Photocatalytic Degradation of Paracetamol and Cefixime Trihydrate Drugs using Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag Nanocomposites

Mansoor Farbod (PhD)[1]* , Vahid Kargar Dehbidi (PhD)[1]

[1]Department of Physic, Faculty of Science, Shahid Chamran University of Ahvaz, Ahvaz, Iran

ABSTRACT

Background: The pharmaceutical residues and their metabolites in water, even at low concentrations, is of concern due to their effects on the aquatic environment.

Objective: The current study aimed to investigate the photocatalytic degradation of paracetamol and cefixime trihydrate drugs from aqueous media using nanocomposites.

Material and Methods: In this experimental study, the photocatalytic degradation of paracetamol and cefixime trihydrate drugs have been investigated using Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites. XRD, FESEM, EDS, elemental mapping (e-mapping) and UV-Visible analysis were used to characterize the nanocomposites.

Results: The photocatalytic performance efficiency of Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites was 45% and 72%, respectively, for paracetamol in 180 min. However, the photocatalytic performance efficiency of Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites for the degradation of cefixime trihydrate was 38% and 55%, respectively during 60 min.

Conclusion: Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites demonstrated effective photocatalytic performance in the removal of paracetamol and cefixime trihydrate drugs.

Introduction

Pharmaceuticals are recognized as a significant category of water pollutants, with growing public and scientific concern about their presence and potential impacts on human health and the environment [1,2]. Pharmaceuticals in wastewater are considered non-biodegradable and toxic pollutants [3]. Although these drugs are prescribed to treat millions of fatal diseases, they can have negative effects on the ecosystem and the environment. Medicinal compounds in water, are resistant to degradation, causing harmful effects on living organisms as active pharmaceutical components. Many pharmacologically active compounds, such as antibiotics, analgesics, steroids, hormones, and nonsteroidal anti-inflammatory drugs, have been frequently detected in water systems due to human, animal, and plant activities [4]. Pharmaceutical industries, individuals, hospitals, sewage treatment plants, and

*Corresponding author:
Mansoor Farbod
Department of Physic, Faculty of Science, Shahid Chamran University of Ahvaz, Ahvaz, Iran
E-mail:
Farbod_m@scu.ac.ir

other medical services are obvious sources of these pollutants. However, their amount in the ecosystem is very low, and their non-stop deposit can have fatal effects on nature and water quality [5]. Cefixime is an important and widely used antibiotic that is chemically instable and unsoluble in water, resulting in low bioavailability, about 40-50% [6]. Its solubility in water depends on pH, increasing as the pH rises. Cefixime is prescribed for a wide range of diseases associated with bacterial infections such as pneumonia, bronchitis, syphilis, gonorrhea, and ear, throat, lung, and urinary tract infections [7]. Cefixime trihydrate is the crystalline form of cefixime, which is very stable and is one of the most important antibiotics used in the world [8]. Paracetamol, as acetaminophen, is one of the most widely used drugs worldwide [9] and an organic compound, which is used as an antipyretic and reliever for migraine, headache, muscle pain, neuralgia, back pain, toothache, and general pain. In addition, paracetamol is frequently used as an important ingredient in the processing of photographic chemicals and dyes [10,11]. In recent years, paracetamol, like other pharmaceutical compounds, has become a global concern due to its environmental stability and resistance to removal by conventional water and wastewater treatment methods [12,13], leading to the bioaccumulation of these medicinal substances and damage to the ecosystem [14]. Consequently, researchers have been increasingly paying attention to understanding its toxic properties and developing effective removal methods.

On the other hand, traditional methods for treating such wastes are not effective methods. Among different chemical methods, advanced oxidation processes using heterogeneous photocatalysts to remove organic pollutants have received more attention [15]. The photocatalytic process starts with the absorption of a photon with an energy greater than the energy band gap of the photocatalyst [16]. Absorption of photons creates electron-hole pairs on the surface of the catalyst, and these pairs create different radicals in aqueous environments that can reduce or oxidize organic substances in aqueous solutions. The main advantage of this method is the conversion of organic pollutants into non-toxic species (CO_2, H_2O) and no need for more separation processes [17]. Semiconductor material such as ZnO is known as one of the best photocatalysts [18]. Although ZnO has many advantages, including non-toxicity, high quantum efficiency, and strong absorption in the ultraviolet region, it does not have ideal photocatalytic performance due to the wideband gap of ZnO, resulting in generating electron holes using only ultraviolet sunlight. Another issue with ZnO is the rapid recombination of electron-hole pairs, which lowers its photocatalytic efficiency [19]. Therefore, various efforts have been made to improve the photocatalytic performance of ZnO, including the precipitation of noble metals, the addition of intermediate metal ions, and coupled semiconductor photocatalysts [8]. Coupling other semiconductors to form non-homogeneous junctions with ZnO is interesting due to the interfacial interactions of the different bilayers that create new properties that do not depend on either nanoparticle alone. Extended carrier lifetime and increased bilayer charge transfer can be obtained from these inhomogeneous structures. Semiconductors with narrowband gaps, such as Fe_2O_3, WO_3, Cu_2O, and CdS are used as semiconductors coupled with ZnO [20].

