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Facile synthesis of ZnO and Co₃O₄ nanoparticles by thermal decomposition of novel Schiff base complexes: Studying biological and catalytic properties



Asma S. Al-Wasidi^{a,*}, Ibtisam I.S. AlZahrani^a, Hotoun I. Thawibaraka^a, Ahmed M. Naglah^{b,c}

^a Department of Chemistry, College of Science, Princess Nourah Bint Abdulrahman University, Riyadh 11671, Saudi Arabia ^b Department of Pharmaceutical Chemistry, Drug Exploration & Development Chair (DEDC), College of Pharmacy, King Saud University, Riyadh 11451, Saudi Arabia

^c Peptide Chemistry Department, Chemical Industries Research Division, National Research Centre, 12622 Dokki, Cairo, Egypt

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Schiff base complexes; Nanoparticles; Photocatalytic degradation; Methylene blue dye; Biological activity

Abstract In this paper, a novel Zn(II) and Co(II) Schiff base complexes were synthesized by template method via refluxing 2,3-Naphthalenedicarboxaldehyde, Metal(II) chloride (Metal = Zn or Co), and L-phenylalanine. ZnO and Co_3O_4 nanoparticles were synthesized by thermal decomposition of Zn(II) and Co(II) complexes, respectively. The products were characterized using different instruments such as CHN, Conductivity, FT-IR, XRD, HR-TEM, and UV-Vis spectrophotometer. The experimental results of elemental analysis for Zn(II) and Co(II) complexes, agree with the calculated results, indicating that the Zn(II) and Co(II) complexes have 1:1 ligand/metal ratios. The molar conductance of the Zn(II) and Co(II) complexes, is less than 5 Ω^{-1} cm⁻¹mol⁻¹, confirming the non-electrolytic nature of the synthesized complexes. The average crystallite diameter of the ZnO and Co_3O_4 samples is 39.64 and 30.38 nm, respectively. The optical energy gap of the ZnO and Co_3O_4 samples are 2.75 and 3.25 eV, respectively. Methylene blue dye was utilized to examine the photocatalytic properties of the synthesized nanoparticles using UV irradiations in the absence and presence of hydrogen peroxide. The % degradation of the methylene blue dye in the presence of hydrogen peroxide using ZnO and Co₃O₄ samples after 40 min is 94.55 and 98.98, respectively. Six pathogenic microbes were utilized to examine the antimicrobial properties of the synthesized Schiff base complexes and their nanoparticles: Staphylococcus aureus, Escherichia coli, Pseudomonas

* Corresponding author.

E-mail address: asalwasidi@pnu.edu.sa (A.S. Al-Wasidi). Peer review under responsibility of King Saud University.



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1878-5352 © 2021 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). aeruginosa, Streptococcus species, Aspergillus species, and Candida species. Zn(II) and Co(II) complexes display inhibition towards all the studied microbes. Besides, ZnO and Co₃O₄ nanoparticles exhibit less inhibition towards Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa, and Streptococcus species. Moreover, ZnO and Co₃O₄ nanoparticles have no activity towards Aspergillus and Candida species.

