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The effects of fuel type in synthesis of NiFe_2O_4 nanoparticles by microwave assisted combustion method

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Abstract. In this study, it was investigated the effects of the used fuels on structural, morphological and magnetic properties of nanoparticles in nanoparticle synthesis with microwave assisted combustion method with an important method in quick, simple and low cost at synthesis of the nanoparticles. In this aim, glycine, urea and citric acid were used as fuel, respectively. The synthesised nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmet-Teller surface area (BET), and vibrating sample magnetometry (VSM) techniques. We observed that fuel type is quite effective on magnetic properties and surface properties of the nanoparticles. X-ray diffractograms of the obtained nanoparticles were compared with standard powder diffraction cards of NiFe_2O_4 (JCPDS Card Number 54-0964). The results demonstrated that diffractograms are fully compatible with standard reflection peaks. According to the results of the XRD analysis, the highest crystallinity was observed at nanoparticles synthesized with glycine. The results demonstrated that the nanoparticles prepared with urea has the highest surface area. The micrographs of SEM showed that all of the nanoparticles have nano-crystalline behaviour and particles indication cubic shape. VSM analysis demonstrated that the type of fuel used for synthesis is highly effective a parameter on magnetic properties of nanoparticles.

1. Introduction

Nanotechnology is area of intense scientific research, due to a wide variety of potential applications in biomedical, optical, and electronic fields. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures.

The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometre the percentage of atoms at the surface is minuscule relative to the total number of atoms of the material.

Nanoparticles have, so far, been used in many applications including ferrofluids, catalysts, microwave devices, gas sensors and magnetic materials [1-3]. Synthesis and applications of magnetic nanoparticles of spinel structured ferrite (AB_2O_4) are among the most important research topics due to their remarkable chemical, physical and magnetic properties. The type of nickel ferrite with spinel structure is an essential composite material for the production of electronic and magnetic components extensively used in advanced technological applications, the most remarkable of which are magnetic ferrofluids, dense information storage system and high frequency systems [4, 5].

The ferrite is an inverse spinel in which eight units of NiFe_2O_4 goes into one unit cell of the spinel structure. Half of the ferric ions preferentially fill the tetrahedral sites (A-sites), while the other occupies the octahedral sites (B-sites). Therefore, the compound can be represented by the formula $(\text{Fe}^{3+})_A[\text{Ni}^{2+}\text{Fe}^{3+}]_B\text{O}_4^{-2}$, where A and B represent tetrahedral and octahedral sites, respectively. Its remarkable electrical and magnetic properties are based on the nature of the ions, their charges and their distribution among the tetrahedral (A) and octahedral (B) sites [6]. Nickel ferrite shows



ferromagnetism, which originates from magnetic moment of anti-parallel spins between Fe^{3+} ions at tetrahedral sites and Ni^{2+} ions at octahedral sites [7, 8].

Various chemical and physical techniques have been developed for the synthesis of NiFe_2O_4 nanoparticles such as sol-gel, hydrothermal, co-precipitation, aerosol, microwave, etc. that have the advantages for instance the low cost, low reaction time, large scale production. Common problems for many of these techniques are factors such as complex processes, expensive precursors and low production rates [9].

Alike the techniques, the combustion method is a promising chemical method for preparation of various nano-sized ferrites in laboratory and semi-pilot scale that is fast and safe furthermore enables the formation of nano-sized metal oxide particles and allows to produce the ferrites without need of sophisticated equipment [3, 10]. Organic compounds like glycine, urea, citric acid, alanine etc. are used as fuels in the combustion method, suitable that they can be mixed directly with the metal salts to enhance the efficiency of the synthesis. Among the organic compounds, urea seems to be the most commonly used compound that it appropriately is cheap, readily available, non-toxic and safe [3, 9, 10].

It is known that synthesis method of nanoparticles is highly effective on the structural, morphology and magnetic properties of nanoparticles. The organic materials used as fuel also has a significant impact on various properties of the nanoparticles in synthesis studies made with microwave assisted combustion method. In the literature, various chemicals have been proposed for use as fuel by various researchers. The most widely used fuels are compounds such as urea, glycine, citric acid, organic thio urea. Among these fuels, the most widely used substance are urea. Because, urea is readily and abundantly available, inexpensive, non-toxic and it can be produced in high purity, etc. Therefore, it finds wider usage area because of these important advantages [11, 12].

