Synthesis and characterization of nanomagnetite for environmental applications

MYSTRIOTI C.[1*], PAPASSIOPI N.[1*] and XENIDIS A.[1]

[1] School of Mining and Metallurgical Engineering National Technical University of Athens Iroon Polytechniou 9 St Athens, 157 80.
*corresponding author: e-mail: chmistrioti@metal.ntua.gr

Abstract Magnetite (Fe_3O_4) in nanoscale has been very attractive due to its unique properties which make it ideal for a wide range of applications. Nanomagnetite can be applied as drug delivery medium, as catalyst and as efficient adsorbent and reducing agent for water treatment. In this study, magnetite nanoparticles were synthesized by co-precipitation of ferrous and ferric iron salts with the addition of a base under microwave-assisted heating. This is a simple, low cost and quick method which results to uniform shape and size of nanomagnetite particles. The effect of heating time and the microwave power were evaluated for the properties of nanoparticles. The mineralogical composition of prepared nanoparticles was determined by X-Ray Diffraction (XRD). The performance of nanomagnetite for Cr(VI) removal from contaminated water streams was evaluated by conducting batch tests. Nanomagnetite exhibited good removal performance for chromates and could easily be separated and recovered under magnetic field.

***Keywords*:** magnetite; magnetic nanoparticles; microwave synthesis; chromium removal; adsorption.

1. Introduction

Iron oxides have been very promising materials because they can be used for a wide range of applications. Iron oxides such as magnetite (Fe_3O_4) due to its nano size can be superparamagnetic which make nanomagnetite very appealing for several applications. Nanomagnetite can be applied in biomedicine as drug carriers, as MRI agent, as useful materials for catalysts and for electronic applications (Wallyn et al. 2019). The nano magnetite particles exhibited super-paramagnetic behavior which make them ideal adsorbent materials for the treatment of polluted waters due to the effective separation from waters using a magnetic field (Aivazoglou et al. 2018). The iron oxides properties (size, chemical composition, magnetic properties) are strongly related with the preparation method which control the nucleation of nanoparticles. The most common synthesis method are the chemical precipitation of ferric and ferrous iron using a strong base (ammonia, NaOH) which requires high temperature and many hours of reaction until the formation of nanomagnetite. However this method results to nanomagnetite with a wide size distribution and irregular shape of particles (Wallyn et al. 2019). This drawback can be overcome applying microwave irradiation for enhancing the nucleation and the uniform synthesis of nanomagnetite particles. Microwave assisted synthesis route have been attractive the last decades for synthesis of inorganic materials. This method can provide homogeneous heating, shorter reaction time, high phase purity, and high yield rate of products (Kostyukhin et al. 2020). Aivazoglou et al. (2018) synthesized nanomagnetite particles ranges from 10.3 to 19.2 nm with negligible coercivity and remanence, illustrating super-paramagnetic behavior by applying microwave-assisted synthesis. Aim of this study was to synthesize nanomagnetite particles by applying microwave assisted heating method. The heating time and the microwave power were evaluated for the optimization of nanomagnetite properties. The hexavalent chromium removal using nanomagnetite particles was investigated by conducting batch tests.

2. Materials and Methods

2.1. Materials

Ferrous and ferric chloride ($FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$), aqueous ammonia 18M (28-30% w/w), and absolute ethyl alcohol were purchased by Sigma Aldrich and were used for the preparation of iron oxide nanoparticles. Potassium dichromate ($K_2Cr_2O_7$) and 1,5 diphenylcarbazide were obtained from Merck, Germany and were used at the batch tests for chromium removal and for Cr(VI) determination respectively.

