**Novel Franklinite-like Synthetic Zinc Ferrite Redox Nanomaterial, with Controlled Composition, for Reductive and Oxidative Degradation of Diclofenac**

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# **Abstract**

The current study investigates a novel redox technology based on synthetic franklinite-like zinc-ferrite nanomaterial with magnetic properties and redox nature for potential use in water treatment. Physicochemical characterization revealed the nanoscale size and AB2O4 spinel configuration of the zinc-ferrite nanomaterial. The redox activity of nanoparticles was tested for degradation of diclofenac (DCF) pharmaceutical in water, without added external oxidant and under dark experimental conditions. Results revealed ~90% degradation in diclofenac (10 µM) within 2 min of reaction using 0.17 g/L Zn1.0Fe2.0O4. Degradation of DCF was due to chemical reduction by surface electrons on zinc-ferrite and oxidation by oxygen-based radicals. Three byproducts from reduction route and eight from oxidation pathways were identified in the reaction system. Reaction pathways were suggested based on the identified byproducts. Results demonstrated the magnetic zinc-ferrite is a standalone technology that has a great promise for rapid degradation of organic contaminants, especially DCF in water.

**Keywords:** Zinc ferrite; Diclofenac (DCF); Advanced oxidation and reduction; Reaction byproducts

**Introduction**

The development and application of homogeneous heterogeneous metal-based catalysts for treatment of contaminants of emerging concern in aqueous media has received considerable scientific attention [1, 2]. While the solubility of such nanomaterial in the reaction medium is an advantage, problems associated with separation of remaining nanomaterial from reaction medium and difficulties of handling air-sensitive catalysts limited their applications in the field of water treatment [3, 4]. Among the existing numerous materials, transition metals-based catalysts have shown various physical and chemical properties that they have been extensively used in promising applications including energy storage, medical, and air and water treatment [5-9]. Owing to its high magnetic anisotropy, spinel zinc-ferrite has been used in magnetic recording applications [10]. Moreover, water disinfection and degradation of organic pollutants in air and water using iron-based spinel metal oxides [11-13]. Historically, photoactivated zinc-ferrite nanoparticles was used to degrade organic contaminants in water [14, 15]. In some cases, oxidants such as hydrogen peroxide and persulfate are added to zinc-ferrite based photocatalytic system for better performance toward degradation of organic contaminants in water[13, 16]. Herein we demonstrate a novel redox system based on spinel zinc-ferrite nanomaterial for an efficient degradation of a model pharmaceutical diclofenac (DCF) in water in absence of any external energy source, without addition of external oxidants.

DCF is an anti-inflammatory, non-steroidal drug that is mainly used as an analgesic drug to reduce inflammation from arthritis and rheumatic conditions [17]. DCF is one of the frequently detected pharmaceuticals in water sources including influent and effluent wastewater in domestic treatment plants [17, 18]. DCF has found its way to surface water and ultimately to drinking water which might impose negative effects on human health [19]. Municipal wastewater treatment plants typically employ specific treatment technologies such as ozonation, Ultraviolet (UV) radiation, and activated carbon adsorption to remediate organic contaminants including DCF, yet, none of these technologies lead to acceptable removal efficiencies [18]. Therefore, it is critical to find efficient, environmentally compatible removal technology for DCF in water.

In this study, recyclable magnetic spinel ZnxFe3-xO4 nanoparticles were synthesized, and characterized using various physical and chemical techniques. The redox activities of synthesized nanoparticles were evaluated for the degradation of DCF in water. Liquid chromatography-mass spectrometry (LC-MS) technique, total organic carbon (TOC), and analysis of inorganic nitrogen-containing products were conducted to evaluate degradation and mineralization of DCF by ZnxFe3-xO4. Finally, proposed reaction pathways, based on identified reaction products and reactivity of involved oxidizing and reducing species such as •OH and e- are presented to rationalize the oxidation and the reduction routes.

# **Experimental**

## **Synthesis of ZnxFe3-xO4 magnetic nanoparticles**

A combustion method was used to synthesize zinc-ferrite nanomaterial. In this method, a mixture of zinc chloride (98%, Sigma Aldrich) and iron (III) nitrate monohydrate (98%, Sigma Aldrich) was initially prepared at a 1:2 molar ratio of zinc to iron (III). This molar ratio was then varied to produce four different stoichiometries where the adequate number of grams of each chemical was determined by multiplying molar ratios by corresponding molecular weight (i.e., Zn1.0Fe2.0O4, Zn 0.7Fe2.3O4, Zn 0.3Fe2.5O4, and Zn0.1Fe2.9O4). Polyvinyl alcohol (PVA, 88% hydrolyzed, average molecular weight of 22,000 g/mol) was added to the reaction mixture in a 1:1 mass ratio. The mixture was grinded and mixed with 15 mL Milli-Q water, placed in a muffle furnace and calcined at 500 °C for 30 min promoting self-ignition of PVA that ultimately generated magnetic nanoparticles of zinc-ferrite.

## **Characterization of** **ZnxFe3-xO4 nanoparticles**

The morphologies of prepared nanomaterial were investigated by an environmental scanning electron microscopy (ESEM, Philips XL 30 ESEM-FEG). Energy-dispersive X-ray spectroscopy (EDS) installed in the ESEM was used to determine chemical compositions of samples. A JEM-2010F (JEOL) HR-TEM with a field emission gun at 200 kV was used after the samples were subject to ultrasonication (2501R-DH, Bransonic) for 30 min in isopropyl alcohol (99.8%, Pharmco). Each sample was fixed on a lacey/carbon 300 mesh copper grid (LC325-Cu, EMS). Selected area electron diffraction (SAED) was obtained with low resolution TEM and analyzed using the open-source program, Diffraction Ring Profiler. Electron diffraction simulations were performed using the commercial software, Desktop Microscopist, with the input of the well-known space group information. Porosimetric analysis was performed using Tristar 300 (Micromeritics) porosimeter analyzer to determine the Brunauer-Emmett-Teller (BET) surface area, pore volume, porosity, Barret- Joyner-Halenda (BJH) pore size and distribution (based on nitrogen adsorption and desorption isotherms). All samples were purged with nitrogen gas for 2 h at 150 °C using Flow prep 060 (Micromeritics) before the porosimetry analysis.

A Cu-Kα wavelength Bruker AXS D8 Discover XRD was used to determine crystal structure of synthesized samples with a receiving slit of 0.3 and 0.2 scan step size from 10 to 70 degrees. Raman spectroscopy measurements were performed with a Renishaw In-Via Reflex dispersive micro-Raman spectrometer with < 2 cm-1 resolution. The laser beam (excitation in the NIR at 785 nm with total laser power below 0.001 mW/µm2) was focused on a spot of about 6.8 µm in diameter with a 20X magnification lens. Rayleigh scattering was rejected with a 200 cm-1 cut-off dielectric edge filter, and analysis of the scattered beam was performed on a 250 mm focal length spectrometer along with suitable diffraction gratings (1200 lines/mm for NIR) and a high-sensitivity charge-coupled device (CCD). All room temperature (RT) Raman spectroscopy measurements were performed in air and at different laser powers to assure that the intensities used did not induce changes in the spectra. The surface analysis studies were performed in a UHV chamber (P<10-9 mbar), equipped with a SPECS LHS-10 hemispherical electron analyzer.

XPS measurements were carried out at room temperature using Kratos Axis Ultra XPS equipped with monochromated (Al) X-Ray source with 12 kV and 10 mA. XPS analysis was performed in spectrum analyzer mode and slot aperture setting with a hybrid lens mode. The XPS core level spectra were analyzed using a fitting routine, which allows the division of each spectrum into individual mixed Gaussian-Lorentzian components after a Shirley and linear background subtraction. The samples were pressed on a ~ 1 cm2 carbon tape and then taped on a metal samples holder. Wide survey scans were recorded for all samples, while the core level peaks that were recorded in detail were: O1s, Fe2p, Zn2p and C1s.

XAFS measurements for Zn and Fe (in ZnxFe3-xO4) were conducted at the Materials Research Collaborative Access Team (MRCAT) beamline Sector 10-ID, at the Advanced Photon Source of Argonne National Laboratory (USA) [20]. The storage ring operated at 7 GeV in top-up mode. A liquid N2 cooled double crystal Si (111) monochromator was used to select the incident photon energies and a platinum-coated mirror was used for harmonic rejection. Calibration was performed by assigning the first derivative inflection point of K edge of zinc (9659 eV) or iron (7112 eV) metal foils with simultaneous collection of the foils for each sample scan for calibration of spectra. Five Zn or Fe K edge X-ray absorption spectroscopy spectra were collected in transmission mode. The collected spectra were analyzed using the Athena software program in the computer package IFEFFIT for data reduction and WinXAS 3.0 for data fitting [21, 22]. The individual spectra for each sample were averaged followed by subtraction of the background through the pre-edge region using the Autobk algorithm and normalized to the atomic absorption of one [23]. The data were converted from energy to photoelectron momentum (k-space) and weighted by k3 using WinXAS. X-ray absorption fine structure spectra were calculated over a typical k-space range with a Bessel window. Fourier transforms were performed to obtain the radial distribution function in R-space. Plotted R-space (Å) data are not phase shift corrected so that the true distances are between 0.3 and 0.5 Å longer than the distances shown. Structural parameters were extracted with fits to the standard XAFS equation. Using the FEFF8 and ATOMS codes, ab initio amplitude and phase functions for single shells were calculated for the mineral franklinite ((Zn,FeII)FeIII2O4) [24, 25]. Structural parameters for Zn and Fe interactions were obtained by least-squares refinements of the theoretical model function χ (k), allowing R, σ2, and ΔE0 to float, to the k3-weighted EXAFS oscillation over the k-range of 2.3–13.5 Å−1 (Zn) and 2.5–14 Å−1 (Fe), after Fourier-filtering in the range of 0.9–6.1 Å. The S02 value was held constant at 0.85 to allow refinements of the coordination number. The accuracy of the mean bond distance R is estimated to be within ±0.02 Å and the coordination number N is estimated to be accurate to ±20%, based on the results of theoretical fits to spectra of reference compounds of known structure.