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1. Introduction

Metal complexes of Schiff base are a field of increasing importance. These metal complexes were used for various applications such as treatment of cancer, antivirus agents, fungicide agents, and antibactericide agents (Kaczmarek et al., 2018; Liang et al., 2021; Al-Resayes et al., 2016; Alaghaz et al., 2015). Also, metal complexes of Schiff base, which were gotten from amino acids, are discovering applications in understanding several in vivo biochemical reactions (Saikumari, 2021; Otani et al., 2021). Besides, the poisoning task of specific metal ions in living organisms is determined by exploiting these complexes via verifying the activity of the drug. Donmez et al. prepared a novel biosensor that is sensitive to glucose using the microspheres modified with (4-formyl-3-methoxyphenoxymethyl)polystyrene (FMPS) with 1glycine. Polymeric microspheres having Schiff bases were prepared from FMPS using the glycine condensation method. Glucose oxidase enzyme was immobilized onto modified carbon paste electrode by cross-linking with glutaraldehyde. Oxidation of enzymatically produced H₂ O₂ (+0.5 V vs. Ag/AgCl) was used for determination of glucose. Optimal temperature and pH were found as 50 °C and 8.0, respectively. The glucose biosensor showed a linear working range from 5.0×10^{-4} to 1.0×10^{-2} M, $R^2 = 0.999$. Storage and operational stability of the biosensor were also investigated. The biosensor gave perfect reproducible results after 20 measurements with 3.3% relative standard deviation. It also had good storage stability (Donmez et al., 2017). Amino acids form the basic structural units of proteins and are chemical kinds required for performing an enormous number of biological purposes, as illustrated via the task of enzymes. Orthophthalaldehyde acts the main role in the assay of amino acids. The residues of amino acids in several biological fluids and enzymes are determined by exploiting ortho-phthalaldehyde. It achieves requests in the clinical area as a high-level antiseptic (Moitessier et al., 2020; Gyimesi-Forrás et al., 2005). Recently, great interest has been established in copper Schiff base complexes as fundamental models for the active position of the copper proteins. In the copper proteins, a distorted environment of mixed donor groups and low symmetry is present (Dinesh Karthik et al., 2020; Srivastava et al., 2021). Also, nickel complexes are existing in the active positions of urease (Thalamuthu and Neelakantan, 2021; Dong et al., 2012). In the presence of oxidizing agents, square planar nickel-salen was used in the cleavage of plasmid DNA as reported by Morrow and Kolasa (Morrow and Kolasa, 1992). Zinc- including bridged-carboxylate complexes have differed structural styles in hydrolytic metalloenzymes, for example, aminopeptidases and phosphatases (Baltulionis et al., 2021; Karmakar and Chattopadhyay, 2020). Latif et al synthesize a Schiff base via the condensation of 4-(dimethylamino)benzaldehyde and Sbenzyldithiocarbazate. Also, Ni(II), Cu(II), and Zn(II) complexes were synthesized. The results of the biological activity of the tested compounds displayed that the complexes were more effective antibiotics than the free Schiff base. The Ni(II) and Cu(II) complexes exhibited high antibacterial effectiveness whereas Zn(II) complex was moderately active against bacteria (Latif et al., 2019). Recently, the complexes have been exploited in the facile and low-cost synthesis of many nanomaterials of small crystallite size by thermal decomposition. Abdelghany et al synthesize Ag and CuO nanoparticles via thermal decomposition of Ag(I) and Cu(II) Schiff base complexes, respectively. The Schiff base was synthesized by the condensation reaction between 2-hydroxy-1-naphthaldehyde and 3-methyl-4-amino-5-mercapto-1,2,4 triazole (Abdelghany et al., 2021). Katouah synthesizes ZnO and Co₃O₄ nanoparticles by thermal decomposition of Zn(II) and Co(II) Schiff base complexes, respectively. The Schiff base was synthesized via condensation of 4-(dimethylamino)benzaldehyde with 4-amino-5ethyl-4H-1,2,4-triazole-3-thiol (Katouah, 2021). Nanomaterials are used in many applications, most notably the treatment of water pollutants by adsorption and photocatalytic degradation techniques (Abdelrahman, 2018; Hegazey et al., 2020; Abdelrahman and Hegazey, 2019; Abdelrahman et al., 2021). The photocatalytic degradation method is an effective and simple way to get rid of many dyes because it depends on the use of light and a catalyst to produce free radicals that can degrade these pollutants (Abdelrahman and Hegazey, 2019; Nguyen et al., 2021b; Nasri et al., 2021; Nguyen et al., 2021a; Nguyen et al., 2021c; Shokouhimehr et al., 2019; Nguyen et al., 2020; Kiani et al., 2020; Nayebi et al., 2020; Zhang et al., 2019). So, in this paper, Zn(II) and Co(II) complexes were synthesized by template method via refluxing 2,3-Naphthalenedicarboxal dehyde, cobalt(II) chloride hexahydrate or zinc(II) chloride, and Lphenylalanine. ZnO and Co3O4 nanoparticles were synthesized by thermal decomposition of the Zn(II) and Co(II) complexes, respectively. The biological and catalytic properties were studied.

