

High Photocatalytic Performance of ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ Nanostructures Thin Films against Methylene Blue Dye under Visible Light Irradiation

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Abstract: Zinc Oxide (ZnO) nanorods and titanium dioxide (TiO₂) nanostructures thin films were deposited onto glass substrates by the chemical bath deposition (CBD) method. The ZnO was in the form of nanorods (NRs) while TiO₂ was grown as nanoflower plate as confirmed by Field-Emission Scanning Electron Microscope (FESEM) images. The ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ nanostructures thin films were prepared via drop-casting Fe₃O₄ NPs onto the grown ZnO and TiO₂ nanostructures thin films. The diameter of Fe₃O₄ NPs deposited onto the ZnO NRs thin films and TiO₂ nanostructures thin films was in the range of 8 to 59 nm. The crystalline structure of prepared samples was investigated through X-ray diffraction (XRD) method. The particle size of Fe₃O₄ was estimated by XRD as well as FESEM images to be around 22 nm. The photocatalytic activity of the as-prepared ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ nanostructures thin films was investigated against methylene blue (MB) dye at room temperature with a pH value of 10 at different exposure time by visible light. The photodegradation rate of MB dye by ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ nanostructures thin films was higher than that of ZnO and TiO₂ nanostructures thin films. The best photodegradation rate of MB dye was 100% after exposure time of 180 min, displayed by ZnO/Fe₃O₄ nanostructures thin film whereas it was 82% for TiO₂/Fe₃O₄ nanostructures thin films after exposure time of 240 min.

Keywords: ZnO/Fe₃O₄, TiO₂/Fe₃O₄, nanostructured, photocatalysis, MB dye.

1. INTRODUCTION

In recent years, pollutants such as organic material were increased in the water as a results to the great expansion of the industry and the spread of factories on the banks of rivers that led to cause a serious environmental problems leading to appear various diseases because of their bio-accumulate in the body of living organisms and capability to be persistent in the environment. Removing these pollutants from the water is very important, but by using environmentally safe and effective methods. Degradation of these pollutants from water can be done using photocatalyst metal oxide materials such as TiO₂ and ZnO which have high removal ability for polluted toxic organic material with simple and low-cost processes [1, 2]. Metal oxides materials in general have a wide band gap in the near-UV region, strong oxidation ability, non-toxic as well as stable chemically [2, 3]. ZnO and TiO₂ can be used to remove and degrade organic dyes like methylene blue (MB) to CO₂ and H₂O under UV light irradiation but the use of ultraviolet light is undesirable because of the

harm it causes to humans [4, 5]. Therefore, various modifications such as metal and non-metal doping, and coupling with other semiconductors and noble metals have been used to enhance the visible light absorption of metal oxide [5, 6]. When metal oxide photocatalyst combine with a magnetic compound such as FeO, Fe₂O₃, and Fe₃O₄, the photocatalytic activity for degradation organic dyes will happen under visible light [7]. The Fe₃O₄ compound has attracted more attention from researchers because of it's the good ability for using as a photocatalytic material. A.V. Tajareh et al. [8] used Fe₃O₄ to enhance photocatalytic hybrid of prepared TiO₂/Fe₃O₄ and TiO₂/Fe₃O₄/MWCNT nanostructures and obtained a high photodegradation rate and better recyclability. Further, C. Karunakaran et al. [9] prepared Fe₃O₄/ZnO nanostructure as a photocatalysts and they found that the compound appeared effective photodegradation of organic pollutants under UV and visible light irradiation [9].

In the present work, ZnO and TiO₂ nanostructures thin films were prepared via chemical bath deposition (CBD) method while ZnO/Fe₃O₄ and

TiO₂/Fe₃O₄ nanostructures thin films were synthesized by casting Fe₃O₄ nanoparticles onto the grown ZnO and TiO₂ thin films. The photocatalytic activity against MB dye of all prepared samples were investigated using a pH of 10 under visible light exposure.

