

Fabrication of nano Ag encapsulated on ZnO/Fe₂V₄O₁₃hybrid-heterojunction for photodecomposition of Methyl Orange

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Abstract

Novel Ag encapsulated nanocomposites $ZnO/Fe_2V_4O_{13}$ (AZF) were synthesized with various wt% of the silver (from 1.0 to 2.5 wt% of Ag) by photo-deposition method using UV-A light. The nanostructure of the AZF was explored by various characterization techniques. Surface functional group was confirmed by FT-IR spectra, the crystalline nature of the material revealed by XRD patterns. Furthermore, surface morphology and optical properties of the composites were analyzed by SEM, HR-TEM UV-DRS and PL respectively. The photoactivity was tested against Methyl Orange (MO) degradation under UV light. The stability of the catalyst was confirmed by reusability measurements. Suitable degradation pathway was proposed based on intermediates obtained during degradation analyzed by GC-MS. Trapping experiments confirmed that super oxide radical anion ($O_2^{-\cdot}$) has been consider as a most active species for this degradation process. Mineralization is confirmed by measurements of chemical oxygen demand (COD).

1. Introduction

Dye pollutants released by the textile industries are becoming a significant source of pollution for the environment. It is estimated that about 150 tons a day will be released into the aquatic system worldwide. The discharge of this dye effluent is a major cause of non-esthetic degradation in the water body and these dyes are also resistant to aerobic degradation and can be converted into carcinogenic aromatic amines under anaerobic conditions [1–4]. Advanced oxidation processes (AOPs) producing hydroxyl radical ('OH) as one of the most effective oxidants were considered promising techniques. Photocatalytic processes based on the application of semiconductors as a photocatalyst for the degradation of toxic organic contaminants to in aqueous phase have been widely studied among various AOPs [5–9]. In the photocatalytic activity of certain dye molecules, zinc oxide (ZnO) is documented to be more effective than TiO_2 [10, 11]. ZnO is becoming a good choice for photocatalyst applications. ZnO is found to be inefficient alternative to TiO_2 since its photodegradation mechanism has been proved to be almost same. However, ZnO has a wide band gap of 3.37 eV, which ultimately limits in photodegradation due to rapid electron-hole recombination. Different attempts have been made to enhance the effective charge separation in ZnO to address this limitation, thus strengthening its photocatalytic ability. Encapsulation of noble metal nanocomposite has been proven efficacious due to strong surface plasma resonance (SPR) of noble metal which extended visible light absorption with charge separation. Recently, Nanosilver (AgNPs) has been paying intense attention due to its high performance of photocatalytic ability when it combined with semiconductors. Ag has been identified as the best elements to encapsulate with ZnO , due to its high solubility [12].

Recently photocatalysts based on Ag have been developed as effective photocatalysts for pollutant degradation [13, 14]. Although both materials show great potential, due to recombination of the e^-/h^+ pair [15–17], they do not operate with high photocatalytic efficiency. The goal of this research work was to use the catalyst $Ag-ZnO/Fe_2V_4O_{13}$ to study the mineralization of MO dye by photodegradation using a technique different from the approaches mentioned above. The synthesized sample is characterized

using techniques such as FT-IR, XRD, BET, SEM-EDX, ECM, HR-TEM, UV-vis-DRS, and PL measurements. The photocatalytic properties of nanocomposites Ag-ZnO/Fe₂V₄O₁₃ (AZF) were assessed through the MO degradation under UV irradiation.

2. Experimental

2.1 Fabrication of Ag coated with ZnO/Fe₂V₄O₁₃

The synthesis of Fe₂V₄O₁₃ and Fe₂V₄O₁₃/ZnO was reported in our previous paper [18, 19]. Different concentrations of Ag⁺ ions were added into the suspension (C₂H₅OH/H₂O as solvent) of 3 g of synthesized Fe₂V₄O₁₃/ZnO such that the Ag⁺ concentration was (X wt%; where X = 1, 1.5, 2, 2.5) in relation to Fe₂V₄O₁₃/ZnO. The mixed suspensions were placed in photoreactor then irradiated for 3 h with 8×8W mercury lamps UV-A light under continuous stirring. During irradiation Ag⁺ converted into Ag and deposited on ZnO/Fe₂V₄O₁₃nanocomposite (AZF). The AZF were centrifuged and dried at 100 °C for 2 h then used as photocatalyst. The chemicals used for this study, instrumental specification for the characterization techniques, the photocatalytic experimental and COD measurements procedures are given in supporting information's. The photoreactor used for this study is given as Fig. S1 (see Supporting information).

3. Results And Discussion

3.1 FT-IR

Figure 1 shows FT-IR spectra of prepared ZnO, Fe₂V₄O₁₃, and X-AZF (X = 1, 1.5, 2 and 2.5 wt%). The stretching vibration of surface hydroxyl group was appeared in the range between 3453 and 3405 cm⁻¹ for all the samples[18, 19]. In Fig. 1a, peaks observed at 420, 447, and 543 cm⁻¹, which could be attributed to the Zn–O stretching modes [19–21].In Fig. 1b, the peaks at 1028, 711 and 510 cm⁻¹ are assigned to V–O, V–O–Fe and Fe–O stretching modes, respectively[19].Bands at 474 and 426 cm⁻¹are attributed to the characteristic stretching mode of Ag–O and Zn–O bonds[22]. Figure 1c–f show various functional groups of AZF and the metal oxide bond present in the compound, Fe–O, Ag–O, and Zn–O vibrations are observed at 1015, 1100, 474, 426, and 413 cm⁻¹. This indicates that Ag was effectively loaded on the ZnO/Fe₂V₄O₁₃ nanocomposite.

