



## Size control in the formation of magnetite nanoparticles in the presence of citrate ions



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### HIGHLIGHTS

- The citrate ion allows the size of the MNPs to be tuned in the range of 4–10 nm.
- Controlling the particle size around superparamagnetic threshold.
- Tuning the processes of agglomeration and the removal of the MNPs from solutions.
- The size control arises from the capping of the magnetite surface by citrate ions.

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### ABSTRACT

A one-pot synthesis method for the controllable growth of magnetite nanoparticles directly during the process of co-precipitation using citrate ions was developed. The effects of the concentration of citrate ions and the solution pH on the characteristics of magnetite particles with sizes in the range of 4–10 nm synthesized by the method of co-precipitation were studied. The results showed that the specified concentration of citrate ions allowed the preparation of magnetite particles with a definite size that exhibited superparamagnetic behaviour in a particular temperature range. As the concentration ratio of citrate to iron ions was increased from 0 to 0.11, the average size of the prepared magnetite particles decreased from 10.5 to 4.4 nm. As a result, the superparamagnetic blocking temperature decreased from 300 to 20 K, the saturation magnetisation decreased from 50 to 20 emu g<sup>-1</sup>, and the average magnetic moment decreased from 8000 μ<sub>B</sub> to 340 μ<sub>B</sub> (at T = 300 K).

The obtained experimental data proved that the size effects of the magnetite nanoparticles can be attributed to the capping of the magnetite surface by adsorbed citrate ions. Thus, the suggested approach allows magnetite nanoparticles to be prepared with an optimum particle size around superparamagnetic threshold that prevents their irreversible agglomeration and simultaneously allows them to be removed from a solution at an acceptable rate.

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### 1. Introduction

Submicron magnetic-particle-based materials find expanding applications, especially in the chemical and biomedical fields, such as in the magnetic separation of radioactive nuclides [1], the removal of heavy-metal cations [2,3] and arsenic [4], the magnetic separation and identification of pathogenic microorganisms [5], cancer hyperthermia [6], *in vivo* magnetic resonance visualisation [7], therapeutic drugs, gene and radionuclide delivery [8,9], and catalysis [10,11].

Currently, the development of catalysts and supports based on magnetic nanoparticles (MNPs) appears to be one of the most urgent problems regarding the application of magnetic transport systems for catalysis [12]. The need for the progress in this area is dictated by both environmental and economic issues and more so by new opportunities that arise from the use of magnetically separable catalysts. The reusability of expensive homogeneous catalysts supported on MNPs allows them to be considered as “quasi-homogeneous” systems that combine the advantages of homogeneous catalysts with the opportunity to remove them from the reaction mixture through simple magnetic separation procedures [13]. Considerable progress has been achieved in the application of magnetic particles and MNP-based catalysts for cross-coupling reactions [14,15], hydrogenation [16,17],

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hydroformylation [18], oxidation and epoxidation [19,20], enantioselective [21,22], and acid–base processes [23], among others [24].

The required properties (e.g., the particle size, the chemical and thermal stability, the magnetic characteristics, the surface state, etc.) for MNPs and MNP-based catalysts vary depending on the application area. For example, micron- and submicron-sized magnetic particles with low toxicity and a high saturation magnetisation value are needed in biomedicine to provide targeted drug delivery and the complete removal of the MNPs by a magnetic field [25].

One of the critical factors for a catalyst system is a high specific surface area and the absence of diffusion difficulties. In this regard, MNPs used for magnetically separable catalysts should be small (~5–50 nm). In addition, the characteristics of magnetic carriers, which can vary due to surface functionalisation, should provide a sufficient rate for the complete removal of the catalysts and simultaneously prevent irreversible agglomeration of particles during the course of a catalytic reaction to maintain a high specific surface area. Catalytic systems based on MNPs should also be stable at high temperatures in reaction media with various acidity levels. Therefore, the development of methods for the synthesis of stable powders with a mean MNP size in the range of ~5–50 nm and a narrow size distribution of particles that exhibit similar magnetic characteristics is necessary.

Chelating ions are known to stabilise highly dispersed nanoparticles. Surface-adsorbed chelating agents form a polyanionic coating that provides both steric and electrostatic potential barriers and prevents the aggregation of nanoparticles due to intermolecular interactions and magnetic dipole–dipole interactions between MNPs. For example, phosphate ions ( $\text{H}_2\text{PO}_4^-$ ) efficiently inhibit nucleation and aggregation of magnetite nanoparticles synthesized by oxidative co-precipitation of  $\text{Fe}^{2+}$  from an acidic solution under heating [26]. This approach allowed particles with sizes smaller than the superparamagnetic threshold for the given material to be prepared. The authors attributed the reduction in particle size not only to the inhibiting effect of phosphate ions, but also to the formation of Fe–phosphate complexes. The influence of chelating agents (e.g., citrate, oxalate, phosphate ions, EDTA) on the formation of haematite particles has also been reported elsewhere [27].

