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Nadia Chekalil, Mohamad Tarhini, Abdelhamid Elaïssari, Salima Saïdi-Besbes. Multi-step synthesis of core–shell magnetic nanoparticles bearing acid-chelating functional moieties. *Research on Chemical Intermediates*, 2019, 45 (10), pp.4847-4861. <10.1007/s11164-019-03868-3>. <hal-02989970>

**HAL Id: hal-02989970**

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Submitted on 17 Nov 2020

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# Multi-steps synthesis of core-shell magnetic nanoparticles bearing acid-chelating functional moieties

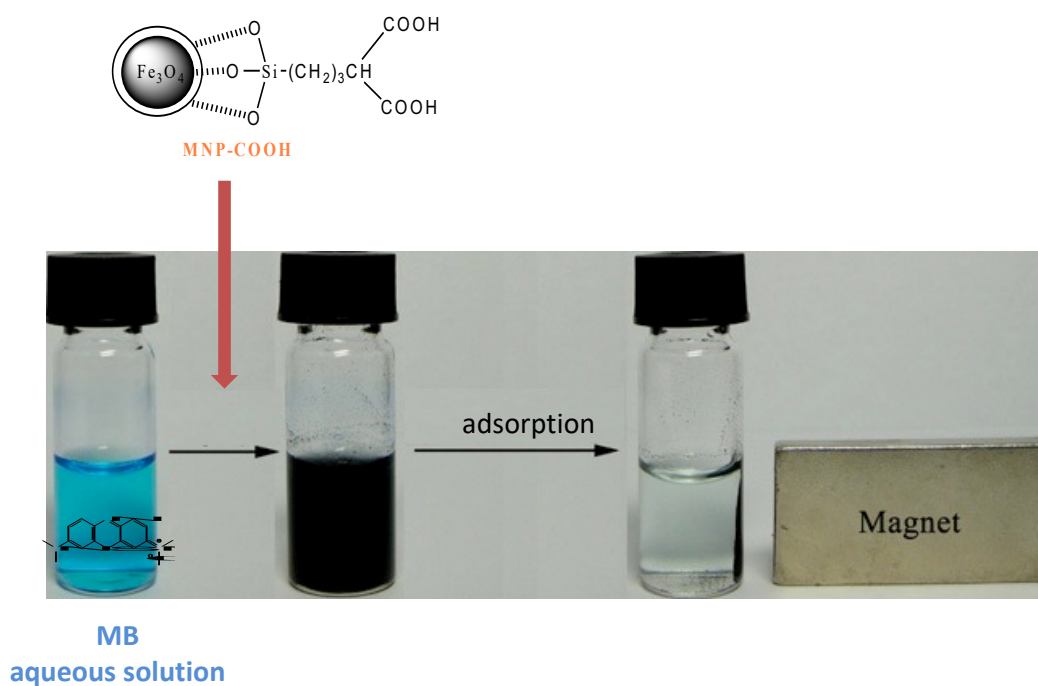
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## Graphical Abstract:



## Abstract:

Two synthetic approaches for the surface modification of core-shell-shaped silica coated magnetic nanoparticles with acid functions have been investigated. The step procedure based on the covalent attachment with diethylmalonate reagent and subsequent hydrolysis of the ester functions has proven to be much efficient and versatile for the incorporation of such functionality than the one-pot method. The changes in surface morphology and chemical functionality were examined by as X-ray diffraction (WAXD), infrared spectroscopy (FTIR), thermogravimetry analysis (TGA), zeta potential analysis and transmission electron

microscopy (TEM). The acid-functionalized  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanomaterial exhibited high adsorption affinity for the cationic dye methylene blue and is as such potentially interesting for wastewater treatment as an effective adsorbent for cationic dyes.

**Keywords:**

$\text{Fe}_3\text{O}_4@\text{SiO}_2$  magnetic nanomaterial, Acid- functionalized, diethylmalonate, cationic dye, adsorbent.

**1. Introduction**

Current trends in the field of environment are aimed at designing tools to obtain fast, specific and automated applications. Magnetic colloids, in particular, are broadly used as magnetizable adsorbents since they make it possible to replace the centrifugation, sedimentation, and filtration heavy separation techniques by using a simple magnetic field, electromagnet, or a permanent magnet.

