## Theoretical and experimental influence of aerosol assisted CVD parameters on the microstructural properties of magnetite nanoparticles and their response on the removal efficiency of arsenic

P.G. Hernández-Salcedo, **P. Amézaga-Madrid**, B.E. Monárrez-Cordero, W. Antúnez-Flores, P. Pizá-Ruiz, C. Leyva-Porras, C. Ornelas-Gutiérrez, M. Miki-Yoshida

## Abstract

The development and optimization of methodologies to generate magnetite nanoparticles is currently an innovation topic. For a desired application such as arsenic removal from waste water, the generation of these nanostructures with specific microstructural properties is determinant. Therefore, it is necessary to understand the phenomenon during the nanoparticles formation process. Thus, in this work it is reported the influence of synthesis parameters of AACVD technique on the formation of magnetite nanoparticles. Parameters were according to: (1) synthesis temperature, (2) tubular reactor diameter, (3) concentration of the precursor solution and type of solvent, (4) carrier gas flow and (5) solvent type in the collection process. The effect of these synthesis parameters on the morphology, size and microstructure are discussed in detail and related with the mechanism of formation of the particles. Theoretical simulations were performed on two of these parameters (1 and 4). The microstructure and surface morphology of the different nanostructures obtained were characterized by field emission scanning electron and transmission electron microscopy. Subsequently two materials, were selected for further microstructural analysis. Finally, to determine the removal efficiency in the



two materials the arsenic adsorption was evaluated. A major contribution of this work was the calculation of the number of spherical particles formed from a single drop of precursor solution. This calculation matched with the value found experimentally.

### 1. Introduction

Currently, solid, hollow or porous magnetite nanoparticles (MNPs) are being extensively studied due to their magnetic properties, porosity, crystallinity and surface area. These properties make particles suitable for biomedical and environmental applications [1]; [2]; [3]; [4]; [5]; [6]; [7]; [8]; [9]; [10]; [11]. In order to properly employ MNPs on those fields, the nanoparticles must achieve several properties such as size, high magnetization, high surface area and crystallinity. All these properties depend on the final morphology, size and structure developed by the MNPs during the synthesis [4]; [8]; [9]; [12]; [13]; [14]. One of the main topics in nanotechnology is the tailoring of the properties from the synthesis process [10]; [15]; [18]. However, it is very important that nanoparticles may be synthesized by low cost methodologies with potential for industrial scale application. In this sense, aerosol assisted chemical vapor deposition (AACVD) is a simple technique for one-step synthesis of hollow and porous MNPs. AACVD technique consists of three stages: (1) the formation of the cloud of the precursor solution, (2) transportation of the cloud by the carrier gas into the furnace where both, the chemical reaction and the solid particle transformation are carried out and, (3) the particle recovery process. The basics of the technique have been reported elsewhere [13]; [16]; [17]; [18]. The final morphology and structure of the MNPs by AACVD method greatly depend on the synthesis parameters such as furnace



temperature, carrier gas flow, concentration and type of precursor and the tubular reactor diameter. In literature there are few works describing the phenomenon occurring inside the tubular reactor and the process of particle formation [18]; other works reported the numerical simulation of the drop–particle transformation process in the spray pyrolysis system [19]; [20]. Hence, it is necessary to study the effect of the processing parameters on the final properties of the MNPs. The aim of the present work is to study the effect of the synthesis parameters of the AACVD method on the final microstructure and adsorption properties of MNPs. Besides the detailed characterization provided, other contributions of the work include the calculation of the number of particles formed from one drop of precursor at two different temperatures of synthesis, and the removal efficiency of MNPs on water containing As\*3 and As\*5 ions.

### 2. Materials and methods

#### 2.1. Theoretical simulation

The actual geometry of the furnace employed in the AACVD experiments was first simulated by SolidWorks-Fluidworks® software. The distribution of temperature, carrier gas velocity and heat transfer from the furnace into the tubular reactor, were calculated in this way. More simulation details were reported in references [13]; [18].

#### 2.2. Synthesis of the MNPs at different conditions

MNPs were synthesized by AACVD technique according to the details previously reported [13]; [18], employing Iron (II) chloride (99.9%, Sigma–Aldrich) as the precursor. The parameters varied during the synthesis of the MNPs were: the concentration and type of solvent used in the precursor solution, temperature of the



furnace, the diameter of the tubular reactor and the type of solvent used during the recovering process. The level of variation on each of the parameters is presented in <u>Table 1</u>. Carrier gas mixture flow rate (Ar:Air) was set at 250:4 cm<sup>3</sup> min<sup>-1</sup>. A total of 11 materials were synthesized, producing different types of MNPs; each experiment was identified with a capital letter from A to K.

