Structural and magnetic characteristics of Nanoferrites and their use in photocatalytic activity of Methylene Blue

Ahmed M. Hammed[1, a*] and Zainab Raheem Muslim[2, b]
[1]Maysan Education Directorate, Maysan, Iraq
[2]Department of physics, College of science, University of Baghdad, Jadiriya, Baghdad, Iraq

Abstract.
The $CoFe_2O_4$, $NiFe_2O_4$ and $MgFe_2O_4$powderswere prepared using wet method.XRD, AFM, and UV-Vis spectrophotometer were used to determine the structure and morphology of the samples, as well as photocatalytic activity to degradethe methylene blue (MB) dye. The samples were exposed to a 2 hours heat treatment at 700°C. $CoFe_2O_4$, $NiFe_2O_4$ and $MgFe_2O_4$had average crystalline sizes of 32.5 nm, 34.7 nm, and 35.3 nm, respectively, while magnetic saturation magnetizations of 84.4 emu/g, 48.1 emu/g, and 26.06 emu/g, respectively.$CoFe_2O_4$, $NiFe_2O_4$ and $MgFe_2O_4$have coercivity (H_c) values of 428.7 Oe, 182 Oe, and 93.075 Oe, respectivelyand degradation percentageof methylene blue (MB)through four hoursbythese materials were 70.1 %, 66.7% and 58.81 %, respectively.

Keywords:photocatalytic activity of methylene blue, Nanoferrites, sol- gel, $CoFe_2O_4$, $NiFe_2O_4$ and $MgFe_2O_4$
DOI Number: 10.14704/nq.2022.20.5.NQ22565 **NeuroQuantology 2022; 20(5):2013-2020**

Introduction

Ferrite materials are magnetic materials with electrical and magnetic properties that are coupled at the same time, high resistance to electric current. The main components of the ferrites are iron oxide and metal oxides such as: nickel, magnesium, cobalt, zinc, lithium and cadmium (SHAMEBO 2018, Jaswal and Singh 2014).M' M''_2O_4denotes spinel-like mixed metal oxides, where M' means a metal ion with two valences and M" denotes a metal ion with three valences such as Al, Cr, Fe, and so on; if M" is Fe (III), ferrites are another name for these metal oxides (Tsvetkov et al. 2019).Due to the narrow band gap (~2 eV), magnetic spinel ferrites, MFe_2O_4 (e.g. M = Co, Ni, Mg, Zn, and Fe), are regarded visible light driven photocatalysts (Heidari andMasoudpanah 2021).The Fe^{2+} ion of Fe_3O_4 was changed by another divalent metal ion (Ni^{2+}, Mg^{2+}, or Mn^{2+}) to enhance the activity and stability of the catalyst under water oxidation conditions.Nickel ferrite ($NiFe_2O_4$), which is widelyemployedin organic oxidation processes, exhibited the best activity for photocatalytic water oxidation when MFe_2O_4 (M = Mg, Mn, Fe, Ni) catalysts were compared in terms of O_2evolution rate and O_2 yield (Hong et al. 2012).

Only 10-15% of all organic pollutants created around the world end up in the environment as waste. Synthetic dyes are chemically stable and difficult to breakdown because they contain complex aromatic groups. Photocatalytic experiments to remove organic pollutants are thought to rely heavily on nanomaterials (Nadumane et al. 2019). Photocatalytic is an area of reaction which employs light to activate a solid catalyst that in turns can increase the rate of a chemical reaction without itself being consumed (Kong et al. 2015).

Precipitation, sonochemical, reverse micelle technique, microwave, hydrothermal synthesis, thermal decomposition, and sol-gel have all been used to make nanosized spinel ferrite particles of various sizes. The sol-gel method is an environmentally friendly and cost-effective method for synthesizing magnetic ferrite particles (Heidari andMasoudpanah 2021, Fardood et al.2017).

The advantages of sol-gel method include its low cost, relative simplicity, ability to be performed at a low temperature without specialized equipment, and ability to achieve a small particle size distribution (Sharma et al. 2015).

