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Photocatalytic Detoxification of Antibiotic- and Bacteria-Contaminated Water using Cobalt-Doped Ni–Zn Ferrites Magnetic Separable Nanopowders

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Abstract

Here, metronidazole (MZ) antibiotic degradation and bactericidal efficacy of Co–Ni_{0.5}Zn_{0.5}Fe₂O₄ (Co–NZF) with and without photoactivation by UV light is reported as a viable cost-competitive water disinfection solution. Co–NZF has a total pore volume of 0.298 cm³ g^{−1}, a specific surface area of 70.2 m² g^{−1} and sufficiently high magnetic properties (80.35 emu g^{−1}). After 360 min of UV–assisted irradiation at pH 3, 10 mg Co–NZF, and 4 mM H₂O₂, the maximum MZ degradation was reached (92.8%). The adsorption result of 10 mg Co–NZF in the dark for 12 h resulted in 70.2% MZ removal, whereas MZ self-degradation was significantly minimal in a blank trial. In the presence of interfering anions and very high molecular weight tylosin antibiotic, Co–NZF maintained 51.7–75.4% degradation efficiency. The effect of the Co–NZF dosage on the viability of *Staphylococcus aureus* and *Escherichia coli* strains showed that 15 mg of the catalyst was sufficient to cause bactericidal activity after 180 min in the presence of UV light, while 25 mg is needed under dark conditions. In addition, when compared to *Escherichia coli* strains, Co–NZF showed higher inhibition against *Staphylococcus aureus* in time-kill experiments under dose variation.

Keywords: Environmental pollution; antibiotic decontamination; Ni-Zn spinel ferrites; bactericidal efficiency; UV-photocatalysis; Cobalt doped nanopowders

Introduction

Pharmaceutical antibiotics are becoming increasingly important globally due to their effectiveness in preventing or treating infections in humans and promoting animal growth (Serna-Galvis et al. 2017; Tran et al. 2019; Azalok et al. 2021ab). The increasing demand for veterinary antibiotics is worrying (Roberts and Zembower 2021), considering the rise in the number of people owning pets like dogs and cats during this pandemic, numerous human diseases, and growing global demand for animal protein for human consumption. Since most antibiotics are poorly absorbed by humans and livestock, this widespread use of antibiotics raises the risk of significant quantities of residual antibiotics ending up in the environment (Li et al. 2015; Estrada-Flórez et al. 2020; Chan et al. 2020).

Antibiotic resistance bacteria and antibiotic-resistant genes are becoming more common as antibiotics and their residues become more prevalent in the ecosystem (Luo et al. 2010; Abureesh et al. 2018). This is in line with the findings of Luo et al. (2010), who noted that the relative abundance of antibiotic-resistant genes (*i.e.*, *sul1* & *2*/16S-rDNA) in the China Haihe River is linked to total sulfonamide antibiotic concentrations. The key threat posed by these antibiotic-resistant bacteria and genes is a rise in pathogenic bacteria, posing a serious threat to humans. According to the World Health Organization (WHO, 2019), at least 700,000 people die each year as a result of drug-resistant diseases, and the United States CDC (Centers for Disease Control and Prevention) estimates that at least 30,000 people die each year in the United States as a result of antibiotic-resistant diseases (Dadgostar 2019).

Metronidazole (MZ) is one of these antibiotics that is commonly used to treat anaerobic bacterial infections, various protozoa, and *Giardia* infections in dogs and cats, as well as being mixed with poultry and fish feeds to aid weight gain (Bashiri et al. 2020; Fakhravar et al. 2020;

Azalok et al. 2021a). MZF has been detected at concentrations ranging from 0.65 to 28.4 $\mu\text{g/L}$ in surface water and groundwater in recent years (Oladipo et al. 2018). Its excessive use by humans and pets, as well as its high solubility ($\sim 10 \text{ mg L}^{-1}$ at 25°C in water) and emission of residues and metabolites, has resulted in its saturation in the environment (Tran et al. 2019; Hena et al. 2020, 2021). The removal of MZ residues and metabolites from aqueous environments is critical because antibiotic resistance caused by the overuse of antibiotics is becoming a global health threat, resulting in higher medical costs and mortality (Varma et al. 2020a). Physical and biological methods have been used in the past to eliminate antibiotics. However, physical methods such as adsorption can adsorb the pollutant and then move it to an adsorbent surface, which involves more disposal (Oladipo et al. 2018). MZ's antibacterial properties, complex structure, and high molecular weight limit the effectiveness of biological methods for its removal.

Because of its low cost, higher performance, strong oxidation potential, and faster reaction rates, semiconductor photocatalysis is a viable and environmentally friendly solution for removing antibiotic and bacteria contamination from water (Aali et al. 2019; Asadi et al., 2019; Tran et al. 2019ab; Varma et al. 2020b; Azalok et al. 2021ab). In recent years, single metal oxide semiconductors such as In_2O_3 , TiO_2 and ZnO have been widely applied and considered efficient to eliminate hazardous contaminants in wastewater owing to their cost-effectiveness, oxidative potential and catalytic stability for widespread environmental applications (Elmolla et al. 2010; Bokare et al. 2013; Tran et al. 2019b). However, the wide bandgap (3.2 eV) and high recombination rate of the aforementioned single metal oxide semiconductors limit their photoresponses in the UV region (4–5% of solar spectrum) and minimize photocatalytic reactions, respectively (Oladipo et al. 2019; Zhao et al. 2020). Apart from that, their separation from the reaction system after spent is a problem.

In recent years, mixed metal oxide spinel ferrites ($M_xM_{1-x}Fe_2O_4$, where M is a different metal cation *i.e.* Ni, Mg, Ca, Zn, Ag, Co, Cr)-based semiconductors have sparked a lot of interest in the field of photocatalysis because of their diverse optoelectronic properties and topological metal sites structure (Manikandan et al. 2015; Kefeni and Mamba 2020); and have been applied to decompose varieties of organic pollutants and inactivate bacteria during water treatment of wastewater (Chen et al. 2017; Asadi and Moeinpour 2019; Tsvetkov et al. 2019). Particularly, spinel Ni–Zn ferrites are particularly appealing for wastewater decontamination because of their small bandgap (2–2.5 eV), intrinsic redox chemistry, tunable electronic properties, and topologically organized metal sites (Qasim et al. 2015; Aali et al. 2019; Nag et al., 2020). Aali et al. (2019) synthesized $Ni_{0.5}Zn_{0.5}Fe_2O_4$ photocatalyst using a solution combustion synthesis technique and observed 85% methylene blue dye photodegradation and 100% bacteria growth inhibition against *E. coli* and *S. aureus* strains, respectively, with a minimum inhibitory concentration of 0.25 mg/mL and 0.125 mg/mL.

