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A facile method to produce magnetic nanoparticles and its influence on their magnetic and physical properties

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This work presents a rapid and facile method to produce and adjust the magnetic and physical properties of magnetic nanoparticles. SEM and DRX characterizations, as well as magnetic hysteresis curves and magnetic susceptibility curves, were performed to study changes in the nanoparticles as a function of two stirring speeds: 1000 and 3000 rpm. The formation of spherical nanoparticles was observed at both speeds, but the small ones (72 nm) were obtained at the highest stirring speed. However, at this speed, the magnetite nanoparticles showed to be partially oxidized to hematite. Magnetic curves reveal the superparamagnetic and spin-glass behavior of both kinds of nanoparticles. The blocking and irreversibility temperature of the nanoparticles was not perceived even at room temperature.

1. Introduction

In recent years, magnetic nanoparticles have been receiving considerable attention due to their multiple applications related to their size and physicochemical properties. Magnetic nanoparticles with superparamagnetic behavior are identified as SPIONs. The hysteresis curves of these particles are characterized by their narrow loops, showing no magnetic remanence [1] and have been used in biomedical applications, such as magnetic resonance imaging, bioseparation and magnetic hyperthermia for cancer treatments [2] or in different catalytic process [3]. Different methods have reported to produce these particles using sol–gel, thermolysis, hydrothermal, coprecipitation and other novel methods [4,5]. The principal aim of this work is to apply a convenient method for the synthesis of high-purity magnetite nanoparticles, thus providing a different approach to tune their magnetic and physical properties.

2. Materials and methods

Magnetic nanoparticles were synthesized by mixing a solution of $FeSO_4 \cdot 7H_2O$, KNO_3, and KOH in distilled water. Firstly, the solution was stirred for 40 min at 90 °C and the pH of the solution was kept between 12 and 14. Secondly, the material was washed with acetone and the separation of the iron particles was performed using a neodymium magnet. Finally, the separated powders were dried at 50 °C. The influence of two stirring speeds (1000 and 3000 rpm) is studied. Fig. 1 shows the schematic of the preparation route of Fe_3O_4 nanoparticles. The morphology of the nanoparticles was observed using a scanning electron microscope (SEM, Vega3 TESCAN). The structural analysis of the magnetic particles was performed using the X-ray diffraction technique (XRD), following the methodology proposed by Agredo Díaz et al. [6]. Magnetic properties of nanoparticles were measured using a vibrating sample magnetometer (VSM). Hysteresis loops with a maximum field of 30 kOe at 300 K were obtained. The zero-field cooling (ZFC) and field cooling (FC) methods were performed to study the magnetic susceptibility $\chi(T)$ of the composites as a function of the temperature (50 K–350 K), under the application of an external field of 100 Oe.

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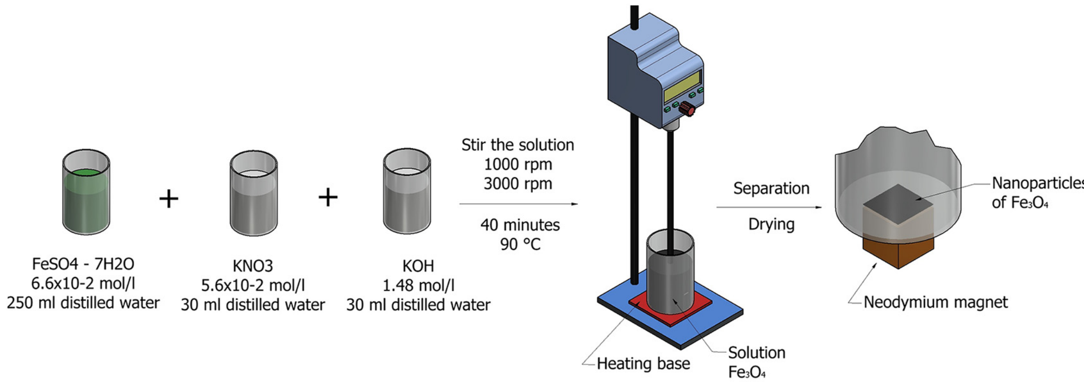

Fig. 1. Schematic of the process for obtaining magnetic nanoparticles.

3. Results and discussion

The effect of the applied field on the magnetic properties of both synthesized nanoparticles is shown in Fig. 2b and e. The absence of hysteresis, high saturation magnetization (M_S) values, low remanence magnetization (M_R) and coercivity (H_C) confirm their soft magnetic and superparamagnetic behavior [7]. The saturation and remanence magnetization for those particles synthesized at 1000 rpm were 85.05 emu/g and 10.32 emu/g, while the measured values of the nanoparticles produced at 3000 rpm were 55.21 emu/g and 8.34 emu/g. The coercivity (H_C) value showed to be higher in the particles obtained at lower stirring speeds with 131.5 Oe versus 117.4 Oe. The so-called soft magnetic character of both kinds of particles was confirmed through the relatively low ratio between the remanence and saturation magnetization ($M_S/M_R\approx0.1$). The reduced M_S and M_R values of the nanoparticles obtained at 3000 rpm are related to their small size and partial oxidation to the hematite phase. Small magnetic nanoparticles have higher surface areas, hence the surface spin disorder increased [8].