To date, different magnetic adsorbents have emerged [1–3]. Magnetic iron oxide nanoparticles MNPs with an average particle size between 5 and 12 nm [4,5] such as maghemite  $\text{Fe}_2\text{O}_3$  and magnetite  $\text{Fe}_3\text{O}_4$ , which can be easily prepared by alkaline co-precipitation, are the most well-known nanoparticles [6]. They acquire a negative charge in solution that allows them to retain cationic pollutants including heavy metals [7]. Iron oxides nanoparticles can be used alone bare, that is to say without recovery. For instance, N. Nasser has shown the effectiveness of the use of magnetite nanoparticles to remove lead ions  $\text{Pb}(\text{II})$  with a good adsorption capacity up to 36 mg /g [8].

However, due to their hydrophobic surfaces and large surface area to volume ratio, magnetic nanoparticles tend to agglomerate in aqueous media which can result on reducing their interaction efficiency with the surrounding molecules. In general, there is the need to disperse MNPs into suitable solvents or to coat them with certain inorganic or organic molecules and polymers in order to form homogeneous solutions called ferrofluids. In addition to avoid agglomeration, such encapsulation, that can be done either covalently or by physical adsorption, provides the iron oxide nanoparticles with protection against external conditions such as oxidation and further functions that enhance the affinity of iron oxides nanoparticles towards targeted molecules. In the biomedical field, the encapsulation of MNPs is of paramount importance to impart them solubility and compatibility in biological environments particularly for the field of diagnosis [9] and for immobilization of viruses [10], enzymes, proteins [11] and

nucleic acids [12].

Among the materials used for chemical modification of magnetic core, silica shell has shown its effectiveness as a protective coating to enhance the chemical stability of magnetic particles particularly in acid media and prevents their aggregation in solution [13]. The silanol groups present at the surface of the silica coating allows also the reaction with different coupling agents to covalently attach specific ligands as proteins, peptides, antibodies, chelating agents... The non-toxicity and biocompatibility of the amorphous silica have been thus extensively explored for several applications in catalysis, environment, and biology.

Several functionalized silica coated magnetic nanoparticles have been designed and used as nanosorbents for metal remediation. The common functional groups used for this purpose are amine, dimercaptosuccinic acid, carboxylic acid, phosphonic acid, natural or synthetic polymers as chitosan [14], alginate, dextrin and poly(acrylic acid) [15].

For example, thiol-modified  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPS were designed as highly effective and recycling magnetic sorbents for mercury removal [16]. The  $\text{SiO}_2$  shell was coated on  $\text{Fe}_3\text{O}_4$  nanoparticles by hydrolyzation of  $\text{Na}_2\text{SiO}_3$ , and then thiol groups were modified on the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  through silanization reaction to form  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$  sorbents. X-ray photoelectron spectroscopy (XPS) analysis suggested that the adsorption was based on the “soft-soft” interaction between thiol group and mercury. Wang et al. used amino-functionalized  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  magnetic nanomaterials with a core-shell structure for the adsorptive removal of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$  heavy metals from aqueous solutions [17].

We investigated recently the ability of 1,2,3-triazole functionalized silica coated magnetite nanoparticles for metal ion remediation [18]. A synergistic effect between magnetite and triazole heterocycle was confirmed that affect positively the adsorption behavior of this adsorbent in comparison with the crude iron oxide material. High adsorption capacities of 87.87, 167.78, 51.20  $\text{mg}\cdot\text{g}^{-1}$  have been achieved for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions, respectively.