Experimental

1. **Synthesis of Ferrites Nanoparticles**

Items x, y and z refer to the $CoFe_2O_4$, $NiFe_2O_4$ and $MgFe_2O_4$, respectively that were obtained. The samples were all prepared using the sol-gel process. Nitrates (cobalt and iron) were mixed with distilled water (20 ml) after citrate added for preparation of item x (1:1:2), the same procedures were repeated for items y and z, the material of y and z were nitrates (nickel and iron) and nitrates (magnesium and iron), respectively.These mixtures were mixed at 80°C for one hour until all of the water had evaporated and the sticky gel had formed. The gel was dried for three hours at 150°C in an oven. To produce the pure crystalline stage, the powder was calcined at 700 °C for two hours in air. Finally, the samples were analyzed using XRD and AFM.

2. **Photocatalytic Activity for Methylene Blue Degradation**

To prepare 5ppm methylene blue (MB) dye solutions, dissolve 0.5 mg of MB powder in 100 mL distilled water at pH 6.7. The itemsx,y and z with weight 0.01gwere added to 20 mL of 5 ppm MB dye solutions at roomtemperature, the solutions were placed on the magnetic stirrer to achieve a homogenous content, each solution was exposed to UV irradiation for four hours until it degraded. The distance between the beaker and the UV source was 30 cm. The dye solution's absorbance decreased as measured by a UV-Vis absorption spectrophotometer.

Result and discussion

Structural characterization: XRD was used to obtain the structural information for all of the samples that were generated, as shown in**(**Figure 1).The samples were operated at 40 kV and 30 mA, respectively, for voltage and current.Item x, item y, and item z (JCPDS Nos. 98-010-9044, 98-020-1149, and 98-015-8402), respectively all have XRD values that match the standard values.Using Debye Scherrer's formula, the crystal size of the produced powder was estimated. The average crystalline size of $CoFe_2O_4$, $NiFe_2O_4$ and $MgFe_2O_4$ were 32.5 nm, 34.7 nm and 35.3nm, respectively.The AFM of the samples shown in (Figure 2).