2. MATERIALS AND METHODS

2.1. Preparation of ZnO NRs and TiO₂ nanostructured thin films

The ZnO nanostructures thin films were prepared onto glass substrates via the chemical bath deposition method as described in our previous work [4] while TiO₂ nanocrystalline thin films were prepared by CBD method onto glass substrates using the same parameters that used by Salman et al. [10]. However, briefly substrates were cleaned by hydrochloric acid (HCl), 2-propanol, ethanol subsequently using ultrasound cleaner. Substrates were vertically immersed in the beaker contains precursor of 4 ml of titanium (III) chloride (TiCl₃) solution, 50 ml deionized water (DI), and 0.1 M of urea [NH₂CONH₂] that was added to adjust the pH of the solution to 0.5. After stirring at room temperature for 1 h, a homogeneous violet solution was obtained. The solution temperature is fixed at 55°C for 3 h and after finishing, substrates were removed from the beaker, cleaned by distilled water (DW), and annealed at 350°C for 1h to enhance the crystallinity of prepared samples.

2.2. Preparation of Fe₃O₄ nanoparticles

The Fe₃O₄ nanoparticles were prepared using a facile hydrothermal method. The FeCl₂ and FeCl₃ with a molar ratio of 1:2 were dissolved in 50 ml of deionized water (DI) and then a drop wise of 1M sodium hydroxide (NaOH) was added to the solution under continuous stirring to adjust pH value at 10. The mixture was transferred to a 70 ml of Teflon-lined stainless-steel autoclave that was fixed inside the oven at a temperature of 200°C for 4hr. After the preparation process was completed, the autoclave was taken out from the oven and left to cool naturally. A dark red precipitate was obtained indicating to form Fe₃O₄ nanoparticles. The obtained product was washed by DI water and ethanol for three times using a centrifuge. Further, the prepared Fe₃O₄ nanoparticles were annealed at 550°C for 2 h to

enhance the crystallinity.

2.3. Synthesis of TiO₂/Fe₃O₄ and ZnO/Fe₃O₄ nanostructured thin films

A 0.1 g of Fe₃O₄ nanoparticles were suspended in 100 ml of DI and the solution was sonicated for 10 min with the power of 800 Watt using sonicator type Tefic Biotech Co., Limited 10 min. The prepared solution is cast on ZnO nanorods and TiO₂ nanostructures thin films to prepare both ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ nanostructures thin films. Prepared samples were annealed at 350°C for 1h to enhance interfacial contact between the core (ZnO& TiO₂) and shell (Fe₃O₄) layer.

2.4. Samples characterization

Surface morphology of prepared ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ nanostructures thin films grown onto glass substrates through the CBD method was investigated through Field-Emission Scanning Electron Microscope (FESEM) type FEI Nova NanoSEM 450. Crystalline structure of prepared samples was studied by X-ray diffraction method using XPertPro (MPD) (Panalytical-The Netherland). All measurements were done at Nanotechnology lab., Department of Physics, College of Science, University of Basrah.

2.5. Photocatalytic Study

Photocatalytic activity of ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ nanostructures thin a film was investigated using an aqueous of 200 ml DW contains 0.001 g of Methylene Blue (MB) dye. Prepared ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ nanostructures thin films were placed in a beaker contains 40 ml of MB dye solution and illuminated by 82 mW/m² of visible light. The degradation ratio of MB day solution is estimated using various values of pH, temperature, and time of exposure. The degradation rate of MB dye was calculated using below formula [11]:

$$\text{Degradation rate}(\%) = \frac{A_0 - A}{A_0} \times 100\% \quad (1)$$

Where A_0 , A are the absorbance value before and after exposure by visible light for several minutes, respectively. However, absorbance spectra of MB dye that catalyzed by ZnO, ZnO/Fe₃O₄, TiO₂, and TiO₂/Fe₃O₄ nanostructures thin film were measured by spectrometer type (PASCO SPECTROMETER PS-2600).

