Characterization and photocatalytic degradation of methyl orange in water by $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ nanoparticles synthesized by gel-auto combustion and microwave-assisted methods

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Abstract

Over the past few decades, magnetic nanoparticles have been considered by many researchers due to their unique physicochemical, magnetic and optical properties and extensive applications in the field of biomedical (such as magnetic resonance imaging (MRI), drug delivery system and magnetic hyperthermia), catalysis, information technology, telecommunication and environmental remediation, destruction of organic pollutants such as dyes, etc. In this work, it has been attempted to synthesize $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ by both gel-auto combustion and microwave-assisted methods and the resulting powders were characterized by different analysis involved, XRD, SEM, IR, EDS, VSM and UV-Vis spectra. The effect of these two ferrites on the absorption and degradation of methylene orange dye was studied at different concentrations (100, 160 and 200 ppm). The average crystalline size of MNPs obtained by gel-auto combustion and MW-assisted, were 77.9 and 44.1 nm, respectively. The specific magnetization curves exhibit ferromagnetism of soft magnetic materials and the (Ms) values of samples were 20.64 and 52.89 (emu/g) for MNPs obtained by gel-auto combustion and MW-assisted, respectively. Finally, both ferrites showed high absorption of methylene orange dye in water under UV-Vis irradiation ($\lambda > 400$ nm).

Keywords: Photocatalyst; Magnetic nanoparticles; Visible light; Methylene orange; $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$.

1 Introduction

Dyes are important pollutants that lead to serious hazards for humans, the other animals and creatures come alive. Dyes can't be decomposed by aerobic treatment processes. Therefore, removing them from industrial wastewater before discharging into the environment requires a great deal of attention. In industries, different types of commercially dyes are used frequently. Factors in the production of these pollutants include the textile, plastics, cosmetics and waste water

[5]. Photocatalysts and their structures are widely contaminated by water resulting from the exposure of light to decomposition of hazardous compounds. Recently, several physical, chemical, and biological methods used to treat water include reversal, adsorption, ultrafiltration, ozonation and biodegradation [6]. Magnetic nanoparticles (MNPs) are another compound capable of absorbing organic pollutants. Nanoparticles and especially ferrite spinel have advantages such as easy preparation, easy changes in nanoparticle size, surface morphology [5]. Except for the above mentioned ferrites are able to be easily separated by magnet due to their good magnetic properties. These advantages have led to the use of ferrites in the water and wastewater pollutants removal industry. In addition, spinel ferrites have been widely used in biomedicine due to their non-toxicity, reduced side effects of cancer drugs and long-distance magnetic guidance, including: imaging contrast probes, hyperthermia agents, magnetic-guided vectors and drug-delivery carriers and etc [7-11]. Spinel ferrites have the general formula MFe_2O_4 known for their magnetic, optical, electronic, catalytic and photoelectric properties [12]. Among ferrites, Ni-Cu-Zn Fe_2O_4 magnetic nanoparticles have received special attention due to their good magnetic properties (high saturation magnetization (Ms)). Nickel increases the magnetic properties and copper improves the size of magnetic nanoparticles [13]. These magnetic vesicles have spinel ferrite structure with general formula $[M_{1-x}Fe_x]^A[MxFe_{2-x}]^BO_4$, where ‘A’ represents tetrahedral site, ‘B’ represents octahedral site, and ‘x’ denotes the degree of inversion [14]. There are different physical and chemical methods for preparing MNPs, including: hydrothermal, co-precipitation, ultrasonic cavitation, thermal decomposition, sol-gel, combustion, microwave, sonochemical, microemulsion etc, each of which has its own advantages and disadvantages [15-23]. In this work, ferrites were synthesized in two self-combustion and microwave methods, and their differences in magnetic, optical and photocatalytic properties were investigated for the absorption of methylene orange dye. The microwave-assisted method was attractive due to its effective thermal energy. On the other hand, this method resulted in increased process speed (short reaction time), improved magnetic properties, improved size distribution of small nanoparticles, and increased contaminant uptake and degradation [24].