## **Catalytic activity of ZnxFe3-xO4 nanoparticles**

To evaluate the zinc-ferrite nanomaterial activities of various ZnxFe3-xO4 (Zn0.1Fe2.9O4, Zn0.3Fe2.7O4, Zn0.7Fe2.3O4 and Zn1.0Fe2.0O4), 5.0 mg of nanoparticle was added to 24 mL Milli-Q water in individual 40 mL glass vials. Sonication for 15 min at 40 kHz (input energy 19 W) was applied to further disperse the zinc-ferrite nanomaterial in water. Then, 6 mL of 50 mM DCF was added to water containing the zinc-ferrite nanomaterial (i.e., final concentration of DCF =10.0 µM). A final volume of 30 mL was achieved in each vial by addition of appropriate amount of Milli-Q water. The vials were placed in a rotating (50 rpm) vial holder to ensure uniform mixing of the solution during the degradation process. The vials were wrapped with aluminum foil to eliminate any light penetrating to solution. Prior to sampling, the nanoparticles were collected at the inner wall of vial using a magnetic bar to maximize retention of nanomaterial during the consecutive sampling process s, Fig. S1. Samples of 300 µL each were drawn at different time intervals (i.e., 0, 1, 2, 4, 8, 16, 30 and 60 min) and were subsequently filtered using a Whatman 0.2 µm syringeless PTFE membrane filter to remove residual nanoparticles. The same degradation experiments were repeated at 30 μM initial DCF concentration to monitor degradation byproducts as well as for quantification of mineralization species (i.e., NO2‒, NO3‒, NH4+) and TOC reduction during the degradation process.

In order to check the zinc-ferrite nanoparticles reusability, nanoparticles collection and regeneration strategies were employed. The suspended nanoparticles were collected at the end of each experiment by placing a magnetic bar near to the vial’s wall for 1 min, Fig. S1. After removing the solution, the collected nanoparticles were regenerated by washing with Milli-Q water and then with ethanol. Finally, the nanomaterial was dried at 60 oC and saved in a refrigerator (at ~ 6 oC) for further reuse.

Among all synthesized zinc-ferrite nanomaterial, primary investigation showed Zn1.0Fe2.0O4 has superior degradation activity for DCF. Therefore, further investigations of chemical properties of Zn1.0Fe2.0O4 were performed to better understand its activity. Chemical reduction property of Zn1.0Fe2.0O4 was investigated by reducing Mn7+ in KMnO4 into Mn2+ in acidic medium. Upon mixing Zn1.0Fe2.0O4 with KMnO4 in acidic medium, permanganate violet color (due to Mn7+) faded out and ultimately disappeared due to the formation of colorless reagent (Mn2+). The color change of reaction mixture was monitored by measuring the solution UV/Vis spectrum using a spectrophotometer. The reaction was performed in a glass vial containing 1.0 eq/L KMnO4 and 5.0 mg Zn1.0Fe2.0O4. Moreover, chemical oxidation property Zn1.0Fe2.0O4 was investigated by investigating the involvement of •OH in DCF degradation. For that purpose, a specific scavenging agent, i.e., *tert*-butanol (*t*-BuOH), was added to the degradation system. In this experiment, 10 µM DCF was mixed with 5.0 mg Zn1.0Fe2.0O4 in the presence of *tert*-butanol (*t*-BuOH) at different concentration levels (i.e., 20, 100, 500 and 1000 mM) and change in DCF concentration was monitored. Moreover, due to reaction between Zn1.0Fe2.0O4 and water in the degradation system, hydrogen peroxide was expected to release in the solution, thus a spectrophotometric determination of hydrogen peroxide was performed by using its reaction with metavanadate in acidic medium [26].

Furthermore, the degradation of DCF was performed in an effluent wastewater collected after microfiltration step (WWE) in the Groundwater Replenishment System (GWRS) located in Orange County, CA, USA. In this experiment, 0.17 g/L of Zn1.0Fe2.0O4 was added to 30 mL WWE water containing 10 µM DCF. Major characteristics of WWE wastewater as provided by GRWS in their 2017 online report are summarized in **Table S1 (Supplementary Information)** [27].

## **Analytical methods**

An HPLC (Agilent 1100 Series) with a photodiode array detector (PDA) was used for the quantification of DCF during the degradation experiments. For separation, a Supelco C18 column (150 mm × 4.6 mm, 5.0 µm) was used with a mobile phase consisted of 0.1% (v/v) formic acid in water and 100% acetonitrile at a ratio of 30:70 (v/v), respectively. The flow rate was 0.30 mL min−1, the injection volume of each sample was 10 µL, the column temperature was 25 oC, and the detection wavelength for DCF was set at 221 nm. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to quantify leached Zn and Fe from the zinc-ferrite during reaction. Quantification of Cl‒ released from DCF during the degradation experiments was performed by using a Dionex Ion Chromatography (model LC20, USA). An IonPac AS18 (2.0 × 250 mm) column was used to elute the ions. NH4+ was measured (as NH3-N) using Hach instrument model SL 1000 by using Chem Key for total ammonia as NH3-N. QuickChem low flow method 10-107-04-1-A for Lachat instrument was used to measure nitrite and nitrate. A Shimadzu VCSH-ASI TOC Analyzer was used for measurement of the change in total organic carbon (TOC) during the degradation experiments to investigate mineralization of DCF by the ZnxFe3-xO4.

An Agilent 1290 infinity HPLC system equipped with a Zorbax Eclipse XDB-C18 Rapid Resolution column (2.1 × 50 mm, 3.5 μm, Agilent Technologies) was used to separate the reaction byproducts from samples taken during DCF (initial concentration of 30 μM) degradation experiments. The mass analysis of the byproducts was performed by an Agilent 6540 UHD accurate-mass quadrupole time-of-flight tandem mass spectrometer (Q-TOF-MS) which was coupled to the 1290 HPLC with an electrospray ionization source (ESI). DCF and transformation product candidates were identified based on mass to charge ratio (*m*/*z*).

# **Results and Discussions**

## **Characterization of zinc-ferrite redox nanomaterial**

The synthesized zinc-ferrite (ZnxFe3-xO4) was characterized by HR-TEM analysis and the average particle size is shown in Fig. S2 (A-D). All nanoparticles were in polycrystalline nanostructures, with average particle size, based on TEM, of 41 nm for Zn0.1Fe2.9O4, 34 nm for Zn0.3Fe2.7O4, 26 nm for Zn0.7Fe2.3O4 and 31 nm for Zn1.0Fe2.0O4. BET surface analysis demonstrated surface of of Zn0.1Fe2.9O4, Zn0.3Fe2.7O4, Zn0.7Fe2.3O4 and Zn1.0Fe2.0O4 were 48.7, 26.1, 15.0 and 14.4 m²/g, respectively. According to SEM analysis, all synthesized zinc-ferrite (ZnxFe3-xO4) possessed octahedral and tetrahedral particle structures as shown in Fig. 1.

XRD analysis of zinc-ferrite nanoparticles revealed diffraction peaks at 18°, 29.9°, 35.2°, 36.8°, 42.8°, 53°, 56.6° and 62.9° which correspond to cubic, spinel crystal planes (111), (220), (311), (222), (400), (422), (511) and (440), respectively (Fig. 2). This result compares favorably with the *hkl* planes of zinc-ferrite that has matching spectra at (220), (311), (222), (400), (422), (511), and (440) (PDF #04-007-6616). The relatively minor peaks of (331), (531), (620), (533), and (622) planes were not observed within the 2*θ* sweep from 0 to 75 degrees, but all have low recorded intensities for zinc-ferrite. The percentage of crystal diffraction in proportion to noise floor suggested the nanoparticles were ~79% crystalline using the Rietvald method [28]. The average sizes of the crystallites for each of the various formulations were determined at (311) which was the dominant peak using the Scherrer equation (Eq. 1) [29].

(1)

where, *K* = 0.9 (shape factor), is the X-ray wavelength 1.5418 Å, is the line broadening at FWHM after subtracting instrumental broadening in radians [Δ(2*θ*)], and *θ* is the Bragg angle of 36.2°. Additionally, peak broadening for the (311) plane was observed when the content of zinc increased for intermediate concentrations, indicating a decreased crystallite size. Using the dominant (311) peak of Zn0.3Fe2.7O4 and Scherrer equation, average crystallite size of 13 nm was obtained. When zinc concentration increased as in Zn0.7Fe2.3O4, the dominant (311) diffraction peak decreased and the average crystallite size was10 nm. Zn0.1Fe2.5O4 produced crystal sizes of 22 nm, while Zn1.0Fe2.3O4 possessed 26 nm average particle size.