Ferrites are also chemically stable, magnetically simple to separate, and inexpensive. It was discovered that doping or combining with other metal oxide semiconductors improved the ferrites' adsorption ability, specific surface area, and light-driven photoactivity (Qasim et al. 2015; Ifebajo et al. 2020; Nag et al. 2020). Doping the photocatalyst with high conductivity metal ions like Co, Ag, and Pt induces highly efficient electron mobility and delays the recombination step of photo-generated electrons/holes, resulting in increased photocatalyst degradation operation (Sinha 2021; Asadi and Moeinpour 2019; Chahal et al. 2020). For example, Sinha 2021 reported that by doping Bismuth-based ferrite with Co dopant, the crystallite size of the nanostructured material was reduced and the bandgap energy was increased from 2.07 eV to 2.43 eV, resulting in increased photocatalysis and remarkable optoelectronic activity. Motivated by the above

considerations, we designed a high-performance light responsive photocatalyst for antibiotic water remediation by doping Co onto $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles. Since cobalt is a hard magnetic material with larger atomic radii, it affects the oxygen position, the vacancy parameter, and the magneto-crystalline anisotropy constant (Debnath et al. 2021), charge transfer efficiency (Sinha 2021), and intrinsic coercivity of the pristine ferrite.

For the first time, a Co-doped $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (Co–NZF) photocatalyst was synthesized through two-step but simple protocols to decontaminate metronidazole antibiotic water and inactivate bacteria strains under UV irradiation. In the presence of other antibiotics or salts as interference, the photocatalytic activity of Co–NZF was investigated. Based on the experimental findings, active species trapping, and theoretical electronic structure estimation, the results obtained are remarkable, and a potential degradation mechanism is highlighted. Since it can degrade organics and inactivate bacterial strains, Co–NZF is expected to have a bright future in the water treatment industry, reducing human reliance on chlorine. It's also worth noting that, because of its magnetic properties, Co–NZF was easily and quickly isolated by an external magnet after repeated reuse cycles.

Experimental section

Reagents

Analytical grade reagents were used without purification. Cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Nickel (II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), hydrochloric acid (HCl, 37%), Zinc (II) sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), ethanol, Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), acetic acid, metronidazole antibiotic (MZ) and sodium hydroxide (NaOH).

Synthesis of Co-doped Ni_{0.5}Zn_{0.5}Fe₂O₄

To start, the co-precipitation method was used to synthesize Ni_{0.5}Zn_{0.5}Fe₂O₄ (NZF) nanoparticles as shown in Scheme 1 (Mustafa and Oladipo, 2021). In 120 mL distilled water, 5.5 g ZnSO₄·7H₂O, 6 g NiSO₄·6H₂O, and 5.7 g FeCl₃·6H₂O were dissolved. The solution was stirred at 250 rpm continuously until it became homogeneous, then 20 mL of 0.3 M acetic acid was added to prevent particle aggregation. The reaction flask was then transferred to an oil bath and vigorously stirred at 800 rpm for 180 min at 80°C. The solution was cooled and dried overnight at 80°C before being calcined in a muffle furnace for 120 min at 800°C. Ni_{0.5}Zn_{0.5}Fe₂O₄ obtained was washed several times with distilled water and dried. The chemical reaction for the formation of Ni_{0.5}Zn_{0.5}Fe₂O₄ is shown as follows:

Co-precipitation stage:

Ferritization stage:

Following that, Co–Ni_{0.5}Zn_{0.5}Fe₂O₄ was prepared by mixing 5 g of NZF with 50 mL of 0.1 M Co(NO₃)₂·6H₂O; then stirred the solution at 250 rpm at room temperature for 45 min. The reaction temperature was then raised to 70°C, and 30 mL of 75 mM NaOH was added dropwise to the mixture and stirred for another 60 min. The precipitate was filtered, washed with water-50% ethanol mixture several times then dried at 100°C for 24 h. The final product was ground and sieved to a uniform size then labelled (Co–NZF).

Scheme 1: Schematic illustration of the synthesis of Co–Ni_{0.5}Zn_{0.5}Fe₂O₄

Characterizations

The Co–NZF was characterized by UV–vis diffuse reflectance spectroscopy (DRS) using a UV–2450 spectrometer (Shimadzu, Japan) from 200 nm to 800 nm. The SEM-EDX was acquired by JSM-6390 scanning electron microscope-coupled EDX (JEOL, Japan). The X-ray powder diffraction (XRD) patterns were recorded using X-ray diffractometer Bruker D8 (Bruker-AXS, Ettlingen, Germany) with a Cu K α ($\lambda = 1.54187 \text{ \AA}$) monochromatic radiation at 40 kV and 30 mA. The measurement was recorded at $2\theta = 5\text{--}70^\circ$ at a rate of 2° min^{-1} and the crystalline phases were clarified using standard JCPDS files. The electrochemical impedance spectroscopy (EIS) was investigated using the PalmSens Sensit smart potentiostat (PalmSens BV, Netherlands) in the frequency range of 50 Hz–200 kHz at room temperature. Fourier Transform Infrared (FTIR)

spectra were recorded in the range 4000–400 cm^{-1} using an FTIR-8700 spectrophotometer (Perkin-Elmer, Japan). Photoluminescence spectrum (PL) was collected by fluorescence spectrophotometer F-7000 (Hitachi High-Tech, Japan) with optical radiation at $\lambda = 340$ nm. At room temperature, a MicroSense Vibrating Sample Magnetometer (Model 10, MicroSense USA) was used to investigate the magnetic properties of samples ranging within $\pm 10,000$ Oe.

Photocatalytic degradation procedure

A 200 mg/L stock solution of the metronidazole antibiotic was prepared by dissolving it in deionized water. The stock solution was kept at 5°C until it was required. Diluting the stock solution with a background solution yielded working solutions with concentrations ranging from 10 to 100 mg/L. The Co–NZF photocatalytic activity was investigated in a batch-type customized-stirred pyrex-flask reactor under UV light (18 W, 385 nm; T8W5, China).

To investigate the effect of pH (3–10) on the performance of the catalyst, desired Co–NZF dose was dispersed in 25 mL of 50 mg L^{-1} MZ solution in the reactor, which was then stirred for 30 min under darkness to achieve the adsorption/desorption state before UV light irradiation for 360 min. The initial pH values of the solutions were adjusted with 0.1 M HCl/NaOH. The Co–NZF particles were separated from the solution using an external magnet periodically, and 2 mL of the sample was taken and analyzed for residual MZ concentration using UV–vis spectroscopy (T90+ UV-vis spectrophotometer PG Instruments Ltd, UK) at the $\lambda_{\text{max}} = 320$ nm with a 1 cm path length quartz cell. The concentrations were determined using a linear regression equation ($y = 0.0375x + 0.1967$) derived from a calibration curve of MZ absorption plotted over a range of concentrations with an R^2 of 0.998. The photocatalytic performance of MZ was examined by varying parameters such as initial MZ concentration (10–100 mg/L), oxidant concentration

(H₂O₂/K₂S₂O₄; 4–7 mM) and dosage of Co–NZF (10–50 mg). To test the stability and reusability of Co–NZF, the spent photocatalyst was eluted with base-spiked distilled water, dried at 40°C, and reused several times.