2.2. Synthesis of nanoFe_3O_4

The synthesis procedure of nanoFe_3O_4 was based on the study of Aivazoglou et al. 2018. In this method, 0.86g of $FeCl_2 4H_2O$ and 2.36g $FeCl_3 6H_2O$ were dissolved in 40 mL of preheated distilled water at 80-90°C. Ammonia solution was added until the pH of the solution was equal to 9 under continuous stirring. The color of the suspension changed from orange to black with the increase of the pH. The suspension was then placed in the microwave synthesis labstation (Microsynth from Milestone). The iron oxide nanoparticles were removed by a neodymium magnet and were washed with 200 mL DW and 50 mL ethanol alcohol. Then the nanoparticles

were dried in an oven at 45°C. Iron nano oxide particles were synthesized varying the heating time (90 sec and 150 sec) and the microwave power (160, 400 and 600 W).

Table 1. Experimental conditions for the production of nanoFe_3O_4 samples

Sample	Microwave power (W)	Heating time(sec)
1	0	150
2	160	90
3	160	150
4	400	90
5	400	150
6	600	150

2.3. Characterisation of nanoFe_3O_4

The nanoparticles were examined by X-Ray Diffraction. The analysis was performed using a Bruker D8-Focus powder diffractometer (Bruker, Karlsruhe, Germany), with nickel-filtered CuKa radiation (λ= 1.5405Å). The point of zero charge (pHpzc) was determined in selected samples by the acid base potentiometric titration method (Uehara and Gillman, 1981). In this method a series of suspensions were prepared by mixing 0.25 g nanoFe_3O_4 with 50 mL NaCl (0.01M). The initial pH was adjusted to values between 2 and 12 and equilibrium pH was measured after 24 hours of mixing.

2.4. Batch experiments for Cr(VI) removal

All the nanoFe_3O_4 samples were evaluated for hexavalent chromium removal. The tests were conducted mixing 0.2g nanoFe_3O_4 with 100 mL of a solution containing 40 mg/L Cr(VI). The effect of pH on Cr(VI) removal capacity was investigated by conducting batch tests in the acidic (3.3-3.9) and in the alkaline (8.5-9.5) pH range. The initial pH of Cr(VI) solution was equal to 3.3 and was mixed with the nanoFe_3O_4 without any pH adjustment. The final pH at the end of adsorption ranged between 3.4 and 3.9. For the alkaline region, the initial pH was adjusted to 9.5 by using NaOH 0.01M and the final pH ranged between 8.5 and 9.0. The experiments were carried out using shaking flasks which were placed in an orbital agitator. The suspensions were agitated at 250 rpm for 90 min and the temperature was kept constant at 25°C. Samples were taken at 90 min and analyzed for Cr(VI). The pH and oxidation reduction potential (ORP) of the samples were also recorded. The separation of nanoFe_3O_4 took place easily using a magnet. The hexavalent chromium was analyzed by using the USEPA 7196a method in a HACH DR-1900 spectrophotometer with detection limit, equal to 15 μg/L.

3. Results

Some representative XRD patterns of nanoFe_3O_4 particles are presented in Fig. 1. The XRD patterns have broad and low intensity peaks which are characteristics of nanomaterials. The six characteristics peaks for magnetite ((220), (311), (400), (422), (511), and (440)) can be seen in the patterns. The mean crystallite size was determined from XRD data using Debye- Scherrer equation:

$$D = (k * \lambda)/(\beta * cos\theta)$$

where k = constant, λ = X-ray wavelength and β = Full Width at Half Maximum (FWHM). The FWHM was calculated using Origin Software. The average crystallite size of the samples prepared by microwave-assisted heating, ranged from 9.8 nm to 11.5 nm in all different synthesis conditions.

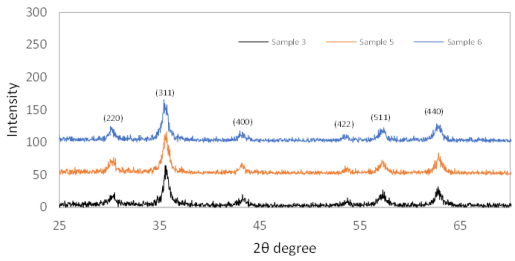

Figure 1. XRD pattern of magnetite nanoparticles

The pH_{pzc}, as determined for sample 3, was found equal to 6.1, suggesting that the electric charge of nanomagnetite surface changes from positive to negative values below and above this pH value, respectively.