The pH value of MB dye solution was fixed at 10 by adding some drops of NaOH solution. The pH was control the type of surface charge of the

photocatalytic where the surface charge of photocatalytic will be positive in the acidic medium and negative in the basal medium. Degradation kinetics (k) of the MB dye can be described using the first-order Langmuir equation represented by [3]:

$$C = C_0 e^{-kt} \quad (2)$$

Where t is the time of the reaction, C_0 is the initial concentration of MB dye, C is the concentration after exposure, and k is the first order constant of the degradation reaction. The concentration is calculated according to Beer–Lambert’s law [12]:

$$A = \varepsilon C l \quad (3)$$

Where A is absorbance, ε is representing of molar absorptivity was taken of value from our previous study [4], and l is the UV light path length (1 cm).

3. RESULTS AND DISCUSSION

3.1. Surface morphology

Figure 1 shows the FESEM image of ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ nanostructures thin films grown onto glass substrates through the CBD method.

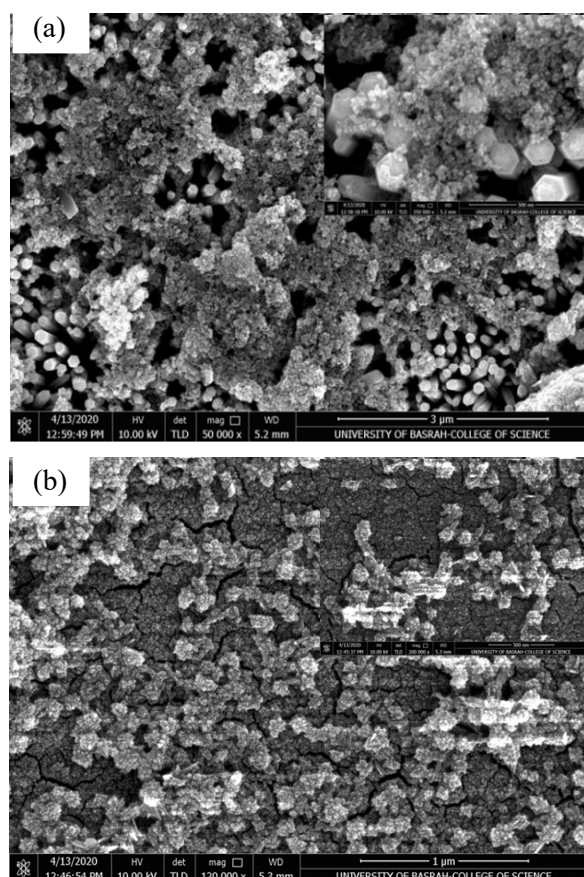


Fig. 1. FESEM images of the (A) ZnO/Fe₃O₄ thin film and (B) TiO₂/Fe₃O₄ thin film.

The ZnO thin film were grown as a nanorods (NRs) with a diameter range of 10–130 nm while the Fe₃O₄ were grown as a nanoparticles (NPs) covered the surface of ZnO NRs as shown in Fig.1A. Figure 1B shows the FESEM image of TiO₂/Fe₃O₄ nanostructures thin film grown onto a glass. Figure 2 shows the distribution of the Fe₃O₄ NPs diameters using ImageJ software and found that the diameter range was 8–59 nm with dominated particles diameter between 10 and 30 nm.