2. Experimental

2.1. Chemicals

Methylene blue dye ($C_{16}H_{18}ClN_3S$), cobalt(II) chloride hexahydrate (CoCl₂·6H₂O), zinc(II) chloride (ZnCl₂), and Lphenylalanine (C₉H₁₁NO₂), ethanol (C₂H₅OH), sodium hydroxide (NaOH), and 2,3-Naphthalenedicarboxaldehyde (C₁₂H₈O₂) were of analytical grade (Purity = 99.99 %) and obtained from Sigma Aldrich Company and utilized without further purification.

2.2. Synthesis of Zn(II) and Co(II) Schiff base complexes

The template method is operated for the synthesis of Zn(II) and Co(II) Schiff base complexes. About 6 mmol (1.11 g) of 2,3-Naphthalenedicarboxaldehyde in 25 mL ethanol was added to an ethanolic solution of proper cobalt(II) chloride hexahydrate or zinc(II) chloride (6 mmol/25 mL) and stirred at room temperature for one hour. To this stirred solution, 12 mmol of L-phenylalanine in 25 mL of ethanol including 12 mmol sodium hydroxide was added then refluxed for six hours. After that, obtained solid product was filtered using filter paper, washed various times using ether, and then recrystallized from ethanol.

2.3. Synthesis of ZnO and Co₃O₄ nanoparticles

The Zn(II) and Co(II) Schiff base complexes were thermally decomposed at 550 °C for 5 h to produce ZnO and Co_3O_4 nanoparticles, respectively.

2.4. Characterization

Elemental analysis of Co(II) and Zn(II) Schiff base complexes was gotten using an Elementar elemental analyzer (Vario EL III). The molar conductance of the Co(II) and Zn(II) complexes in ethanol was assessed utilizing a conductivity bridge (Systronics 304). The Fourier transform (FT-IR) spectra of the complexes, ZnO, and Co₃O₄ samples, on KBr pellets, were gotten at room temperature using a Shimadzu spectrometer (IRTracer 100) in the range from 4000 to 400 cm^{-1} . Thermal analysis of the Co(II) and Zn(II) complexes was performed using TG/DTG instrument (Perkin-Elmer Diamond) through an oxygen atmosphere at a heating rate of 10 °C/min. The X-ray diffraction (XRD) patterns of the ZnO and Co₃O₄ samples were conducted utilizing a Bruker diffractometer (D8 Advance) with Cu-K α irradiation ($\lambda = 0.15$ nm) at 40 mA and 40 kV. The high-resolution transmission electron microscopy (HR-TEM) images of the ZnO and Co₃O₄ samples were taken using JEOL model 2100. Optical energy gaps of ZnO and Co₃O₄ samples were obtained using a UV-Vis spectrophotometer (Cintra 101).

2.5. Photocatalytic degradation of methylene blue dye

Degradation experiments of the methylene blue dye were achieved in a photochemical batch reactor containing a magnetic stirrer. 15 W four UV lamps ($\lambda = 365$ nm) were operated as a UV radiation source. All the experiments of adsorption and photocatalytic degradation started with a 60 mL aqueous solution of 60 mg/L of methylene blue dye and 0.15 g of ZnO or Co₃O₄. The adsorption experiments were achieved in the dark. The degradation of methylene blue dye in the absence and presence of hydrogen peroxide under the effect of UV light and catalyst (ZnO or Co₃O₄) was observed using a UV–Vis spectrophotometer at different periods. The concentration of methylene blue dye was determined from a preset calibration curve at 663 nm (maximum absorption wavelength of the methylene blue dye).

% Adsorption (% A) was calculated using Eq. (1) whereas % degradation (% D) was calculated using Eq. (2).

$$\% \boldsymbol{A} = [\boldsymbol{Z}_1 - \boldsymbol{Z}_2] \times \frac{100}{\boldsymbol{Z}_1} \tag{1}$$

$$\% \boldsymbol{D} = [\boldsymbol{Z}_2 - \boldsymbol{Z}_3] \times \frac{100}{\boldsymbol{Z}_2} \tag{2}$$

where Z_1 (mg/L) is the initial concentration of methylene blue dye, Z_2 (mg/L) is the concentration of methylene blue dye after adsorption in the dark place, and Z_3 (mg/L) is the concentration of methylene blue dye after exposure to UV light.