2 Experimental

2.1 Materials

Iron(III) nitrate nonahydrate (>98% $Fe(NO_3)_3 \cdot 9H_2O$), zinc (II) nitrate hexahydrate (>98% $Zn(NO_3)_2.6H_2O$), nickel (II) nitrate hexahydrate (>98% $Ni(NO_3)_2.6H_2O$), copper (II) nitrate terryhydrate (>98% $Cu(NO_3)_2.3H_2O$), ammonium nitrate (25% NH_4NO_3), glycine (as fuel) and deionized water (H_2O) were used and were supplied from Merck Millipore.

2.2 Synthesis of $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ NPs by gel-auto combustion method

The stoichiometric amounts of the nitrate salts of zinc, nickel, copper and iron with ammonium nitrate and glycine (as fuel) were dissolved in distilled water and heated to 80 ° C until the excess water evaporated and were obtained a reddish-brown gel. Subsequently, the heater temperature was increased to 300 ° C and after 10 minutes the combustion reaction was carried out. The brown powder of the nanoparticles obtained was ball milled for 12 min at a frequency of 30 W (Retsch-MM400, 60 Hz with maximum power 150 W). MNPs stored and kept at room temperature for different analyses.

2.3 Synthesis of $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ by microwave-assisted

The stoichiometric amounts of the nitrate salts of zinc, nickel, copper and iron with ammonium nitrate and glycine were dissolved in distilled water and heated to 80 ° C until the excess water evaporated and were obtained a reddish-brown gel. Then the resulting gel was placed into a domestic microwave oven (LG-MC61, 230 Hz operated with the maximum power of 900 W) [3]. Finally, the ball milling to ensure nanoscale particles was carried out for 12 min at the same frequency. So, MNPs stored and kept at room temperature for different analyses.

2.4 Preparation of methylene orange solution and photocatalytic activities

Initially, 5, 10 and 15 ppm solutions of methylene orange ($C_{14}H_{14}N_3NaO_3S$) were prepared to investigate the adsorption and degradation of this pollutant by the samples. Then dissolve 0.03 g of each sample in 30 ml of 5, 10 and 15 ppm solutions and stir at three different times for 20, 40 and 60 minutes in the dark. At the end of the three times the solution was magnetically separated from the ferrite. The stored samples were then centrifuged for 5 min and stored for UV-Vis analysis. Exactly the same was done at three times of 20, 40 and 60 min for each sample in the presence of visible light and the samples were stored for investigation amount of pollutant degradation. Photocatalytic activity of the samples was evaluated by the percentage of degradation of methylene orange dissolved in distilled water under the LED lamp (10W) in the visible area (λ = 462 nm) [4].

3 Result and discussion

3.1 Physicochemical properties

3.1.1 XRD pattern

Fig. 1 shows the X-ray diffraction pattern of the single-phase spinel ferrite cubic structure for both samples prepared by gel-auto combustion and microwave-assisted methods, which means that neither of the two methods makes any changes to the spinel ferrite structure. Also, the average size of NPs prepared by microwave irradiation and gel-auto combustion method were 77.9 and 44.1 nm, respectively. Therefore, microwave waves improve the size of nanoparticles that are more suitable for the applications mentioned.

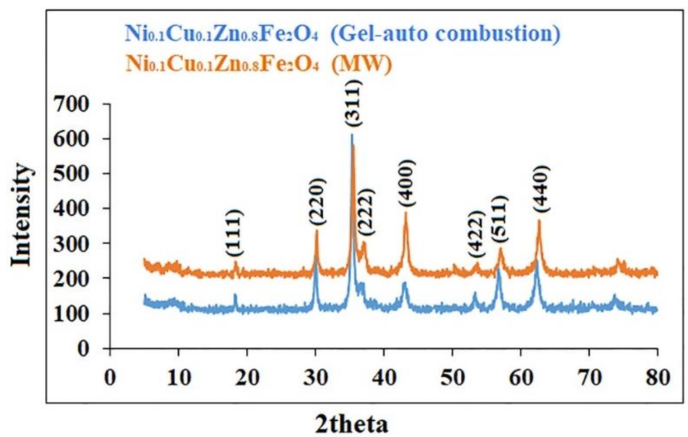

Fig. 1. The XRD pattern of $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ nanoparticles prepared by two different methods.

