Photocatalytic Removal of Polyester Polyurethane, and Polyethylene Microplastics via ZnO-Fe-Mg-C Nanocomposite to H₂

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Abstract: - In this work H₂ generation was studied via polyester, polyurethane, and polyethylene microplastics using a novel nanocomposite namely zinc oxide-iron-magnesium-carbon (ZnO/Fe/Mg/C). The probability of H₂ production from plastic wastes was researched. The characterization of this nanocomposite were performed by XRD, FTIR, Raman, SEM, EDS and TEM analysis. XRD analysis showed that lattice planes of ZnO/Fe/Mg/C nanocomposite were distributed as (100), (002), (101), (102), (110), (103), (200), (112) and (004) according to FTIR analysis, it was found that the ligth abundances at 610, 682 and 779 cm⁻¹ were associated with the Zn and O moeities, while the maximum peak at 399 cm⁻¹ can be defined with Zn, Fe and Mg oxides and they connected to Zn and OH radicals. Raman spectra exhibited the G-band at 1499 cm⁻¹ as special properties of sp² carbonated moeities. SEM results showed that a brittle and porous structure containing spherical nanosized particles was detected in the ZnO/Fe/Mg/C nanocomposite, where various voids were formed, while the zinc particle size containing carbon-Mg-Fe was increased by excess carbon and ZnO/Fe/Mg/C nanocomposite. Furthermore the effects of some operational conditions (time, nanocomposite concentration, temperature) on the yields of H₂ productions from both micropollutants were examined. The maximum H₂ production was detected at 250 mg/l polyethylene microplastic as 9800 ml/h with ZnO/Fe/Mg/C nanocomposite a, containing 2% Fe while the H₂ production was detected as 7800 ml/h from polyester polyurethane with the same nanocomposite. Optimum operating conditions; maximum H₂ production efficiencies of 99% polyethylene and 88% polyester polyurethane were achieved at 3 mg/l ZnO/Fe/Mg/C nanocomposite a, concentration, at 3 minutes and at 5 minutes experimental times and at 125°C temperature, respectively.

Key-Words: - Hydrogen (H₂) production; H₂ fuels; Microplastics; Polyester Polyethylene; Polyurethane; Photocatalytic removal; ZnO/Fe/Mg/C nanocomposite.

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1 Introduction

In recent years microplastic wastes affect negatively the ecosystem. Microplastics are plastic wastes with a diameter < 5 mm. they cannot be treated from the ecosystems with some conventional processes since they have very small bodies, [1], [2]. Nanoplastics have a dimension of 0.1 μm. The remediation of microplastics is very important phenomenon since they have extensively used, [3], [4]. The novel progress is the recovery of microplastics to the economical valor having organics as ultimate end products. The polymers containing no olefins exhibited completely different structures from the plastics containing olefin. These products were: polyethylene (PE), polypropylene (PP), and polystyrene (PS), [5], [6], [7], [8], [9]. The physicochemical properties of microplastics based on fabrication procedure is effective in microplastic transformation. From remediation processes the polymers can be emitted to the ecosystems, [10]. Polystyrene, polyurethane and polyethylene was detected in municipal sludge and in environments containing garbage.

Polyethylene contained low weight carbon benzene and can be generated from the degradation of ethylene, [11], [12], [13], [14], [15], [16], [17], [18]. Polyethylene is a resin from polyolefin group. It is extensively utilized microplastic and can be generated from the food wrap and some plastic bottles and fuel boxes. It can degraded to fibers or and emitted from the rubbers. Types of polyethylene were summarized as follows, [19], [20], [21], [22], [23], [24]:

1. Low-Density Polyethylene (LDPE): LDPE is used extensively since it was not expensive. It can be suitable for plastic film applications like
grocery bags and food packaging. Despite its lower tensile strength and temperature resistance, LDPE’s flexibility and toughness make it a popular choice in the market.

2. High-Density Polyethylene (HDPE): HDPE is praised for its high strength and stiffness. These attributes, combined with its resistance to many solvents, make it appropriate for extensive utilizations, from milk bottles to fuel tanks and piping systems.

3. Linear Low-Density Polyethylene (LLDPE): Bridging the gap between LDPE and HDPE, LLDPE offers superior tensile strength, large-scale deformability, and excellent resistance to environmental stress cracking. It is used in applications like stretch wrap, toys, and flexible tubing.

