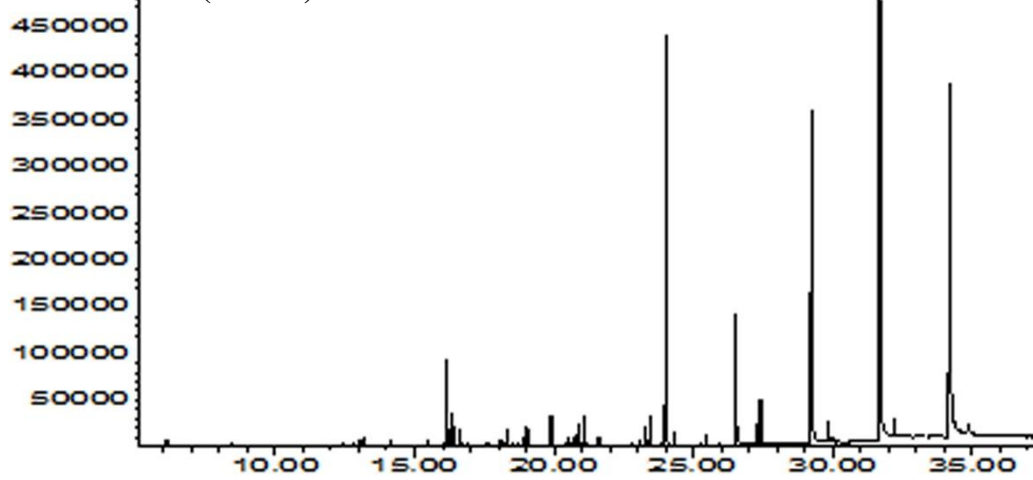
As auxiliary pieces of information for Figs. S8-S10, Fig. S11 shows the total ion chromatograms of the components extracted from the reaction mixture after the corresponding periods of irradiation, while Fig. S12 displays the mass spectra of the typical components (with the corresponding retention times) extracted from the reaction mixture.

Figure S11. Total ion chromatograms of the components extracted from the reaction mixture after 0 min (A), 60 min (B), 90 min (C), 240 min (D), 360 min (E) irradiation.



Abundance

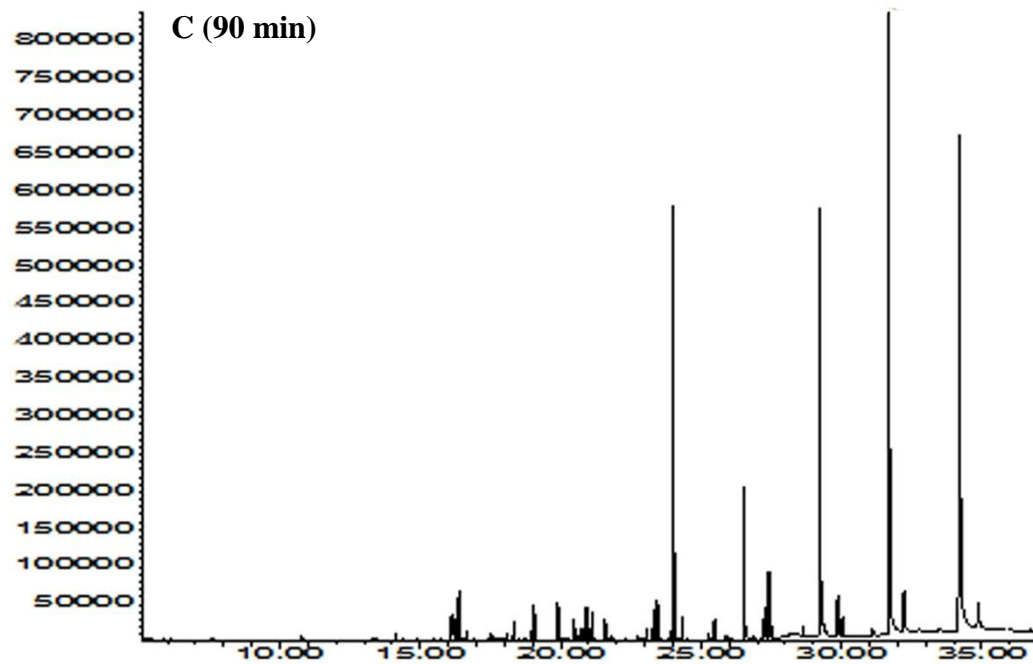
B (60 min)



