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Removal of methyl orange using combined ZnO/Fe₂O₃/ZnO-Zn composite coated to the aluminium foil in the presence of simulated solar radiation

Nemanja Banić^{1,*}, Jugoslav Krstić², Maria Uzelac¹

¹University of Novi Sad Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg D. Obradovića 3, 21000 Novi Sad, Serbia

²University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Department of Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Serbia

*nemanja.banic@dh.uns.ac.rs

Abstract

Four immobilized ZnO/Fe₂O₃ photocatalysts with different molar ratios of Zn to Fe (0.42, 0.84, 1.68, and 3.36) were synthesized via the chemical precipitation method on optimized electrochemically synthesized ZnO-Zn coating on aluminium foil support (ZnAF). The efficiency of these catalysts for methyl orange removal in the presence of simulated solar radiation (SSR) was investigated. The optimal molar ratio of Zn towards Fe, in the presence of the SSR, was 1.68. The possibility of potential reusing the catalyst was examined six times in a row. It was determined that the application of the 1.68Zn/Fe/ZnAF/H₂O₂/SSR system after the dye removal generates hydrogen at a rate of 186.5 μmol g⁻¹ after 6 h. Using the HPLC method for 1.68Zn/Fe/ZnAF/SSR system, five primary intermediates were found to be formed.

Keywords: Photodegradation; Adsorption; Methyl orange; ZnO/Fe₂O₃; Immobilized catalyst; H₂ generation.

Introduction

In recent years, pollution by dyes has received great attention due to their increasing amount of water supplies and wastewaters from industrial effluents. There are many unwanted properties of dyes such as carcinogenicity, mutagenicity, allergenicity, resistance to natural degradation, and it is known that they can cause damage to human beings and animals [1]. The effluent streams coming from textile plants must be treated to remove the dye residues and their by-products, whereas an effective effluent decolorization is usually required by most government regulations [2,3]. Due to the higher stability of modern synthetic dyes, the conventional biological treatment methods are ineffective for the complete dye removal and degradation of these pollutants [4]. Various traditional treatment methods for removing azo dyes in wastewater, such as physical [5,6], chemical [7,8] and biological [9,10], have been investigated. However, these methods cannot destroy contaminants. Only transfer dyes from the solution to the adsorbent happen. Thus, inexpensive and environment-friendly processes for the complete conversion of pollutants must be developed [11]. Nowadays, advanced oxidation processes (AOPs) Photo-Fenton [12], H₂O₂/UV [13,14], O₃/UV, heterogeneous photocatalysis [15,16] have attracted a great deal of attention owing to their very high efficiency and without generation of secondary contamination [17]. Photocatalysis, a protuberant off-shoot of AOPs, has emerged as one of the most efficient methods for the complete mineralization of toxic organic pollutants. However, most reported photocatalysts have some disadvantages, making them unsuitable for any practical applications in wastewater due to their high cost, low photocatalytic efficiency, and difficulty to be recycled [18]. Heterogeneous photocatalysis based on nanostructured TiO₂ has been extensively studied as an essential destructive technology that leads to the total mineralization of a wide range of organic dyes, which has been an international hot topic for decades. While TiO₂ is probably the most frequently used photocatalyst, ZnO is an alternative

photocatalyst with low cost. It has a similar band gap energy compared to TiO_2 (3.2 eV) [19] and can absorb over a larger fraction of the UV spectrum [20]. Higher photocatalytic efficiency of ZnO compared to TiO_2 has been reported, especially for degradation of organics in aqueous solutions [21]. Despite the positive attributes of ZnO photocatalyst, there are some drawbacks associated with its use: (I) charge carrier recombination occurs very fast [22], and (II) the large band gap does not allow the utilization of visible light [23]. The photocatalytic activity of ZnO can be improved by combining some semiconductors with different band gaps to form heterojunctions in photocatalytic systems, because their somewhat unique properties not existed in the individual nanomaterial arising from the interfacial interaction at the nanoscale [24]. Among the combinations reported, ZnO has been successfully fabricated combined with Fe_2O_3 [25] and with MnO_2 [26], showing in both cases enhanced catalytic properties. While significant progress has been made on increasing the visible light-harvesting efficiency of various photocatalysts, their recovery and regeneration in large-scale applications remain a big challenge. It was reported that synthesized powder ZnO/ Fe_2O_3 was successfully used for photodegradation of Dicamba and 2,4-dichlorophenoxyacetic acid (2,4-D herbicides) using simulated solar radiation [27]. On the other hand, ZnO/ $\gamma\text{-Fe}_2\text{O}_3$ exhibited enhanced photoactivity compared to pure ZnO in photodegradation of 2,4-D herbicides under the influence of UV radiation [28]. However, complete mineralization of contaminants was not achieved. All above implies that immobilization of photocatalysts with appropriate adsorptive material will facilitate the easy recovery of catalysts [29,30] and enhance photodegradation *via* bringing the pollutants near the active sites of catalysts [31].