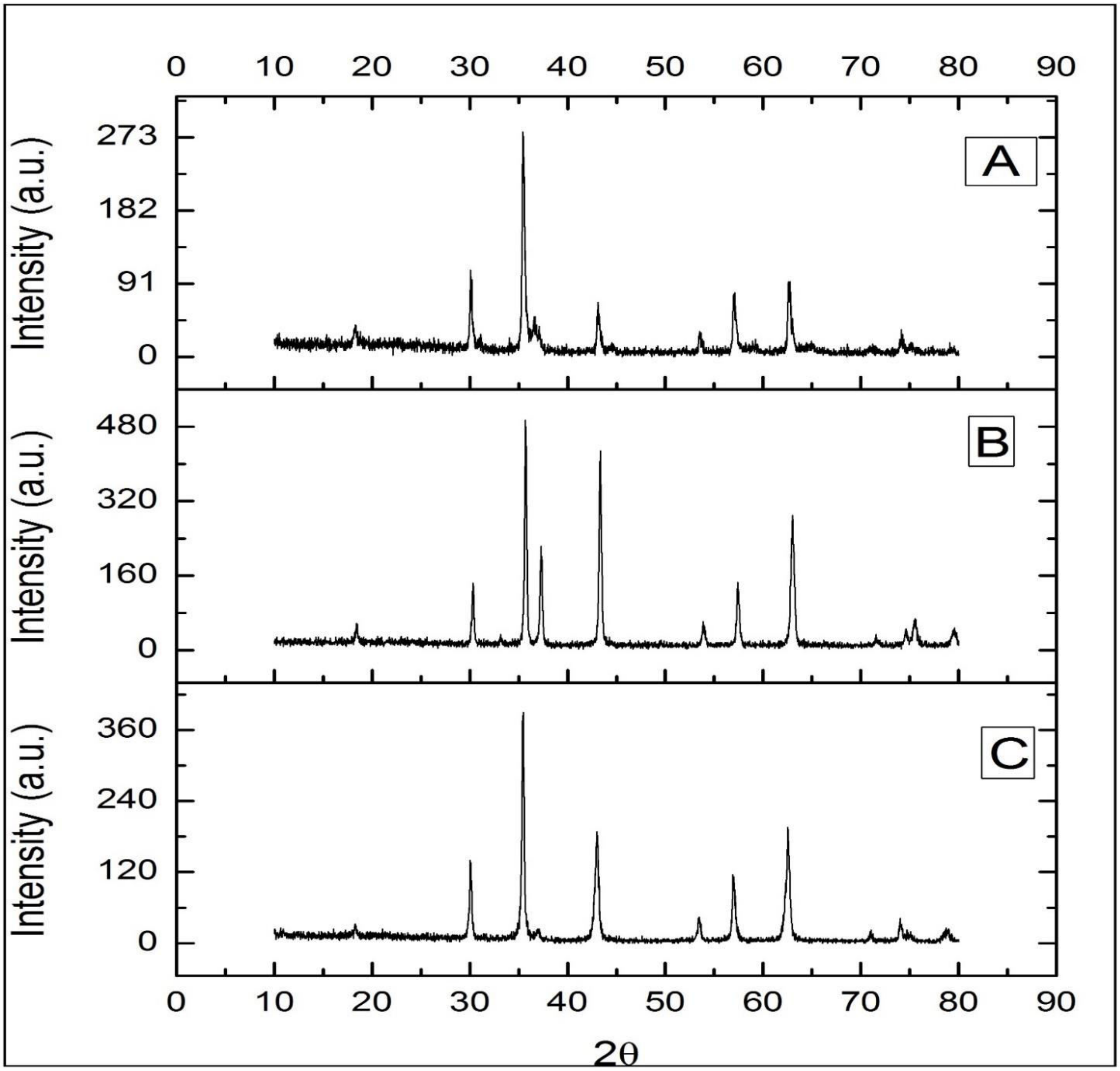


Figure. 1: XRD pattern for; A-$CoFe_2O_4$, B-$NiFe_2O_4$ and C-$MgFe_2O_4$.

