Synthesis and Structural Studies of Manganese Ferrite and Zinc Ferrite Nanocomposites and Their Use as Photoadsorbents for Indigo Carmine and Methylene Blue Dyes

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ABSTRACT: Solar-moderated adsorptions of indigo carmine and methylene blue dyes were investigated using manganese and zinc ferrite capped with biochar prepared from the root of Chromolaena odorata. TEM micrograph of the as-prepared manganese ferrite nanocomposites (MnFe₂O₄@BC) revealed octagonally shaped particles with an average size of 42.64 nm while the zinc ferrite nanocomposite (ZnFe₂O₄@BC) micrograph revealed mixtures of rod- and cone-shaped particles with an average size of 43.82 nm. Biochar capping of MnFe₂O₄@BC reduced the band gap from 3.63 to 2.08 eV. The nanocomposite surface areas were 197.64 and 92.14 m²/g for MnFe₂O₄@BC and ZnFe₂O₄@BC, respectively. Photoadsorption of the as-prepared nanocomposites showed that 10 mg of ZnFe₂O₄@BC effectively removed 69.07 and 98.60% of 70 mg/L indigo carmine and methylene blue dyes while MnFe₂O₄@BC removed 77.65 and 94.83% of indigo carmine and methylene blue dyes after 2 h of equilibration under visible light irradiation, respectively. The nonlinear form of the Langmuir isotherm had a better approximation to the experimental solid-phase concentration (qₑ) for the adsorption of indigo carmine dye using both nanocomposites. In contrast, the linear form gave a better goodness-of-fit for the adsorptions of methylene blue dye. The manganese ferrite (MnFe₂O₄@BC) and zinc ferrite (ZnFe₂O₄@BC) nanocomposites showed no inhibition of Escherichia coli and Staphylococcus aureus, which indicates that they could be used for both biological and environmental applications.

1. INTRODUCTION

Water scarcity is predicted to increase as demand for water is significantly expected to surge for use in agriculture, household, and other industrial applications.¹⁻³ This has exacerbated the need to develop cheap, smart, and effective water decontaminators and conservation technologies. However, the fate and safety of nanoresidue in biological and environmental media has received little attention. In pursuit of green technology, biocompatible and environment-friendly nanomaterials are necessary for sustainable ecological frameworks. Metal-based inorganic photocatalysts have optimum performance because of their narrow band gaps, wideband edges, high electron flow, and conductivity but are limited by their low surface area and biocompatibility.⁴⁻⁵ In comparison, organic photocatalysts have large surface areas and more active sites but generate secondary pollutants.⁶⁻⁷ A hybridized composite would harness the properties of both inorganic and bioinspired composites to provide economic and environmental gains.

Adsorption is a popular and cost-effective process to remove pollutants from wastewater.⁸ The adsorption process is primarily moderated by the temperature and pH of the reaction medium. It is thus desirable to develop wastewater treatment technologies that can harness natural sources of energy to drive a future green economy. Smart composites are stimuli-responsive or environmentally sensitive composites.⁹ Temperature-responsive composites promote the capture and utilization of visible radiation, which accounts for over 90% of the solar energy spectrum.¹⁰ Magnetic biochars have enormous potentials for wastewater treatment because of their thermal stability, porosity, high surface area, reduced band gaps, low cost, and ability to adsorb different pollutants.¹¹⁻¹⁵

In addition, biochars are good sequesters for greenhouse gases. They can act as both donors and acceptors of electrons via protonation and deprotonation of the hydroxyl group, which is desirable for photocatalysis.⁶⁻¹⁰ Biochar-capped nanoparticles accelerate the separation of photogenerated carriers, reduce metal aggregation, and are inhibitive to photocorrosion.¹⁴⁻¹⁰

Recently, Saber and Kotb designed a dual-function material using layered double hydroxides (LDHs) and graphene oxide.²¹
Incorporation of graphene oxide reduced the band gap of the nanostructure from 5.5 to 2.5 eV, while the nanoadsorbent effectively combined adsorption with photocatalytic degradation in the decolorization of organic dyes under sunlight. In this study, we present the synthesis of MnFe₂O₄ and ZnFe₂O₄ nanoparticles capped with biochar from Chromoleana odorata and their photosorption of indigo and methylene blue dyes. Adsorption studies under simulated solar energy were extensively investigated using Langmuir, Freundlich, and Temkin isotherm equations to develop a model for industrial wastewater treatment. Antimicrobial activities of the nanocomposites as a measure of environmental and biological compatibility were also investigated.