In this paper, the novelties are that optimized electrochemically synthesized ZnO-Zn coating on aluminium foil support (ZnAF) was used for the first time to synthesize four immobilized ZnO/ Fe_2O_3 /ZnAF photocatalysts via the chemical precipitation method. The efficiency of these catalysts for methyl orange removal in the presence/absence of simulated solar radiation (SSR) was investigated. Removal studies also included determining the optimal Zn/Fe molar ratio, H_2O_2 concentration, and the formation of intermediates. Also, the possibility of potential reusing ZnO/ Fe_2O_3 /ZnAF was examined. Furthermore, it has also been shown that the ZnO/ Fe_2O_3 /ZnAF materials may have a new way of practical application in the future because the synthesized catalyst can be applied in the first step for dye removal, and after that, the formed adsorbed dye/catalyst system for photocatalytic hydrogen generation, which is experimentally confirmed in this paper.

Materials and methods

Materials

Methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$, > 99.9%), and zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, > 99.5%) were manufactured by Kemika (Zagreb, Croatia); phosphoric acid (H_3PO_4 , 85%), and acetonitrile (ACN, $\text{C}_2\text{H}_3\text{N}$, > 99.9%) were obtained from Merck (Darmstadt, Germany); iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, > 99.1%) and ammonium hydroxide (NH_4OH , > 25%) were purchased from NRK Inženjering (Belgrade, Serbia); hydrogen peroxide (H_2O_2 , containing stabilizer, 30%) was obtained from Centrohem (Stara Pazova, Serbia). All solutions were prepared using ultrapure water (pH 6.56, $\kappa = 0.055 \mu\text{S cm}^{-1}$, total organic carbon TOC < LOD). The concentration of the aqueous stock solution of dye was $2.45 \cdot 10^{-2}$ mM.

Fabrication of ZnO/ Fe_2O_3 /ZnAF catalysts

As a support for the preparation of the catalysts, ZnAF was used. For the synthesis of the immobilized ZnO/ Fe_2O_3 composite [32], a suspension consisting of $\text{Zn}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ was used. The suspension was prepared by dissolving the appropriate amounts (depending on the required molar ratio of Zn to Fe) of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 300 mL of ultrapure water. Precipitation was carried out by adding ammonia to pH 7. During the synthesis, the

suspension was stirred vigorously using a magnetic stirrer. Thus, suspensions with different molar ratios of Zn and Fe were obtained (0.42, 0.84, 1.68, and 3.36). Electrochemically synthesized ZnAFs placed in Plexiglas holders were immersed in the obtained suspensions, and mixing was continued for the next 24 hours. After that, the foils with the resulting composites were removed from the holder and washed with distilled water from the excess suspension, after which they were annealed at 300 °C in an air atmosphere for 10 min.

By applying this procedure, four ZnO/Fe₂O₃ composites on ZnAF with a different molar ratio of Zn : Fe of 0.42Zn/Fe, 0.84Zn/Fe, 1.68Zn/Fe, and 3.36Zn/Fe were prepared. Hereinafter, the obtained catalysts will be denoted as 0.42Zn/Fe/ZnAF, 0.84Zn/Fe/ZnAF, 1.68Zn/Fe/ZnAF, and 3.36Zn/Fe/ZnAF.

Removal activity test

A typical experiment was carried out in a batch reactor (Fig. 1) made of Pyrex glass (total volume of ca. 170 mL, solution depth 65 mm). The efficiency of the composite was tested for the removal of 30 mL of methyl orange concentration of $2.45 \cdot 10^{-2}$ mM under the influence of SSR ($I_{UV} = 0.223 \text{ mW cm}^{-2}$; $I_{Vis} = 208.5 \text{ mW cm}^{-2}$). The halogen lamp (Philips, Netherlands; type: ESS / MR16 / Alu / 50W / GU10 / 240V / 36D / 4C15) was used as SSR source. The halogen lamp was placed under the lens. For experiments in the presence of a catalyst, a foil with a synthesized catalyst was placed between two plexiglass plates, one of which had an opening of 24 mm × 38 mm. The two plexiglass plates were fastened to each other employing plastic clamps, this securing the foil. The immobilized catalyst was facing the opening of the plexiglass plate. The plexiglass plates with the immobilized foil were immersed in the solution so that the opening of the plate was facing the radiation source. The photoreactor is then mounted on a lens, which serves to focus the radiation on the immobilized catalyst.