Time-->

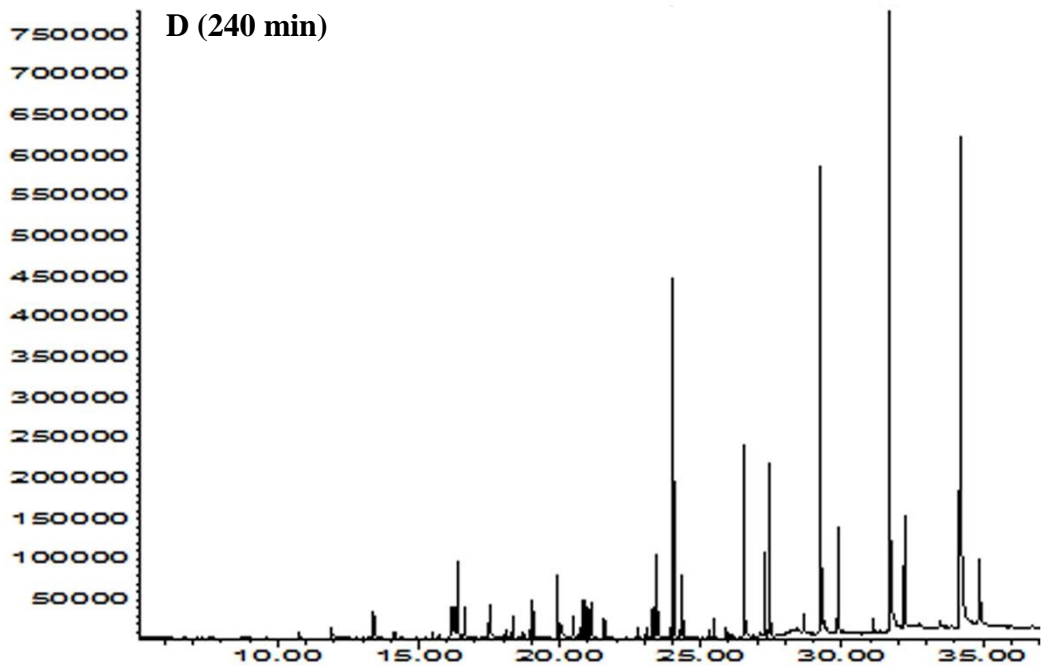
Abundance

C (90 min)