2.6. Biological activity

Six pathogenic microbes were utilized to examine the antimicrobial activity of the synthesized Schiff base complexes and their nanoparticles: Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa, Streptococcus species, Aspergillus species, and Candida species. The antimicrobial activity of the extracts was qualitatively estimated via a modified disc diffusion approach (Almehizia et al., 2021). A lawn of microorganisms was synthesized via pipetting and equally spreading inoculums $(10^{-4} \text{ cm}^3, \text{ adjusted turbidometrically to } 10^{-5} \text{ cfu}$ cm³) onto agar group in petri dishes, utilizing potato dextrose agar in the case of fungi and Muller Hinton nutrient agar in the case of bacteria. The liquid media including the bacterial divisions was autoclaved for twenty minutes at 15 lb pressure and 120 °C before inoculation. Then, the bacteria were cultured at 37 °C in an incubator for one day. The samples (50 µg) to be examined were dissolved in dimethyl sulfoxide then dropwise added to a Whatman No. 1 filter paper disc (10 mm diameter) placed at the center of each agar plate. These filter paper discs were then kept at 5 °C for one hour then transported to an incubator maintained at 37 °C. After four days, the inhibition zone, which formed around the discs in each plate, was determined. Commercially available nystatin was utilized as antifungal control whereas ampicillin was utilized for antibacterial control.

3. Results and discussion

3.1. Characterization of Zn(II) and Co(II) complexes

The experimental results of elemental analysis for the Zn(II) and Co(II) complexes agree with the calculated results indicating that the Zn(II) and Co(II) complexes have 1:1 ligand/metal ratios as clarified in Scheme 1 and Table 1. The molar conductance of the Zn(II) and Co(II) complexes in ~0.001 M ethanol at room temperature is 3.87 and 4.12 Ω^{-1} cm⁻¹mol⁻¹, respectively. These values confirming the non-electrolytic nature of the synthesized complexes because of the absence of counterions in the suggested structure of the complexes as shown in



Scheme 1 The Structure of the synthesized complexes.

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% Element	Zn(II) complex Formula: C ₃₀ H ₂₈ N ₂ O ₆ Molecular weight: 576.	Zn 12	Co(II) complex Formula: C ₃₀ H ₂₈ N ₂ O ₆ Co Molecular weight: 571.13		
	Calculated	Found	Calculated	Found	
%C	62.34	62.12	63.05	63.15	
%Н	4.88	4.67	4.94	4.90	
%N	4.85	4.80	4.90	4.92	
%O	16.61	16.45	16.80	16.88	
%Zn	11.32	11.96	_	-	
%Co	-	-	10.31	10.15	

Table 1 (Abdelghany et al., 2021; Katouah, 2021). Fig. 1 represents the FT-IR spectra of the Zn(II) and Co(II) complexes, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 480 and 430 cm⁻¹, are due to the stretching vibration of Zn-O and Co-O, respectively (Abdelghany et al., 2021; Katouah, 2021; Nakamoto, 2008). The bands, which were observed in the Zn(II) and Co(II) complexes at 582 and 570 cm⁻¹, are due to the stretching vibration of Zn-N and Co-N, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 582 and 570 cm⁻¹, are due to the stretching vibration of Zn-N and Co-N, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes in the range 690–960 cm⁻¹ and 680–950 cm⁻¹, are due to CH out of plane bend-

ing vibration of aromatic rings, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 1390 and 1385 cm⁻¹, are due to the symmetric stretching vibration of COO, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes in the range 1450–1530 cm⁻¹ and 1460–1540 cm⁻¹, are due to the stretching vibration of C = C aromatic, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 1601 and 1610 cm⁻¹, are due to the asymmetric stretching vibration of COO, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 1601 and 1610 cm⁻¹, are due to the asymmetric stretching vibration of COO, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 1601 and 1610 cm⁻¹, are due to the asymmetric stretching vibration of COO, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 1601 and 1610 cm⁻¹, are due to the asymmetric stretching vibration of COO, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 1601 and 1610 cm⁻¹, are due to the asymmetric stretching vibration of COO, respectively. The bands, which were observed in the Zn(II) and Co



Fig. 1 The FT-IR spectra of the Zn(II) (A) and Co(II) (B) complexes.