3.1.2 FT-IR spectroscopy

As shown in Fig. 2, the formation of ferrite structure is confirmed by the IR analysis of both samples. Peaks shown in the 600-400 cm^{-1} region are assigned to octahedral (B) and tetrahedral (A) sites of Fe–O bonding.

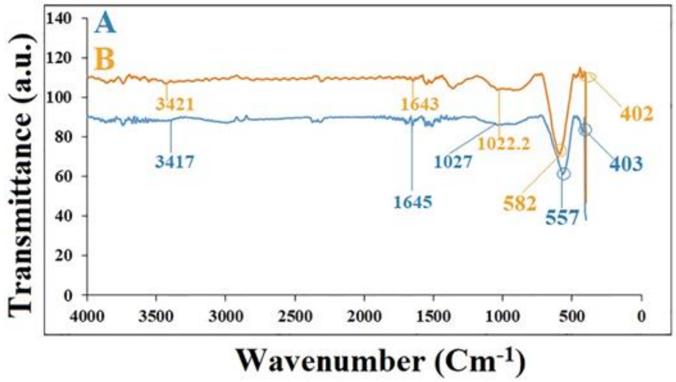

Fig. 2. IR spectroscopy of MNPs. (A) $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ synthesized by gel auto-combustion method and under microwave irradiation (B).

3.1.3 DRS analysis

To investigate the optical properties of the nanoparticles, DRS analysis was applied (Fig. 3). The optical properties of the samples appeared at 462 and 464 nm, respectively. So again, through his analysis, we came to the conclusion that microwave waves improve optical properties.

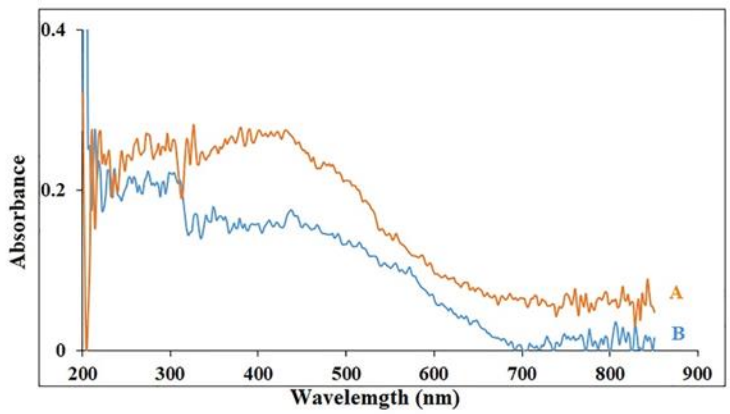

Fig. 3. DRS analysis for $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ synthesized by gel-auto combustion (A) and under microwave irradiation (B) respectively.

3.1.4 EDS analysis

EDS analysis shows the purity of the samples at room temperature (Fig. 4). According to this analysis, only the Ni, Cu, Zn, Fe and O elements were found in both samples and no secondary phase was observed.

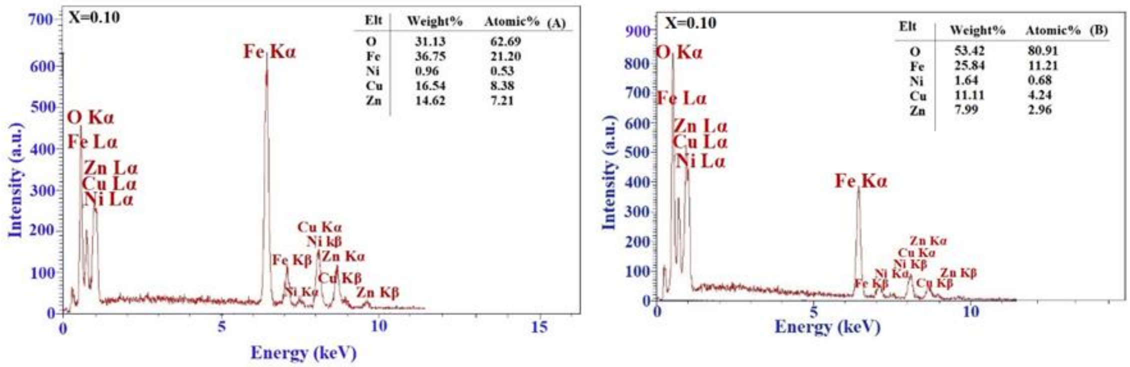

Fig. 4. EDX analysis for $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ synthesized by gel auto-combustion method, (A) and under microwave irradiation (B).