NiFe_2O_4 nanoparticles can synthesis with various methods such as combustion, sol-gel, hydrothermal etc... In this study, NiFe_2O_4 nanoparticles were synthesized with microwave assisted combustion method. In this method; some substances have to be used as fuel. The aim of this work was to investigate the effect of fuel type above structural, morphology and magnetic properties of NiFe_2O_4 nanoparticles synthesized with microwave assisted combustion method.

2. Materials and method

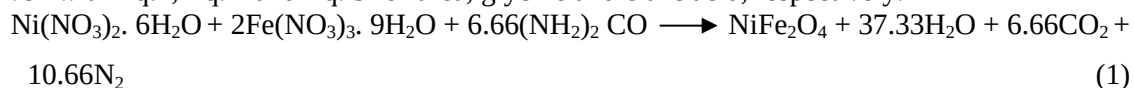
The preparation of materials

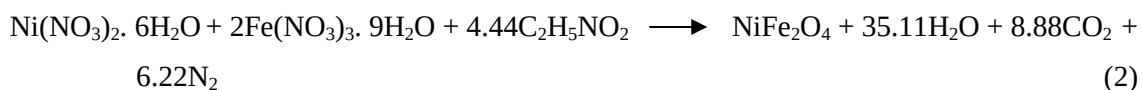
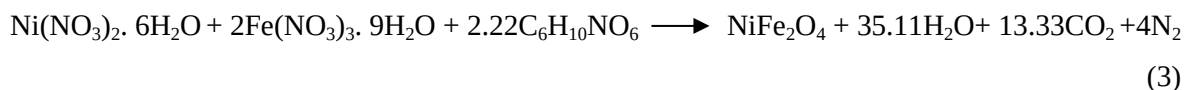
All chemicals used in this study have analytical purity, and these materials commercially produced is used without any additional purification. Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, >99%), iron (II) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, >99%), urea ($\text{CO}(\text{NH}_2)_2$, > 99%), glycine ($\text{NH}_2\text{CH}_2\text{COOH}$, > 99%), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, > 99%) and all other necessary chemicals were purchased from Sigma-Aldrich company.

Synthesis

Nickel ferrite was prepared from an exothermic reaction of a mixture of metallic nitrates and urea. Nickel nitrate, ferric nitrate and fuel reagent were mixed in certain stoichiometric ratios in a baker. The mixture was formed due to the hygroscopicity of metal nitrates, which absorbs air humidity [13]. Therefore, this method does not require the use of water or any solvent. Then, the mixture was placed in a laboratory-type microwave oven at a maximum power of 800 W for 10 min. When the solution reached the point of spontaneous combustion, it started burning by releasing a very dense gas and heat, and then the sample instantaneously became a solid [9].

In the experiments made to investigate the effects of fuel type in the synthesis of the NiFe_2O_4 nanoparticles with microwave assisted combustion method were used urea, glycine and citric acid as fuel reagent, respectively. The reactions occurred between nickel nitrate, iron nitrate and fuel reagents were given with Eq.1, Eq. 2 and Eq. 3 for urea, glycine and citric acid, respectively.





According to the reactions given above, nickel ferrite nanoparticles were obtained as a single product in the all of the reactions. However, H₂O, CO₂ and N₂ gases were evolved as gases in the products.

Characterization

In this study, XRD analysis were performed for the structural characterization of the synthesised nanoparticles. X-ray diffraction (XRD) analysis were performed with CuK α irradiation ($\lambda=1.5418 \text{ \AA}$) in the 2θ range $10-80^\circ$. The microscopic and morphological properties of the nanoparticles were characterized by Nova NS450 scanning electron microscopy (FEI, USA). The surface areas and the other surface characteristics were measured by the nitrogen adsorption principle the particle surfaces at low temperature. These measurements were made with Gemini VI model surface analyzer (Micromeritics Instruments, USA). Magnetic hysteresis loops were determined at room temperature, for fields up to 3 T.

3. Results

The synthesised nanoparticles should to have small grains, high surface area and adequate level of saturation magnetization values. It is known that these characteristics significantly depend on the type of the fuel used as reagent. In this study, glycine, urea and citric acid were used as fuel, respectively. Then the obtained samples were characterized by XRD, SEM, BET and VSM techniques. The results are presented below, respectively.

