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SYNTHESIS AND CHARACTERIZATION OF MAGNETITE NANOPARTICLES

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Abstract:

Magnetite (Fe_3O_4) nanoparticles have garnered the attention of researchers in the fields of renewable energy, electronics, and medicine over the past decade due to their magnetic and high magnetic susceptibility. The unique properties of magnetite make it an essential material for the development and advancement of renewable technologies. To obtain magnetite powder through hydrothermal synthesis, the precursors used were $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ aqueous solutions with a molar ratio of 1:2, and NaOH solution with a concentration of 2 M was used as the hydrolysis agent. The reaction took place at varying temperatures of 85°C, 150°C, and 200°C, and a pressure of 20 bar. The resulting powders were then subjected to morpho-structural characterization using techniques such as scanning electron microscopy and X-ray diffraction.

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1. INTRODUCTION

Renewable energy is an increasingly important topic nowadays in the context of global warming and climate change. One solution to reduce our dependence on fossil fuels and protect the environment is to rely more on renewable energy sources, such as solar energy, and eolian energy. To this end, researchers around the world are developing new technologies and materials to improve the efficiency and performance of renewable

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energy systems.

One such material is magnetic nanoparticles, which are obtained through hydrothermal synthesis. There is a compound called iron oxide that can be found naturally in different forms. Hematite, magnetite and maghemite are the three most frequently found types of iron oxide (Poonam Lathiya, Jing Wang, 2022).

Magnetite (Fe_3O_4) is a magnetic iron oxide nanoparticle that goes by the name black iron oxide. Of the transition metal oxides, it manifests the highest magnetism (Wu Wei et all, 2010).

At room temperature, Magnetite (Fe_3O_4) displays distinctive ferromagnetic characteristics that set it apart from other iron oxide variants. Based on the available literature, magnetite nanomaterials exhibit susceptibility to oxidation when exposed to air at temperatures exceeding 150°C (L. M. Cursaru et all, 2020). This is due to its unique composition of both divalent and trivalent iron. Fe_3O_4 is considered a semiconductor with both *p*-type and *n*-type properties. Despite this, Fe_3O_4 has the least resistivity among iron oxides, which can be attributed to its reduced band gap of 0.1 eV (Teja S.A., et all 2009).

Magnetic nanoparticles are extremely small particles, ranging in size from 1 to 100 nm, that exhibit magnetic properties. These properties make them ideal for a range of applications, including renewable energy (F. Wang et all, 2022).

Popular routes include sol-gel synthesis, hydrothermal synthesis, co-precipitation, microemulsion, thermal decomposition, ultrasonic synthesis, etc. (F. Zhao et all, 2012).

In the last decade, hydrothermal synthesis has become a very interesting method to obtain various nanostructured materials (powders and thin films) with controlled composition, particle size, and texture. The main advantages of the hydrothermal process include versatility, reduction of the number of technological operations, minimization of energy costs and chemical agent consumption, elimination or reduction of pollution, production of nanocrystalline powders with high reactivity at low cost and energy consumption (A. G. Plăiaşu et all, 2014).

In high-pressure hydrothermal synthesis, an external pressure higher than the equilibrium water vapour pressure is applied. These conditions lead to outstanding quality of the nanoparticles obtained, as the solubility of inorganic materials increases with increasing pressure (L. M. Cursaru et all, 2020).

By the hydrothermal reaction of ferrous sulphate, sodium hydroxide, and sodium thiosulphate at a temperature of 140°C, nanocrystalline magnetite particles were obtained. X-ray analysis of the powders showed that the magnetite formed has a single-phase, inverse spinel cubic structure. The composition of the magnetite particles was determined through conventional chemical analysis as well as XPS. Additionally, TEM images showcased that the particles have a quasi-spherical polyhedron shape that is uniform throughout, with an average diameter of 50 nm. (R. Fan et all, 2001).