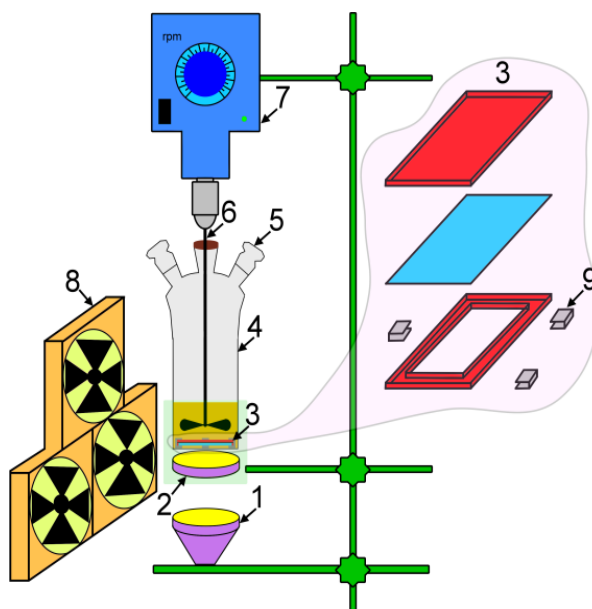


Figure 1. Schematic representation of the photocatalytic reactor: (1) halogen lamp, (2) lens, (3) plexiglass with immobilized foil (4) photochemical cell, (5) sampling port, (6) glass impeller shaft, (7) overhead stirrer, (8) ventilators, (9) plastic clamps

The stirring was carried out using an overhead stirrer with a stirring speed of 588 rpm. The propeller blades' dimensions were 10 mm × 5 mm, and the diameter of the stirrer shaft was 6 mm. The reactor content was mixed continuously in darkness for 15 min before irradiation. The mixing was also performed during irradiation, and the reactor was cooled with three fans, and the

temperature was (44 ± 1) °C. Experiments were also conducted in the dark to investigate the contribution of adsorption to the overall removal efficiency. For studying the influence of hydrogen peroxide concentration on the removal efficiency of methyl orange, different volumes of 30% H₂O₂ were added.

Photocatalytic hydrogen production from water splitting

The photocatalytic property of synthesized 1.68Zn/Fe/ZnAF catalyst was evaluated also by the H₂ evolution from aqueous methyl orange ($2.45 \cdot 10^{-2}$ mM) solution in the presence of H₂O₂ (193.0 mM) under SSR. The photocatalytic reaction was carried out in a laboratory-made batch reactor [33]. The photocatalytic reactor was made of Pyrex glass with a double wall for water cooling. An appropriate mass of scraped coating of 1.68Zn/Fe/ZnAF catalyst (21.5 mg) from a sheet of aluminium foil was suspended in a solution of methyl orange and H₂O₂ (300 mL) by a magnetic stirrer. The air remaining in the reactor was removed by purging three times with N₂ (5.0), and then the reactor was closed. The SSR source was a set of eight 50 W halogen lamps ($\lambda > 360$ nm, Philips, Netherlands, type: ESS / MR16 / Alu / 50W / GU10 / 240V / 36D / 4C15) which were placed in a symmetrical way around the reactor. UV and Vis radiation intensities for applied SSR were $2.8 \cdot 10^{-4}$ W cm⁻² and 0.21 W cm⁻², respectively; the reaction temperature was held at 40 °C. The amount of evolved H₂ was determined using a gas chromatograph (5880A, Hewlett Packard, molecular sieve 4Å packed column, TCD detector, N₂ carrier).

Analytical procedure

For the kinetic studies of dye removal, 2.0 mL aliquots of the solution were sampled at the beginning of the experiment and at various time intervals. Absorption spectra were recorded on a double-beam T80+ UV/Vis spectrometer (UK), at a fixed slit width (2 nm), using quartz cell (1 cm optical length) and computer-loaded UV Win 5 data software. Absorption was monitored at the absorption maximum of methyl orange, which was at 460 nm.

For chromatographic measurements, aliquots of 0.30 mL were taken from the reaction mixture at the beginning of the experiment and at regular time intervals. The solutions were filtered through a Millex-GP, Millipore 0.22 µm syringe filter. Afterwards, a 40 µL sample was injected and analyzed using a High Pressure Liquid Chromatography with Photodiode Array Detection (HPLC – PDA, Shimadzu), equipped with an Eclipse XDB – C18 column (150 mm × 4.6 mm i.d., particle size 5 µm, 30 °C). The UV/Vis PDA detector was set at 507 nm and 222 nm (wavelength of maximum absorption for detection of intermediates). To follow the degradation kinetics of the initial compound, it is necessary to separate peak originating from methyl orange and intermediates formed in the degradation process. Therefore, HPLC – PDA isocratic mod of analysis was used. The mobile phase (flow rate 1 mL min⁻¹) was a mixture of ACN and water (20 : 80, v/v); the water is acidified with 0.1% H₃PO₄. The reproducibility of repeated runs was 3% – 10%. The retention time for methyl orange was (11.0 ± 0.1) min.

The radiation energy fluxes were measured using a Delta Ohm HD 2102.2 (Padova, Italy) radiometer which was fitted with the LP 471 UV (spectral range 315 nm – 400 nm) and LP 471 RAD (spectral range 400 nm – 1050 nm) sensors.