#### 2.3. MNPs microstructural characterization

The microstructure of the MNPs was analyzed in two field emission microscopes. The surface morphology was observed in a scanning electron microscope (SEM) JEOL JSM-7401F, while the microstructure was analyzed in a high resolution transmission electron microscope (HRTEM) JEOL JEM-2200FS. After analyzing the 11 materials by these techniques, two materials were selected (D and E) for further microstructural characterization such as particle size distribution, percentage of porosity and arsenic removal tests. Crystalline phases were identified by X-ray diffraction (XRD) in a Panalytical X-Pert system using Cu Kα radiation at 40 kV and 35 mA. Raman spectroscopy was employed for identifying the magnetite phase in the powders. The specific surface area was determined by the BET method using liquid nitrogen. Magnetic properties were evaluated with a vibrating sample magnetometer. All these tests allowed to properly determining the differences in microstructure, elemental composition, morphology, porosity and particle size, to correlate all these changes with the influence of the synthesis parameters [13]; [14].



#### 2.4. Arsenic ions removal tests

Sodium arsenite (III) (>99%) and sodium arsenate heptahydrate (>98%) (both from Sigma–Aldrich) were dissolved separately in tridistilled water (JT Baker) to obtain stock solutions of As<sup>+3</sup> and As<sup>+5</sup>, respectively. Stock solutions were prepared a concentration of 0.05 ppm in a fixed volume of 100 mL. A sample of 10 mg of MNPs was added to each arsenic solution and thoroughly mixed with a mechanical stirrer during times of 1, 5, 10 and 15 min (this first part of the experiment is called contact time). After elapsing the contact time, mechanical agitation was stopped, and begins the second part of the experiment, which is the time of separation. In this time, MNPs were left to sediment by placing the beaker on a magnet of 1 T.

Variation of synthesis parameters in the AACVD method to obtain different materials.				
Material	Temperature (K)	Precursor concentration (mol L <sup>-1</sup> ]	Tubular reactor inner diameter (mm)	Solvent used in precursor solution- and the recovering process
Α	773	0.01	9	Methanol-methanol
В	873	0.01	9	Methanol-methanol
C	973	0.01	9	Methanol-methanol
D [14]	723	0.05	15	Methanol-methanol
E [14]	773	0.05	15	Methanol-methanol
F	873	0.05	15	Methanol-methanol
G	773	0.05	6	Methanol-water
Н	773	0.05	9	Methanol-water
I	773	0.05	15	Methanol-water
J	723	0.05	15	Methanol-water
K	723	0.05	15	Water-water

Table 1 Variation of synthesis parameters in the AACVD method to obtain different materials

Solution was maintained undisturbed by a recovery time of 30 min. To determine the real time of adsorption efficiency of nanoparticles, experiments were made by eliminating the separation time, the experiment was made under the same conditions described considering two contact times 1 and 10 min, after the contact



time, samples were centrifuged immediately at 3500 rpm by 5 min. Then, the supernatant solution was removed and stored in a flask for further analysis. Each test was done in duplicate, together with a solution free of arsenic ions (blank solution). The remaining concentration of As<sup>+3</sup>, As<sup>+5</sup> and Fe in the solutions was quantified by atomic absorption spectroscopy (AAS GBC, model Avanta Sigma). After the removal tests, MNPs were dried and analyzed by both SEM and HRTEM. The relative concentration of the adsorbed arsenic was determined by energy dispersive spectroscopy (EDS) analysis.

## 3. Results and discussion

# 3.1. Theoretical simulation of the temperature distribution inside the furnace and the carrier gas flow

The actual geometry of the furnace employed in the AACVD experiments, the distribution of temperature, carrier gas velocity and heat transfer from the furnace into the tubular reactor, were simulated by SolidWorks – FluidWorks®. New calculations were performed employing the following starting data: nominal temperature 773 K, diameter of the tubular reactor of 15 mm and carrier gas flow ratio of 1:0.015. Fig. 1a shows the temperature distribution inside the furnace for a nominal temperature of 773 K and Fig. 1(b and c) shows the carrier gas flow behavior inside the tubular reactor. Along the tubular reactor at approximately 23 cm from the entrance, the temperature reached 703 K. According to thermogravimetric analysis (TGA), this value is the minimal temperature required for the chemical decomposition of the iron precursor and the subsequent formation of iron oxide into the magnetite phase. In the middle zone of the furnace, about 25–70 cm after the entrance, the temperature inside the tubular reactor is close to the nominal



temperature (Fig. 1a). Low temperatures at the entrance and exit of the tubular reactor were observed. This low temperature was reached in these zones because both ends of the tubular reactor are open and exposed to room temperature. Fig. 1b shows the temperature distribution in the carrier gas. The carrier gas enters at room temperature into the tubular reactor and starts to warm up as it travels through the reactor. This behavior is similar to that simulated with a nominal temperature of 723 K [14]. Fig. 1c shows the carrier gas velocity profile. Velocity is low near the wall of the tube, while the maximum velocity is achieved at the center of the reactor. This is a typical behavior provoked by the friction of gas molecules on the walls of the tubular reactor.