Among the different phases of iron oxide, Fe_2O_3 has the most thermodynamic stability under environmental conditions. It is cheap and environmentally friendly. It has high resistance to photon erosion, and is usually used as a photocatalyst in the visible light region [21]. Composites of ZnO semiconductors with Fe_2O_3 can increase the photocatalytic activity by accelerating the separation rate of charge carriers. On the other hand, the sites of noble metals (Cu, Ag, Au) can trap the generated photoelectrons and also increase the light

absorption by ZnO by Surface Plasmon Resonance (SPR). Both effects markedly facilitate the redox reactions and increase the photocatalytic activity [22]. Specifically, Ag nanoparticles on the photocatalyst surface have two different characteristics: (1) an increase in the light absorption range due to SPR absorption and (2) a decrease in the recombination rate due to the formation of Schottky junction at the interface, which creates an internal electric field at the junction [23]. In the present research, the Fe_2O_3-ZnO nanocomposite with the ratio (10:90) was first prepared. The photocatalytic performance of Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites was investigated for the removal of paracetamol and cefixime trihydrate drugs, with a focus on the role of Ag in enhancing the performance of the Fe_2O_3-ZnO/Ag nanocomposite.

Material and Methods

Materials

In this experimental study, sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$), iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), zinc oxide nanostructures (ZnO), silver nitrate ($AgNO_3$), and ethanol, all manufactured by Merck, were utilized. Paracetamol and cefixime trihydrate were sourced from Solarbio, and all materials were of laboratory-grade purity and used without further purification.

Synthesis of Fe_2O_3 nanoparticles

Fe_2O_3 nanoparticles were synthesized, as follows [24]: First, 0.0070 g of $NaH_2PO_4.2H_2O$ was dissolved in 100 ml of water and heated to 95 °C. A total of 1.8 ml of $FeCl_3 \cdot 6H_2O$ solution with a concentration of 1.48 mol l^{-1} was added drop-vised to the above solution and kept at 100 °C for 14 hours. After the product was collected and washed several times with deionized water and pure alcohol, it was dried in an oven at 60 °C. At the end, the product was heated at 550 °C for 2 h.

Preparation of Fe_2O_3-ZnO nanocomposite

To prepare the Fe_2O_3-ZnO nanocomposite with the ratio (10:90), two separate suspensions were prepared. First, 0.180 g of ZnO powder was completely dispersed in 180 ml of water, and then 0.020 g of Fe_2O_3 particles was dispersed in 20 ml of water. In this research, the sonication method was used to disperse the particles uniformly in water. Then, these two suspensions were mixed together and strongly dispersed for 30 min. Finally, the obtained product was dried at 60 °C for 48 h.

Synthesis of Fe_2O_3-ZnO/Ag nanocomposite

In order to synthesize Fe_2O_3-ZnO/Ag nanocomposite, first, 0.0005 g of $AgNO_3$ was dissolved in 30 ml of ethanol for 15 min, and 0.0995 g of Fe_2O_3-ZnO nanocomposite was added to the solution and strongly dispersed for 40 min. The obtained solution was then vigorously stirred at 60 °C for 30 min. After reaching room temperature, the product was washed several times with water and acetone and then dried at room temperature [25].

Characterization of the samples

The samples were characterized by X-ray diffraction (XRD) using a PHILIPS (PW1730) diffractometer, at room temperature utilizing Cu K_α radiation with a wavelength of $\lambda = 1.54056$ Å and in the range of 10 to 80 degrees. FESEM-TESCAN-Mira4 was used to examine the size and shape of nanocomposite particles, and energy dispersive X-ray spectroscopy (EDS), and elemental mapping (e-mapping) were also used to study the elements in the nanocomposites and their distribution. The optical properties were performed using Photonix Ar 2015 spectrophotometer.

Photocatalytic decomposition tests

Decomposition of paracetamol and cefixime trihydrate drugs in aqueous solution was performed under UV radiation with the help

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of photocatalytic activity of Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites, using four 8 W UV lamps (Osram) placed at a distance of 10 cm above the reaction container. First, 50 ml of the drug solution with a concentration of 0.01 g/L and 0.025 g of the nanocomposite were kept in the dark for 45 min to achieve the proper balance of absorption and desorption of the drug molecules on the surface of the nanoparticles. The dark experiment is necessary to separate the surface absorption from the photocatalytic process. After that, the solution was exposed to UV radiation, and samples were taken at 15-minute intervals, and the amount of drug degradation was measured by measuring the UV-Vis spectrum. It is to be noticed that one of the standard ways to measure the concentration of dyes or drugs is to use their optical absorption. The intensity of the absorption peak is directly related to the concentration of dye or drug. In the photocatalytic degradation of dyes and drugs from aqueous media, the relative intensity of absorption peaks is used. Here, the concentration of paracetamol and cefixime trihydrate drugs is determined by the peak intensity at the

characteristic absorption wavelength of these drugs, which is at λ_{max}=244 nm and λ_{max}=286 nm, respectively.

A control experiment was conducted under optimal conditions since the photocatalytic process is the primary mechanism of drug degradation. This experiment involved drug photolysis under UV radiation without the use of a photocatalyst [26].

The photocatalytic degradation efficiency was measured using the absorption spectrum of the drug solution. The photocatalytic degradation efficiency was calculated using following Equation 1 [27]:

$$\frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

where C_0 and C_t are the initial drug concentration and the concentration after the photocatalytic reaction in different time intervals (t), respectively. For photon decomposition reaction kinetics, the Langmuir-Hinshelwood model was used, which is given by Equation 2 [28].

