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## Dual functional novel catalytic $Cu_{1-x}Zr_xFe_2O_4$ (x=0, 0.5, 1) nanoparticles for synthesis of polysubstituted pyridines and sunlight-driven degradation of methylene blue

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Harminder Singh, Department of Chemistry, Dr B. R. Ambedkar National Institute of Technology, Jalandhar – 144011, Punjab, India. Email: harmindersingh87@gmail.com The effect of varied zirconium content on the structural, morphological, magnetic, optical, thermal and catalytic properties of nanoparticles of the ferrite  $Cu_{1-x}Zr_{x}Fe_{2}O_{4}$  (x = 0, 0.5, 1) was investigated. The mixed ferrite was synthesized by the auto-combustion method using nitrates of respective metals and citric acid as a chelating agent. The as-prepared nanoparticles showed dual benefits. They were employed as a heterogeneous catalyst for one-pot synthesis of polysubstituted pyridine derivatives as well as for catalytic degradation of industrial waste dyes such as methylene blue (MB). The highlight of the research reported is the catalytic degradation of industrial waste (MB) with high efficiency in eluent of a wide range of pH (3-13). The proposed nanoparticles arguably offer certain great advantages that include: low cost, facile nature, anti-leaching property, magnetic recoverability and recyclability. The characterization of the as-synthesized nanoparticles was done using various techniques. The leaching study was carried out using inductively coupled plasma optical emission spectroscopy. The formation of organic products was confirmed using Fourier transform infrared and <sup>1</sup>H NMR spectroscopies and examination of degradation products of MB dye was carried out using mass spectrometry and UV-visible spectroscopy.

#### **KEYWORDS**

degradation, methylene blue, polysubstituted pyridines, recyclable, reusable

## **1** | INTRODUCTION

Among heterocyclic compounds, N-heterocyclic compounds are of immense interest due to their momentous contribution in medicinal chemistry. They have a significant position in the field of natural products and synthetic organic compounds due to their being key elements of diverse drugs. Pyridine structures are important heterocyclic compounds found in many natural products, agrichemicals, pharmaceuticals and functional materials.<sup>[1]</sup> Among the various derivatives, 2-amino-3cyanopyridine derivatives possess multiple activities such as anti-pyretic,<sup>[1]</sup> anti-tumour,<sup>[2]</sup> antimicrobial,<sup>[3,4]</sup> antiinflammatory,<sup>[5,6]</sup> antibacterial,<sup>[7]</sup> anticonvulsant,<sup>[8]</sup> fungicidal,<sup>[9]</sup> cannabinoid receptor agonist,<sup>[1]</sup> 1 KK-b inhibitory,<sup>[3]</sup> analgesic,<sup>[10]</sup> HIV-1 integrase<sup>[11,12]</sup> and antiexcitotoxic<sup>[10]</sup> activities and are intermediates for the production of an extensive variety of important heterocycles.

Methylene blue (MB) is a strongly coloured compound which is used in dyeing and printing industries and is a common water pollutant.<sup>[13–15]</sup> It is also used as a probe in many biochemical systems. It causes various health problems such as eye burns by direct contact, anaemia, nausea, vomiting, bladder irritation, mental confusion, profuse sweating, gastrointestinal problems and methemoglobinemia.<sup>[16,17]</sup> A number of techniques such as physical (adsorption, ultrafiltration, coagulation and ion exchange) and biological (bacteria and yeasts) have been reported in the literature for the removal of coloured effluents coming out with industrial and textile waste. The reported techniques do not convert the contaminants into less harmful and useful products.<sup>[7]</sup> Moreover, they do not cause complete degradation and also are not capable of discontinuing their movement from one phase to another. These methods do not work well due to high stability and resistance to chemical and biological degradation of dyes. So, a more suitable method is still in demand which overcomes these problems for wastewater treatment.<sup>[8]</sup>

Photocatalysis has proven to be a convenient, simple and eco-friendly way for the degradation of harmful dyes due to the use of oxygen as an oxidant, low-temperature oxidation of organic compounds and complete mineralization.<sup>[18-22]</sup> Photocatalysis is a process that uses the energy from incident radiation and the catalytic properties of the surface of a material to bring about or speed up important chemical reactions (oxidation and reduction reactions) without the material itself being consumed.<sup>[23-25]</sup> When irradiated with light energy, an electron (e<sup>-</sup>) is excited from the valence band to the conduction band of the photocatalyst, leaving behind a photogenerated hole (h<sup>+</sup>). The production of electronhole pairs after the absorption of light energy is further responsible for occurrence of a redox reaction. The main oxidant (i.e. OH') causes the oxidation of organic compounds. It is produced by the reaction of hydroxide ion with a photogenerated hole  $(h^+)$ , when the photocatalytic reaction occurs in an aqueous medium.<sup>[26]</sup>

Metal oxides containing iron as the main component are called ferrites with general formula MFe<sub>2</sub>O<sub>4</sub> (M = Co, Ni, Cu, etc.).<sup>[10-12,27-30]</sup> Ferrites are important magnetic materials with high magnetic character, low cost of production, high thermal and chemical stability, and a wide range of applications in scientific and industrial fields such as in transformer cores, permanent magnets, radio wave circuits, magnetic resonance imaging, high-quality filters, antenna rods, magnetic recording media, operating devices, magnetic resonance amplifiers, etc.<sup>[31]</sup> Nowadays, ferrite materials are used in sensor materials, as catalysts for the oxidation of alcohols into aldehydes and also as antibacterial agents.<sup>[32-36]</sup> Among the ferrites, spinel ferrites are of great interest due to their wide-ranging applications in modern technology. These materials are broadly studied due to their electric, magnetic, catalytic<sup>[37,38]</sup> and structural properties.<sup>[28]</sup> When spinel ferrites are in the nanometric size range, they display superparamagnetic nature, which is of great interest due from the point of view of their application.<sup>[27]</sup> Further, in a catalytic system, they can be easily separated from reaction media using an external magnet.<sup>[39,40]</sup> This property enhances their use as heterogeneous catalysts in many organic synthetic transformation reactions.<sup>[9]</sup> Further, due to low band gap and easy availability of catalytic active sites, spinel ferrites can be used in the degradation of industrial toxic waste and dyes.<sup>[41]</sup> Of the various spinel ferrites, copper ferrite ( $CuFe_2O_4$ ) is one of the most studied by various experimental techniques because of the relatively small energy difference between Cu<sup>2+</sup> ions at the tetrahedral (A) and octahedral (B) sites, and cation rearrangement is probable and strongly dependent on the microstructure, calcination temperature, cooling rate and other parameters.<sup>[42,43]</sup> Incorporation of various substituents of magnetic and nonmagnetic nature like Zn,<sup>[44]</sup> Al,<sup>[45]</sup> Ni and Co,<sup>[46]</sup> Ti,<sup>[47]</sup> etc., has been done in copper ferrite to transform the properties. However, to the best of our knowledge, zirconium has not been substituted in copper ferrite. Numerous excellent properties are exhibited by zirconium, a lustrous, greyish-white, soft, ductile and malleable metal, which is solid at room temperature, though it becomes hard and brittle at lower purities. Zirconium is highly resistant to corrosion by alkalis, acids, salt water and other agents.