#### 3.2. Influence of each parameter varied in the characteristics of the MNPs

<u>Fig. 2</u> shows SEM and TEM images of the MNPs synthesized at the different conditions (materials A–K in <u>Table 1</u>). As observed in the figure, small variations in the parameters produce changes in morphology, microstructure and particle size. 3.2.1. The effect of temperature

This parameter was studied at three different temperatures: 773, 873 and 973 K. For the tubular reactor of 9 mm in diameter, these variations in temperature correspond to images A–C in Fig. 2, respectively. At 773 K, the material A is conformed of well-defined nanostructured hollow spheres with a porous surface formed of crystallites. The average spherical particle size was 250 nm. The fact of obtaining this material with these characteristics by the AACVD technique can be described by the following mechanism: the first step is the production of a cloud of



droplets or aerosol, which is generated by the ultrasonic nebulizer. This cloud is transported into the tubular reactor by the carrier gas.



Fig. 1. (a) Temperature profile distribution inside the furnace and in the tubular reactor of 15 mm in diameter. Nominal temperature of 773 K. Distribution profile of: (b) temperature and (c) carrier gas velocity inside the tubular reactor with the same diameter and nominal temperature. Longitudinal section.

Once inside the reactor, the droplets rapidly warm up, undergoing the evaporation of the solvent. Thus, as the aerosol travels along the reactor, the size of the droplets decreases while the concentration of solute in the drop increases. The original size of the droplet shrinks to a smaller size, which may explains the nanometric size of the particles produced from micrometric droplets [20]; [22]. As the solvent evaporates, the solute concentration on the surface of the droplet



reaches a critical supersaturation (CSS) where the nucleation of the solute begins [19]. After the nucleation of the solid, if the concentration of solute inside the drop is larger than the equilibrium saturation (ES), an abrupt precipitation of the solid on the drop occurs. Therefore, the hollow particles are likely to be formed if, at the time of nucleation on the surface, the concentration of the solute at the center of the droplet is smaller than the ES [20]. On the contrary, if the concentration of the solute at the center of the droplet is higher than the ES, a solid particle will be formed [20]. This occurs because the process is so fast that the solute does not have enough time to diffuse from the surface of the drop, where the solute concentration is higher, toward the center. After the formation of the crust, the solution trapped in the center of the droplet continuous evaporating, resulting in an increase in the internal pressure. If the permeability of the crust is high, the internal pressure inside the drop is relieved by the sudden escape of vapors and the formation of hollow and porous nanoparticles [19]; [20]. By increasing the temperature from 773 to 873 and 973 K (Fig. 2 materials B and C, respectively) spherical morphology is lost, observing agglomerated nanoparticles resembling the structure of material in bulk. At these conditions of temperature, is difficult to determine whether these materials are solid or hollow since not well-defined boundaries are distinguished in the agglomerated particles. The difference in morphology among materials A-C, may occur because the evaporation process becomes faster: the drop is rapidly heated causing the abrupt formation of the surface crust with less pores and the subsequent rupture due to a higher internal pressure of the evaporated solvent. Another possible effect of the abrupt warming is the breaking of the drop [23] or the explosive



evaporation [24] which produces the formation of several nanoparticles from a single drop, which is consistent with the smaller particle size observed in material C. The effect of employing a tubular reactor larger in diameter was analyzed at the same three temperatures. Images D–F, correspond to the 15 mm tubular reactor and temperatures of 773, 873 and 973 K, respectively. At these conditions, for all the experimented temperatures, the MNPs were comprised of regular shape hollow and porous spheres. These results are similar to those found in material A. The effect of temperature was evaluated by measuring the size of both, spherical particles and crystallites. As temperature increased (773, 873 and 973 K), the average sphere size increased (300, 380 and 617 nm, respectively). The same effect was observed for the average crystallite size, which varied as: 19, 25 and 39 nm. Unlike the 9 mm tubular reactor at 873 and 973 K, where agglomerated particles were formed, in the 15 mm reactor spherical particles were produced. This effect is most noticeable in this experiment due to the smaller diameter of the tube reactor utilized (9 mm), which increases the flow velocity of gas therein and thus a reduction of residence time occurs, and an increase of the heating rate.

3.2.2. Effect of the diameter of tubular reactor

To evaluate the influence of the diameter of the tubular reactor at a given temperature, materials G–I were synthesized at 773 K in





Fig. 2. SEM and TEM images showing the morphology of the materials obtained (A–K) by AACVD, at the different synthesis conditions.

tubular reactors with diameters of 6, 9 and 15 mm, respectively. At these conditions, all materials showed a homogeneous well-defined spherical morphology. The average spherical particle sizes were 270, 310 and 400 nm, while the average crystallite sizes were 17, 22 and 27 nm. This behavior can be explained by the larger residence time exerted on the drops of iron precursor as the diameter of the tubular reactor increases. The carrier gas flow velocity decreases with larger tube



diameters, thus the drops in the precursor cloud travel more slowly through the tubular reactor. Therefore, MNPs have more time for nucleation and growth, producing larger spherical particles and crystallites.