Nano sized ZnO, was extensively utilized in drinking and polluted water remediations, since has elevated redox potential, elevated electron activity and good photocatalytic activity, [12], [14]. ZnO nanocomposite exhibited elevated surface and high durability compared to other metal oxides. This, cause to an excellent photodegradation activity, [15]. In order to extend the photocatalytic yields of ZnO, nonmetals, and carbonated chemicals can be doped on ZnO surface to improve the activity of electrons in holes, [20]. By combining of a metal, the photodegradation yields can be elevated since redox reactions improve the light activity. These improves the surface resonance of the photocatalyst. Electromagnetic band gap energies of the metal nanocomposites resulting in transformation of electrons from valence band (VB) to conduction band (CB) ending with photocatalysis, [14], [19], [20], [21], [22], [23]. The presence of Ni$^{2+}$ and Fe$^{3+}$ in the nanocomposites cause to super magnetic structure of Ni ferrites, [11], [12], [14], [19], [20], [21], [22], [23]. Combining of ZnO with some metals like Fe, and Ni was performed to improve its ferro magnetic properties, [15], [24], [25]. The recent studies showed that photodegradation properties were performed by ZnO connected with certain ratios of NiFe$_2$O$_4$, [26], [27]. The Photoactivity of nano composites are influenced by the generation rules, nanocomposite diameter, and certain ratios of dopant molecules. Fe-Ni nanocomposites were utilized are used to photodegrade the microplastic residues with excessive H$_2$ productions.

The doping of Fe to Ni improved the nanocomposite activity, [28], [29], [30], [31], [32]. Physicochemical analysis results indicated that doping of Ni increase the metal nanocomposite diameter and oxygen releasing. Fe-Ni nanocomposite show high catalytic performance resulting in 98% hydrogen production from microplastic residues. Ni having nanocomposites exhibited excellent performance due to C and H bond degradation ending with excellent photocatalytic performances, [20], [22]. Nano metal oxides having Zn, Mg and Ca exhibits excellent microbial inhibitions, [33], [34], [35], [36], [37], [38]. In recent works, it was found that, ZnO nanocomposites exhibited inhibitions versus microorganisms, [39], [40], [41], [42], [43], [44], [45], [46], [47]. The recent literature showed that antimicrobial effects of ZnO NPs. In some studies, emissions of Zn$^{2+}$ from nanocomposites cause to death of microorganisms, [48], [49], [50]. It is important to note that the solubility of ZnO is very low.

Carbon nanotubes (CNT) were used for remediate the pollutants. CNT structure and its electro equations can be changed quickly by doping of some metals to its surface, [21]. CNT was effectively used since is elastic and has some mechanical, and electrical structures ending with hydrogen production, drug transportation and treatment of polluted ecosystems. CNT can be utilized to energy storage with high electrolyte properties, and equilibrium. CNT exhibits excessive surface, fast reaction kinetic and degradation of pollutants like Pb$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and, dyes, [19], [23]. CNT have also been utilized for treatment of pollutants with perfect structure, conductive, and chemical structures, [11], [16], [24]. CNTs have a mesoporous structure and provides effective adsorption, [9], [15], [25].

In this study, the photodegradation of ZnO was improved by connecting Fe, Mg and C nanoparticles on the its structure, and the photodegradation capacity of ZnO/Fe/Mg/C nanocomposite was examined to produce H$_2$ from polyester polyurethane and polyethylene microplastics. The effect of time, temperature and nanocomposite concentrations on H$_2$ yields were studied for polyester polyurethane, and polyethylene microplastics.

2 Materials and Methods

2.1 Production of ZnO/Fe/Mg/C Nanocomposite

ZnO particles were produced from Zn(NO$_3$)$_2$.6H$_2$O and NaOH was added to adjust the pH. 5.990 g of Zn(NO$_3$)$_2$.6H$_2$O was mixed with 100 ml distilled water. The temperature was elevated and at a temperature of 70°C, 1 ml of 4 M NaOH was added up to the mixture pH was become 10.0. After 2 h mixing a precipitate was found. This section was separated by a centrifuge. The filtered precipitate was dried at 90°C for 10 h. The temperature was adjusted...
to 500°C for 2 h in an incubator. Then 10 g ZnO(NO₃)₂·4H₂O was mixed in 200 ml of water. 1 ml of 6 M NaOH (6 M) was added to reach a pH of 9.0. To produce the ZnO/FeO₂⁺ (30%) nanocomposite, 0.600 g ZnO was added. 0.420 g Fe(NO₃)₃·9H₂O was dissolved mixed in 20 ml water. The produced mixture was added to an autoclave at 190°C for 28 h. The settled mass was dried.

