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ADVANCED MATERIALS BASED ON MAGNETIC NANOPARTICLES USED IN BIOMEDICAL AND ENVIRONMENTAL APPLICATIONS

PhD Thesis – Abstract
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Scientific supervisor,
Prof.univ.dr.eng. Cornelia PĂCURARIU

Author,
eng. Diana-Aylin CĂPRARU (m. SCHULZE)

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INTRODUCTION

The aim of the thesis consists in the synthesis of magnetic nanoparticles using the combustion method and the solvothermal method respectively, their characterization, the comparison of their properties with those obtained by using other methods reported in the literature, as well as their use in different applications.

In this regard, the following objectives were taken into account:

- Study of the influence of fuel type and the combustion reaction conditions on the characteristics of iron oxide nanoparticles.
- Study of the influence of residual carbon on the characteristics of iron oxide nanoparticles.
- Establishing the optimal conditions for obtaining colloidal suspensions starting from magnetic nanoparticles of iron oxides synthesized by the combustion method and evaluation of their potential applicability in the biomedical field.
- Study of the adsorption capacity of a Fe_3O_4/Ag/C nanocomposite obtained by the combustion reaction.
- Study of the influence of surfactant type on manganese ferrite powders $MnFe_2O_4$ and manganese ferrite-polyaniline hybrid materials $MnFe_2O_4$/PANI via solvothermal method.

To achieve the previously described objectives, the following activities were carried out:

- → Iron oxide nanoparticles were synthesized by solution combustion synthesis and the influence of the fuel nature as well as the oxidizing agent-fuel molar ratio on the iron oxide nanoparticles properties were evaluated.
- → Nanoparticles of iron oxides were synthesized by the combustion method using comparatively the conventional reaction initiation, with a heating mantle and using microwave initiation.
- → The influence of residual carbon on the properties of iron oxides and its removal by treatment with hydrogen peroxide was investigated.
- → Magnetic colloidal suspensions were obtained and characterized using different surfactants and dispersed in various carriers.
- → The colloidal suspensions were characterized and their potential use in biomedical applications was evaluated.
- → The Fe_3O_4/Ag/C nanocomposite was synthesized via combustion method and characterized.
- → The adsorption capacity of the Fe_3O_4/Ag/C nanocomposite was tested using three dyes in mono- and multi-component systems in aqueous media.
- → Manganese ferrite powders $MnFe_2O_4$ and $MnFe_2O_4$/PANI hybrid materials were synthesized and characterized, working comparatively with two surfactants which were previously not reported in literature. Their electrical and magnetic properties were evaluated.

I. Theoretical Study

I.1. The importance of iron oxide nanoparticles

Iron oxide nanoparticles have been intensly studied in the recent years due to thier use in a variety of applications: from nanomedicine, used in cell separation, drug delivery, tumor treatment via hyperthermia [1], to biotechnology, such as chemical sensors, catalysts or electromagnetic materials [2].

Among the magnetic nanomaterials, magnetite (Fe_3O_4) and/or maghemite (γ-Fe_2O_3) present the most outstanding characteristics such as: superparamagnetism, high saturation magnetization values, low Curie temperature, high magnetic susceptibility as well as biocompatibility, which makes them attractive for a variety of applications [3, 4].

The importance of nanoparticles results primarily from their controllable size (between 1 and 100 nm), which makes them suitable for various applications where small particles are required. For example in bimedicine, the size of nanoparticles is comparable to that of cells (10 - 100 μm), viruses (20 - 450 nm), proteins (5 - 50 nm) and genes (2 nm wide and 10 - 100 nm long) [5].

The surfaces of iron oxides are endowed with strong adsorption forces of diverse nature, such as electrostatic interactions, ion-exchange and ion-association tendencies, complex formations, thus being adequate materials for the removal of pollutants from waste environments [6].

I.2. Properties of iron oxide nanoparticles

The characteristics of iron oxide nanoparticles are very important because they determine their subsequent use. Fields of activity such as biomedicine, wastewater treatment, high-density data storage, ferrofluids, magnetic resonance imaging, bioseparations, catalysts, and electrode materials require nanomaterials of specific sizes, shapes, surface characteristics, and magnetic properties [7].

The crystallographic phase depends, for example, on the oxidation state, crystallite size and thermodynamic parameters such as pressure and temperature. Magnetite contains Fe^{2+} ions, which will oxidize even under ambient conditions to Fe^{3+}, resulting in maghemite. Maghemite transforms at temperatures higher than 300 °C into hematite, which is the most stable phase under ambient conditions [8].

