

Characterization of Manganese Ferrites Synthesized Using a Combustion Method

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ABSTRACT

Magnetic manganese ferrites were created in the laboratory using a novel combustion method in order to blend the catalytic properties of manganese (Mn) with the magnetic and structural properties of ferrites. The developed synthesis method involved mixing Mn and iron (Fe) nitrate (NO₃) salts with polyvinyl alcohol (PVA) followed by calcination. The resulting synthesis method is a scaleable and a simplified synthesis pathway. Preparation studies varying the Mn:Fe stoichiometric ratio and PVA content during synthesis revealed that PVA content above 1:1.5 NO₃:PVA is required to form manganese ferrites. XRD, SEM-EDS, carbon content, and BET surface area analysis confirmed that the developed method yielded manganese ferrites of the form Mn_{2.5}Fe_{0.5}O₄, MnFe₂O₄, and Mn_{0.5}Fe_{2.5}O₄. The manganese ferrites were then used to remove methylene blue dye from an aqueous solution as a proof-of-concept study to demonstrate their reactivity and use as a treatment technology.

Keywords: manganese, ferrites, synthesis, combustion, magnetic

1 INTRODUCTION

Manganese ferrite particles are of interest because of their large surface to volume ratio and their many uses in the areas of biosensors [1], electronics [2], and pharmaceutical delivery [3]. Because the structural characteristics of manganese ferrite are controlled by the synthesis approach, different preparation methods have been explored. Reported synthesis methods include ceramic, co-precipitation, sol-gel, spray drying, freeze drying, and high temperature and pressure hydrothermal methods [4-7].

Manganese ferrites belong to the class of ferros spinels represented by the general formula AB₂O₄ where A and B refer to tetrahedral and octahedral cation sites and O represents the anionic oxygen site. Different electrical, magnetic, and catalytic properties of ferros spinels are governed by the distribution of metals between the octahedral and tetrahedral sites. Manganese based

ferros spinels show interesting catalytic properties in the oxidative dehydrogenation of hydrocarbons [8], oxidative gas phase CO oxidation [9], decomposition of peroxides [10], and oxidation of alkenes [11].

The purpose of this research was to synthesize and characterize of manganese ferrites using a combustion method. The developed synthesis method involved mixing Mn and Fe salts with PVA followed by calcination. Proof-of-concept studies were used to demonstrate the reactivity of the prepared manganese ferrites to remove methylene blue (MB) dye from aqueous solutions in order to demonstrate their application for water treatment. While MB is used as a surrogate organic, dyes are widely used in variety of industries including textiles, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries. Wastewater discharge from these industries into natural streams has caused significant environmental contamination.

2 METHODS

2.1 Preparation of magnetic manganese ferrites

Magnetic manganese ferrite was prepared by mixing Mn(NO₃)₂ and Fe(NO₃)₃ in the stoichiometric ratio of 1:2 within a ceramic crucible. Poly-vinyl alcohol (PVA) was added to the mixture according to nitrates:PVA ratios of 10:1; 5:1; 10:3; 2:1; 1:1; 1:1.5 and 1:2. The total weight of NO₃ in each NO₃:PVA composition was 10 g. Therefore, a prepared manganese ferrite with a label 'MnFe₂O₄ PVA10' refers to a composition with 10 g total NO₃, a Mn:Fe ratio of 1:2, and a total PVA weight of 10 g.

100 mL DI water was added to dissolve the NO₃ salts. The solution was allowed to stand for 8 hours to ensure dissolution. 20 mL DI water was then added and the solution was mixed. The mixture was fired in a muffle furnace at 773K for a period of 60 minutes. After 60 minutes the furnace was turned off and allowed to cool. Once the furnace cooled down, the crucible was removed and the particles within the crucible were transferred into a

40 mL glass vial, capped, and stored at room temperature. Particles with different stoichiometric ratios of the two NO₃ salts were also created by varying the Mn percentage.

2.2 Characterization studies

All prepared samples were characterized using X-Ray Diffraction (XRD), carbon analysis, Brunauer-Emmett-Teller (BET) surface area, and Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS). A PANalytical Xpert Pro theta-two theta diffractometer with Cu K α radiation at 45kV and 40 mA ($\lambda = 1.5406 \text{ \AA}$) was used to identify the crystal phase and primary crystallite size of the created manganese ferrites. XRD pattern analysis was performed using the Jade+ software (version 7, MDI, Inc., Livermore, CA) according to ASTM D934-80 and using ICDD reference patterns (2002 PDF-2 release, International Center for Diffraction Data, Newtown Square, PA).