3.2 XRD

Figure 2 show the typical X-ray diffraction (XRD) patterns of the prepared ZnO(Fig. 2a),Fe₂V₄O₁₃ (Fig. 2b) [19] and ZnO/Fe₂V₄O₁₃ samples with different loading concentrations of Ag (X = 1, 1.5, 2 and 2.5 wt%) (Fig. 2c–f). The wurtzite ZnO (JCPDS Card No. 36-1451) planes were observed for the prepared ZnO at 2θ values of 31.75, 34.40, 36.23, 47.53, 56.60, and 62.34° corresponds to (100), (002), (101), (102), (110), and (103) planes, respectively[23, 24].In Fig. 2b, Fe₂V₄O₁₃ shows three diffraction peaks at 2θ angles of

12.5, 22.7, and 26.7° that correspond to (002), (022), and (014) planes of $\text{Fe}_2\text{V}_4\text{O}_{13}$, respectively and the peaks are well matched to the monoclinic phase of $\text{Fe}_2\text{V}_4\text{O}_{13}$ (JCPDS Card No. 00-039-0893). The good crystallinity is confirmed by high and narrow diffracted peaks[19]. Face centered cubic (FCC) geometry is indexed to the three additional peaks at 38.06, 44.29, and 64.43° corresponding to (111), (200), and (220) planes of $\text{ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$ doped with silver nanocomposites (JCPDS Card No. 4-0783)[25, 26] in Fig. 2c-f. The average crystallite size of 2 wt% of AZF was 28.5 nm.

3.3 BET surface area

The pore structure and surface area of the prepared $\text{Ag-ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$ was analyzed using N_2 absorption-desorption isotherms are shown in Fig. 3. The $\text{Ag-ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$ is type II isotherm at IUPAC level[27] and the distribution of pore size is given in the inset of Fig. 3. The BET surface area and pore volume of $\text{Ag-ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$ are given in Table 1.

Table 1
Texture parameters of 2 wt% $\text{Ag-ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$

$S_{\text{BET}} (\text{m}^2 \text{ g}^{-1})$	$V_p (\text{cm}^3 \text{ g}^{-1})$	$D_p (\text{nm})$	$S_{\text{micro}} (\text{m}^2 \text{ g}^{-1})$	$V_{\text{micro}} (\text{cm}^3 \text{ g}^{-1})$
0.9043	0.1044	461.86	16.53	0.0089

S_{BET} = BET surface area, V_p = total pore volume, D_p = average uniform pore size distribution, S_{micro} = surface area of micropores, V_{micro} = pore volume of micropores.

Table 2
Mass spectral data of intermediates (MO)

Compounds	Retention time (min)	m/z values
$\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$ (D1)	19.796	292.0 ($M + 1$), 258.0, 229.0, 181.0, 152.0, 126.0, 111.0, 75.0
$\text{C}_{12}\text{H}_9\text{N}_2\text{NaO}_3\text{S}$ (D2)	18.533	284.0 (M^+), 282.0, 211.0, 111.0, 85.0, 71.0, 57.0, 54.0
$\text{C}_6\text{H}_5\text{N}_2\text{NaO}_3\text{S}$ (D3)	16.665	209.0 (M^+), 111.0, 97.0, 85.0, 71.0, 57.0
$\text{C}_6\text{H}_7\text{NO}$ (D4)	15.512	109.0 (M^+), 83.0, 71.0, 67.0, 57.0

3.4 SEM-EDX with color mapping

SEM measurements have described the surface morphology of the AZF. Figure 4 shows that the 2 wt% Ag-loaded $\text{ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$ with different magnifications. The irregular-shaped $\text{ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$ agglomerates are shown in all SEM images. EDX can generally accurately detect up to trace amount of metal present on the surface of base materials. Figure 5 shows the EDX recorded from the selected area, which reveals that

the presence of Zn, Fe, V, Ag, and O in the catalyst. The presence of these elements in Ag-ZnO/Fe₂V₄O₁₃ was also confirmed by elemental color mapping. The different color areas in Fig. 6 indicate Ag, Zn, Fe, V, and O enriched areas of the Ag-ZnO/Fe₂V₄O₁₃ sample.

3.5 HR-TEM

Figure 7 shows that the HR-TEM images of the 2 wt% Ag-ZnO/Fe₂V₄O₁₃. From Fig. 7a, some of the hexagonal particles are clearly seen, and corresponding to ZnO in Ag-ZnO/Fe₂V₄O₁₃, although the identification of Fe₂V₄O₁₃ in Ag-ZnO/Fe₂V₄O₁₃ was impossible. The lattice fringes of the Ag-ZnO/Fe₂V₄O₁₃ catalyst are shown in Fig. 7d. The interplanar spacing values for the nanocrystalline Ag-ZnO are shown in Fig. 7e. From the HR-TEM images, the average diameters (28.545±5.453nm) of the nanoparticles (Ag-ZnO/Fe₂V₄O₁₃nanocomposite) were computed by Image J analysis. The histogram shows that the average particle diameter of 2wt% Ag-ZnO/Fe₂V₄O₁₃in Fig. 7f.

3.6 UV-vis-DRS

Figure 8A shows the DRS results of ZnO, Fe₂V₄O₁₃, and samples with various wt % of X-Ag-loaded ZnO/Fe₂V₄O₁₃ (X = 1.0, 1.5, 2 and 2.5 wt%) catalyst. In visible regions, Ag-ZnO/Fe₂V₄O₁₃ composites display higher absorption than ZnO, resulting in higher visible light active catalytic behavior and also an increase in the absorption at 350–380 nm (UV-region) this can contribute to enhanced e⁻/h⁺pair production, which consequently improves the photocatalytic activity under UV light[28]. Figure 8B shows K-Mplots for ZnO, Fe₂V₄O₁₃, and ZnO/Fe₂V₄O₁₃ with various wt % of Ag loading. The band gap energies of ZnO, Fe₂V₄O₁₃, and X-Ag-ZnO/Fe₂V₄O₁₃ (X = 1, 1.5, 2, and 2.5 wt%) were 3.25, 2.21, 3.23, 3.23, 3.15, and 3.16 eV, respectively.

3.7 Photoluminescence (PL) emission spectra

The effective suppression of photogenerated charge carriers and the transfer of the photogenerated e⁻/h⁺were investigated by photoluminescence (PL) emission spectra[29]. Figure 9 shows the PL spectra of the prepared ZnO (Fig. 9a) and 2 wt% Ag-ZnO/Fe₂V₄O₁₃ (Fig. 9b). Three emission bands are observed at 395, 431, and 586 nm. Although all the peaks are almost identical, PL intensities are different. The higher intensitywas observed in bare ZnO at 395 nm due to high e⁻/h⁺recombination than Ag-ZnO/Fe₂V₄O₁₃. The Ag particles loaded with the ZnO/Fe₂V₄O₁₃nanocompositeact as trapper for photo-generatedelectrons, and quench the PL emission [30].The maximum intensity shows the higher e⁻/h⁺ recombination and resultslow photocatalytic activity[31, 32].The lowest intensity shows that the well suppression of e⁻/h⁺recombination and results higher photocatalytic activity[33].

