Microwave-Assisted Catalytic Degradation of Brilliant Green by Spinel Zinc Ferrite Sheets

Sandhya Mishra, ‡ Tumesh Kumar Sahu, ‡ Priyanshu Verma, ‡ Prashant Kumar, * ‡ § and Sujoy Kumar Samanta * ‡

‡ Department of Chemical and Biochemical Engineering and ‡ Department of Physics, Indian Institute of Technology Patna, Bihta, Patna, Bihar 801106, India
§ Birck Nanotechnology Centre, Purdue University, West Lafayette 47906, United States

ABSTRACT: Microwave (MW)-assisted catalytic degradation, being an emerging technique, can potentially fill in the technological gap which promises on-demand, prompt, and efficient catalysis, and therefore, suitable MW catalysts are curiously being hunted. Candidature of spinel zinc ferrite (SZFO) atomic sheets as a MW catalyst has thoroughly been investigated in this article. Analytical techniques prove SZFO atomic sheets to be highly crystalline, thermally stable, good dielectric, and superparamagnetic, which render it a potentially strong MW catalyst. Brilliant green (BG) has been demonstrated to be chemisorbed on the SZFO atomic sheets, which upon MW irradiation gets mineralized within 5 min, and the overall efficiency has been observed to be >99%. Total organic carbon removal of ∼80% has been obtained. Ionic chromatography proves the formation of SO₄²⁻ and NO₃⁻ anions which increase with MW exposure time. Liquid chromatography mass spectroscopy studies have established intermediate formations during catalysis. SZFO, established as a uniquely suited and highly efficient MW catalyst for BG, is expected to broaden the horizons of MW-assisted catalytic degradation and lead it toward its broader applications.

INTRODUCTION

Organic pollutants (BG, i.e., brilliant green, a triarylmethane group of dye; being one of them) in water due to industrial waste are carcinogenic and mutagenic in nature and cause skin diseases, eye irritation and breathing problems. BG exhibits exceptionally high visibility even in minute concentration. It can cause diarrhea and abdominal pain when being ingested and is said to be toxic to plants and aquatic lives as well. To treat organically polluted water, electro-chemical treatment, ultrasound treatment, photocatalysis, ion exchange, photo-fenton process, and so forth have already been employed. Most of these existing techniques are slow and inefficient. Attaining high degradation efficiency is very crucial and therefore, is presently being sought in desirable future technologies for wastewater treatment, as otherwise it will cost severe health hazards. Microwave (MW)-assisted catalytic degradation seems to be extremely promising, as it would cut short the time needed for the treatment and is supposed to be extremely efficient as well. However, research on MW-assisted catalytic degradation is still in its infancy. MW is capable of an extreme level of achievable power density and fast delivery. Achieving high absorption of MW by the catalyst is however very crucial. Along this line of research, activated carbon, carbon nanotubes, polymers, and transition metal oxides such as MnO₂ have earlier been reported as MW catalysts. However, structural stability against MW irradiation is a cause of concern to practically realize MW degradation, and that is why the selection of MW catalyst is pivotal. Spinel ferrites have earlier been suggested to have potential as a MW catalyst because of their structural stability. Nanoscale spinel zinc ferrite (SZFO) appears to have good candidature for MW catalyst because of the (a) economic cost of precursors, (b) easy synthesis protocol, (c) room-temperature magnetic behavior, (d) semiconducting nature (metals are avoided in MW), (e) magnetic retrievability of the catalyst, and (f) robustness under thermal spike generated in an MW oven. Even though SZFO seems to have great candidature as the MW catalyst, yet it has never been employed for this purpose, which makes it urgent to explore.

Gauging the need of the hour, we have therefore explored the potential of SZFO atomic sheets as a MW catalyst. Transmission electron microscopy (TEM), atomic force microscopy (AFM), and scanning electron microscopy (SEM) have been employed to investigate morphology and surface features of the synthesized sheets of SZFO. X-ray and electron diffraction have been used to establish structure identity. Raman, X-ray photoelectron (XPS), photoluminescence (PL), and Fourier transform infrared (FTIR) spectroscopy techniques have been employed to investigate the
synthesized sheet regarding its physical and chemical behavior. A vibrating sample magnetometer (VSM) and vector network analyzer (VNA) were used to explore magnetic and dielectric behavior of SZFO atomic sheets. To establish MW-assisted catalytic degradation by SZFO for degrading BG and to analyze products, the host of analytical techniques, for example, UV−vis spectroscopy, ion chromatography (IC), total organic carbon (TOC), liquid chromatography mass spectroscopy (LCMS), and FTIR spectroscopies were employed.