A carbon analyzer was used to determine the carbon content. The BET surface area, porosity and pore size distribution of the resulting manganese ferrites were measured with a surface area and porosimetry (Tristar 3000, Micromeritics). Surface morphology of the manganese ferrites was assessed using an environmental SEM (ESEM, Philips XL 30 ESEM-FEG) at an accelerating voltage of 10-30 kV.

2.3 Proof-of-Concept Dye Removal Studies

A stock solution of 40 mg/L MB in DI water was used throughout the proof-of-concept experiments. Experiments were conducted in a 250 mL Erlenmeyer flask. 90 mL of DI water was placed in each flask and spiked with 10 mL of MB stock solution to achieve a 4 mg/L MB concentration in solution. 0.2 g of created manganese ferrite was added to each flask and reactions for individual manganese ferrite compositions were completed in triplicate. Flasks containing DI water, MB, and manganese ferrite were sealed with parafilm and placed on a gyrotory shaker. Multiple samples were pulled from each flask within two hours and observed for MB removal. Each withdrawn sample was immediately passed through a 0.2 μm Iso-Disc Teflon filter to ensure manganese ferrites were removed from solution in order to stop the reaction. Absorbance within each sample was measured using a UV-Spectrophotometer at a wavelength of 665 nm.

Based upon the resulting absorbance data, MB removal percentage within a reactor was calculated as:

$$\text{Removal (\%)} = 100 * (1 - C_t / C_o)$$

where: t = reaction duration at time of sample withdrawal and quenching; C_t = concentration of the dye solution at time t, and C_o = the initial dye concentration (4 mg/L).

3 RESULTS AND DISCUSSION

3.1 Characterization studies

XRD analysis demonstrated that PVA was required to form pure manganese ferrite. PVA acts as a fuel during synthesis helping to crystallize the manganese ferrite structure. At NO₃:PVA ratios below 1:1 there was a complete shift of peaks from Fe₂O₃ and Mn to MnFe₂O₄. Below this ratio (i.e. MnFe₂O₄ PVA15 and MnFe₂O₄ PVA20), the XRD pattern observed matches Jacobsite (Figure 1).

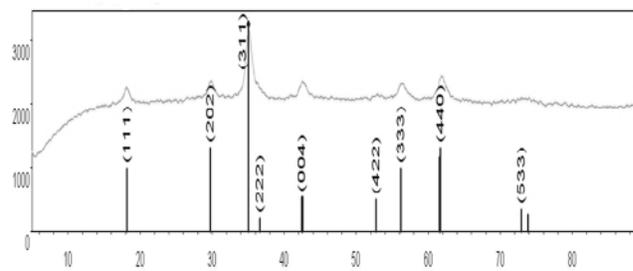


Figure 1: XRD spectra of manganese ferrites. The peaks are observed at $2\theta = 30.195^\circ, 35.543^\circ, 43.217^\circ, 53.60^\circ, 57.067^\circ, 62.665^\circ$ and 71.15° which represent the Bragg reflections from the (220), (311), (400), (422), (511), (440) and (533) planes respectively.

3.2 Carbon composition and BET surface area

Table 1 presents the carbon and BET surface area analysis results. A slight increase in the carbon percentage was observed as PVA content increased. However, the carbon content was always less than 0.2% by weight. The BET surface area of the prepared manganese ferrites ranged between 46 and 58 m²/g and depended upon the PVA content used during synthesis.

Table 1: Manganese ferrite % carbon and BET surface area.

Catalyst	% Carbon	BET Surface Area (m ² /g)
MnFe ₂ O ₄ 10PVA	Non Detectable	48.8
MnFe ₂ O ₄ 15PVA	0.14	57.4
MnFe ₂ O ₄ 20PVA	0.22	39.9

3.3 SEM-EDS analysis

Figure 2 presents the SEM images of the created manganese ferrites.