Time-->

Abundance



Abundance

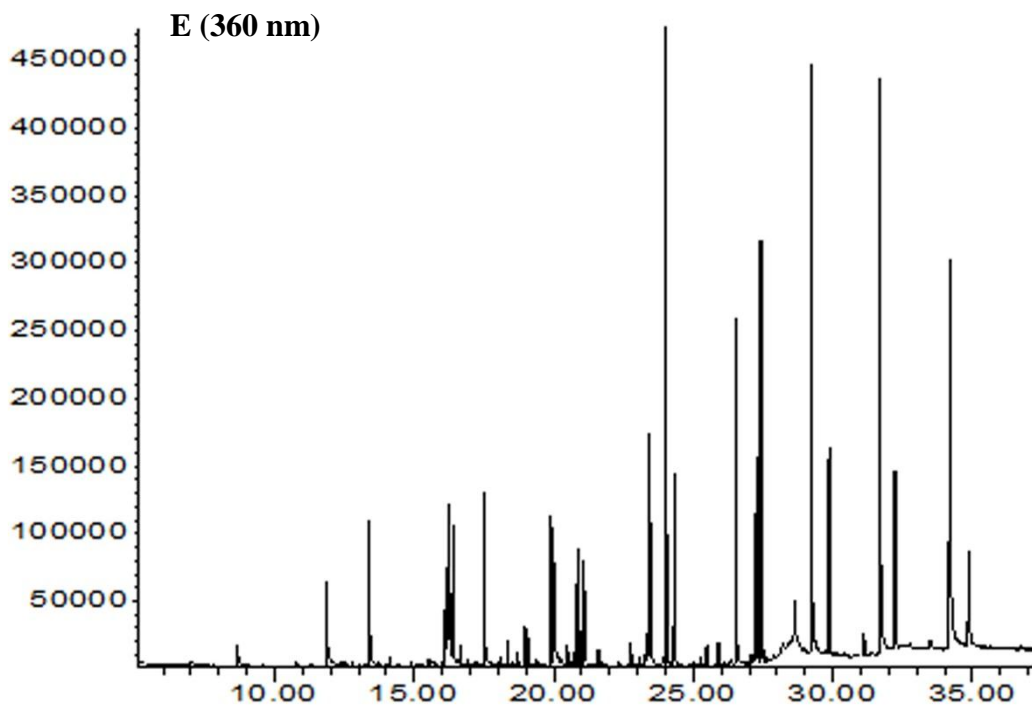
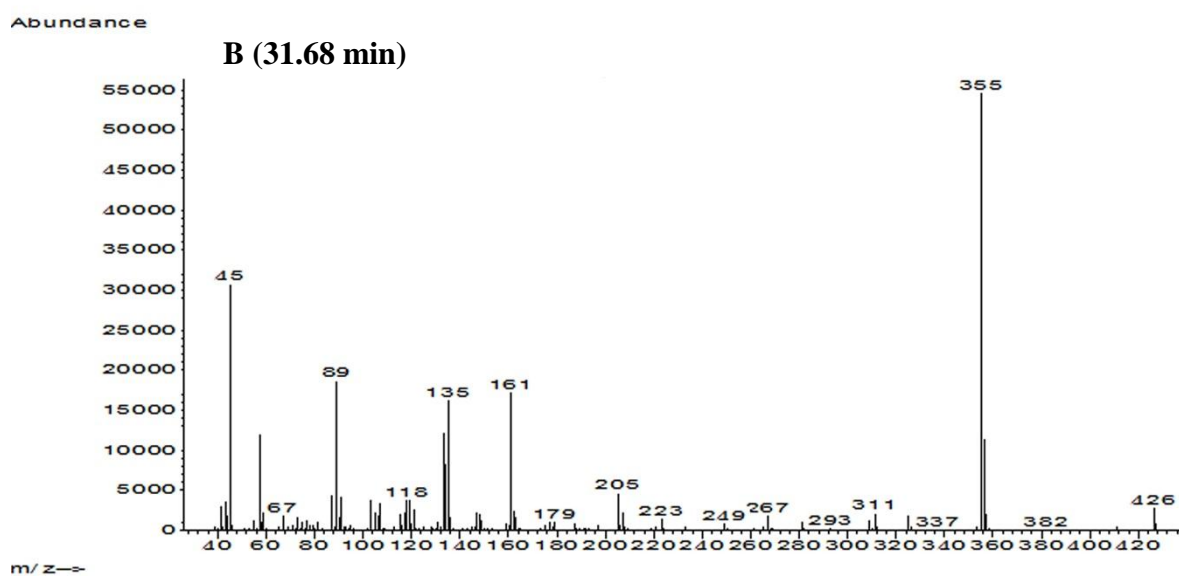