The magnetic behavior of iron oxide nanoparticles is crucial for their efficiency in various applications [9].

I.3. Synthesis methods

There is a correlation between the field of use of the nanoparticles obtained and the properties of the respective material, and at the same time, the properties are influenced by the applied synthesis method and conditions. An ideal synthesis method should be able to reliably adjust the properties of iron oxide nanoparticles, such as particle distribution, size control, shape control, phase composition, crystallinity and purity, by controlling synthesis parameters such as: temperature, pH, stirring speed, concentration of the reactants and so on [10].

Numerous chemical, physical and biological methods for obtaining iron oxides nanoparticles have been reported in the literature. By far the most used techniques are chemical ones due to the low production cost and high production yield [11].

However, these synthesis methods present limitations due to sensitive working parameters, require long working times or additional calcination steps, which lead to additional costs. Therefore, the development of new reliable synthesis methods is an ongoing challenge.

II. Experimental work

This doctoral thesis foscuses on the synthesis of magnetic iron oxides nanoparticles, with tailored properties, with the aim of their subsequent use both in the biomedical and technological fields. To obtain these materials, the solution combustion synthesis and the solvothermal method were used.

The solution combustion synthesis involves an exothermic, self-propagating redox reaction in a liquid medium between an oxidizing agent and a reducing agent (fuel). According to the most recent publications in the field [12, 13], the solution combustion synthesis meets all the conditions imposed on a synthesis method, as it is efficient, versatile, simple, involving short reaction time (several tens of seconds), low costs of raw materials, minimal energy consumption (no subsequent calcination of the reaction product is required), while being environmentally friendly (secondary reaction products are N_2, H_2O and CO_2, environmentally friendly gases).

The high versatility of the solution combustion synthesis is mainly due to the large number of parameters that can be modified in order to obtain materials with properties necessary for their subsequent use. The most important parameters that influence the characteristics of the finished product are: the type of fuel used, the ratio between the amount of fuel and the metal cation, the type of metal precursor, the conditions in which the reaction takes place (in the presence or absence of air) or the manner of initiating the reaction combustion [14, 15, 16, 17, 12].

Within the doctoral thesis, contributions were also made in the synthesis of manganese ferrite ($MnFe_2O_4$) and the corresponding hybrid materials, manganese ferrite/polyaniline ($MnFe_2O_4$/PANI), using the solvothermal method and in the presence of two surfactants which have previously not been reported in the literature, i.e. tetra-n-butylammonium bromide (TBAB) and Tween 80 (TW), respectively.

II.1. Solution combustion synthesis of magnetic iron oxide nanoparticles with tailored properties

In this chapter, the correlation between the most important parameters that influence the combustion reaction (the type of fuel used, the atmosphere in which the reaction takes place, the molar ratio between the metal cation and the fuel, the way the reaction is initiated, the influence of residual carbon) and the properties of the resulted iron oxide nanoparticles is investigated.

II.1.1. Effect of the fuel type and reaction atmosphere on iron oxide properties

Eight different organic compounds were used as fuel: glucose, citric acid, Tween80, hexamethylenetetramine, ethylenediaminetetraacetic acid, triethanolamine, glycine and urea, and the combustion reactions were conducted comparatively in the presence of air, in a capsule, respectively in absence of air, in a round bottom flask sealled with a stopcock.

Carrying out the combustion reaction in the presence of air, in the capsule, regardless of the nature of the fuel, allows the formation of hematite, α-Fe_2O_3, as the dominant phase, respectively of maghemite, γ- Fe_2O_3, as a secondary phase. Iron oxide powders prepared in a controlled atmosphere, in the absence of air, yield a mixture of maghemite, γ- Fe_2O_3, as the main phase and magnetite, Fe_3O_4, as a secondary phase, regardless of the type of fuel used.

Hexamethylenetetramine is an exception, since the reaction products are the same, regardless of the reaction atmosphere: hematite, as well as hematite as the main phase together with maghemite as the secondary phase.

The characteristics of iron oxides varied depending on the nature of the fuel used, but

also according to the working atmosphere chosen. Thus, the specific surfaces of the powders obtained in the absence of air are higher than those obtained in the presence of air and vary between 1.29 and 134.3 m^2/g. The high values of the specific surface areas were obtained for the samples prepared in the absence of air, in the flask with triethanolamine (134.3 m^2/g), glucose (86 m^2/g) and ethylenediaminetetraacetic acid (78 m^2/g).