3.8 Primary analysis

The photocatalytic behavior of nanocomposite Ag-ZnO/Fe₂V₄O₁₃ with 1, 1.5, 2, and 2.5 wt percent of Ag loading was assessed in terms of MO degradation. Controlled experimentswere conducted under different reaction conditions (Fig. 10). The dye/ZnO/UV-A process underwent 68% degradation in 90 min (curve a).

The dye/ZnO/Fe₂V₄O₁₃/UV light process showed curve b, which yielded 75% degradation in 90 min. Only 19% adsorption was observed in dye/2 wt% Ag-ZnO/Fe₂V₄O₁₃/dark process (curve e). Curves c, d, f, and g demonstrate the degradation of dye on irradiation with the Ag-ZnO/Fe₂V₄O₁₃ catalyst with different percent wt of Ag loading. The 2 wt% Ag-ZnO/Fe₂V₄O₁₃ hybrid-heterojunction catalyst showed higher MOdegradation (curve f, 93%) in 90 min and also almost complete degradation was achieved at 120 min. Hence, 2 wt% of Ag is the optimum loading of Ag-ZnO/Fe₂V₄O₁₃.

3.9 Effect of pH

pH is the important parameters for the application of industrial point of view. By adjusting the pH of the MO solution, the effect of pH on the MO photodegradation was studied. Fig. S2demonstrates that pH has an important effect on the rate of photodegradation and decolorization. The maximum degradation and decolorization of MO is observed at pH 7. Above pH 7, the rate of degradation and decolorization decreases. Effect of catalyst loading (Fig. S3) and initial dye concentration (Fig. S4) are discussed in supporting information's.

3.10 Reusability

Figure 11 shows the stability of the catalyst for the degradation of MO. In the first run, approximately 99% of MO degradation achieved. The same catalyst was again reused for further runs. All the remaining cycles gave almost 98.5% of degradation in 90 min. Hence, the 2 wt% Ag-ZnO/Fe₂V₄O₁₃ is stable, recoverable and reusable.

3.11 Mineralization studies

3.11.1 GC-MS analysis

Sometimes intermediates are more hazardous than starting materials, so it is necessary to analyze the intermediates for the degradation process. An attempt has been made to find out the degradation intermediates of MO photodegradation with 2wt% Ag-ZnO/Fe₂V₄O₁₃ (AZF) hybrid-heterojunction/UV process. GC-MS studied performed with the solutions obtained after 30 and 60 minutes of irradiation and predicted a degradation pathway for MO by AZF based on the m/z ratio, retention time and molecular weight(Scheme 1). For these identified intermediates, molecular ion and fragmentation peak values are stated inTable 2.Although, in photocatalytic degradation of azo dyes, it was expected that the cleavage of azo bond take place first, however, formation of compounds observed (**D1** and **D2**)with azo groups at the retention time of 19.796 and 18.533 min, respectively. Hydroxyl radicals were thus considered to be the most reactive species for degradation, the compound **D1** undergoes azo link cleavage and replacement of sulfonic acid group by hydroxyl group through the repetitive attack of ·OH radicals produced intermediates *N*-methylbenzene-1,4-diamine (Compound **I**) and 4-aminophenol (**D4**). The intermediate product **D2** further undergoes C–N cleavage produced **D3** which on further undergoes azo link cleavage produced 4-aminophenol (**D4**). Finally, it is expected that the compound **D4** and compound **I** would be mineralized to CO₂, water and mineral acids [34, 35].

3.11.2 FT-IR spectral analysis

The early adsorption of the dye under dark by 2 wt% Ag-ZnO/Fe₂V₄O₁₃nanocomposite is 33.4%, although complete degradation occurred at 90 min irradiation. The experiments were carried out to determine whether the adsorbed dye molecules had been degraded completely. Comparisons made with FT-IR spectra of the fresh dye and catalyst ((Fig. S5a and S5b), and dye adsorbed composite before and after irradiations (Fig. S5c and S5d). The characteristic bands of MO (Fig. S5a) are observed at 1604, 1366, and 1042 cm⁻¹ due to N = N stretching, C–N bond vibrations, and S = O bond of MO, respectively [36]. When compared Fig. S5a and Fig. S5c, the characteristic MO dye peaks are observed in the dye adsorbed catalyst. However, upon irradiation, *i.e.* after complete degradation, the FT-IR spectrum of the composite (Fig. S5d) resembles with fresh catalyst (Fig. S5b) revealed that the adsorbed dye molecules underwent complete degradation. Thus, the 2 wt% Ag-ZnO/Fe₂V₄O₁₃nanocomposite shows better catalytic performance for MO.

3.11.3 UV-Vis spectral analysis

Figure 12 shows UV-vis spectra for the degradation and decolorization of MO by 2 wt% Ag-ZnO/Fe₂V₄O₁₃nanocomposite under UV-A light irradiation for 0–90 min. UV-vis spectrum of MO shows strong absorption in the range of 200–600 nm with λ_{max} at 464 nm, which is due to the presence of the azo group (N = N), and another band is observed at 272 nm in the UV region due to aromatic part of the dye. Upon continues irradiation with 2 wt% Ag-ZnO/Fe₂V₄O₁₃nanocomposite, both peaks were diminished with respect to time, and finally almost completely disappeared. From these observations we conclude that the degradation of the dye with respect to time[37]. Moreover, no new peakswere observed during irradiation, indicating that MO was degraded gradually and intermediates do not absorb at analytical wavelengths. The color of the suspension changed from the orange to colorless (inset of Fig. 12).

3.11.4 Chemical oxygen demand (COD) measurements

The mineralization of the dye further confirmed with reduction of COD values. Under optimum condition, COD measurements were made and the percentageof COD reduction of the dye at different times of UV-A light irradiation is given in Table 3. Percentages of COD reduction increases with respect to irradiation time reveals that the mineralization of the dye.

Table 3
Percentages of COD reduction at different irradiation times for the degradation of MO by 2 wt% Ag-ZnO/Fe₂V₄O₁₃ catalyst

Dye	0 min	30 min	60 min	90 min	120 min
MO	0	31.6	57.4	79.3	88.0

[MO] = 4·10⁻⁴ M, 2 wt% Ag-ZnO/Fe₂V₄O₁₃ = 3 g L⁻¹, airflow rate = 8.1 mL s⁻¹, pH = 7, $I_{\text{UV}} = 1.381 \cdot 10^{-6}$ einstein L⁻¹ s⁻¹.