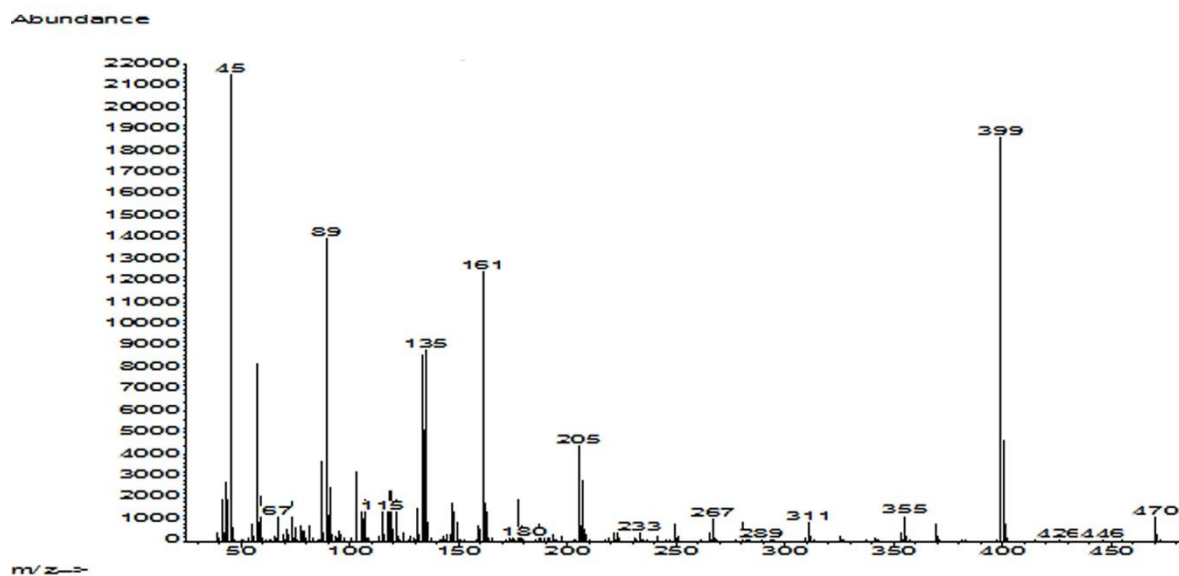
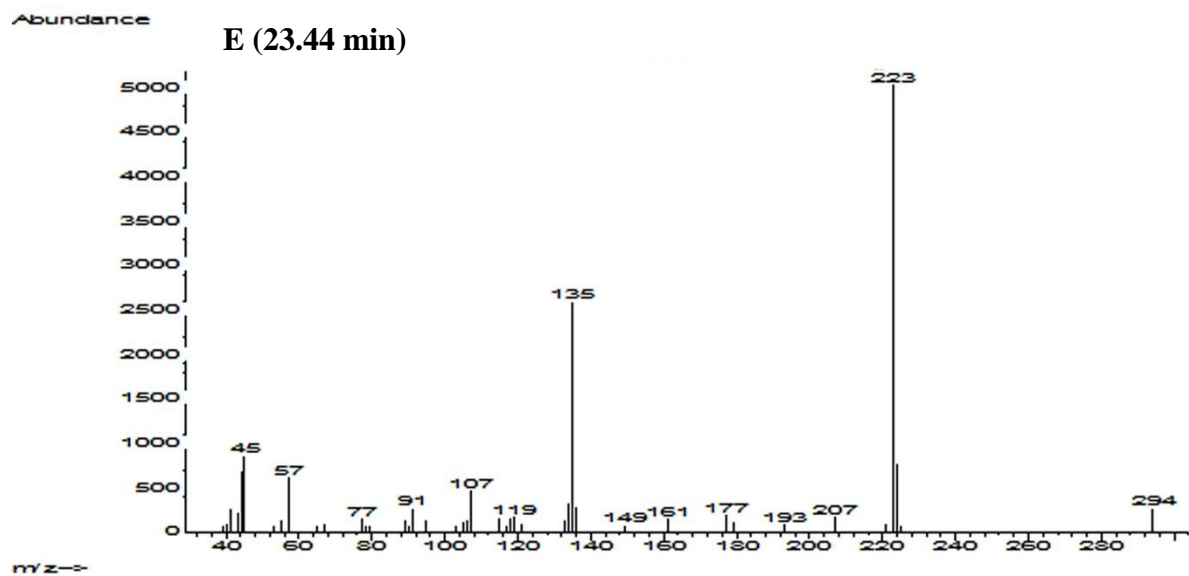