MgO was produced by addition of Mg(NO₃)₂·6H₂O as Mg²⁺ addition, and settled by using NaOH, [29]. For MgO production, 0.32 M Mg(NO₃)₂ was added to 150 ml of distilled. Afterwards, 1 ml 2M NaOH solution was added to Mg(NO₃)₂ to reach a pH of 9.0. The settling of Mg(OH)₂ was performed. The produced precipitate was centrifuged and dried in an incubator at 140°C for 6 h. Then, the powder was calcined at 700°C for 7 h in an oven. The produced nanocomposite was ZnO/Fe/Mg/C nanocomposite.

2.2 Detection of Polyethylene and Polyester Polyurethane in GC-MS

600 mg of liquids were autoclaved at 141°C for 30 min. The samples were centrifuged at 8000 rpm for 10 min at 4°C. Then the liquids were maintained at 25°C while the suspension was withdrawn. The pH was adjusted to 2.0 after 2 h. Then extracted with the passage of N₂ gas to a volume of 70 µl. The liquids were extracted with N₂O-bis(trimethylsilyl)trifluoroacetamide before measurements in an Agilent 6890 model gas chromatography (GC) coupled with an Agilent model 5973 mass spectrometer (MS), in an GC-MS. The samples were separated on HP-5ms capillary column (40 m x 0.30 mm diameter x 0.35 µm film). The temperature was adjusted as follows: the initial temperature of 90°C for 5 min and then at a temperature of 10°C up to 230°C.

2.3 Measurement of the Photodegradation Yield of the ZnO/Fe/Mg/C Nanocomposite

Photocatalytic degradation of catalysts was performed in 250 mg/l liquids. About 5 mg of ZnO/Fe/Mg/C nanocomposite was dissolved in 70 ml of deionized water. The microplastic photodegradations were performed in an GC-MS as aforementioned.

3 Results and Discussions

3.1 XRD Analysis Results of ZnO/Fe/Mg/C Nanocomposite

The first two and third specimen diffraction line profiles are determined from 2θ = 2° to 2θ = 100°. The created lattice planes of ZnO/Fe/Mg/C nanocomposite samples are indicated as (100), (002), (101), (102), (110), (103), (200), (112) and (004) (Fig. 1). These 2θ values were measured as 31.62°, 34.38°, 36.11°, 56.32°, 62.61°, 65.06°, 68.06° and 72.52°, respectively (Fig. 1). These planes are consistent with the standard spectra of the hexagonal phase of wurtzite-type ZnO with space group P6₃mc, defined by interpretation of the resulting PDF number 5-664. The diffraction peaks of the ZnO/Fe/Mg/C nanocomposite sample are of medium height and appear to be single peaks originating from the sample. Moreover, it is stated in the studies in the literature that no other peak from other crystalline phases provides the crystallinity conformation of ZnO, [26], [27], [51], [52], [53], [54].

* Fig. 1 can be found in the Appendix section.

XRD patterns of Fe-doped samples containing 2% and 4% Fe, ZnO/Fe/Mg/C nanocomposite a and ZnO/Fe/Mg/C nanocomposite b, showed corresponding diffraction peaks for another phase with ZnO crystallites without any peaks. Additionally, biomimetic production of ZnO using egg white and doping of various concentrations of iron oxide (Fe₂O₃) appeared to cause changes in all diffraction peaks and the height of both. 2% Fe₂O₃ doping brought about a decrease in the peak height in crystallites. The opposite behaviour was noticed in the case of the sample treated with 4 mol% Fe₂O₃. 2 mol% Fe₂O₃ Surface-doped ZnO/C system led to a gradual decrease in the crystallite size of ZnO, followed by an increase in strain and dislocation density. In the case of doping using 5 mol% Fe₂O₃, the opposite effect was observed. In general, doping the studied system with 2 or 5 mol% Fe₂O₃ caused a shift of one atom to its neighbour and an increase in the lattice constants.

