Mn-Zn spinel ferrite synthesis by solution combustion method and applications in adsorption of dyes

I.Beri, M. Ayoub, N. Fatma and H.S.Dosanjh*

Department of Chemistry, School of Chemical Engineering and Physical Science, Lovely ProfessionalUniversity Phagwara, 144411, Punjab, India

*Corresponding Author: harmanjit.singh@lpu.co.in

ABSTRACTDyes are hazardous chemicals that are commonly found in textile industries' effluent water. Adsorption techniques are more efficiently used for the removal of various dyes from wastewater. The present work deals with the synthesis of Mn-Zn (Mn0.3Zn0.7Fe2O4) spinel ferrite through the solution combustion method. The solution combustion method has many advantages over other conventional methods. Single-phase spinel ferrite materials can be synthesized by using this method at lower temperatures and in a shorter time. Synthesized Mn-Zn spinel ferrite material has been characterized by using FT-IR spectroscopy. As synthesized ferrite material has been employed for the adsorption of various dyes with different concentrations from their aqueous solutions. Results related to dyes' adsorption have been reported using UV-Visible spectroscopy. Mn-Zn spinel ferrite has worked efficiently as an adsorbent and its magnetic nature is useful for its extraction from the aqueous solution.

Keywords. ferrites, solution combustion method, adsorption

1 INTRODUCTION

Dyes are compounds absorbing light in the visible region of spectra, have a conjugated system, and exhibit resonance of electrons providing stability, making dyes chemically stable and complex in nature and as a result very hard to degrade [1]. Textile industries are known to be the major cause of water effluents caused by dyes. Among the many wastewater treatment technologies available, including oxidation, flocculation, coagulation, membrane filtration, chemical precipitation, ion exchange, and biological treatment, adsorption is a widely used method for the treatment of wastewater containing colors and other organic contaminants as it is recognized as a straightforward, low-cost, secure, and effective method for dye removal [2-5]. In the past decade or two spinel ferrites have attracted a huge amount of attention due to their numerous uses in biomedicine, wastewater treatment, pharmaceuticals, biomedicine, electronics, and photocatalysis among other fields. Spinel ferrites have exceptional magnetic and electric characteristics with great magnetic and thermal stability expressed with the formula MFe₂O₄ and can be synthesized by a number of methods which includes sol-gel, microwave, sol-gel auto combustion, co-precipitation method, solution combustion method, etc. [6-8]. Among the methods, the solution combustion method is preferred for the studies because it is a simple, convenient, economical, environmentally friendly, versatile, self-sustained, and rapid method with application in optical devices, nanoceramics, energy conservation, and storage, etc. [9-11]. The solution combustion method is found to be very useful for the synthesis of nanosized materials as it is an energy-saving and efficient approach [12]. Simultaneously, the combustion method efficiently synthesizes a diverse spectrum of ferrites with large surface areas and yields [13-14]. This synthetic material was then tested as a dye adsorbent.

2 EXPERIMENTAL

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Material: Mn-Zn ($Mn_{0.3}Zn_{0.7}Fe_2O_4$) ferrite was synthesized via the solution combustion method. All the materials and reagents used in this work are of analytical grade; ferric nitrate nonahydrate, zinc nitrate hexahydrate, manganese nitrate tetrahydrate, hydrazine hydrate, diethyl oxalate, methyl orange, congo red, methylene blue and crystal violet.

General Procedure: for the synthesis of Mn-Zn (Mn0.3Zn0.7Fe2O4)

The synthesis of the Mn-Zn ($Mn_{0.3}Zn_{0.7}Fe_2O_4$) ferrite begins with the creation of stoichiometric aqueous solutions made up of nitrates from metals in a small amount of distilled water individually, followed by the mixing of all of these aqueous solutions in a single container with the necessary initiator oxalyl dihydrazide (ODH) and constant stirring. As an exothermic reaction involves in the combustion method, ODH is introduced in minute amounts to the nitrate solution combination, while it is continuously stirred. After the addition of ODH, the mixture solution was concentrated on a water bath for two hours at 70-75°C. The concentrate was then transferred to a crucible and combusted in a muffle furnace at 650 °C for 5 hours. A dark brown powdered product was obtained and characterized using FTIR spectroscopy. A schematic diagram of the synthesis of Mn-Zn ($Mn_{0.3}Zn_{0.7}Fe_2O_4$) ferrite is shown in Fig 1.