2. RESULTS AND DISCUSSION

2.1. Morphological Studies of the Magnetic Composites. The X-ray diffraction patterns of ZnFe₂O₄@BC (Figure 1a) revealed diffraction peaks at 2θ of 21.24° (111), 35.42° (220), 43.02° (222), 44.69° (400), 53.37° (422), 56.92° (511), 62.51° (440), and 82.20° (533) that correspond well to the spinel phase of zinc ferrite (ICDD card no: 01-089-1012). The X-ray diffraction patterns of MnFe₂O₄@BC (Figure 1b) correlate well with the spinel cubic MnFe₂O₄ (ICDD card no: 00-010-0319). Peaks observed at 2θ of 36.01, 38.46, 44.66, and 59.86° represent Bragg reflections from (220), (311), (400), and (511), respectively; the crystallite size of the nanocomposite using the most intense peak (311) was 43.82 nm. The X-ray diffraction patterns of MnFe₂O₄@BC (Figure 1b) correlate well with the spinel cubic MnFe₂O₄ (ICDD card no: 00-010-0319). Peaks observed at 2θ of 36.01, 38.46, 44.66, and 59.86° represent Bragg reflections from (220), (311), (400), and (511), respectively; the crystallite size of the nanocomposite using the most intense peak (311) was 42.64 nm.

TEM micrograph of MnFe₂O₄@BC showed octagonally shaped particles with sizes in the range of 54.53–87.11 nm, while the ZnFe₂O₄@BC micrograph revealed mixtures of rod- and cone-shaped particles with a size range of 72.53–122.11 nm (Figure 2). The uniform distributions of white particles among the black in the SEM images indicate an even distribution of the nanoparticles to the biochar.25,28 The marked reduction in the pore sizes of MnFe₂O₄@BC, within the mesoporous region, agrees with its H4 hysteresis loop assertion. The reported low recovery of the adsorbate after the sorption process. Type H4 hysteresis loop for MnFe₂O₄@BC is associated with a mesoporous composition.25 BET surface areas (S_BET) of ZnFe₂O₄@BC and MnFe₂O₄@BC are 92.15 and 197.64 m²/g, respectively. Pore size distributions (inset in Figure 3a,b) within 50 nm confirmed the mesoporous composition of the composites, but MnFe₂O₄@BC was less distributed (≤20 nm) in comparison to ZnFe₂O₄@BC (≤50 nm). The homogeneity of the pore sizes of MnFe₂O₄@BC, within the mesoporous region, agrees with its H4 hysteresis loop assertion. The reported low surface area of ZnFe₂O₄@BC might be attributed to the blockage of carbon deposition from the biochar on the nanoparticles as a result of the bulky zinc atom.26,27

The Zn——O and Fe——O stretching vibrations in ZnFe₂O₄@BC were observed at 615 and 777 cm⁻¹, while the Mn——O and Fe——O stretching vibrations in MnFe₂O₄@BC were observed at 572 and 752 cm⁻¹, respectively. The presence of the metal—oxide bonds confirms the attachment of the nanoparticles to the biochar.25,28 The marked reduction in the intensity of OH_δ+ vibration (3360 cm⁻¹) suggests the involvement of the OH group in bond formation. The bands at 1611 and 1051 cm⁻¹ are assigned to C=C and C==O, respectively. Band gap energy is an indicator of the material’s ability to harvest solar energy; the band gap value is indicative of the energy needed to move an electron from the valence to the conduction band. The ultraviolet-visible (UV—vis) spectra of the nanocomposites (Figure S2) were used to estimate the band gap energy. The Tauc’s plot value for the band gap of MnFe₂O₄@BC showed a remarkable reduction from 3.63 to 2.08 eV while that of ZnFe₂O₄@BC was slightly blue-shifted.
from 2.25 to 2.53 eV (Figure S4). This shows that the visible light response of the nanoparticles can be improved by doping with biochar. The filled d-orbital of zinc might be responsible for the blue shift in the band gap value of ZnFe₂O₄@BC.