3.12 Mechanism

Under light irradiation, the photoexcited electrons in the CB of $\text{Fe}_2\text{V}_4\text{O}_{13}$ can jump to the CB of ZnO. The CB potential of ZnO was found to be more electronegative than the reduction potential of $\text{O}_2/\text{O}_2^{\cdot-}$ (-0.34 eV vs NHE), and therefore, the electrons concentrated in the CB of ZnO can generate $\text{O}_2^{\cdot-}$ for dye degradation(Fig. 13). Further, Ag can shuttle the photogenerated electron from ZnO in Ag-ZnO/ $\text{Fe}_2\text{V}_4\text{O}_{13}$ and reduces the recombination of electron-hole pair effectively. However, owing to the less positive VB potential of $\text{Fe}_2\text{V}_4\text{O}_{13}$, the holes do not generate $\cdot\text{OH}$. Meanwhile, $\text{Fe}_2\text{V}_4\text{O}_{13}$'s holes created in the VB would be transferred to its surface and then directly involved in the MO degradation.By these two processes the lifetimes of electron and hole increase, leading to enhanced photocatalytic activity.

The increased transfer of charge between the interface of $\text{Fe}_2\text{V}_4\text{O}_{13}$ and ZnO strongly suppressed the rate of recombination, which is beneficial to improve the photocatalyticability. The reduction of PL intensity in Ag-ZnO/ $\text{Fe}_2\text{V}_4\text{O}_{13}$ as compared to that of pure undopedZnOreveals the effective prohibition of recombination of e^-/h^+ pairs, indicating thatloadingof Ag and $\text{Fe}_2\text{V}_4\text{O}_{13}$ could substantiallysuppress the charge transfer rate in ZnO. The band gap energy of Ag-ZnO/ $\text{Fe}_2\text{V}_4\text{O}_{13}$ lowered than that of pure ZnO.

In general, for a higher formation rate of $\cdot\text{OH}$ radicals, a separation efficiency of electron-hole pairs would be greater. The photocatalytic activity therefore shows a positive association with the rate of radical formation of $\cdot\text{OH}$, i.e., a faster rate of radical formation of $\cdot\text{OH}$ contributes to a higher photocatalytic activity of the nanocomposite. Moreover, the formation of superoxide radical anions increased due to electrons transferred to the adsorbed oxygen molecules by Ag *via* the ZnO conduction band. Hydroxyl radicals and superoxide radical anions are potent oxidants, so that organic molecules and intermediate species can completely oxidizedtotheir respective end-products.

Trapping experiments were performed to identify the active species involved in photocatalytic degradation process[38–40] and the results are shown in Fig. 14. No scavenger, the degradation efficiency is 99% at time of 90 min. Under the same condition, with TBA ($\cdot\text{OH}$ scavenger), KI (h^+ scavenger), BQ ($\text{O}_2^{\cdot-}$ scavenger) and AgNO_3 (e^- scavenger) gave 93.9, 86.8, 84.6 and 89.6 percentages of degradation, respectively. From these values, more or less all the species are equally contributed in the degradation process. However, the addition of BQ suppress the photocatalytic activity of the composite insomewhat extent, hence superoxide radical anion ($\text{O}_2^{\cdot-}$) has been consider as a most active species for this degradation process.

4. Conclusions

Ag loaded ZnO/ $\text{Fe}_2\text{V}_4\text{O}_{13}$ nanocomposites have been prepared using photo-deposition method. The prepared nanocomposite was characterized by various technique. The photocatalytic activities of Ag-ZnO/ $\text{Fe}_2\text{V}_4\text{O}_{13}$ nanocomposite were evaluated using degradation of MO under UV-A light irradiation, and almost complete degradation was observed with 2 wt% Ag loaded $\text{Fe}_2\text{V}_4\text{O}_{13}/\text{ZnO}$ composite. The neutral pH (7) facilitate the degradation efficiently with3 g L^{-1} catalyst loading. The stability of the catalyst was

observed by multiple runs of the catalyst. Almost 99% of degradation was observed for all the five runs. GC-MS reveals that the formation of three azo compounds (**D1**, **D2** and **D3**) and 4-aminophneol (**D4**) as intermediates during degradation process. Trapping experiments confirms that the super oxide radical anion ($O_2^{\cdot-}$) has been considered as a most active species for this degradation process. The complete mineralization was confirmed by COD measurement. A suitable degradation mechanism is also proposed.

Declarations

Conflicts of interest

There is no conflict of interest declare

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Electronic supplementary information (ESI)

Figs. S1–S5, the chemicals used for this study, instrumental specification for the characterization techniques, the photocatalytic experimental and COD measurements procedures are given in supporting information's.

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Scheme

Scheme 1 is available in supplementary section.