XRD Analysis

X-ray analysis performs to identify the atomic and molecular structure of a crystal. XRD is one of the key analysis in the determining of the structure. The synthesis mixture prepared in stoichiometric rates was put in to the kitchen type microwave oven. In the end of reaction time was obtained a brown-black solid and this solid was milled in a balling mill. Then obtained this powder were characterized with X-Ray powder diffraction system. The X-ray diffractograms of the obtained particles were given in Fig. 1.

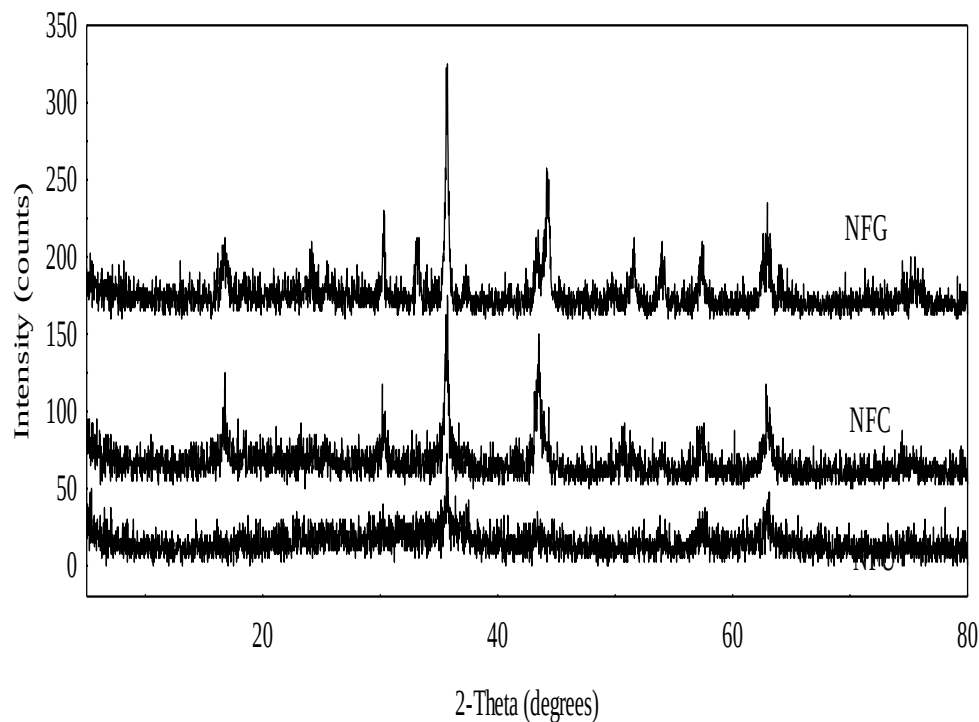


Figure 1. The X-Ray diffractograms of the nanoparticles prepared with various fuels

According to the XRD patterns given in Fig. 1., narrow and sharp reflection peaks were observed in the measured diffraction pattern for three fuel types. Moreover, it can be said that the glycine between used fuels have the most significant positive effect on the crystal structure and the conversion. However, all the diffraction patterns of the obtained nanoparticles were matched with standard powder diffraction cards of NiFe_2O_4 (JCPDS Card Number 54-0964) and determined to be fully compatible with standard reflection peaks.

Electron Microscopy (SEM) Analysis

The NiFe_2O_4 nanoparticles prepared with microwave assisted combustion method used different fuel type were characterized with scanning electron microscopy. The SEM images of the NiFe_2O_4 nanoparticles synthesized were given in Fig. 2.