During the photocatalytic reaction, trapping experiments were carried out to investigate the contribution of radicals and active species. Before adding the Co–NZF, the MZ solution was spiked with 5 mM 1,4-benzoquinone (BQ), *tert*-butyl alcohol (*t*-BuOH), methanol and sodium oxalate (NaOx) to scavenge $\cdot\text{O}_2^-$, $\cdot\text{OH}$, $\cdot\text{SO}_4^-$ and h^+ scavengers, respectively. The catalytic activity of Co–NZF was also studied when 50 mg L⁻¹ MZ interfered with antibiotics (1 mg L⁻¹ Tylosin and tetracycline) and various salts (0.1 M of NaCl, KNO₃ and Na₂SO₄).

Bacterial inactivation activities of Co–Ni_{0.5}Zn_{0.5}Fe₂O₄ via time-kill assays

Time-kill assays were used to investigate the antimicrobial efficacy of Co–NZF against *Staphylococcus aureus* (*S. aureus*, ATCC 2921) and *Escherichia coli* (*E. coli*, ATCC 25922) as shown in Scheme 2. In Muller Hinton Agar (MHA, Biomerieux, France) and MacConkey agar (MCA, Biomerieux, France), *S. aureus* and *E. coli* cultures were incubated overnight at 37°C, respectively. Mueller Hinton Broth (MHB, Merck, Germany) was used to prepare the bacterial stock solutions, then standardized using 0.5 McFarland scale and diluted to 1 × 10⁷ CFU mL⁻¹ using sterile saline solution (0.85%) as shown in Scheme 2. 5–25 mg of Co–NZF was mixed with the bacterial solutions and agitated at 200 rpm either in the dark, or were exposed to the UV light ($\lambda_{\text{max}} = 365$ nm) at a distance of 4 cm. Flasks containing bacterial solutions that did not contain Co–NZF were used as a control group. Periodically, 10 mL of each sample was withdrawn and diluted with 90 mL of MHB. Finally, the diluted solutions were dropped onto the agar plate and incubated for 24 h at 37°C. Following that, the colonies were counted, and the bacteria concentrations (CFU per mL) and bacteria-killing efficacy (A%) were calculated using Eqs. 4 and 5.

Scheme 2: Outline of the bacteria killing due to the catalytic reaction of $\text{Co-Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$

Data analysis

Each experiment was replicated twice, with an average outcome of $\pm 1.5\%$ error. The photocatalytic degradation efficiency, η (%), degradation kinetics and the electrical energy per order, E_{EO} ($\text{kWh m}^{-3} \text{ order}^{-1}$) required to decrease the concentration of MZ were calculated following Eqs. 1–3:

$$\eta = \frac{1 - C_t}{C_0} \times 100 \quad (1)$$

$$\ln \frac{C_t}{C_0} = -k_{obs} t \quad (2)$$

$$E_{EO} = \frac{1000 \times P \times t}{V \times 60} \times \log \frac{C_0}{C_t} \quad (3)$$

$$\text{CFU mL}^{-1} = \frac{\text{No.of colonies} \times \text{dilution factor}}{\text{Volume of culture plated}} \quad (4)$$

$$A(\%) = \frac{\text{No.of CFUs in control group} - \text{No.of CFU in exp.group}}{\text{No.of CFU(control group)}} \times 100 \quad (5)$$

where C_t and C_o (mg/L) denote the MZ concentrations at time t (min) and before the reaction, respectively; while k (min^{-1}) is the apparent rate constant, V (L) denotes the reaction volume, P is the electrical power consumed during the process (kW) and t represents reaction time (min). GraphPad Prism (ver.7, USA) was employed for data visualization.

Results and discussion

The NZF and Co–NZF FTIR spectra are shown in Fig. 1a. We used the abbreviations ν and δ to denote stretching and bending vibrations, respectively, when interpreting infrared (IR) spectra. Main assignments of IR wave-numbers are listed accordingly for NZF and Co–NZF;

NZF: 1145 – 983 cm^{-1} δ (Fe–O–H/M= Ni or Zn); 845–832 cm^{-1} ν (Fe–O–M); 578 cm^{-1} ν (M – O/metal-oxygen tetrahedral (Fe $\leftrightarrow$ O)); 465 cm^{-1} ν (M – O/octahedral (Ni $\leftrightarrow$ O and Zn $\leftrightarrow$ O)); 415 – 600 cm^{-1} (characteristics bands of the spinel structure).

Co–NZF: 1153–1089 cm^{-1} δ (Fe–O–H); 476–469 cm^{-1} ν (M – O/octahedral and tetrahedral (Ni $\leftrightarrow$ O and Zn $\leftrightarrow$ O)); 445 cm^{-1} ν (Co–O); 415 – 600 cm^{-1} (characteristics bands of the spinel structure).

As previously stated, the tetrahedral and octahedral sites are strongly preferred by Zn and Ni atoms, respectively. Fe^{3+} cations, on the other hand, can occupy octahedral and tetrahedral sites (Thakur et al. 2016; Debnath et al. 2021). According to Fig.1a, the changes of IR spectra of the doped catalyst compared to the undoped catalyst can be outlined as follows. The Fe–O–H absorption bands in Co–NZF deviated marginally to long-wave regions and decreased in intensity, which is

likely due to the transformation of bond lengths or particle enlargement and crystal structure perfection as a result of Co doping onto NZF (Sivaranjani et al.2019; Ivanovskaya et al. 2009). Furthermore, in the Co–NZF spectrum; the Fe $\leftrightarrow$ O tetrahedral and the octahedral bands (Ni $\leftrightarrow$ O and Zn $\leftrightarrow$ O) merged into a sharp peak centred at 473 cm^{-1} . A new peak at 445 cm^{-1} was observed, which was due to the stretching of the Co–O and confirmed the existence of Co atoms in the $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ lattice. When the sample was sintered at 800°C, the stretching vibrations induced by the C–O bond with peaks around 1091–1143 cm^{-1} were noticeably weakened which is similar to the observation reported by Thakur et al. 2016.

Fig.1: Characterization of NZF and Co–NZF (a) FTIR (b) UV–vis DRS (inset: band energy gap from Tauc plots) (c) Transient photocurrent response (d) PL spectra.