In terms of nanocrystalline character, the smallest maghemite/magnetite crystallite size was obtained using triethanolamine (5 nm), glucose (7 nm), and ethylenediaminetetraacetic acid (10 nm).

II.1.2. Effect of the iron nitrate/ fuel ratio on iron oxide properties

Three organic compounds (glucose, EDTA, or TEA) were used as fuel, under and over stoichiometric molar ratio between iron nitrogen and fuel.

Regardless of the type of fuel used, its presence in excess contributes to the formation of maghemite, alongside magnetite. On the other hand, it was observed that the use of a fuel deficit does not ensure the formation of γ-Fe_2O_3 or Fe_3O_4; the resulting powder is practically amorphous.

The way in which the crystallite size varies with the molar ratio of iron nitrogen to fuel depends on the nature of the fuel used. Thus, in the case of samples obtained with EDTA and TEA, the presence of excess fuel favored the reduction of crystallite size compared to samples prepared under identical conditions, but with a stoichiometric ratio. A distinct behavior was observed in the case of glucose, for which the use of excess fuel led to an increase in crystallite size compared to the stoichiometric counterpart.

The thermal analyzes of the samples obtained with different molar ratios of iron nitrogen/fuel showed that the use of an excess of fuel contributes to the increase of the residual carbon content, compared to the samples prepared under identical conditions, but with a stoichiometric molar ratio.

Samples obtained with excess of fuel show lower specific surface areas compared to those obtained with a stoichiometric ratio between iron nitrate and fuel. A similar evolution was observed in the magnetic properties.

II.1.3. Effect of the combustion reaction ignition on iron oxide properties

Initiation of the combustion reaction was achieved by heating the precursor mixtures in a heating mantle and in a microwave oven. Iron nitrate was used as a source of iron and three different reagents were used as fuel, namely: citric acid, ethylenediaminetetraacetic acid (EDTA) and triethanolamine (TEA).

From the point of view of the effect of the initiation manner of the combustion reactions, the crystalline products of the combustion reactions are the same (maghemite and/or magnetite), in the case of using citric acid, EDTA or TEA as fuels.

It was noted that the samples prepared with citric acid or EDTA activated in the microwave oven have smaller crystallite sizes compared to the heating mantle activated samples (except TEA).

The specific surfaces obtained by microwave initiation are considerably smaller and the saturation magnetization values are higher compared to those obtained in the heating mantle when using EDTA and TEA as fuels.

The sample prepared with citric acid with a stoichiometric ratio is an exception as it shows smaller crystallite and particle sizes, higher specific surface area and lower values of saturation magnetization compared to the sample activated in the heating mantle.

II.1.4. Effect of residual carbon on iron oxide properties and removal by treatment with hydrogen peroxide

A two-step method for the preparation of maghemite nanopowders with high specific surface area was designed: the first step consists in the synthesis by solution combustion synthesis of magnetic iron oxide nanoparticles embedded in an amorphous carbon matrix. The second phase involves the removal of the residual carbon matrix by treatment with hydrogen peroxide and thus, releasing the magnetic nanopowder.

The combustion reaction conducted in the absence of air using iron nitrate as well as, glucose, EDTA, TEA and triethylenetetramine as fuels, yields a mixture of nanocrystalline maghemite dispersed in an amorphous residual carbon matrix of black colour. After applying the chemical treatment by addition of hydrogen peroxide, the color of the powders changes from black to brown.

The thermal analyzes show that after the oxidative treatment of the powder prepared with triethylenetetramine, the carbon content decreases from 59.6% in the untreated sample to only 6.2% in the sample treated with hydrogen peroxide.

Subsequently to the treatment of the powders with hydrogen peroxide, a significant increase of the specific surface area from 93 m^2/g to 191.9 m^2/g and of the saturation magnetization from 21.6 emu/g to 56.5 emu/g depending on the nature of the fuel used is noted.

The results obtained show that this approach avoids the removal of carbon by heat treatment, thus preserving the nanometric size of the maghemite nanoparticles allowing the increase of the specific surface area and the saturation magnetization of the samples, irrespective of the nature of the fuel used.