$$-\ln\left(C_t / C_0\right) = k_{app}t \qquad (2)$$

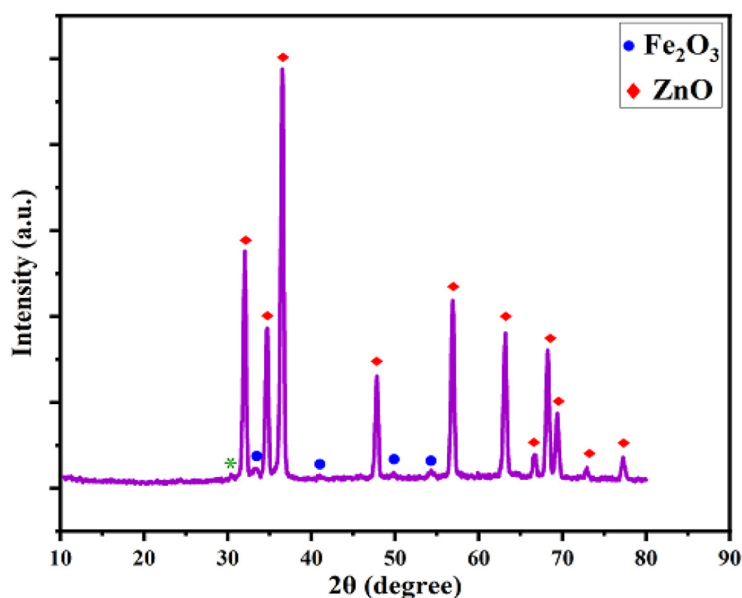where k_{app} is the pseudo-first-order rate

Figure 1: X-ray diffraction pattern of Fe_2O_3-ZnO nanocomposite, peaks related to Fe_2O_3 and ZnO are marked with a circle and diamond, respectively.

constant (min^{-1}), and t is the irradiation time (min).

Results

X-ray and structural analysis

The XRD pattern of the Fe_2O_3-ZnO nanocomposite is plotted in Figure 1. For Fe_2O_3 and ZnO phase analysis, JCPDS standard cards No. 33-0664 and 36-1451 were used, respectively. In Figure 1, the peaks related to ZnO and Fe_2O_3 are marked with diamonds and circles, respectively, according to the standard cards. The matching of the peaks with the standard cards and the absence of specific extra peaks in the XRD pattern indicate the high purity of the nanocomposite. Fe_2O_3 has a hematite phase with a rhombohedral corundum structure, and ZnO has a hexagonal crystal structure.

The observed tiny peak at about 31° is an impurity peak, attributed to the Fe_3O_4 phase (less than 0.1%). Meanwhile, the peak at 61° has no width and is background noise.

FESEM and morphological analysis

Figure 2 shows FESEM images of ZnO, Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites. The average diameter of these particles was measured using Digimizer software. ZnO has a mixed morphology of nanoparticles and nanorods with an average particle size of 83 nm and an average diameter of 72 nm, respectively. Fe_2O_3 has a particulate morphology with an average size of 28 nm. Since Ag particles are very small, it is practically impossible to identify them from FESEM images. On the other hand, by adding Ag particles to the Fe_2O_3-ZnO nanocomposite, the shape of this nanocomposite remains unchanged.

The EDS spectrum of Fe_2O_3-ZnO/Ag nanocomposite is shown in Figure 3, showing that the samples are almost free of any impurities. Fe_2O_3-ZnO/Ag nanocomposite contains Fe, O, Zn, and Ag elements. The presence of gold elements in the EDS spectrum is due to the use of gold coating on the sample in the preparation stage for taking the FESEM images.

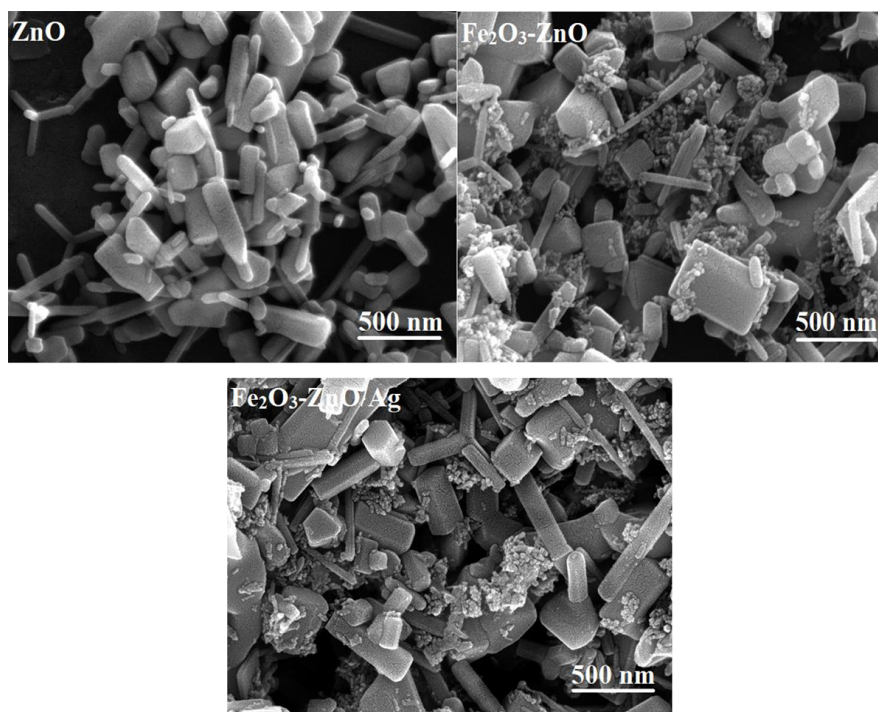In order to investigate the distribution of

Figure 2: FESEM images of ZnO, Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites.

elements in Fe_2O_3-ZnO/Ag nanocomposites, the elemental mapping test for Fe_2O_3-ZnO/Ag nanocomposite is shown in Figure 4. As can be seen, Fe, O, Zn and Ag elements have almost uniform distribution in this nanocomposite.