The UV–vis DRS absorption spectra of the NZF and Co–NZF over the wavelength range of 200–800 nm are represented in Fig.1b. Both samples have high absorption in the ultraviolet range; NZF, in particular, has an absorption in the UV region (345–396 nm) due to intrinsic band transitions between the M^+ cations and $M^+ - O_2^-$, which is consistent with other studies (Qasim et al. 2015; Asadi and Moeinpour 2019; Aali et al. 2019; Nag et al., 2020). NZF has an absorption edge at 392 nm. The absorption edge of the Co–NZF wavelength region extends into the visible region (437 nm), with an absorption enhancement in the region of 450–595 nm, which is due to the interaction of the localized d -electrons of Co^{2+} and s - and p - electron of the host NZF (Kaphle et al. 2019). The absorption intensity of Co–NZF is greater than that of NZF in the 300–800 nm range, implying that it may have better catalytic activity in the UV and visible regions. The optical band gap (E_g) of the samples was calculated using Eq.6 (Oladipo et al.2019; Oladipo 2021ab) to be 2.84 eV and 2.99 eV for Co–NZF and NZF respectively.

$$E_g = \frac{1240}{\lambda_{AbsorpEdge}} \quad (6)$$

Note that doping with Co ions generates oxygen vacancies, which promotes the formation of M^{x-1} from M^x (host metal ions) (Chahal et al. 2020; Kaphle et al. 2019). This raises the number of M^{x-1} states, resulting in the creation of localized energy states closer to the conduction band and thus lowering the bandgap (Saranya et al. 2014).

Fig.1c displays the light response profiles of the NZF and Co–NZF during multiple irradiations of On/Off light. The photocurrent density increased rapidly when the irradiation light was activated for both samples, then decreased to a constant value when the light was shut off. The light response profiles of the NZF and Co–NZF during multiple irradiations of On/Off light are shown in Fig.1c. When the irradiation light was turned on for both samples, the photocurrent

density increased rapidly but decreased to a constant value when the light was turned off. Co–NZF, in particular, showed a photocurrent response of 1.73 A cm^{-2} , which is 1.4 times higher than NZF.

The photoluminescence (PL) technique was used to investigate the transfer and recombination rate of the photogenerated charge carrier. Both samples had two emission bands about $\sim 360\text{--}485 \text{ nm}$, as shown in Fig.1d. The broad 389 nm emission originates from an exciton-exciton collision mechanism from the recombination of the free excitons and is typically referred to as UV band edge emission (Ahmad et al. 2020). At 468 nm, the broad blue-green emission band is possibly due to the direct recombination of electrons in CB and holes in VB and oxygen defects (Saranya et al. 2014). On doping NZF with Co, the emission peaks redshifted and more oxygen defects were formed which resulted in a weak green emission band observed at $\sim 559 \text{ nm}$. In contrast to NZF, Co–NZF had a lower PL intensity; note that the lower the PL intensity, the lower the e^- and h^+ recombination rate.

SEM micrographs of NZF and Co–NZF are shown in Fig.2a. When examined closely, the Co–NZF has a spongy morphology with agglomerated irregular grain shapes which is consistent with the SEM of Ni–Zn ferrite reported by Džunuzović et al 2015. The crystallites' dipole interactions might have caused the agglomeration. The crystals are not completely monodisperse, and the average particle size of the samples is found to be between 23 and 28 nm. In both samples, several grain surfaces have hexagonal shapes and distorted edges, which is the basic crystal cell unit of ferrites (Thakur et al. 2016; Mustafa and Oladipo 2021). The presence of metal ions with compositions consistent with the predicted stoichiometry of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ was verified by energy-dispersive X-ray spectroscopy (EDX) analysis of the samples (Fig.2b). It's worth noting that the Pd and Au peaks in the spectra correspond to the metallic coater used in the experiments.

Fig.2c depicts the magnetic hysteresis loop for NZF and Co–NZF samples at room temperature. The magnetization results revealed ferromagnetic activity which is common for soft magnetic material (Džunuzović et al 2015). NZF's saturation magnetization (M_s) is 79.28 emu g⁻¹, which is less than Co–NZF's (85.94 emu g⁻¹); while these values are higher than the 57–78 emu g⁻¹ stated previously (Džunuzović et al 2015; Thakur et al. 2016). Because of the Co doping, Co–NZF has a higher crystallinity and saturation magnetization moment than NZF. The Co which is magnetic caused Fe³⁺ ions to migrate from tetrahedral to octahedral sites, disrupting ion equilibrium and increasing magnetization. Co doping, on the other hand, resulted in a slight increase in grain size in Co–NZF, with a lower coercivity (H_c) of 57.94 Oe than NZF (61.21 Oe). The M_r/M_s varies from 0.935 to 0.969 for both samples, which is closer to the average value of 1 for single-domain ferromagnetic particles. An external magnet can easily extract Co–NZF from aqueous solutions due to its high magnetic properties.

The electrochemical properties of the samples were investigated using impedance spectroscopy. Semicircular arcs were observed in both NZF and Co–NZF due to grain boundary conduction at low frequencies and high frequencies. The radius of the arc represents the interfacial charge transfer resistance (R_{ct}) in the EIS Nyquist plots in Fig.2d. Co doping resulted in increased defects (vacancies), which led to a decrease in Co–NZF's resistance, as predicted by the PL study. The decrease in resistivity can also be due to the reduction in the number of grain boundaries caused by the increase in grain size in the Co–NZF (Džunuzović et al 2015; Mustafa and Oladipo 2021). The Co–NZF has a lower R_{ct} value, indicating that it has a higher charge transfer efficiency than NZF. Under UV irradiation, Co–NZF had the smallest semi-circle diameter and a significantly lower R_{ct} value than NZF, implying a greater separation of photogenerated electron-

hole pairs and transfer efficiency, resulting in the highest photocatalytic activity against MZ degradation.

Fig.2: (a) SEM images (b) EDX spectra (c) magnetic parameters and (d) EIS Nyquist plots of NZF and Co-NZF.

Fig.3 shows the XRD pattern of NZF, with all major diffraction peaks corresponding to the standard pattern of the cubic spinel structure of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite (JCPDS# 52-0278, JCPDS# 10-0325 and JCPDS# 08-0234) at the position of $2\theta = 18.36^\circ, 30.14^\circ, 35.58^\circ, 37.11^\circ, 43.18^\circ, 51.94^\circ, 57.18^\circ, 62.88^\circ, 71.5^\circ$ and 75.14° matching (111), (220), (311), (222), (400), (422),

(511), (440), (620) and (533) Miller indices (Qasim et al. 2015; Džunuzović et al 2015; Thakur et al. 2016; Nag et al. 2020).

Similar diffraction peaks were observed in Co–NZF. As a result, cobalt (Co^{2+}) ion doping in NZF ferrite does not affect the NZF spinel phase because cobalt occupies interstitial space in the ferrite's cubic structure. However, other unidentified peaks between $21.14^\circ - 27.5^\circ$ disappeared and there was a minor change towards the lower angle in the 2θ position for each peak, which may be due to the replacement of Fe^{3+} having ionic radii of $0.65 \text{ \AA}$ by Co^{2+} with higher ionic radii of $\sim 0.74 \text{ \AA}$ (Debnath et al. 2021; Sinha 2021). According to the Debye Scherrer equation ($D=0.9\lambda/\beta \cos \theta$), the average crystallite size of NZF and Co–NZF was estimated from the intense peaks (220), (311) and (440) as 19.9 and 25.6 nm, respectively.