Results and discussion

Study of methyl orange removal efficiency using Zn/Fe/ZnAF photocatalysts

First, the adsorption efficiency for each Zn/Fe/ZnAF was examined in the dark to determine the possibility of removing methyl orange by adsorption on Zn/Fe/ZnAF (Fig. 2a). The degree of adsorption was high, and after 300 min, it was in the range from 88.4% to 91.9% on Zn/Fe/ZnAF composites. The adsorption efficiency increased with the increasing molar ratio of Zn/Fe, while at

1.68Zn/Fe/ZnAF, adsorption was the highest (91.9%) and for the further increased Zn/Fe, adsorption efficiency was the same (91.9% for 3.36Zn/Fe/ZnAF). Also, the influence of temperature on the adsorption efficiency was examined since the temperature of the solution during irradiation was 44 °C, the experiments of adsorption were conducted at 44 °C. Based on the obtained results, it can be concluded that an increase in the temperature of the solution leads to a decrease in the adsorption efficiency of the studied catalysts. For 0.42Zn/Fe/ZnAF this decrease was 11.5%, while for 1.68Zn/Fe/ZnAF the decrease in adsorption efficiency was 1.7%.

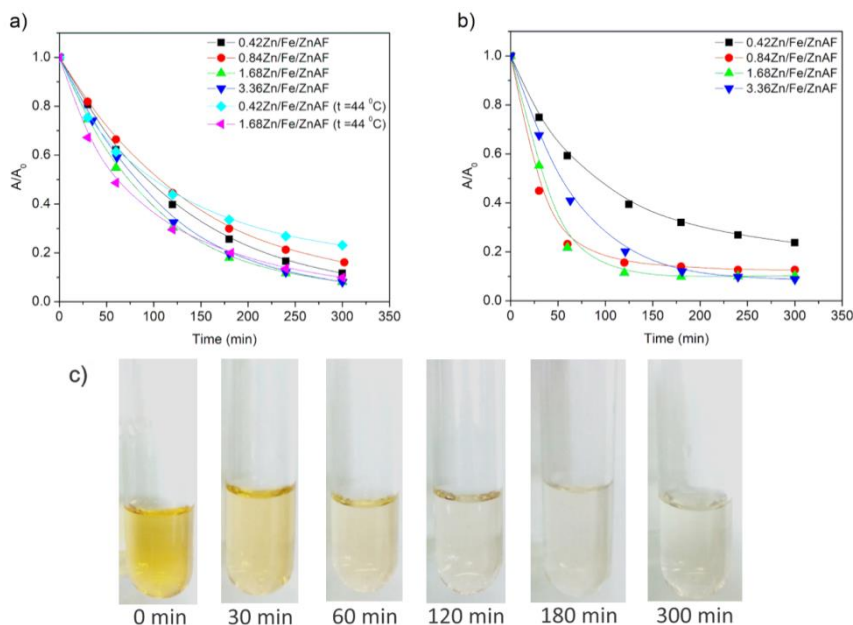


Figure 2. Kinetic curves for methyl orange ($c_0 = 2.45 \cdot 10^{-2}$ mM) removal efficiency in the presence of different Zn/Fe/ZnAF photocatalysts at a stirring rate of 588 rpm: (a) darkness, (b) in the presence of SSR, (c) photos of methyl orange solution during removal process using a 1.68Zn/Fe/ZnAF under SSR

In addition to adsorption, the presence of SSR was also examined on the removal efficiency of methyl orange in the presence of Zn/Fe/ZnAF. Comparing Figs. 2a and b, it can be seen that radiation contributes to the overall removal efficiency. After 120 min of irradiation, the contributions to the overall methyl orange removal efficiency were 28.8% for 0.84Zn/Fe/ZnAF, 17.6% for 1.68Zn/Fe/ZnAF, and 9.9% for 3.36Zn/Fe/ZnAF. In contrast, it was found that radiation did not affect the methyl orange removal efficiency by 0.42Zn/Fe/ZnAF. It was reported that radiation did not contribute to the removal of methyl orange by synthesized 0.13TiO₂-Chitosan nanocomposite (with 0.13 M titanium(IV) isopropoxide), which had the smaller concentration content of titanium(IV) isopropoxide. Other synthesized materials with higher concentrations of titanium(IV) isopropoxide (0.33, 0.65, and 1.3TiO₂-Chitosan nanocomposite) exhibited contribution to overall methyl orange removal together with adsorption [34]. When compared photocatalysis and adsorption in the initial period of reaction, adsorption contributes to the overall efficiency. Removal rate constant of methyl orange, calculated after 60 min, indicated that higher rate constant were observed in the case of 0.84Zn/Fe/ZnAF (0.0244 min^{-1} , $R^2 = 0.996$) and 1.68Zn/Fe/ZnAF (0.0255 min^{-1} , $R^2 = 0.988$). With further increase of Zn molar ratio to the 3.36 removal rate constant decreases (0.0141 min^{-1} , $R^2 = 0.998$). Since 1.68Zn/Fe/ZnAF was found to be the most efficient in removing methyl orange, this composite was used in further examinations. The disappearance of the methyl orange solution during removal under the influence of SSR and in the presence of 1.68Zn/Fe/ZnAF is given in Fig. 2c. Increasing removal efficiency of methyl orange with increasing dopant ion to a certain content was reported in the literature, and our research is in line with

experiments by using different nanopowders [35,36]. Still, so far there are no available literature data about using Zn/Fe on ZnAF support to remove contaminants.