Optical properties

The UV-Vis absorption spectrum at room temperature of Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites is shown in Figure 5a. Nanocomposites with a concentration of 0.001 g
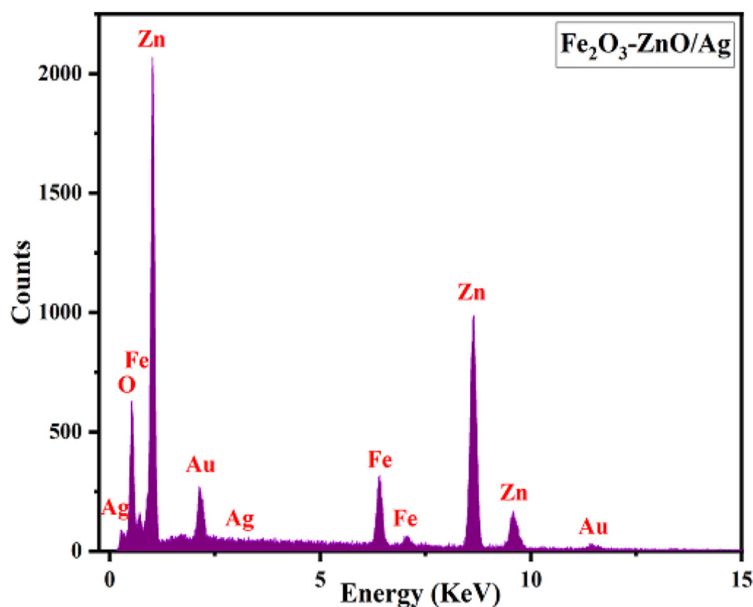

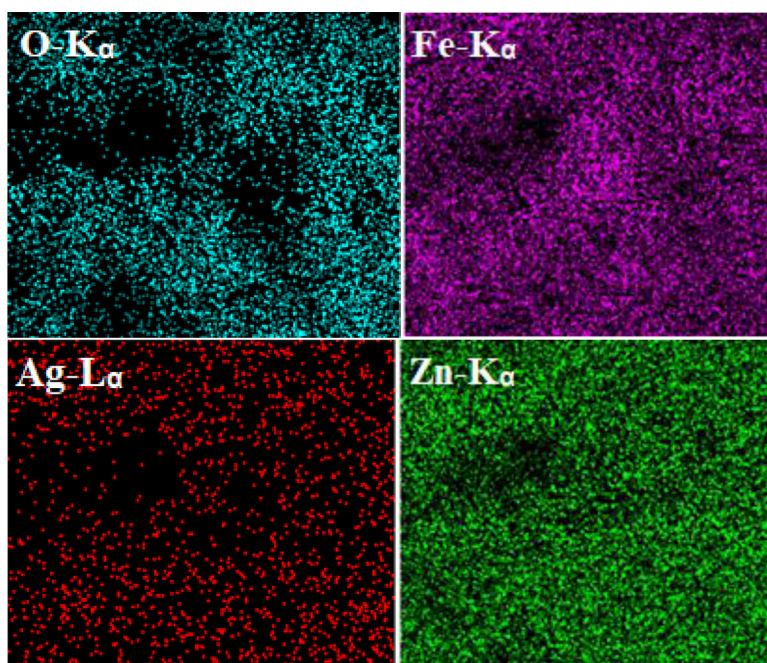**Figure 3:** Energy dispersive X-ray spectroscopy (EDS) spectrum of Fe_2O_3-ZnO/Ag nanocomposite.

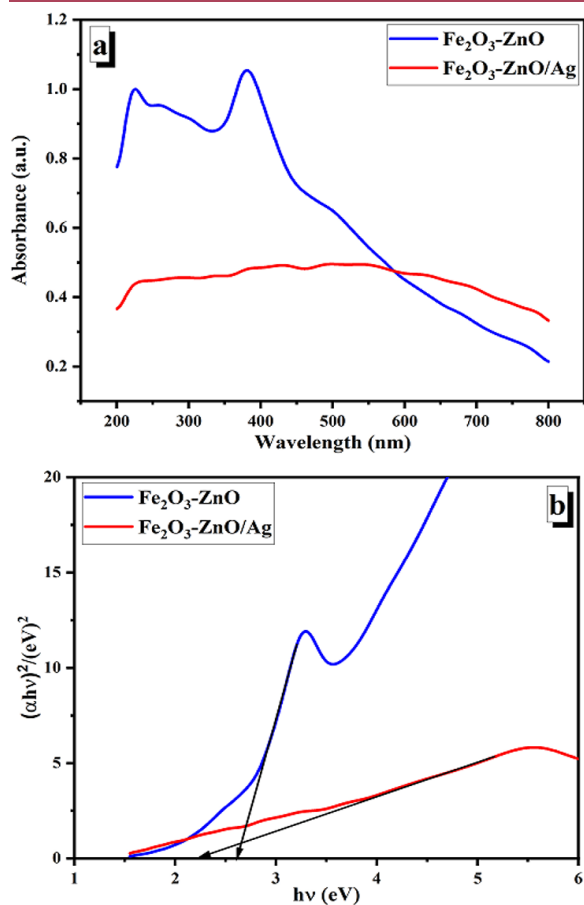**Figure 4:** Elemental mapping images of Fe_2O_3-ZnO/Ag nanocomposite.

Figure 5: a) UV-Vis spectrum and **b)** optical gap calculation of Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites.

$$(\alpha h\nu)^n = B(h\nu - E_g) \tag{3}$$

Where E_g is the optical gap energy, $h\nu$ is the photon energy, α is the absorption, B is the material constant, and n is equal to 2 for direct transitions and 1/2 for indirect transitions. The optical gap is obtained by plotting the linear part of the graph of $(\alpha h\nu)^n$ in terms of $h\nu$ and extrapolating towards zero. The absence of a linear relationship for n=1/2 indicates the directness of the transition in this energy for this nanocomposite. According to Figure 5b, the optical band gap for Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites is 2.60 eV and 2.22 eV, respectively. Adding Ag to the Fe_2O_3-ZnO nanocomposite reduces the band gap, which can increase the application potential of the Fe_2O_3-ZnO/Ag nanocomposite as a photocatalyst.