Fig.3: XRD patterns of the Co–NZF and NZF

Also, note that the Co–NZF exhibited higher crystallinity, slightly lower X-ray density, decreased dislocation density and increased average lattice constant (Table 1) due to the substitution of ions with smaller ionic radii in the ferrite structure by cobalt with larger atomic

radii ($\sim 0.74 \text{ \AA}$) (Debnath et al. 2021; Mustafa and Oladipo 2021). In addition, the strain has been induced in the system as a result of lattice expansion, and the positive sign indicates tensile stress (Chahal et al. 2020). Table 1 lists the textural characteristics of Co–NZF and NZF. According to the findings, both samples have meso and micropores. However, the mesopore volume of Co–NZF is ~ 1.4 times larger than that of NZF and its specific surface area is slightly lower which is likely due to (i) the aggregation of small cobalt particles into larger bulk particles of Co during the doping process (ii) owing to the doping of Co^{2+} (which is magnetic) onto NZF, the Co–NZF has a higher magnetization saturation than the NZF, which further enhances its agglomeration. Ali et al. (2016) also found that doping Ag onto a FeAlO sample reduced its surface area. Also, the specific surface areas of NZF and Co–NZF were determined as $56.2 \text{ m}^2 \text{ g}^{-1}$ and $44.0 \text{ m}^2 \text{ g}^{-1}$ respectively based on crystallite size. Since most of the grain boundaries in the crystallite are not accessible, these values are significantly lower than those obtained using the BET. Since the particle size increased with Co doping, the surface area of Co–NZF is less than that of NZF, which is consistent with the BET results.

Table 1: Surface and crystal characteristics of NZF and Co–NZF

Parameters	Notes	^a NZF	Co–NZF
Surface area and pore volume			
$S_{\text{BET}} (\text{m}^2 \text{g}^{-1})$	Brunauer–Emmett–Teller specific surface area obtained via N_2 adsorp. isotherm at $P/P_0 = 0.05\text{--}0.35$.	73.5	70.2
$V_t (\text{cm}^3 \text{g}^{-1})$	Total pore volume measured at $P/P_0 \sim 0.99$.	0.287	0.298
$V_{\text{mic}} (\text{cm}^3 \text{g}^{-1})$	Micropore pore volume.	0.158	0.117
$V_{\text{mes}} (\text{cm}^3 \text{g}^{-1})$	Mesopore volume obtained by deducting V_{mic} from V_t .	0.129	0.181
XRD structural data			
$D (\text{nm})$	Average crystallite size calculated through Debye Scherer's formula $= k\lambda/\beta \cos\theta$, $k = 0.94$; $\beta = \text{FWHM}$.	19.9	25.6
$\delta \times 10^{-3} (\text{nm}^{-2})$	Dislocation density calculated from $\delta = 1/D^2$	2.52	1.52

$\varepsilon \times 10^{-3} \text{ (nm}^{-2}\text{)}$	Lattice strain = $\beta/4 \tan \theta$	2.11	2.56
X (%)	% Crystallinity = $I_{\text{crystal, peaks}}/(I_{\text{crystal, peaks}} + I_{\text{amorph, peaks}})$	66.8	69.9
a (nm)	Average lattice constant	0.838	0.840
d (nm)	Average lattice spacing	0.206	0.209
V (nm ³)	Volume of the cubic unit cell = a^3	0.588	0.593
$\rho \text{ (g cm}^{-3}\text{)}$	X-ray density = $8M/N_{\text{avogadro}} * V$, M: molecular mass	5.37	5.33
S (m ² g ⁻¹)	Specific surface area based on crystallite particle size = $6000/D * \rho$	56.2	44.0

Magnetic parameters					EDX parameters Wt. (%)				
Samples	M _s (emu g ⁻¹)	M _r (emu g ⁻¹)	H _c (Oe)	M _r /M _s	Co	Fe	Ni	Zn	O
Co–NZF	85.94	80.35	57.94	0.935	7.2	49.7	12.9	13.3	16.9
^a NZF	79.28	76.81	61.21	0.969	0	51.3	13.7	15.6	19.4

^aMustafa and Oladipo 2021

Evaluation of Co–NZF under varying experimental conditions

Note that NZF's performance is noticeably lower than Co–NZF's, which was achieved at a longer reaction time in a series of tests. As a consequence, only Co–NZF findings are presented in this article.

Effect of pH variation

When the pH of 50 mgL⁻¹ MZ solution was varied in the absence and presence of oxidants (4 mM H₂O₂ or 5 mM K₂S₂O₈) at 200 rpm, a preliminary test was performed to evaluate the photocatalytic degradation of MZ using 25 mg Co–NZF. The pH-dependent speciation of MZ (pK_a =2.5) and the surface chemistry of Co–NZF (pH_{pzc} = 6.69; Fig.4a) are used to explain the MZ degradation behaviour here. The Co–NZF degradation efficiency reached a maximum of 74.9% without an oxidant at pH 3 then decreased steadily with increasing pH. MZ degradation reached 93.4% at pH 3 in the presence of H₂O₂ and Co–NZF, while when the solution pH was increased beyond pH 3, MZ degradation decreased remarkably and reached 16.3% at pH 9. In the K₂S₂O₈/Co–NZF system,

maximum degradation was observed at pH 3 which decreased to 32.6% at pH 9 (Fig.4b). Except in the presence of $K_2S_2O_8$, the pH of the final solutions increased before remaining marginally stable at pH 6.87.

The following is an interpretation of the removal behaviour as a function of pH variation: the anionic MZ^- , which are electron-deficient species, are dominant in the solution at pH 3 due to its pK_a and are electrostatically attracted to the positively charged $Co-NZF^+$ (since the pH is less than the $pH_{pzc} = 6.69$), resulting in higher degradation efficiency (Fakhravar et al. 2020). The higher degradation of MZ at acidic pH compared to that at pH 6 may likely be attributed to the hydrolysis of MZ (Azalok et al. 2021b). The formation of $\cdot OH$ radicals, which can boost the reaction rate and photocatalytic efficiency of the $Co-NZF$, is responsible for the higher degradation observed in the presence of H_2O_2 . MZ adsorption on the surface of $Co-NZF$ (during photocatalytic degradation) can occur through a combination of processes such as electrostatic attraction, hydrogen bonding, and complex formation between MZ π -electrons and the $Co-NZF$ metal ions between pH 3 and 7. At pH 9, lower degradation efficiency occurred due to repulsion between the negatively charged MZ^- , hydroxyl ions and the negatively charged $Co-NZF^-$. Other researchers have identified similar photodegradation activities for MNZ (Farzadkia et al. 2015; Bashiri et al. 2020); hence, subsequent studies were conducted at pH 3.