3.2 FTIR Analysis Results of ZnO/Fe/Mg/C Nanocomposite

Fig. 2 shows the FTIR spectra of the components present in the nanocomposite. The metal-oxygen release mode corresponds to the Zn–OH group, whereas the characteristic broad band at 399 cm⁻¹ is attributed to metal–oxide stretching vibrations of the Zn-O bond, [26], [27]. Vibrational modes of carbon groupings, together
with Mg and Fe, may be responsible for the bands at 1090 and 1480 cm\(^{-1}\). Due to the capping agent in egg white, these bands are attributed to C–H, C–O and C–OH vibrations with the aforementioned metals, [26], [27], [28]. The strong bands at 1640 and 5000 cm\(^{-1}\) are due to the stretching vibrations of O–H bonds with C, indicating the presence of the aforementioned metal during the preparation of the nanocomposite pellet, [29], [51]. As can be observed from the FTIR spectra, the addition of iron ions during doping caused a modest repositioning of every absorption band and a subsequent alteration in their intensities.

### 3.3 Raman Analysis Results of ZnO/Fe/Mg/C Nanocomposite

With Raman spectra, the vibrational properties of three separate samples materials are investigated. Fig. 3 displays the Raman spectra of the examined materials between 0 and 5000 cm\(^{-1}\) at room temperature. The Raman spectra of the ZnO/Fe/Mg/C nanocomposite a, and ZnO/Fe/Mg/C nanocomposite b samples did not reveal the distinctive vibrational modes connected to ZnO crystals. However, these spectra show two large peaks in the G and D bands at 1499 cm\(^{-1}\) and 2199 cm\(^{-1}\), respectively.

* Fig. 3 can be found in the Appendix section.

Typical carbon compounds exhibiting these bands showed distinctive features, [55]. Indeed, the appearance of the G-band at 1499 cm\(^{-1}\) is a significant characteristic of sp\(^2\) hybridized carbon materials. This band can provide specific points in the in-plane vibration of sp\(^2\) bonded carbon regions, [56]. On the other hand, the D-band occurs at 2199 cm\(^{-1}\) indicates the existence of sp\(^3\) defects or abnormalities inside the hexagonal graphitic structure, [33]. Additionally, the edges of this band may violate the symmetry and selection criteria, and may consist of amorphous carbon and hexagonal graphite structure, or a combination of these, [35], [53]. The crystallite shape of Fe with nanocomposites exhibiting Mg and Fe and is proportional to the relationship (I\(_D\)/I\(_G\)) corresponding to the intensities of these bands, confirming the formation of crystallized carbon.

It has been stated that increasing the dopant content in ZnO/Fe/Mg/C nanocomposite b causes an increase in the formation of amorphous carbon due to the severe weakness in the intensities of the G and D bands, [23], [26], [27], [57]. This finding indicates that the standard error of the carbon material decreases.

### 3.4 SEM Analysis Results of ZnO/Fe/Mg/C Nanocomposite

The SEM analysis is conducted to study the morphology of the biosynthesized pure and Fe-Mg doped ZnO/C nanoparticles (Fig. 4).

* Fig. 4 can be found in the Appendix section.

SEM images showed that the shape and size of the display fragile and porous flakes containing spherical nanosized particles with the formation of various voids in ZnO/Fe/Mg/C nanocomposite a, (Fig. 4a). In other words, the as-synthesized materials are easily broken or destroyed and also are easily crumbled. The carbon-Mg-Fe containing zinc particle size reduced via excess carbon and Fe in the ZnO/Fe/Mg/C nanocomposite b since it was a capping agent in the nanoparticles (Fig. 4b).

### 3.5 EDS Analysis Results of ZnO/Fe/Mg/C Nanocomposite

Table 1 describes the less fragmentation structure of the nanocomposite. As the surface area of the nanocomposite decreased, while the percentage of ZnO decreased to 3%. Under these conditions a slight decrease in the pores and voids sizes was detected due to the agglomeration of smaller nanoparticles, especially, in the ZnO/Fe/Mg/C nanocomposite b. This nanocomposite contains high amounts of Fe additives. This is demonstrated by the presence of the lowest surface area in the above-mentioned nanocomposite, [23], [26], [27], [57].

* Table 1 can be found in the Appendix section.

