

ARSENIC REMOVAL FROM WATER USING MAGNETIC NANOPARTICLES OBTAINED BY ACCVD

REMOCIÓN DE ARSÉNICO DE AGUA USANDO NANOPARTÍCULAS MAGNÉTICAS OBTENIDAS POR ACCVD

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Abstract

The development of magnetic nanoparticles by ACCVD is a powerful technique to synthesize material with high purity. The size and composition of magnetic nanoparticles was tailored, by variation of the flow ratio Ar-Air and furnace temperature. Different types of nanoparticles were obtained from metallic Fe until Fe₂O₃. The size of magnetic nanoparticles was between 195 nm and 272 nm. The synthesis temperature was between 440 and 590 °C. The nanoparticles were collected by using an impactor plate at 120 °C. The obtained materials were characterized by high resolution electron microscopy, X-ray diffraction and ICP-MS. These particles were used to remove arsenic from contaminated water. The magnetic nanoparticles showed a high capacity to adsorb arsenic. The initial concentration of arsenic in water was 20 ppbs and after removal with hematite the arsenic disappeared from solution. To remove arsenic from solution the ultrasonic method was used

to mix the magnetic nanoparticles with arsenic and subsequent precipitation with super magnets.

Keywords: ACCVD, arsenic removal, hematite.

Resumen

El desarrollo de nanopartículas magnéticas por ACCVD es una poderosa técnica para sintetizar materiales con alta pureza. El tamaño y composición de las nanopartículas magnéticas fue conseguido, por la variación en la relación de flujo de Ar- Aire, así como la temperatura del horno. Se obtuvieron diferentes tipos de nanopartículas desde Fe metálico hasta Fe_2O_3 . El tamaño de las nanopartículas magnéticas estuvo entre 195 nm y 272 nm. La temperatura de síntesis varió de 440 a 590 °C y el método de recolección de las nanopartículas se realizó con una placa impactor plana a 120 °C. El material obtenido fue caracterizado por microscopia electrónica de alta resolución, ICP-MS y difracción de rayos X. Estas nanopartículas fueron usadas para remover arsénico de agua contaminada. Las nanopartículas magnéticas mostraron una alta capacidad para adsorber el arsénico. La concentración inicial de arsénico en agua fue de 20 ppbs y después de la remoción con la hematita el arsénico desapareció de la solución. Para remover el arsénico de la solución fue usado el método de ultrasonificación para mezclar las nanopartículas magnéticas con el arsénico y su posterior precipitación con super imanes.

Palabras clave: ACCVD, remoción de arsénico, hematita.

Introduction

There are as many as 15 phases formed by Fe and O as oxides of iron. There are abundant in earth's crust. They can be synthesized in pure, mixed oxides as well as doped structures. Iron oxides are used as an electrode in non aqueous and alkaline batteries and as a cathode in brine electrolysis. Recently, Fe_2O_3 is found to have large third-order non-linear optical susceptibility and faster response time showing potential applications in optical

computing [1]. Magnetic particles are of great interest for magnetic fluids, biotechnology, biomedicine, magnetic resonance imaging, data storage and environmental remediation. Depending on the Fe oxidation state (Fe^{+2} or Fe^{+3}), iron oxides exhibit different crystal structures that include hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) on which hematite is the thermodynamically more stable form as well as magnetite (Fe_3O_4). Various methods have already been applied for synthesis of Fe_2O_3 and Fe_3O_4 particles. These include wet chemical routes such as co-precipitation, thermal decomposition in non-aqueous liquids and microemulsions or hydrothermal synthesis, but also particle formation in the gas phase such as thermal decomposition in hot-wall reactors or flame synthesis. Different flame reactors have already been used for the synthesis of Fe_2O_3 particles including diffusion flames and flame spray pyrolysis reactors operating with Fe-precursors dissolved in a combustible liquid [2].

Magnetic nanoparticles offer attractive possibilities abundant in technology, particularly in biotechnological applications, the synthesis route is very important for the characteristic of material and application; the magnetic particles obtained by ACCVD were collected in an impactor plate and stored it for analysis. ACCVD use an ultrasonic nebulizer for atomizing a precursor solution in droplet form. Spray aerosol generators can be applied to the formation of thin films and preparation of fine particles by ACCVD for film generation; an aerosol of a solution is formed and then deposited onto a surface where solvent evaporation and chemical reaction take place resulting in a film. The advantage of ACCVD lies in the ability to use a wide variety of precursors with low vapor pressure as long as they have a suitable solvent [3].