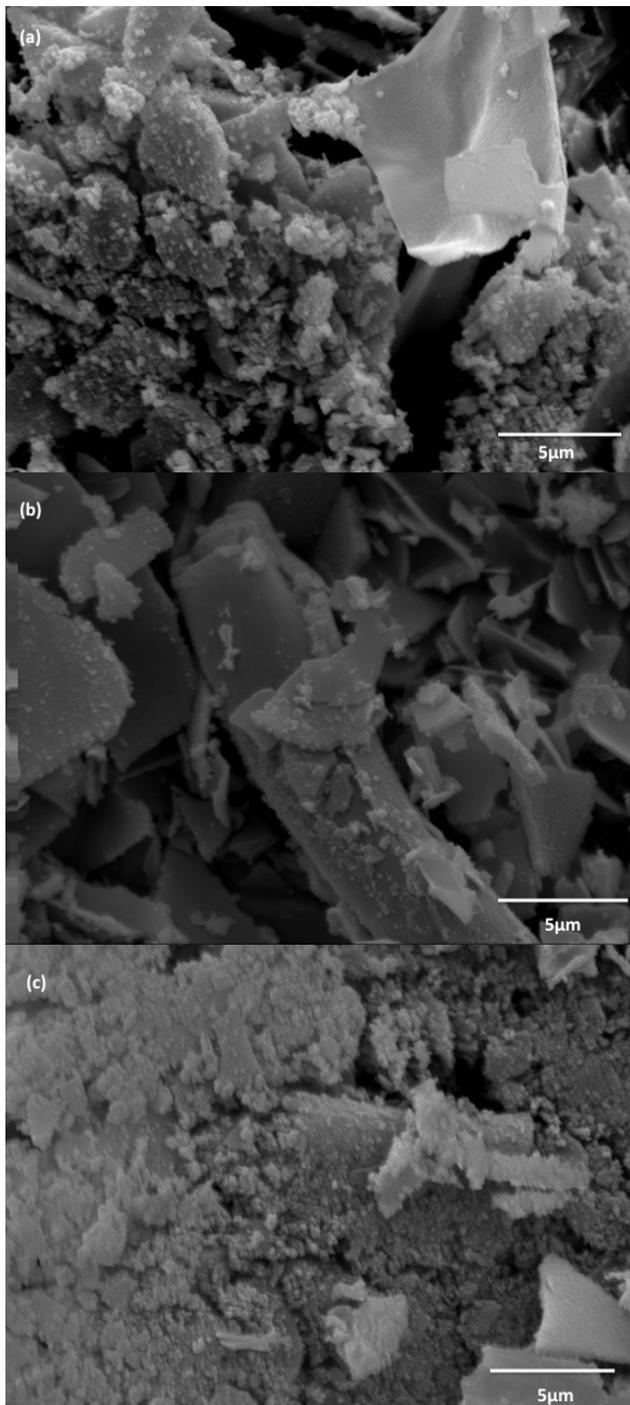


Figure 2: SEM images of MnFe_2O_4 (a) PVA10, (b) PVA15, and (c) PVA20.

Prepared manganese ferrites were agglomerated and formed dense, flake-like structures. The formation of MnFe_2O_4 was confirmed with EDS as shown in Figure 3. Peak heights of manganese and iron vary according to the different stoichiometric ratios used in their preparation.