3.2.3. The effect of the type of solvent

The solvent used in the precursor solution was also studied. Two different solvents were tested, methanol and water, corresponding to materials J and K, respectively. Images in Fig. 2 shows large differences in morphology. While the MNPs synthesized with methanol developed a regular spherical hollow morphology, the material synthesized with water was solid particles with irregular shape. The average particle size for materials J and K were 310 and 420 nm, while the crystallite size were 20 and 9 nm, respectively. These variations may be explained in terms of differences in the evaporation rate and temperature of the solvents. As the precursor cloud enters the tubular reactor it starts to warm up. As the drops travel along the tubular reactor, continues warming while the solvent is evaporating. Evidently, the evaporation of the solvent produces shrinkage in the drop, which in turn results in the coalescence of the dissolved iron precursor molecules in the drop for further nucleation and growth. Jayanthi et al. [19] reported the formation of solid particles when the evaporation of the solvent is slower than the diffusion rate of the solid inside the drop. Since the evaporation rate of water is slower than that of methanol, then solid particles were expected when employing the former for dissolving the iron precursor. The decreasing sizes of crystallite using water instead of methanol is consistent with the nucleation in the entire volume of the droplet, which increases the number of nucleation sites, thus diminishing the size, because



the concentration of solute within the droplet is fixed.

3.2.4. The effect of the precursor concentration

Two concentrations of the precursor were analyzed: 0.01 and 0.05 M of Fe (II) chloride in methanol. The corresponding images in Fig. 2 were labeled as A and E. At the concentration of 0.01 M, the average spherical particle size and crystallite were 280 and 20 nm, while for a concentration of 0.05 M were 310 and 22 nm. As observed, there is not a significant change in dimensions under these conditions of synthesis. This result is in agreement with that reported by Monárrez-Cordero et al. [13].

3.2.5. The type of solvent employed in the recovering system

The last effect analyzed was the type of liquid employed in the recovering system. This was tested with two different solutions: methanol and water. The corresponding images in Fig. 2 were identified as D and J. Both liquids used in the recovery process showed similar results: hollow spherical particles. This was expected, since the whole process of particle formation was previously carried out inside the tubular reactor.

# 3.3. Size of nanostructured spherical particles, crystallites and crust thickness

For a desired application such as heavy metals removal from wastewater, MNPs must fulfill some properties such as high surface area and porosity. In a previous work, the surface area of MNPs synthesized at the same conditions as the materials D and E was analyzed [14]. The results showed that at these conditions of



synthesis, both materials meet the requirements of high surface area and porosity. Based on the electron microscopy images acquired in the SEM and TEM, size of the spherical particles, crystallites and crust thickness were measured in the materials synthesized in experiments D and E. For these materials, particle size distribution was calculated measuring more than 500 MNPs employing dedicated software (Digital Micrograph<sup>™</sup> from Gatan). Fig. 3(a–d) shows all the measurements performed on materials D and E (723 and 773 K respectively). The summary of these results is reported in Table 2. MNPs in material E presented a larger value in all the measured guantities. This result was expected since powder of material E was synthesized at higher temperature than that of material D. Crystallite volume was almost the double for material E. This result suggests that the density of the powder is lower but may present a higher surface area. Crust thickness remained almost unchanged for the two materials. As explained in the previous section, crust thickness is affected mainly by two variables, temperature and precursor solution concentration. Thus, an increment of 50 degree in temperature had a negligible effect on the thickness, since the concentration of the precursor solution was the same in the two experiments (0.05 M).

Average crystallite was determined by measuring at least 500 crystallites in each material and crust thickness was calculated by averaging more than 100 particles. From these measurements, the percentage of porosity was estimated according to Eq. (1):

$$Porosity~(\%) = \frac{A_{Empty}}{A_{Total}} \cdot 100$$

where  $A_{\text{Empty}}$  represents the free area between the crystallites and  $A_{\text{Total}}$  is the



area occupied by the crystallites in a single spherical particle. <u>Table 3</u> shows the data necessary to perform the molar balance and the theoretical approximations indicated that only one nanostructured spheres is formed from a single drop of precursor solution. As reported in <u>Table 3</u>, the estimated porosity in material E was 59%, while that for material D was 30% [14]. The larger value in material E indicates a larger pore size than in material D. An increment of 50 degree on the temperature of synthesis in material E produced an increase in the size of spherical particles, crystallites and pores. During the coalescence of crystallites, the void-space in between crystallites increases according to the square of the crystallite

radius  $2\frac{\sqrt{3}-\pi}{6}R^2$ . Therefore, as the crystallite size increases, the overall spherical particle size and porosity increase as well. Since the amount of iron precursor was fixed in a single droplet, the calculated volume of the spherical shell for material D was similar to that from material E. <u>Table 4</u> shows the calculated data to obtain the number of nanostructured spheres and crystallites formed from a droplet of precursor solution. Diameter of nebulized drop was previously estimated approximately as 2.2 µm; this value was used in all calculations. According to the theoretical calculations every single drop forms a nanostructured sphere; this result is consistent with those reported in the literature [19]; [20]. Regarding the number of crystallites, it was observed that increasing the synthesis temperature in 50 degrees results in a decrease in the number of crystallites. For material D, from one drop, is formed one hollow spherical particle of magnetite with an average size of 300 nm in diameter, crust thickness of 26 nm and 30% of porosity. The iron mass balance showed that the spherical particle is composed of 1007 crystallites with



19 nm in diameter. For material E, experimental measurements showed and average particle size of 380 nm, crust thickness of 27 nm and 59% of porosity. After calculating the iron mass balance, the particle is composed of 578 crystallites with 25 nm in diameter. Once again the effect of temperature is observed in these calculations. As temperature of synthesis increased, the number of crystallites forming the spherical particle decreased but they were larger in size [19]; [20].