In the work presented here,  $Cu_{1-x}Zr_{x}Fe_{2}O_{4}$  (x = 0, 0.5, 1) nanoparticles with good magnetic response properties and high specific surface area were prepared from metal nitrates by the auto-combustion route using citric acid as a chelating agent. They were subsequently used as a heterogeneous catalyst for the synthesis of polysubstituted pyridines at room temperature and in the photocatalytic degradation of MB in aqueous solution under sunlight irradiation with optimization of various reaction conditions. The structural phase of the as-prepared nanoparticles was characterized using X-ray diffraction (XRD) analysis. The particle size and morphologies were determined using transmission electron microscopy (TEM) and the chemical composition was determined using X-ray photoelectron spectroscopy (XPS). Thermal stability was determined using thermogravimetric analysis (TGA). Magnetic properties were investigated with vibrating sample magnetometry (VSM). The effect of doping of zirconium ions on various properties of copper ferrite, like structural, morphological, optical, thermal and magnetic properties, was investigated.

### 2 | EXPERIMENTAL

### 2.1 | Materials

All the reagents used in the study were of analytical grade and they were used as such without further purification. Zirconyl nitrate, copper nitrate (extra pure), ferric nitrate (extra pure), citric acid (pure) and ammonium hydroxide (25%) were purchased from Loba Chemie.

#### 2.2 | Methods

The crystal structure of the prepared magnetic nanoparticle catalyst was investigated using XRD with a PANalytical X'Pert PRO (NPD) X-ray diffractometer with Cu K aradiation ( $\lambda = 0.154$  nm), in the 2 $\theta$ range 10-80°. Fourier transform infrared (FT-IR) spectroscopy was carried out using an Agilent Cary 600 in the range 400-4000 cm<sup>-1</sup>. The morphology was studied using TEM. Samples were prepared by dispersion of nanoparticles in ethanol, which were deposited on a carbon-coated Cu grid, and, after drying, analysis was performed using a Hitachi S7500 instrument. The magnetic properties were measured using a VSM instrument (Princeton Applied Research model 155) at room temperature with a maximum magnetic field range of +1 to -1 T. TGA of the catalyst was performed using an EXSTAR6000TG/DTA 6300 instrument in the temperature range 50-700°C at a heating rate of 10°C min<sup>-1</sup> under nitrogen atmosphere. Light intensity was measured with digital lux meter (HTC <sup>™</sup>model LX-101A). A mercury lamp of power of 15 W in a photocatalytic chamber was used as a source of artificial UV radiation and the distance of dye solution (when stagnant) was set as 50 cm from the lamp. An ultrasonic cleaner (sonication) (JSGW model 1236/2) of a frequency of 33  $\pm$ 3 kHz with internal dimensions of 228 mm  $\times$  140 mm  $\times$  100 mm was used. Surface area and pore characteristics were characterized using a Quanta Chrome Nova-1000 surface analyser instrument at liquid nitrogen temperature with vacuum degassing at 110°C for 3 h. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. Surface properties were studied using XPS (PHI 5000 Versa Prob II, FEI Inc.). Calcination was done in a muffle furnace (Labco model 1541, with inner size of  $10'' \times 5'' \times$ 5"). Leaching study was carried out using inductively coupled plasma optical emission spectroscopy (ICP-OES; Thermo ICAP 7600). The organic products were characterized using <sup>1</sup>H NMR spectroscopy at 400 MHz with an Advance 400 spectrophotometer using tetramethylsilane as the internal standard and CDCl<sub>3</sub> as solvent. Software used for NMR analysis was MNOVA and for drawing chemical structures was ChemDraw ultra 8.0.

## 2.3 | Synthesis of $Cu_{1-x}Zr_xFe_2O_4$ (x = 0, 0.5, 1) Nanoparticles

 $Cu_{1-x}Zr_xFe_2O_4$  (x = 0, 0.5, 1) nanoparticles were synthesized by the auto-combustion method using citric acid as

a chelating agent. In a typical synthesis, metals salts and chelating agent were taken in a 1:3 ratio (copper nitrate mmol)/citric acid (3 mmol) and ferric nitrate (1 (2 mmol)/citric acid (6 mmol) or zirconyl nitrate (0.5 mmol)/citric acid (1.5 mmol), copper nitrate (0.5 mmol)/citric acid (1.5 mmol) and ferric nitrate (2 mmol)/citric acid (6 mmol), or zirconyl nitrate (1 mmol)/citric acid (3 mmol) and ferric nitrate (2 mmol)/citric acid (6 mmol)) in 5 ml of deionized water separately followed by sonication for 10 min. The solutions were stirred for 30 min separately. Then, the solutions were mixed and again stirred for 30 min to afford a homogeneous mixture. Ammonium hydroxide was used to make the pH of the mixture to 7 by neutralization of nitrate-citric acid solution. After this, the mixture was put on a hot plate for 1 h at 100°C and autocombustion took place with evolution of N<sub>2</sub>, CO<sub>2</sub>, HCl gases, etc., leaving behind a black-coloured fluffy ash material. Further, the solid material was subjected to thermal treatment at 600°C for 4 h in a muffle furnace.

# 2.4 | Synthesis of Polysubstituted Pyridine Derivatives

For the synthesis of substituted derivatives, malononitrile (1 mmol, 55.51  $\mu$ l), cyclohexanone (1 mmol, 103.53  $\mu$ l) and ammonium acetate (1.5 mmol, 0.115 g) were added to ethanol (2 ml) and then anisaldehyde (1 mmol) in the presence of 5 mg of Cu<sub>1 - x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (*x* = 1). The resultant mixture was stirred for an appropriate time at room temperature. The completion of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was removed simply using an external magnet. The obtained precipitates were washed with ethanol. The filtrate was then recrystallized from acetone and water (9:1) to afford the pure product in excellent yield.

## 2.5 | Degradation of MB Catalysed by $Cu_1 - {}_xZr_xFe_2O_4$ (x = 1) Nanoparticles

In a typical experiment, 10 ml of 10 ppm MB dye solution and 10 mg of Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 1) catalyst were placed in a round-bottom flask. Before irradiation, the reaction suspension was magnetically stirred at 800 rpm for 30 min in the dark to establish adsorption equilibrium between the catalyst, dye and water. Afterwards, the suspension was put under sunlight for an appropriate time for complete degradation. The experiments were carried out under direct solar radiation for consecutive sunny days in March–April 2017 from 11.30 a.m. to 2.30 p.m. with an average light intensity of 75 000–85 000 lux. All experiments were carried out in the temperature range 30–36°C.

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## 3 | RESULTS AND DISCUSSION

A stoichiometric combustion reaction scheme of metal nitrates with citric acid as chelating agent for the formation of Cu<sub>1 - x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1) nanoparticles is given below:

an increase in the amount of Zr doping. The decrease in band frequency is due to the fact that the stretching band frequency is inversely proportional to the reduced mass, i.e.  $\mu = m_1 m_2/(m_1 + m_2)$ , and  $\nu = 1/2\pi \sqrt{k/\mu}$ , where  $m_1$  and  $m_2$  are the masses of atoms and k is the force constant.<sup>[50,51]</sup> As the masses of atoms increase the value

$$Cu(NO_3)_2 + 2Fe(NO_3)_3 + 13/6 C_6H_8O_7 \xrightarrow{\bigtriangleup} CuFe_2O_4 + 13CO_2 + 26/3 H_2O + 4N_2 \qquad (x=0) \qquad (1)$$

$$\frac{1}{22rO(NO_3)_2 + 1}{2Cu(NO_3)_2 + 2Fe(NO_3)_3 + 13.5}{6 C_6H_8O_7} \xrightarrow{\bigtriangleup} Cu_{0.5}Zr_{0.5}Fe_2O_4 + 13.5CO_2 + 27/3 H_2O_4 + 4N_2$$
(x=0.5) (2)

$$ZrO(NO_3)_2 + 2Fe(NO_3)_3 + 14/6 C_6H_8O_7 \longrightarrow ZrFe_2O_4 + 14CO_2 + 28/3 H_2O + 4N_2$$
 (x=1) (3)