RESULTS AND DISCUSSION

MW-assisted catalytic degradation of BG (C27H33N2·HSO4−) by SZFO atomic sheets has been demonstrated for the first time. A normal SZFO structure has molecular sheets weakly interacting with each other (see Figure 1a).23 Molecular sheets of SZFO can be exfoliated; however, there is no report explicitly describing the exfoliation.24 Coprecipitation (at low temperature ~60 °C) using zinc and iron chloride precursors and distilled water (DW) solvent has been employed to synthesize SZFO nanopowder, which upon calcination looks dark brown (see Figure 1b). Aqueous solution of BG which has bluish green appearance upon adsorption turns light green (cyan shade), and the supernatant achieved by MW treatment of the cyan solution for up to 5 min followed by centrifugation is visibly transparent (see Figure 1c). The first proof that SZFO has sheet-like features was evidenced in the SEM image (Figure 1d). AFM imaging reveals molecular sheets having lateral dimensions ~20−60 nm and measured thickness ~2.4 nm which would be 3−4 layers (Figure 1e). TEM imaging reveals tinnier sheets (see Figure 1f). Sheets in Figure 1f are electron transparent and as is apparent, they are very thin;
which seems to be just few molecular layers. Atoms are above 5 Å apart, and the material is crystalline.

Selected area fast Fourier transform (FFT) shows intersecting hexagonal pattern (see the inset in Figure 1g) and such a pattern is usual in spinel ferrites. Interplanar distances were observed to be 0.30 and 0.47 nm at two different locations in TEM image of the SZFO sheets (see Figure 1h) which is matching with the existing literature. Hydrodynamic particle size distribution seems to be uniform, as this is apparent from nanoparticle tracking analysis (NTA) (see Figure 1i), and the approximate particle size is ∼100 nm. As the NTA experiment was carried out in the aqueous form, uniformity suggests stability of the dispersion, and it is also supported by Tyndall effect experiments (see Figure 1j).

Obtained X-ray diffraction (XRD) patterns shown in Figure 2a establish a spinel cubic structure (JCPDS no. 22-1012) of the synthesized SZFO sheets. Higher calcination temperature (700 °C) gives rise to heat diffusion which in turn helps uniform crystallization. SZFO sheets exhibited characteristic Raman vibrational modes. Raman peaks positioned at ∼332.2 and 652.7 cm⁻¹ shown in Figure 2b attest to the phase purity. The XPS survey reveals that the synthesized sheet exhibited Zn 2p, Fe 2p, and O 1s peaks (see Figure 2c). When individual peaks were resolved and deconvoluted (see Figure 2d−f), we could get further information. The Zn 2p spectrum shows two peaks at binding energy (BE) of 1020.6 and 1044 eV, which refers to Zn 2p₁/₂ and Zn 2p₃/₂, respectively.

Oxidation state of zinc, that is, +2 is thus revealed. A fine scan of Fe 2p peak exhibits two subpeaks. Upon deconvolution, the first peak (Fe 2p₃/₂) is resolved into 713.7 and 710.7 eV, and another peak (Fe 2p₁/₂) gets resolved into 725.3 and 719.2 eV. The oxidation state of Fe, that is, +3 is thus revealed. Furthermore, the O 1s peak (Figure 2f) can be resolved into two subpeaks (upon deconvolution) viz. 529.2 eV (for lattice oxygen) and 530.7 eV for (surface adsorbed oxygen species). A Tauc plot is obtained from optical reflectance data employing the Kubelka–Munk function (i.e., \( \alpha = (1 - R)^2/2R \)), where \( \alpha \) is the absorption coefficient and \( R \) is the diffuse reflectance that reveals band gap energy of ZnFe₂O₄ to be 2.47 eV, which characterizes the semiconducting nature of the synthesized sheets (see Figure 2g).