3.4. Microstructure and magnetic characterization in materials D and E

High resolution transmission electron microscope (HRTEM) images and electron diffraction patterns (EDP) are shown in Fig. 4, Fig. 5, Fig. 6 ; Fig. 7, for MNPs synthesized in experiments D and E. At low magnifications, the spherical particle is comprised of hundreds of small crystallites. The EDP shows the typical well defined concentric rings from a polycrystalline material. The indexation of these rings with a given diffraction plane (*h k l*) corresponded to the magnetite phase (Fig. 4 ; Fig. 6) [26]. HRTEM images confirm the single-crystal nature of the crystallites forming the spherical particle. The inset in Fig. 5 ; Fig. 7 shows the atomic planes and the distance in between, for two particles found in materials D and E, respectively. In Fig. 8 are shown the Raman spectroscopy results from the two materials. Magnetite phase (Fe<sub>3</sub>O<sub>4</sub>) presents a





Fig. 3. Distribution graphics of materials D and E. (a) Nanostructured particle sizes, (b) crystallite sizes, (c) crystallite volume and (d) thickness of the shell.

Table 2		
Summary of results f	rom measurements	presented in Fig. 3.

Material	Particle size (nm)	Crystallite size (nm)	Crystallite volume (nm <sup>3</sup> )	Crust thickness (nm)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )
D	$300 \pm 78$	19 ± 5	4272	26 ± 9	66 [14]
E	$380 \pm 100$	25 ± 6	7450	27 ± 5	47 [14]



Specific data	Value
Drop diameter [14] Precursor solution concentration Density ( $\rho$ ) of Fe <sub>3</sub> O <sub>4</sub> Molar mass of Fe <sub>3</sub> O <sub>4</sub> Porosity material D Porosity material E Volume of a drop	$\begin{array}{c} 2.2 \ \mu m \\ 0.05 \ mol \ L^{-1} \\ 5 \ g \ cm^{-3} \\ 231.5 \ g \ mol^{-1} \\ 30\% \ [14] \\ 59\% \ [14] \\ 5.58 \ \times \ 10^{-15} \ L \end{array}$
Table 4 Calculated data to obtain the number of nanostructured crystallites formed from a droplet of precursor solution.	spheres and
Calculated data	Value
Number of moles of FeCl <sub>2</sub> in a drop Occupied volume of a hollow sphere material D Occupied volume of a crystallite material D Mass of Fe <sub>3</sub> O <sub>4</sub> in a hollow porous sphere Number of moles of Fe <sub>3</sub> O <sub>4</sub> in a hollow porous sphere Number of moles of Fe in a hollow porous sphere Mass of Fe <sub>3</sub> O <sub>4</sub> in a crystallite Number of moles of Fe <sub>3</sub> O <sub>4</sub> in a crystallite Number of moles of Fe in a crystallite Number of moles of Fe in a crystallite Number of crystallites contained in a single sphere material D	$\begin{array}{c} 2.79 \times 10^{-16} \text{ mol} \\ 4.31 \times 10^{-15} \text{ cm}^3 \\ 4272 \text{ nm}^3 \\ 2.15 \times 10^{-14} \text{ g} \\ 9.30 \times 10^{-17} \text{ mol} \\ 2.79 \times 10^{-16} \text{ mol} \\ 4.27 \times 10^{-18} \text{ cm}^3 \\ 9.23 \times 10^{-20} \text{ mol} \\ 2.77 \times 10^{-19} \text{ mol} \\ 1007 \ [14] \end{array}$
Number of crystallites contained in a single sphere material E	578 [14]

Table 3 Specific data necessary for the theoretical estimation.

well-defined vibration band at 670 cm-1, while maghemite phase ( $\gamma$ -Fe2O3)

presents wide bands at 460, 500 and 700 cm-1 [25]; [27]. Clearly, the two powders

presented a single vibration band at



Fig. 4. Material D, synthesized at 723 K, (a) image by HRTEM-BF and (b) electron diffraction pattern (EDP).



Fig. 5. HRTEM image of crystallites from material D. The inset shows the crystallographic planes of magnetite.

 $673 \text{ cm}^{-1}$ , which confirms the formation of the magnetite phase. The magnetic characterization results are presented in <u>Fig. 9</u>. In the figure are presented the curves of magnetic field against the magnetization, showing a typical ferromagnetic behavior. The corresponding cohercitivity (*H*<sub>c</sub>) and remanent magnetization (*M*<sub>c</sub>)



Fig. 6. Material E, synthesized at 773 K, (a) image by HRTEM-BF and (b) electron diffraction pattern (EDP).