Fig. 3(A-D) depicts SAED patterns of ZnxFe3-xO4.The diffraction rings are consistent with spinel zinc-ferrite crystal structure [30]. The rings of Zn0.1Fe2.9O4 corresponding to (200) and (311) planes (Fig. 3A) match with zinc-ferrite *hkl* planes (PDF #04-007-6616). The diffraction rings of Zn0.3Fe2.5O4 from planes (111), (220), (311), (400), and (511) also match with spinel zinc-ferrite (Fig. 3B). Zn0.7Fe2.3O4 also resembles zinc-ferrite with diffraction from planes (220), (311), (400), (422), (511) and (440) (Fig. 3C). Lastly, Zn1.0Fe2.0O4 crystal spectra again agree very well to those of zinc-ferrite with diffraction from planes (111), (220), (311), (511), and (440) (Fig. 3D).

Zinc lattice constants of different nanomaterial were calculated from the reciprocal of space rings in Fig. 3 using the equation , where *d* is the interplanar spacing, *α* represents the lattice constant, and *hkl* are Miller indices. Lattice constants of Zn 0.1Fe2.9O4 were 0.1491 nm for [220] and 0.1250 nm for [311], with an average lattice constant of 0.1370 nm. Using the same equation, lattice constants and their average values for all synthesized nanomaterial were calculated and summarized in Table 1. Generally, as the concentration of zinc in ZnxFe3-xO4 increased, the average lattice constant of corresponding nanomaterial increased (Table 1).

The results of SAED diffraction rings and XRD lattice plane reflection suggested zinc-ferrite nanomaterial were in cubic crystalline zinc-ferrite structure, with spinel configuration (i.e., AB2O4, Fig. S3). In AB2O4 structure, [A] and [B] are occupying the tetrahedral and octahedral sites, respectively [31]. The spinel ferrite unit cell is of cubic structure (space group Oh7-F3dm) that forms a cube with eight ZnOFe2O4 molecules consisting of 32O2- anions. The oxygen anions construct a face-centered cube packing, consisting of 64 tetrahedral (A) and 32 octahedral (B) empty spaces that are partially populated by Fe3+ and Zn2+ cations [32]. In all synthesized nanomaterial, cubic spinel ferrites displayed high percentages of Fe at the tetrahedral location of 80% [33], 66% [34], and 84% [35]. The crystal structure was altered correspondingly with the shift in percentage of Fe at the tetrahedral site. This accounted for the alteration in crystal structure with changing stoichiometry.

The vibration modes in the Znx-1Fe3-xO4 nanoparticles were investigated by Raman spectroscopy, Fig. 4. The synthesized Znx-1Fe3-xO4 material showed Raman active modes at around 212, 272, 390, 493, 603, 1100, 1330 cm-1 with intensities changing according to stoichiometry [36]. Position of these vibration modes varies with the synthesis process [36, 37] and/or with the incorporation of Zn ions in the crystal lattice [38]. In the current study, zinc-ferrite possessed low frequency spectral vibrations (equal or below 490 cm-1) attributed to those of metal cations and oxygen ions at the octahedral sub-lattice (O-side modes) of ZnxFe3-xO4. Other vibrational spectra were noticed at higher frequencies (603, 1100, and 1330 cm-1) that were consistent with vibrations of tetrahedral sub-lattice (T-side modes) [36-38]. Apart from zinc-ferrite, isolated zinc oxide and ferrite were also detected, such as the vibrational modes at 212, 272, 390 and 493 cm-1 of hematite (a-Fe2O3) found in zinc-ferrite nanoparticle with lowest zinc content (i.e., x= 0.1) [39]. nanomaterial with higher zinc content were found in higher crystallinity, in spinel structure with traces of impurities. These impurities were randomly formed among the different Znx-1Fe3-xO4 samples, without showing a specific tendency; the broad bands at 1100 cm-1 (for x equal to 0.7 or 1.0) and 1330 cm-1 (for x equal to 0.5 or 0.7) were assigned to Zn3O4 phase [40] and iron oxides [41], respectively.

Surface analysis (from the top 0 to 10 [nm](https://en.wikipedia.org/wiki/Nanometre) deep) of the synthesized ZnxFe3-xO4 was performed using X-ray photoelectron spectroscopy (XPS), Fig. S4 -S9. Analysis of the XPS spectra revealed Fe, Zn, O, and C were the major elements composing all zinc-ferrites in the current study. With regard to Zn0.1Fe2.9O4, deconvolution of C1s core level peak resulted in three components at binding energies 284 eV, 286 eV, ~288.5 eV corresponding to C-C, C-O, and O-C=O bonds, respectively, Fig. S4(B). These peaks were very intense in case of Zn1.0Fe2O4, and C1s peak shape was characteristic to iron carbonate, FeCO3 [42]. On the other hand, less intense C1s deconvolution peaks with similar bond energies were obtained for the remaining zinc-ferrite materials (i.e., Zn0.7Fe2.3O4, Zn0.3Fe2.5O4, and Zn0.1Fe2.9O4). Zn0.7Fe2.3O4 possessed three C1s deconvolution peaks C-C bond at 284 eV, C-O bond at ~286 eV and C=O bond at 288.5 eV with reduced peak intensities as the Zn to Fe ratio decreases, Fig. S5 (B). The remaining mixtures, Zn0.3Fe2.5O4, and Zn0.1Fe2.9O4 also display peaks I, II, and III at the same bonding energies with a reduction in the peak intensity respectively.

The O1s core level XPS peaks of all zinc-ferrites were also deconvoluted and results are shown in Fig. S4-S9. Peaks analysis resulted in three deconvolution peaks centered at 530 eV, 531 eV, and 534 eV for all zinc-ferrites, with the sane peak intensities. The sub-figures (D) in Fig. S4-S9 of zinc-ferrites show the core level spectra of Fe2p doublet. The binding energy centered at 710.2 eV (in Zn1.0Fe2O4) assigned to Fe2p3/2 was deconvoluted into two peaks assigned to 63.49% Fe2+ (711 eV) and 36.51% Fe3+ (713 eV) of the overall envelope peak. As zinc content decreased in zinc-ferrites, binding energy for Fe2p3/2 increased, e.g., 710.6 eV in Zn0.7Fe2.3O4, to 711.3 eV in Zn0.3Fe2.7O4, and to 712 eV in Zn0.1Fe2.9O4. The XPS binding energy at 710.2 eV was previously reported to be characteristic to Zn1.0Fe2O4 [43] or iron carbonates FeCO3 [42]. Moreover, the binding energy at ~713.5 eV featured Fe3+ in Fe2O3 particles [44], hematite (α-Fe2O3) nanoparticles [45] or FeOOH [46]. Accordingly, Fe2p3/2 peaks of different zinc-ferrites in the current study were concluded to be a sum of two contributions: at the low binding energy (zinc ferrite, iron carbonate) and at the high binding energy (Fe2O3 or FeOOH). As zinc content decreases, the component at high binding energy was more intense in the whole spectrum, probably due to the absence of zinc-ferrite compounds on the surface. Finally, all zinc-ferrites unveiled two Zn2p XPS spectra at 1022 eV (for Zn2p3/2) and 1044 eV (for Zn2p1/2) which were identical to ZnxFe3-xO4 structure. In the Zn0.1Fe2.9O4 sample, traces of Zn appeared because of a small amount of Zn atoms. Moreover, the binding energy at 780.0 eV confirmed the existence of characteristic bonding between Zn and Fe in all zinc-ferrites [43].

The average percentage (%) relative to atomic concentration of elements in the analyzed regions of the zinc-ferrites were determined using total peak area of Zn2p, Fe2p and O1s peaks after contribution from substrate was subtracted, appropriate sensitivity factors were applied (i.e., based on Wagner’s collection) and adjusted to transmission characteristics of analyser EA10 with applying corresponding equations for the electron transport properties in the matrix [47].

XPS analysis was also performed to the collected used Zn1.0Fe2.0O4 material from DCF degradation system to monitor changes in elemental composition of the zinc-ferrites. Fig. S8 and S9 depict XPS analysis of Zn1.0Fe2.0O4 after one-time use and two-times uses, respectively, for degradation of DCF in water. Resulted shoed the same elemental contents in both samples (i.e., O, C, Zn, and Fe), however, with changes happened to the concentrations of iron species in the zinc-ferrites. With respect to the pre-used C1s core level peak, there was no change in its three major components corresponding to binding energies 284 eV, 286 eV, and ~288.5 eV after uses. Deconvolution of O1s peaks of the two used Zn1.0Fe2.0O4 samples resembled similar binding energy peaks to that of pre-used sample, i.e., at 530 eV, 531 eV, and 532 eV, however, with a reduction of ~ 2 eV in binding energy of the last peak. Deconvolution peaks of core level spectra of Fe2p3/2 were obtained for the used Zn1.0Fe2.0O4 samples. Yet, the composition (%) of Fe2+ and Fe3+ species composing the original Fe2p3/2 envelope peak changed significantly from 63% and 36% in pre-used sample into 50% and 50% in the used sample, respectively (fig. 5).

Characterization of the atomic bonding environment for Zn1.0Fe2.0O4 nanoparticles was conducted by XAFS analysis from both Zn and Fe perspective. Table 3 shows the optimized parameters highlighting the coordination number (CN) and interatomic bond distance (R) for the Zn and Fe K-edge of franklinite and Zn1.0Fe2.0O4. Natural franklinite has a chemical formula of (Zn,Fe2+)Fe3+2O4 where minor levels of Fe2+ can substitute for Zn in the mineral structure. Evident in Table 3, the structural parameters for franklinite are interestingly similar to that of Zn1.0Fe2.0O4 nanoparticles in the current study. Additional XAFS data can be found in Supporting Information including normalized X-ray absorption near-edge structure (XANES) spectra and derivatives of the normalized XANES spectra (Fig. S10), k3-weighted χ functions (Fig. S11), and radial structure functions (Fig. S12) for Zn and Fe K-edge data for Zn1.0Fe2.0O4.