vibration of C = N, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 2900 and 2950 cm⁻¹, are due to the stretching vibration of CH aliphatic, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 3200 and 3300 cm^{-1} , are due to the stretching vibration of CH aromatic, respectively. The bands, which were observed in the Zn(II) and Co(II) complexes at 3450 and 3500 cm^{-1} , are due to the stretching vibration of H-O-H, respectively (Abdelghany et al., 2021; Katouah, 2021; Nakamoto, 2008). Table 2 represents the data of TG and DTA analyses for Zn(II) and Co(II) complexes. There are three decomposition steps. The first exothermic step, which was observed in the temperature range of 30-300 °C, is due to the loss of two coordinated water molecules. The second exothermic step, which was observed in the temperature range of 300-550 °C, is because of the decomposition of the organic moiety. The third step, which was observed in the temperature range of 550-1000 °C, is because of oxidation of metal (Zn or Co) i.e., formation of ZnO or Co_3O_4 .

3.2. Characterization of ZnO and Co₃O₄ nanoparticles

The ZnO and Co₃O₄ samples were analyzed using X-ray diffraction (XRD) to check their crystalline phases and structures. The XRD patterns of the ZnO and Co₃O₄ samples are presented in Fig. 2A-B, respectively. In the case of ZnO, the principal reflections observed at the 2θ values of 31.80° , 34.40°, 36.30°, 47.50°, 56.60°, 62.90°, 67.90°, 68.80°, 69.90°, 72.50°, and 78.60° assigned (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) plains, respectively as clarified from the JCPDS No. 36-1451 (Katouah, 2021). In the case of Co_3O_4 , the principal reflections observed at the 20 values of 36.80°, 38.50°, and 44.80° assigned (311), (222), and (400) plains, respectively as clarified from the JCPDS No. 78-1970 (Katouah, 2021). The average crystallite diameter of the ZnO and Co₃O₄ samples is 39.64 and 30.38 nm, respectively. The FT-IR spectra of the ZnO and Co₃O₄ samples are presented in Fig. 3A-B, respectively. The band, which was appeared in the case of ZnO at 485 cm^{-1} , is because of the stretching vibration of Zn-O. The bands, which were appeared in the case of ZnO at 1615 and 3445 cm^{-1} , are because of the bending and stretching vibration of adsorbed water, respectively (Katouah, 2021). The bands, which were appeared in the case of Co₃O₄ at 530 and 630 cm^{-1} , are because of the stretching vibration of Co(II)-O and Co(III)-O, respectively. The bands, which were appeared in the case of Co_3O_4 at 1620 and 3450 cm⁻¹, are because of the bending and stretching vibration of adsorbed water, respectively (Katouah, 2021). The morphology of the ZnO



Fig. 2 The XRD patterns of the ZnO (A) and Co_3O_4 (B) samples.

and Co_3O_4 samples was examined via HR-TEM as shown in Fig. 4A-B, respectively. The ZnO and Co_3O_4 samples consist of irregular and spherical shapes with an average diameter of 35.04 and 26.48 nm, respectively. UV–Vis spectrophotometer was utilized for determining the bandgap via the Tauc plot method (Eq. (3)) for the ZnO and Co_3O_4 samples as shown in Fig. 5A-B, respectively (Katouah, 2021).

$$(\rho h v)^M = G(h v - E_g) \tag{3}$$

where G, ρ , M are a constant, the absorption coefficient, and an integer depending on the type of transition. In the case of a direct allowed transition M equals 2. Besides, in the case of an

 Table 2
 Thermal analysis of the synthesized complexes.