## 3.1 | Characterization of As-Synthesized Nanoparticles

#### 3.1.1 | FT-IR spectral analysis

FT-IR spectral technology was used for the determination of characteristic bands of spinel ferrite-structured materials. The effect of zirconium substitution on CuFe<sub>2</sub>O<sub>4</sub> was explored. In general, spinel ferrites exhibit mainly two absorption bands, i.e. tetrahedral ( $\nu_1$ ) and octahedral ( $\nu_2$ ) in the ranges 500–600 and 400–435 cm<sup>-1</sup>, respectively.<sup>[48,49]</sup> These bands arise because of the vibrational modes of tetrahedral and octahedral metal–oxygen (M– O) bonds. The tetrahedral site has a band at a higher frequency than the octahedral site.<sup>[9]</sup> The  $\nu_1$  and  $\nu_2$  bands were found at 534, 530, 520, 435, 432 and 428 cm<sup>-1</sup> for Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0), Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0.5) and Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 1), respectively, as depicted in Figure 1. Both stretching band frequencies decrease with



**FIGURE 1** FT-IR spectra of Cu<sub>1 - x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub>: (a) x = 0, (b) x = 0.5 and (c) x = 1

of reduced mass increases and the corresponding value of stretching band frequency decreases.<sup>[52]</sup> Further a broad peak of low intensity in the range 3000–3500 cm<sup>-1</sup> was also found in the case of Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1) nanoparticles. This was attributed to the adsorption of a very small amount of water on the surface of the nanoparticles.

## 3.1.2 | XRD analysis

The structural and phase purity of as-synthesized materials was studied by exploring XRD patterns. The patterns of nanocrystalline  $Cu_1 - _xZr_xFe_2O_4$  (x = 0, 0.5, 1) are shown in Figure 2. The reflections (220), (311), (320), (400), (422), (511) and (440) belong to desired cubic spinel phases as demonstrated in XRD patterns.<sup>[53]</sup> These reflections confirmed the absence of impurity phases in the materials. A peak shift can be seen for the corresponding reflection angles for  $Cu_{1-x}Zr_xFe_2O_4$  (x = 0.5, 1) in comparison to  $Cu_{1-x}Zr_{x}Fe_{2}O_{4}$  (x = 0). This was attributed to the increase in zirconium ion substitution in CuFe<sub>2</sub>O<sub>4</sub> nanoparticles.<sup>[54]</sup> It is known that copper ferrite in its inverse spinel form shows tetrahedral sites occupied by half Fe<sup>3+</sup> ions and octahedral sites occupied by half Fe<sup>3+</sup> and Cu<sup>2+</sup>, mostly depending upon the method of synthesis used. Since the size of the Zr<sup>4+</sup> ion is larger than that of the  $Fe^{3+}$  ion, its substitution results in a peak shift of reflection angles which is due to the occupying nature of Zr ions in the position of Fe<sup>3+</sup> ions.<sup>[55]</sup> Further, the average particle size was calculated using the Scherrer formula:  $D = k\lambda/\beta \cos \theta$ , where  $\lambda$  is the wavelength,  $\beta$  is the corrected diffraction line full width at half maximum, k is a constant (having a value of 0.94) and  $\theta$  is the Bragg angle. The average particle size of the  $Cu_1 - {}_xZr_xFe_2O_4$ 



**FIGURE 2** XRD patterns of  $Cu_{1-x}Zr_xFe_2O_4$ : (a) x = 0, (b) x = 0.5 and (c) x = 1

(*x* = 0, 0.5, 1) nanoparticles was found to be 67, 42 and 33 nm, respectively. The average particle size decreased with increasing content of Zr ions. The reason behind this decrease in average particle size was attributed to the broadening of the diffraction planes, i.e. (220), (311), (320), (400), (422), (511) and (440), with increasing Zr ion content, which increases  $\beta$ and correspondingly decreases *D* (average particle size) in the Scherrer formula as shown in Figure 2. Further, the reduction in average particle size with increasing Zr content may be due to the requirement of high energy for Zr<sup>4+</sup> ions to enter the CuFe<sub>2</sub>O<sub>4</sub> lattice.<sup>[29]</sup>

The lattice parameter was also determined, as presented in Table 1. It was observed that the lattice parameter increased from 8.357 Å (Cu<sub>1 - x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0)) to 8.556 Å (Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 1)) with an increase in Zr dopant. This is mainly due to the replacement of smaller ionic radius Cu<sup>2+</sup> (0.73 Å) ions in the CuFe<sub>2</sub>O<sub>4</sub> spinel by larger ionic radius Zr<sup>4+</sup> (0.87 Å) ions.<sup>[56–58]</sup>

#### 3.1.3 | VSM analysis

The magnetic properties of the as-synthesized nanoparticles were investigated using VSM with the sweeping range from  $-10\ 000$  to  $+10\ 000$  Oe, as depicted in Figure 3. The value of saturation magnetization ( $M_s$ ) of Cu<sub>1 - x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1) nanoparticles was found to be 20.97, 27.51 and 22.74 emu g<sup>-1</sup>, respectively. The hysteresis loss in the magnetization curves was almost

**TABLE 1** Average particle size, Lattice parameter, band gap energy, surface area, pore volume and pore diameter of  $Cu_{1 - x}Zr_xFe_2O_4$  (x = 0, 0.5, 1) nanoparticles

Sample	Average particle size (nm)	Lattice parameter (Å)	Band gap energy (eV)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore diameter (nm)
x = 0	67	8.357	1.62	3.94	0.064	1.758
x = 0.5	42	8.457	1.52	21.44	0.059	1.756
x = 1	33	8.556	1.44	49.77	0.145	1.755



**FIGURE 3** VSM curves of  $Cu_{1-x}Zr_xFe_2O_4$ : (a) x = 0, (b) x = 0.5 and (c) x = 1

zero, i.e. both the magnetization and de-magnetization curves passed through zero. The value of  $M_s$  increases with increasing content of  $Zr^{4+}$  from x = 0 to 0.5. The reason for this behaviour can be explained on the basis that when substitution of Zr<sup>4+</sup> ion was carried out in the CuFe<sub>2</sub>O<sub>4</sub> nanoparticles, it occupied A-site by displacing Fe<sup>3+</sup> ion from A-site to B-site. This leads to an increase in the magnetic moment at B-site compared to A-site, i.e. a dilution of magnetization of A sub-lattice by nonmagnetic Zr<sup>4+</sup> ions or causing a net increase in magnetic saturation. Further decrease in  $M_s$  for x > 0.5 can be explained on the basis of the Neel sub-lattice model. According to which, due to dilution in A sub-lattice, the A-B sub-lattice interaction is no longer strong and causes a strong B-B sub-lattice interaction.<sup>[59,60]</sup> This causes a disturbance in the spin magnetic moment on the B-site and hence spin canting occurs which leads to a decrease in  $M_{\rm s}$  value.<sup>[44,55]</sup> This clearly indicates that the nanoparticles exhibited a superparamagnetic property. This larger value of  $M_s$  further encouraged us to use the nanoparticles as a recoverable catalyst in organic synthesis transformation reactions and dye degradation.