The carboxylic acid-functionalized MNPs adsorbents demonstrated outstanding ability to remove a wide variety of heavy metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{2+}$ , and  $\text{Cd}^{2+}$  from aqueous solutions owing to the strong metal complexing capability of carboxylic acid groups [19,20]. For instance, Humic-acid-coated  $\text{Fe}_3\text{O}_4$  nanoparticles prepared by the coprecipitation method were found to effectively sorb  $\text{Hg(II)}$ ,  $\text{Pb(II)}$ ,  $\text{Cd(II)}$ , and  $\text{Cu(II)}$  from water [21]. Polyacrylic acid grafted superparamagnetite nanoparticles were synthesized by modification of magnetite core subsequently with 3-aminopropyl triethoxysilane (APTES) and

acryloyl chloride (AC) followed by graft polymerization with acrylic acid. The grafted magnetite nanoparticles showed their potential for the separation of heavy metal cations such as  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  [22]. Hematite nanoparticles have been functionalized with a self-assembled monolayer of undecanoic acid by covalent attachment via siloxane groups and used for the capture of cadmium ions [20]. It is worth mentioning that common investigated carboxylic acid –functionalized magnetic sorbents are based on bare iron oxide nanoparticles that are susceptible to leaching under acidic conditions, environment where their regeneration usually takes place.

Thus, we were interested in this work to develop an efficient and versatile synthetic procedure for the preparation of silica coated magnetite particles  $\text{MNP}@SiO_2$  functionalized with acid functions. Such material can be potentially used for the adsorption of cationic pollutants as metallic ions or dyes. Two strategies were investigated as presented in figure 1: a) a 3 steps strategy based on the functionalization of  $\text{MNP}@SiO_2$  with 3-(chloropropyl)trimethoxysilane followed by reaction with diethyl malonate and hydrolysis of the ester functions and, b) a *one-pot* reaction to accede to the diesters derivatives from  $\text{MNP}@SiO_2$  NPs followed by their subsequent hydrolysis. The efficiency of these two procedures will be discussed regarding different characterization methods as IR spectroscopy, Zeta potential, thermogravimetry analysis and transmission electron microscopy.

## 2. Material and methods

### 2.1 Materials

Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 98%), ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 99%), tetraethylorthosilicate ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ , TEOS >99%), (3-Chloropropyl)trimethoxysilane (CPTES,  $\geq 97\%$ ), diethylmalonate, sodium hydride (NaH, 60 % dispersion in mineral oil), potassium hydroxide (90%) hydrochloric acid (37%), ammonia solution (28-30%) were purchased from Sigma-Aldrich (Prochima Sigma, Tlemcen, Algeria). The solvents were of commercial grade quality and were dried and distilled before use. Ethanol (99%) and tetrahydrofuran ( $\geq 99.9\%$ ) were purchased from Sigma-Aldrich (Prochima Sigma, Tlemcen, Algeria). Toluene (99%) was obtained from Biochem, Algiers.

### 2.2. Characterizations

The Fourier-transform infrared spectroscopy spectra were recorded on an alpha Bruker spectrometer. The average infrared radiation was ranging from 4000 to 400 cm<sup>-1</sup>. The dry powders of magnetic particles were used as such for measurements.

Thermogravimetry analyses of particles were carried out on a TG 209 Netzsch apparatus by measuring the mass variation of the samples as a function of temperature. Alumina crucibles were filled with accurately weighted samples of about 10 mg. The temperature program ranged from 93.49 C° to 721.37C° at a heating rate of 10 °C/min. All experiments were conducted under nitrogen atmosphere. The weight loss was recorded as a function of temperature and time.

Zeta potentials of magnetic nanoparticles were determined as function of pH values using a Zeta sizer nanoseries “zs” of Malvern instruments (England). Zeta potential is related to the electrophoretic mobility by the HENRY EQUATION:

$$\zeta = 3\mu\eta / (3\epsilon f(\kappa a))(1)$$

with  $\zeta$  is the zeta potential,  $\epsilon$  is the dielectric constant,  $\eta$  is the viscosity,  $f(\kappa a)$  is Henry's function,  $\kappa$  is the Debye parameter,  $a$  is the particle radius and  $\mu$  is the electrophoretic mobility. Different pH solutions were prepared using 1 mM NaCl solution and the pH values were adjusted by 1 mM NaOH or 1 mM HCl solution using a pHmeter. The samples were diluted in the corresponding solution before measuring the electrophoretic mobility.