Applications already explored for SZFO include high-density data storage, radio sensitization, gas sensing, photocatalysis, drug delivery, and heterogeneous catalysis. UV photocatalysis is usually employed for photocatalysis, as it has higher photon energy in contrast to visible light. However, colored wastewater is opaque for UV light, and therefore, the degradation is inefficient and takes prolonged time to achieve the decoloring. MW degradation fits in this context, as catalyst, solvent, and dyes all are dielectric in nature, and therefore, one expects dielectric absorption of MW which in effect is expected to break functionalities in dye molecules.

Absorption spectra of BG adsorbed on the SZFO catalyst surface at various MW exposure times (0, 1, 2, 3, 4, and 5 min) are shown in Figure 3a. The inset in Figure 3a indicates pseudo first-order kinetics. In fact, purely, adsorption itself would reduce absorption of dye (by ∼26%) (see Figure S3a). Adsorption of dye molecules plays the active role in final degradation efficiency, as it helps in interaction between the dye and catalyst. To explore the role of a catalyst, MW exposure was carried out in the absence of any catalyst, and we found that it causes ∼19% reduction in absorption peak intensity (see Figure S3a). To obtain the degradation rate, \( C_0 \) was plotted against time (see Figure 3b). Before any MW treatment would commence, adsorption was attained, which helps MW degradation, as it brings molecules closer to the dye. SZFO sheets possess a negative zeta potential (\( \zeta \)) of ∼26.8 mV, which may cause these sheets to adsorb cationic BG molecules. To explore the interaction between the dye molecule and the catalyst, we carried out Raman spectroscopy of dyes adsorbed on the catalyst. Interestingly enough, catalyst Raman modes (340, 480, and 645 cm⁻¹) have been shifted and new peaks arise upon adsorption (see Figure S3b). Thus, Raman peak shifts ∼7 cm⁻¹ have been registered which in vivid terms indicate chemisorption. Langmuir and Freundlich isotherms corresponding to adsorption are shown in Figure S3c,d, respectively, and parameters can be found in Table S1. It is interesting to note that Langmuir model fits better with the data.

The absorption peak of BG at \( \lambda = 624 \text{ nm} \) was decreased upon increasing MW exposure time, and it was totally decolorized (approx. 99% degradation) after 5 min (see Figure 3a). As it turns out that with respect to the other parameters, MW power is the most crucial determining factor in this experiment. MW power was varied in 200−800 W range, and other parameters such as concentration of BG solution (20 mg/L), weight of SZFO catalyst (0.05 g), and MW exposure time (5 min) were kept constant.

The degradation extent was gradually increased with the MW power from 200 to 800 W; however, it technically saturates ∼360 W (see Figure 3c). Therefore, the output power of 360 W was considered for further studies. For practical applications, however, initial concentration of dyes is the most influential factor, and therefore, the effect of initial concentration of BG (in 10−100 mg/L range) on the extent of degradation was investigated. As can be observed in Figure 3d, for concentration below 80 mg/L, more than 99% degradation has been realized within 5 min of MW irradiation, and about 73.2% degradation was observed in 5 min for an initial
concentration of 100 mg/L. There will thus be a maximum concentration of BG which will suffice to make an adsorbed layer, above which it would cause the formation of a second or third layer (clustering of dye molecules could also not be ruled out) which will make dye layers opaque medium for MW and the catalyst would not be exposed and therefore would not be activated, resulting in the decrease of degradation efficiency. To explore how pH of an aqueous solution of dye influences degradation, we carried out an experiment with various pH of solutions (pH = 3–11), and we found that below pH = 5, degradation is poor (see Figure 3e). To test whether the SZFO catalyst can be used in cycles, we carried out experiments over four cycles, and the result was wonderful. Up to four cycles of usage, the catalyst delivers over 97.1% degradation efficiency (see Figure 3f) and interestingly, the structural quality of the catalyst is intact even after four cycles, as has been verified by XRD pattern (see Figure S1b).