Fig. 7. HRTEM image of crystallites from material E. The inset shows the crystallographic planes of magnetite.

were 97 Oe and 6 emu g<sup>-1</sup> for material D, while for material E were 177 Oe and 13 emu g<sup>-1</sup>. The increase in the magnetic values corresponded to the increase in the crystallite size between the two materials. This result is in agreement with those reported by Goya et al. [29], Xu et al. [28] ; [30] and Monárrez-Cordero et al. [13] who have found a relation between the particle size and the magnetic



Fig. 8. Raman spectrum of materials D and E.

cimar)20

Table 5



Fig. 9. Room-temperature magnetization curves of materials D and E.

Material	Adsorption time (min)	Removal efficiency As <sup>+3</sup> (%)	Removal efficiency As <sup>+5</sup> (%)	Concentration of Fe detected by AAS <sup>*</sup> (ppm)
D	1 <sup>a</sup>	0	59 ± 3	No detected
D	10 <sup>a</sup>	10 ± 5	65 ± 2	No detected
D	31 <sup>b</sup>	36 ± 3	100	No detected
D	35 <sup>b</sup>	84 ± 4	100	No detected
D	40 <sup>b</sup>	100	100	No detected
D	45 <sup>b</sup>	100	100	No detected
E	31 <sup>b</sup>	49 ± 2	100	No detected
E	35 <sup>b</sup>	61 ± 9	100	No detected
E	40 <sup>b</sup>	100	100	No detected
E	45 <sup>b</sup>	100	100	No detected

<sup>b</sup> Contact and separation time including. <sup>\*</sup> Atomic absorption spectroscopy.

behavior for magnetite nanoparticles. Thus, these results suggest that temperature does not affect the crystalline phase only, but the particle size and in consequence the magnetic properties. However, the overall values of magnetization for both materials were quiet lower than those reported for bulk magnetite. This behavior can be explained in terms of Bloch wall thickness and spins orientation [31]. In bulk magnetite, where particles size is larger than 1 micron, magnetic domains are oriented in all directions. When an external magnetic field is



exerted on these particles, magnetic domains change as the Bloch walls are modified by the action of the field. As the particle size decreases to nanometric sizes, the formation of Bloch walls is no longer energetically favorable and the magnetic order or domains inside the particle do not change by the action of the field, consequently the magnetization is lower. Thus, the magnetic changes in this type of particles do not occur thought the movement of magnetic domain walls. Furthermore, ferromagnetism is originated by the parallel arrangement at short range, of the magnetic moment in atoms. Therefore, when particles are very small, magnetic order on the surface of the particles is lost because the surface anisotropy, which is produced by the discontinuity of the magnetic moments beyond the surface particle. The arrangement of the spins on the surface produces a null magnetization, because for every spin parallel to the surface there is an opposite spins on the other side of the particle counteracting the magnetization effect. Factors such as spherical morphology, hollow structure, small crystallite size and nanometric particle size, enlarge this effect, producing a lower magnetization value on the particles as those synthesized in this work.

#### 3.5. Arsenic removal tests

MNPs produced in materials D and E were tested for the removal of As<sup>+3</sup> and As<sup>+5</sup> from water. The ionic form of As<sup>+3</sup> is more difficult to adsorb since is very soluble in water [32]; [33]. As shown in <u>Table 5</u>, at adsorption times lower than 35 min, the efficiency for material D is higher than that for material E. After 40 min of contact As<sup>+3</sup> was fully removed from water. This behavior is explained in terms of hollow



morphology, porosity and particle size, where material D presented a smaller particle and crystallite size and in consequence a larger specific surface area than material E [14]. After testing adsorption times of 1 and 10 min for As<sup>5+</sup>, a 65% of removal efficiency was achieved and after 31 min of adsorption time, a 100% was fully removed from water. This result demonstrates the lower solubility of As<sup>+5</sup> in water and the fast adsorption on magnetite particles. Overall, these results showed larger efficiencies and shorter adsorption times than those previously reported in literature. [[21]; [34]; [35]; [36] ; [37]].

Although the magnetic behavior of the MNPs does not affect the adsorption of arsenic, still it is a very important feature during the recovery of MNPs, since this type of nanoparticles may be easily collected with the aid of a magnet. After the removal tests were performed, magnetite powders were separated from the treated water. As described in the experimental section, a magnet was employed for attracting the magnetite particles. The powders were dried and analyzed by TEM– EDS for quantifying the relative concentration of Arsenic adsorbed on the particles. Fig. 10(a and b) shows these results. Arsenic concentration was larger in particles synthesized in material D. As explained before, this was an effect of particle size. Other elements detected by the EDS were C, Na and Si; the majority of them originated from the precursor employed during the synthesis and the glass tube where magnetite particles were produced.