Investigation of photocatalytic activity

Figures 6 and 7 show the absorption spectrum of paracetamol and cefixime trihydrate solutions along with the normalized C/C_0 concentration graph and its logarithm versus UV irradiation time degraded by Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites. By increasing the irradiation time, the intensity of the absorption peak of these drugs gradually decreases, showing the photonic degradation of drugs by nanocomposites. In Figure 6, after 180 min, only 45% of the paracetamol has been destroyed by Fe_2O_3-ZnO nanocomposite, while using Fe_2O_3-ZnO/Ag nanocomposite, 72% of this drug has been removed. As a result, by adding Ag to Fe_2O_3-ZnO nanocomposite, the amount of paracetamol degradation has increased. The value of k_{app} for Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites was obtained as 0.003 and 0.007 min^{-1}, respectively, which indicates the increase of k_{app} value by adding Ag to Fe_2O_3-ZnO nanocomposite. In order to evaluate the photocatalytic activity of Fe_2O_3-ZnO/Ag nanocomposite in paracetamol degradation, the obtained removal efficiency was compared with other similar studies. For

were dispersed in 10 ml of water and then used for UV-Vis measurement. In the Fe_2O_3-ZnO nanocomposite, the characteristic absorption peak of ZnO at the wavelength of 381 nm is attributed to the intrinsic absorption band of ZnO [29]. In addition, this sharp peak shows the nanoscale and narrow size distribution of ZnO particles [30]. Figure 5 illustrates adding Ag nanoparticles to the Fe_2O_3-ZnO nanocomposite, and the absorption in the UV region (wavelength=200-400 nm) has decreased, while in the visible region, the amount of absorption in the wavelength range of 400-585 nm shows a decrease and an increase from 585-800 nm. The optical gap is determined based on the optical absorption spectrum using the Tauc's relation (Equation 3) [31]:
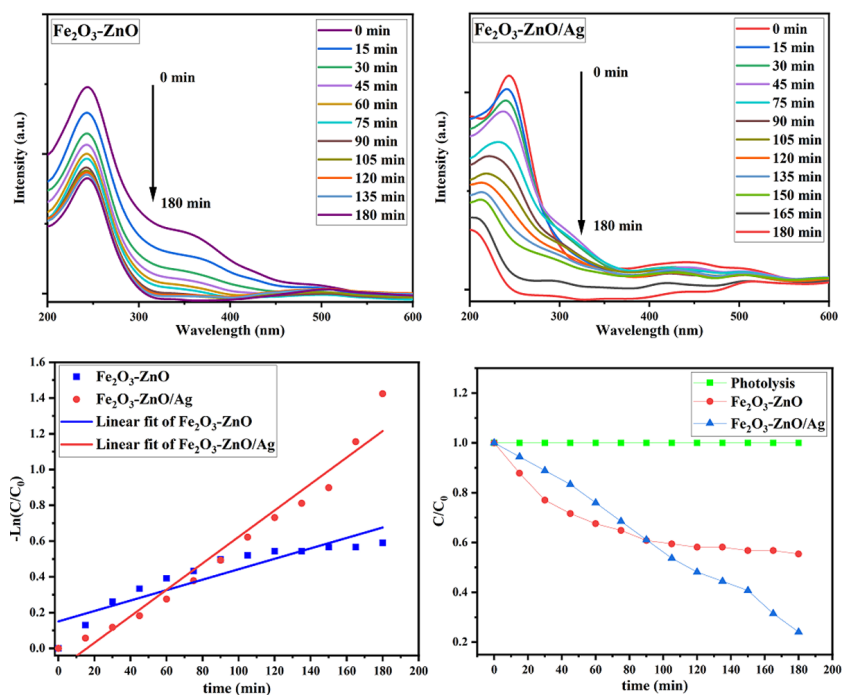
Figure 6: Absorption spectrum of Paracetamol solution along with the graph of normalized concentrations of C/C$_0$ and its logarithm versus UV irradiation time in the presence of Fe$_2$O$_3$-ZnO and Fe$_2$O$_3$-ZnO/Ag nanocomposites.
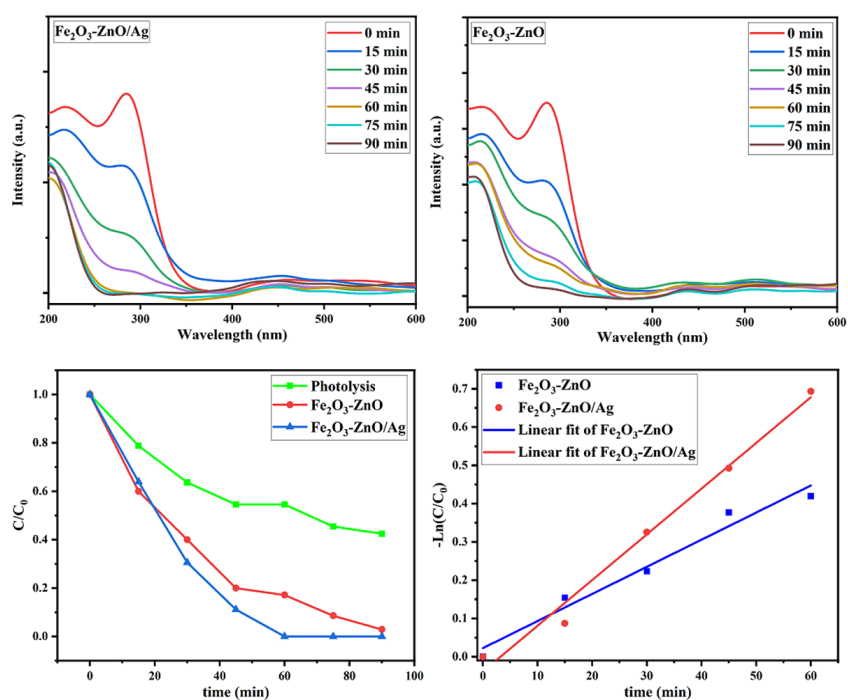