II.1.5. Preparation of colloidal suspensions with magnetic properties and biomedical application

Colloidal suspensions were prepared starting from magnetic nanoparticles (previously obtained by the combustion method under different conditions), by coating with several types of surfactants (oleic acid, Tween 80, citric acid, SiO_2) and dispersing in different carrier media, such as water or phosphate-buffered saline (PBS).

Colloidal suspensions stabilized with oleic acid show high stability, confirmed by significant negative values of the Zeta potential, ranging between - 42.07 mV and - 87.01 mV, regardless of the dispersion medium, water or PBS.

The stabilization of colloidal suspensions with Tween 80 (nonionic surfactant) leads to values of the Zeta potential between -11.82 mV and -15.51 mV, much lower compared to those resulting from stabilization with oleic acid, which proves that the steric stabilization of the suspensions colloidal provided by Tween 80 is less efficient compared to the electrosteric stabilization provided by oleic acid.

The nature of the dispersion medium, distilled water or PBS, does not significantly influence the stability of the colloidal suspensions, only a slight decrease in stability is noted when PBS is used as the dispersion medium.

It is also noted that the polydispersity index (PDI) shows values close to zero which indicates a small polydispersity, so a dimensional homogeneity of the colloidal suspensions.

The hydrodynamic diameter of the particles shows values between 54.1 nm and 145.7 nm which indicates that the prepared suspensions are suitable for biomedical applications, also considering their stability as well as their good solubility in aqueous solutions.

Four of the colloidal suspensions prepared under different conditions were tested in order to evaluate the toxicological profile/biological activity in relation to human tumor liver cells, as well as in relation to healthy human liver cells.

The viability of tumor cells is not affected, regardless of the tested colloidal suspension

and the concentration used, while in the case of healthy cells, a decrease in cell viability is observed starting from the concentration of 20 μg/mL.

A rare phenomenon of enucleation was observed in tumor cells, but also in healthy ones in the case of suspensions stabilized with Tween 80, while in the case of the suspension stabilized with oleic acid and dispersed in PBS this phenomenon appears starting with high concentrations, of 25 μg/mL.

During the evaluation of the toxicological profile/biological activity in relation to tumor and healthy liver cells, the best results were achieved in case of the suspension obtained from magnetic iron oxide nanoparticles resulting from initiation of the combustion reaction in microwave oven, working with a stoichiometric molar ratio of ferric nitrate to citric acid, as fuel. The synthesized nanoparticles were then coated with double layer oleic acid and dispersed in PBS.

II.1.6. Combustion synthesis of Fe_3O_4/Ag/C nanocomposite with magnetic properties and its environmental application

A nanocomposite based on magnetite, silver and carbon (Fe_3O_4/Ag/C) was prepared by solution combustion synthesis, with properties suitable for its use as an adsorbent for the removal of anionic and cationic dyes from mono- and multi-component systems.

Solution combustion synthesis allows obtaining of the Fe_3O_4/Ag/C nanocomposite with a specific surface area of 744.7 m^2/g and a saturation magnetization of 2.6 emu/g, which are favorable characteristics for its use as an adsorbent for the removal of anionic and cationic dyes from mono- and multi-component systems.

It was established that the Fe_3O_4/Ag/C nanocomposite shows a very high yield (>90%) for the removal of the three investigated dyes (Metylene Blue, Acid Orange 7 and Rodamine 6G) from aqueous solutions over the entire analyzed pH range (2.7 - 12.1) and for a dose of 1 g/L.

In the case of ternary systems, the removal efficiency decreases as the pH increases for the anionic dye (acid orange 7) and increases for the cationic dyes (methylene blue and rhodamine 6G) due to electrostatic interactions, but the differences are not significant.

For all investigated systems, the adsorption kinetics can be described by the pseudo-second order kinetic model, and the Sips isotherm model describes the adsorption process in the single system. The estimated maximum adsorption capacities were 152.62 mg/g, 154.57 mg/g, and 168.68 mg/g for Methylene Blue, Acid Orange 7, and Rhodamine 6G, respectively, which are higher or comparable to the values reported in literature in the case of using other magnetic nanocomposites.

The obtained results showed that Fe_3O_4/Ag/C presents both the advantage of a high adsorption capacity for anionic and cationic dyes in aqueous solutions and that of easy phase separation with the help of a magnet, which recommends it as a viable alternative for applications in the field of environmental protection.