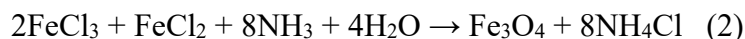
Transmission Electron Microscopy, TEM, was performed with a Philips CM120 microscope at the “Centre Technologique des Microstructures” (CT $\mu$ ) of the University of Lyon 1 (Villeurbanne, France). Before observation, carbon grids were plunged in nanoparticle powders, the excess were then removed. The samples were observed by TEM under 120 kV acceleration voltages.

The magnetic properties of the samples were examined by an automatic bench for magnetic measurement (ABMM) at CNRS-IRC laboratory Lyon. Magnetization of the samples was investigated by decreasing magnetic field (H) from 20,000 to 15,000 Oersted.

## 2.3. Methods

### 2.2.1. Synthesis of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>)

Magnetic particles were prepared by the chemical precipitation method [23]. In brief, 5.4 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 2 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (molar ratio 2:1) were dissolved in 100 mL of demineralized water. The solution was bubbled with nitrogen for 20 min under vigorous mechanical stirring. Then 55 mL of ammonia solution 28% was added drop wise into the solution under vigorous mechanical stirring for 30 min at room temperature. Black colored precipitates begin to form that corresponds to  $\text{Fe}_3\text{O}_4$  particles according to the following chemical reaction:



The mixture was heated to  $70^\circ\text{C}$  and was allowed to proceed for further 2 hours at 300 rpm. Particles were then separated by an external magnet, washed with demineralized water until the pH becomes neutral, then three times with ethanol and finally dried using a vacuum pump.

### **2.2.2 Synthesis of silica coated magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@\text{SiO}_2$ )**

Magnetic nanoparticles were coated with a silica protective layer as follows: 100 mg of magnetite  $\text{Fe}_3\text{O}_4$  particles were dispersed in a mixture of 80 ml of anhydrous ethanol and 20 ml of demineralized water using an ultrasonic bath during 15 minutes to ensure the total dispersion of the powders. The pH of the solution was adjusted to  $\text{pH} = 9$  with ammonia solution (28%). Then, 200  $\mu\text{l}$  of TEOS were added and the mixture was stirred under nitrogen atmosphere at 300 rpm for 4 h at room temperature. The solid was separated with an external magnet and washed three times with 50 mL demineralized water then with 50 mL of ethanol and dried under vacuum.

### **2.2.3 Functionalization of magnetic nanoparticles with CPTES (MNP-Cl)**

The surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  was modified by the reaction with the grafting reagent (3-Chloropropyl)trimethoxysilane (CPTES) by the following general procedure: In a 500 mL round-bottom tricol flask, a solution of 250 mg of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  in 100 mL of dichloromethane was sonicated for 30 minutes. 100 ml of dichloromethane were then added followed by a drop wise addition of 1.2 g (5mmol) of CPTES. The sonication was maintained for 2 h then the solution was magnetically stirred for further 6 h at room temperature then 10 h at  $60^\circ\text{C}$  under nitrogen atmosphere. The solid product was recovered using an external magnet, washed four times with 50 mL of dichloromethane and finally dried under vacuum.

### **2.2.4. Functionalization of MNPs with diethylmalonate (MNP-COOEt)**

#### **Method 1 (step method)**

0.416g (2.6 mmol) of diethylmalonate was reacted with 0.0624g (2.6 mmol) of sodium hydride in 10 mL of dry toluene : THF mixture (1: 1) for 30 minutes. 130 mg of MNP-Cl were then

added under nitrogen atmosphere and the mixture was stirred at reflux during 17h. The product was separated using an external magnet, washed three times with 50 mL of demineralized water then with 50 mL of ethanol and finally dried under vacuum.