## **Degradation of DCF by ZnxFe3-xO4**

The redox activities of the synthesized zinc-ferrites nanomaterial were evaluated for the degradation of DCF under dark experimental conditions (Fig. 6). Unlike previous studies established for degradation of organic contaminants using zinc-ferrite as a photocatalyst, the current ZnxFe3-xO4 material showed unique enhanced degradation properties for DCF in water, without any added oxidants or external energy. Fig. 6 depicts the degradation profile of 10 µM DCF in Milli-Q water by using different ZnxFe3-xO4 at an initial solution pH of 6.45. DCF degradation deemed super-fast that in some cases degradation reached ~ 90 % complete within the first 2 min of the reaction, yet, no appreciable change in DCF concentration was noted beyond 2 min. Results also revealed as Zn:Fe ratio increased in the zinc-ferrite nanomaterials, degradation of DCF increased. For example, respective removals of DCF at 2 min of reaction by Zn0.1Fe2.9O4, Zn0.3Fe2.7O4, Zn0.7Fe2.3O4 and Zn1.0Fe2.0O4 were 5, 25, 38 and 90 %. Moreover, using pure ZnO pellets only promoted 5 % removal of DCF under the same experimental conditions, which is similar to the zinc-ferrite with the lowest level of Zn, Zn0.1Fe2.9O4. These findings implied the synergistic role of Zn and Fe in DCF degradation, among the zinc-ferrites tested, zinc-ferrite with Zn:Fe ratio of 1:2 were clearly superior to the materials with lower Zn levels.

For practical assessment of zinc-ferrites, DCF degradation was conducted in a wastewater effluent (WWE) collected after microfiltration process in the groundwater replenishment system GWRS (Orange County, CA, USA), the world's largest water purification system for indirect potable reuse. In this experiment, 10 µM DCF was spiked in WWE and mixed with 0.17 mg/L Zn1.0Fe2.0O4 in a glass vial. Figure 6 compares removal percentages of DCF at different reaction times in Milli-Q water and WWE samples. With respect to degradation in Milli-Q water, slightly lower DCF removal was observed in WWE sample. Approximately 90% removal of 10 µM initial DCF was achieved in two min reaction time when Milli-Q water was used, compared to only 60 % removal in WWE sample. Longer reaction time did not lead to a notable improvement in DCF degradation in Milli-Q water, yet degradation in WWE sample continued to increase up to ~75% at 60 min reaction time. The decreased removal in DCF in WWE was due to the complex organic and inorganic matrix of the WWE sample (**Table 2)**. Presence of organic and inorganic species (e.g., chloride, bromide, bicarbonate, etc.) has been previously reported to inhibit degradation of organic contaminants by AOPs in water. Natural organic matter and inorganic ions tend to quench/react with active species such as hydroxyl radical generated during AOPs that typically lead a decrease degradation efficiency. Indeed, the synthesized zinc-ferrite nanomaterials showed a promising result for the removal of DCF even in field water matrices such as EWW.

### *Redox properties of zinc-ferrite and formation of H2O2*

Zinc-ferrite material was suggested to release electrons upon contact with aqueous solution due to via oxidation of its Fe2+ into Fe3+ (**Eq. 2**). This hypothesis was confirmed by XPS analysis of Zn1.0Fe2.0O4 before and after degradation experiment (**Fig. 5**). Zn1.0Fe2.0O4 lattice consisted of 63 % Fe2+ (Fe2p 3/2; 710.5) and 37 % Fe3+ (Fe2p 3/2; ~ 713.5) for the as-prepared zinc-ferrite nanomaterial before use (**Fig. 5**). After degradation process, the same zinc-ferrite nsanomaterial exhibited a decrease in its Fe2+ content by 13% and increase Fe3+ content by the same percentage due to redox process that took place during degradation process [48]. As a result, several chemical processes could take place based on these electrons at the synthesized ZnXFe3-XO4 surface [49].

To further confirm the chemical reduction property of zinc-ferrite, reaction with KMnO4 (a strong oxidizing agent; *E*= +1.3 V) in acidic medium was investigated. KMnO4 is characterized with a purple reddish color due to presence of Mn7+ in its composition. In presence of a reducing agent (i.e., electron donating substrate), Mn7+ undergoes a chemical reduction process due to five electrons transfer in acidic medium and convert into Mn2+ (colorless reagent) [50, 51]. When KMnO4 was mixed with Zn1.0Fe2.0O4 in acidic medium the characteristic purple color of the solution faded out slowly until complete disappearance, **Eq. 3** and **Fig. S14**. The change in spectra of reaction solution was collected at different reaction times as shown in **Fig. S13**. Upon monitoring change in absorbance intensity corresponding to [Mn7+] (i.e., 450-600 nm), a fast decrease in the light absorbance was noticed in the first 15 min of the reaction, followed by a gradual decrease until 30 min then the absorbance was almost halted at 60 min. These results confirmed the reducing properties of Zn1.0Fe2.0O4 in aqueous medium due to oxidation reaction in **Eq. 2,** that resulted in reducing KMnO4 and changed the color of solution **Eq. 3**. [50, 51]

(2)

(3)

The generated electrons at the Zinc-ferrite nanomaterials surface were suggested to interact withmolecular oxygen in water to generate superoxide anion that further led to formation of hydrogen peroxide (**Eq. 4**). Previous studies also suggested H2O2 release during reaction involving zinc ions or zinc-ferrites in aqueous solutions [52-55]. Therefore, formation of H2O2 in the degradation medium in the current study was investigated by its reaction with ammonium metavanadate in acidic medium. In this reaction, a red-orange color is produced due to reaction between H2O2 and ammonium metavanadate to form peroxovanadium cation. The latter was then monitored spectrophotometrically (at 450 nm) as a response to H2O2 formation [26]. **Fig. 9** shows time-based evolution profile of H2O2 in an aqueous solution containing Zn1.0Fe2.0O4. Initially, a fast formation of H2O2 was observed, i.e., [H2O2] increased from 0.14 µM at 4 min to a maximum of 0.23 µM at the 8 min, followed by a sudden decrease with time until it was almost disappeared from the solution at 60 min. The consumption of H2O2 could be explained by its reaction with iron (i.e., Fe2+ and Fe3+) from the zinc-ferrite to ultimately produce hydroperoxyl radicals that were responsible for DCF degradation (**Eqs. 5-8**) [52-55]. Hydroxyl radicals could also combine to form H2O2 in the system (**Eq. 5)**. Due to the rapid evolution of H2O2 at the beginning of the reaction, a fast formation hydroxyl radical was observed, and thus a fast degradation in DCF was observed. As the reaction proceeded, H2O2 was consumed progressively and ultimately disappeared from the solution at the end of experiment.

(4)

(5)

(6)

(7)

(8)

To further investigate the role of •OH in DCF degradation by zinc-ferrite, quenching experiments were conducted in presence of *t*-BuOH as a common quenching agent, with a known second order rate constant of its reaction with •OH (i.e., 3.8 – 7.6 × 108 M-1 s-1) [56]. **Fig. 8A** illustrates the degradation profile of 10 µM DCF by Zn1.0Fe2.0O4 in presence of different *t*-BuOHat different initial concentrations (i.e., 20, 100, 500 and 1000 mM). At 5 min reaction time, the addition of 20, 100, 500, and 1000 mM *t*-BuOH resulted in a drop in DCF removal % to 87, 54, 28, and 15%, respectively. This suggested •OHwas majorly involved in DCF degradation. A similar observation was reported by Zhang et al. (2017) for the contribution of •OH in the degradation of PBSA by PMS in presence of CuFe2O4 as a catalyst and Li et al. (2018) in the degradation of DCF by Fe0/H2O2[57, 58]. Moreover, 12% reduction in DCF was observed under nitrogen purging and 38% reduction when 15.0 M Dimethyl Sulfoxide (DMSO) was added to the reaction as shown in **Fig. 8B**. These results also confirmed •OH was primarily involved in the degradation process.

### *Role of Fe and Zn in DCF degradation*

As explained above, the generated electrons from ZnxFe3-xO4 were the driving force for DCF direct reductive degradation and also through indirect oxidation by reactive oxygen species (i.e., O2•−, HOO• and •OH) produced in the system. Fe2+ and Fe3+ in ZnxFe3-xO4 were also suggested to react with the generated H2O2 in the system via Fenton and Fenton-like reactions, respectively, and yield •OH that participated in DCF degradation (**Eqs. 4-7).** It is also possible for Zn2+ in the zinc-ferrites to be reduced into Zn+ and/or Zn0 at the zinc-ferrite surface; these Zn species played an important role in Fe2+ regeneration in the zinc-ferrite via reduction of Fe3+ which extended the lifetime of the zinc-ferrite nanomaterial during the degradation process (**Eq. 9**). Possible reductive degradation route of DCF is explained in section 3.3.2.1.