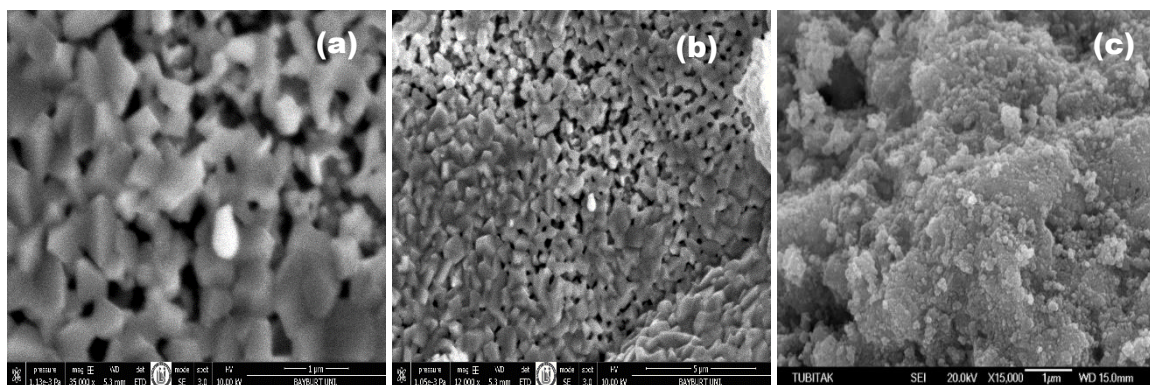


Figure 2. The SEM images of the NiFe_2O_4 nanoparticles synthesized (a) glycine, (b) citric acid, (c) urea

According to the results of SEM analysis, all nanoparticles prepared with three different fuel types consists of nanoscale particles. In addition, it was appeared that particles form large agglomerates. It was thought that formation of agglomerates originated from the electrostatic interactions between particles. Moreover, sintering may have occurred due from the happened high temperature during chemical reaction.

BET Analysis

To investigate the effects onto the surface properties of nanoparticles prepared with different fuels, BET analysis were made by using a surface analyzer. A sample contained in an evacuated sample tube is cooled (typically) to cryogenic temperature, and then is exposed to an analysis gas at a series of precisely controlled pressures. With each incremental pressure increase, the number of gas molecules adsorbed on the surface increases. The equilibrated pressure (P) is compared to the saturation pressure (P_0) and their relative pressure ratio (P/P_0) is recorded along with the quantity of gas adsorbed by the sample at each equilibrated pressure.

As adsorption proceeds, the thickness of the adsorbed film increases. Any micropores in the surface are filled first, then the free surface becomes completely covered, and finally the larger pores are filled by capillary condensation. The process may continue to the point of bulk condensation of the analysis gas. Then, the desorption process may begin in which pressure systematically is reduced resulting in liberation of the adsorbed molecules. As with the adsorption process, the changing quantity of gas on the solid surface at each decreasing equilibrium pressure is quantified. These two sets of data describe the adsorption and desorption isotherms. Analysis of the shape of the isotherms yields information about the surface and internal pore characteristics of the material. The obtained results in the end of measurement are shown in Figure 3. Various surface properties of the NiFe_2O_4 nanoparticles prepared with different fuels were presented in Table 1.

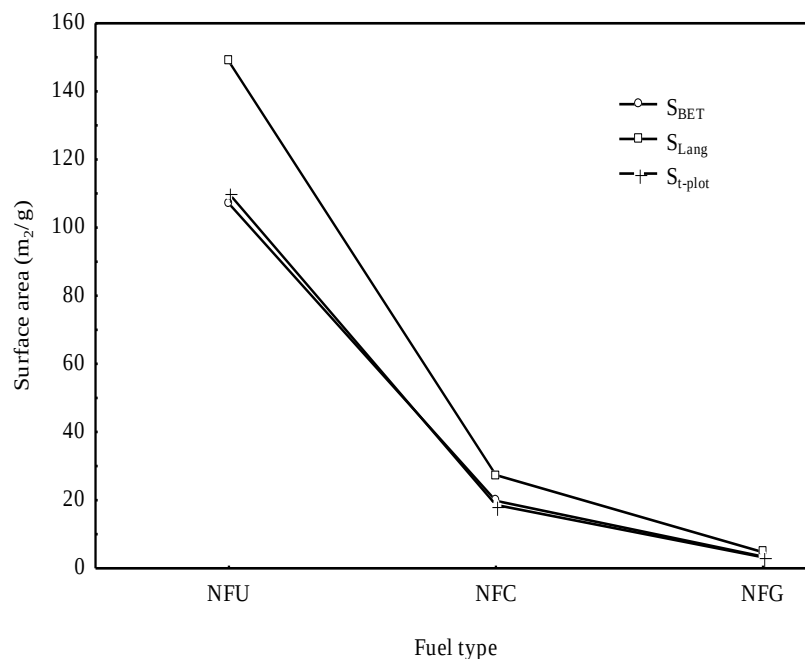


Figure 3. Effect of type of fuel used over the surface area of the NiFe_2O_4 nanoparticles

Table 1. Various surface properties of the NiFe₂O₄ nanoparticles prepared with different fuels