As a technology, MW-assisted catalytic degradation is still a new and, several ferrites have been demonstrated as MW catalysts.15,33 Crucial determining parameters for catalysis include dielectric and magnetic behavior of catalysts, as they are responsible for the absorption of MW radiation, which in turn will degrade dye molecules. To gauge magnetic behavior of the catalyst, vibrating sample magnetometry was carried out, and in fact, we obtained the signature of the superparamagnetic nature of SZFO (see Figure 2h) which is characterized by minimal coercive field (~4 Oe). Magnetization per unit mass was found to be ~4 emu/g which indicates sufficient response to the applied external magnetic field. The magnetoresistance value measured for SZFO is exceedingly high (~360%) (see Figure S2), which is a significant result, especially because of the 2D nature of SZFO sheets (and it indicates prospective magnetic memory applications as well). The magnetic nature of the catalyst would help focusing of the EM wave inside the oven and in retrieving the catalyst after the degradation as well. To explore dielectric behavior of the catalyst, VNA was employed. Frequency-dependent real and imaginary parts of dielectric constant and loss tangent for SZFO are plotted in Figure 2i. One can readily observe that the real part is ~4.4 and imaginary part is 0.2 at 2.45 GHz (frequency used in the MW catalytic experiment). Water being polar has a high dielectric constant (~80) and BG has dielectric constant ~8.5 at 2.45 GHz. MW absorption being dependent on the effective dielectric function of the catalyst + solvent + dye molecule, we expect effective focusing of the EM wave in our case, as all of the three components have high values of ε.

Time-averaged dissipated power density is given by

$$P_{\text{diss}}(r) = \frac{\alpha}{2} \left( \varepsilon_0 \epsilon'_0 \tilde{E}(r)^2 + \mu_0 \mu' \tilde{H}(r)^2 + \frac{\sigma}{\omega} \tilde{E}(r)^2 \right)$$

(1)

However, magnetic field dependence is not as strong as that of the electric field, and therefore, one can ignore the magnetic field term. In such a case, therefore, dissipative power will turn to

$$P_{\text{diss}}(r, T) = \frac{\alpha \epsilon_0 \epsilon'_0 \omega(T)}{2} \left( E(r, \epsilon'_0(T), T), \epsilon'_0(T) \right)^2$$

(2)

where ω is the angular frequency, ε0 is dielectric permittivity of vacuum, ε'0 is dielectric loss, E(r) is the electric field amplitude, μ0 is the magnetic permeability of vacuum, μ' is the magnetic loss, and H(r) is the magnetic field amplitude.34,35

Upon efficient absorption of MW, local electric field and hence temperature at the central region of the oven and at the catalyst surface will be high (estimated temperature > 1000 °C),15–15,36 which has an equivalent energy of 0.1 eV = 1.6 × 10^-19 J. Bond dissociation energy for C≡N, C≡C, and C–H (primary bonds in BG) are 615, 614, and 413 kJ/mol, respectively. Energy needed to break C≡N and C≡C bonds in one molecule is about 1.02 × 10^-18 J. Thus, the absorbed energy would be sufficient to break these bonds and hence decolorization of BG. Thermal stability of the catalyst is crucial in MW degradation as the peak temperature goes high. Delightfully though, SZFO sheets have been found to have appreciably high thermal stability even in high-temperature range, and weight loss (marginal though) can be attributed to moisture desorption (see Figure S1a). While MW is ON, because of the interaction with the catalyst, dye molecules will experience generated local electric field and thermal spike. Such a directional field would increase vibration of bonds, and local temperature adds to that effect. Bonds in BG which are weaker (e.g., C–H) will break first, and then, relatively stronger bonds (e.g. C≡C or C≡N) will break later. In such a scenario, bond angle changes are also envisaged. Moreover, the formation of intermediates is expected as well, and in fact, we have obtained a proof of intermediate products in LCMS measurements. As shown in Figure 5, four different m/z peaks, namely 385.2, 340.2, 227.1, and 226.9 were detected. The corresponding intermediate and possible degradation mechanism of BG found due to MW irradiation are similar to that of UV photocatalysis by anions or by Fenton processes.37,38 The formation of the first intermediate with m/z value of 340.2 results due to the elimination of −C2H3N and −H2 from the BG structure which originally exhibited an m/z value of 385.2. It attests to the degradation of BG. The intermediate has gone through further transformation because of direct substitution of OH• radical with the liberation of ethylbenzene (C6H1–C3H3) and ethylene (C2H4), and this resulted in further reduction of the m/z value down to 227.1. After that, the abstraction of H atom from the resulting intermediate causes m/z to dip further into the lowest value of 226.9.