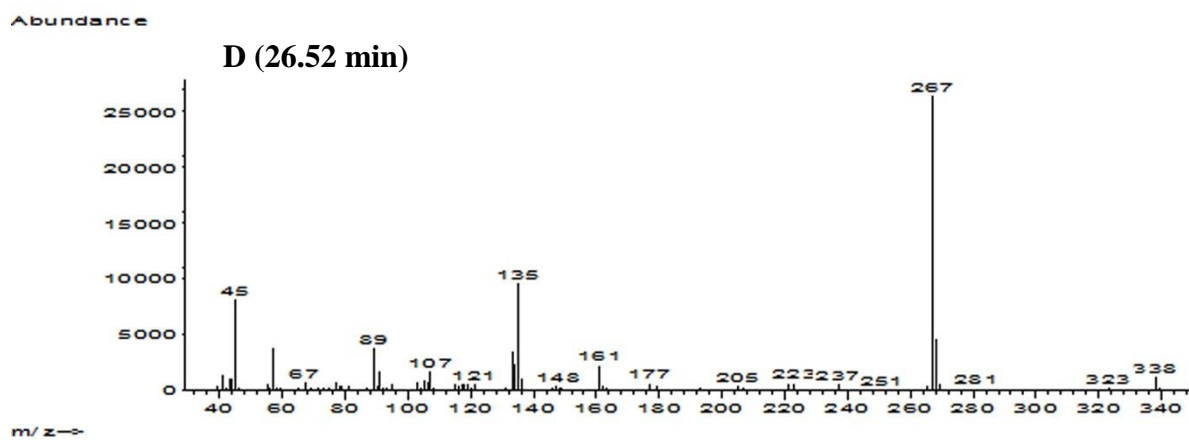
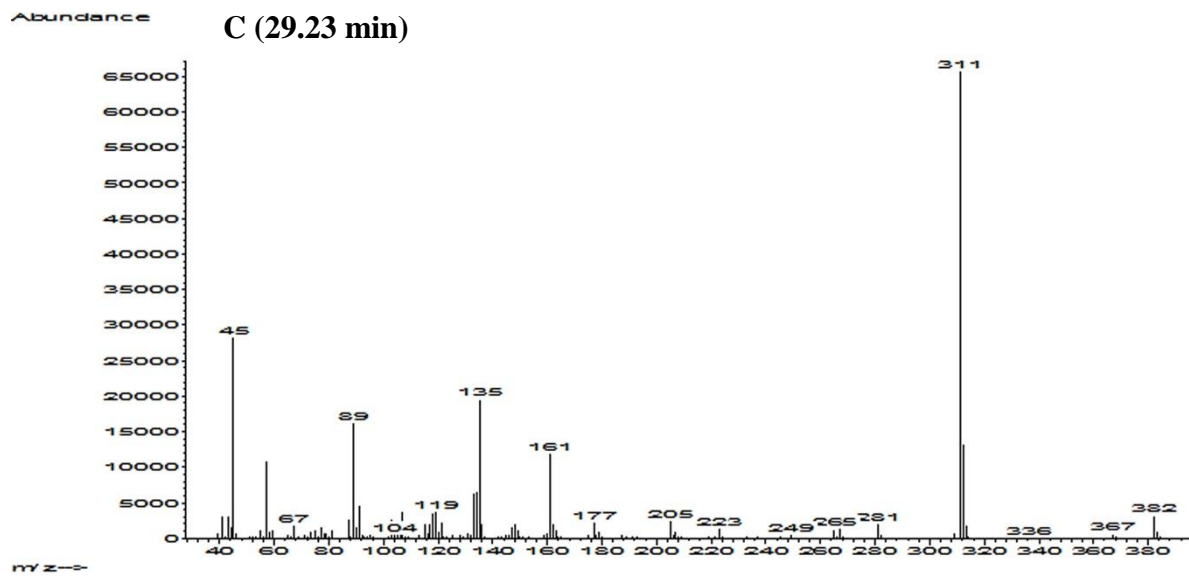
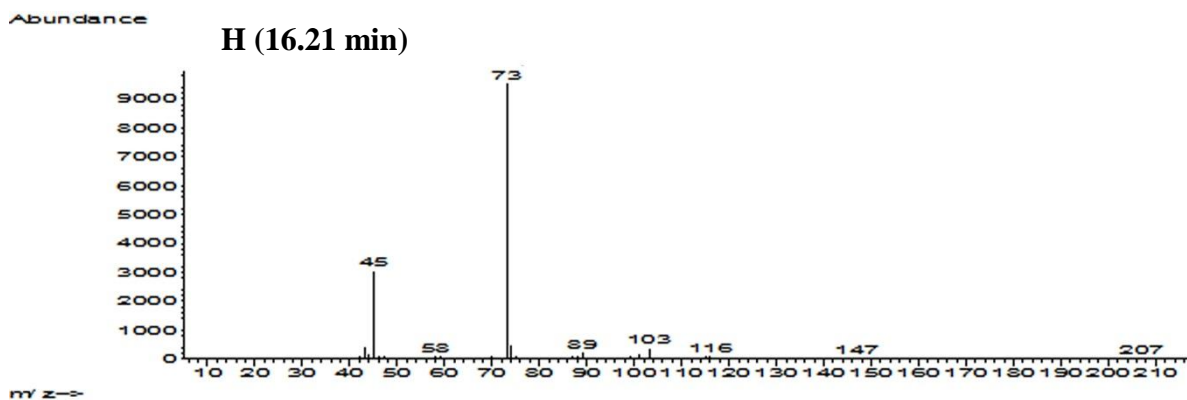