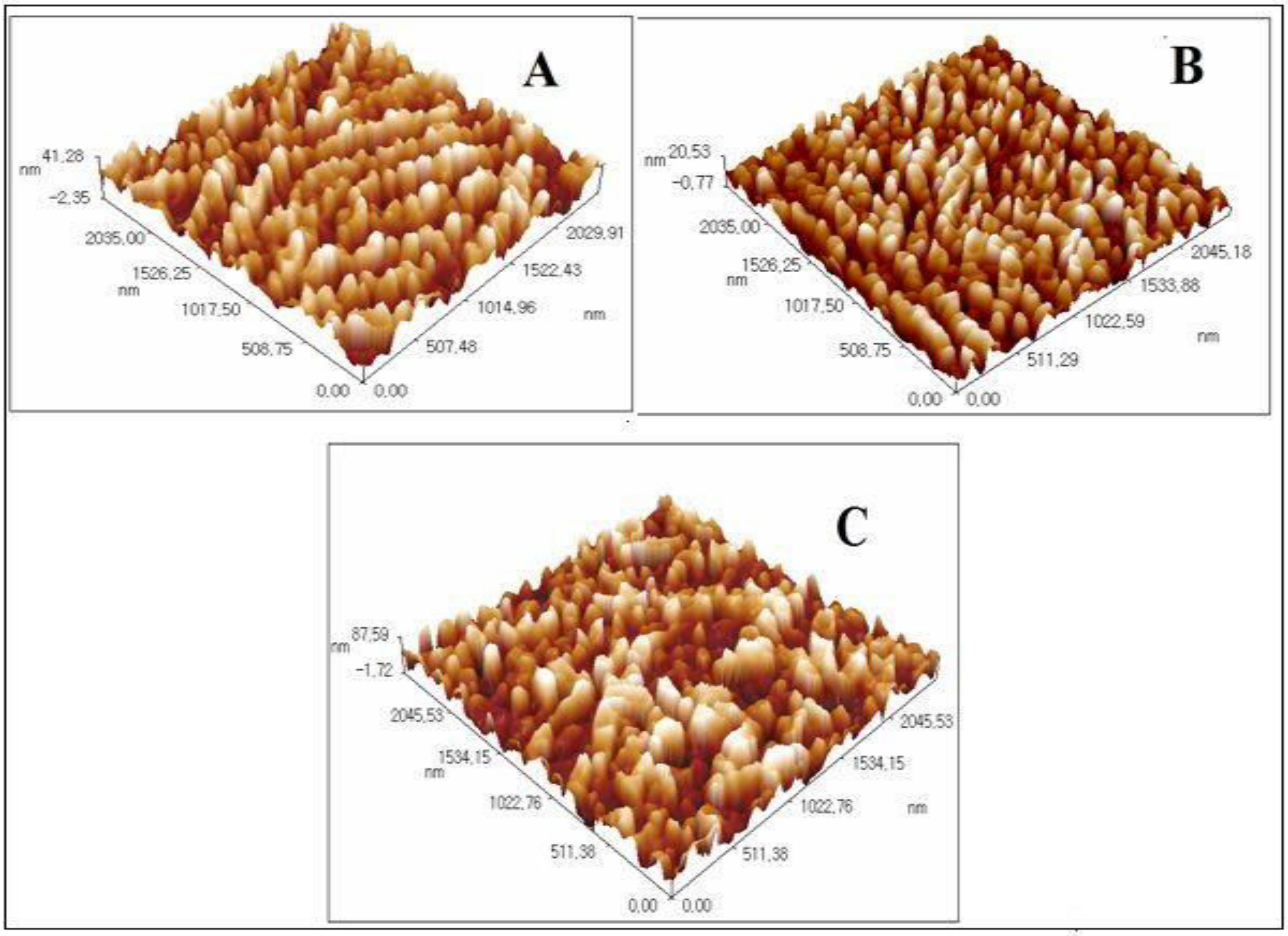


Figure 2: AFM for;A-$CoFe_2O_4$, B-$NiFe_2O_4$ and C-$MgFe_2O_4$.

Magnetic studies: VSM was used to measure magnetization versus applied field at room temperature with a magnetic field of -10kOe≤ H ≤10kOe.The magnetic characteristics of the samples are shown in (Table 1 and Figure 3), indicating that they are all soft ferromagnetic materials.The item x had the greatest saturation magnetization value of 84.4 emu/g and the lowest value of 26.06 emu/g for the item z, while the item y had the saturation magnetization value of 48.1 emu/g.

The lower grain size was most likely to blame for the rise in saturation magnetization. The saturation magnetization increased due to thermal disorder, which opposes the alignment of the applied magnetic field, and it occurred as a result of an increase in applied magnetic field, which could not increase the material's magnetization. Additionally the coercivity value increased as the grain size decreased, so the item x has $M_s$higher than items y and z and $H_c$of item z smaller than itemsx and y, agree with (Nejati and Zabihi 2012)