	I I I I I I I I I I I I I I I I I I I							
Steps Zn(II) complex (C ₃₀ H ₂₈ N ₂ O ₆ Zn)		Co(II) complex (C ₃₀ H ₂₈ N ₂ O ₆ Co)						
	Chemical equations	Weight loss%		Chemical equations	Weight loss%			
		Calculated	Found		Calculated	Found		
First step	$\begin{array}{l} C_{30}H_{28}N_2O_6Zn \rightarrow C_{30}H_{24}N_2O_4Zn \\ + \ \mathbf{2H_2O}\uparrow \end{array}$	6.25	6.38	$\begin{array}{l} C_{30}H_{28}N_2O_6Co \rightarrow C_{30}H_{24}N_2O_4Co \\ + \ \mathbf{2H_2O}\uparrow \end{array}$	6.30	6.15		
Second step	$C_{30}H_{24}N_2O_4Zn \rightarrow Zn + C_{30}H_{24}N_2O_4\uparrow$	82.65	82.26	$C_{30}H_{24}N_2O_4Co \rightarrow Co + C_{30}H_{24}N_2O_4 \uparrow$	83.37	83.49		
Third step	$Zn + 1/2O_2 \rightarrow ZnO$	-	-	$3\text{Co} + 2\text{O}_2 \rightarrow \text{Co}_3\text{O}_4$	-	-		



Fig. 3 The FT-IR spectra of the ZnO (A) and Co₃O₄ (B) samples.

indirect allowed transition M equals 0.5. The extrapolating of each graph so as $(\rho h \upsilon)^2$ equals zero gives the optical energy gap (E_g) of the direct allowed transitions. The optical energy gap of the ZnO and Co₃O₄ samples are 2.75 and 3.25 eV, respectively.

3.3. Photocatalytic degradation of methylene blue dye

% A of the methylene blue dye in the dark place using ZnO and Co_3O_4 samples is 8.33 and 18.33 %, respectively. To deter-

mine the influence of UV irradiation time on % D of methylene blue dye using ZnO and Co_3O_4 samples in the absence and presence of H_2O_2 , experiments were performed by the analysis of irradiation time variations versus % D as shown in Fig. 6A-B, respectively. In the absence of hydrogen peroxide, % D increased with increasing UV irradiation time from 20 to 80 min. After that, % D almost remains stable when the UV irradiation time increased from 80 to 120 min owing to the saturation of the active centers. Consequently, the



Fig. 4 The HR-TEM images of the ZnO (A) and Co₃O₄ (B) samples.



Fig. 5 The optical energy gap of the ZnO (A) and Co_3O_4 (B) samples.

optimum UV irradiation time is 80 min. The % D of the methylene blue dye using ZnO and Co_3O_4 samples after 80 min is 67.27 and 75.51, respectively. In the presence of hydrogen peroxide, % D increased with increasing UV irradiation time from 10 to 40 min. After that, % D almost remains stable when the UV irradiation time increased from 40 to 60 min owing to the saturation of the active centers. Consequently, the optimum UV irradiation time is 40 min. The % D of the methylene blue dye using ZnO and Co_3O_4 samples after 40 min is 94.55 and 98.98, respectively. Photocatalytic degradation of methylene blue dye fitted well with the first-order kinetic model (Eq. (4)) (Katouah, 2021).

$$\ln\left(\frac{\mathbf{Z}_2}{\mathbf{Z}_3}\right) = \mathbf{K}\mathbf{t} \tag{4}$$

where K (1/min) is the first-order constant. The plots of ln (Z_2/Z_3) versus t in the absence and presence of hydrogen peroxide using ZnO and Co₃O₄ samples are shown in Fig. 7A-B, respectively. The values of the K and correlation coefficient (\mathbf{R}^2) are shown in Table 3. The photocatalytic degradation mechanism of the methylene blue dye can be described as shown in Scheme 2 (Katouah, 2021). Under the impact of UV light irradiation, the ZnO or Co₃O₄ photocatalyst can absorb energy greater than or equals to its energy gap and produce the electron-hole (e^{-}/h^{+}) pairs on the surface of ZnO or Co₃O₄. The adsorbed oxygen reacts with electrons to produce oxygen anion radicals. Besides, water molecules react with holes producing hydroxyl radicals. Accordingly, the active kinds produced, especially holes and hydroxyl radicals, react effectively to degrade the methylene blue dye into carbon dioxide, water, or other products. The % D of the methylene blue dve was compared with some catalysts in the literature, for example, Co alloyed CdZnS, ZnWO₄, TiO₂ supported on magnetic core shell, ZnSe, and CdSe as shown in Table 4 (Geetha et al., 2021; de Moura et al., 2021; Sridevi et al., 2020; Ivanets et al., 2021; Ivanets et al., 2019; Ivanets et al., 2021). The



Fig. 6 The plot of % D versus time.