Figures

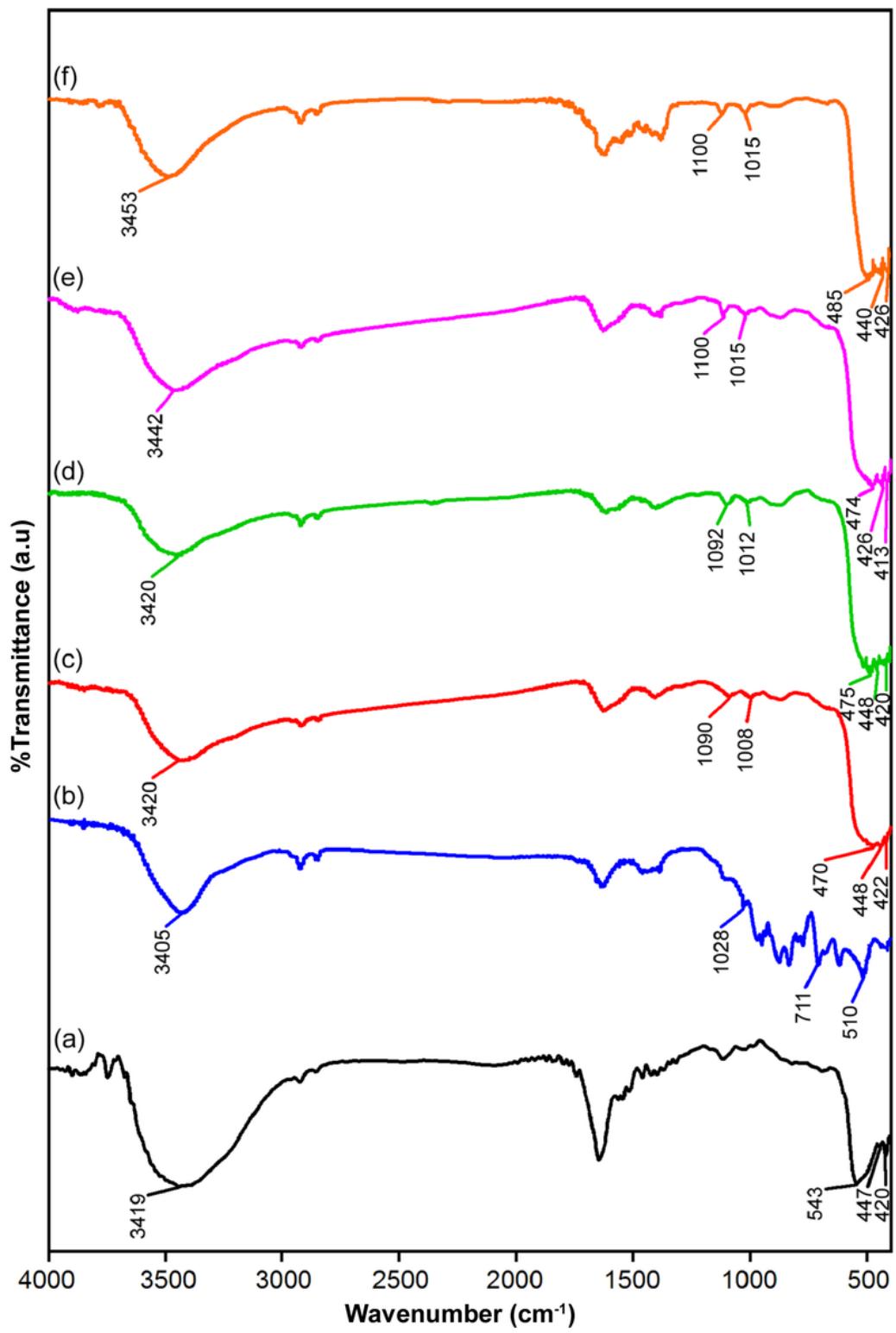


Figure 1

FT-IR spectra of a) ZnO, b) $\text{Fe}_2\text{V}_4\text{O}_{13}$, c) 1 wt% Ag-ZnO/ $\text{Fe}_2\text{V}_4\text{O}_{13}$, d) 1.5 wt% Ag-ZnO/ $\text{Fe}_2\text{V}_4\text{O}_{13}$, e) 2 wt% Ag-ZnO/ $\text{Fe}_2\text{V}_4\text{O}_{13}$ and f) 2.5 wt% Ag-ZnO/ $\text{Fe}_2\text{V}_4\text{O}_{13}$.

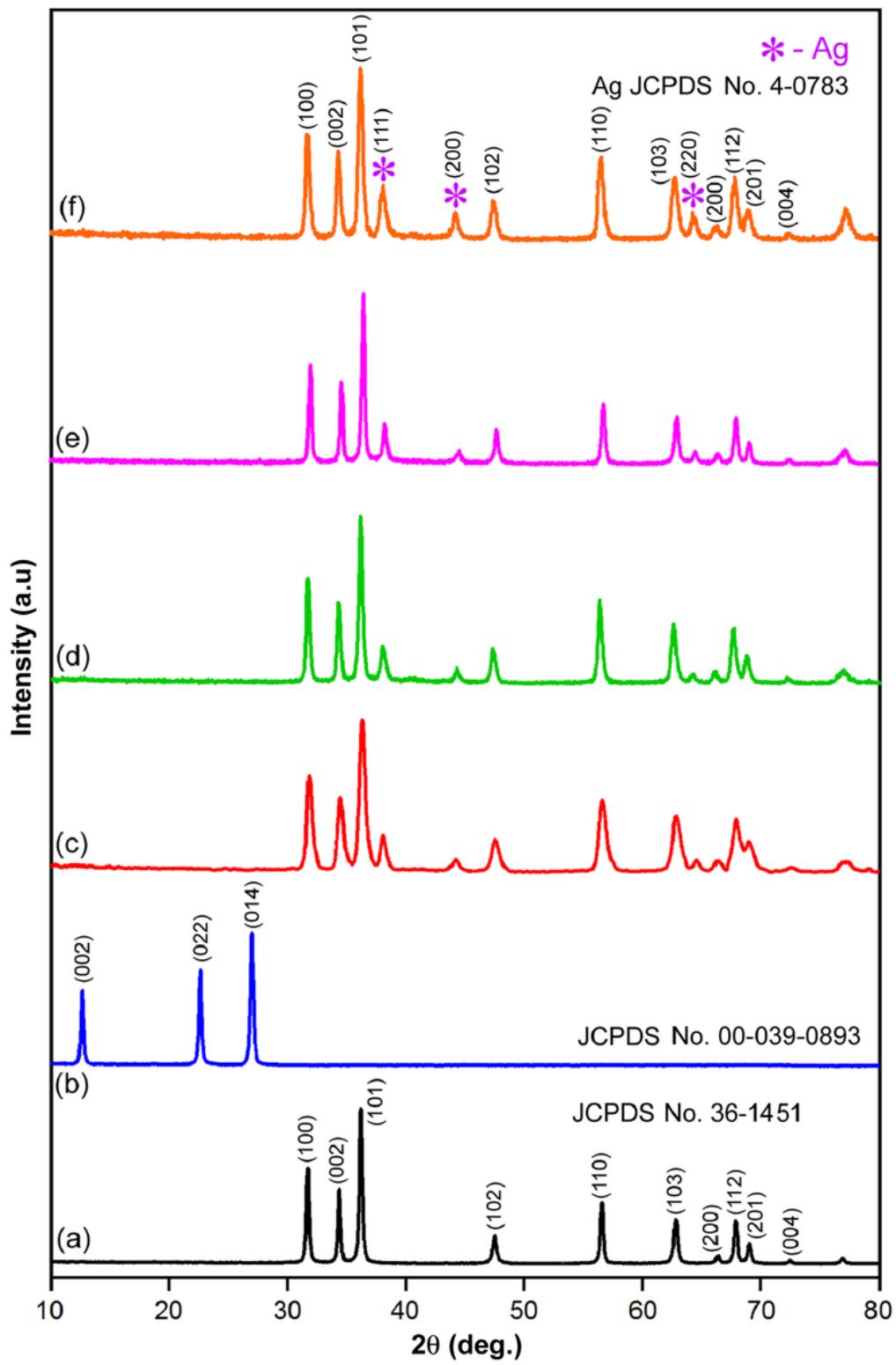


Figure 2

XRD patterns of a) ZnO , b) $\text{Fe}_2\text{V}_4\text{O}_{13}$, c) 1 wt% $\text{Ag-ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$, d) 1.5 wt% $\text{Ag-ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$, e) 2 wt% $\text{Ag-ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$ and f) 2.5 wt% $\text{Ag-ZnO}/\text{Fe}_2\text{V}_4\text{O}_{13}$.