Other technique for obtaining nanoparticles shows the possibility for synthesis of magnetic nanoparticles under controlled atmosphere. This way controlled and flame synthesis of Fe_2O_3 and Fe_3O_4 [2]. The process of spray is commonly used to form a wide variety of materials in powder form. The method of spray offers specific advantages over conventional material processing techniques [4, 5]. This method consist of five steps: (i) generation

of a spray from a liquid precursor by an appropriate droplet generator, (ii) spray transport by an air flow during which solvent evaporation occurs then solute precipitation when the solubility limit exceed inside droplets, (iii) thermolysis of the precipitated particles at higher temperatures to form micro/nano porous particles, (iv) intra- particulate sintering to form dense particles and (v) finally, extraction of the particles from the gas flow [6].

Magnetic nanoparticles are used to remove arsenic from contaminated water [7], magnetite has been used for the arsenic remotion and it is obtained for different methods [8, 9]. The magnetic phase and size of particles is very important to remove arsenic. In the future the process to remove the arsenic must be redefined and well as the analysis of the difference between magnetic nanoparticles of magnetite and hematite.

Experimental Procedure

Magnetic nanoparticles were synthesized by ACCVD method using reagent grade materials: Iron (III) Chloride Hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (JT Baker)) in tridistilled water how solvent.

By varying concentration of reactive in aqueous solution of Chloride Hexahydrate 0.01 M to 0.1 M and temperature in furnace, different magnetic particles were synthesized. An aqueous solution of Chloride Hexahydrate was atomized using in a mixture Air-Ar as the carrier gas. The temperature furnace was 440 °C to 590 °C where the solution was evaporated for the formation of nanoparticles, with the variation of gas mixed and the solution concentration and furnace temperature, the particles size and composition was modified. In table 1 the variation of concentration solution or ratio of air-argon makes it possible to obtain pure Fe or Hematite, or obtain particles of different sizes. Hematite is simple to obtain for this method, pure Fe is obtained in the absence of oxygen in this method. The nanoparticles were collected in heat plate with a special design and removed washing them with ethanol for posterior characterization. The technical characterizations used to analyze the samples are DRX, SEM, TEM and ICP-MS.

The magnetic nanoparticles were used to remove arsenic of contaminated water by using ultrasonification and separated for elemental analysis technique and detect the arsenic remotion. The initial amount of arsenic in water was 20 ppbs and after remotion the arsenic disappears, the method to quantify is an ICP-MS.

Sample	Reagent	Flow (L/min)	Furnace Temperature (°C)	Solution Concentration
MF (Fe ₂ O ₃)	FeCl ₂ ·4H ₂ O	0.2 (Air)	440	0.1 M
MK (Fe ₂ O ₃)	FeCl ₂ ·4H ₂ O	2 (Air)	500	0.1 M
ML (Fe ₂ O ₃)	FeCl ₂ ·4H ₂ O	1 (Air)	500	0.1 M
MM (Fe ₂ O ₃)	FeCl ₂ ·4H ₂ O	1 (Air)	500	0.01 M
MO (Fe)	FeCl ₂ ·4H ₂ O	1 (Ar)	500	0.01 M
MQ (Fe ₂ O ₃)	FeCl ₂ ·4H ₂ O	1 (Ar)/ 0,015(Air)	500	0.01 M
MR (Fe ₂ O ₃)	FeCl ₂ ·4H ₂ O FeCl ₃ ·6H ₂ O	1 (Ar)/ 0,015(Air)	500	0.01 M
MS (Fe ₂ O ₃)	FeCl ₂ ·4H ₂ O	1 (Ar)/ 0,015(Air)	590	0.01 M

TABLE 1. *Samples with different experimental conditions*

Results and Discussion

HEAT PLATE

Figure 1 shows the experimental setup utilized for the synthesis, where (1) is a flow control for Ar and Air, (2) is a generator of droplets from the solution, (3) the initial solution (4) is a quartz tube of 9 mm which allows the pass of droplets of solution towards (5) furnace and (6) is a plate to collect the nanoparticles for analysis.

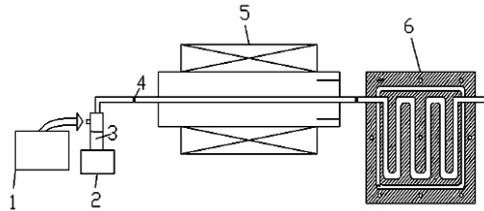


FIGURE 1. System to produce magnetic particles

SEM

The figures 2a and 2b show SEM images of magnetic nanoparticles of different sizes where the only variation is the solution concentration. In figure 2a there are some particles of 272 nm size to concentration 0.1M and figure 2b shows particles of 195 nm to concentration of 0.01 M. The furnace temperature was 500 °C and with an air flow.