Fig. 3a shows the nanoparticles obtained at 1000 rpm and characterized by their spherical morphology with an average particle size of 109.6 ± 24 nm. The nanoparticles synthesized at 3000 rpm (Fig. 3b) exhibited irregular spherical shapes related to the high energy supplied by the stirring speed, consequently, small particles were produced (72.5 ± 14.9 nm). Fig. 2a shows the XRD results for both synthesized nanoparticles. Their elemental composition was related to the Fe_3O_4 (magnetite), with characteristics peaks at 35.41°, 43.04°, 53.4° and 62.5°. For stirring speeds of 3000 rpm, the presence of characteristics peaks from the hematite (Fe_2O_3) phase were located at 24.16°, 33.18°, 39.91°, and 49.4°. The presence of the hematite phase was a result of the partial surface oxidation, even at room temperature, of the magnetite nanoparticles [9].

Fig. 2c and f show the measured magnetic susceptibility for both synthetized nanoparticles. Their profiles differ from the common susceptibility curve of the bulk magnetite [7] as they show instead the typical behavior of the nano-sized magnetite particles [10] in which the absence of the blocking temperature

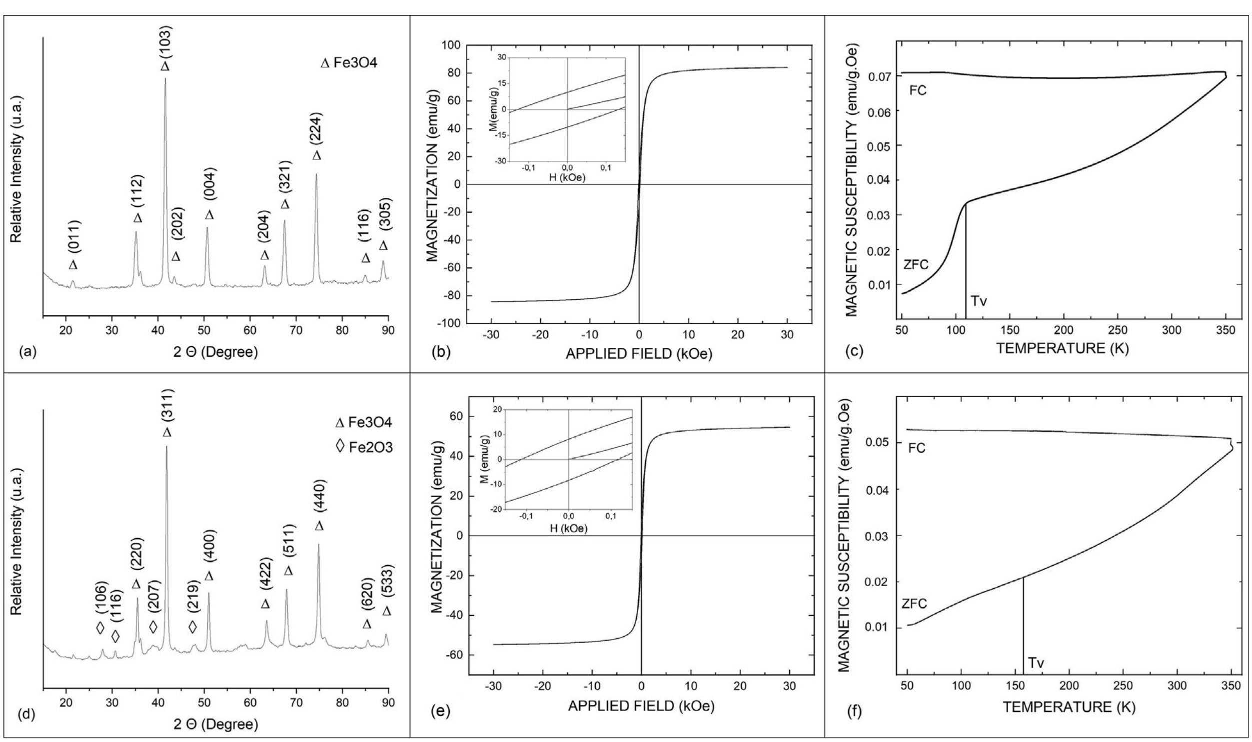

Fig. 2. Particles synthetized at stirring speeds of 1000 rpm: (a) XRD pattern, (b) hysteresis loop and (c) magnetic susceptibility. Particles synthetized at stirring speeds of 3000 rpm: (d) XRD pattern, (e) hysteresis loop and (f) magnetic susceptibility.