Figure 7: Absorption spectrum of cefixime trihydrate solution along with the graph of normalized C/C$_0$ concentrations and its logarithm versus UV irradiation time in the presence of Fe$_2$O$_3$-ZnO and Fe$_2$O$_3$-ZnO/Ag nanocomposites.

this purpose, a comparative study in terms of the initial concentration of the target pollutant (mg/L), solution pH, catalyst concentration (g/L), light source and intensity, irradiation time, and removal efficiency is presented and listed in Table 1.

Several parameters influence the photocatalytic degradation of a dye or drug, including the concentration of the dye or drug, the concentration of the photocatalyst, the power and wavelength of the light source, and the irradiation time. As the concentration of the photocatalyst, light source power, and irradiation time increase, the extent of degradation increases. Considering that in the current research, the concentration of Fe_2O_3-ZnO/Ag nanocomposite is 0.5 g.L^{-1}, and the initial concentration of the drug is 10 mg.L^{-1}; the type and power of lamp used (UV light of 32 W) and the irradiation time (60 min), the efficiency of photocatalytic degradation was (55%), it can be concluded that Fe_2O_3-ZnO/Ag nanocomposite had a much reasonable performance in the photocatalytic removal of cefixime trihydrate drug.

According to Figure 7, in 60 min, the total degradation of cefixime trihydrate in the presence of Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites was achieved with 83% and 100% efficiency, respectively. Meanwhile, 45% of this destruction was caused by the photolysis process of cefixime trihydrate. As a result, the efficiency of photocatalytic degradation for Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites during this period was calculated as 38% and 55%, respectively. k_{app} was calculated as 0.007 min^{-1} for Fe_2O_3-ZnO nanocomposite and 0.012 min^{-1} for Fe_2O_3-ZnO/Ag nanocomposite. As a result, by adding Ag to Fe_2O_3-ZnO nanocomposite, the photocatalytic performance has increased in the degradation of cefixime trihydrate.

The maximum destruction efficiency of 99.1% was obtained for the concentration of 0.41 g.L^{-1} of ZnO/α-Fe_2O_3 nanocomposite and 10.11 mg.L^{-1} of cefixime trihydrate, the intensity of UV-Vis light of 8 W.m^{-2} and the irradiation time of 127 min, [8]. Table 2 summarizes the results of photocatalysis of paracetamol and cefixime trihydrate using Fe_2O_3-ZnO and

Table 1: Comparison of the efficiency of different photocatalysts for paracetamol degradation.

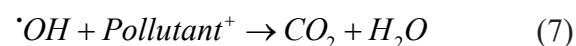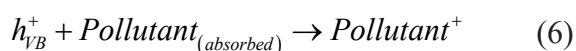| Catalyst	Concentration (mg/L)	pH	Catalyst dose (g/L)	Light source (Power)	Irradiation time (min)	Degradation efficiency (%)	Ref.
TiO_2-Fe_2O_3	50	NA	1.2	Mercury lamp (450 W)	90	100	[9]
Fe_2O_3-TiO_2	30	11	1.25	Solar simulator	180	95.5	[12]
Fe_2O_3-ZnO/Ag	10	7	0.5	UV lamp (32 W)	180	72	This study

Table 2: Kinetic constant and percentage of drug degradation using Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites.

Photocatalyst	Drug	k_{app} (min^{-1})	Time (min)	Photocatalytic degradation (%)
Fe_2O_3-ZnO	Paracetamol	0.003	180	45
Fe_2O_3-ZnO/Ag	Paracetamol	0.007	180	72
Fe_2O_3-ZnO	Cefixime trihy-drate	0.007	60	38
Fe_2O_3-ZnO/Ag	Cefixime trihy-drate	0.012	60	55

Fe_2O_3-ZnO/Ag nanocomposites.

Discussion

The photocatalytic degradation mechanism of drugs using Fe_2O_3-ZnO photocatalyst can be summarized as (4-7) [31]:

$$Fe_2O_3 - ZnO + hv \rightarrow h_{VB}^+ + e_{CB}^- \qquad (4)$$

$$h_{VB}^+ + H_2O \rightarrow {}^{\cdot}OH + H^+ \qquad (5)$$

$$h_{VB}^+ + Pollutant_{(absorbed)} \rightarrow Pollutant^+ \qquad (6)$$

$${}^{\cdot}OH + Pollutant^+ \rightarrow CO_2 + H_2O \qquad (7)$$
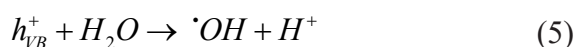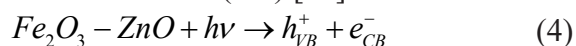
Furthermore, the addition of Fe_2O_3 and Ag affects the photocatalytic activity of ZnO semiconductor in different ways: (1) the Ag noble metal increases the surface plasmon resonance, which leads to an increase in the absorption capacity in the visible light range, (2) the formation of Schottky junction at the interface of ZnO/Ag nanostructure increases the separation of charge carriers and reduces the time rate of recombination, (3) with the addition of Fe_2O_3/Ag to the ZnO semiconductor, the volume of oxygen vacancies in the semiconductor increases, as a result, the generated electrons can be trapped [32].