#### 3.1.4 | UV-visible spectral analysis

UV-visible spectral analysis was carried out for the determination of the band gap. The nanoparticles show a strong absorption in the visible region, which is related

to the band gap energy. The Tauc equation was used for the estimation of the band gap:  $(\alpha h\nu)^n = B(h\nu - E_g)$ , where  $\alpha$ , h,  $\nu$ ,  $E_{g}$  and B are the absorption coefficient, Planck constant, light frequency, band gap energy and a constant, respectively. The values of  $E_g$  of  $Cu_{1-x}Zr_xFe_2O_4$ (x = 0, 0.5, 1) were found to be 1.62, 1.52 and 1.44 eV, respectively, as demonstrated in Figure 4 and presented in Table 1. The value of band gap decreased with increasing concentration of Zr ions. The observed trend was well matched with that of earlier reports.<sup>[61]</sup> Further increasing the concentration of Zr ions results in the generation of sub-bands between the energy band gap and assimilation of conduction band with these sub-bands forms a continuous band.<sup>[62]</sup> Other factors were also responsible for the same trend, such as crystalline size, carrier concentration and formation of some impurities which might not be detected even by XRD.<sup>[62]</sup> The decrease in band gap of the Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1) nanoparticles with decreasing average particle size is the result of quantum confinement effects arising from the small size regime.<sup>[61,63,64]</sup> It may also be attributed to the sp-d exchange interactions between the localized d-electrons of the Zr<sup>4+</sup> and band electron of CuFe<sub>2</sub>O<sub>4</sub>.<sup>[49,65,66]</sup>

#### 3.1.5 | BET analysis

For the investigation of the catalytic activity of the nanoparticles, parameters like surface area play an important



**FIGURE 4** UV-visible analysis of  $Cu_{1-x}Zr_xFe_2O_4$ : (a) x = 0, (b) x = 0.5 and (c) x = 1

role. For this purpose, BET analysis of the as-synthesized nanoparticles was carried out. The values of BET surface area of Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1) nanoparticles were 3.94, 21.44 and 49.77 m<sup>2</sup> g<sup>-1</sup>, respectively, presented in Table 1 and shown in Figure 5. This observation is in agreement with the XRD analysis, i.e. small-sized particles exhibited high surface area. This high value of surface area confirmed that the material consists of a large number of catalytic active sites which further enhances its use as a heterogeneous catalyst.<sup>[67,68]</sup> Further, pore volumes of 0.064, 0.059 and 0.064 cm<sup>3</sup> g<sup>-1</sup> and pore diameters of 1.758, 1.756 and 1.755 nm were found for the Cu<sub>1 - x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1) nanoparticles. The pore size indicates that all three types of nanoparticles were microporous in nature.<sup>[69]</sup> Further, BET isotherm plots indicated a type IV porous material characteristic for the Cu<sub>1 - x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1) nanoparticles<sup>[70]</sup> as shown in Figure 6.

### 3.1.6 | Thermogravimetric analysis

TGA curves for Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1) are shown in Figure 7. The weight loss in all three types of catalysts occurred in three different steps. The first step involved weight loss of 1.28, 2.31 and 4.02% from 0 to 200°C for Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1), respectively. This was attributed to the elimination of water or moisture from the surface of the catalysts. This weight loss was also matched with the earlier FT-IR analysis in which all three types of nanoparticles showed an absorption band of water molecule in the range 3000–3500 cm<sup>-1</sup> (Figure 1). The second step involved weight loss of 0.80, 1.82 and 3.26% from 200 to 450°C for Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1), respectively. Removal of nitrates and other impurities were responsible for this loss. The final step involved weight loss of 1.3, 3.83 and 7.93% from 450 to 700°C for Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1), respectively. The reason for this was the elimination of trapped gases from the samples.<sup>[71]</sup> No weight loss above 700°C was observed for all three samples.

## 3.1.7 | TEM analysis

For the investigation of particle size and morphology, TEM analysis was conducted using a copper grid. The particle size calculated from this technique was found to be 33 nm, which was in good agreement with that calculated from XRD analysis. The shape of the nanoparticles was found to be spherical as depicted in Figure 8.



**FIGURE 5** Surface area analysis of  $Cu_{1-x}Zr_xFe_2O_4$ : (a) x = 0, (b) x = 0.5 and (c) x = 1



**FIGURE 6** Isotherm analysis of  $Cu_{1-x}Zr_xFe_2O_4$ : (a) x = 0, (b) x = 0.5 and (c) x = 1



**FIGURE 7** TGA curves of  $Cu_{1-x}Zr_xFe_2O_4$ : (a) x = 0, (b) x = 0.5 and (c) x = 1



**FIGURE 8** TEM image of  $Cu_{1 - x}Zr_xFe_2O_4$  (x = 1) nanoparticles

#### 3.1.8 | XPS analysis

To study the surface nature of the as-synthesized  $Cu_1 - {}_xZr_xFe_2O_4$  (x = 1) nanoparticles, XPS was used, as shown in Figure 9. The results indicate that the product is composed of zirconium, iron and oxygen. In Figure 9(a), the Zr 3d signal constitutes two peaks at 179.86 and 182.17 eV which represent Zr 3d<sub>5/2</sub> to Zr  $3d_{3/2}$  spin-orbital splitting with a value of 2.3 eV, confirming the +2 oxidation state of Zr.<sup>[72,73]</sup> For iron, two distinct peaks were observed at 708.74 and 722.29 eV for Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  spin-orbital components, respectively, as shown in Figure 9(b). This is characteristic of iron being is in the +3 oxidation state. The single peak at 527.75 eV suggested that oxygen is in the  $O^{2-}$  state<sup>[74]</sup> shown in Figure 9(c). Thus, the XPS analysis confirmed that the as-synthesized nanoparticles are composed of  $Cu_1 - {}_xZr_xFe_2O_4$  (x = 1).

3.2 | Use of  $Cu_{1-x}Zr_xFe_2O_4$  (x = 0, 0.5, 1) Nanoparticles as Heterogeneous Catalyst for Synthesis of Polysubstituted Pyridine Derivatives

## 3.2.1 | Optimization of various conditions for model reaction

Optimization was carried out of a model reaction for the synthesis of polysubstituted pyridine derivatives using malononitrile (1 mmol), cyclohexanone (1 mmol), ammonium acetate (1.5 mmol) and anisaldehyde (1 mmol). Various types of reaction conditions, like type of catalyst, dose of catalyst, temperature and type of solvent, were studied (Scheme 1).

The reaction was first tried with the different as-synthesized nanoparticles, i.e.  $Cu_{1 - x}Zr_xFe_2O_4$  (x = 0, 0.5, 1) by fixing the amount (5 mg) of each in ethanol at room temperature. The yield of product was found to be 69, 73 and 96% for  $Cu_{1 - x}Zr_xFe_2O_4$  (x = 0, 0.5, 1), respectively (Table 2, entries 1–3). The reason for the increase in yield of product can be explained on the basis that as we increased Zr content in the  $Cu_{1 - x}Zr_xFe_2O_4$  (x = 0, 0.5, 1) nanoparticles, the size of nanoparticles decreased and surface area increased as explained in the earlier discussion of XRD and BET analyses. As the surface area increases, more catalytic active sites are available on the surface of the catalyst, resulting in enhanced catalytic activity.