(9)

### *Effect of Zn:Fe stoichiometry and pH on DCF degradation*

Fig. 6 shows the effect of change in zinc-ferrite composition on DCF degradation process. The removal percentages for DCF (initial concentration of 10 µM) at 10 min reaction using Zn1.0Fe2.0O4, Zn0.7Fe2.3O4, Zn0.3Fe2.7O4 and Zn0.1Fe2.9O4 were 10, 20, 35, and 90%, respectively (Fig. 6). Degradation of DCF was notably increasing as the Zn content in Zn-ferrite increased, indicating the important role of zinc in regeneration of Fe2+ in the zinc-ferrite nanomaterial during the process. With respect to other prepared Zn-ferrite materials, Zn1.0Fe2.0O4 showed superior reactivity towards DCF degradation and a very fast removal for DCF at the beginning of the reaction. This was explained by the fast chemical reduction of DCF by electrons at the surface of Zn1.0Fe2.0O4, in addition to the oxidation by reactive radical species, especially •OH, generated in the first 2-5 min of the degradation process [62]. Rapid degradation of DCF was also reported by Moreira et al. by different hydroxyl radical initiated processes [63]. The decomposition percentage of DCF did not significantly change as the reaction proceeded beyond 5 min in all degradation system, that was likely due to surface poisoning of the zinc-ferrite and decreased generation rate of radical species in the systems [64]. Degradation of DCF by Zn1.0Fe2.0O4 was slightly enhanced to 95 % in moderately acidic medium (i.e., pH 5.0) in the first 4 min of reaction. Increasing the solution pH to 8.0 resulted in a notable decrease in DCF degradation % to 88 and 24%, respectively (Fig.8). Based on the enhanced performance of Zn1.0Fe2.0O4 for DCF removal, it was used in the further experiments to examine the roles of Zn-ferrite loading and oxidant initial concentration on the degradation process.

## **Transformation products and pathways of DCF**

### *Degradation products*

Identification of DCF transformation products during the degradation by Zn1.0Fe2.0O4 was accomplished by analyses of peak areas of extracted ion chromatograms, retention time (Rt), suggested formula and *m/z* values given by the analytical software (Agilent Qualitative Analysis B.04.00) [65]. A relatively high initial DCF concentration (i.e. 30 µM) was used in this experiment to maximize the efficiency of detection of transformation products by the currently employed analytical method. Eleven transformation products were detected during a reaction period of 60 min; their corresponding formulas and detection parameters are presented in **Table S1**. The assigned transformation products comprised eight compounds from the oxidation pathways and three compounds from the reduction pathways. **Fig. 10** (A) and (B) depicts the kinetics profile in terms of change in peak area of DCF and its transformation products during the experiments.

Chemical reduction of DCF comprised three transformation products including **R1**; *m/z* 262, **R2** (*m/z* 226) and **R3** (*m/z* 228) [66]. Yu et al. has reported **R1** and **R2** as reduction products from DCF using hydrated electrons ( generated from 60Co γ-irradiation to degrade DCF [61]. To the best of authors’ knowledge, **R3** was for the first time detected along with R1 and R2 in the current study (**scheme1**).

Eight transformation products were tentatively identified from the oxidation pathway, including **P1** (*m/z* =152), **P2** (*m/z* =146), **P3** (*m/z* =169), **P4** (*m/z* =194), **P5** (*m/z* =178.9), **P6** (*m/z* =310), **P7** (*m/z* 268), **P8** (*m/z* =282) and **P9** (*m/z* 266), **Scheme 2**. The formation of DCF transformation products, and their further degradation varied from one to another in terms of their peak areas. Among all identified byproducts, **P1** and **P4** showed the highest abundance, with respect to their chromatogram peak area. Generally, all recognized transformation products were evolved quickly in the solution in the first 2 - 4 min of the degradation process and then sustained in the solution till the end of the reaction. About 12% reduction in the peak area of **P1** was observed at 4 min and then the compound stayed unchanged in the solution. **P5** lost nearly 72% of its maximum peak area after only 2 of reaction time while **P4** experienced 14% removal at 4 min. Among all byproducts, **P3**, **P6**, **P8** and **P9** showed the lowest peak areas and insignificant decrease in their volumes were observed till the end of reaction. Hofmann et al. [67] have reported the formation of **P1** (*m/z* =152)**,** **P2** (*m/z* =146) **and P7** (*m/z* =268) among other transformation products detected during the degradation of DCF by sonolysis of catalysts in water, yet, **P2** was not detected in the current study and only assumed. Moreover, **P3** (*m/z* =169), **P4** (*m/z* =194), **P5** (*m/z* =178), **P6** (*m/z* =310), **P8** (*m/z* =282) and **P9** (*m/z* 266) were reported in other studies conducted on oxidation of DCF by aqueous chlorine dioxide-based AOP [68, 69].

### *Degradation pathways*

Dechlorination of DCF was the main degradation pathway for the reduction route, and cyclization was suggested to occur after dechlorination as shown in **Scheme 1**.

The potential pathways of DCF oxidation pathways are presented in **Scheme 2**; cleavage of the C-N bond, hydroxylation of DCF prompted by •OH, and decarboxylation reaction, were recognized as the main degradation pathways for the oxidation route.

### *Reduction Route*

The reduction of DCF was initiated by electronic attack resulting in the dechlorination of the molecule and the formation of **R1** (*m/z* 262).Further reductive dechlorination of intermediate **R1** (*m/z* 226) promoted complete dechlorination and the formation of **R3** *m/z* 228. Formation of **R2** (*m/z* 226) was justified by further dichlorination and intermolecular cyclization of **R1**.Another possible formation pathway for **R2** (*m/z* 226) was expected via direct dichlorination and cyclization of the parent compound (DCF). Indeed, the formation of dechlorinated-DCF byproducts as well as cyclization process in DCF has confirmed the involvement of chemical reduction by surface electrons in the degradation process. The identification of the transformation products from the reduction route is in agreement with the presented above XPS analysis confirming once more the generation of electrons.

### *Oxidation Route*

Initially, DCF experienced C6-N bond cleavage to form **P1** (*m/z* =152) and **P2** (*m/z* =146; *not detected in the current study*). Via further successive hydroxyl radical attack to **P1** at C8 and C11 and deamination (loss of amino group NH2), **P3** (*m/z* =169) was formed. Moreover, further hydroxylation of compound **P2** was explained to produce **P4** (*m/z* =194) that underwent additional hydroxyl radical attack to form **P5** (*m/z* =178, polyhydroxy dichlorobenzene). A second possible DCF degradation pathway was via hydroxylation prompted by •OH attack at C11 position to form **P6** (*m/z* =310; monohydroxylated-DCF). This compound underwent two types of transformations, the first involved decarboxylation to form P**7** (*m/z* 268), and the second pathway comprised C-N bond cleavage to generate **P3** (*m/z* =169). Compound P**8** (*m/z* =282) was possible formed via sequential hydroxylation and oxidation of the terminal methyl group in **P7** into aldehyde moiety. Again, the byproducts **P4** and **P5** were expected to be produced from **P8** after a succeeding C-N bond cleavage and hydroxylation processes. The third major degradation pathway for DCF occurred due to sequential decarboxylation/hydroxylation/oxidation of the terminal acetate group (-CH2-COOH) to form an aldehyde derivative of DCF **P9** (*m/z* 266). Further hydroxylation of **P9** (*m/z* 266) prompted by •OH electrophilic addition led to formation of **P8** (*m/z* =282). P9 was also suggested to experience C-N bond cleavage followed by successive hydroxylation to form **P4** and **P5**. Ultimately, all byproducts were suggested to mineralize under the current reductive/oxidatiove conditions and yield NH4+, NO2−, H2O2 and CO2.

### Hydroxylation products of DCF degradation

Due to the high electron density of phenylacetic acid ring of DCF, it is progressively attacked by •OH to generate various hydroxylated products including DCF-OH [70, 71]. Hydroxylation of DCF can take place upon •OHattack to one of its carbon atoms containing α-hydrogen [57, 70, 72, 73]. Mechanism of DCF hydroxylation by •OH is illustrated in **scheme 3**. A carbon-centered radical is generated upon electrophilic addition of •OH to DCF benzene ring. The carbon-centered radical can react quickly with dissolved O2 to form the transient peroxyl radical, that ultimately is converted into monohydroxylated DCF product (i.e., **P6**) with simultaneous release of hydroperoxyl radical (H2O•) [73]. Further hydroxylation of DCF can also take place via the same pathway to yield more hydroxylated products [57, 70, 71, 73].

## **Mineralization of DCF into Cl−, NH4+ and NO2−, and TOC removal**

Mineral residues based on N atoms are expected from the degradation of DCF by ZnxFe3-xO4. Moreover, reduction in the total organic carbon (TOC) content of the DCF degradation system was also expected as a result of the complete oxidation of DCF and its transformation products. Fig. 9 reveals the concentration profile of NO2– and NH4+ released during the degradation process. The formation of NH4+ and NO2**−** during DCF degradation was justified as **P1** (*m/z* =152), **P6** (*m/z* =310), **P8** (*m/z* =282) and **P9** (*m/z* 266) compounds lost N-atoms dudegradation process, then this nitrogen was mineralized into NH4+ and NO2**−** in the solution Similar release of N-atoms in the form of NH4+ and NO2**−** was previously reported during the degradation of DCF by ultrasonic irradiation [74]. Nitrite ions were detected in the current study at considerably low concentrations as compared to NH4+ (fig. 9). There was no noticeable formation of NH4+ at the beginning of the degradation process (till 10 min). Then, a sudden increase in NH4+ concentration was observed in the solution that reached 0.4 mg/L at 16 min, , that was maintained almost unchanged till 30 min before it resume again a rapid formation until it reached 0.6 mg/L at 60 min. NO2– has rapidly evolved early in the solution and reached 56 µM at the first 1 min of the reaction, then it continued increasing steadily and slowly in the solution and reached 79 µM at 60 min. Overall, formation of NO2– was marginal during the degradation process as compared to formation of NH4+ in the same system. The nature of NO2– under the operated experimental conditions was explained via its low release (i.e., 79 µM) in the 60 min of the reaction. In accordance with above mentioned findings, previous studies reported the rapid oxidation of nitrite ions into nitrate species, especially in oxidative systems [75, 76]

Fig. 9 also shows the result of TOC reduction in the degradation system. About 78% of the theoretical total TOC was removed in the first 8 min of the reaction, yet, longer reaction time (>8 min) did not exhibit any further removal of TOC.