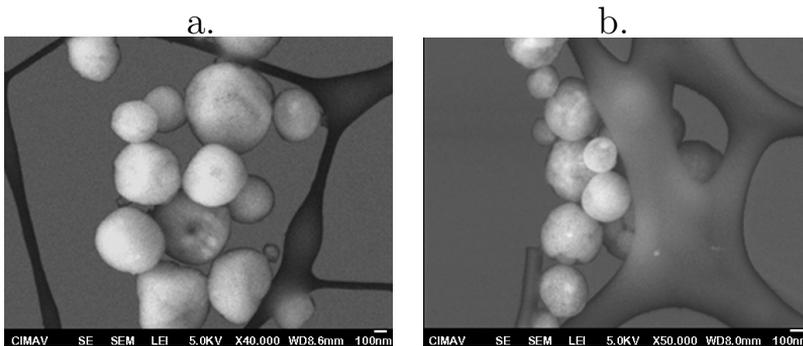


FIGURE 2. **a.** Magnetic particles with concentration 0.1 M. **b.** Magnetic particles with concentration 0.01 M.

TEM

At AACVD can obtain Fe metallic and Hematite Fe_2O_3 . The figure 3a shows rings of characteristic patron diffraction of metallic Fe and figure 3b. shows a particle which have some nanometric crystals size. The nanoparticle is an agglomerate but inside there are nanoparticles of 5 nm; the variation in nanoparticles composition was obtained with the variation of air in carrier gas in the obtaining process of nanoparticles. The composition of nanoparticles affects

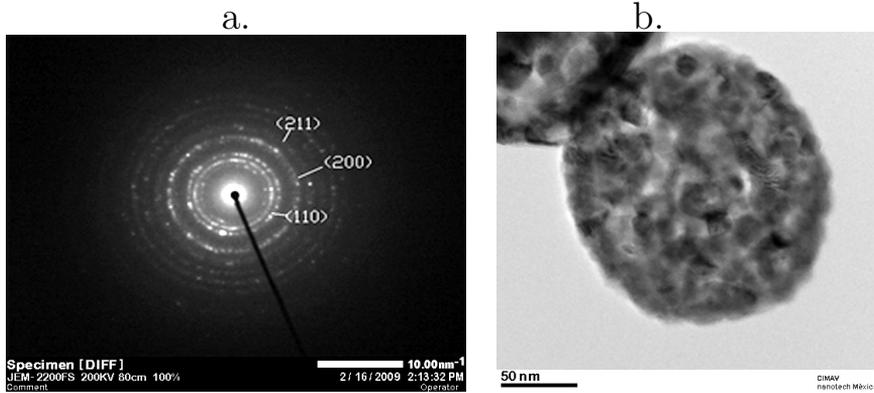


FIGURE 3. *a.* Diffraction pattern rings of magnetic nanoparticles of metallic Fe. *b.* Agglomerates magnetic nanoparticles.

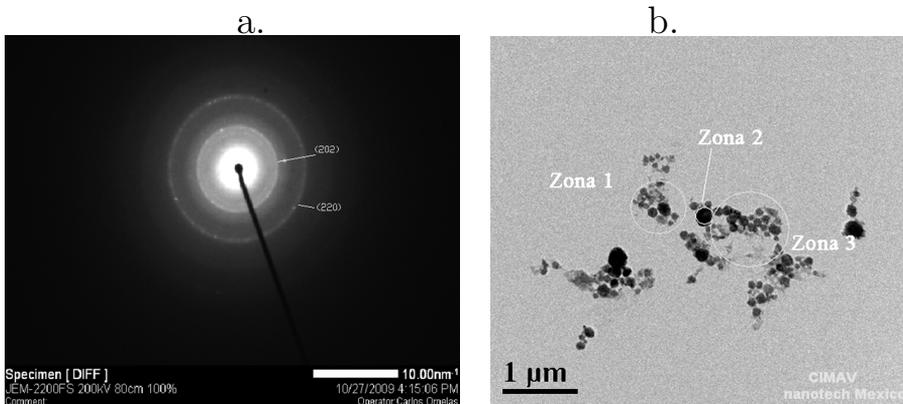


FIGURE 4. *a.* Diffraction pattern rings of magnetic nanoparticles of hematite. *b.* Agglomerates magnetic nanoparticles.

the internal structure where we can obtain metallic Fe or different magnetic phases.