II.2. Synthesis of manganese ferrite powders and manganese ferrite-polyaniline hybrid materials via solvothermal method. Electrical and magnetic properties

The effect of the surfactant nature on the properties of the $MnFe_2O_4$ powder and the $MnFe_2O_4$/PANI hybrid materials obtained by the solvothermal method was studied.

The use of surfactants influences both the characteristics of ferrite nanopowders and their coresponding composites with PANI. The best results were obtained in the case of samples prepared with Tween 80.

The $MnFe_2O_4$ powders exhibit a specific surface area between 79.8 and 97.1 m^2/g, much higher compared to that obtained in the case of $MnFe_2O_4$/PANI hybrid materials with values

between 21.6 and 34.0 m^2/g. In the case of $MnFe_2O_4$/PANI hybrid materials, the highest specific surface area value was obtained using Tween 80 as a surfactant (34.0 m^2/g).

The presence of surfactants TBAB and Tween 80 does not significantly change the value of the saturation magnetization neither in the case of $MnFe_2O_4$ nor in the case of $MnFe_2O_4$/PANI composites. The saturation magnetization of $MnFe_2O_4$/PANI hybrid materials shows values between 15.1 and 19.1 emu/g, which are much lower compared to those of $MnFe_2O_4$ synthesized in the absence and presence of the two surfactants, which vary between 46, 8 and 48.4 emu/g.

The electrical conductivities of the composites with PANI increased significantly, showing values between $15.3 \cdot 10^{-5}$ and $54.5 \cdot 10^{-5}$ S/m, compared to those of manganese ferrite powders which have values between $0.588 \cdot 10^{-5}$ and $0.780 \cdot 10^{-5}$ S/m. The highest value of electrical conductivity was obtained in the case of the MnFeTW/PANI composite, using Tween 80 as a surfactant ($54.5 \cdot 10^{-5}$ S/m) which is close to the pure PANI value ($61.2 \cdot 10^{-5}$ S/m).

The main **original contributions** that resulted from experimental research are:

- The versatility of the combustion method was demonstrated, which allows the attainment of iron oxide magnetic particles with specific surface area, particle size and magnetic properties that can be tailored by the nature of the fuel used and by the molar ratio between ferric nitrate and fuel.
- Ethylenediaminetetraacetic acid was used for the first time as a fuel in the combustion reaction and the characteristics of the powders obtained with a stoichiometric ratio, as well as with an excess of fuel were established.
- An innovative method was applied to remove the residual carbon from the magnetic powders obtained via the combustion reaction by treating them with hydrogen peroxide; this method is more efficient compared to the thermal treatment of the samples, mentioned in literature, which has the disadvantage of energy consumption and the change in the phase composition of the samples with the increase in temperature.
- It was shown that stable colloidal suspensions can be prepared, using different surfactants and different carrier media, starting from magnetic powders obtained under different conditions via combustion synthesis.
- A rare phenomenon of enucleation (expulsion of the nucleus) was observed in the case of colloidal suspensions tested on tumor and healthy human liver cells; this behavior offers the possibility of a new direction of research regarding their potential use in cancer therapy.
- It was demonstrated that the combustion method allows the synthesis of the Fe_3O_4/Ag/C nanocomposite with tailored properties, which presents both a large specific surface due to carbon and magnetic properties due to magnetite. The innovation of this material combines on the one hand the excellent adsorption capacity provided by activated carbon, the advantage of magnetic separation given by magnetite with the good catalytic and antibacterial activity offered by silver.
- The Fe_3O_4/Ag/C nanocomposite was tested for the first time as an adsorbent for the removal of both an anionic dye (acid orange 7) and two cationic dyes (methylene blue and rhodamine 6G) from aqueous solutions. The obtained results demonstrated that Fe_3O_4/Ag/C presented a high adsorption capacity of dyes from mono- and multi-component systems, which were higher or comparable to the results obtained for similar materials in literature.
- The effect of two surfactants which were not previously reported in literature (TBAB and Tween 80) on the characteristics of $MnFe_2O_4$ and $MnFe_2O_4$/PANI hybrid materials via solvothermal method was studied.
- It was established that the use of Tween 80 as a surfactant in the synthesis of the $MnFe_2O_4$/PANI composite determined a very high value of electrical conductivity

($54.5 \cdot 10^{-5}$ S/m) which is close to the value of pure polyaniline ($61.2 \cdot 10^{-5}$ S/m).

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