Further, it can also be explained on the basis of XPS analysis in which when a photon of light is absorbed by an atom of a molecule, ionization and emission of inner shell electrons occur. In the case of Zr, inner electrons were present in 3d orbital (with binding energy of 179.86 and 182.17 eV), whereas in Fe they were present in 2p orbital (with binding energy of 708.74 and 722.29 eV) as shown in Figure 9(a,b). In the case of Cu, the inner electrons were present in 2p orbital (with binding energy of 932.3 and 942.8 eV).<sup>[75]</sup> The low value of binding energy of Zr as compared to Cu and Fe confirmed that 3d inner electrons require low ionization energy (experience less nuclear charge) for ionization as compared to 2p orbital of Fe and Cu (experience more nuclear charge). Therefore, Zr shows high oxidative property or high Lewis acidic character to initiate the reaction as clear from Scheme 2. So as we increase the Zr content in the Cu<sub>1 - x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1) nanoparticles, the Lewis acidic character is enhanced, which in turn speeds up the reaction and increases the yield of product.<sup>[76,77]</sup> So on the basis of performance,  $Cu_1 - xZr_xFe_2O_4$  (x = 1) was a better catalyst for obtaining the desired product.

After the selection of the best catalyst for the formation of desired product, the next step involves



**FIGURE 9** XPS analysis of  $Cu_{1-x}Zr_xFe_2O_4$  (x = 1) nanoparticles



**SCHEME 1** Synthesis of polysubstituted pyridines using various reaction conditions

investigation of the appropriate amount of optimized catalyst for the reaction. Different amounts of the  $Cu_{1 - x}Zr_xFe_2O_4$  (x = 1) nanoparticles, i.e. 2.5, 5.0, 7.5, 10.0 and 15 mg, were considered and the yield was found to be 23, 96, 78, 85 and 71%, respectively (Table 2, entries 4, 3, 5, 6 and 7). The maximum yield, i.e. 96%, was obtained with 5 mg of catalyst. It was observed that increasing or decreasing the amount of catalyst neither increases the yield of product nor decreases the time for completion of the reaction. So, 5 mg was considered as a suitable amount to afford a maximum amount of product.

Next, suitable conditions for the reaction to occur were examined. For this purpose, various temperatures were employed for the model reaction such as room temperature, 40 and 60°C and refluxing and the yield was found to be 96, 67, 69 and 71%, respectively (Table 2, entries 3, 8–10). The reaction at room temperature exhibited the highest yield and less time for the production of the desired product as compared to other reaction conditions.

After establishing the suitable amount of catalyst and conditions for the reaction, the next study focused on the screening of the solvent. For this purpose, polar and nonpolar solvents were used. The reaction was run in various solvents, namely ethanol, methanol, EtOAc, water, *n*-hexane and toluene (Table 2, entries 3, 11–15). It was found that ethanol was the best solvent for carrying out the synthesis of polysubstituted pyridines in respect of yield and time (Table 2, entry 3). The reaction was also tried under solvent-free condition, but no reaction occurred at all (Table 2, entry 16).

After optimizing the various reaction conditions for the model reaction, the next step was to determine the applicability of the presented protocol for synthesizing various derivatives under identical conditions. For this purpose, various aldehydes, both electron-withdrawing and electron-releasing, were employed (Table 3). The

#### TABLE 2 Optimization of reaction conditions<sup>a</sup>



<sup>a</sup>Reaction conditions: malononitrile (1 mmol), cyclohexanone (1 mmol), ammonium acetate (1.5 mmol) and anisaldehyde (1 mmol), solvent (2 ml). <sup>b</sup>Isolated yield.



**SCHEME 2** Proposed mechanism of reaction for synthesis of polysubstituted pyridines

desired products were obtained in good yields and were characterized using various spectroscopic techniques such as FT-IR and <sup>1</sup>H NMR.

The first step of the proposed mechanism involved the formation of arylidene malononitrile (a) as an intermediate

as a result of the Knoevenagel condensation. Then Michael-type addition of cyclohexanone (b) occurred, which results in the activation of arylidene. Further, intramolecular cyclization of as-produced adducts and subsequent oxidation yielded the desired product (Scheme 2).<sup>[80]</sup>

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TABLE 3 Synthesis of various polysubstituted pyridines using various aromatic aldehydes<sup>a</sup>

		CHO + NC CN + DCH <sub>3</sub>	CH <sub>3</sub> COONH <sub>4</sub> +	OCH3 OCH3 Cu <sub>1-x</sub> Zr <sub>x</sub> Fe <sub>2</sub> O <sub>4</sub> (x=1)[5mg] r.t, EtOH (2ml)	°N IH <sub>2</sub>
	1	a-k 2a	3a 4a	5a-k	
Entry	Reactant	Product	Tim	e (min) Yield (%	6) <sup>b</sup> M.p. (°C)
1	сно осн <sub>5</sub> 1а	OCH3 CCH3 CCH NH 5a	4 1 <sub>2</sub>	96	233–235/232–234 <sup>[78]</sup>
2	CHO CI Ib		10 N H2	76	256-258/257-258 <sup>[79]</sup>
3	CHO NO <sub>2</sub> Ic	NO <sub>2</sub> CN NH 5c	3	81	>300/>300 <sup>[79]</sup>
4	CHO Br Id	Br CN NH 5d	2	82	256–257/256–258 <sup>[78]</sup>
5	CHO F Ie	F CN NH Se	3	80	245-248
6	CHO L NO <sub>2</sub> If		NO <sub>2</sub> 10	87	231-234/230-232 <sup>[79]</sup>
7	Lg	O <sub>2</sub> N Cl N Sg	4 N	81	180-182

(Continues)

#### **TABLE 3** (Continued)



<sup>a</sup>Reaction conditions: malononitrile (1 mmol), cyclohexanone (1 mmol), ammonium acetate (1.5 mmol) and aromatic aldehyde (1 mmol), EtOH (2 ml). <sup>b</sup>Isolated yield.

## 3.2.2 | Recyclability and Leaching of Catalyst

The recyclability of the catalyst was investigated in the model reaction under identical conditions. Due to its superparamagnetic character, the catalyst was recovered from the reaction mixture after completion of the reaction using an external magnet.<sup>[81–83]</sup> The obtained catalyst was washed with ethanol and dried in an oven at 50°C. After this, it was reused for up to five cycles with very little loss in activity and product yield. The average isolated yield for up to five successive runs was 92.3% as shown in Figure 10.

For checking the leaching of the as-synthesized catalyst, precipitation tests were performed, which identify whether Zr ions leached or not from the surface of the catalyst during repeat reactions. For this purpose, the firstly solid product formed at the end of the fifth cycle of the reaction was filtered and washed with distilled water. Then the filtrate was divided into two parts. In the first part, sodium hydroxide was added, and no gelatinous white precipitate of zirconium hydroxide was added, and no gelatinous white precipitate of zirconium hydroxide was added, and no gelatinous white precipitate of zirconium hydroxide test was also performed for Fe<sup>3+</sup> ions, but no solid precipitate

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**FIGURE 10** Recyclability of  $Cu_1 - _xZr_xFe_2O_4$  (x = 1) nanoparticles up to five cycles

of ferric hydroxide was obtained. These precipitation tests demonstrated that no Zr and Fe ions were leached from the surface of the catalyst.

Further study of the leaching of metal ions of  $Cu_1 _ xZr_xFe_2O_4$  (x = 1) was also conducted using ICP-OES. The amounts of Zr and Fe leached from  $Cu_1 _ xZr_xFe_2O_4$  (x = 1) were found to be 0.00010 and 0.00007%, respectively. These results clearly demonstrated that there was no significant amount of leaching.