NiFe ₂ O ₄ Samples	Fuel type	S _{BET} (m ² /g)	S _{Lang.} (m ² /g)	S _{t-plot} (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (nm)
NFU	urea	107.094	148.8080	110.082	0.187014	6.8648
NFC	citric acid	19.0784	27.3815	18.6425	0.052319	10.2866
NFG	glycine	3.4268	4.7601	3.2934	0.016057	15.1929

According to the results given in Fig. 3., the highest surface area was measured for the NiFe₂O₄ nanoparticles prepared with urea. The surface area properties of NiFe₂O₄ nanoparticles depend on the fuel type used in the synthesis. According to Table 1, the BET surface area of nanocrystalline NiFe₂O₄ was determined as ~108 m²/g for urea, ~19 m²/g for citric acid, ~4 m²/g for glycine. The pore volume per mass was determined to be 0.1870 cm³/g for urea, 0.0523 cm³/g for citric acid, 0.0160 cm³/g for glycine. The effect of fuel type used on the total pore volume and average pore diameter of the NiFe₂O₄ nanoparticles is given in Fig. 4.

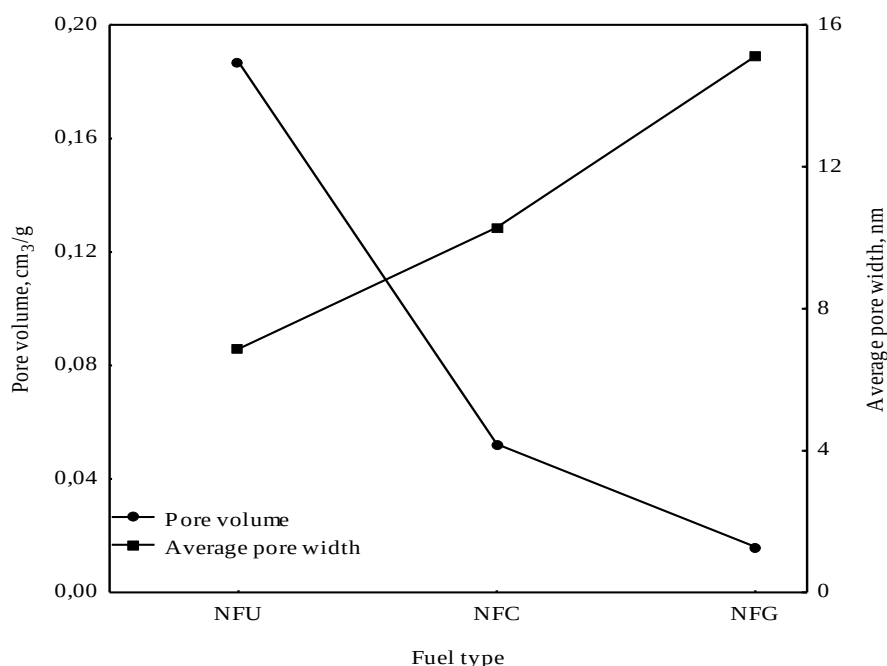


Figure 4. The effect of fuel type used on the total pore volume and average pore diameter of the NiFe₂O₄ nanoparticles

The highest value of average pore diameter was measured for the NiFe₂O₄ nanoparticles prepared with glycine. However, the highest value of total pore volume was measured for the NiFe₂O₄ nanoparticles synthesized using urea as fuel. Despite synthesized NiFe₂O₄ nanoparticles by using urea have the smallest pore diameter, they have the highest pore number. The smallest value of total pore was measured for sample prepared with glycine. Adsorption-desorption isotherms of the NiFe₂O₄ nanoparticles prepared with different fuels are showed Fig. 5. Hysteresis loop of adsorption and desorption isotherms were associated with a characteristic type IV and with mesoporous materials.