Methyl orange removal with the reused 1.68Zn/Fe/ZnAF photocatalyst

From the economic point of view and for practical applications, deactivation of photocatalyst is an underlying aspect to consider for the designing of photocatalysts [37]. There are different methods in the literature used for catalyst regeneration, including the use of agents such as NH_4OH or NaOH , thermal processes [12,38], $\text{H}_2\text{O}_2/\text{UV}$ oxidation, and the use of UV radiation [39].

To examine the photostability and reusability of 1.68Zn/Fe/ZnAF, the foil after the process of methyl orange removal was collected, thoroughly washed twice with ultrapure water, and annealed for 10 min at 300 °C. For this type of Zn/Fe preparation on ZnAF support, no one has applied regeneration by this procedure so far. Six successive photodegradation experiments were conducted while other experimental conditions were kept unchanged. Regeneration of photocatalyst was done after each photodegradation experiment. Fig. 3 shows that in the case of five consecutive experiments (performed in a time interval of 24 h), there was a decrease in photocatalytic efficiency by: 22.0% (second time), 48.9% (third time), 62.5% (fourth time), and 76.8% (fifth time) compared to the first use of 1.68Zn/Fe/ZnAF foil.

Since the melting point of methyl orange is above 300 °C, after five applications, the foil was regenerated by increasing the annealing temperature to 400 °C. The 1.68Zn/Fe/ZnAF foil prepared in this way was again used as a photocatalyst (sixth time), and there were no changes in the removal efficiency compared to the fifth time. It is reported that using combustion synthesized TiO_2 Degussa P25 after only three successive runs, the degradation efficiency of dyes decreased by 80% [40].

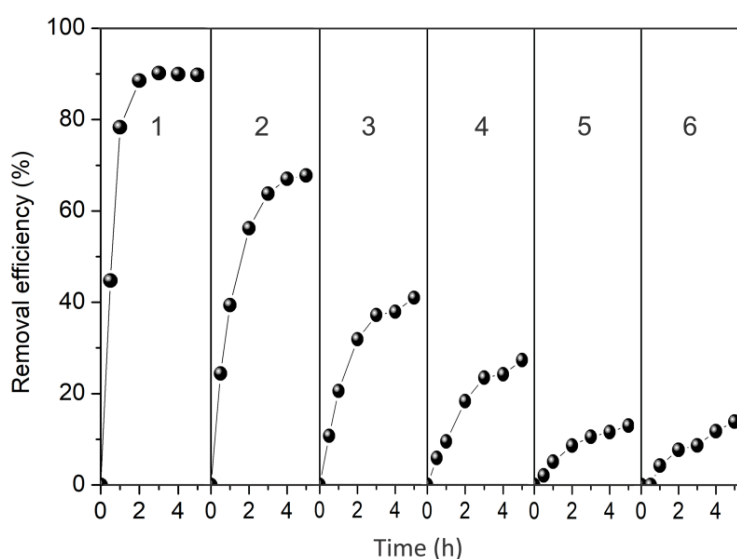


Figure 3. Methyl orange ($c_0 = 2.45 \cdot 10^{-2}$ mM) removal efficiency in the presence of reused 1.68Zn/Fe/ZnAF photocatalyst in six runs at a stirring rate of 588 rpm in presence SSR. Each run lasted 5 h

This points out that dyes are very persistent contaminants, and there are not so many practical applications for their removal from the environment. 1.68Zn/Fe/ZnAF is promising material due to its physical characteristics for easy removal of the foil from the dye solution, and it can be used at least twice for efficient removal of methyl orange.

Influence of H_2O_2 on the methyl orange removal efficiency and H_2 production

Since H_2O_2 could be formed in reduction and oxidation processes in the photocatalytic reaction, dimerization of $\cdot\text{OH}$, reduction and disproportionation of O_2 , it is essential to take the concentration of

H_2O_2 into account to understand details of photocatalytic reactions. It has been reported that H_2O_2 could be photocatalytically reduced by O_2 or photoinduced e^- to produce $\cdot\text{OH}$. However, H_2O_2 could also be oxidized by $\cdot\text{OH}$ or photoinduced h^+ to give O_2 , inhibiting photocatalysis efficiency [41]. Consequently, it is imperative to observe and investigate the effect and behavior of H_2O_2 in the photocatalytic reaction.