Polyanionic coatings, including the citrate-based ones, are widely used for post-synthesis nanoparticles and MNPs stabilisation [28–33].

However, little research devoted to the application of a capping agent during the MNPs synthesis has been reported. In one example [34], the authors obtained nanocrystalline cobalt-doped magnetite  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  ( $0.05 \leq x \leq 0.20$ ) using preliminarily synthesized citrate complexes. In another example [35], cobalt nanoparticles were synthesized via the reduction of  $\text{CoCl}_2$  with sodium borohydride in the presence of citric acid. The authors found that, as the molar ratio between citrate and  $\text{Co}^{2+}$  ions was increased from 0.01 to 1, the size of the cobalt nanoparticles decreased by a factor of almost 5 (from 78 nm to 17 nm). Other authors [36] have suggested a method for the synthesis of haematite nanoparticles by the oxidation of magnetite, which, in turn, was prepared by co-precipitation in the presence of various concentrations of citrate ions. The size of haematite nanoparticles decreased from 8 to 2 nm as the ratio of citrate ions to iron ions was increased from 0 to 0.03. Unfortunately, the size and magnetic characteristics of the magnetite nanoparticles were not studied.

Despite the publication of numerous papers devoted to the preparation of magnetic particles, the problem of controlling the synthesis of iron-oxide particles to produce particles with a certain structure with sizes on the order of a few nanometres is still a challenge, especially with respect to the preparation of

nanoparticles for catalytic applications. The currently available information indicates that the development of a one-pot method for the synthesis of magnetite nanoparticles directly through co-precipitation using citrate ions to control the growth is possible.

Here, we report the effects of citrate ions during co-precipitation on the size-dependent properties of magnetite particles. Structural and size characteristics of the particles were studied by XRD (X-ray diffraction) and HR TEM (high-resolution transmission electron microscopy) methods. As expected, the studies of the magneto-static and the magnetic resonance properties of the synthesized systems showed the transition from superparamagnetic behaviour to a ferrimagnetic state with nonzero residual magnetisation in the given size range at room temperature. The citrate ions allowed the controlled synthesis of magnetite nanoparticles in the size range of 4–10 nm with a rather narrow particle size distribution. Thus, the suggested approach enables the average size of the magnetite nanoparticles to be tuned to within a few nanometres around superparamagnetic threshold; it also allows the magnetic properties to be tuned to those required for the magnetic transport systems in catalysis (a) to avoid irreversible aggregation and simultaneously allows (b) complete removal of the MNPs from the system (within an acceptable time period).

## 2. Materials and methods

### 2.1. Materials

The following reagents of chemical purity grade were used: citric acid monohydrate (Acros Organics), 99.5%; 23.5% ammonia aqueous solution (Sigma–Aldrich),  $\geq 99.99\%$ ;  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Acros Organics), 99+%;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Sigma–Aldrich), ( $\geq 98\%$ ). To prepare the initial solution of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  salts with a total iron concentration of  $0.900 \text{ mol L}^{-1}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in distilled (deoxygenated) water at a  $\text{Fe}^{3+}/\text{Fe}^{2+}$  molar ratio of 2.

The obtained solution was filtered through a filter paper (pore diameter 1–2.5  $\mu\text{m}$ ) and was used within two weeks after being prepared.

### 2.2. Synthesis of $\text{Fe}_3\text{O}_4$

Magnetite particles were synthesized by co-precipitating  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  salts ( $[\text{Fe}^{3+}]/[\text{Fe}^{2+}] = 2$ ) in the presence of citrate ions. Total concentration of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions was  $0.15 \text{ mol L}^{-1}$ . The molar ratio of citrate to iron ions varied from 0 to 1.2, and the pH varied from 7.5 to 11.6. We performed the synthesis under an Ar atmosphere at room temperature (18–24 °C) by mixing  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  solution under intensive mechanical stirring (500 rpm) with solution of ammonium hydroxide and citric acid in preliminarily deoxygenated water. Magnetite nanoparticles were aged for 3 days at room temperature before characterization.

### 2.3. Testing methods

pH measurements were performed using a Hanna pH 213 pH meter equipped with a regular refillable glass electrode.

High-resolution transmission electron microscopy (HR TEM) images were obtained with a JEOL JEM-2010 microscope with a resolution of 1.4 Å operated at an accelerating voltage of 200 kV. The size distribution of the nanoparticles was calculated based on a representative set of HR TEM images taken at different areas of the sample. The number of measured particles was 546, 557 and 491 for samples Cit-0, Cit-20 and Cit-100, respectively.

The X-ray diffraction (XRD) analysis was performed using an XTRA powder diffractometer (Switzerland) equipped with a  $\text{CuK}_\alpha$

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