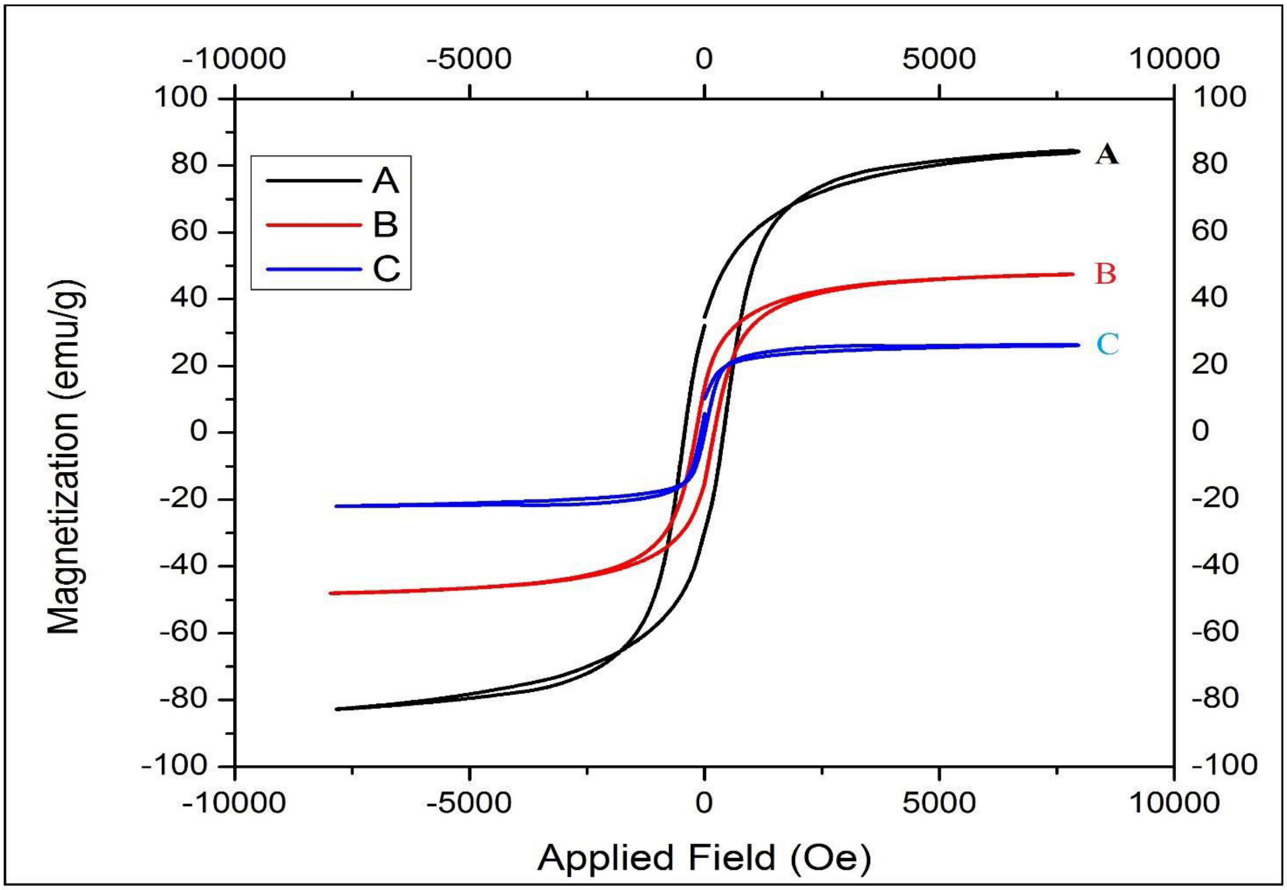


Figure 3: Magnitzation versus applied field for ; A-$CoFe_2O_4$, B-$NiFe_2O_4$ and C-$MgFe_2O_4$.

Table 1: The magnetic properties that characterize the powder.

magnetic parameters	Item x	Item y	Item z
M_s (emu/g)	84.4	48.1	26.06
M_r (emu/g)	35.6	17.5	11.82
H_c (Oe)	428.7	182	93.075

Photocatalytic studied

Under visible light irradiation, photocatalytic degradation of MB (= 663 nm) dyes was carried out in the presence of itemx, y, or z. Figure 4 represented the absorbance of MB dyes in the presence of photocatalyst, where the dyes' absorbance decreases with increasing time of visible light irradiation. The degradation of MB was found to be 70.1%, 66.7% and 58.81% in four hours of irradiation for itemsx, y and z, respectively, shown in (Figure 5). In comparison between item xwith item y and item z,itwas found that the item x has better efficiency for degradation of MB dye, due to lower energy gap (1.97, 3.75 and 3.9 eV)as shown in figure 6. The crystallite nature, unique charge separation, and surface morphology all play a role in degrading efficiency.