The EDS pattern of ZnO/Fe/Mg/C nanocomposite a, elementally, respectively; It shows the presence of Zn (28.39 wt%), O (13.60 wt%), C (26.74 wt%), Fe (12.67 wt%) and Mg (11.67 wt%) (Table 2).

* Table 2 can be found in the Appendix section.

The EDS patterns of ZnO/Fe/Mg/C nanocomposite b showed the elemental content of these samples, respectively: Zn (25.00 wt%), Fe (20.01 wt% and 5.36 wt%), Mg (8.99 wt%), O (12.67 wt%) and Mg (11.67 wt%) (Table 2).

* Table 2 can be found in the Appendix section.

The EDS patterns of ZnO/Fe/Mg/C nanocomposite b showed the elemental content of these samples, respectively: Zn (25.00 wt%), Fe (20.01 wt% and 5.36 wt%), Mg (8.99 wt%), O (4.32 wt%) and C (10.06 wt%). All of these nanocomposites; It consists of the elements Zn, Fe, O, C and Mg.

### 3.6 TEM Analysis Results of ZnO/Fe/Mg/C Nanocomposite
The results of the TEM analysis confirm that both nanocomposite samples were encapsulated in graphitic carbon layers (Fig. 5).

* Fig. 5 can be found in the Appendix section.

In the ZnO/Fe/Mg/C nanocomposite an exhibited better dispersion, depending on a decrease in the agglomeration formation rate of the nanocomposite (Fig. 5a). While the average diameter of ZnO/Fe/Mg/C nanocomposite a was measured as 8.3 nm (Fig. 5a), ZnO/Fe/Mg/C nanocomposite b exhibited an increase in the agglomeration process, with a size diameter of 5.9 nm (Fig. 5b).

### 3.7 The Selected Area Electron Diffraction (SAED) Patterns of ZnO/Fe/Mg/C Nanocomposite

In Fig. 6a, Fig. 6b, and Fig. 6c, various bright spots were observed within the concentric rings, indicating the polycrystalline structure of pure and Fe-doped ZnO/C/Mg nanoparticles.

* Fig. 6 can be found in the Appendix section.

The Fe-doped ZnO/C/Mg nanoparticles b, demonstrated maximum intensity of these bright spots diminishes. In addition, increasing the Fe dopant content exhibited an increase in the number of concentric rings. These originated from the Fe-doped ZnO/C/Mg nanoparticles b size reduction, with the self-aggregation of some bulk layers, [58], [59], [60], [61].

### 3.8 H₂ Productions from 250 mg/l Polyester Polyurethane, and 250 mg/l Polyethylene via 3 mg/l ZnO/Fe/Mg/C Nanocomposite after 10 min Irradiation under 60 W/m² UV

The hydrolysis reaction of polyester polyurethane and polyethylene to H₂ was carried out within a 36-hour reaction time using Fe-doped samples containing 2% ZnO/Fe/Mg/C nanocomposite a and 4% ZnO/Fe/Mg/C nanocomposite b. The H₂ productions were 7800 ml/h and 5600 ml/h, respectively for polyester polyurethane while the H₂ productions were measured as 9800 ml/h and 8700 ml/h for polyethylene reduction at 125°C (Table 3).

* Table 3 can be found in the Appendix section.

The H₂ productions were extremely high since polyethylene carbon bonds were lower than that of polyester polyurethane, [59], [60], [61]. ZnO/Fe/Mg/C nanocomposite a, with a Fe content of 2%, exhibited higher H₂ production than the other. Microplastic yields at low temperatures were 100% at 130°C and 54% yield at 110°C (Table 3).

The hydrolysis ratio of the polyethylene was found to be higher since was readily degraded to H₂. However, polyester polyurethane showed ineffective depolymerisations and small amounts of polyurethane oligomers were observed. High hydrolysis rate of water-soluble polyethylene ending with high H₂ productions. When polyester polyurethane conversion is not completed; A metabolite residue was recovered, indicating that polyester polyurethane polymers consist of a metabolite with a lower molecular weight. After use, the ZnO/Fe/Mg/C nanocomposite catalyst can be easily recovered by centrifugation, and reused in other catalytic experiments under the same conditions; this shows a slight decrease in H₂ production of 3% (data not shown), [47], [60], [61], [62], [63].