In this article, we present a study on the synthesis of magnetic nanoparticles by hydrothermal method at 20 bar pressure and various temperatures. To obtain these particles, Fe^{2+} and Fe^{3+} precursors were used in a molar ratio of 1:2. The magnetic magnetite nanoparticles thus obtained have potential use in the development of catalysts for hydrogen production by electrolysis of water. The use of these catalysts, based on magnetic nanoparticles, can improve the efficiency of the hydrogen production process, thus having the potential to contribute to the more efficient production of renewable energy.

2. EXPERIMENTAL

2.1. Materials and methods

To elaborate magnetic powders, the following precursors $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ were used, with NaOH as a hydrolysis agent. The powders were washed seven times with distilled water and ethyl alcohol to eliminate chloride ions.

The chemicals used were purchased from Sigma-Aldrich.

2.2. Magnetite nanoparticles elaborated by hydrothermal synthesis

Hydrothermal synthesis is a pressurized heat treatment process that takes place in an autoclave containing an aqueous solution of precursors and hydroxides. This method was used at the Nanostructured Materials Laboratory of the National Research and Development Institute for Nonferrous and Rare Metals in Bucharest. The synthesis was carried out at a pressure of 20 bar and different temperatures (85°C, 150°C, and 200°C). Aqueous solutions of $FeCl_2{\cdot}4H_2O$, and $FeCl_3{\cdot}6H_2O$ in a molar ratio of 1:2 were used for the synthesis, together with a 2 M NaOH solution as hydrolysis agent. After obtaining the magnetite nanoparticles, they were cleaned using distilled water to remove Cl^-, and ethyl alcohol to prevent agglomeration. The equipment used in the hydrothermal synthesis was a Berghof autoclave.

The parameters used for hydrothermal synthesis are presented in the following Table 1.

Table 1. Experimental parameters for hydrothermal synthesis

Sample	Precursor	Precursor concentration	Precipitating Agent	Reaction parameters	
				t^0C	P (bar)
GP1	$FeCl_2{\cdot}4H_2O$ $FeCl_3{\cdot}6H_2O$	0.4 M Fe^{3+}	2M NaOH	85^0C	20 bar
GP2				150^0C	
GP3				200^0C	

2.3. Characterization

The morphology and size of the nanoparticles were observed using scanning electron microscopy (SEM) with the HITACHI SU8230 equipment. X-ray diffraction analysis was conducted for the obtained powders with the Rigaku Ultima IV diffractometer, which was equipped with a D/teX ultra detector, graphite monochromator for kβ radiation, and a vertical goniometer in Bragg-Brentano focusing. The range of the 2θ angle was set between 15° and 100°, with a step size of 0.05° and a scanning rate of 3°/min. CuKα radiation was used to record the XRD diffractogram, and PDXL 2 software was utilized to carry out XRD spectrum analysis. The PDF 4+ 2022 database was used to identify the crystalline compound.

3. RESULTS

3.1. Magnetite nanoparticles synthesis

Magnetite nanoparticles are a type of nano ferrite with a crystalline structure. They are composed of the iron mineral Fe_3O_4, which consists of a combination of Fe^{2+} and Fe^{3+} oxides. The synthesis of magnetite nanoparticles was performed by the hydrothermal route, which involves a chemical reaction as shown in the equation below:

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O$$

The magnetite powder obtained from hydrothermal synthesis exhibits magnetic properties (it can be attracted to a magnet when brought close to it, as shown in Figure 1).