In order to illustrate the catalytic activity of the assynthesized catalyst, we compared the results with those for various catalysts reported in the literature, as summarized in Table 4. The present magnetically separable catalyst leads to higher yield of product in the least reaction time compared to other catalysts. The attractive feature of our catalyst is that it was separated from the reaction mixture using an external magnet, which reduces the catalyst loss during separation. Moreover, our catalyst was synthesized using a cost-effective method and recycled up to five times without considerable loss in activity. This catalyst is better in terms of stability, reusability, cost and ease of separation from the reaction mixture.

## 3.2.3 | Spectral data of selected compounds

Table 3, entry 2 (**5b**): 2-amino-4-(2-chlorophenyl)-5,6,7,8tetrahydroquinoline-3-carbonitrile. Melting point: 256–258°C. White crystalline solid. FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3450, 3360, 3206, 2925, 2220, 1622. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$ , ppm): 0.75–0.78 (m, 1H), 1.30–1.38 (m, 2H), 1.60 (br s, 1H), 2.03–2.11 (m, 2H), 2.81 (br s, 1H), 3.82–3.85 (m, 1H), 5.71 (s, 2H), 7.39–7.47 (m, 2H), 7.56–7.58 (m, 1H), 7.71–7.73 (m, 1H).

Table 3, entry 3 (**5c**): 2-amino-5,6,7,8-tetrahydro-4-(4nitrophenyl)quinoline-3-carbonitrile. Melting point: >300°C. Yellow solid. FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3448, 3352, 3224, 2928, 2210, 1644. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$ , ppm): 0.85–0.91 (m, 1H), 1.40–1.44 (m, 2H), 1.69 (br s, 1H), 2.05–2.08 (m, 1H), 2.17–2.22 (m, 1H), 2.91 (br s, 1H), 3.90 (d, 1H), 5.75 (s, 2H), 7.43 (s, 1H), 7.73–7.75 (m, 1H), 7.90–7.92 (m, 1H), 8.32–8.36 (m, 1H).

Table 3, entry 4 (**5d**): 2-amino-4-(4-bromophenyl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile. Melting point: 256–257°C. White solid. FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3425, 3346, 3229, 2930, 2212, 1644. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz,  $\delta$ , ppm): 0.83–0.89 (m, 1H), 1.43–1.46 (m, 2H), 1.66 (br s, 1H), 2.04–2.08 (m, 1H), 2.16–2.18 (m, 1H), 2.79 (br s, 1H), 3.63 (d, 1H), 5.73 (s, 2H), 7.39 (s, 2H), 7.54–7.56 (m, 1H), 7.65–7.70 (m, 1H).

Table 3, entry 5 (**5e**): 2-amino-4-(4-fluorophenyl)-5,6,7,8-tetrahydroquinoline-3-carbonitrile. Melting point: 245–248°C. White crystalline solid. FT-IR (KBr,  $\nu$ , cm <sup>-1</sup>): 3440, 3345, 3240, 2956, 2216, 1645. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$ , ppm): 0.82–0.88 (m, 1H), 1.09–1.17 (m, 1H), 1.43–1.65 (m, 3H), 2.00–2.16 (m, 1H), 3.63 (d, 1H), 3.96–3.98 (m, 1H), 5.72 (s, 2H), 7.34–7.38 (m, 2H), 7.59–7.62 (m, 2H).

Table 3, entry 6 (**5f**): 2-amino-5,6,7,8-tetrahydro-4-(3nitrophenyl)quinoline-3-carbonitrile. Melting point: 231– 234°C. Yellow solid. FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3449, 3360, 3207, 2928, 2217, 1623. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$ , ppm): 1.00–1.06 (m, 1H), 1.46–1.49 (m, 2H), 1.68 (br s, 1H), 2.08–2.22 (m, 2H), 3.00 (br s, 1H), 4.06 (d, 1H), 5.77 (s, 2H), 7.44 (s, 1H), 7.74–7.78 (m, 1H), 7.91–7.94 (m, 1H), 8.00–8.02 (m, 1H), 8.07–8.08 (m, 1H).

Product	Catalyst	Solvent	Temp.	Time (min)	Yield (%)	Ref.
5a	[bmim]OH	[bmim]OH	80 °C	240	88	[79]
	Fe <sub>3</sub> O <sub>4</sub> /cellulose	Ethanol	r.t	180	98	[78]
	Cu <sub>1 - x</sub> Zr <sub>x</sub> Fe <sub>2</sub> O <sub>4</sub> ( $x = 1$ ) nanoparticles	Ethanol	r.t	4	96	Present work
5d	[bmim]OH	[bmim]OH	80 °C	300	80	[79]
	Fe <sub>3</sub> O <sub>4</sub> /cellulose	Ethanol	r.t	300	75	[78]
	Cu <sub>1 - x</sub> Zr <sub>x</sub> Fe <sub>2</sub> O <sub>4</sub> ( $x = 1$ ) nanoparticles	Ethanol	r.t	2	82	Present work

 TABLE 4
 Comparison of catalytic activity of as-synthesized catalyst with that of reported catalysts

## 3.3 | Use of $Cu_{1-x}Zr_xFe_2O_4$ (x = 0, 0.5, 1) Nanoparticles as Heterogeneous Photocatalyst for Degradation of MB

The photocatalytic activity of as-synthesized  $Cu_{1 - x}Zr_xFe_2O_4$  (x = 0, 0.5, 1) nanoparticles as a heterogeneous catalyst was evaluated for degradation of MB without the addition of any additives. Various factors such as the type of catalyst, pH, dose of catalyst, reaction conditions, amount of dye solution, dye concentration and time were explored. Further, a study of the reusability, stability and adsorption/degradation of the nanoparticles was carried out. The degradation efficiency was determined using the formula

Degradation (%) = 
$$\frac{C_0 - C_t}{C_0} \times 100$$
 (1)

where  $C_0$  is the initial concentration of MB and  $C_t$  is the concentration at time *t*.

#### 3.3.1 | Optimization of type of catalyst

The effect of the different types of as-prepared  $Cu_1 - xZr_xFe_2O_4$  (x = 0, 0.5, 1) catalyst on the photodegradation of MB was explored. For this investigation, a dye solution (10 ml) of pH  $\approx$ 6.39 was stirred for 30 min in the dark (for good dispersion and to attain the adsorption-desorption equilibrium between photocatalyst, MB and water) and further 60 min under sunlight in the presence of a constant amount (10 mg) of the catalyst. The degradation of MB was found to be 46, 51 and 67 for  $Cu_1 - xZr_xFe_2O_4$  (x = 0, 0.5, 1), respectively. Or we can say that with an increase in Zr content the degradation increased. This behaviour can be explained on the basis that the  $Cu_1 - {}_xZr_xFe_2O_4$ (x = 1) catalyst had the smallest band gap (1.44 eV; the increase in photocatalytic activity with decrease in band gap was due to the production of inter-band or heterojunction which reduces the electron-hole recombination<sup>[10,84]</sup>), small particle size (33 nm; with a decrease in particle size, photocatalytic activity is enhanced<sup>[85]</sup>) and high surface area (49 m<sup>2</sup> g<sup>-1</sup>; increase in surface area has a positive influence on photocatalytic activity<sup>[86]</sup>) compared to the other  $Cu_1 - {}_xZr_xFe_2O_4$ (x = 0,0.5) catalysts, as discussed earlier with UV spectral, XRD and BET analyses, respectively (Table 1). Thus on the basis of the performance exhibited by the  $Cu_{1} - xZr_{x}Fe_{2}O_{4}$  (x = 1) catalyst for the degradation of MB dye, it was selected as the best catalyst for degradation experiments.