3.1.5 Vibrating sample magnetometer (VSM) analysis

The specific magnetization curves exhibit ferromagnetism of soft magnetic materials and the saturation magnetization (Ms) values of samples were 20.6 and 52.9 emu/g for $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ obtained by gel-auto combustion (Fig. 5A) and microwave irradiation (Fig. 5B), respectively. Therefore, microwaves improve the magnetic properties of the NPs.

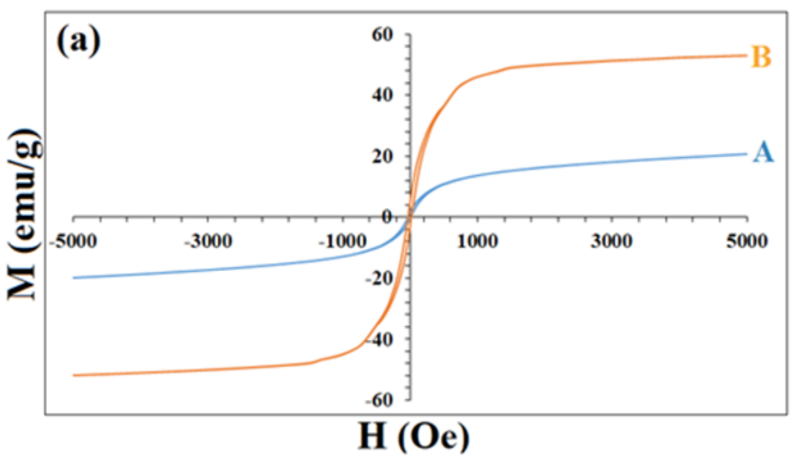

Fig. 5. M–H hysteresis curve of the magnetic ferrite nanoparticles, synthesized by gel-auto combustion (A) and MW irradiation (B).

3.1.6 Photocatalytic activity of ferrite as an absorbent of methylene orange by UV spectroscopy

Fig. 6 shows the degradation of methyl orange after one hour by two ferrites synthesized by gel-auto combustion method and microwave-assisted. The main absorption is at 464 nm and according to the ferrite form A (gel-auto combustion) and B (MW-assisted), 21% and 92% of the pollutants were degraded, respectively and methyl orange not had any damage. So, Microwave-assisted ferrite Cu

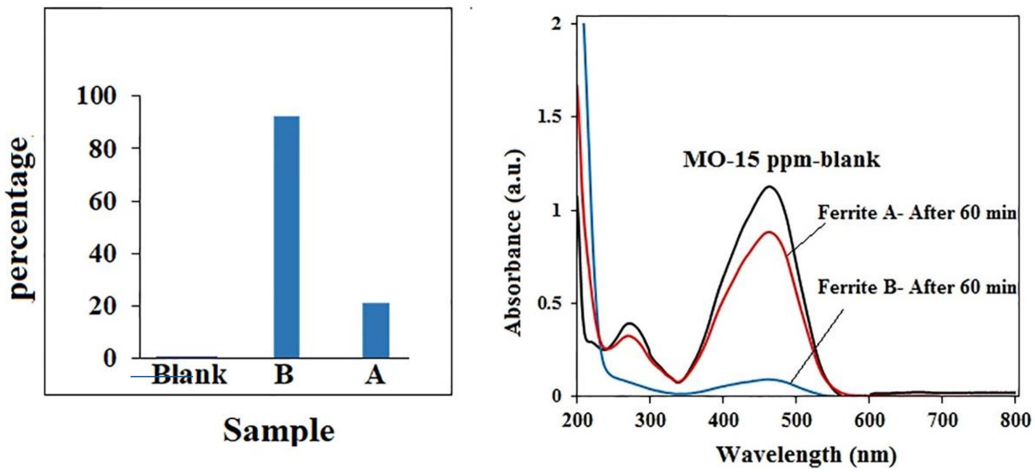

Fig. 6. UV–visible absorption spectrum of methyl orange (15 ppm) by $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ A (gel-auto combustion) and B (MW-assisted).