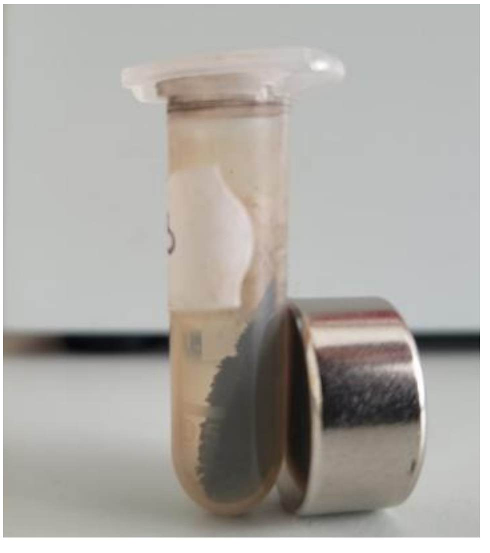

Figure 1. Powder of magnetite attracted by the magnet

Black iron oxide, commonly referred to as magnetite, possesses the property of serving as a black pigment. Conversely, various other iron oxides, namely hematite, maghemite, and goethite, can be utilized as pigments of red, brown, and yellow hues.

3.2. Morphological and elemental characterization

The HITACHI SU8230 scanning electron microscope was used to characterize the morphology and elements of the nanoparticles obtained by hydrothermal synthesis. Particle sizes were determined using ImageJ image analysis software. The morphology of the iron oxide particles was revealed by micrographs obtained by these methods, and the results are shown in the following figures:

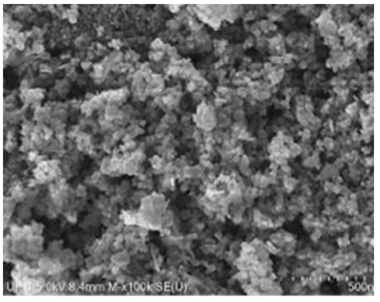

Figure 2. SEM micrograph of GP1 powder at 85°C (×100k mag.)

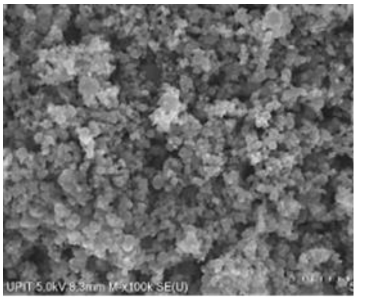

Figure 3. SEM micrograph of GP2 powder at 150°C (×100k mag.)

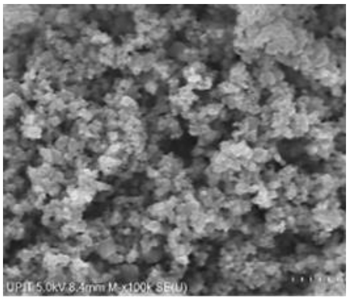

Figure 4. SEM micrograph of GP3 powder at 200°C (×100k mag.)

The GP1 powder, synthesized at 85°C, shows a uniform, predominantly polyhedral morphology, as can be seen in Figure 2. This morphology is similar to that present in the micrographs of the GP2 powder, obtained by hydrothermal synthesis at 150°C (Figure 3). In the case of the GP3 powder, obtained at 200°C, it can be seen that the morphology of the particles has not changed significantly (Figure 4).

Using ImageJ image analysis software, ten measurements were made to accurately estimate the particle size of GP1, GP2, and GP3 powders. For the GP1 powder, polyhedral particles with diagonals between 19-28 nm were identified. For GP2 powder, the diagonals of the polyhedral particles identified range from 18 nm to 34 nm, and for GP3 powder, the diagonals of the polyhedral particles range from 21-34 nm. By making ten measurements, the aim was to obtain as accurate an estimate of the particle sizes as possible.

The results are presented in the table 2.

Table 2. Average particle size for samples GP1, GP2, and GP3

Sample	Technological parameters /Precursor Concentration/ pH / Temperature Synthesis	Average particle size (nm)	Morphology
GP_1	0.4 M Fe^{3+}, pH=11/ **85°C**	21	polyhedron
GP_2	0.4 M Fe^{3+}, pH=11/ **150°C**	23	polyhedron
GP_3	0.4 M Fe^{3+}, pH=11/ **200°C**	27	polyhedron

Different particle sizes can be observed depending on the synthesis temperature. Particle sizes range from 21 nm at 85°C, 23 nm at 150°C and 27 nm at 200°C. This change in particle size is explained by the increase in nucleation rate with increasing synthesis temperature. EDS elemental analysis of the processed powders shows the presence of elements in the composition (Figure 5).