2.2. Photocatalytic and Kinetics Studies. The photocatalytic degradation of indigo carmine (IC) and methylene blue (MB) dyes was examined by comparing their change in concentration at time (t) against the time (t = 0) of exposure to visible light using a UV–visible spectrophotometer. MnFe₂O₄@BC degraded indigo carmine by 50.12% after 120 min of visible light irradiation (Figure 4). The degradation of indigo carmine dye by MnFe₂O₄@BC reached a maximum after...
and also as an electron tank; this inherent quality hinders electron–hole recombination, thus sustaining the lifetime of the reactive species. The biochar capping of the nanoparticles, therefore, maintains the stability of the photocatalytic process.

The reaction kinetics of the dye degradation was investigated using the pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion model (IDM) reaction kinetics. Based on the coefficient of determination ($R^2$), the IDM model best explained the kinetics for the sorption of indigo carmine and methylene blue dyes, respectively, on MnFe$_2$O$_4$@BC with $R^2$ values of 0.851 and 0.996 ($p \leq 0.05$) (Figure 6a). This implies good linearization of the sorption process at a low concentration of the adsorbate, owing to micropore and mesopore contributions from the nanocomposites. Pseudo-second-order (PSO) gave a better kinetic interpretation for the adsorption of indigo carmine dye on ZnFe$_2$O$_4$@BC. At the same time, pseudo-first-order (PFO) better explained the sorption of methylene blue with $R^2$ values of 0.982 and 0.867 ($p \leq 0.05$) (Figure 6b,c).

2.3. Adsorption Studies. Adsorption data were fitted using the Langmuir, Freundlich, and Temkin equations. Further, 10–70 mg/L of both indigo carmine (IC) and methylene blue (MB) dyes were used for the adsorption studies at an equilibration time of 120 min (Tables S1–S4). The final absorbance for the dyes was measured using a UV–visible spectrophotometer. The maximum adsorption capacity of indigo carmine dye on MnFe$_2$O$_4$@BC as predicted by the nonlinear Langmuir isotherm was 173.47 mg/g (Table S1). Though the linear form of the Langmuir equation had a better $R^2$ of 0.99 as against the nonlinear one at 0.94, based on closeness to the experimental and theoretical $q_e$ values (Tables S1 and S3), the nonlinear form is preferred. The same applies to the adsorption of the dyes on ZnFe$_2$O$_4$@BC. The calculated $q_e$ value of 129.91 mg/g ($R^2 = 0.87$) is closer to the experimental value of 96.70 mg/g than the estimated value of 10.52 mg/g ($R^2 = 0.59$) by the linear Langmuir equation. Comparatively, the adsorption of methylene blue dye on both nanocomposites was better explained using the linear Langmuir equation. The maximum adsorption capacity ($Q_e$) of 131.58 mg/g ($R^2 = 0.99$) (Table S2) of the dye on MnFe$_2$O$_4$@BC is close to the experimental solid-phase concentration of the adsorbate ($q_{exp}$) at 70 mg/L (132.76 mg/g) (Table S5). The $Q_e$ of the dye on ZnFe$_2$O$_4$@BC was 123.46 mg/g ($R^2 = 0.97$). Even though the extrapolated $Q_e$ from the nonlinear equation was higher, there was an error in the coefficient of determination estimates. The linear equation gave a better goodness-of-fit and a better approximation to the experimental values. The Freundlich constant $(1/n)$ was less than 1, suggesting a favorable sorption process. The Temkin constant $(B)$ (Tables S1 and S2) was greater than 1 for all sorption processes, indicating an exothermic behavior. This is indicative of electrostatic interaction between the adsorbent and the adsorbate, a physisorption process rather than a chemisorption one.