Fig.4: (a) pH point zero charge determination, and variation in (b) solution pH (c) Co-NZF dosage (d) oxidant concentration. *Reaction conditions:* reaction time = 360 min; initial MZ conc. = 50 mgL^{-1} and MZ vol. = 25 mL.

Variation in Co-NZF dosage and oxidant concentration

The degradation efficiency of 50 mgL^{-1} MZ and the final concentration as the dose of Co-NZF was varied at pH 3 in the presence of 4 mM H_2O_2 are shown in Fig.4c. When the Co-NZF dosage was increased from 10 mg to 35 mg, the degradation efficiency increased marginally from 92.8% to 93.9%. When the Co-NZF dose was increased to 50 mg, the degradation efficiency decreased slightly to 87.7%. The observed decreasing trend in degradation efficiency when the Co-NZF dosage reached 50 mg is most likely due to one of three factors: (i) increased suspension turbidity due to increased catalyst in the bulk, which resulted in decreased UV light penetration and

photoactivation efficiency (Sathya et al. 2017; Bajorek et al. 2019; Oladipo 2021ab); (ii) the aggregation of excess Co–NZF might decrease its effective surface area and adsorption of the MZ species (Aram et al. 2020) or (iii) as the amount of catalyst in the suspension increased, photon-activated Co–NZF species were deactivated by collision with excess Co–NZF, as shown in Eq. 7.

Arghavan et al. 2021 reported a similar phenomenon when they used a nickel ferrite-based nanocomposite to degrade metronidazole under simulated sunlight irradiation. They observed an increase in activity from 0.005 to 0.04 gL⁻¹ in catalyst dose, then a decrease at higher catalyst loadings. In this study, further experiments were carried out using 10 mg of Co–NZF per 25 mL of MZ because there were no major variations in Co–NZF performance when 10 mg and 35 mg were used.

When the oxidants' initial concentrations were varied from 4 mM to 7 mM, the MZ degradation efficiency is shown in Fig.4d. When H₂O₂ concentration was increased from 4 mM to 6 mM, MZ degradation efficiency decreased from 92.8% to 73.3%, then remained nearly unchanged when 7 mM H₂O₂ was used. The decreasing trend is most likely due to an excess of H₂O₂ in the system scavenging the produced [•]OH radicals, potentially resulting in less reactive hydroperoxyl radicals ([•]OOH) (Azalok et al. 2021ab). Based on the findings, a concentration of 4 mM of H₂O₂ was chosen for subsequent experiments.

When the concentration of K₂S₂O₈ was increased from 4 mM to 5 mM, MZ degradation increased from 30.2% to 50.8%. Increased K₂S₂O₈ concentration resulted in more oxidative radicals ([•]SO₄⁻ and [•]OH), which favoured MZ degradation. However, the degradation efficiency decreased to 25.8% when K₂S₂O₈ concentration was elevated to 7 mM. This is likely due to the

competitive consumption of the free $\text{SO}_4^{\cdot -}$ radicals by the excess $\text{K}_2\text{S}_2\text{O}_8$ or generation of comparatively weaker $\text{SO}_5^{\cdot -}$ (1.1 eV) (Chen et al. 2018); hence, the rate of degradation reduced. Subsequent studies were carried out using 5 mM $\text{K}_2\text{S}_2\text{O}_8$.

Variation in initial MZ concentration

The photocatalytic degradation efficiencies of MZ when the concentration was varied from 10 to 100 mgL^{-1} in the presence of 10 mg Co-NZF/4mM H_2O_2 per 25 mL of MZ at pH 3 are shown in Fig.5a. The degradation efficiency shows an increasing pattern as the initial concentration of MZ was increased from 10 to 50 mgL^{-1} , and then dramatically decreased. The degradation efficiency reached 92.8% after a 6 h reaction with a 50 mgL^{-1} MZ concentration; however when the MZ concentration was increased to 100 mgL^{-1} , it decreased to 52.3%. The lower degradation efficiency observed at 100 mgL^{-1} of MZ is due to an insufficient number of reaction sites or active radicals to satisfy the increasing MZ species, as the Co-NZF dosage remained constant.

The MZ degradation was investigated under optimized conditions. In preliminary adsorption experiments conducted in the dark for 12 h using 10 mg Co-NZF, 70.2% MZ adsorption was observed while MZ self-degradation was significantly negligible in a blank experiment (without Co-NZF in the dark). As shown in Fig.5b, without the catalyst, 5.86% of MZ was photolytically degraded (under UV irradiation alone), but when 4mM H_2O_2 and 5 mM $\text{K}_2\text{S}_2\text{O}_8$ were added within 360 min, the degradation increased to 33.9% and 44.8%, respectively. After 6 h of UV irradiation in the presence of 10 mg Co-NZF and no oxidant, the MZ degradation efficiency reached a peak of 68.6%. Even though the degradation efficiency in the dark is higher than under UV, the UV synergistically stimulated Co-NZF, causing it to generate photoinduced charge carriers and aided the degradation rate as compared to when it was dark.

The 10 mg Co–NZF/H₂O₂/UV and 10 mg Co–NZF/K₂S₂O₈/UV systems reached 92.8% and 50.8% degradation, respectively. However, according to the kinetic studies shown in Fig.5c, the Co–NZF/H₂O₂/UV system had a faster degradation rate and reached the maximum before 6 h. When compared to photolysis (UV alone), H₂O₂/UV and K₂S₂O₈/UV systems, the photodegradation activity of Co–NZF/H₂O₂/UV increased remarkably by 15.8, 2.74 and 1.74 times, respectively. The increased performance is attributed to Co–NZF's activation of H₂O₂ that generated •OH radicals to enhance the degradation of MZ as represented in Eqs. 8–10.

In comparison to using Co–NZF alone, the Co–NZF/K₂S₂O₈ system showed less degradation. K₂S₂O₈ is available in the form of S₂O₈²⁻ in a wide pH range between 2 and 14 due to its low pK_a = –1.30 and may firmly attach to the positively charged catalyst's surface (pH_{pzc} = 6.69) at pH 3, decreasing MZ adsorption for photocatalytic degradation. Based on these findings, we can deduce that while photolysis and oxidants play minor roles in MZ degradation individually, the synergistic effects of photocatalysis (Co–NZF/H₂O₂/UV) are critical.

Fig.5: (a) Degradation efficiencies of Co–NZF based on initial MZ concentration (b) degradation efficiencies of various processes (c) degradation of MZ as a function of UV irradiation time using Co–NZF/H₂O₂ (inset: kinetic linear simulation curve). *Reaction conditions:* K₂S₂O₈ = 5 mM; H₂O₂ = 4 mM; Co–NZF dosage = 10 mg; MZ vol.= 25 mL; pH = 3 and 360 min.