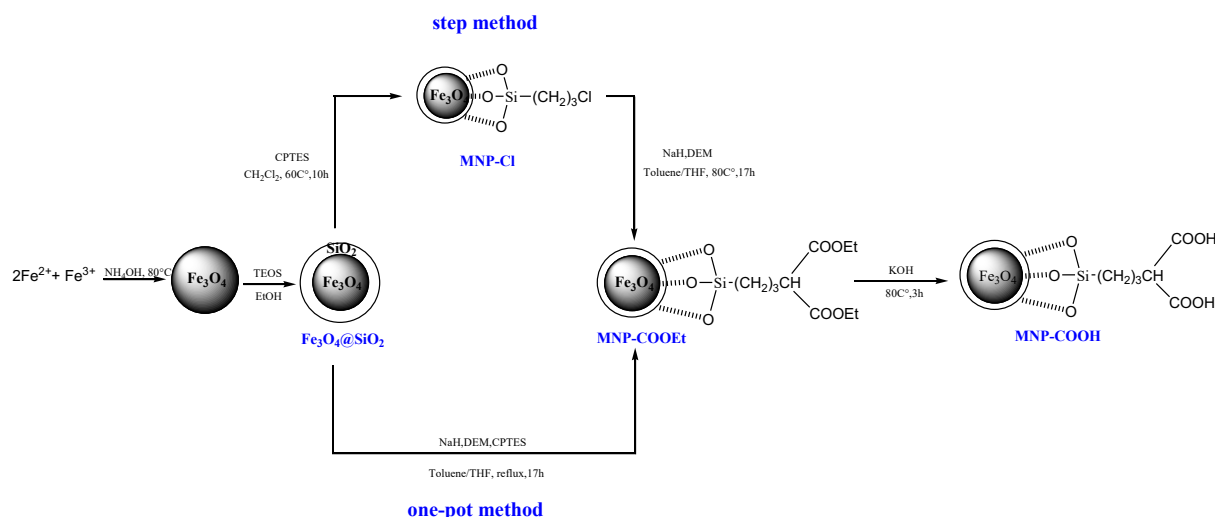
### Method 2 (one-pot method)

0.32 g (2 mmol) of diethylmalonate was reacted with 0.048 g (2 mmol) of sodium hydride in 7 ml of toluene: THF mixture (1:1) for 30 minutes. 0.48 g (2 mmol) of CPTES was then added and the mixture was stirred under nitrogen atmosphere at reflux for 5 h. After that, 100 mg of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  was added, and the mixture was maintained under reflux during 14h. The solution was allowed to cool then the product was recovered using an external magnet and washed successively three times with 50 mL of demineralized water and 50 mL of ethanol then dried under vacuum.

### 2.2.5. Hydrolysis of ester-functionalized MNP (MNP-COOH)

A solution of 0.15 g (2.67 mmol) of KOH dissolved in 10 mL of a mixture of water: ethanol (1: 2) was added to 15.4 mg of MNP-COOEt. The mixture was stirred under reflux during 3h then its pH was adjusted, at ambient temperature, with a hydrochloric solution (0.5M). The recovered product was washed three times with 50 mL of demineralized water then with 50 mL of ethanol, dried under vacuum and stored in a desiccator.

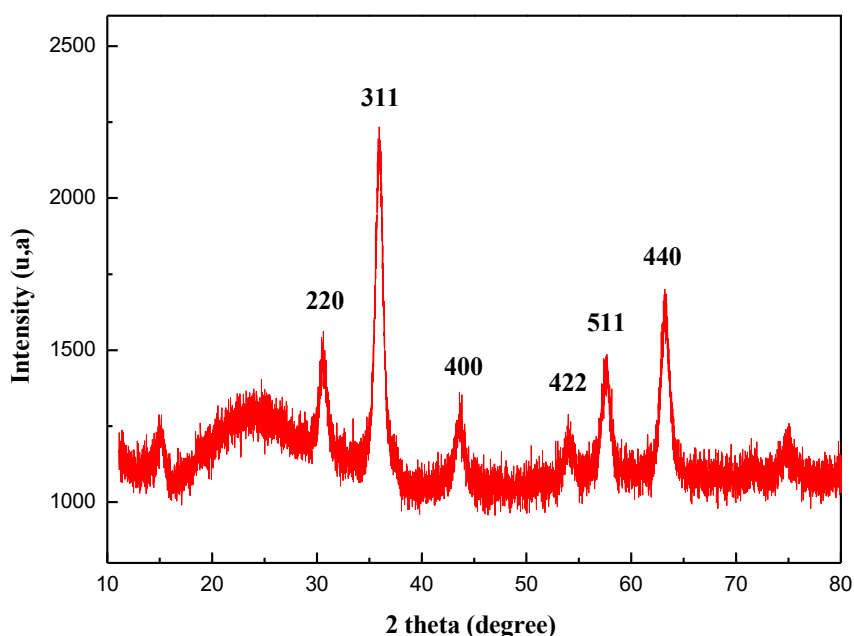
## 2.4. Results and discussion



Scheme 1. Synthetic procedures used for the preparation of acid functionalized magnetic nanoparticles MNP-COOH