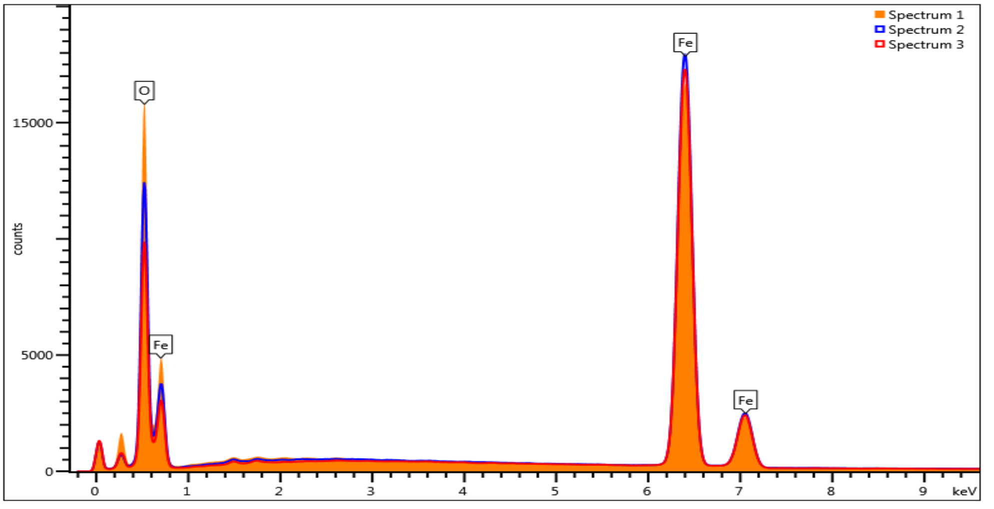

Figure 5. Overlap of EDS spectra of GP1, GP2 and GP3 powders

The EDS spectra show X-ray fluorescence peaks corresponding to Fe and O elements, without the presence of impurities. This finding confirms that hydrothermal synthesis is an optimal method for producing nanostructured iron oxide.

3.3. Structural characterization

Using the PDF 4+2022 database, all powders were identified as having a single crystalline phase with a cubic structure, magnetite (as shown in Table 3), as shown in the XRD spectra shown in Figure 6. Comparing the diffraction picks for GP3 powder with GP2 and GP1, it can be seen from the XRD spectra that it shows higher and narrower intensities at higher temperatures (200°C). The crystallinity of magnetite powders occurred at 200°C.