The electrical energy consumed per order, coefficient of determination (R^2) values, treatment cost, half-life ($t_{50\%}$) corresponding to 50% MZ degradation efficiency and rate constant (k_{obs} , min^{-1}) of the pseudo-first order model are listed in Table 2. The R^2 values in the MTZ concentration range studied were greater than 0.97, showing that the photocatalytic degradation of MZ using Co–NZF follows pseudo-first-order kinetics. When the MZ concentration was increased from 50 to 100 mg L^{-1} , the rate constant reduced from 0.0117 to 0.0074 min^{-1} . This decrease, according to Arghavan et al. 2021, is due to a larger concentration of intermediate products, which

limits interaction with active hydroxyl radicals, decreasing the rate constant. In addition, a cost estimate based on a 0.05\$ per kWh electricity price in the Turkish Republic of Northern Cyprus in 2021 shows that the E_{EO} value for 50 mg L⁻¹ MZ solution is roughly 2 times lower than that for 100 mg L⁻¹.

Table 2: Comparative MZ degradation efficiency of Co–NZF and other catalysts

#Process	pH	MZ Conc. (mg L ⁻¹)	#Time (min)	k_{obs} (min ⁻¹)	# $t_{50\%}$ (min)	R^2	η (%)	E (kWh m ⁻³)
Co–NZF/H ₂ O ₂	3	50	360	0.0093	74.5	0.987	92.8	17.11
Co–NZF/H ₂ O ₂	3	100	360	0.0062	111.8	0.976	52.3	25.78
ⁱ Ag–d–NZF/H ₂ O ₂	3	50	360	0.0103	67.3	0.997	99.9	26.84
ⁱⁱ MnFe–LDO–biochar/K ₂ S ₂ O ₈	3	20	240	0.212	3.27	0.996	92.1	11.31
ⁱⁱ MnFe–LDO–biochar/H ₂ O ₂	3	20	240	0.0868	7.98	0.987	99.0	10.26
ⁱⁱⁱ UV/BiOI–MWCNTs	7	10	90	0.0740	9.36	0.952	99.9	32.09
^{iv} FeNi ₃ /chitosan/BiOI	7	20	200	0.0092	75.3	0.983	100	–
^v N–TiO ₂ /ZnFe ₂ O ₄ /zeolite/O ₃	5	100	120	0.0196	35.6	0.998	94	–
^{vi} 25% BiVO ₄ /BiPO ₄	–	5	120	0.0203	34.1	–	90	–

[#]Each process is under UV irradiation at a given reaction time. $t_{50\%}=0.693/k_{obs}$.

i: Mustafa and Oladipo 2021; ii: Azalok et al.2021b; iii: Balarak et al. 2019; iv: Arghavan et al. 2021; v: Aram et al. 2020; vi: Yunhui et al.2019.

Active radicals trapping test and metronidazole UV-catalytic degradation mechanism

The radical trapping test, shown in Fig.6a, was used to validate each radical's contribution to the MZ degradation process. The application of BQ under the same optimum conditions significantly hampered the Co–NZF degradation efficiency, resulting in 64.7% MZ degradation compared to 92.8% without the BQ. In the presence of *t*-BuOH and Na-Ox, respectively, the degradation efficiency decreased to 77.6% and 81.7%. The results revealed that $\bullet O_2^-$ was the most prevalent radical; this is most likely owing to active defects in the Co–NZF structure, which are responsible for O₂ adsorption and reduction to generate reactive oxygen species (ROS) $\bullet O_2^-$. Both $\bullet OH$ radicals and photoinduced holes (h^+) contributed to the decomposition processes.

Fig.6: (a) Active radicals quenching during degradation process (b) performance of Co-NZF in presence of interfering species (c) Co-NZF reuse studies. *Reaction conditions:* pH =3, catalyst dosage = 10 mg and MZ initial concentration = 50 mgL⁻¹ under 360 min UV illumination.

Considering the radical scavenging results and UV-vis DRS data, the likely mechanism of MZ photodegradation by Co-NZF is postulated. Eqs. 11 and 12 were used to calculate the conduction band (C_b) and valence band (V_b) potentials of Co-NZF, which were found to be -0.53 eV and 2.31 eV, respectively; and χ represents the calculated absolute electronegativity of Co-NZF.

$$C_b = V_b - E_g \quad (11)$$

$$V_b = \chi + 0.5E_g - 4.5 \text{ eV} \quad (12)$$

In the initial dark adsorption step, the reactive sites of Co–NZF absorbed both MZ species and oxygen. Electrons are promoted from the V_b to the C_b when the Co–NZF was irradiated with photon energy greater than that of its bandgap. As indicated in Eq.8, this mechanism produces electron (e^-)–holes (h^+) in the exterior shell of Co–NZF, which generates extremely reactive radicals by oxidizing O_2 and H_2O molecules as shown in Eqs. 13–14.

This is thermodynamically feasible because Co–NZF's C_b is more negative than the reduction potential of $\text{O}_2/\bullet\text{O}_2^-$ (–0.33 eV vs. NHE) and its V_b is more positive than ($\bullet\text{OH}/\text{H}_2\text{O}$, 2.10 eV vs. NHE) (Karimi et al. 2019; Ekande and Kumar, 2021; Oladipo 2021ab). If no suitable charge carrier scavengers are available, the generated e^- and h^+ pairs recombine, generating heat; however, MZ molecules can be degraded if charge separation is established. Because of its localized surface plasmon resonance effect (Braik et al. 2021; Sinha 2021; Debnath et al. 2021), the Co dopant can act as an electron reservoir and delayed the recombination of photoinduced charge carriers as validated by the results of the PL investigation. Also, the conversion between Co^{3+} and Co^{2+} (1.81 V vs NHE) gives priority to capture electrons, hence can inhibit electron-hole pair recombination (Hu et al. 2018). Based on the results of the radical quenching studies, the $\bullet\text{O}_2^-$ radicals and the photogenerated charge carriers can either directly degrade the adsorbed MZ or react with H_2O_2 in the system to form $\bullet\text{OH}$ radicals, as represented in Eqs. 15–16 and Scheme 3.