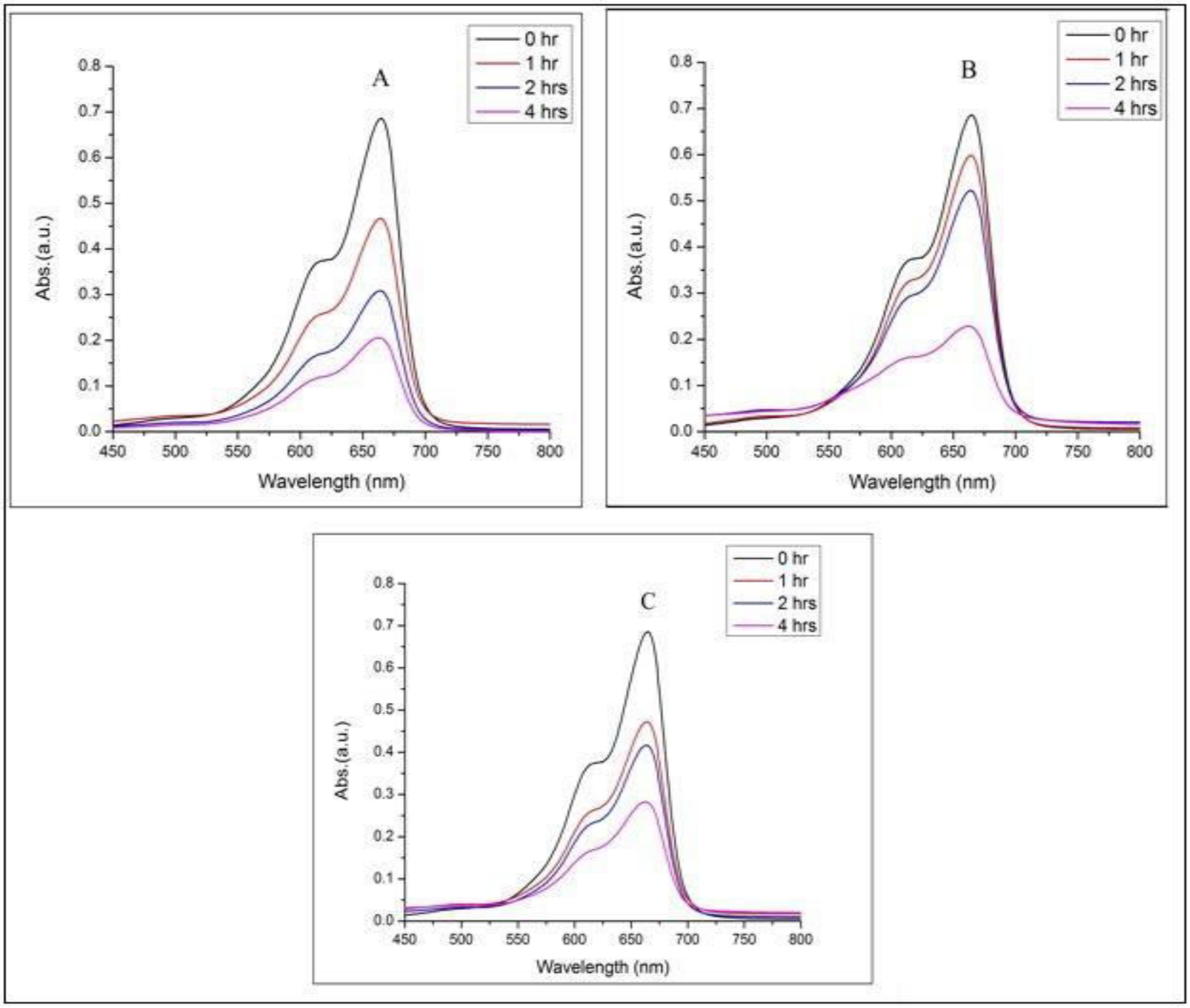
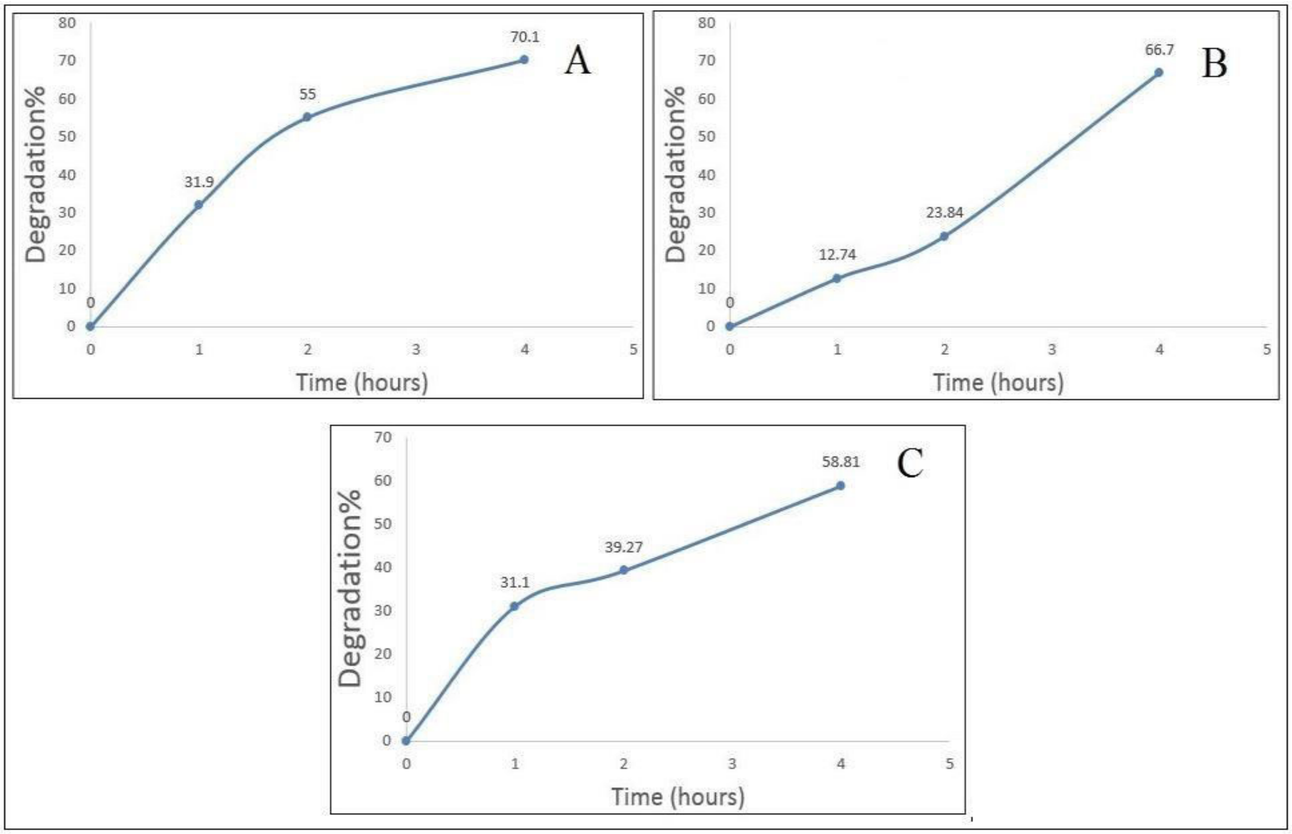