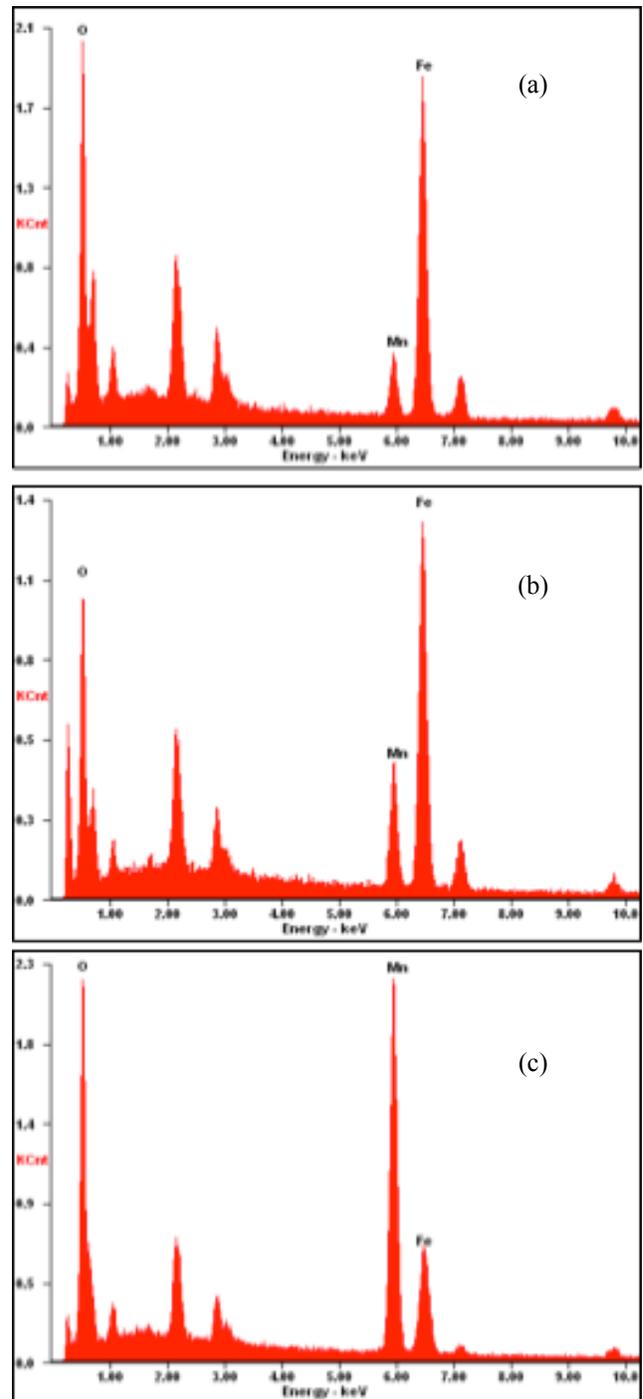


Figure 3: EDS spectra for (a) $\text{Mn}_{0.5}\text{Fe}_{2.5}\text{O}_4$, (b) MnFe_2O_4 , and (c) $\text{Mn}_{2.5}\text{Fe}_{0.5}\text{O}_4$.

3.4 Proof-of Concept MB Dye Removal

MB was removed from each reactor when manganese ferrite was present. Figure 4 presents a characteristic absorbance spectra observed when MB is reacted with MnFe_2O_4 PVA15. The absorbance caused by MB within samples decreased as a function of reaction time in all cases. MB removal observed within the reactors was greater than 90% within one hour.

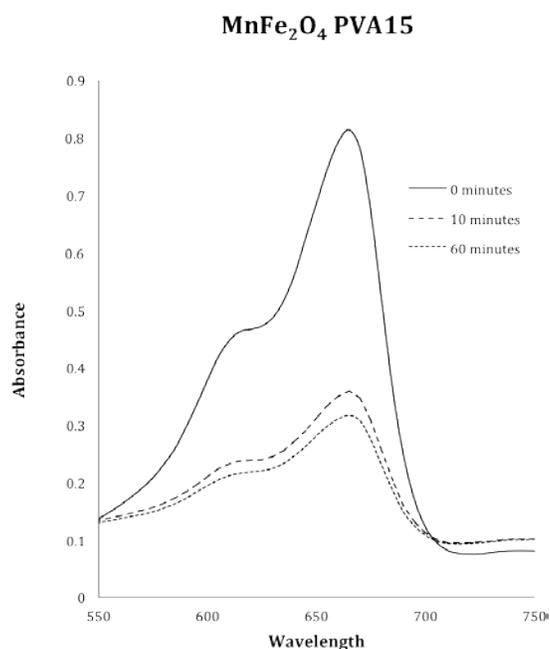


Figure 4: Typical removal pattern for MB in the presence of prepared manganese ferrites observed as a decrease of absorbance within reactor samples.

4 CONCLUSION

This research verified that a simple combustion method can be used to create magnetic manganese ferrite. The created manganese ferrites were demonstrated to remove MB dye as a surrogate for organics. The particles were created for the purpose of creating reactive surfaces that could easily be removed within by a magnetic field when used within water and watertreatment processes. The simplified combustion method used to make manganese ferrites results in the creation of reactive surfaces that offer a wide range of applications while being easily scalable.

5 REFERENCES

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