Conclusion

The Fe_2O_3-ZnO with ratio (10:90) and Fe_2O_3-ZnO/Ag nanocomposites were successfully synthesized with high purity. Elemental analysis confirmed the presence of Ag element in Fe_2O_3-ZnO/Ag nanocomposites. The optical gap for Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites was calculated to be 2.60 eV and 2.22 eV, respectively. Next, the photocatalytic performance of Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites was studied for the photocatalytic degradation of paracetamol and cefixime trihydrate drugs. After 180 min, only 45% of paracetamol was decomposed by Fe_2O_3-ZnO nanocomposite, while 72% of this drug was removed by using Fe_2O_3-ZnO/Ag nanocomposite. Also, the overall degradation of cefixime trihydrate in the presence of Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag nanocomposites in 60 min by subtracting the photolysis effects was 38% and 55%, respectively. Although compounds Fe_2O_3-ZnO and Fe_2O_3-ZnO/Ag were successful in the degradation of paracetamol and cefixime trihydrate, according to the results, it seems that the presence of Ag in the nanocomposite improves the photocatalytic performance and nanocomposite Fe_2O_3-ZnO/Ag performs better in the degradation of these drugs. Also, compared to previous works, Fe_2O_3-ZnO/Ag nanocomposite showed much better performance in the degradation of paracetamol and cefixime trihydrate drugs.

Authors' Contribution

M. Farbod planned the scheme, initiated the project, proposed the experiments, and analyzed the results. V. Kargar Dehbidi conducted the experiments and analyzed the empirical results. The manuscript was written through the contribution of all authors. All authors discussed the results, and reviewed, and approved the final version of the manuscript.

Ethical Approval

The ethics approval is not applicable.

Conflict of Interest

None

References

1. Gorgaslidze N, Sulashvili N, Gabunia L, Pruidze-Liparteliani N, Giorgobiani M. The impact of pharmaceuticals on the ecology and human health. *World Med J Biomed Sci.* 2024;**1**:65-89.

2. Ojha S, Tripathi SM, Vishwakarma PK, Mishra S. Pharmaceuticals in the Water: Emerging Concerns and Innovative Remediation Solutions. *Curr Green Chem.* 2024;**11**(1):50-62. doi: 10.2174/0122133461 2725262231012064151.

3. Kaushik B, Rao G, Vaya D. Photocatalytic Degrada-

tion of Drugs: Sustainable solution of Waste water treatment. In: Handbook of Green and Sustainable Nanotechnology: Fundamentals, Developments and Applications. Cham: Springer; 2023 p. 1-29.

4. Malakootian M, Yaseri M, Faraji M. Removal of antibiotics from aqueous solutions by nanoparticles: a systematic review and meta-analysis. *Environ Sci Pollut Res Int.* 2019;**26**(9):8444-58. doi: 10.1007/s11356-019-04227-w. PubMed PMID: 30706272.

5. Bilal M, Mehmood S, Rasheed T, Iqbal HM. Antibiotics traces in the aquatic environment: persistence and adverse environmental impact. *Curr Opin Environ Sci Health.* 2020;**13**:68-74. doi: 10.1016/j.coesh.2019.11.005.

6. Alaei S, Ghasemian E, Vatanara A. Spray drying of cefixime nanosuspension to form stabilized and fast dissolving powder. *Powder Technol.* 2016;**288**:241-8. doi: 10.1016/j.powtec.2015.10.051.

7. Visalakshi M, Bai GS, Sinduri V, Praveena G, Ushasree G, Swapna G. Photocatalytic degradation of outdated antibiotics by nano-crystalline ZnO. International Conference on Advanced Nanomaterials & Emerging Engineering Technologies; Chennai, India: IEEE; 2013. p. 409-11.

8. Shooshtari NM, Ghazi MM. An investigation of the photocatalytic activity of nano α-Fe2O3/ZnO on the photodegradation of cefixime trihydrate. *Chem Eng J.* 2017;**315**:527-36. doi: 10.1016/j.cej.2017.01.058.

9. Abdel-Wahab AM, Al-Shirbini AS, Mohamed O, Nasr O. Photocatalytic degradation of paracetamol over magnetic flower-like TiO2/Fe2O3 core-shell nanostructures. *J Photochem Photobiol A.* 2017;**347**:186-98. doi: 10.1016/j.jphotochem.2017.07.030.

10. Dalida ML, Amer KM, Su CC, Lu MC. Photocatalytic degradation of acetaminophen in modified TiO2 under visible irradiation. *Environ Sci Pollut Res Int.* 2014;**21**(2):1208-16. doi: 10.1007/s11356-013-2003-4. PubMed PMID: 23888349.

11. Idris M, John C, Ghosh P, Shukla SK, Baggi TR. Simultaneous determination of methaqaulone, saccharin, paracetamol, and phenacetin in illicit drug samples by hplc. *J Anal Sci Technol.* 2013;**4**:1-6.

12. Khasawneh OF, Palaniandy P, Ahmadipour M, Mohammadi H, Hamdan MR. Removal of acetaminophen using Fe2O3-TiO2 nanocomposites by photocatalysis under simulated solar irradiation: optimization study. *J Environ Chem Eng.* 2021;**9**:104921. doi: 10.1016/j.jece.2020.104921.

13. Quesada HB, Baptista ATA, Cusioli LF, Seibert D, De Oliveira Bezerra C, Bergamasco R. Surface water pollution by pharmaceuticals and an alternative of removal by low-cost adsorbents: A review. *Chemosphere.* 2019;**222**:766-80. doi: 10.1016/j.chemosphere.2019.02.009. PubMed PMID: 30738319.

14. Vaiano V, Sacco O, Matarangolo M. Photocatalytic degradation of paracetamol under UV irradiation using TiO2-graphite composites. *Catal Today.* 2018;**315**:230-6. doi: 10.1016/j.cattod.2018.02.002.