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## 3.3.2 | Optimization of pH

As it is known that industrial waste has various pH values, so it becomes very important to determine the catalytic activity of as-synthesized nanoparticles at various pH values. Variation in pH affects the surfacecharge properties of the catalyst and the production of ionic species in solution.<sup>[87]</sup> So it is one of the most important parameters which influences the degradation of dyes. Solution of MB dye (10 ppm) was prepared at various pH, i.e. 1, 3, 5, 7, 9, 11 and 13. The solutions of various pH were prepared using HCl and NaOH solutions of 1 N each. The degradation using the catalyst (10 mg) was found to be 42.52, 97.83, 95.54, 94.50, 95.74, 92.80 and 76.10% for pH of 1, 3, 5, 7, 9, 11 and 13, respectively. Maximum degradation of the dye was at a pH of 3, i.e. 97.83%. So, pH = 3 was the optimized value for conducting the photocatalytic experiment at which the as-synthesized catalyst led to maximum degradation as shown in Figure 11. Our catalyst shows marked activity at various pH (1, 3, 5, 7, 9, 11 and 13), so the catalyst activity is almost pH-independent.

#### 3.3.3 | Dose of catalyst

After determining the optimum pH value, in the next step we explored various amounts of the  $Cu_1 - _xZr_xFe_2O_4$ (x = 1) catalyst, i.e. 0, 2.5, 5.0, 7.5 and 10 mg, keeping the concentration of dye (10 ppm), amount of dye solution (10 ml) and pH (3) constant, under sunlight and degradation was found to be 9.82, 73.84, 76.15, 96.30 and 97.83%, respectively. The increase in degradation with increasing dose of catalyst was due to the increase in catalytic active sites which were present on the surface



**FIGURE 11** Variation of MB degradation with pH. (Reaction conditions: 10 ml (10 ppm) dye solution),  $Cu_{1 - x}Zr_xFe_2O_4$  (x = 1) (10 mg), 30 min stirring in dark, 60 min stirring under sunlight)

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of the catalyst. These catalytic active sites were further responsible for an increase in the production of hydroxyl and superoxide radicals which were necessary for the photocatalytic reaction.<sup>[88]</sup> But when we further increased the catalyst amount, i.e. 15 mg, the degradation was found to be decreased, i.e. 86.07%. The reason for this behaviour was attributed to scattering of light and decrease in penetration of light through the dye solution. Further collisions of the ground-state molecules with the active molecules caused a decrease in degradation efficiency of the as-synthesized catalyst<sup>[51,89]</sup> as shown in Figure 12.

## 3.3.4 | Effect of concentration of dye

To determine the appropriate concentration of dye solution for the nanoparticles to show superior catalytic activity, various concentrations of dye solution were employed, i.e. 10, 15 and 25 ppm, keeping the amount of  $Cu_{1-r}Zr_{r}Fe_{2}O_{4}$ (x = 1) (10 mg/10 ml) constant. The degradation of MB was found to decrease with an increase in dye concentration as depicted in Figure 13. As we increased the dye concentration the adsorption of molecules on the surface of the catalyst increased and it further enhanced the requirement of reactive species (OH and  $O_2^{\bullet-}$ ) for degradation. But at a fixed irradiation time, catalytic dose and intensity of light, the generation of reactive species is also constant, which results in the decrease in degradation of dye solution.<sup>[90]</sup> On further increasing the dye concentration the colour becomes more and more intense which shields the sunlight radiation, resulting in a decrease in the path length of photons entering into the solution. And this causes a decrease in the generation of hydroxyl and superoxide radicals as fewer photons reach the surface of the catalyst.<sup>[91]</sup> So, from



**FIGURE 12** Effect of catalyst dose on degradation. (Reaction conditions: 10 ml (10 ppm) dye solution), pH = 3,  $Cu_{1-x}Zr_xFe_2O_4$  (x = 1), 30 min stirring in dark, 60 min stirring under sunlight)



**FIGURE 13** Effect of dye concentration on degradation. (Reaction conditions: 10 ml dye solution, pH = 3,  $Cu_{1 - x}Zr_xFe_2O_4$  (*x* = 1) (10 mg), 30 min stirring in dark, 60 min stirring under sunlight)

the above discussion, it was clear that the as-synthesized catalyst led to maximum degradation (97.83%) of dye solution for a concentration of 10 ppm.

## 3.3.5 | Effect of amount of dye solution

After deciding on the concentration of dye, i.e. 10 ppm, our next step was to examine the effect of different amounts of dye solution. For this purpose, various amounts of dye solution, 10, 20, 30 and 40 ml at pH = 3, were taken with fixed amount of  $Cu_{1 - x}Zr_xFe_2O_4$  (x = 1) catalyst (10 mg) and under sunlight. The degradation was decreased as we increased the amount of dye solution. The degradation was found to be 97.83, 66.07, 64.61 and 51.92% for 10, 20, 30 and 40 ml, respectively, as shown in Figure 14. This was attributed to the fact that as we increased the amount of dye solution the adsorption of molecules on the surface of the catalyst increased which in turn decreased the catalytic activity of the as-synthesized catalyst, so decreasing the degradation of dye.<sup>[92]</sup>

#### 3.3.6 | Effect of reaction conditions

Next, we explored the reaction under various conditions, such as under UV irradiation, ultrasonication and under sunlight irradiation. The effect on degradation of dye was analysed. It was found that the degradation of dye was 42.43, 52.23 and 97.83% for UV irradiation, ultrasonication and sunlight, respectively, as shown in Figure 15. Since our catalyst showed maximum catalytic activity under sunlight irradiation, this makes the presented protocol



**FIGURE 14** Effect of amount of dye solution on degradation. (Reaction conditions: 10 ppm dye solution, pH = 3,

Cu<sub>1 – x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 1) (10 mg), 30 min stirring in dark, 60 min stirring under sunlight)



**FIGURE 15** Effect of reaction conditions on degradation. (Reaction conditions: 10 ml (10 ppm) dye solution, pH = 3,  $Cu_{1 - x}Zr_{x}Fe_{2}O_{4}$  (x = 1) (10 mg), 30 min stirring in dark, 60 min stirring under sunlight (SL), ultrasonication (US) and UV irradiation)

greener, because sunlight is a natural source of light, present in abundance, easily available, cost-effective and environmentally benign. On the other hand, UV irradiation and ultrasonication are costly and dangerous to health.<sup>[3]</sup> The reason for the better catalytic activity of as-synthesized catalyst under sunlight was attributed to its narrow band gap ( $E_g = 1.44$  eV), which effectively allows utilization of visible light for the degradation of organic compounds in an aqueous medium. So, reaction under sunlight was suitable for conducting the experiment.

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## 3.3.7 | Effect of stirring time

We further studied the effect of stirring time on the degradation of MB. Figure 16 shows the photodegradation of dye using optimized conditions as a function of stirring time under solar irradiation. The intensity of the main absorption peak (663 nm for MB)<sup>[93]</sup> decreased with irradiation time which indicates a decrease in the concentration of the dye, without the appearance of any other new peak, further confirming that MB has undergone complete decomposition rather than conversion to another structure. The results showed the high activity of the as-prepared catalyst which causes the degradation of MB in such a short illumination time and the catalyst has active sites for carrying out the reaction.