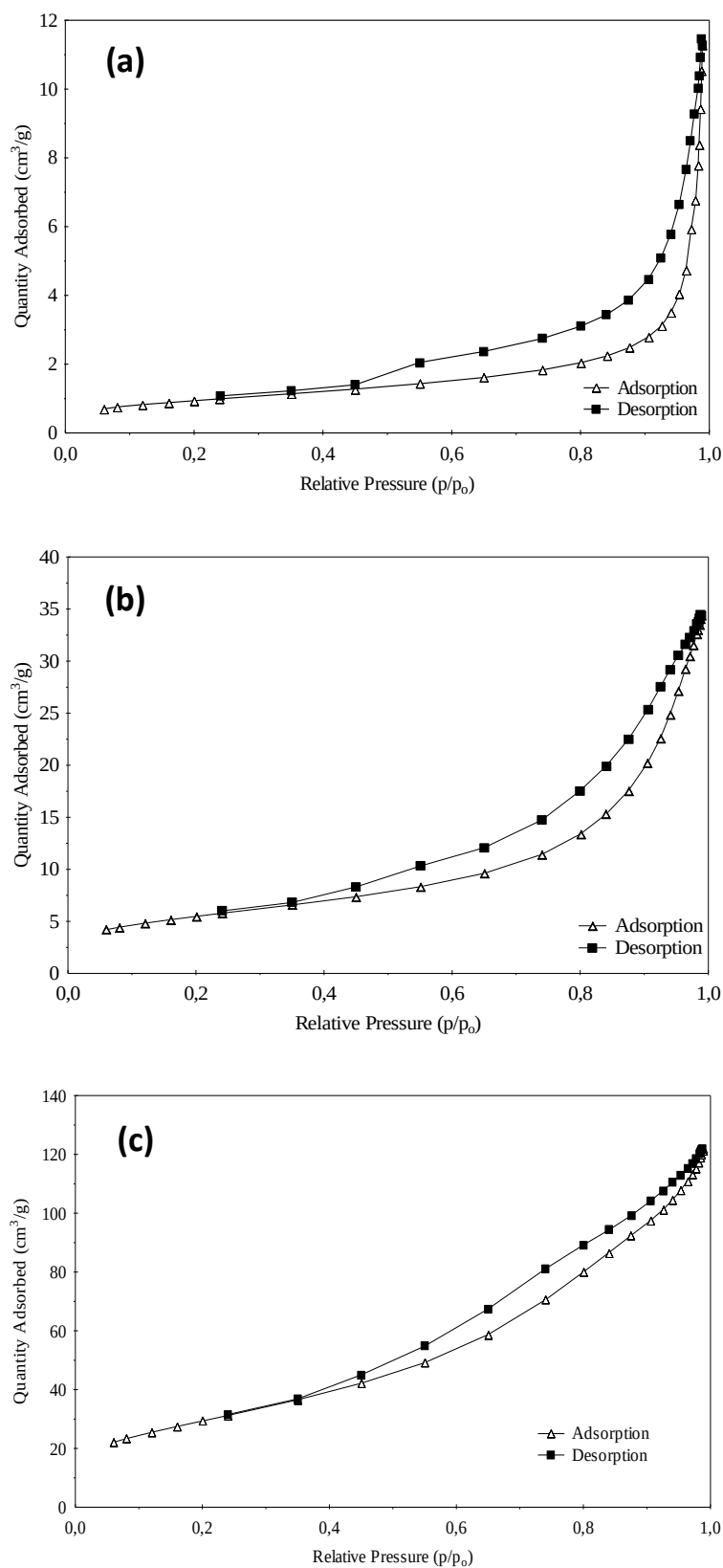


Figure 5. Adsorption-desorption isotherms of samples prepared with different fuels, (a) glycine, (b) citric acid, (c) urea

VSM analysis

In this study, it was investigated the effect of fuel type above magnetic properties of NiFe_2O_4 nanoparticles synthesized with microwave assisted combustion method. The fuel type used in synthesis of nanoparticles is quite effective above the crystal structure of nanoparticles. The crystal structure is the most important parameter on the magnetic properties of the nanoparticles. The magnetic properties of the materials are dependent on the sample shape, crystallinity, magnetization direction, etc. [14]. Magnetic characterization of the nickel ferrite nanoparticles is performed using a vibrating sample magnetometer (VSM) at room temperature with a maximum of 10kOe. The hysteresis loop curves of the nanoparticles were formed with the measured experimental data. The obtained results were given graphically in Fig.6.