The initial concentration of H_2O_2 in the range of 6.4 mM – 193.0 mM and 1.68Zn/Fe/ZnAF for removal of methyl orange under SSR was investigated (Fig. 4). It is noted that the addition of H_2O_2 does not increase the removal of methyl orange, which means that H_2O_2 was oxidized by $\cdot\text{OH}$ or photoinduced h^+ , and therefore the production of additional $\cdot\text{OH}$ radicals was inhibited, while production of $\cdot\text{OH}$ was reduced. Namely, with the addition of 6.4 mM of H_2O_2 , methyl orange removal efficiency decreased by 1.9%, compared to 1.68Zn/Fe/ZnAF alone. With a higher concentration of H_2O_2 of 45.0 mM and 193.0 mM, removal efficiency decreased by 10.9% and 6.1%, respectively. During direct photolysis, methyl orange remains unchanged after 300 min of irradiation. However, in indirect photolysis (193.0 mM H_2O_2) after 300 min, the degradation of methyl orange was 17.2%. This indicates that although H_2O_2 showed some efficiency in degradation by indirect photolysis, in the process with a photocatalyst it leads to the inhibition of the process due to the above mentioned side effects that interfere with the removal process.

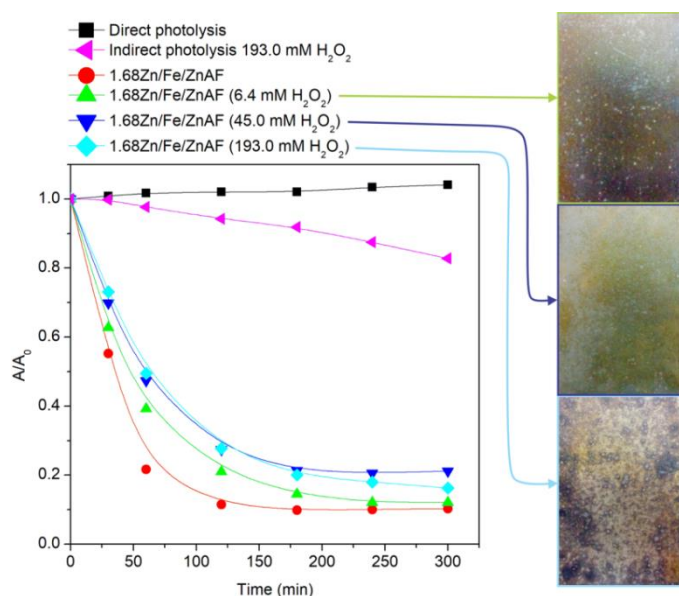


Figure 4. Influence of H_2O_2 concentration on methyl orange ($c_0 = 2.45 \cdot 10^{-2}$ mM) removal efficiency using 1.68Zn/Fe/ZnAF at a stirring rate of 588 rpm and in presence SSR (left). The appearance of foil surface after 300 min of methyl orange removal in the presence of different H_2O_2 concentrations (right)

This foil behavior in the presence of H_2O_2 indicates the possibility of a competitive process happening, such as photocatalytic hydrogen production [42], which reduces methyl orange removal efficiency. The appearance of the coated foil after removal of methyl orange in the presence of different concentrations of H_2O_2 is shown in Fig. 4. It can be seen that when comparing the surface look of coated foil 1.68Zn/Fe/ZnAF treated with 6.4 mM and 45.0 mM H_2O_2 , a smaller area of the foil was covered with dye in the case of higher H_2O_2 concentration. With a further increase of H_2O_2 concentration, it can be seen that corrosion occurred on the surface of plate. This change in appearance indicates the possibility of hydrogen separation at higher H_2O_2 concentrations from the coated foil surface and corrosion due to its separation.

To determine the nature of the competitive process on the 1.68Zn/Fe/ZnAF foil, experiments in which the coated foil potential was measured in relation to the saturated calomel electrode (SCE)

potential in the presence of 193.0 mM H₂O₂ were performed. From Fig. 5, it can be seen that a light-assisted reduction process is taking place on the coated foil surface. Furthermore, with SSR in the time interval between 150 min and 180 min, the potential difference decreased by -0.192 V, which indicated the formation of hydrogen. Additional confirmation for hydrogen production was obtained by hydrogen generation measurement. The same figure shows that after 180 min, there was no significant increase in hydrogen generation efficiency (12.8 μmol g⁻¹). On the other hand, the highest hydrogen generation efficiency of 186.5 μmol g⁻¹ was achieved after 360 min of irradiation. A possible explanation for the sharp increase in hydrogen generation efficiency can be found by comparing Figs. 2a and 5. The significant hydrogen generation begins after approximately all of the methyl orange has been adsorbed (80% in the case of the immobilized catalyst (Fig. 2a)) on the catalyst surface. The percentage of adsorption was undoubtedly higher since, for hydrogen generation experiments, the catalyst was scraped from the foil and suspended (21.5 mg). Also, the presence of H₂O₂ contributed to faster photodegradation of methyl orange in the solution, and the solution was more transparent for SSR. Therefore, the radiation utilization for the adsorbed dye/catalyst system was significantly higher. This is in agreement with previous studies, in which it was found that dye can absorb visible light, and the electrons can be transferred from the HOMO to the LUMO state, generating excited electrons and cationic radicals, which are followed by electron-injection from dyes to the host photocatalyst [43]. However, the dye needs to be adsorbed on the photocatalyst surface to continue the above process. On the other hand, dye will absorb light, leading to light energy loss, decreasing the hydrogen generation rate [44,45].