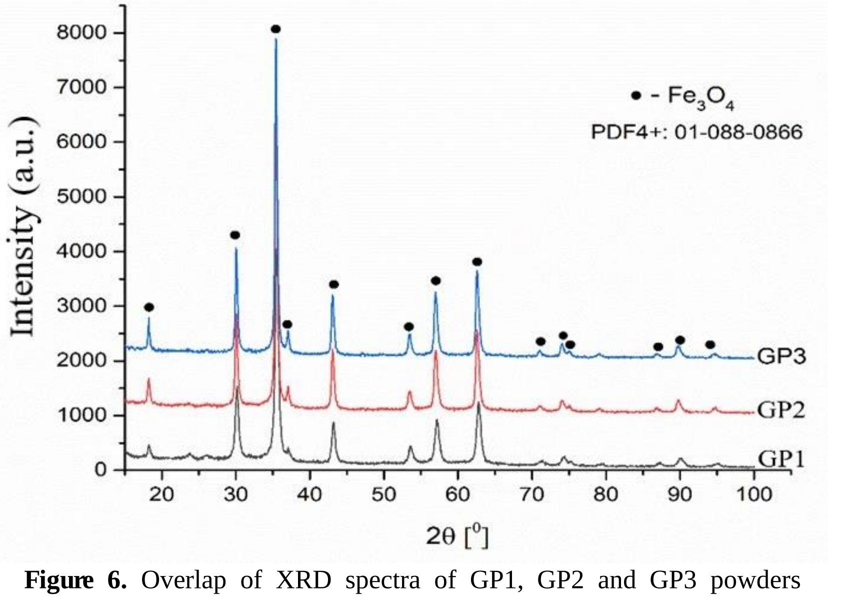

Figure 6. Overlap of XRD spectra of GP1, GP2 and GP3 powders

Table 3 displays the findings of the qualitative and quantitative phase analyses conducted through the utilization of the PDF 4+ database and Scherer relation on chosen crystal planes {104}.

Table 3. Qualitative and quantitative phase analysis of nanostructured iron oxide

Sample	Technological parameters /Precursor Concentration/ pH / Temperature synthesis /	Qualitative phase analysis			Crystallite size (nm)
		Phase name	Chemical formula	PDF4+2022- DB	
GP_1	0.4 M Fe^{3+}, pH=11/**85^0C**	magnetite	**Fe_3O_4**	01-088-0866	13 ± 1.3
GP_2	0.4 M Fe^{3+}, pH=11/**150^0C**	magnetite	**Fe_3O_4**	01-088-0866	16 ± 0.3
GP_3	0.4 M Fe^{3+}, pH=11/**200^0C**	magnetite	**Fe_3O_4**	01-088-0866	27 ± 0.4

As the synthesis temperature increases, an increase in crystallite size from 13 nm to 27 nm is observed, according to the experimental results. These findings are in agreement with research by Phong and co-workers presented in the paper "*Iron oxide nanoparticles: tunable size synthesis and analysis in terms of core-shell structure and mixed coercive model*", which indicates that crystallite sizes in iron oxide powders obtained by the hydrothermal method at different temperatures (100°C-180°C) increase from 5.8 nm to 19.5 nm (Phong P. T. et all, 2017).

4. CONCLUSIONS

Three types of powders have been obtained from experimental investigations on the hydrothermal synthesis of magnetite. Morpho-structural analysis was approved out by SEM and XRD, and ImageJ image analysis software revealed a particle size variation between 21 nm and 27 nm with increasing synthesis temperature from 85°C to 200°C. All samples showed a single crystalline phase, magnetite, in agreement with PDF4+2022-DB: 01-088-0866. The crystallite size of the powders increased from 13 nm to 27 nm with increasing synthesis temperature from 85°C to 200°C. The hydrothermal method was found to be optimal for obtaining nanostructured iron oxide as magnetite. The optimum parameters for hydrothermal synthesis of nanostructured iron oxide with crystallite size below 25 nm are $FeCl_2 \cdot 4H_2O$: $FeCl_3 \cdot 6H_2O$ = 1:2, 2M NaOH, t_1 = 85°C, t_2 = 150°C, $t_{synthesis}$ = 1h30min, pH = 11. The obtained results can be considered an original contribution to the field of nanostructured iron oxide synthesis.

In conclusion, the hydrothermal synthesis method yields magnetic nanoparticles that show significant promise in increasing the efficiency of solar panels, wind turbines, advanced batteries, and hydrogen production catalysts, thus proving valuable for renewable energy applications.

Author Contributions: Ecaterina Magdalena Modan analyzed/interpreted the data and draft the manuscript, Roxana Mioara Piticescu and Laura Madalina Cursaru realized hydrothermal synthesis procedure, Denis Aurelian Negrea performed SEM analysis and interpretation, Sorin Georgian Moga Negrea performed XRD analysis and interpretation, Cătălin Marian Ducu has reviewed and approved the final version for publication.

Conflict of Interest Statement: There is no conflict of interest in this article.

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