15. Su R, Zhu Y, Gao B, Li Q. Progress on mechanism and efficacy of heterogeneous photocatalysis coupled oxidant activation as an advanced oxidation process for water decontamination. *Water Res.* 2024;**251**:121119. doi: 10.1016/j.watres.2024.121119. PubMed PMID: 38219690.

16. Khan I, Liu W, Zada A, Raziq F, Ali S, Shah MI, et al. Recent progress in emerging materials and hybrid nanocomposites for peroxymonosulfate and peroxydisulfate activation towards solar light-driven photocatalytic degradation of emerging pollutants. *Coord Chem Rev.* 2024;**499**:215466. doi: 10.1016/j.ccr.2023.215466.

17. Lanjwani MF, Tuzen M, Khuhawar MY, Saleh TA. Trends in photocatalytic degradation of organic dye pollutants using nanoparticles: A review. Inorganic Chemistry Communications. *Inorg Chem Commun.* 2024;**159**:111613. doi: 10.1016/j.inoche.2023.111613.

18. Farbod M, Jafarpoor E. Fabrication of different ZnO nanostructures and investigation of morphology dependence of their photocatalytic properties. *Materials Letters.* 2012;**85**:47-9. doi: 10.1016/j.matlet.2012.06.080.

19. Kadhim MJ, Mahdi MA, Selman AM, Al-Ani SK, Hassan JJ, Ahmed NM. The most important parameters that affect the photocatalytic activity of ZnO nanostructures against organic dyes: a review. *Iran J Catal.* 2023;**13**:1-21. doi: 10.30495/ijc.2023.1969439.1966.

20. Zou X, Fan H, Tian Y, Yan S. Synthesis of Cu 2 O/ZnO hetero-nanorod arrays with enhanced visible light-driven photocatalytic activity. *CrystEngComm.* 2014;**16**(6):1149-56. doi: 10.1039/C3CE42144A.

21. Hitam CNC, Jalil AA. A review on exploration of Fe2O3 photocatalyst towards degradation of dyes and organic contaminants. *J Environ Manage.* 2020;**258**:110050. doi: 10.1016/j.jenvman.2019.110050. PubMed PMID: 31929077.

22. Wang Y, Fang HB, Zheng YZ, Ye R, Tao X, Chen JF. Controllable assembly of well-defined monodisperse Au nanoparticles on hierarchical ZnO microspheres for enhanced visible-light-driven

photocatalytic and antibacterial activity. *Nanoscale.* 2015;**7**(45):19118-28. doi: 10.1039/c5nr06359k. PubMed PMID: 26524158.

23. Jadhav J, Biswas S. Surface plasmon enhanced near-UV emission in monodispersed ZnO: Ag core–shell type nanoparticles synthesized by a wet chemical method. *Superlattices and Microstructures.* 2016;**91**:8-21. doi: 10.1016/j.spmi.2015.12.040.

24. Zhang S, Wu W, Xiao X, Zhou J, Ren F, Jiang C. Preparation and characterization of spindle-like Fe3O4 mesoporous nanoparticles. *Nanoscale Res Lett.* 2011;**6**(1):89. doi: 10.1186/1556-276X-6-89. PubMed PMID: 21711591. PubMed PMCID: PMC3212238.

25. Chidambaram S, Pari B, Kasi N, Muthusamy S. ZnO/Ag heterostructures embedded in Fe3O4 nanoparticles for magnetically recoverable photocatalysis. *J Alloys Compd.* 2016;**665**:404-10. doi: 10.1016/j.jallcom.2015.11.011.

26. Pourtaheri A, Nezamzadeh-Ejhieh A. Photocatalytic properties of incorporated NiO onto clinoptilolite nano-particles in the photodegradation process of aqueous solution of cefixime pharmaceutical capsule. *Chem Eng Res Des.* 2015;**104**:835-43. doi: 10.1016/j.cherd.2015.10.031.

27. Motahari F, Mozdianfard MR, Soofivand F, Salavati-Niasari M. NiO nanostructures: synthesis, characterization and photocatalyst application in dye waste-water treatment. *RSC Adv.* 2014;**4**(53):27654-60. doi: 10.1039/C4RA02697G.

28. Zak AK, Abrishami ME, Majid WA, Yousefi R, Hosseini SM. Effects of annealing temperature on some structural and optical properties of ZnO nanoparticles prepared by a modified sol–gel combustion method. *Ceram Int.* 2011;**37**:393-8. doi: 10.1016/j.ceramint.2010.08.017.

29. Zak AK, Razali R, Majid WH, Darroudi M. Synthesis and characterization of a narrow size distribution of zinc oxide nanoparticles. *Int J Nanomedicine.* 2011;**6**:1399-403. doi: 10.2147/IJN.S19693. PubMed PMID: 21796242. PubMed PMCID: PMC3141867.

30. Anandan K, Rajendran V. Structural, optical and magnetic properties of well-dispersed NiO nanoparticles synthesized by CTAB assisted solvothermal process. *Nanosci Nanotechnol Int J.* 2012;**2**(4):24-9.

31. Choina J, Duwensee H, Flechsig G, Kosslick H, Morawski A, Tuan V, Schulz A. Removal of hazardous pharmaceutical from water by photocatalytic treatment. *Open Chem.* 2010;**8**:1288-97. doi: 10.2478/s11532-010-0109-9.

32. Sabry RS, Aziz WJ, Rahmah MI. Enhanced photocatalytic activity of Ag and Fe2O3 co-doped ZnO nanostructure under visible light irradiation. *Materials Technology.* 2020;**35**(6):326-34. doi: 10.1080/10667857.2019.1681717.