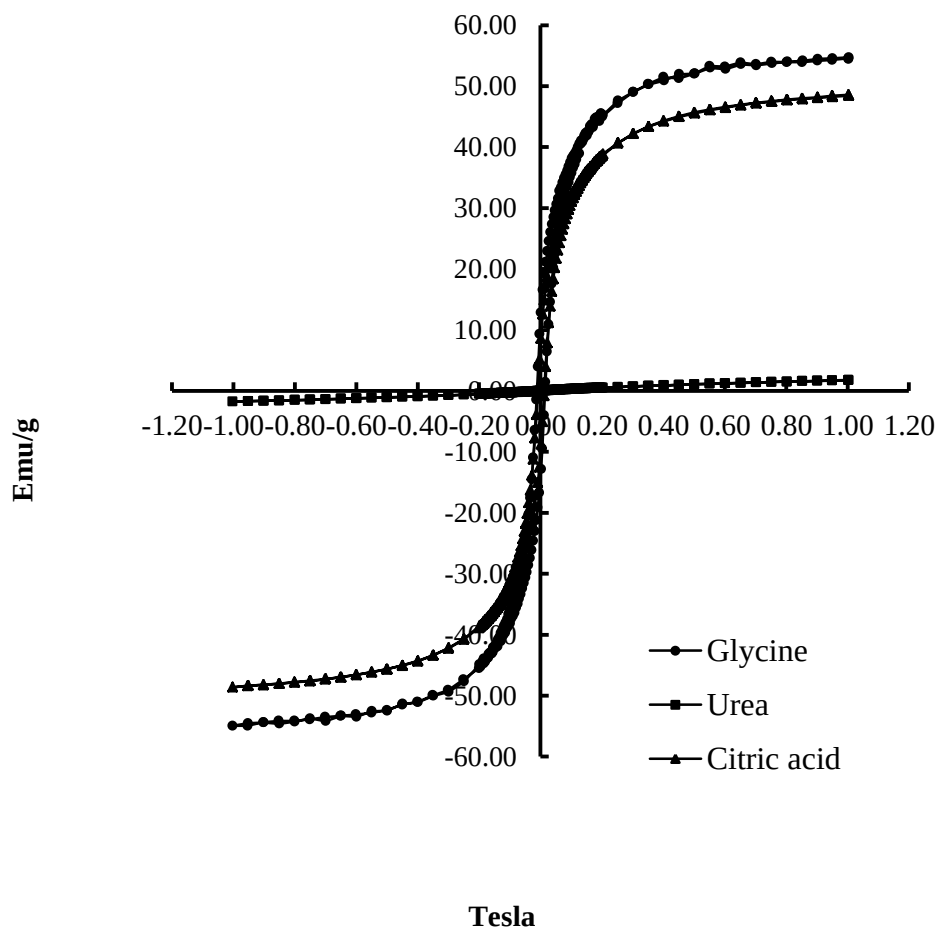


Figure 6. The hysteresis loop curves of the nanoparticles prepared with various fuels