FTIR spectroscopy carried out on dye chemisorbed on the SZFO catalyst surface before and after MW treatment reveals that MW exposure reduces some peaks substantially (blue shaded), and even new peaks have evolved (red and green shaded) as one can observe in Figure 4a. To gauge carbon contents in the intermediate and final products, TOC measurement was carried out, and the results revealed 80.1%
disappearance of organic carbon of BG chemisorbed on the SZFO catalyst when MW treatment was carried out in contrast to 60.8% TOC level upon adsorption without MW treatment (see Figure 4b). To confirm the final degradation products of BG in aqueous solution, IC was also employed. It could be observed that the IC peaks (see Figure 4c) corresponding to NO$_3^-$, SO$_4^{2-}$ gradually increases along with the increasing MW irradiation time. It seems that C==N and weak electrostatic sulfur bonding of BG were broken gradually, and then, nitrogen and sulfur were oxidized into NO$_3^-$ and SO$_4^{2-}$ anions, respectively. It means that BG in aqueous solution could be mineralized into simple and innoxious inorganic ions under MW irradiation in the presence of an SZFO catalyst.

To explore the species, that is, ions and radicals forming while decomposition of BG takes place, scavenging experiments were carried out with trapping reagents, for example, ammonium oxalate (AO) (1 mM), isopropyl alcohol (IPA) (1 mM), p-benzoquinone (BQ) (1 mM) for holes, hydroxyl, and superoxide radicals$^{30,39,40}$ (see Figure S4a). Without scavenging, degradation efficiency was found to be about 99.6%. While IPA (*OH scavenger) or BQ (*O$_2^-$ scavenger) were introduced to the BG solution, the degradation rate was decreased (degradation efficiency was found to be 83.2 and 92.7% respectively). Thus, it is established that decolorization is significantly influenced by active species such as *OH and *O$_2^-$. Degradation efficiency dropped down from 99.6 to 8%, hinting at the active role of holes in the catalytic process.

To establish the participation of *OH in the MW degradation process of BG, terephthalic acid (TPA) was employed as a probe molecule in the fluorescence spectrophotometer. TPA instantly reacts with *OH radical to result in fluorescent 2-hydroxy TPA which has excitation and emission wavelength at ~315 and ~425 nm, respectively. Fluorescence spectra from 0.3 mM TPA solution at various irradiation times are shown in Figure S4b. As MW exposure increases, there is a gradual enhancement in fluorescence peak intensity at ~425 nm, which reaffirms the generation of *OH radicals (see Figure S5). When BG chemisorbed on the SZFO sheet catalyst was exposed to MW irradiation >360 W in aqueous solution, extreme local electric field and hence spike in temperature is attained (see Figure 6). Under these extreme conditions, SZFO ($E_g = 2.47$ eV) being a semiconductor gets excited, and electrons and holes are generated. Electrons give *O$_2^-$ upon reaction with O$_2$, and holes give *OH upon reaction with H$_2$O. These radicals then oxidize BG into harmless intermediates along with the formation CO$_2$ and H$_2$O.

Catalysis employing electromagnetic waves are most sought after, as it provides green technology for wastewater treatment (see the detailed overview in Figure 7). Among electromagnetic waves, sunlight is available free of cost. However, there is no selectivity of wavelength, and energy delivered per unit volume of the catalyst is very less which are the reasons for a long time and less efficiency of catalysis. Other artificial sources of visible light can also be employed and in fact, several such attempts have been made to use highly focused light utilizing several lenses. However, because photon energy ($hc/\lambda$) is less and that is why even after focusing, it is difficult to attain high beam energy. Ultraviolet light sources are better in that sense, and photon energy is relatively higher, and therefore, even without much effort, one can in principle get better beam energy and hence improved catalytic efficiency.$^{41-45}$ MW energy is highly tunable in a controlled manner with extremely high precision by externally controlled MW power. That is the reason that in recent years, it has been employed in catalysis and still is an emerging technology as far
as catalysis is concerned. However, the choice of catalysts (which efficiently responds to MW) and catalyst−organic dye interaction is of essence (chemisorption is desirable though) and these have to be suitably and adequately be satisfied so as to attain higher efficiency. Our present effort has been to improve on these vital aspects of MW-assisted catalytic degradation which has indeed worked well, and the results obtained in the present report is better than the existing literature in MW-based catalytic degradation.