Figure 3

N_2 adsorption-desorption isotherm of 2 wt% Ag-ZnO/Fe₂V₄O₁₃. Inset shows pore size distribution.

Figure 4

SEM images of 2 wt% Ag-ZnO/Fe₂V₄O₁₃: a, b) 1 mm and c, d) 200 nm.



Figure 5

EDX of 2 wt% Ag-ZnO/Fe₂V₄O₁₃.

Figure 6

Elemental color mapping images of 2 wt% Ag-ZnO/Fe₂V₄O₁₃: a) 2 wt% Ag-ZnO/Fe₂V₄O₁₃ composition, b) O, c) Ag, d) V, e) Fe and f) Zn.

Figure 7

HR-TEM images of 2 wt% Ag-ZnO/Fe₂V₄O₁₃: a) 100 nm, b) 50 nm, c) 20 nm, d) 2 nm, e) SAED pattern and f) particle size distribution.

Figure 8

a) UV-DRS and B) K.M plot of a) ZnO, b) Fe₂V₄O₁₃, c) 1 wt% Ag-ZnO/Fe₂V₄O₁₃, d) 1.5 wt% Ag-ZnO/Fe₂V₄O₁₃, e) 2 wt% Ag-ZnO/Fe₂V₄O₁₃ and f) 2.5 wt% Ag-ZnO/Fe₂V₄O₁₃.

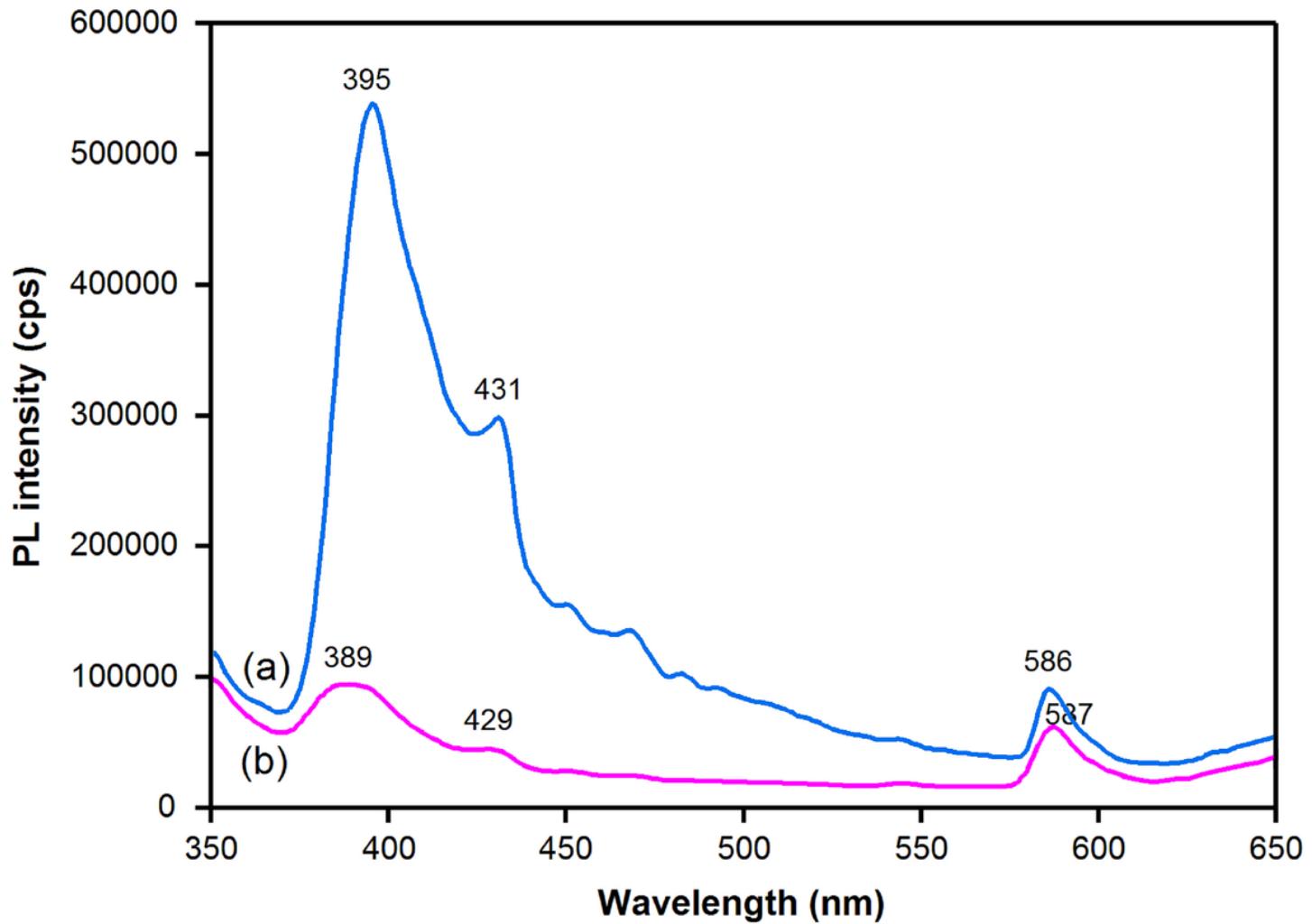


Figure 9

PL spectra of a) ZnO and b) 2 wt% Ag-ZnO/Fe₂V₄O₁₃.