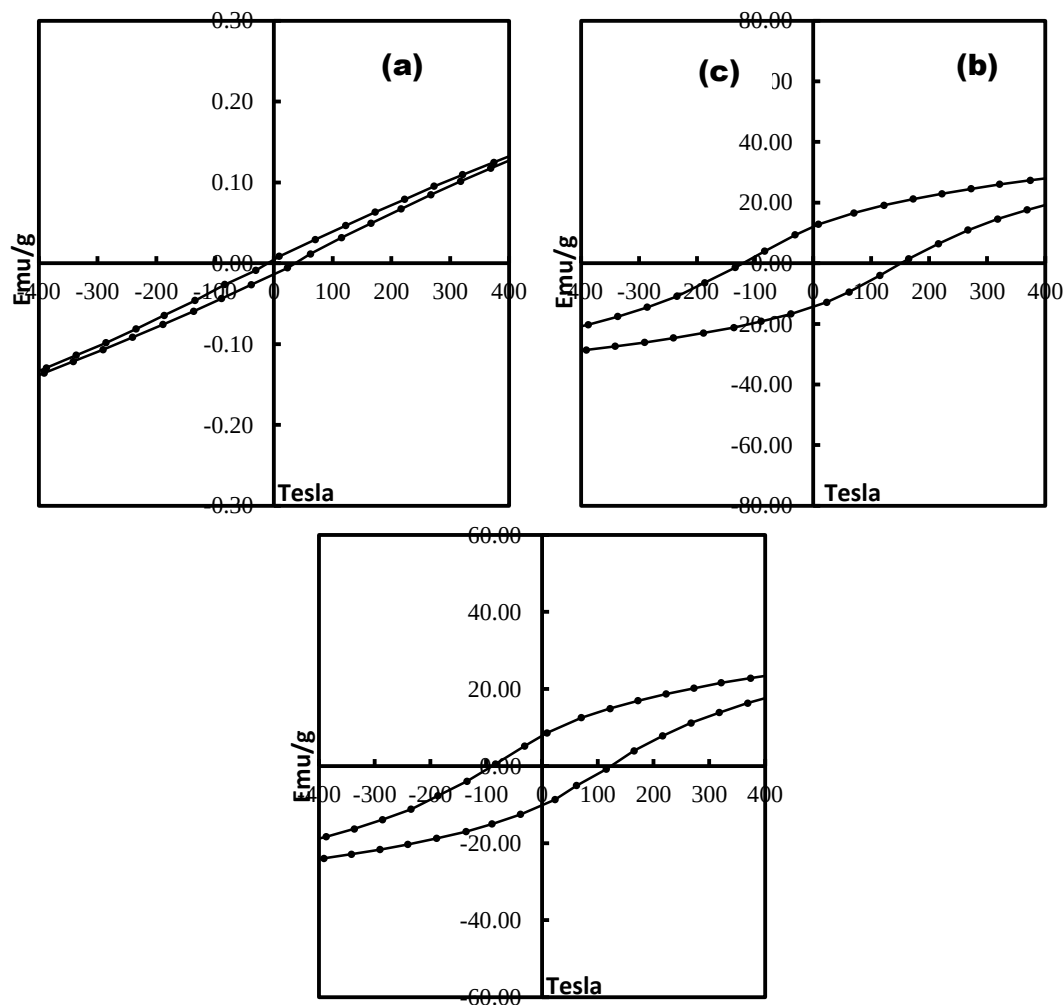
VSM measurements performed at room temperature show that all of the nanoparticles synthesized with different fuel type exhibited ferromagnetic behaviour. The magnetic properties of an substance alike saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) can be calculated from the hysteresis curve. Accordingly, magnetic properties measured at room temperature for nickel ferrite nanoparticles prepared with various fuels were presented in Table 2.

Table 2. The magnetic properties measured at room temperature for nickel ferrite nanoparticles prepared with various fuels.

NiFe ₂ O ₄ examples	Fuel Type	Saturation magnetization M _s (emu/g)	Remanent magnetization M _r (emu/g)	M _r / M _s	Coercivity field H _c (Oe)
NFU	Urea	1.73	0.0084	0.00490	23
NFC	Citric Acid	48,43	5.1950	0.10727	112,4
NFG	Glycine	54.55	9,3259	0.17096	128,6

The expanded graphs of origin region on the hysteresis curve in the range of approximately -400 to +400 Oe for the clear examination of hysteresis are given in Fig. 7. Accordingly, the largest saturation magnetization value was measured as 54,55 emu/g for the nanoparticle prepared with glycine and the smallest value was measured as 1.73 emu/g for the nanoparticles produced with urea.

The saturation magnetization values of the nickel ferrite nanoparticles are observed to change with different fuel type. The changing in saturation magnetization values is associated with the crystallinity of particles. According to graph given in Fig. 1, depending on the improvement in the crystal structure, the magnetization values of the nanoparticles were observed to increase.

**Figure 7.** The expanded graphs of origin region on hysteresis curve in the range of nearly -400 to +400 Oe. (a) urea, (b) glycine, (c) citric acid

4. Conclusion

NiFe₂O₄ nanoparticles can synthesis with various methods such as combustion, sol gel, hydrothermal etc... In this study, NiFe₂O₄ nanoparticles were synthesized with microwave assisted combustion method. In this method; some substances have to be used as fuel. The aim of this work was to investigate the effect of fuel type above structural, surface and magnetic properties of NiFe₂O₄ nanoparticles synthesized with microwave assisted combustion method. We observed that fuel type is quite effective on structural, surface and magnetic properties of the particles. The nanoparticles synthesized by using urea as fuel have got the highest surface area. But they have quite poor crystallinity. On the other hand, the nanoparticles synthesized by using glycine and citric acid have got more than better crystallinity. But their surface areas are smaller than the particles produced with urea.

According to the hysteresis loop curves of the nanoparticles, the magnetic properties of the NiFe₂O₄ nanoparticles changed with fuel type. The all of the samples showed ferromagnetic behaviour. But, the nanoparticles prepared by using glycine as fuel have got the more better saturation magnetization than the others.

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