The degradation behavior of DCF by recycled Zn1.0Fe2.0O4 was studied and results are depicted in Fig. S17. DCF degradation decreased with subsequent reuse of the same Zn-ferrite nanomaterial, that was likely due to the decrease in Fe2+ content in the Zn-ferrite that was the main factory for electrons’ generation and further formation of radical species responsible of DCF degradation in the system. Upon investigating the amount of metal leached out off the Zn-ferrite nanomaterial, about 0.21 mg/L Zn metal was released in the solution at 60 min of the reaction, while almost no iron species were found in the solution (i.e., concentrations were below detection limit of the instrument), Fig. 6B. Accordingly, another possible factor for the decreased DCF degradation when recycled Zn1.0Fe2.0O4 was used is the partial release of Zn2+ (i.e., as was investigated by ICP-AES) from the Zn-ferrite nanomaterial that inhibited the regeneration of Fe2+

# **Conclusion**

The current study work provided an efficient DCF treatment approach based on spinel ZnxFe3-xO4 nanoparticles. A combustion method was used for the synthesis of redox nanomaterial. The synthesized magnetic nanoparticles demonstrated novel reductive and oxidative properties when used in the degradation of DCF in water. Studies on the role of various Zn:Fe stoichiometries showed Zn1.0Fe2.0O4 was the most effective by removing ~90% DCF in 60 min reaction time, under ambient experimental conditions. DCF degradation in wastewater matrix was also achieved and results showed ~76% of initial 10 µM DCF was removed by Zn1.0Fe2.0O4 in 8 min. Magnetic zinc ferrite resox nanomaterial showed a reasonable efficiency over three consecutive reuse cycles, with only ~8% decrease in its efficiency for DCF degradation after the first use. Both reduction and oxidation properties of zinc ferrite were justified by its reaction with potassium permanganate and using *t*-BuOH as a scavenging agent for hydroxyl radical, respectively. Mineralization of DCF was majorly in the form of nitrite and ammonium. Furthermore, 78% of the total theoretical TOC was reduced in the first 8 min of the reaction. Eight transformation products from DCF degradation were identified using LC/MS analysis via oxidation route and three transformation products where identified via reduction route. Degradation pathways of DCF were also suggested based on the detected transformation products. Overall, ZnxFe3-xO4 was shown to be a promising magnetic nanomaterial for the degradation of organic contaminants, especially DCF, in wastewater matrix.

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**Captions**

**Figures;**

**Fig. 1:** SEM imaging of (A) Zn0.1Fe2.7O4 (B) Zn0.3Fe2.7O4 (C) Zn0.7Fe2.3O4 and (D) Zn1.0Fe2.0O4.

**Fig. 2:** XRD diffraction patterns of various mixtures of zinc ferrite spanning from Zn0.1Fe2.7O4, Zn0.3Fe2.7O4, Zn0.7Fe2.3O4, and Zn1.0Fe2.0O4.

**Fig. 3:** SAED images of (A) Zn0.1Fe2.7O4 (B) Zn0.3Fe2.7O4 (C) Zn0.7Fe2.3O4 (D) Zn1Fe2O4.

**Fig. 4**: Raman spectra of ZnxFe3-xO4, for x equal 0.1, 0.3, 0.7 and 1.0, respectively.

**Fig. 5:** (A) Fe2p XP core level from Zn1.0Fe2.0O4 before use

(B) Fe2p XP core level from Zn1.0Fe2.0O4 after use

**Fig. 6:** (A) Effect of various stoichiometry’s of zinc ferrite in addition to the effect of zinc oxide alone used in to remove DCF from water samples over 240 minutes. Experimental conditions are: ZnxFe3-xO4 = 0.17 g/L, [DCF]0= 10 µM.

(B)The releasing of Zn2+ and the generation of H2O2 during the degradation of DCF. Experimental conditions are: Zn1.0Fe2.0O4 = 0.17 g/L, [DCF]0= 10 µM.

**Fig. 7:** The effect of different pH on the degradation of DCF using Zn1.0Fe2.0O4 = 0.17 g/L, [DCF]0= 10 µM.

**Fig. 8:** (A) Effect of different concentrations (0, 20, 100, 0, 500 and 1000 mM) of quenching agent *t*-BuOH on the overall degradation of DCF and DCF removal percentage at 5 min. Experimental conditions are: Zn1.0Fe2.0O4 = 0.17 g/L, [DCF]0= 10 µM.

(B) Effect of different quenching agent DMSO (5.0 M and 15 M) on DCF removal and the effect of Nitrogen purging in DCF removal. Experimental conditions are: Zn1.0Fe2.0O4 = 0.17 g/L, [DCF]0= 10 µM

**Fig. 9:** The generation of NH4+, NO2ˉ, Clˉ, and TOC as a result of DCF degradation by Zn1.0Fe2.0O4 = 0.17 g/L, [DCF]0= 10 µM.

**Fig. 10:**  (A) the evolution of transformation products results from DCF degradation (oxidation) by Zn1.0Fe2.0O4 = 0.17 g/L, [DCF]0= 10 µM.

(B) the evolution of transformation products results from DCF degradation (reduction) by Zn1.0Fe2.0O4 = 0.17 g/L, [DCF]0= 10 µM.

**Schemes:**

**Scheme 1:**  Suggested reaction pathways for the DCF degradation (reduction) using Zn1.0Fe2.0O4 = 0.17 g/L, [DCF]0= 10 µM

**Scheme 2:**  Suggested reaction pathways for the DCF degradation (oxidation) using Zn1.0Fe2.0O4 = 0.17 g/L, [DCF]0= 10 µM.

**Scheme 3:**  HO• attack, a carbon-centered radical is produced upon electrophilic addition of HO• to DCF benzene ring.

**Tables:**

**Table 1:** Calculated interplanar lattice spacing and the resulting lattice constant for each of the planes for samples consisting of (A) Co0.1Fe2.9O4 (B) Co0.5Fe2.5O4 (C) Co0.7Fe2.3O4 and (D) Co1.0Fe2.0O4.

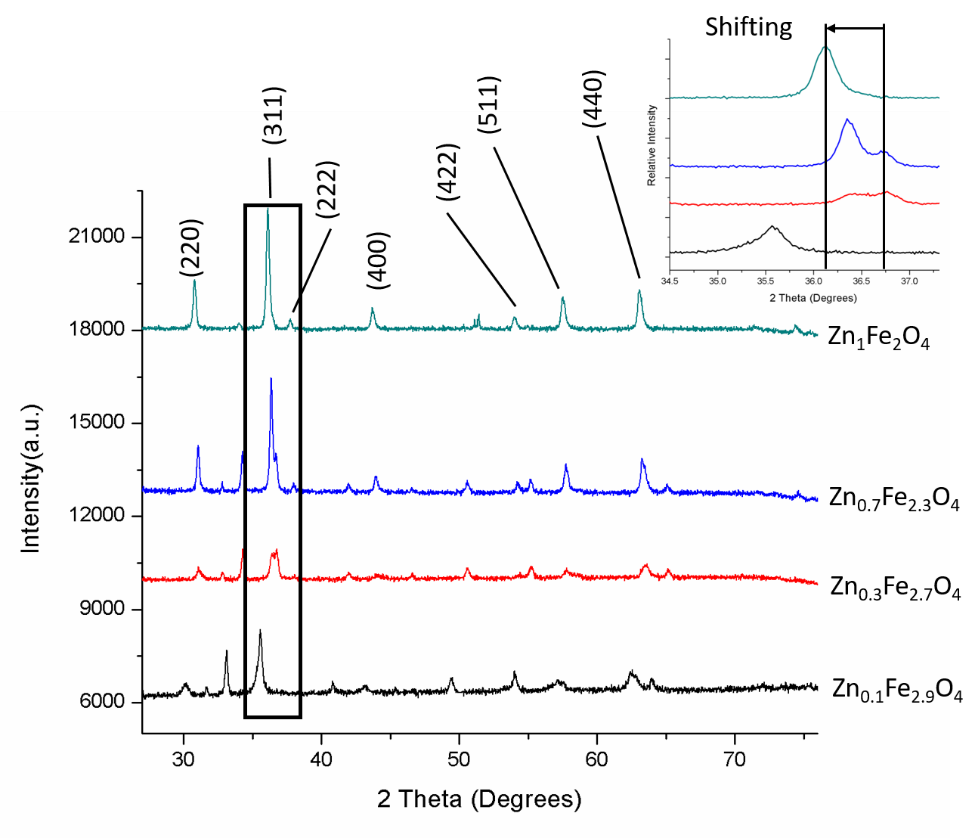
**Table 2:** The water sample parameters from a microfiltration effluent system.

**Table 3:** Optimized parameters of Zn and Fe K-edge XAFS data of natural franklinite and sample Zn1.0Fe2.0O4. CN is coordination number, R is radial distance, and σ2 is the Debye-Waller factor. CN for franklinite was fixed to calculated values and S02 was fixed to 0.85.