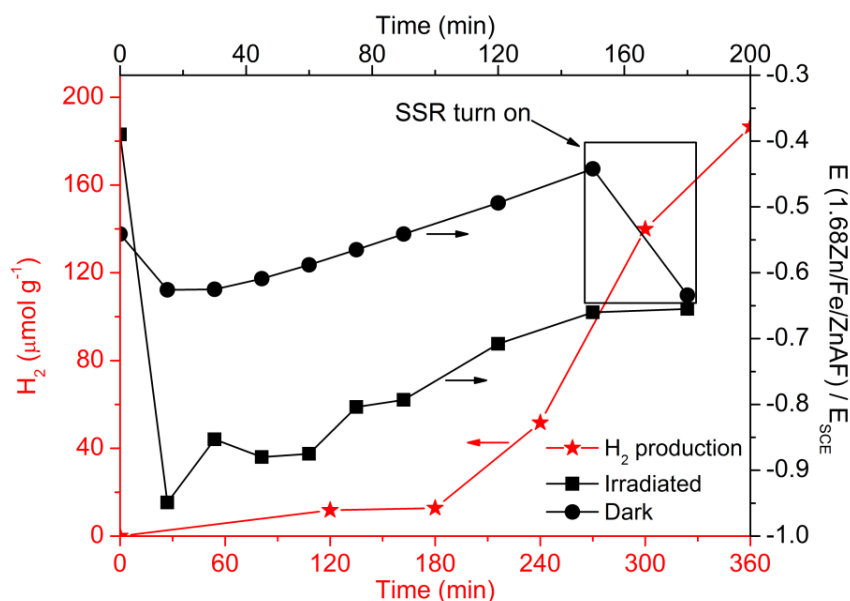


Figure 5. H₂ production amount for suspended 1.68Zn/Fe/ZnAF (71.7 mg L⁻¹) under the influence of SSR (red curve), and change in potential difference immobilized 1.68Zn/Fe/ZnAF related to SCE (black curves), in a solution of methyl orange ($c_0 = 2.45 \cdot 10^{-2}$ mM) and hydrogen peroxide (193.0 mM) at a stirring rate of 588 rpm

This behavior could have practical applications in the future because the synthesized catalyst can be applied for dye removal and then the formed adsorbed dye/catalyst system for photocatalytic hydrogen generation.

HPLC analysis of methyl orange degradation

HPLC analysis was performed to identify the number of intermediates formed during the removal of methyl orange by 1.68Zn/Fe/ZnAF under SSR. As expected, the peak of methyl orange was detected at 508 nm (Fig. 6a). On this wavelength, intermediate P1 was detected with an absorption

maximum at 496 nm (Fig. 6a). Peak P1 is formed during the first 125 min and then decreasing during the next 180 min of irradiation. Also, the kinetic curve obtained for methyl orange removal by 1.68Zn/Fe/ZnAF under SSR by chromatographic analysis (Fig. 6b) is in good correlation with spectrophotometric measurement (Fig. 2b). Besides this intermediate that absorbs in the visible range, some other intermediates that absorb in the UV region were also detected (Fig. 7). In the UV range, at 222 nm, the peak of methyl orange was barely noticeable. On the other hand, formed intermediates P2, P3, P4, and P5 absorb in the UV region, P2 < 200 nm, P3 \approx 234 nm, P4 \approx 218 nm, and P5 \approx 226 nm. Peaks P2 and P5 were formed during the first 125 min, and then are disappearing while peaks P3 and P4 were formed during all 305 min of irradiation. Future research with the use of MS detectors will try to provide insight into the composition of degradation products.