## 4. Conclusions

MNPs differing in morphology, microstructure and particle size were synthesized by the AACVD method. The effect of the synthesis parameters were studied and explained in terms of particle size and microstructure: (i) temperature and reactor tube diameter have a large effect on morphology and particle size, (ii) the type of solvent employed for dissolving the iron precursor influences the morphology, and (iii) the concentration of iron precursor solution affects less the size of spherical particles and crystallites. A mechanism of particle formation was proposed for describing the



Fig. 10. Elemental analysis of the materials D (a) and E (b) by energy dispersive spectroscopy (EDS). Arsenic was detected in the analyzed MNPs.

development of the hollow, porous and nanostructured shell of the magnetite sphere. The final crystalline phase characterized by HRTEM, XRD and Raman spectroscopy, was unaffected by the parameters studied, resulting in all cases the magnetite phase. Based on the overall iron mass balance, only one spherical nanostructure was obtained from one drop of precursor solution. Calculations



showed a very good matching with the experimental measurements. Two materials were tested in the removal of arsenic ions (As<sup>+3</sup> and As<sup>+5</sup>) from water, finding a 100% of efficiency at short periods of time.

## Acknowledgements

The authors would like to thank E. Torres-Moye, K. Campos-Venegas, D. Lardizabal, A. Benavides, S. Miranda, C. Santillán, for their technical assistance.

## References

[1] C. Sun, J.S.H. Lee, M. Zhang, Magnetic nanoparticles in MR imaging and drug delivery, Adv. Drug Delivery Rev. 60 (2008) 1252–1265.

 [2] J. Murbe, A. Rechtenbach, J. Topfer, Synthesis and physical characterization of magnetite nanoparticles for biomedical applications, Mater.
Chem. Phys. 110 (2008) 426–433.

 [3] S. Guo, D. Li, L. Zhang, J. Li, E. Wang, Monodisperse mesoporous superparamagnetic single-crystal magnetite nanoparticles for drug delivery,
Biomaterials 30 (2009) 1881–1889.

[4] Y.F. Shen, J. Tang, Z.H. Nie, Y.D. Wang, Y. Ren, L. Zuo, Tailoring size and structural distortion of Fe3O4 nanoparticles for the purification of contaminated water, Biores. Technol. 100 (2009) 4139–4146.

[5] S.K. Giri, N.N. Das, G.C. Pradhan, Synthesis and characterization of magnetite nanoparticles using waste iron ore tailings for adsorptive removal of dyes from aqueous solution, Colloid Surf. A 389 (2011) 43–49.

[6] A. Reza, M. Al-Sadat, Efficient separation of heavy metal cations by anchoring polyacrylic acid on superparamagnetic magnetite nanoparticles through



surface modification, Chem. Eng. J. 159 (2010) 264–271.

[7] Y.F. Shen, J. Tang, Z.H. Nie, Y.D. Wang, Y. Ren, L. Zuo, Preparation and application of magnetic Fe3O4 nanoparticles for waste water purification, Sep. Purif. Technol. 68 (2009) 312–319.

[8] J. Mayo, C. Yavuz, S. Yean, L. Cong, H. Shipley, W. Yu, J. Falkner, A. Kan, M. Tomson, V.L. Colvin, The effect of nanocrystalline magnetite size on arsenic removal, Sci. Technol. Adv. Mat. 8 (2007) 71–75.

[9] S. Yean, L. Cong, Effect of magnetite particle size on adsorption and desorption of arsenite and arsenate, J. Mater. Res. 20 (2005) 3255–3264.

[10] A. Andrade, M. Valente, J. Ferreira, J. Fabris, Preparation of sizecontrolled nanoparticles of magnetite, J. Magn. Magn. Mater. 324 (2012) 1753– 1757.

[11] Y. Li, J. Wang, Y. Zhao, Z. Luan, Research on magnetic seeding
flocculation for arsenic removal by superconducting magnetic separation, Sep. Purif.
Technol. 73 (2010) 264–270.

[12] Z. Huang, F. Tang, Preparation, structure, and magnetic properties of mesoporous magnetite hollow spheres, J. Colloid Interface Sci. 281 (2005) 432–436.

[13] B. Monárrez-Cordero, P. Amézaga-Madrid, W. Antúnez-Flores, C. Leyva-Porras,

P. Pizá-Ruiz, M. Miki-Yoshida, Highly efficient removal of arsenic metal ions with high superficial area hollow magnetite nanoparticles synthesized by AACVD method, J. Alloys Comp. 586 (2014) S520–S525.

[14] B. Monárrez-Cordero, P. Amézaga-Madrid, P.G. Hernández-Salcedo,



W. Antúnez-Flores, C. Leyva-Porras, M. Miki-Yoshida, Theoretical and experimental analysis of the aerosol assisted CVD synthesis of magnetite hollow nanoparticles, J. Alloys Comp. 615 (2014) S328–S334.

[15] T.T. Kodas, M.J. Hampden-Smith, Aerosol Processing of Materials, first ed., Wiley-VCH, 1999. ISBN 978-0-471-24669-5.

[16] C. Roger, T.S. Corbitt, T.T. Kodas, M.J. Hampden-Smith, Aerosol assisted chemical vapor deposition of copper, J. Aerosol Sci. 25 (1994) S221–S222.