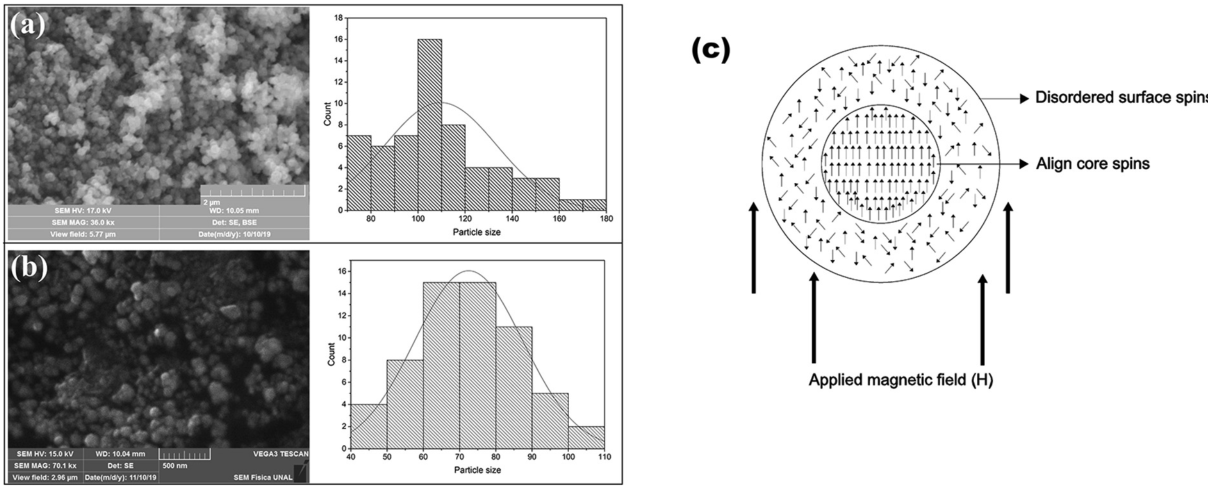

Fig. 3. SEM micrographs and particle size distribution histogram of the nanoparticles obtained at stirring speeds of: (a) 1000 rpm, (b) 3000 rpm, and (c) core–shell magnetic behavior of the nanomagnetite particles.

(T_B), even at room temperature, is highlighted. The irreversibility temperature (T_{irr}), defined as the splitting point between the ZFC and FC curves, was not observed in neither of the two types of nanomagnetic particles. This absence, as well as the T_B value above the room temperature, is distinctive of systems with strong dipole–dipole magnetic interactions, which restrain the effect of the thermal energy. These strong interactions in both samples of nanoparticles were further confirmed by the constant flatness in their FC curves, without remarkable changes in their magnetic susceptibility values with the increasing temperature. The strong dipole interparticle interactions found in the nanoparticles produced at both stirring speeds leads to a spin-glass-like or spin-glass order within the particles [8]. Due to the nature of some magnetic nanoparticles, this behavior can be explained in terms of core–shell morphology, as illustrated in Fig. 3c [11]. The nanoparticles have a core of aligned spins with ferrimagnetic behavior, and a spin-glass-like surface where the spins are non-collinear. Consequently, when an external magnetic field was applied during the ZFC procedure, the core spins and surface spins were decoupled. First, the core spins align at a certain level, while the external ones remain disordered. On the contrary, when the FC procedure was applied, the spin coupling was achieved at high temperatures. Therefore, when the measuring is recorded while the temperature is decreasing, the path of χ (T) becomes irreversible.

The principal difference in the susceptibility curves of the magnetite nanoparticles produced at stirring speeds of 1000 rpm and those obtained at 3000 rpm was the Verwey transition (T_V). Stichometry magnetite at ≈120 K undergo a structural transition, from monoclinic ($T < T_V$) to cubic ($T > T_V$). T_V in nano-sized magnetite is still a matter of research [10] but it has been documented that its value is lower than that reported for bulk magnetite. The Verwey transition for both produced magnetite nanoparticles were identified at 112 K. However, this inflection point was more evident in the magnetite nanoparticles synthesized at 1000 rpm. This transition, as well as the T_B, is sensitive to the stoichiometry of the magnetite, its surface anisotropy and its particle size [10]. Consequently, as previously reported, the small size of the magnetite particles obtained at 3000 rpm and their partial oxidation to hematite vanishes the T_V in their susceptibility curve. This partial oxidation also decreases the magnetic parameters (M_S, M_R, H_C, and χ (T)), but it does not affect the superparamagnetic character of the magnetite nanoparticles.

4. Conclusions

The principal aim of this work was to produce nano-sized magnetite by the co-precipitation method in which the size and the magnetic properties of the nanoparticles could be adjusted using two stirring speeds: 1000 and 3000 rpm. The stirring speeds influenced the size of the obtained ferrites. The nanoparticles obtained at 3000 rpm are 33% smaller than those obtained at 1000 rpm. Besides, the magnetite nanoparticles produced at the highest stirring speed showed partial oxidation to hematite. Nanoparticles showed superparamagnetic behavior and their magnetic parameters, such as MS, MR, HC and χ (T), depended on the particle size. The magnetic susceptibility curves also showed strong effects of anisotropy and spin glass type behavior.

CRediT authorship contribution statement

Nicolas Ortiz-Godoy: Investigation. **Dayi Gilberto Agredo-Diaz:** Investigation. **Andrés Orlando Garzón-Posada:** Methodology and review & editing. **Carlos A. Parra Vargas:** Resources. **David A. Landínez Téllez:** Resources, Supervision. **Jairo Roa- Rojas:** Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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