When the atmosphere is varied, Air-Ar concentration can be obtained Fe_2O_3 . Figure 4a shows patron rings of Fe_2O_3 and figure 4b shows nanoparticles with different sizes and indicates that the particles are solid and spherical.

Preliminary results indicate that the particles size is a function of several parameters. Figure 5 shows the results for relation atmosphere Air-Ar and amount Oxygen in the samples, without Air is metallic Fe; to Fe_2O_3 near to “m” sample shows the percentage

of O in 48% and Fe in 52% present in hematite to 0.98 l/min of Air.

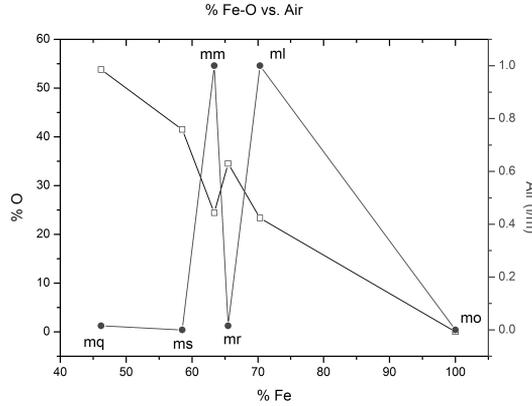


FIGURE 5. Oxygen variation with mixture of flow inside furnace

XRD

Figure 6 shows a XRD pattern of magnetic nanoparticles of hematite, this particles were used to remove arsenic from contaminated water, the peaks are narrows and display high intensity which is due to particle size. The particle size in TEM is 195 nm and 55 nm from XRD by using the Scherrer's formula.

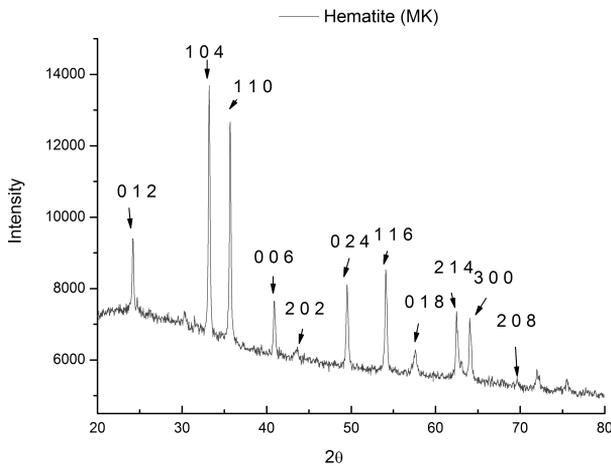


FIGURE 6. DRX particles of Fe₂O₃.

Table 1 shows the nanoparticles with different conditions which display different structural characteristic and composition. With

this technique we can produce some materials only with the variation of furnace temperature and the mix flow. Hematite is obtained in oxygen presence, particle size is varied by the solution concentration, 272 nm particles is obtained by 0.1 M solution and 195 nm particles is obtained by 0.01 M solution. Pure Fe is obtained in Ar atmosphere. The MR sample is obtained with Iron (III) Chloride Hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and Iron (II) Chloride Hexahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$). The particles size is 272 nm, MS is obtained with Iron (II) Chloride Hexahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), the particles size are 195 nm, the ratio Air-Ar and furnace temperature is the same, the difference in particles size is the reactant, when the solution contained $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ the particles size are 272 nm.

MQ and MS samples are obtained with the same solution concentration, the furnace temperature is different. When the temperature is high the particles size decreases.

Table 2 shows a comparison between contaminated water and clean water after remotion with magnetic nanoparticles of hematite. The process for remotion was very simple, the magnetic nanoparticles were mixed by ultrasonification process during few minutes, and then the magnetic nanoparticles were separated by precipitation with super magnets.

Sample	Ultrasonification time (min)	As mg/L	Fe mg/L	% Removal
Water contaminated with arsenic	0	0,020	0	0
Water after mixing with magnetic nanoparticles of hematite (MK)	5	N.D.	0	100

TABLE 2. Treatment of 200 mL of contaminated water (Ar 0.02 mg/L) with 0.05 mg magnetic nanoparticles of 195 nm size.

Conclusions

- The variation of solution concentration modified size of particles.

- Varying the concentration of carrier gas the composition of nanoparticles and internal structure are modified, we can obtained metallic Fe and Fe₂O₃.
- The nanoparticles obtained have sizes of few nanometers, the nanoparticles have 5 nm in some agglomerates and the samples have a crystalline structure.
- The magnetic nanoparticles of hematite in this method have high capacity to remove arsenic from contaminated water.

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