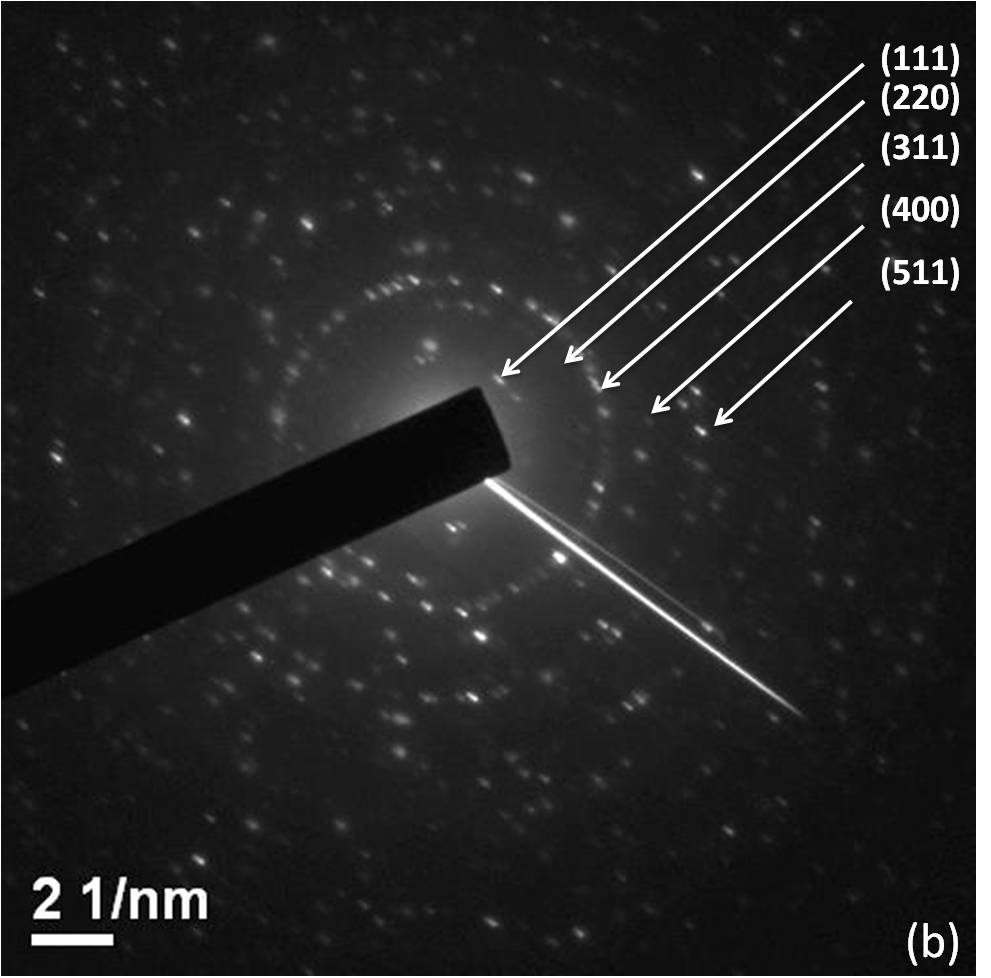
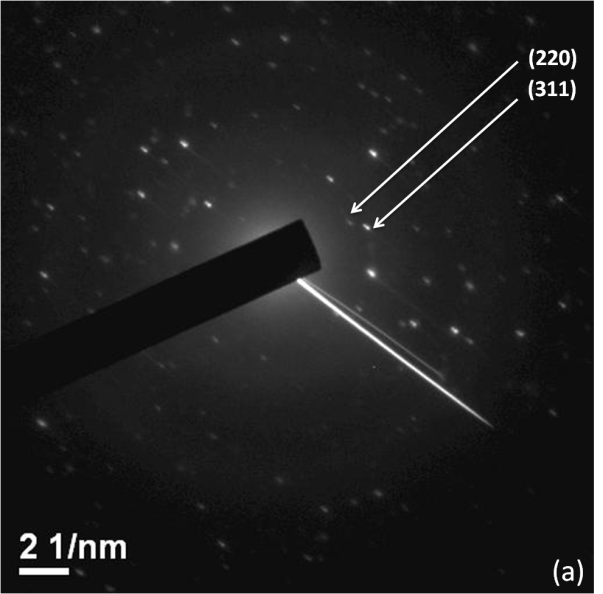
**Fig. 1 (A, B, C and D)**

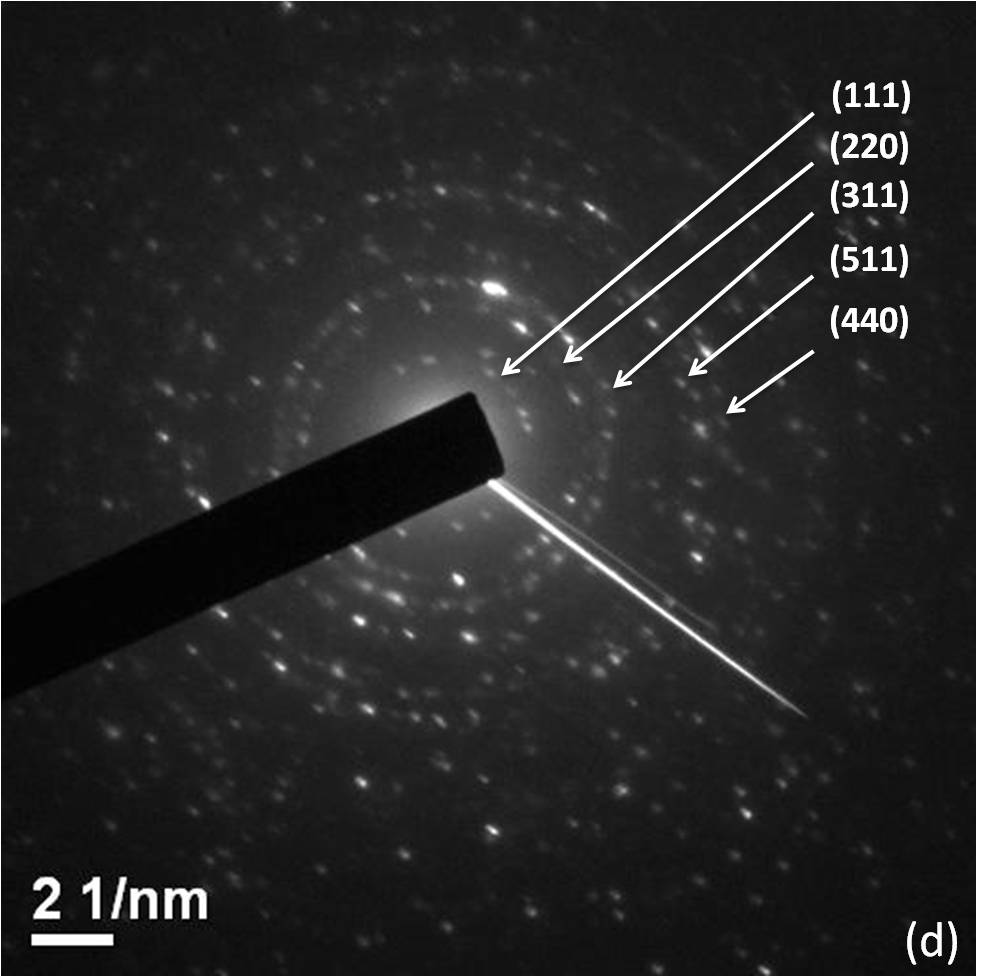
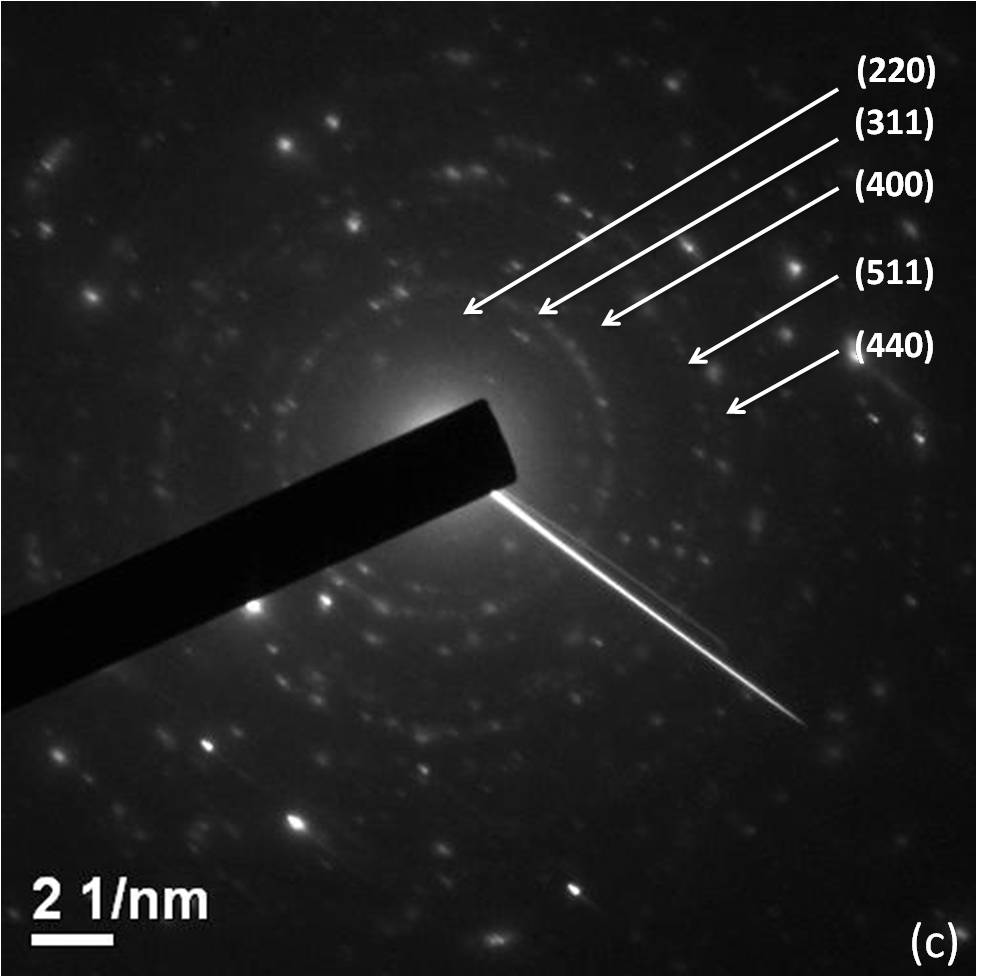
|  |  |
| --- | --- |
| **(A)** | **(B)** |
| **(C)** | **(D)** |