Figure 4: photocatalytic activity for;A-$CoFe_2O_4$, B-$NiFe_2O_4$ and C-$MgFe_2O_4$.

*e***ISSN** 1303-5150
www.neuroquantology.com



2019

Figure 5: Degradation percentage for;A-$CoFe_2O_4$, B-$NiFe_2O_4$ and C-$MgFe_2O_4$.

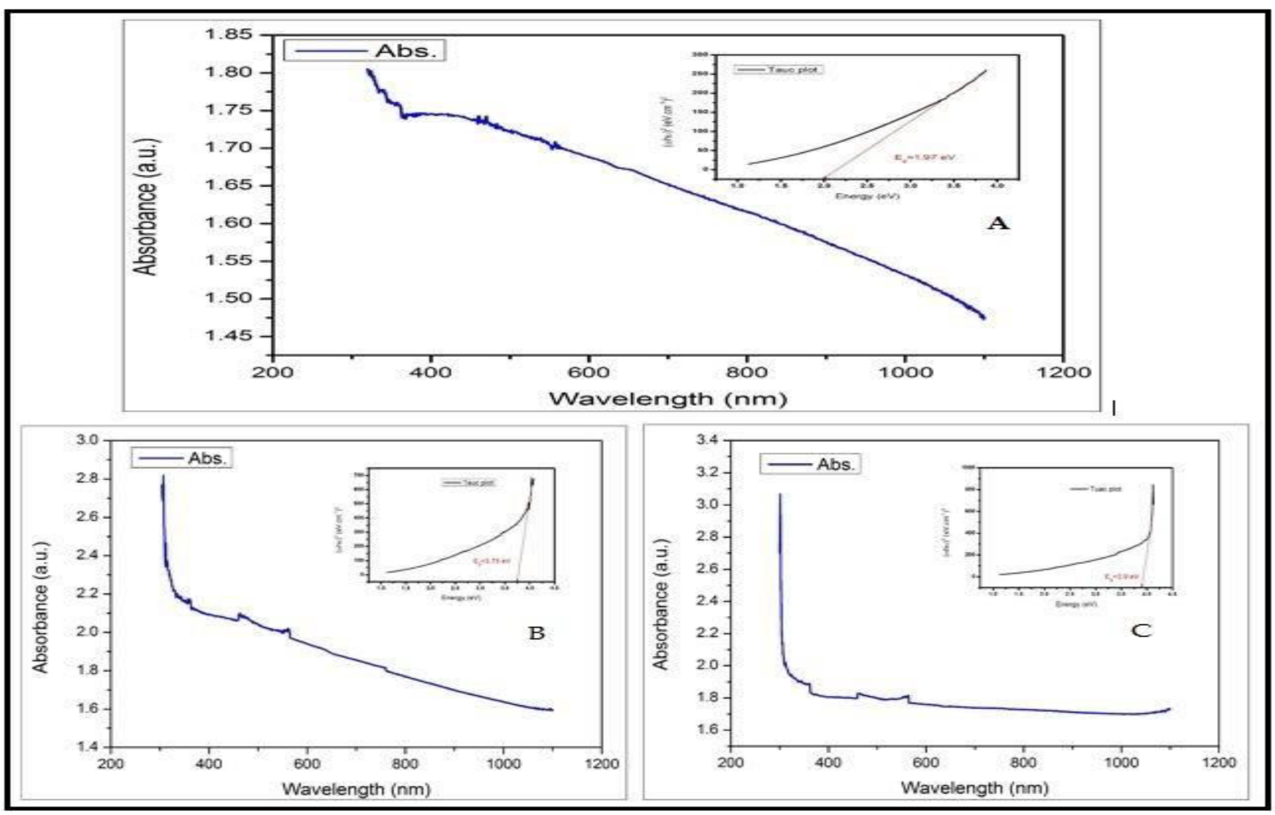


Figure 6: Energy gap for;A-$CoFe_2O_4$, B-$NiFe_2O_4$ and C-$MgFe_2O_4$.

Conclusion

Due to the values of the magnetic characteristics, all samples are ferromagnetic materials. The average crystalline size of $CoFe_2O_4$, $NiFe_2O_4$ and $MgFe_2O_4$ were 32.5 nm, 34.7 nm and 35.3nm, respectively and these materials have saturation magnetizations of 84.4 emu/g, 48.1 emu/g, and 26.06 emu/g, respectively.According to magnetic measurements.The residual magnetization of $CoFe_2O_4$, $NiFe_2O_4$ and $MgFe_2O_4$ were 35.6 emu/g, 17.5 emu/g and 11.82 emu/g, respectively. The values of coercivity (H_c) of the $CoFe_2O_4$, $NiFe_2O_4$ and $MgFe_2O_4$ are 428.7 Oe, 182 Oe and 93.075 Oe and degradation percentage of methylene blue (MB) through four hours by these materials were 70.1 %, 66.7% and 58.81 %, respectively. The magnetic properties and degradation percentage increase with decrease in crystalline size.

References

1. SHAMEBO S," Studies on structural, electric, dielectric and magnetic properties of nickel-based ferrite materials", MSc thesis, Arbaminch University, Ethiopia, 2018.
2. Jaswal L and Singh B, "History and applications of important ferrites", Integr. Res. Adv., vol.1, no.1, pp.11-13, 2014.
3. Tsvetkov M P, Ivanova I R, Valcheva E P, Zaharieva J T and Milanova M M"Photocatalytic activity of $NiFe_2O_4$ and $Zn_{0.5}Ni_{0.5}Fe_2O_4$ modified by Eu(III) and Tb(III) for decomposition ofMalachite Green", Open Chem., 17, (2019) 124-1132.