## CONCLUSIONS

In tune with the emergence of MW-assisted catalytic degradation technology, we have demonstrated for the first time the use of SZFO atomic sheets as a MW catalyst. We have employed the SZFO catalyst because of its unique set of magnetic as well as dielectric attributes and in addition because of its appreciable thermal stability. Atomically thin SZFO sheets acted as an excellent anchor for BG molecules which got chemisorbed on the catalyst surface due possibly to π−π interactions. SZFO being semiconducting in nature, upon MW exposure, results in the formation of electron and holes which react with water and oxygen to finally mineralize dye molecules. This is the first report of its kind employing SZFO sheets as the MW catalyst. In contrast to UV photocatalysis which suffers from poor efficiency and needs prolonged duration for finishing reaction, MW-assisted catalytic degradation is yet an emerging technology for wastewater treatment, which seems to have enormous potential, as it is highly efficient, and the whole reaction finishes within few minutes. We have demonstrated that SZFO sheets (which are easily synthesizable) are environmentally benign. It is delightful to note that MW-assisted catalytic degradation by SZFO sheets is exemplary by any means, as evident from excellent efficiency (>99%) and prompt degradation (within ~5 min) for completion of the degradation reaction vis-à-vis existing catalysis technologies. It is noteworthy that SZFO catalysts exhibit recyclability upon magnetic retrieval (due to magnetic nature of SZFO). In light of all these qualities, therefore, we propose SZFO sheets as an extraordinary MW catalyst. Extensive experiments have been carried out to figure out a mechanism/pathway of MW degradation of BG molecules. Our research findings are poised to give new directions to MW-assisted catalytic degradation and relevant future research, we believe.

## MATERIALS AND METHODS

### Materials

All chemical reagents viz. ferric chloride hexahydrate (FeCl₃·6H₂O), zinc chloride (ZnCl₂), BG that is BG (C₆H₄O₂), AO ((NH₄)₂·O−O=C(O)−C(O)=O), BQ (C₃H₈O), IPA (C₃H₈O) were >99% purity (purchased from Sigma-Aldrich), and NaOH pellet were purchased from Merck. Double distilled water (DW) water was employed throughout the experiments.

### Synthesis of ZnFe₂O₄

SZFO sheets were synthesized by the coprecipitation method. ZnCl₂ (1.36 g) and FeCl₃·6H₂O (5.40 g) were dissolved in 100 mL of DW water under vigorous magnetic stirring at 60 °C for 1 h. Then, NaOH was added dropwise into the above solution until pH increased to ~11. Finally, the obtained brown precipitates were collected by centrifugation and washed with DW water and ethanol six times, and the precipitate was then dried in an oven at 100 °C for 5 h. After that SZFO nanopowder was obtained upon calcination at 700 °C for 3 h in a muffle furnace.

### Characterizations

Powder XRD patterns of the catalyst sample was obtained in reflection mode using a Rigaku TTRX-III instrument equipped with Cu Kα (λ = 1.54 Å) line operating at a scan rate of 2°/min. SEM images were obtained by using the Carl Zeiss AG SUPRA 55VP instrument operating at 5 kV. High-resolution TEM images were acquired using a Tecnai 210 TEM instrument working at 200 kV. Diffuse reflectance UV−visible spectroscopy of SZFO catalyst was obtained in a Shimadzu UV-2600 spectrometer instrument with IRS-2600 Plus attachment using BaSO₄ powder as a standard reference. XPS was attained using ESCA + omicron nanotechnology, Oxford Instruments, Germany equipped with a monochromator Al as the excitation source (Al Kα radiation with hν = 1486.7 eV). The instrument was operated at 15 kV and 20 mA. All of the BE values were taken as referenced to the C 1s peak of carbon at 284.6 eV. FTIR spectra of solid samples were measured in a Shimadzu, IRAffinity-1S, Japan, instrument. Thermal gravimetric analysis was performed in the PerkinElmer STA 6000 apparatus with a heating rate of 20 °C/min from 40 to 850 °C under a N₂ gas atmosphere (20 mL/min). Raman spectroscopy was carried out employing an STR 500 Confocal Micro Raman spectrometer, Japan using Nd:YAG laser (λ = 514.5 nm). Magnetic measurements (M−H hysteresis loop) for SZFO were carried out using a MicroSense EZ-9 VSM and the measurement was done at room temperature. The mean hydrodynamic diameter spectra and z potential were obtained using NTA in NanoSight NS300, Malvern Panalytical and Malvern Zetasizer Nano ZS instrument. Dielectric properties (ε′, ε″) were obtained employing the VNA (Keysight Technologies E5071C, USA) instrument. AFM measurements were carried out on SZFO sheets employing the Agilent 5500 model instrument in dynamic force mode at room temperature and ambient environment. To find magnetoresistance, magnetic field was produced by constant current power supply (DPS-50), magnetic field was measured by a digital gauss meter (DGM-102), and 2-probe resistance measurement was done at room temperature.