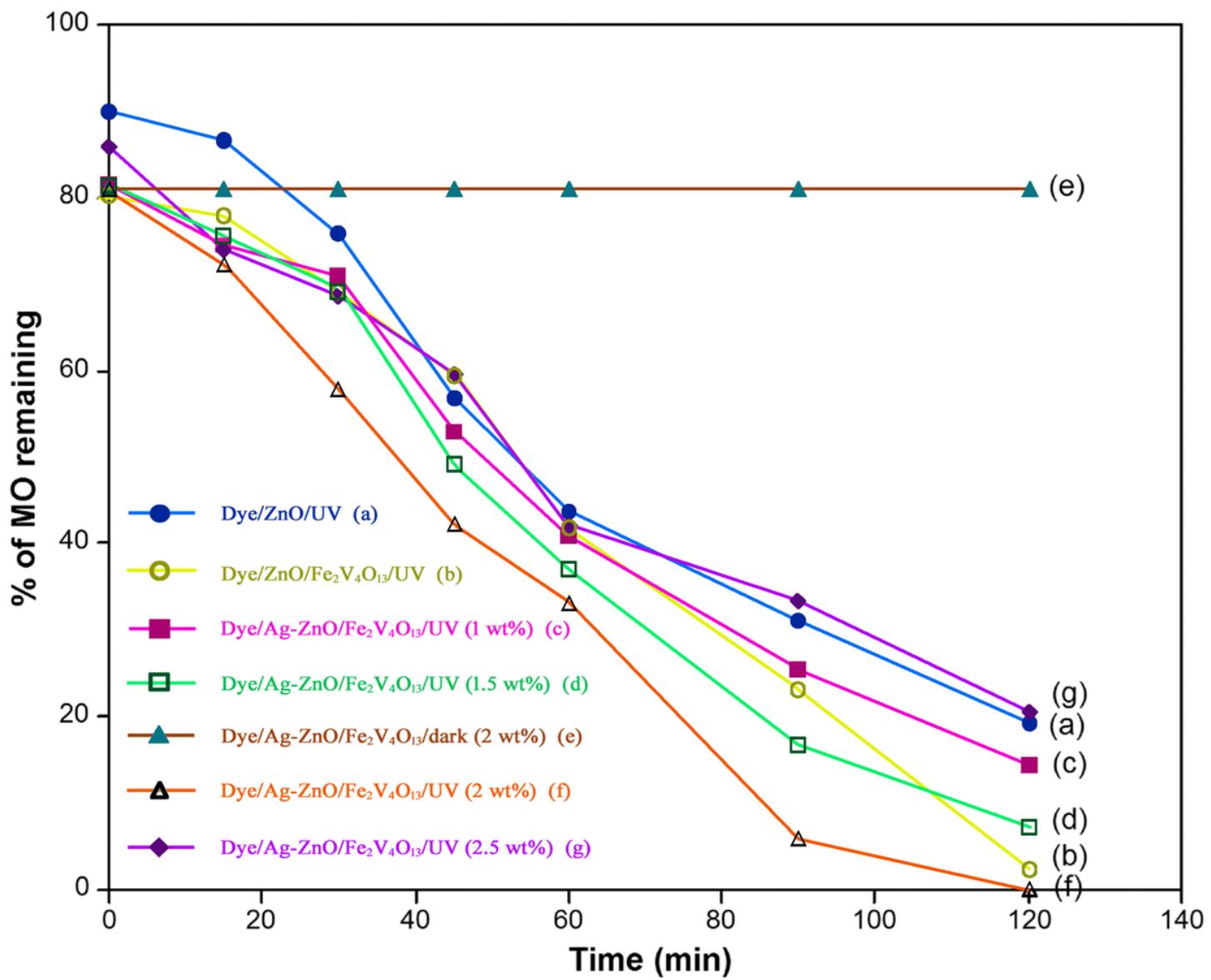


Figure 10

Primary analysis of Ag-ZnO/Fe₂V₄O₁₃ catalyst with MO under UV-A light. [MO] = $4 \cdot 10^{-4}$ M, 2 wt% Ag-ZnO/Fe₂V₄O₁₃ = 2 g L⁻¹, airflow rate = 8.1 mL s⁻¹, pH = 7.0, I_{UV} = $1.381 \cdot 10^{-6}$ einstein L⁻¹ s⁻¹.