Mn-Zn Ferrites

Fig 1:Schematic diagram of the synthesis of Mn-Zn (Mn_{0.3} Zn_{0.7} Fe₂O₄) ferrite

3 RESULTS AND DISCUSSION

Spinel ferrite's crystal structure is made up of octahedral and tetrahedral voids. These spaces are inhabited by ions of metal, while the lattice positions in this configuration are occupied by oxygen atoms. Due to the two metal ion interactions, two types of peaks are expected in the IR spectrum of ferrites.

a) divalent metal ion like Mn^{2+} , Zn^{2+} interaction with oxygen.

b) Trivalent metal ion like Fe³⁺ interaction with oxygen.

Fig. 2 shows the FTIR spectrum of Mn-Zn $(Mn_{0.3}Zn_{0.7}Fe_2O_4)$ ferrite. The recorded spectrum show two absorption peaks, one ranging between 400-450 cm⁻¹ and another ranging between 500 and 600 cm⁻¹. These bands are typically assigned to the

vibration of ions in crystal lattices[15]. In a spinel structure, these bands are assigned to octahedral (low frequency) sites and tetrahedral (high frequency) sites, respectively [16-17].



Fig 2: indicates FTIR spectra of Mn-Zn ferrite

4 Adsorption studies

The synthesized ferrite material was used for adsorption of dyes such as congo red, crystal violet, methylene blue, and methyl orange from aqueous solutions.[18] Different dye concentrations (30ppm, 50ppm, 70ppm, and 100ppm) were utilized for this purpose, and a set amount of ferrite material (0.1g) was applied.[19] Adsorption investigations were performed using a UV-Vis spectrophotometer, and the results were compared to blank dye solutions of the same concentrations.[20] The absorbance values at wavelengths for each dye in non-blank solutions were significantly reduced in the UV-Vis spectra (Figure 3-4), as shown in Table-1. According to the findings, ferrite material adsorbed Congo red, Crystal Violet, and Methylene blue dyes more efficiently.[21,22]

Table-1 Absorbance values for blank and non-blank dye solutions at the maximum absorption wavelength.

Dye Concentration	Congo red (CR)		Crystal violet (CV)		Methyl orange (MO)		Methylene blue (MB)	
	Blank	With	Blank	With	Blank	With	Blank	With
		ferrite		ferrite		ferrite		ferrite
30ppm	1.376	0.036	1.399	0.524	2.021	1.816	3.403	0.447
50ppm	2.348	0.081	2.044	0.719	3.399	2.754	3.567	0.546
70ppm	3.33	0.130	2.805	0.809	3.992	3.553	3.598	1.419

100ppm	4.00	0.313	3.277	0.803	4.00	3.989	3.783	1.018



3: UV-Visible absorption spectra for congo red and crystal violet at 30ppm, 50ppm, 70ppm & 100ppm concentration

Fig



Fig 4: UV-Visible absorption spectra for Methyl orange and Methylene blue at 30ppm, 50ppm, 70ppm & 100ppm concentration

5 CONCLUSIONS

The current study includes a full description of the synthesis of spinel ferrite by the combustion process, characterization of ferrite by FT-IR analysis, and application of ferrite material in dye adsorption from aqueous solutions. The formation of the spinel phase in synthesized ferrite material is confirmed by FT-IR analysis, which shows two absorption peaks for metal ion-oxygen interactions at tetrahedral and octahedral sites, respectively. UV-Vis spectroscopy tests have revealed that ferrite material has a substantial adsorption capacity. As per reported results, Mn-Zn doped transition metal ferrite act as efficient adsorbent for removing dyes from aqueous solutions for methyl orange, congo red, crystal violet, and methylene blue.

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7 CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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