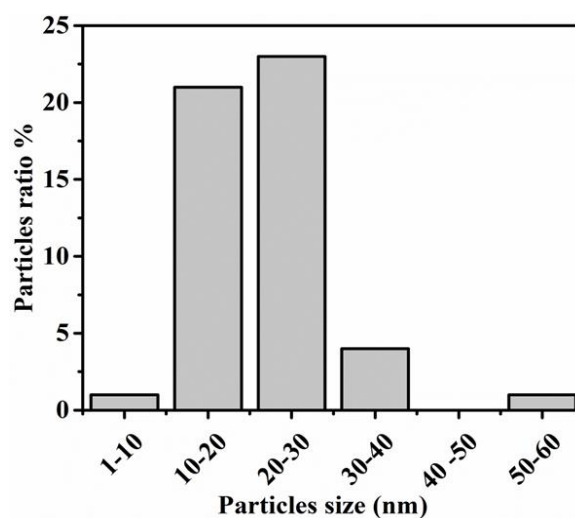


Fig. 2. Statistical distribution of the Fe₃O₄ NPs.

3.2. Crystalline structure

Figure 3A shows XRD pattern of Fe₃O₄ NPs that appeared diffraction peaks at 2θ of 30.10°, 35.57°, 43.20°, and 57.17° that corresponding to crystalline planes of (220), (311), (400), and (511), respectively of Face Center Cubic (FCC) of Fe₃O₄ according to standard XRD database (JCPDS card no. 19-0629). However, the XRD results confirmed that no other phase of other compounds was formed. Furthermore, the crystal size of Fe₃O₄ was 22 nm which is calculated using the Scherrer equation [13]. Figure 3B shows XRD pattern of ZnO/Fe₃O₄ nanostructures thin films that appears XRD peaks at 2θ of 31.78°, 34.43°, 36.24°, 47.52°, and 56.56° that related to crystalline planes of (100), (002), (101), (102), and (110), respectively of hexagonal (wurtzite) structure of ZnO (JCPDS card No., 36-1451) [14, 15]. Figure 3C shows the XRD pattern of TiO₂/Fe₂O₃ nanostructures and observed XRD peaks at 2θ of 25.17°, 38.31°, 47.782°, and 54.753° which corresponding to planes of (011), (110), (020), and (121), respectively of anatase TiO₂ compound

(JCPDS file No. 96-900-4143 and 96-900-8216) [16]. However, the low XRD intensity indicates to poor crystallinity of TiO_2 as well as the absence the diffraction peaks that corresponding to Fe_3O_4 is due to the low ratio in sample.

3.3. Photocatalytic degradation of MB dye

Figure 4 shows the relationship between photodegradation rate of MB dye and irradiation time for ZnO , $\text{ZnO}/\text{Fe}_3\text{O}_4$, TiO_2 , and $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanostructures thin film and noted the photodegradation rate of ZnO NRs is 28% at 240 min while for $\text{ZnO}/\text{Fe}_3\text{O}_4$ nanostructures thin film at 150 min is 87% and reached to 100% after exposure by visible light for 180 min. Moreover, the photodegradation rate of TiO_2 nanostructures thin film is 26% at 240 min while $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanostructures thin film appears photo-degradation rate of 82% at the same time of the irradiation.

Although, the base medium of the MB solution increases formation of hydroxyl radicals OH

that leads to increase photocatalysis process [16, 17]. The obtained results show the $\text{ZnO}/\text{Fe}_3\text{O}_4$ and $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanostructures thin films appeared photocatalysts higher than the photocatalysis that aobtained by ZnO and TiO_2 thin films because of the synergic effect between metal oxides material and magnetic material of Fe_3O_4 . The Fe^{3+} ions in Fe_3O_4 will work to prevent recombination charge carriers in metal oxide catalysts that could be led to improve the photocatalysis process [17–19]. Y. Lei et al. got a photodegradation rate of 18.9% obtained by $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanostructure at 180 min of illumination [20] while T. Tan et al. obtained a photodegradation rate of 87.9% for $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanostructure [21]. The degradation mechanism of $\text{ZnO}/\text{Fe}_3\text{O}_4$ depending of absorbing photons by both ZnO and Fe_3O_4 and form the electron/hole pairs. However, ZnO and Fe_3O_4 have a positions of conduction bands (-0.45 eV and -0.58 eV vs NHE) and valence bands ($+2.75$ eV and $+0.99$ eV vs NHE), respectively [22].