Scheme 3: Probable MZ degradation and bacterial disinfection mechanisms of Co-NZF

Effect of interference on degradation performance and reusability of Co-NZF

Under optimal conditions, different salts (Na_2SO_4 , KNO_3 and $NaCl$) and antibiotics (tetracycline and tylosin) were added into the system as interference. In the presence of ionic salts and antibiotics, the Co-NZF degradation efficiency decreased to 53.3–75.4% ($SO_4^{2-} > NO_3^- > Cl^-$) and 51.7–67.3%, respectively, after 360 min of interaction (Fig.6b). The size of the interfering species, the magnitude of the surface charge, and the generation of less reactive species may all contribute to the inhibition of Co-NZF. Tylosin and tetracycline, in particular, have a molecular

weight of ~5.4 and 2.6 times that of the MZ, respectively. As a result, their adsorption on the surface of Co-NZF could prevent MZ from adsorbing further. The hydroxyl radicals are scavenged by sulphate, chloride, and nitrate ions, resulting in the formation of less reactive inorganic species such as $\text{NO}_2^\bullet$, Cl^- , $\text{SO}_4^{\bullet-}$ and $\text{Cl}_2^{\bullet-}$ (Devi et al. 2013); hence, MZ degradation was subsequently reduced as a result of this. The Co-NZF was effectively recycled for five photocatalytic reuse cycles and retained more than 50% after the third cycle but the performance decreased remarkably beyond this stage (Fig. 6c). This decrease in degradation efficiency could be related to the diminishing reactive sites and Co-NZF concentration in the bulk solution as a result of sequential separation, filtration, and washing operations.

Bacterial disinfection activity performance of Co-NZF

The *in vitro* antibacterial activity of Co-NZF against *S. aureus* and *E. coli* at different dosages are shown in Fig.7; the viability curves were created by counting colony-forming units (CFU). Co-NZF displayed bacteriostatic and bactericidal effects after 60–180 min of UV light irradiation against the bacterial colonies, as seen in time-kill studies in Fig.7a–b. At 5–25 mg mL⁻¹, Co-NZF was bacteriostatic against both bacterial species for the first 180 min afterwards then exhibited bactericidal effects. In comparison to the control (without Co-NZF), 41.1, 66.8, and 74.1% *E. coli* degradation were obtained in the first 60 min in the presence of 5, 15, and 25 mg mL⁻¹ Co-NZF/UV system, respectively. But when the time was extended to 120 min; both 15 and 25 mg mL⁻¹ of Co-NZF inactivated nearly 98% of the *E. coli* colonies (Fig.7a). After 120 min (Fig.7b), 5 mg of Co-NZF had a bactericidal effect against *S. aureus*, which was most likely owing to the interaction of the positively charged Co-NZF⁺ with the bacteria proteins or/and the induction of ROS, which resulted in bacterial death.

Fig.7: Time-kill assays as a function of Co–NZF doses for inhibition of *E. coli* and *S. aureus* under UV-light assisted inhibition (**a and b**); **c** and **d** show antibacterial inhibition performance of Co–NZF in the dark and under UV in 60 min.

The performance of Co–NZF was examined after 60 min in the absence and presence of UV light to further understand the contribution of UV light during the bacteria degradation process (Fig.8). After 60 min, without UV light irradiation, 5, 15, and 25 mg mL⁻¹ of Co–NZF showed 22.2, 28.1, and 76.9% degradation efficiency, respectively, as shown in Fig.7c for *E. coli*. When the Co–NZF dosage was increased from 5 to 15 mg mL⁻¹, the degradation efficiency of *S. aureus* in the dark decreased from 94.4% to 72.9%. Only 23.4% bacterial degradation efficiency was attained when the dose was increased to 25 mg mL⁻¹ (Fig.7d). Suggesting that 5 mg of Co–NZF is sufficient to remarkably inactivate *S. aureus* in the dark condition. It is worthy to note that under both the dark

and UV-light conditions; Co–NZF demonstrated better antibacterial action against *S. aureus* strains than *E. coli* strains, which could be attributed to differences in their composition and cell membrane structure.

Fig.8: Comparative performance of varying doses of Co–NZF against *Escherichia coli* in the dark and UV-light after 60 min catalyst exposure.

Different mechanisms for the bactericidal effects of ferrites and metal oxides have been proposed in previous investigations (Asadi et al. 2019; Aali et al. 2019; Mizwari et al. 2021; Mmlesi et al. 2021). According to Méndez-Pfeiffer et al. 2019, atomic force microscopy images revealed damage to the *E. coli* cellular wall in the presence of photoactivated Ag nanoparticles. They believe that the Ag NPs' positive charge can easily interact with the phosphate groups of the bacteria membrane's phospholipids and penetrate the bacteria, causing the membrane to rupture and release the cellular contents. In line with their report, the antibacterial activity of the Co–NZF in the dark, herein, is likely due to the interaction of positively charged metal ions in the catalyst's external shell with sulfhydryl groups and phosphorus-containing compounds in the bacterial cell

membrane, causing damage to the DNA's replication potential. The enhanced antibacterial activity of Co–NZF under UV light could be related to the production of reactive oxygenated species, which damaged the membrane and caused cell death.

Conclusion

Ni-Zn ferrites (NZF) were synthesized using a slightly modified co-precipitation procedure and then doped with Co^{2+} ions to produce an effective photocatalyst (Co–NZF) for decontamination of bacterial-contaminated and metronidazole antibiotic (MZ) water. Both NZF and Co–NZF were characterized using various spectroscopic and electrochemical tools. Co–NZF has a bandgap of 2.84 eV, an average crystallite size of 25.6 nm, a specific surface area of $70.2 \text{ m}^2 \text{ g}^{-1}$, total pore volume of $0.298 \text{ cm}^3 \text{ g}^{-1}$, spongy morphology with agglomerated irregular grain, and can be easily separated from the solution by an external magnet, according to the results. The use of Co doping resulted in an increase in impurity levels, which helped to separate and transport photogenerated electron-hole pairs more effectively. Also, Co–NZF had the highest photocurrent intensity and smallest arc radius (R_{ct}) which decreased its electron transfer impedance with increased charge mobility due to the variation in ionic and electronic conductivity induced by Co incorporation.

Under optimal conditions (4 mM H_2O_2 , 360 min reaction time, 50 mgL^{-1} MZ, and pH 3); 10 mg of Co–NZF degraded 92.8% of the MZ with a rate constant of 0.0093 min^{-1} and consumed total electrical energy of 17.11 kWh m^{-3} . Even in the presence of very high molecular weight antibiotic interferences, the catalyst retained more than 50% of its performance with adequate reuse efficiency. Notably, 15 mg Co–NZF achieved a complete inhibition of both *E. coli* and *S. aureus* strains when photoactivated for 180 min. In the dark, 5 and 25 mg of Co–NZF exhibited 94.4% and 77% bacteriostatic effects on *S. aureus* and *E. coli*, respectively within 60 min.

Authors' contributions All authors contributed to the conceptualization, read and approved the final manuscript. **FSM** performed the experiments, collected and analyzed the data. **AAO** formulated the research ideas, designed the methodology, interpreted the data and was a major contributor in writing the manuscript. **ZMM** characterized the synthesized materials and interpreted results. **MG** provided reagents, instrumentation and administration.

Data availability The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests The authors declare that they have no competing interests.

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