### 3.9 Effect of Nanocomposite Concentration on H₂ Productions in 250 mg/l Polyester Polyurethane and Polyethylene Microplastics after 10 min Irradiation under 60 W/m² UV

The effects of increasing ZnO/Fe/Mg/C nanocomposite a, catalyst concentration from 1, 3, 5, 7 and to 10 mg/l was detected on H₂ productions in both microplastics (Table 4).

* Table 4 can be found in the Appendix section.

The maximum degradation capacity of 250 mg/l polyester polyurethane was 89% while the degradation yield was 99% at 250 mg/l polyethylene concentration at 3 mg/l ZnO/Fe/Mg/C nanocomposite a with a Fe ratio of 2% (Table 4). Then, the degradation yields of both microplastics dropped slightly from 99% to 94% and from 89% to 80% at 7.0 mg/l nanocomposite concentrations, for polyethylene and polyester polyurethane microplastics. This may be because, at low nanocomposite dosages, nanocomposite sites are more exposed to microplastics and degradation has occurred more rapidly. On the other hand, there is additional numbers of unoccupied nanocomposite sites at higher nanocomposite concentrations, which reduces the photodegradation capacity.

### 3.10 Effect of Time on H₂ Productions in 250 mg/l Polyester Polyurethane and Polyethylene Microplastics via 3 mg/l ZnO/Fe/Mg/C Nanocomposite a

The maximum degradation capacity of 250 mg/l polyester polyurethane was 89% while the degradation yield was 99% at 250 mg/l polyethylene concentration at 3 mg/l ZnO/Fe/Mg/C nanocomposite a with a Fe ratio of 2% (Table 4). Then, the degradation yields of both microplastics dropped slightly from 99% to 94% and from 89% to 80% at 7.0 mg/l nanocomposite concentrations, for polyethylene and polyester polyurethane microplastics. This may be because, at low nanocomposite dosages, nanocomposite sites are more exposed to microplastics and degradation has occurred more rapidly. On the other hand, there is additional numbers of unoccupied nanocomposite sites at higher nanocomposite concentrations, which reduces the photodegradation capacity.
The effects of contacting time (3–30 min) on the photocatalytic degradation of both microplastics to H$_2$ were studied. The results showed that the degradation efficiencies of polyester polyurethane and polyethylene microplastics increase readily with increasing irradiation time interval from 3 min up to 6 mins. At the beginning the microplastic concentration is more for degradation which later decreased with time (Table 5).

* Table 5 can be found in the Appendix section.

This also may be because initially large number of metal radicals present in the solution and they were attacked on microplastic molecules with the time. When the metal radicals lowered, the speed of degradation process may also decrease. The percentage of degradation efficiency for polyester polyurethane and polyethylene microplastics were 88% and 99% after 4 min and 6 min, respectively. The degradation efficiency increased sharply at the beginning while the degradation rate of increases very rapidly up to 10 min in polyester polyurethane, and then the degradation rate decreases slightly after the optimum time. The maximum degradation time of polyethylene was detected after 4 min photodegradation then the yields decreased after 5 min.

3.11 Effect of Temperature on H$_2$ Production from Polyester Polyurethane and Polyethylene Microplastics via 3 mg/l ZnO/Fe/Mg/C Nanocomposite a

The effect of temperature on the thermal degradation rates of polymers has been extensively explored because of the need to predict the service lifetime of consumer plastics. In some studies, it was found that the results are consistent with an Arrhenius relationship, [14], [20], but other studies have found non-Arrhenius behavior, [21], [22], [23]. There is some indication that the non-Arrhenius behavior is due to the complex degradation pathways referred to above, and therefore the relatively straightforward degradation process in polymers with metal–metal bonds might provide some fundamental insights that are not obtainable with standard carbon-chain polymers.

The temperature dependence of the quantum yields for the degradation of polymer could depend on: (1) the inherent temperature dependence of the photolysis and radical trapping reaction of the ZnO/Fe/Mg/C nanocomposite a, (2) the temperature dependent behaviour of the polymer morphology, or (3) a temperature-dependent dynamical property of the photogenerated radicals in the polymer. There is a significant increase in the quantum yields for polyester polyurethane with increasing temperature. In contrast, for polyethylene dispersed with Mg–Fe-ZnO chromophores are unattached to the polymer chains there are only slight increases the quantum yields over this temperature range, [23], [26], [27], [47], [57], [58], [59], [60], [61], [62], [63]. Big increase in the quantum yield with temperature for polyester polyurethane is not attributable to an inherent temperature dependence of the photolysis and subsequent radical trapping reaction of the nanocomposite (Table 6).