2.4. Antimicrobial Activity. The antimicrobial activities of MnFe$_2$O$_4$@BC and ZnFe$_2$O$_4$@BC were tested to gain insight into their cytotoxicities. Eight concentrations of the nanocomposites of low (3, 6, 9 mg/L), medium (50, 100, 250 mg/L), and high (500, 1000 mg/L) were prepared and tested against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) bacteria on an agar plate. The results showed that both nanocomposites did not inhibit the tested bacteria at any of these concentrations. In contrast, distilled water used in culturing (negative control) equally showed no inhibition.

![Figure 4. (a) Photodegradation of dyes on MnFe$_2$O$_4$@BC and (b) ZnFe$_2$O$_4$@BC.](https://dx.doi.org/10.1021/acsomega.0c04404)
compared to ethanol (positive control), which showed inhibition of the growth of both bacteria. Though the mechanism of inhibition of nanoparticles on microorganisms is not well known, the noninhibitory action of the nanocomposites on the bacteria in the current study may be attributed to their inability to cause loss of DNA replication upon treatment and stop the expression of ribosomal subunit proteins and some other cellular proteins and enzymes essential for adenosine triphosphate (ATP) production. It can also be suggested that the nanocomposites could not bind with the cytoplasmic membrane to kill the bacterial cell. This might be ascribed to a nonmembrane disruptive electrostatic interaction between MnFe2O4@BC and ZnFe2O4@BC and the cell membrane of these bacteria. Another probable reason for the noninhibitory effect by the nanocomposites on S. aureus and E. coli could be due to the average particle size of 40 nm. The antibacterial effect of nanoparticles is known to be dependent on particle size. Reports have shown that smaller particles have a higher inhibitory effect due to increased interfacial area that provides better contact and a more significant impact on bacteria.

Furthermore, the noninhibitory effect could also be due to the inability of the nanocomposites to produce enough reactive oxygen species (ROS) to destroy the bacterial cells. Other studies have shown that the ions released from metal nanoparticles are probably the driving force of antibacterial properties of nanoparticles. We can also infer that the biochar capping was adequately bonded to the nanoparticles and thus controlled the release of elemental ions in solution. The inability of the nanocomposites to destroy the tested microorganisms implies that they are biocompatible and could be useful in both biological and environmental applications.

Figure 5. Electronic spectra showing dye degradation with time, (a) indigo carmine on ZnFe2O4@BC and (b) MnFe2O4@BC, and (c) methylene blue on ZnFe2O4@BC and (d) MnFe2O4@BC.

Further study will be required to ascertain some inherent biocompatibility properties of these nanocomposites.

2.5. Desorption Study. The recoverability of dyes is indicative of the sorption process and the probable mechanism of clearance from aqueous solution. The desorption of indigo carmine dye from MnFe2O4@BC was investigated using a reported method. Immediately after the sorption process (10 mg of the adsorbent, 10 mL of the dye, 1 h), the adsorbent was left to dry at room temperature. Afterward, 10 ml aliquots of distilled water were utilized in recovering the adsorbed dye at room temperature. The concentration of the leached dye was determined using a UV–visible spectrophotometer. At the first run, 27 mg/L (67.5%) was recovered. A total of 83.65% of the dye was desorbed after two consecutive runs. The ease of desorption of the dye from the adsorbent using distilled water is indicative of the existence of a weak adsorbate–adsorbent bond, suggesting a physisorption process.