### MW Catalytic Degradation

The decolorization performance of the SZFO catalyst was determined under a dark environment as well as under MW exposure. The adsorption behavior of BG on the SZFO surface was evaluated by a batch adsorption process in the dark. The targeted aqueous solution (50 mL) of organic pollutant BG was placed in a beaker, and an SZFO catalyst (50 mg) was added to it by using a magnetic stirrer at a speed of 600 rpm at room temperature (RT). The beaker was completely covered and sealed with aluminum foil to remove the effect of photocatalytic degradation. After adsorption−desorption equilibrium was attained, aqueous solution was added into a 250 mL flat bottom flask, and the solution was then exposed to MW irradiation (in a temperature controlled domestic MW oven (Panasonic, 2.45 GHz) attached with a reflux condenser) at various power levels (see experimental setup, Figure S6). After MW irradiation was carried out, the solution was then centrifuged, and the concentration of centrifuged solution was determined employing UV−vis spectroscopy.

### Analytical Methods

The BG concentrations were recorded according to the absorbance at 624 nm wavelength using UV−vis spectroscopy. TOC measurements were carried out for original solution, after adsorption and 5 min of
treatment in the MW using an OI-Analytical (Aurora 1030) analyzer. PL spectra obtained from the fluorospectrometer (PerkinElmer, LS-55) instrument were recorded between 350 and 550 nm at 315 nm excitation. To further identify reaction products, IC (Metrohm IC 82) has been used for sample examination. The sample flow rate was 0.7 mL/min. Note that Na₂CO₃ and NaHCO₃ were used as eluents. The reaction intermediates were detected by LCMS (Agilent G6545B, USA). The samples were chromatographically separated using an Agilent 1290 Infinity 1 UHPLC system on a ZORBAX RRHD eclipse plus C 18 column (2.1 × 50 mm, 1.8 μm) with a flow rate of 0.4 mL/min and injection volume of 0.4 μL. The solutions A and B were 0.1% formic acid and 100% acetonitrile, respectively. The ion mode was set on positive mode, and mass fragments were observed from m/z 100 to 1000.

Analysis of Active Species. To confirm the effective role of some active species on the catalytic performance of the catalyst, trapping experiments were followed up. The main trapping agents, that is, scavengers such as AO, IPA, and BQ for h⁺, *OH, and *O²⁻ radicals, respectively, were used.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00914.

Thermal decomposition curve of ZnFe₂O₄ and XRD plot after MW treatment; magnetoresistance curve of ZnFe₂O₄; UV-vis absorption spectogram of BG solution at different conditions, Raman spectra after adsorption, and adsorption isotherm of BG onto MW catalyst ZnFe₂O₄ fitting; adsorption isotherms of BG onto the MW catalyst SZFO fitting; effects of a series of scavengers on the degradation efficiency of BG and fluorescence spectra of terephthalic acid; formation of luminescent 2-hydroxyterephthalic acid from terephthalic acid; and schematic diagram for microwave irradiation with the condenser unit setup (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: prashantkumarj@iitp.ac.in, magmemory@gmail.com. Phone: +91-612 302 8141, +91-9102830953 (P.K.).
*E-mail: sksamanta@iitp.ac.in. Phone: +91-612 302 8173, +91-9835355046 (S.K.S.).

ORCID

Sujoy Kumar Samanta: 0000-0001-5823-6786

Author Contributions
S.M. carried out the synthesis of zinc ferrite sheets, characterized it, and explored its candidature as MW catalyst. T.K.S. helped with AFM and magnetoresistance measurements. P.V. gave consultation for catalysis experiments. S.M. and P.K. wrote the manuscript and S.K.S. corrected it. P.K. and S.K.S. supervised the project.

Notes
The authors declare no competing financial interest.

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