* Table 6 can be found in the Appendix section.

Since the quantum yields for polyethylene dispersed show only a slight temperature dependence, the temperature dependence observed for polyester polyurethane. The maximum H$_2$ production rates were detected at a temperature of 125°C with H$_2$ yields of 99% and 88% for polyethylene and polyester polyurethane microplastics, respectively. Like higher temperatures like 150°C and 175°C did not improve the H$_2$ yields.

4 Conclusions

H$_2$ production was examined by producing ZnO/Fe/Mg/C, a new nanocomposite from polyester polyurethane and polyethylene microplastics. The potential for converting plastic wastes to H$_2$ was studied in this study as fuel. Physicochemical analyses were performed to determine ZnO/Fe/Mg/C nanocomposite a, and ZnO/Fe/Mg/C nanocomposite b containing 2% and 4% Fe ratios.

Raman analyses showed that the G band at 1499 cm$^{-1}$ is an important feature of sp$^2$ hybridized carbon materials. The D-band occurs at 2199 cm$^{-1}$, and indicates the presence of sp$^3$ defects or abnormalities within the hexagonal graphite structure. The crystallite shape of Fe with nanocomposites exhibiting Mg, ZnO and C, and is proportional to the relationship (I$_D$/I$_G$) corresponding to the intensities of these bands, confirming the formation of crystallized carbon.

The selected area electron diffraction (SAED) results of the ZnO/Fe/Mg/C nanocomposite exhibited bright spots inside concentric rings, indicating the polycrystalline nature of the Fe-doped ZnO/C/Mg nanocomposites a. The 4% Fe-doped ZnO/C/Mg nanocomposites b, demonstrated maximum intensity of these bright spots. Elevated high Fe dopant content.
exhibited an increase in the number of concentric rings resulting in size reduction.

Selected area electron diffraction (SAED) results of ZnO/Fe/Mg/C nanocomposite a exhibited bright spots within concentric rings; This case is based on Fe-doped ZnO/C/Mg nanocomposite a; It shows polycrystalline nature. ZnO/C/Mg nanocomposite b, containing 4% Fe exhibited an increase in the number of concentric rings, leading to size reduction.

The XRD analysis showed that lattice planes of ZnO/Mg/C/Fe nanocomposite were distributed as (100), (002), (101), (102), (110), (103), (200), (112) and (004).

According to FTIR analysis, the weak bands at 610, 682 and 779 cm\(^{-1}\) are related to the Zn-OH group, while the characteristic broad band at 399 cm\(^{-1}\) is; It was observed that metal-Zn-O with Mg and C bonds had oxide stretching vibrations.

Additionally, the effects of some operating conditions (time, nanocomposite concentration, temperature) on H\(_2\) production from both micropollutants were investigated. The maximum H\(_2\) production was detected at 250 mg/l polyethylene microplastic as 9800 ml/h with ZnO/Fe/Mg/C nanocomposite a, containing 2% Fe while the H\(_2\) production was detected as 7800 ml/h from polyester polyurethane with the same nanocomposite.

Optimum operating conditions; maximum H\(_2\) production efficiencies of 99% polyethylene and 88% polyester polyurethane were achieved at 3 mg/l ZnO/Fe/Mg/C nanocomposite a, concentration, at 3 min and at 5 min experimental times and at 125\(^\circ\)C temperature, respectively.

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**Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)**

Prof. Dr. Delia Teresa Sponza and Post-Dr. Rukiye Öztekin took an active role in every stage of the preparation of this article. The authors equally contributed in the present research, at all stages from the formulation of the problem to the final findings and solution.