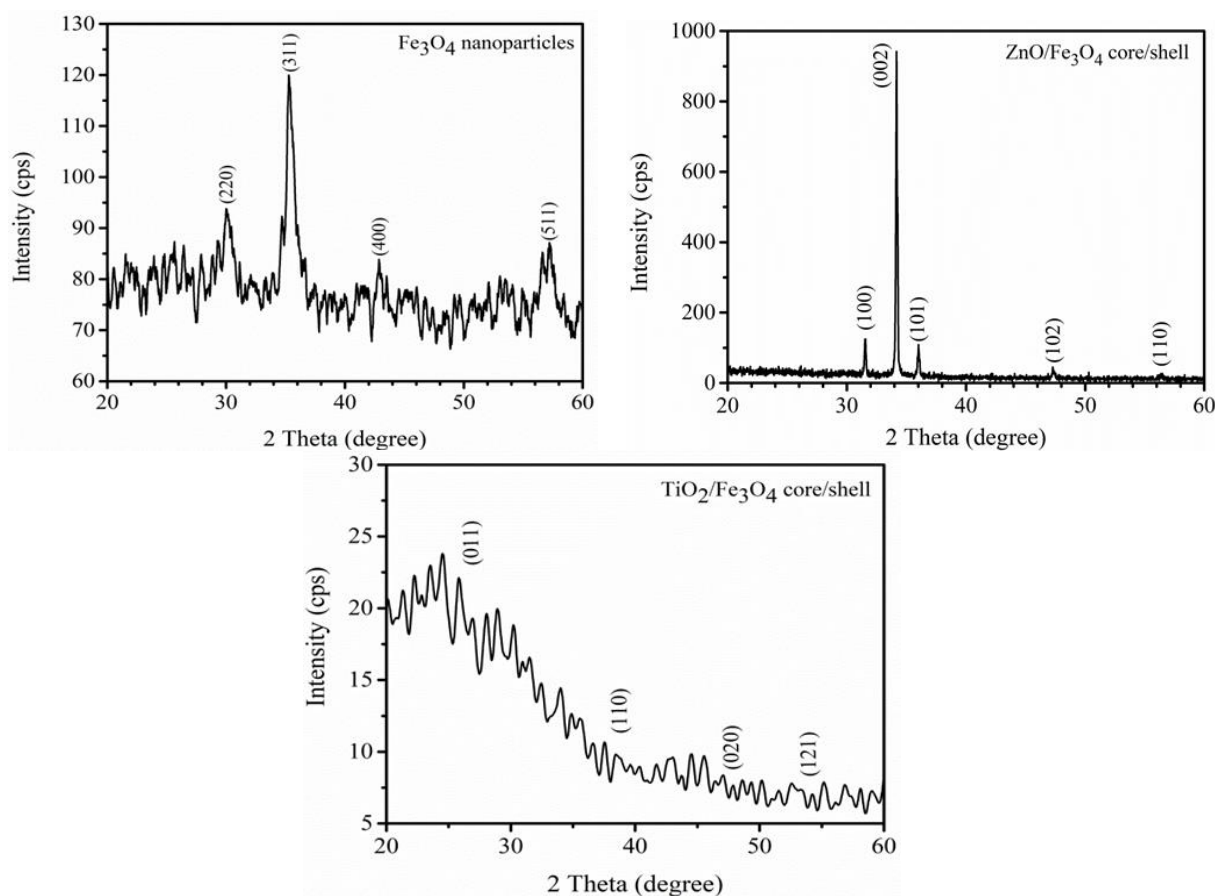


Fig. 3. XRD patterns of Fe_3O_4 NPs, $\text{ZnO}/\text{Fe}_3\text{O}_4$ thin film, and $\text{TiO}_2/\text{Fe}_3\text{O}_4$ thin film.