The efficiency of nanoFe_3O_4 particles for Cr(VI) removal was investigated in the acidic and in the alkaline pH ranges. Table 2 presents the adsorption capacity q_e (mg/g) of the nanomagnetite particles. The effect of microwave power is also presented in Figure 2.

Table 2. Efficiency of nanomagnetite samples for Cr(VI) removal at acidic and alkaline pHs.

	Micro-wave power (W)	Heating time (s)	qe (mg/g) pH 3.3-3.9	qe (mg/g) pH 8.5-9.5
1	0	150	11.23	3.67
2	160	90	10.15	4.67
3	160	150	11.90	2.64
4	400	90	8.11	2.54
5	400	150	11.38	3.99
6	600	150	13.80	4.52

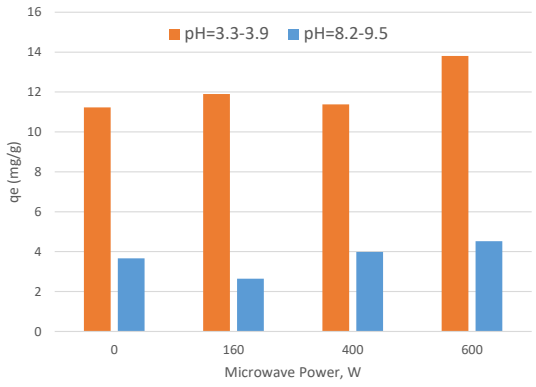

Figure 2. The effect of microwave power

As expected, higher removal efficiencies varying between 8.1 and 13.8 mg/g were recorded at the acidic pH values. The corresponding removal at the alkaline pHs ranged between 2.5 and 4.5 mg/g. The maximum removal, i.e. 13.8 and 4.5 mg/g at acidic and alkaline pHs respectively, was obtained with the nanomagnetite produced at the higher microwave power (600 W).

4. Conclusions

In this study the synthesis of nanoFe_3O_4 particles applying a microwave-assisted method was evaluated. Magnetite nanoparticles with average particle size from 9.8 nm to 11.5 nm have been prepared in few minutes. The process is easy and quick. The effect of microwave power and the heating time were investigated. The nanoFe_3O_4 particles presented good adsorption capacity for Cr(VI). At initial concentration of Cr(VI) at 40 mg/L and with a Fe_3O_4 dose of 2.0 g/L the maximum adsorption capacities reached were 13.8 mg/g and 4.6 mg/g, for initial pH 3.3 and 8.5 respectively. Loaded nanoparticles can be easily removed from treated solutions by magnetic separation.

ACKNOWLEDGMENTS

This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project "Reinforcement of Postdoctoral Researchers - 2nd Cycle" (MIS-5033021), implemented by the State Scholarships Foundation (IKY).

References

Aivazoglou E., Metaxa E., and Hristoforou E. (2018), Microwave-assisted synthesis of iron oxide nanoparticles in biocompatible organic environment, *AIP Advances* **8**, 048201.

Kostyukhin E., Nissenbaum V., Abkhalimov E., Kustov A., Ershov B., and Kustov L. (2020) Microwave-Assisted Synthesis of Water-Dispersible Humate-Coated Magnetite Nanoparticles: Relation of Coating Process Parameters to the Properties of Nanoparticles *Nanomaterials*, **10**, 1558.

Wallyn J., Anton N. and Vandamme T. F. (2019) Synthesis, Principles, and Properties of Magnetite Nanoparticles for In Vivo Imaging Applications- A Review Pharmaceutics, **11**, 601.

Uehara G., and Gillman G. (1981) The mineralogy, chemistry, and physics of tropical soils with variable charge clays. Boulder, CO: Westview Press **145**.