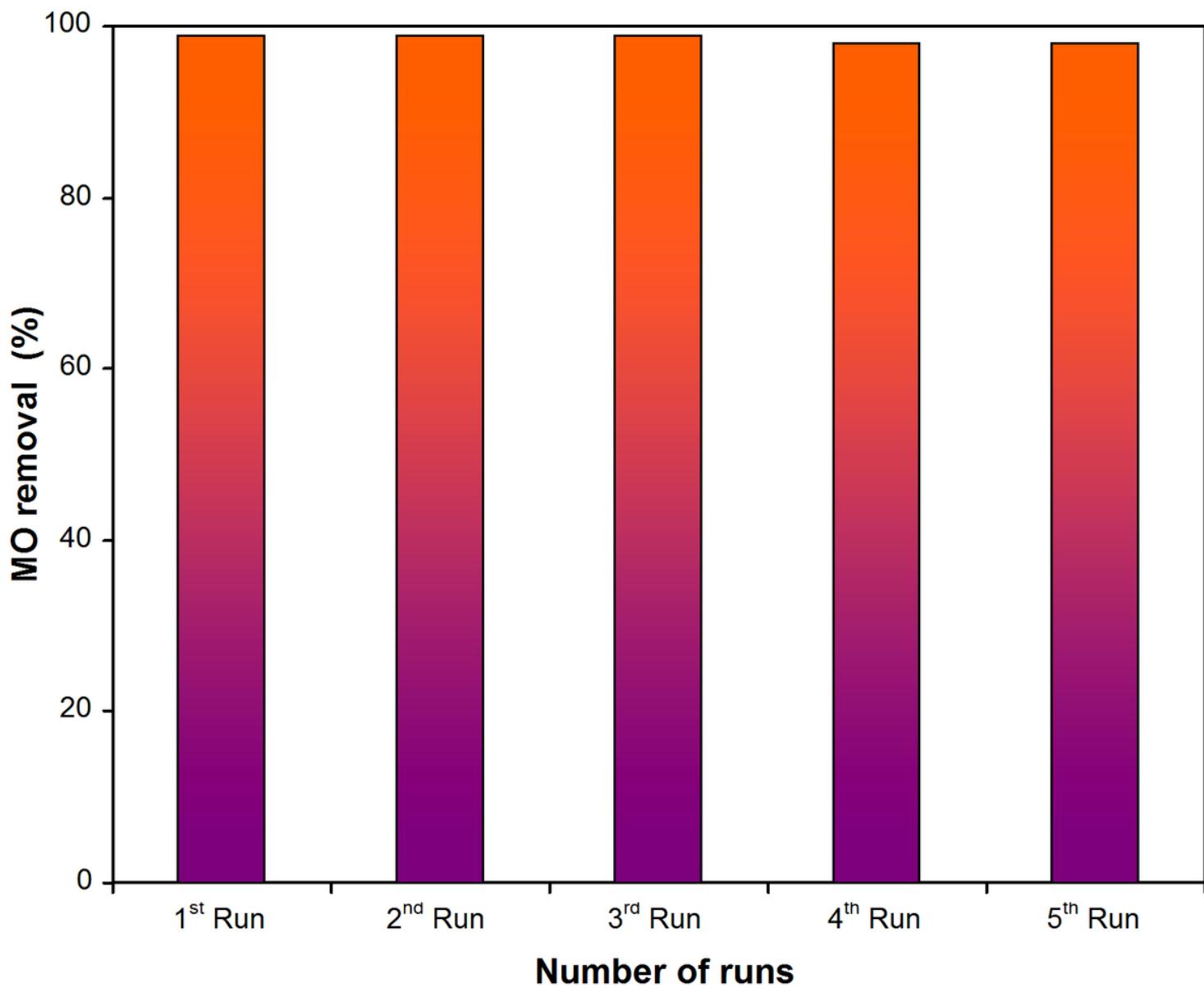


Figure 11

Reusability. $[MO] = 4 \times 10^{-4} M$, 2 wt% Ag-ZnO/Fe₂V₄O₁₃ = 3 g L⁻¹, airflow rate = 8.1 mL s⁻¹, pH = 7.0, irradiation time = 90 min, $I_{UV} = 1.381 \times 10^{-6}$ einstein L⁻¹ s⁻¹.

Figure 12

Overlay spectrum of MO. $[MO] = 4 \times 10^{-4} M$, 2 wt% Ag-ZnO/Fe₂V₄O₁₃ = 3 g L⁻¹, pH = 7.0. a) 0 min, b) 15 min, c) 30 min, d) 45 min, e) 60 min, and f) 90 min

Figure 13

Schematic representation of Ag-ZnO/Fe₂V₄O₁₃ nanocomposite mechanism of dye degradation.

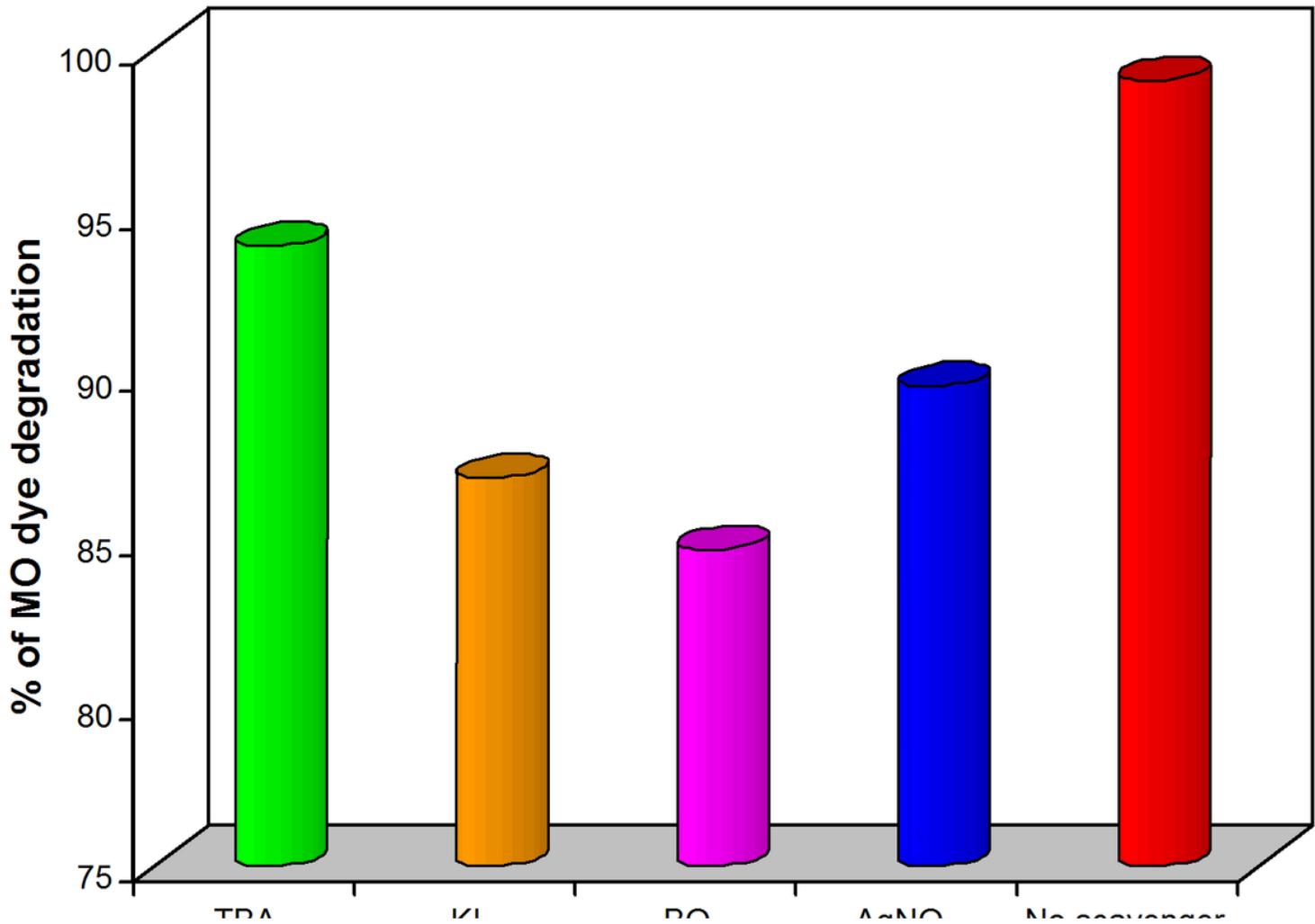


Figure 14

Effect of different scavengers on MO degradation with Ag-ZnO/Fe₂V₄O₁₃

Supplementary Files

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- 04Supplementarymaterial.doc
- GraphicalAbstract.doc
- Scheme01.png