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**Conflict of Interest**

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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APPENDIX

Fig. 1. XRD spectra of ZnO/Fe/Mg/C nanocomposite
Fig. 2. FTIR spectra of ZnO/Fe/Mg/C nanocomposite
Fig. 3. Vibrational Raman spectra of ZnO/Fe/Mg/C nanocomposite
Fig. 4. SEM analysis results in ZnO/Fe/Mg/C nanocomposite a (a) and ZnO/Fe/Mg/C nanocomposite b (b) (SEM images size: 50 nm).
Table 1. Energy dispersive spectroscopy of the ZnO/Fe/Mg/C nanocomposite

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<th>Raman Shifts (cm(^{-1}))</th>
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<td>1740</td>
</tr>
<tr>
<td>4500</td>
<td></td>
<td>2000</td>
<td>1740</td>
</tr>
<tr>
<td>5000</td>
<td></td>
<td>2000</td>
<td>1740</td>
</tr>
</tbody>
</table>

Table 2. Elements of ZnO/Fe/Mg/C nanocomposite a, and ZnO/Fe/Mg/C nanocomposite b

<table>
<thead>
<tr>
<th>Elements (wt%)</th>
<th>Names of Nanocomposite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>28.39</td>
</tr>
<tr>
<td>C</td>
<td>26.74</td>
</tr>
<tr>
<td>Fe</td>
<td>12.67</td>
</tr>
<tr>
<td>Mg</td>
<td>11.67</td>
</tr>
<tr>
<td>O</td>
<td>13.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elements (wt%)</th>
<th>Names of Nanocomposite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>25.00</td>
</tr>
<tr>
<td>C</td>
<td>10.06</td>
</tr>
<tr>
<td>Fe</td>
<td>20.01</td>
</tr>
<tr>
<td>Mg</td>
<td>8.99</td>
</tr>
<tr>
<td>O</td>
<td>4.32</td>
</tr>
</tbody>
</table>
Fig. 5. TEM images of the ZnO/Fe/Mg/C nanocomposite a (a) and ZnO/Fe/Mg/C nanocomposite b (b) (TEM images size: 100 nm).
Fig. 6. SAED patterns of the ZnO/Mg/C nanocomposite a (a), Fe-doped ZnO/C/Mg b (b) and ZnO/Fe/Mg/C (c)
Table 3. H₂ productions from polyester polyurethane, polyethylene via ZnO-Mg-Ni-Fe-C nanocomposite a and ZnO-Mg-Ni-Fe-C nanocomposite b

<table>
<thead>
<tr>
<th>Microplastic Names</th>
<th>ZnO/Fe/Mg/C Nanocomposite a</th>
<th>ZnO/Fe/Mg/C nanocomposite b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester polyurethane</td>
<td>7800</td>
<td>5600</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>9800</td>
<td>8700</td>
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</table>

Table 4. Effect of ZnO/Fe/Mg/C nanocomposite a, concentration on H₂ productions in 250 mg/l polyester polyurethane and polyethylene microplastic concentrations

<table>
<thead>
<tr>
<th>Nanocomposite a, Concentration (mg/l)</th>
<th>Microplastic Names and Yields</th>
<th>Photodegradation Yield of Polyethylene (%)</th>
<th>Photodegradation Yield of Polyester Polyurethane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>99</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>98</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>94</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>89</td>
<td>70</td>
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</tr>
</tbody>
</table>

Table 5. Effect of time on H₂ productions in the presence of polyester polyurethane and polyethylene microplastics via 3 mg/l ZnO/Fe/Mg/C nanocomposite a

<table>
<thead>
<tr>
<th>Time</th>
<th>Microplastic Type and H₂ Yield Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polyester Polyurethane</td>
</tr>
<tr>
<td>3</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>99</td>
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<td>10</td>
<td>97</td>
</tr>
<tr>
<td>15</td>
<td>97</td>
</tr>
<tr>
<td>30</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>Polyethylene</td>
</tr>
<tr>
<td>3</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>77</td>
</tr>
<tr>
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<td>15</td>
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<tr>
<td>30</td>
<td>85</td>
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</table>
Table 6. Effect of temperature increase on H₂ production yields of polyethylene and polyester polyurethane

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>H₂ Production Yield (%) from Polyethylene</th>
<th>H₂ Production Yield (%) from Polyester Polyurethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>97</td>
<td>60</td>
</tr>
<tr>
<td>70</td>
<td>98</td>
<td>70</td>
</tr>
<tr>
<td>90</td>
<td>99</td>
<td>80</td>
</tr>
<tr>
<td>125</td>
<td>99</td>
<td>88</td>
</tr>
<tr>
<td>150</td>
<td>99</td>
<td>88</td>
</tr>
<tr>
<td>175</td>
<td>99</td>
<td>99</td>
</tr>
</tbody>
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