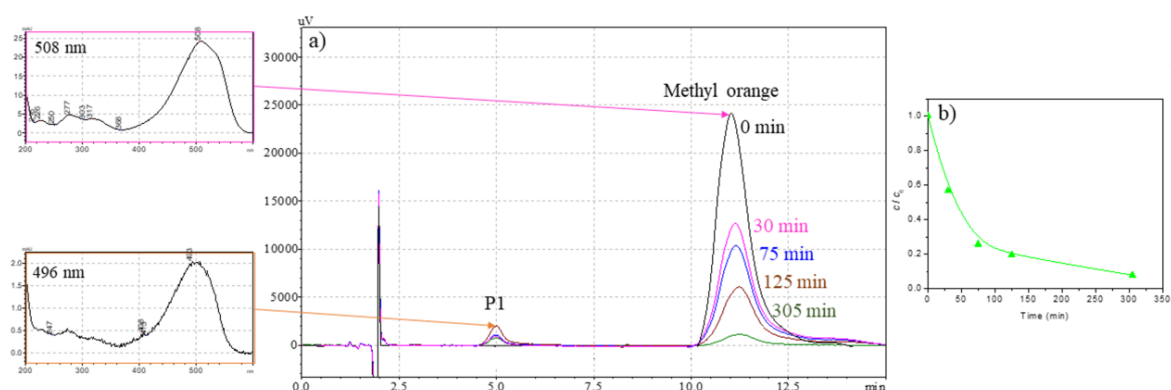


Figure 6. Formed intermediates (a) and efficiency of methyl orange ($c_0 = 2.45 \times 10^{-2}$ mM) removal (b) using 1.68Zn/Fe/ZnAF at a stirring rate 588 rpm and under SSR. Retention time: $t_R = (5.0 \pm 0.1)$ min (P1), and $t_R = (11.0 \pm 0.1)$ min (methyl orange), $\lambda_{det} = 508$ nm

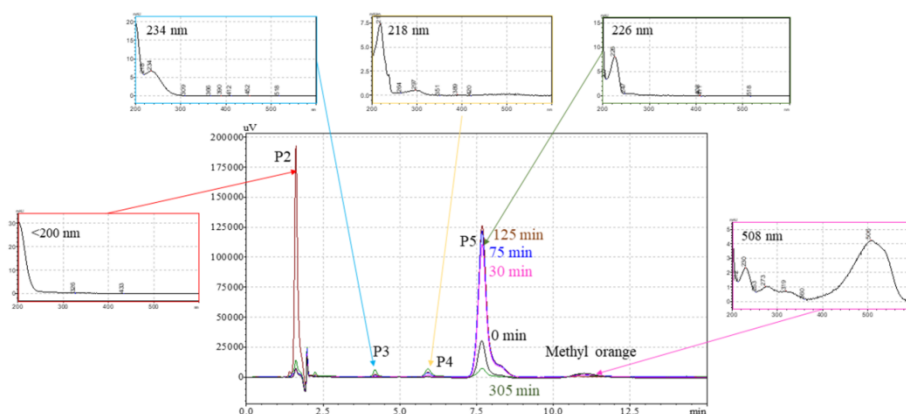


Figure 7. Formed intermediates during methyl orange ($c_0 = 2.45 \cdot 10^{-2}$ mM) removal using 1.68Zn/Fe/ZnAF at a stirring rate 588 rpm and under SSR. Retention time: $t_R = (1.6 \pm 0.1)$ min (P2), $t_R = (4.2 \pm 0.1)$ min (P3), $t_R = (5.9 \pm 0.1)$ min (P4), $t_R = (7.7 \pm 0.1)$ min (P4), and $t_R = (11.0 \pm 0.1)$ min (methyl orange), $\lambda_{det} = 222$ nm

Conclusions

In this paper, research was focused on synthesizing four immobilized ZnO/Fe₂O₃ photocatalysts with a different molar ratio of Zn to Fe (0.42, 0.84, 1.68, and 3.36) via the chemical precipitation method on optimized electrochemically synthesized ZnAF support. For all Zn/Fe/ZnAF materials, the degree of methyl orange adsorption was high, and after 300 min was in the range from 88.4 to 91.9%. In the presence of the SSR removal rate constant indicated that the highest rate constant was observed in the case of 1.68Zn/Fe/ZnAF (0.0255 min^{-1} , $R^2 = 0.988$). 1.68Zn/Fe/ZnAF is promising

material due to its physical characteristics for easy removal of the foil from the dye solution, and it can be used at least twice for efficient removal of methyl orange. In the presence of higher H₂O₂ concentrations of 45.0 mM and 193.0 mM, removal efficiency decreased by 10.9 and 6.1%, respectively. Hydrogen generation was confirmed for the 1.68Zn/Fe/ZnAF/H₂O₂/SSR system, with the maximum hydrogen generation efficiency of 186.5 μmol g⁻¹, achieved after 360 min.

Hydrogen generation occurred after the dye was completely adsorbed on catalyst surface. This behavior could have practical application in the future because the synthesized catalyst can be applied for dye removal and then the formed adsorbed dye/catalyst system for photocatalytic hydrogen generation. HPLC measurements for 1.68Zn/Fe/ZnAF/SSR system showed that five primary intermediates were found to be formed. Materials obtained showed great potential for dye removal, which makes them good candidates for broader use.

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