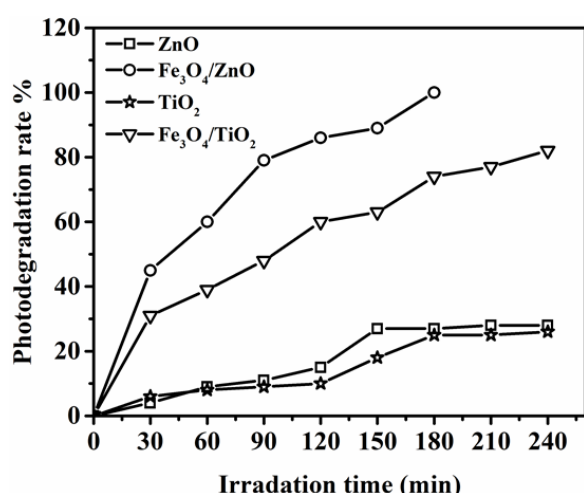
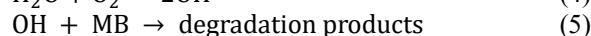
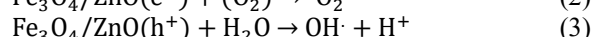
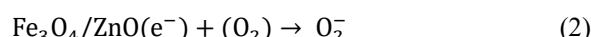
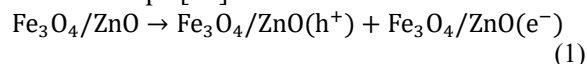


Fig. 4. MB dye photodegradation rate vs. illumination time for ZnO, TiO₂, ZnO/Fe₃O₄, and TiO₂/Fe₃O₄ nanocrystalline thin films.

Therefore, the electrons of the conduction band (CB) of Fe₃O₄ would migrate to the ZnO while holes at the valence band (VB) of Fe₃O₄ would remain that led to reduce the electron/hole recombination. Thus, the photocatalytic activity of the Fe₃O₄/ZnO is better than of pure ZnO. Then, the OH⁻ present in the aqueous solution will capture by the hole of the valence band to form highly reactive OH radical. Finally, the dye molecules attacked by the radical to decompose into simple products as shown by the following reaction steps [23]:



The enhancement of the photocatalytic activity of Fe₃O₄/TiO₂ nanoparticles can be interpreted by energy level theory: the energy level of Fe³⁺/Fe²⁺ closes to the energy level of TiO₂'s conduction band, and the energy level of Fe³⁺/Fe⁴⁺ closes to the energy level of TiO₂'s valence band. Thus, the Fe³⁺ ions that dissolved from Fe₃O₄ nanoparticles can act as a capture electron position as well as work as a hole capture position that led to decrease the electron-hole pair recombination of TiO₂ [24]. Figure 5A shows the C/C₀ plot vs. irradiation time of ZnO, ZnO/Fe₃O₄, TiO₂, and TiO₂/Fe₃O₄ nanostructures thin film catalyzed MB dye and found that the concentration of MB dye was decreased when irradiation time was increased. Figure 5B shows the variation of -ln(C/C₀) vs. irradiation time for the prepared catalysts nanostructures thin films. Furthermore, the kinetic rate of degradation of MB dye was calculated from the slope and it was 0.00156 min⁻¹ and 0.0141min⁻¹ for ZnO and ZnO/Fe₃O₄ nanostructures thin films, respectively. The kinetic rate of TiO₂ and TiO₂/Fe₃O₄ nanostructures thin films was 9.9333 x 10⁻⁴ min⁻¹ and 0.0068 min⁻¹, respectively. Increasing the kinetic rate value led to convert the reaction kinetics and the equilibrium properties of the adsorbent process [25].