4 Conclusion

The samples were synthesized by microwave and gel-auto combustion methods and investigated by XRD, IR, DRS, EDS, VSM and UV-Vis spectra. Studies have shown that micro-waves improve the size of nanoparticles, their magnetic and optical properties, and high absorption of pollutants. $Ni_{0.1}Cu_{0.1}Zn_{0.8}Fe_2O_4$ synthesized by MW-assisted with 92% uptake of pollutants can be used as a good sorbent for removal of organic pollutants in water and wastewater.

References

[1] Thi, H., Thanh, T., Nguyen Tran, D.H., Bach, L.G., Vu-Quang, H., Nguyen, D.C., Park, K.D. and Nguyen, D.H., 2019. Functional Magnetic Core-Shell System-Based Iron Oxide Nanoparticle Coated with Biocompatible Copolymer for Anticancer Drug Delivery. Pharmaceutics, 11(3), p.120.

[2] Gabal, M.A. and Al-Juaid, A.A., 2019. Cr-substitution effect on structural and electromagnetic properties of Mg-Ni ferrite synthesized via sucrose auto-combustion method. Journal of Alloys and Compounds, p.152250.

[3] Nabiyouni, G., Ghanbari, D., Ghasemi, J. and Yousofnejad, A., 2015. Microwave-assisted synthesis of $MgFe_2O_4$-ZnO nanocomposite and its photo-catalyst investigation in methyl orange degradation. Journal of Nanostructures, 5(3), pp.289-295.

[4] Xu, S., Shangguan, W., Yuan, J., Shi, J. and Chen, M., 2007. Preparations and photocatalytic degradation of methyl orange in water on magnetically separable Bi12TiO20 supported on nickel ferrite. Science and Technology of Advanced Materials, 8(1-2), pp.40-46.

[5] Naik, M.M., Naik, H.B., Kottam, N., Vinuth, M., Nagaraju, G. and Prabhakara, M.C., 2019. Multifunctional properties of microwave-assisted bioengineered nickel doped cobalt ferrite nanoparticles. Journal of Sol-Gel Science and Technology, pp.1-18.

[6] Naik, M.M., Naik, H.B., Kottam, N., Vinuth, M., Nagaraju, G. and Prabhakara, M.C., 2019. Multifunctional properties of microwave-assisted bioengineered nickel doped cobalt ferrite nanoparticles. Journal of Sol-Gel Science and Technology, pp.1-18.

[7] Issa, B. and Obaidat, I.M., 2019. Magnetic Nanoparticles as MRI Contrast Agents. In Magnetic Resonance Imaging. IntechOpen.

[8] Simeonidis, K., Martinez-Boubeta, C., Serantes, D., Ruta, S., Chubykalo-Fesenko, O., Chantrell, R., Oró-Solé, J., Balcells, L., Kamzin, A.S., Nazipov, R.A. and Makridis, A., 2019. Controlling magnetisation's reversal mechanism and hyperthermia efficiency in core/shell magnetic nanoparticles by tuning the interphase coupling. arXiv preprint arXiv:1910.03914.

[9] Akutsu, S. and Tanaka, M., Honda Motor Co Ltd, 2019. Automated guided vehicle. U.S. Patent Application 16/202,376.

[10] Dunuweera, S.P., Rajapakse, R.M.S.I., Rajapakshe, R.B.S.D., Wijekoon, S.H.D.P., Thilakarathna, N., Sasanka, M.G.G. and Rajapakse, R.M., 2019. Review on Targeted Drug Delivery Carriers Used in Nanobiomedical Applications. Current Nanoscience, 15(4), pp.382-397.

[11] Yang, Z., Cui, B., Bu, Y. and Wang, Y., 2019. Preparation of flower-dewdrops Fe_3O_4/carbon-SiO_2 microsphere for microwave-triggered drug delivery. Journal of Alloys and Compounds, 775, pp.826-835.

[12] Guo, X., Xu, Y., Wang, K., Zha, F., Tang, X. and Tian, H., 2019. Synthesis of magnetic $CuFe_2O_4$ self-assembled hollow nanospheres and its application for degrading methylene blue. Research on Chemical Intermediates, pp.1-17.