**Fig. 2**

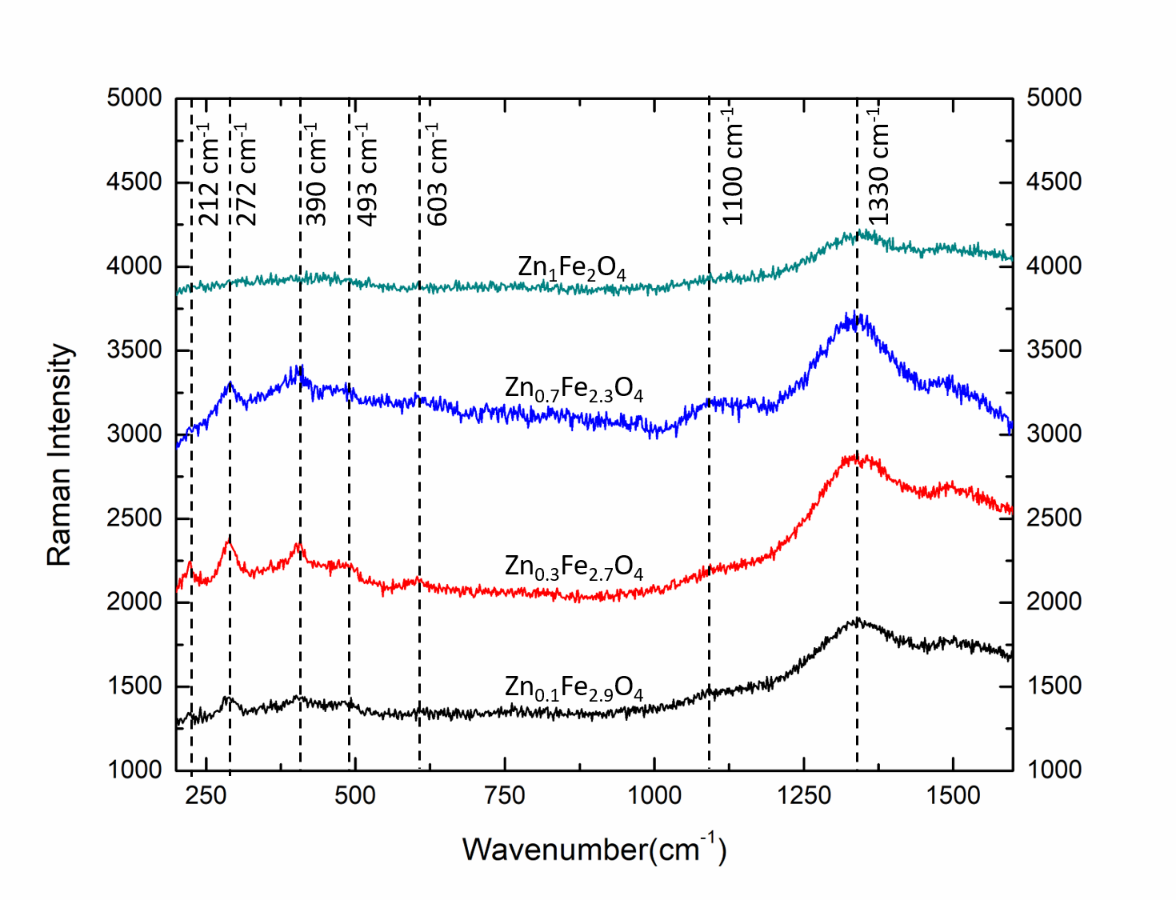


**Fig. 3**





**Fig. 4**



**Fig. 5**

**Fig. 6 (A&B)**





**Fig. 7**

**Fig. 8 (A&B)**





**Fig. 9**



**Fig. 10 (A&B)**





**Scheme 1.**



**Scheme 2.**

**Scheme 3**



**Table 1**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | a |  | b |  | c |  | d |
|  |  | **Zn0.1Fe2.9O4 (nm)** |  | **Zn0.3Fe2.5O4 (nm)** |  | **Zn0.7Fe2.3O4 (nm)** |  | **Zn1.0Fe3.0O4 (nm)** |
| [111] |  |  |  | 0.2463 |  |  |  | 0.2410 |
| [220] |  | 0.1491 |  | 0.1445 |  | 0.1434 |  | 0.1450 |
| [311] |  | 0.1250 |  | 0.1239 |  | 0.1214 |  | 0.1209 |
| [400] |  |  |  | 0.1015 |  | 0.1034 |  |  |
| [511] |  |  |  | 0.0845 |  | 0.0872 |  | 0.8417 |
| [440] |  |  |  |  |  | 0.0809 |  | 0.0709 |
| Mean(nm) |  | 0.1370 |  | 0.1401 |  | 0.1072 |  | 0.1338 |

**Table 2**

|  |  |  |
| --- | --- | --- |
| Parameter |  | Reading |
|  |
| EC |  | 1499 mS/cm |
| pH |  | 7.38 |
| Temp. |  | 27.7 °C |
| ORP |  | +431 mv |
| TOC |  | 9.68 mg/L |

**Table 3**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **Zn Edge** | | | | | | |  |  | **Fe Edge** | | | | | | |
|  | **Franklinite** | | |  | **Zn1.0Fe2.0O4** | | |  |  | **Franklinite** | | |  | **Zn1.0Fe2.0O4** | | |
|  | **CN** | **R (Å)** | **s2 (Å)** |  | **CN** | **R (Å)** | **s2 (Å)** |  |  | **CN** | **R (Å)** | **s2 (Å)** |  | **CN** | **R (Å)** | **s2 (Å)** |
| **Zn-O1** | 4.00 | 2.00 | 0.003 |  | 4.28 | 2.03 | 0.004 |  | **Fe-O1** | 6.00 | 2.02 | 0.004 |  | 5.97 | 2.02 | 0.007 |
| **Zn-Fe2** | 12.00 | 3.50 | 0.001 |  | 11.92 | 3.51 | 0.004 |  | **Fe-Fe2** | 6.00 | 2.99 | 0.005 |  | 5.97 | 3.00 | 0.006 |
| **Zn-O2** | 12.00 | 3.53 | 0.002 |  | 11.60 | 3.58 | 0.002 |  | **Fe-O2** | 2.00 | 3.49 | 0.002 |  | 2.04 | 3.54 | 0.001 |
| **Zn-Zn2** | 4.00 | 3.66 | 0.002 |  | 4.07 | 3.73 | 0.001 |  | **Fe-Zn2** | 6.00 | 3.50 | 0.004 |  | 6.22 | 3.61 | 0.006 |
| **Zn-O3** | 12.00 | 4.49 | 0.005 |  | 12.61 | 4.51 | 0.006 |  | **Fe-O2** | 6.00 | 3.72 | 0.006 |  | 5.99 | 3.79 | 0.003 |
| **Zn-O4** | 12.00 | 5.35 | 0.006 |  | 12.70 | 5.56 | 0.006 |  | **Fe-O3** | 12.00 | 4.68 | 0.006 |  | 11.84 | 4.70 | 0.004 |
| **Zn-Fe4** | 16.00 | 5.48 | 0.007 |  | 15.59 | 5.49 | 0.007 |  | **Fe-O3** | 12.00 | 4.85 | 0.007 |  | 12.35 | 4.96 | 0.009 |
| **Zn-O4** | 4.00 | 5.65 | 0.002 |  | 4.88 | 5.63 | 0.003 |  | **Fe-Fe3** | 12.00 | 5.17 | 0.003 |  | 12.55 | 5.18 | 0.009 |
| **Zn-Zn4** | 12.00 | 5.97 | 0.005 |  | 12.85 | 5.99 | 0.006 |  | **Fe-Zn3** | 8.00 | 5.48 | 0.007 |  | 8.48 | 5.54 | 0.008 |
|  |  |  |  |  |  |  |  |  | **Fe-Fe4** | 12.00 | 5.97 | 0.006 |  | 11.61 | 5.95 | 0.007 |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **DE (eV)** | 1.723 |  |  |  | 1.921 |  |  |  | **DE (eV)** | 3.547 |  |  |  | 3.396 |  |  |
| **S02** | 0.85 |  |  |  | 0.85 |  |  |  | **S02** | 0.85 |  |  |  | 0.85 |  |  |
| **R-Factor** | 0.009 |  |  |  | 0.013 |  |  |  | **R-Factor** | 0.007 |  |  |  | 0.012 |  |  |

**Table 3.** Optimized parameters of Zn and Fe K-edge XAFS data of natural franklinite and sample Zn1.0Fe2.0O4. CN is coordination number, R is radial distance, and σ2 is the Debye-Waller factor. CN for franklinite was fixed to calculated values and S02 was fixed to 0.85.