3. MATERIALS AND METHOD

3.1. Materials and Method. All chemicals were used as obtained without further purification (Table 1). The bacterial strains used in the study (E. coli and S. aureus) were obtained from the Microbiology department of the University of KwaZulu-Natal, Pietermaritzburg, South Africa. Magnetic composites were synthesized via a co-precipitation method. A 2:1 molar ratio of iron(II) or (III) with respect to manganese(II) and zinc(II) precursors was used for the synthesis of the nanoparticles. An equal mass ratio of the binary nanoparticles and C. odorata biochar was adopted for the composites. Then, 1000 mg/L solutions of the dyes were prepared by dissolving 1 g (±0.0005) of the powder in a 1000 mL volumetric flask, and working solutions were prepared from
the stock solution. Origin 9.1 software was employed for data analysis.

3.2. Synthesis of Zinc and Manganese Ferrite Nanoparticles. Zinc ferrite nanoparticles were synthesized using 0.34 g of zinc precursor and 0.99 g of iron(II) chloride, while manganese ferrite nanoparticles were prepared using 0.40 g of manganese precursor and 1.62 g of iron(III) nitrate. The powders were dissolved in 50 mL of deionized water and quantitatively transferred to a three-neck round-bottom flask and left under stirring for 30 min. Then, the solution pH was increased to 12 using aqueous ammonia. The co-precipitation process was completed by heating the mixture at 70 °C for 1 h under a continuous flow of N2.

3.2.1. Synthesis of C. odorata-Capped Zinc and Manganese Ferrite Nanocomposite. After cooling the zinc and manganese ferrite nanoparticles to room temperature, 0.5 g of C. odorata biochar was added to the mixture and stirred for 1 h. The final product was washed several times with deionized water till the pH was set to 7 and finally with acetone. The black crystalline residue was dried in an electric oven for 12 h at 70 °C and stored in a plastic Petri dish for characterization and experimental studies.

3.3. Antimicrobial Assay. Nutrient broth medium was used to subculture the pure culture of E. coli and S. aureus separately and was incubated at 37 °C for 24 h. A fresh overnight-grown culture aliquot of 100 μL was spread on the nutrient agar plates to cultivate the bacteria. Duplicate agar plates for concentrations (3, 6, 9, 50, 100, 250, 500, and 1000 mg/L) of the nanocomposite were investigated. Ethanol and distilled water were used as positive and negative controls, respectively. A paper disc was dipped in different concentrations of the nanocomposite and inserted in solidified nutrient agar; then, the impregnated plates were incubated at 37 °C for 24 h. The antibacterial activity of each bacterium was determined by measuring the diameter (in mm) of the inhibition zone around the impregnated disc.

3.4. Photocatalytic Studies. Photocatalysis was done in a dark room using a high-pressure sodium lamp OSRAM VIALOX (65600 lumens) as a controlled visible light radiation source. Circular metal support bearing seven circular holes and a passage for the sodium bulb was used as a sample holder. Photocatalytic studies were carried out using 5 mg of the adsorbent and 5 mL of 30 mg/L dyes. Sample tubes were removed at intervals of 20 min in a 2 h equilibration period, while the unadsorbed dye was determined using a UV−visible spectrophotometer. Percentage removal was calculated by comparing absorbance at each interval to the absorbance of the dye (0 min) in the absence of a visible light source.

3.5. Characterization. X-ray diffraction (XRD) was carried out on an XPert-PRO X-ray diffractometer with Cu Kα radiation in the 2θ angular range of 4.01−89.9°. TEM images were captured on a JEOL JEM 1400 transmission electron microscope. Scanning electron microscopy (SEM-EVOLS15, ZEISS) combined with EDX was used to investigate the composition of the nanocomposite.
nanoparticles. Fourier transform infrared (FT-IR) spectra were recorded in the region of 4000−500 cm\(^{-1}\) using a Perkin Elmer Spectrum 100 FT-IR spectrometer while a Cary100 UV−vis spectrophotometer (Agilent Technology) was used to study the electronic range of the composites. The surface area \(S_{\text{BET}}\) of the composites was analyzed with a Micromeritics Tristar II 3020 analyzer using N\(_2\) as the adsorbate at 77 K.