[13] Lassoued, A., Karolak, F., Dkhil, B., Ammar, S. and Gadri, A., 2017. Synthesis and magnetic characterization of Spinel ferrites MFe_2O_4 (M= Ni, Co, Zn and Cu) via chemical co-precipitation method. Journal of Materials Science: Materials in Electronics, 28(24), pp.18857-18864.

[14] Wu, Z.Y., Zou, Y., Liu, Q.X., Ma, C.B., Tang, X.G. and Chen, B.T., 2013. Preparation of Magnetic $Ni_{0.5}Co_{0.5}Fe_2O_4$ Nanoparticles and their Applications in Adsorption of Bovine Serum Albuminn. Integrated Ferroelectrics, 142(1), pp.128-134.

[15] Ahmadian-Fard-Fini, S., Ghanbari, D. and Salavati-Niasari, M., 2019. Photoluminescence carbon dot as a sensor for detecting of Pseudomonas aeruginosa bacteria: Hydrothermal synthesis of magnetic hollow $NiFe_2O_4$-carbon dots nanocomposite material. Composites Part B: Engineering, 161, pp.564-577.

[16] Sagayaraj, R., Aravazhi, S. and Chandrasekaran, G., 2019. Tuning of ferrites (Co x Fe 3-x O 4) nanoparticles by co-precipitation technique. SN Applied Sciences, 1(3), p.271.

[17] Kharat, P.B., Chavan, A.R., Humbe, A.V. and Jadhav, K.M., 2019. Evaluation of thermoacoustics parameters of $CoFe_2O_4$–ethylene glycol nanofluid using ultrasonic velocity technique. Journal of Materials Science: Materials in Electronics, 30(2), pp.1175-1186.

[18] Goudarzi, M., Salavati-Niasari, M., Yazdian, F. and Amiri, M., 2019. Sonochemical assisted thermal decomposition method for green synthesis of $CuCo_2O_4$/CuO ceramic nanocomposite using Dactylopius Coccus for anti-tumor investigations. Journal of Alloys and Compounds, 788, pp.944-953.

[19] Omelyanchik, A., Singh, G., Volochaev, M., Sokolov, A., Rodionova, V. and Peddis, D., 2019. Tunable magnetic properties of Ni-doped $CoFe_2O_4$ nanoparticles prepared by the sol–gel citrate self-combustion method. Journal of Magnetism and Magnetic Materials, 476, pp.387-391.

[20] Kombaiah, K., Vijaya, J.J., Kennedy, L.J. and Kaviyarasu, K., 2019. Catalytic studies of $NiFe_2O_4$ nanoparticles prepared by conventional and microwave combustion method. Materials Chemistry and Physics, 221, pp.11-28.

[21] Ghobadifard, M., Farhadi, S. and Mohebbi, S., 2019. Catalytic performance of $ZnFe_2O_4$ nanoparticles prepared from the $[ZnFe_2O\ (CH_3COO)_6\ (H_2O)_3] \cdot 2H_2O$ complex under microwave irradiation. Research on Chemical Intermediates, 45(2), pp.379-400.

[22] Wang, G., Zhou, F., Du, T., Lu, Z., Ma, Y., Mu, J., Wang, Y., Zhang, Z., Che, H., Zhang, X. and Yu, R., 2019. Controlled assembly of $MnFe_2O_4$ nanoparticles on MoS_2 nanosheets by a facile sonochemical method. Journal of Magnetism and Magnetic Materials, 476, pp.453-458.

[23] Mohammadikish, M., Masteri-Farahani, M. and Mahdian, T., 2019. Optical properties of copper tungstate nanoparticles prepared by microemulsion method. Inorganic and Nano-Metal Chemistry, 49(3), pp.63-68.
[24] Fariñas, J.C., Moreno, R., Pérez, A., García, M.A., García-Hernández, M., Salvador, M.D. and Borrell, A., 2018. Microwave-assisted solution synthesis, microwave sintering and magnetic properties of cobalt ferrite. Journal of the European Ceramic Society, 38(5), pp.2360-2368.