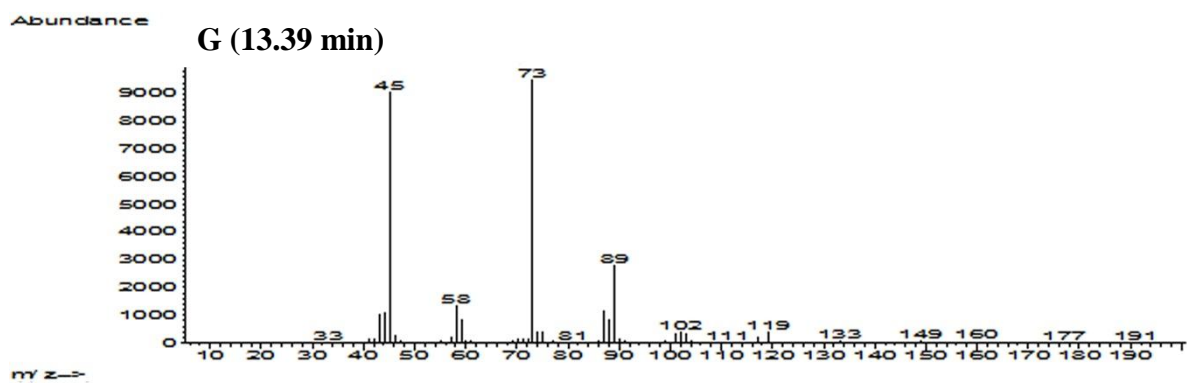
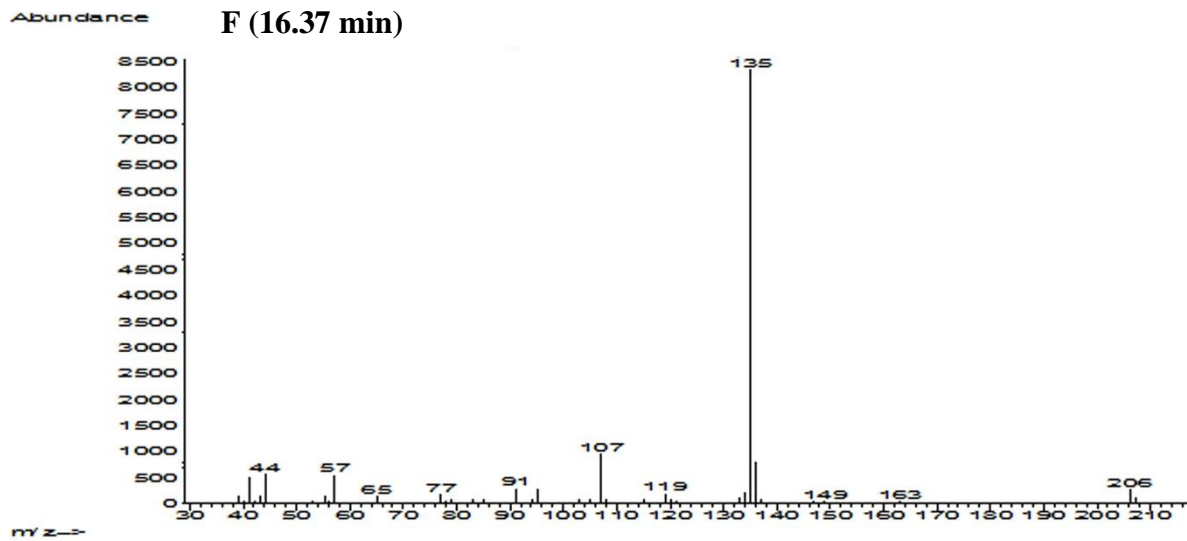