4. Heidari P and Masoudpanah S M,"Structural, magnetic and optical properties and photocatalytic activity of magnesium-calcium ferrite powders",Journal of Physics and Chemistry of Solids, 148 (2021) 109681.
5. Hong D, Yamada Y, Nagatomi T, Takai Y and Fukuzumi S,"Catalysis of Nickel Ferrite for Photocatalytic Water Oxidation Using $[Ru(bpy)_3]^{2+}$ and $S_2O_8^{2-}$", J. Am. Chem. Soc., 134 (2012) 19572-19575.
6. Nadumane A, Shetty K, Anantharaju KS, Nagaswarupa H P, Rangappa D, Vidya YS, Nagabhushana H, Prashantha SC," Sunlight photocatalytic performance of Mg-doped nickel ferrite synthesized by a green sol-gel route", Journal of Science: Advanced Materials and Devices, 4 (2019) 89-100.
7. Kong ZY, Wong N X, Lum S W, Tan SY, Khan MR , Cheng C K , "The application of magnesium ferrite photocatalyst for photo treatment of methylene blue", Journal of Engineering Science and Technology, vol. 4 (2015)1-10.
8. Fardood S T, Golfar Z and Ramazani A,"Novel sol–gel synthesis and characterization of superparamagnetic magnesium ferrite nanoparticles using tragacanth gum as a magneticallyseparable photocatalyst for degradation of reactive blue 21 dye and kinetic study,"J Mater Sci: Mater Electron, (2017).
9. Sharma R, Bansal S and SonalSinghal, "Tailoring the photo-Fenton activity of spinel ferrites (MFe_2O_4) by incorporating different cations (M=Cu, Zn, Ni and Co) in the structure", RSC Advances, 5, pp. 6006–6018, 2015.
10. Nejati K and Zabihi R," Preparation and magnetic properties of nano size nickel ferrite particles using hydrothermal method", Chemistry Central Journal, 23, (2012) 6.