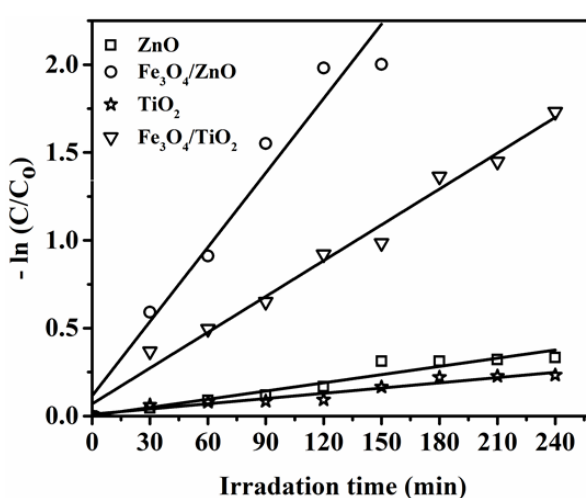
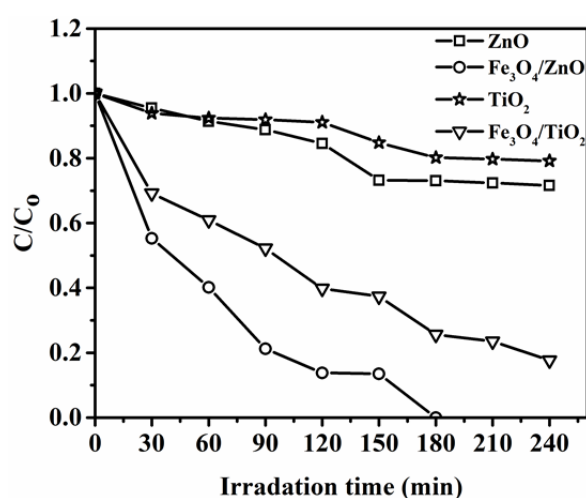


Fig. 5. (A) Kinetics of photocatalytic degradation with irradiation time (B) Variation of -ln(C/C₀) with irradiation time under visible light for ZnO, TiO₂, ZnO/Fe₃O₄, TiO₂/Fe₃O₄ nanostructured thin films.

Table 1. Photocatalytic activity of different Fe₃O₄ nanostructures

Photocatalysts	Morphology	Photodegradation rate %	Irradiation of time (min)	Dye type	K(min ⁻¹)	Reference
Fe ₃ O ₄ /ZnO	Core-Shell NPs	18.9	180	MB	0.00958	[20]
Fe ₃ O ₄ /ZnO	Core-Shell NPs	73	60	MO	0.00221	[26]
Fe ₃ O ₄ -ZnO	Core-Shell NPs	94	120	MB	208x10 ⁻⁴	[15]
TiO ₂ /Fe ₃ O ₄	NPs	80.8	120	MB	--	[27]
TiO ₂	NPs	19.04	240	MO	--	[8]
TiO ₂ /Fe ₃ O ₄		19.02			--	
ZnO/Fe ₃ O ₄	Nanostuctur	100	180	MB	0.01411	Current work
TiO ₂ /Fe ₃ O ₄	Nanosrtuctur	82	240	MB	0.0068	Current work

4. CONCLUSIONS

ZnO NRs thin films and TiO₂ nanostructures thin films were grown onto glass substrates by the CBD method. The ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ thin films were prepared by drop casting of Fe₃O₄ NPs onto the grown ZnO and TiO₂ nanostructures thin films. The photocatalytic activity against MB dye was investigated at pH value of 10 under visible light irradiation. The photodegradation rate of MB was increased when used as-prepared ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ nanostructures thin films photocatalysts with increasing irradiation time. The enhancement of the photocatalytic activity of the as-prepared ZnO/Fe₃O₄ and TiO₂/Fe₃O₄ nanostructures thin films could be due to the absorbance of light by Fe₃O₄ nanoparticles in the visible region. Moreover, the Fe⁺³ could act to prevent recombination carriers in metal oxide (ZnO) catalysts which can lead to improved photocatalytic activity.

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