Figure S12. Mass spectra of the typical components extracted from the reaction mixture. The corresponding retention times: 34.19 min (A), 31.68 min (B), 29.23 min (C), 26.52 min (D), 23.44 min (E), 16.37 min (F), 13.39 min (G), 16.21 min (H), 24.00 min p-terphenyl (standard) (I).







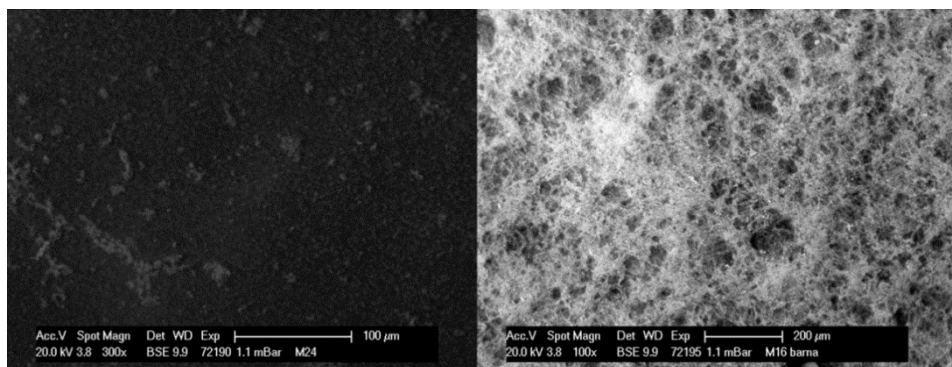
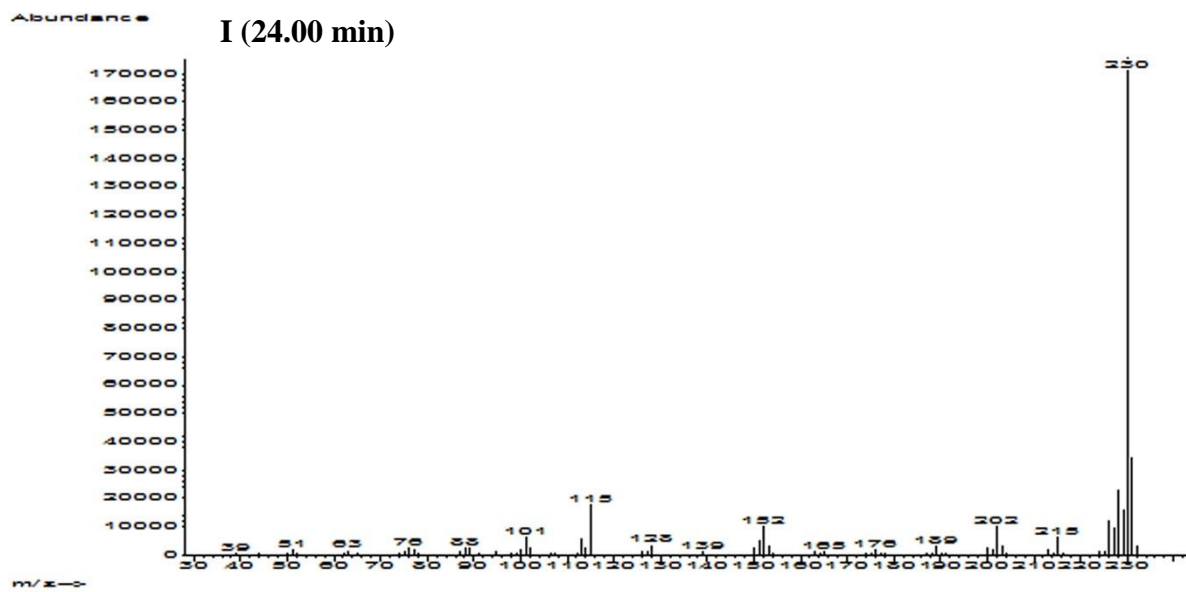


Fig. S13. SEM picture of the foil surface before and after its soaking upon irradiation.