[17] Ch. Xu, M. Nyman, J. Caruso, M.J. Hampden-Smith, T.T. Kodas, Aerosol assisted chemical vapor deposition (AACVD) of binary films of Ag–Pd, Cu– Pd, and Ag–Cu alloys, and SnO2: the role of precursor chemistry, J. Aerosol Sci. 26 (1995) S603–S604.

[18] M. Miki-Yoshida, P. Amézaga-Madrid, W. Antúnez-Flores, P. Pizá-Ruiz, C. Leyva-Porras, C. Ornelas- Gutiérrez, O. Solís-Canto, Aerosols: Synthesis, Optical Properties and Environmental Applications, Nova Science Publishers, Inc., New York, 2014. Cap. 3: Aerosols processing of nanostructured oxides for environmental applications, pp. 63–123.

[19] G. Jayanthi, S. Zhang, G. Messing, Modeling of solid particle formation during solution aerosol thermolysis: the evaporation stage, Aerosol Sci. Technol. 19 (1993) 478–490.

[20] I. Wuled, T. Hata, F. Iskandar, M. Lunden, K. Okuyama, An experimental and modeling investigation of particle production by spray pyrolysis using a laminar flow aerosol, React. J. Mater. Res. 15 (2000) 733–743.

[21] I. Akin, G. Arslan, A. Tor, M. Ersoz, Y. Cengeloglu, Arsenic (V) removal



from underground water by magnetic nanoparticles synthesized from waste red mud, J. Hazard. Mater. 235–236 (2012) 62–68.

[22] S.C. Zhang, G.L. Messing, M. Borden, Synthesis of solid, spherical zirconia particles by spray pyrolysis, J. Am. Ceram. Soc. 73 (1990) 61–67.

[23] K. Okada, A. Tanaka, S. Hayashi, N. Otsuka, J. Mater. Sci. Lett. 12 (1993) 854.

[24] M. Shusser, T. Ytrehus, D. Weihs, Kinetic theory analysis of explosive boiling of a liquid droplet, Fluid Dyn. Res. 27 (2000) 353.

[25] F. Márquez, T. Campo, M. Cotto, R. Polanco, R. Roque, P. Fierro, J.M. Sanz, E. Elizalde, C. Morant, Synthesis and characterization of monodisperse magnetite hollow microspheres, Soft Nanosci. Lett. 1 (2011) 25–32.

[26] Join Committee on Power Diffraction Standards, Powder DiffractionFile, International Center for Diffraction Data, Swarthmore P.A., Card 00-088-0315,2011.

[27] F. Froment, A. Tournié, P. Colomban, Raman identification of natural red to yellow pigments: ochre and iron-containing ores, J. Raman Spectrosc. 39 (2008) 560–568.

[28] J. Xu, H. Yang, W. Fu, K. Du, Y. Sui, J. Chen, Y. Zeng, M. Li, G. Zou,Preparation and magnetic properties of magnetite nanoparticles by sol–gel method,J. Magn. Magn. Mater. 309 (2007) 307–311.

[29] G. Goya, T. Berquó, F. Fonseca, Static and dynamic magnetic properties of spherical magnetite nanoparticles, J. Appl. Phys. 94 (2003) 3520– 3528.



[30] N. Guan, J. Xu, L. Wang, D. Sun, One-step synthesis of aminefunctionalized thermo-responsive magnetite nanoparticles and single-crystal hollow structures, Colloid Surf. A 346 (2009) 221–228.

[31] J.M.D. Coey, Magnetism and Magnetic Materials, Cambridge University Press, 2009. ISBN-T3 978-0-511-677434, p. 296..

[32] P. Mondal, C.B. Majumder, B. Mohanty, Laboratory based approaches for arsenic remediation from contaminated water: recent developments, J. Hazard. Mater. B 137 (2006) 464–479.

[33] W. Tang, Q. Li, S. Gao, J. Ku Shang, Arsenic (III, V) removal from aqueous solution by ultrafine a-Fe2O3 nanoparticles synthesized from solvent thermal method, J. Hazard. Mater. 192 (2011) 131–138.

[34] Z. Bujnáková, P. Baláz, A. Zorkovská, M.J. Sayagués, J. Kovác, M. Timko, Arsenic sorption by nanocrystalline magnetite: an example of environmentally promising interface with geosphere, J. Hazard. Mater. 262 (2013) 1202–1214.

[35] W. Tang, Q. Li, S. Gao, J. Ku Shang, Arsenic (III, V) removal from aqueous solution by ultrafine a-Fe2O3 nanoparticles synthesized from solvent thermal method, J. Hazard. Mater. 192 (2011) 131–138.

[36] W. Yang, A. Kan, W. Chen, M. Tomson, PH-dependent effect of zinc on arsenic adsorption to magnetite nanoparticles, Water Res. 44 (2010) 5693–5701.

[37] T. Türk, I. Alp, H. Deveci, Adsorption of As (V) from water using nanomagnetite, J. Environ. Eng. 136 (4) (2010) 399–404.