## 3.3.8 | Kinetic study of photodegradation

The photocatalytic degradation rate of most organic compounds follows pseudo-first-order kinetics. The photodegradation rate of organic compounds on the surface of a semiconductor is described by the Langmuir–Hinshelwood model:<sup>[94]</sup>

$$R = \frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_{\mathrm{r}}KC}{1+KC} \tag{2}$$

where  $k_r$  is the reaction rate constant, *K* the adsorption coefficient of the reaction and *C* the reactant concentration.

The effect of light intensity is also included in  $k_r$ , and K expresses the equilibrium constant for adsorption–desorption phenomenon on an interface between surface



**FIGURE 16** Effect of stirring time on degradation. (Reaction conditions: 10 ml (10 ppm) dye solution, pH = 3,  $Cu_{1 - x}Zr_xFe_2O_4$  (x = 1) (10 mg), 30 min stirring in dark, 0–60 min stirring under sunlight)

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**FIGURE 17** Plot of photodegradation rate of MB on  $Cu_{1-x}Zr_xFe_2O_4$  (x = 1) nanoparticles as a function of irradiation time under sunlight

monolayer and bulk solution. Integration of equation (2) gives the following:

$$\ln\left(\frac{C_0}{C}\right) + K(C_0 - C) = k_{\rm r}Kt \tag{3}$$

When the initial concentration  $C_0$  is small, equation (3) becomes equation (4), which reveals pseudo-first-order reaction kinetics:

$$\ln\left(\frac{C_0}{C}\right) = k_{\rm r}Kt = kt \tag{4}$$

For a pseudo-first-order reaction, half-life  $t_{1/2} = 0.693/k$ , where *k* is the pseudo-first-order reaction rate constant in min<sup>-1</sup>. Figure 17 shows a plot of ln ( $C_0/C$ ) versus time of MB dye degradation reaction. Rate constant *k* was calculated from the slopes of the respective curves<sup>[95,96]</sup> as in Figure 17. The values of rate constant *k* and half-life  $t_{1/2}$ were found to be 0.02 min<sup>-1</sup> and 23.57 min, respectively.

## 3.3.9 | Mass spectrometric study of degradation products

MB has the formula  $C_{16}H_{18}ClN_3S$  and showed a molecular ion peak at m/z 284.06 in its mass spectrum before degradation (Figure 18a) because Cl<sup>-</sup> ion dissociates



FIGURE 18 Comparison of mass spectra of MB (a) before degradation and (b) after degradation



**FIGURE 19** Proposed mechanism of degradation of MB catalysed by  $Cu_{1-x}Zr_xFe_2O_4$  (x = 1) nanoparticles



**FIGURE 20** Recyclability of  $Cu_{1-x}Zr_xFe_2O_4(x=1)$  nanoparticles

when MB is dissolved in water. In the mass spectrum of MB after degradation, no peak corresponding to the molecular ion was found, which signifies that the dye was degraded. Other peaks were observed corresponding to the degraded products of the dye. The peaks obtained at m/z 319, 303, 279, 269, 216, 192 and 135 were attributed to the fragmented ions which were fully matched with earlier reports.<sup>[97–99]</sup> In addition to these peaks, numerous peaks of insignificant intensity were also present in the spectrum (Figure 18b) which indicated that most of the MB molecules have been mineralized.

## 3.3.10 | Mechanism of degradation of MB

According to our results, a possible mechanism of degradation of MB under sunlight irradiation using the



**FIGURE 21** FT-IR spectra of  $Cu_{1-x}Zr_xFe_2O_4$  (x = 1) (a) before and (b) after use

as-synthesized catalyst is shown in Figure 19. The first step involves the generation of an electron-hole pair (responsible for the redox reaction occurring). This further results in the formation of hydroxyl radicals ('OH) and superoxide radicals (O<sub>2</sub>'). The strong oxidative properties of these radicals cause the oxidation of MB.<sup>[10]</sup> The enhanced photocatalytic activity with increasing Zr content in Cu<sub>1 - x</sub>Zr<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (x = 0, 0.5, 1) nanoparticles is due to the decrease in band gap energy, increase in surface area and decrease in particle size, as discussed earlier (Table 1). The mechanism of degradation of MB is illustrated below:

Further, our catalyst was not light-sensitive; this was determined by leaving the recovered catalyst at room temperature for 48 h. It was found that there was no change in colour observed in the recovered catalyst. This study demonstrated the light-insensitivity of the assynthesized catalyst after recycling. Similarly, in FT-IR analysis, there was no change in peaks before and after recycling (Figure 21). In addition, no special care has to be taken to handle or store the as-prepared catalyst for further use during the recycling process.<sup>[101,102]</sup>

The similarity in the FT-IR spectrum of the as-synthesized catalyst after being reused up to five cycles to that of



## 3.3.11 | Reusability, Stability and Adsorption/Degradation Study of Catalyst

It is known that the stability and reusability of the as-synthesized catalyst are important factors for numerous applications in environment protection processes. For this investigation, the photodegradation experiment was repeated for five cycles and the degradation rates of MB were measured. For each cycle, the catalyst was separated from the reaction mixture using an external magnet. The catalyst was washed with water and dried in an oven at 50°C. Then it was used in consecutive cycles for the degradation of MB, as shown in Figure 20. The average degradation yield for up to five successive runs was found to be 95.9%. The very slight change in performance of the catalyst with each cycle might be due to the reduction in catalytic active sites.<sup>[100]</sup> the as-synthesized catalyst before use as discussed above showed that there were no peaks of dye molecules adsorbed on the surface of the as-synthesized catalyst after recycling. This clearly indicated that the decolorization of the dye did not occur through adsorption phenomena but through the degradation process (Figure 21). This observation matches well with the mass spectral analysis discussed earlier, which showed that MB had undergone degradation.

### 4 | CONCLUSIONS

Zirconium-substituted copper ferrite  $Cu_1 \_ _xZr_xFe_2O_4$ (x = 0, 0.5, 1) magnetic nanoparticles were synthesized via the auto-combustion method using citric acid as a chelating/fuelling agent. The characterization of assynthesized powder samples was done with various techniques. The XRD results confirmed the crystalline nature and effect of substitution on average size of as-synthesized nanoparticles. UV-visible spectroscopy demonstrated that band gap energy decreased with substitution. VSM results confirmed the superparamagnetic nature of the as-prepared nanoparticles. BET analysis showed that surface area increased with substitution. The chemical composition was determined using XPS analysis. ICP-OES analysis confirmed that there was no significant leaching from the nanoparticles after recycling. Comparison of catalytic activity of different copper ferrites in one-pot zirconium-substituted multicomponent reactions and degradation of an organic pollutant was conducted. Out of the three types of zirconium-substituted copper ferrite nanoparticles,  $Cu_{1-x}Zr_{x}Fe_{2}O_{4}$  (x = 1) showed excellent activity as a heterogeneous catalyst for the formation of polysubstituted pyridine with product yields of 74-96% in 2-40 min and in the degradation of MB at 97.83% in 60 min. Additionally, due to its superparamagnetic character, it was separated from the reaction media in both cases by applying an external magnet. Recyclability, reusability, magnetic separation and ease of formation of the as-synthesized catalyst and its utilization in the formation of biologically important heterocyclic compounds and water purification for environmental protection open a new era in catalytic research. Further, our catalyst was almost pH-independent in the photodegradation of the dye. Light-insensitivity, pH-independence and anti-leaching properties are prominent features of the catalyst.

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