Fig. 7 The plot of $\ln (Z_2/Z_3)$ versus time.

Table 3 Constants of first order model.						
Factors	Parameters					
	R^2	K (1/min)				
ZnO + UV irradiation	0.986	0.0131				
$ZnO + UV$ irradiation + H_2O_2	0.998	0.0801				
$Co_3O_4 + UV$ irradiation	0.926	0.0187				
$Co_3O_4 + UV$ irradiation $+ H_2O_2$	0.995	0.1338				



ZnO or Co₃O₄ + UV light \longrightarrow h⁺ at (VB) + e⁻ at (CB) h⁺ + OH⁻ \longrightarrow OH⁺ e⁻ + O₂ \longrightarrow O²₂⁻ O²₂⁻ + H⁺ \longrightarrow HOO⁺ 2 HOO⁺ \longrightarrow H₂O₂ + O₂ H₂O₂ \xrightarrow{UV} OH⁺



Photocatalyst	Dye		Е	% Degradation		Ref	
Name	W (g)	C (mg/L)	V (mL)		Value	Time (min)	
Co alloyed CdZnS	0.03	25	25	UV light	83	100	(Geetha et al., 2021)
ZnWO ₄	0.1	10	200	UV light	87	60	(de Moura et al., 2021)
TiO ₂ supported on magnetic core shell	0.03	10	200	UV light	96	120	(Sridevi et al., 2020)
ZnSe	0.05	10	50	UV light	78	150	(Ivanets et al., 2021)
CdSe	0.05	10	50	UV light	56	150	(Ivanets et al., 2021)
ZnO	0.15	60	60	UV light	94.55	40	This study
Co ₃ O ₄	0.15	60	60	UV light	98.98	40	This study

 Table 4
 Comparison between % D of methylene blue dye using synthesized nanoparticles and that using different photocatalysts in the literature.

E = Excitation source, V = Volume, C = Concentration, and W = Weight.

Table 5Biological activity of the synthesized samples.

Sample	Inhibition zone diameter (mm/mg sample)							
	Staphylococcus aureus	Escherichia coli	Pseudomonas aeruginosa	Streptococcus species	Aspergillus species	Candida species		
Control	15	13	12	9	12	11		
Zn(II) complex	22	21	17	19	17	14		
Co(II) complex	19	15	15	16	14	12		
ZnO	12	8	8	11	0	0		
C03O4	11	10	9	10	0	0		

results confirmed the superiority of the ZnO and Co_3O_4 samples for their degrading a high concentration of the methylene blue dye in a shorter time.

3.4. Biological activity

In vitro antimicrobial activities of the metal complexes and their nanoparticles were examined against six microbes using the modified disc diffusion procedure (Katouah, 2021). The zone of inhibition versus the growth of microbes for the metal complexes and their nanoparticles is given in Table 5. The complexes and their nanoparticles diffused into microbes through the lipid layer of spore membranes to the site of action eventually killing them via combining with -OH groups of specific cell enzymes (Katouah, 2021). The diversity in the efficiency of different biocidal agents against different organisms relys on the impermeability of the cell. It is clear that Zn(II) and Co(II) complexes display inhibition towards all the studied microbes. Besides, ZnO and Co₃O₄ nanoparticles exhibit less inhibition towards Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa, and Streptococcus species. Moreover, ZnO and Co₃O₄ nanoparticles have no activity towards Aspergillus and Candida species.

4. Conclusions

ZnO and Co_3O_4 nanoparticles were facilely synthesized using the thermal decomposition of novel Zn(II) and Co(II) Schiff base complexes. The average crystallite diameter of the ZnO and Co_3O_4 samples is 39.64 and 30.38 nm, respectively. The % degradation of the methylene blue dye in the presence of hydrogen peroxide using ZnO and Co_3O_4 samples after 40 min is 94.55 and 98.98, respectively. Compared to Schiff base complexes, ZnO and Co_3O_4 nanoparticles exhibit less inhibition towards Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa, and Streptococcus species. Moreover, ZnO and Co_3O_4 nanoparticles have no activity towards Aspergillus and Candida species.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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