4. CONCLUSIONS

Zinc ferrite and manganese ferrite were successfully capped with biochar from the root of \(C.\) odorata to prepare manganese ferrite \((\text{MnFe}_2\text{O}_4@\text{BC})\) and zinc ferrite \((\text{ZnFe}_2\text{O}_4@\text{BC})\) nano-composites. The surface area of \(\text{MnFe}_2\text{O}_4@\text{BC}\) was 197.64 m\(^2\)/g while that of \(\text{ZnFe}_2\text{O}_4@\text{BC}\) was 92.14 m\(^2\)/g with estimated energy band gaps of 2.08 and 2.53 eV, respectively. The nanocomposites showed appreciable removal of both indigo carmine and methylene blue dyes. Methylene blue dye was better adsorbed on \(\text{ZnFe}_2\text{O}_4@\text{BC}\) with a percentage removal of 98.60% while indigo carmine dye had more affinity for \(\text{MnFe}_2\text{O}_4@\text{BC}\) with a percentage removal of 77.65%. The nonlinear Langmuir equation better explained the adsorption process of indigo carmine dye. Comparatively, the linear Langmuir was more suitable in interpreting the sorption of methylene blue dye on both nanocomposites. The magnetic composites were solar-responsive and showed no inhibition at 1000 mg/L to both \(E.\) coli and \(S.\) aureus bacterial cell lines. Then, 83.65% of the adsorbed indigo carmine dye was effectively desorbed from \(\text{MnFe}_2\text{O}_4@\text{BC}\) after two consecutive runs using distilled water. This study shows that both composites are eco-friendly and adaptable as low-cost adsorbents for wastewater treatment.

**ASSOCIATED CONTENT**

Supporting Information The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04404.

- Adsorption parameter (Tables S1 and S2); EDX spectra for (a) \(\text{MnFe}_2\text{O}_4-\text{BC}\) and (b) \(\text{ZnFe}_2\text{O}_4-\text{BC}\) (Figure S1);
- Electronic spectra overlay for nanocomposites (Figure S2); adsorption isotherm (Figure S3); band gap energy (Figure S4); sorption calibration curve (Figures S5 and S6); EDS spectrum of biochar (Figure S7); XRD diffraction patterns for \(\text{ZnFe}_2\text{O}_4\) nanoparticles (Figure S8); and agar plate showing zero inhibition on \(E.\) coli (Figure S9) (PDF)

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Table 1. Sample Description Table for Chemicals Used in the Experimental Work

| Component     | CAS     | Reg no. | Source                                |
|---------------|---------|---------|---------------------------------------|
| Zinc chloride | 7646-85-7| Sigma-Aldrich, South Africa.          |
| Fe(NO\(_3\))\(_2\)-9H\(_2\)O | 7782-61-8| Sigma-Aldrich, South Africa.          |
| FeCl\(_2\)-4H\(_2\)O | 13478    | Sigma-Aldrich, South Africa.          |
| MnCl\(_2\)-4H\(_2\)O | 13446-34-9| Sigma-Aldrich, South Africa.          |
| NH\(_3\)-H\(_2\)O | 1336-21-6| Sigma-Aldrich, South Africa.          |

| Molecular structure | Name     | Molecular formula | Molecular weight (g/mol) | Melting point (°C) | Solubility at 25°C |
|---------------------|----------|-------------------|--------------------------|--------------------|---------------------|
| Indigo carmine       |          | \(\text{C}_19\text{H}_16\text{N}_2\text{Na}_2\text{O}_5\text{S}_2\) | 466.35               | > 300              | Soluble             |
| Methylene blue       |          | \(\text{C}_4\text{H}_8\text{ClN}_3\text{S}\) | 319.85               | 190 °C              | Soluble             |
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Notes
The authors declare no competing financial interest.

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