The procedure for preparing acid-functionalized magnetic nanoparticles MNP-COOH is shown in Scheme 1. Firstly, uniform  $\text{Fe}_3\text{O}_4$  NPs were synthesized by the coprecipitation method from  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  aqueous solutions. The black color of the resulted precipitate is an indication that magnetite iron oxide particles have been obtained. This was confirmed by XRD analysis where the six characteristic peaks of the cubic spinel structure of magnetite were observed with  $2\theta$  values of  $30.3^\circ$ ,  $35.6^\circ$ ,  $43.1^\circ$ ,  $53.7^\circ$ ,  $57^\circ$  and  $62.7^\circ$  that can be indexed as (220), (311), (400), (422), (511) and (440), respectively. The deduced lattice constant  $a = 8.37 \text{ \AA}$  was consistent with the reported value (JCPDS Card No. 88-0315,  $a = 8.375 \text{ \AA}$ ).



**Fig 1. Powder X-ray diffractogram of magnetite  $\text{Fe}_3\text{O}_4$ .**

The silica coating of the magnetic core was then performed by the sol-gel process known as the Stöber process.[24]  $\text{Fe}_3\text{O}_4$  NPs were reacted with tetraethoxysilane (TEOS) as precursor in the presence of ammonia solution as catalyst. The hydrolysis and subsequent condensation of the precursor, leads to the formation of a three-dimensional silica shell network via siloxane bonds (Si-O-Si).

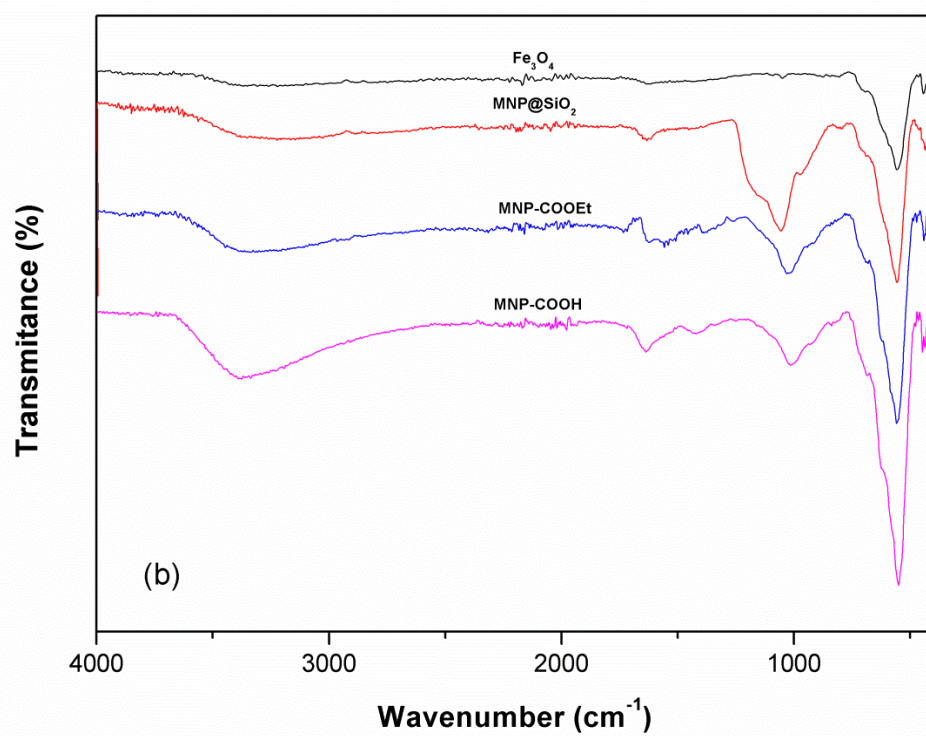
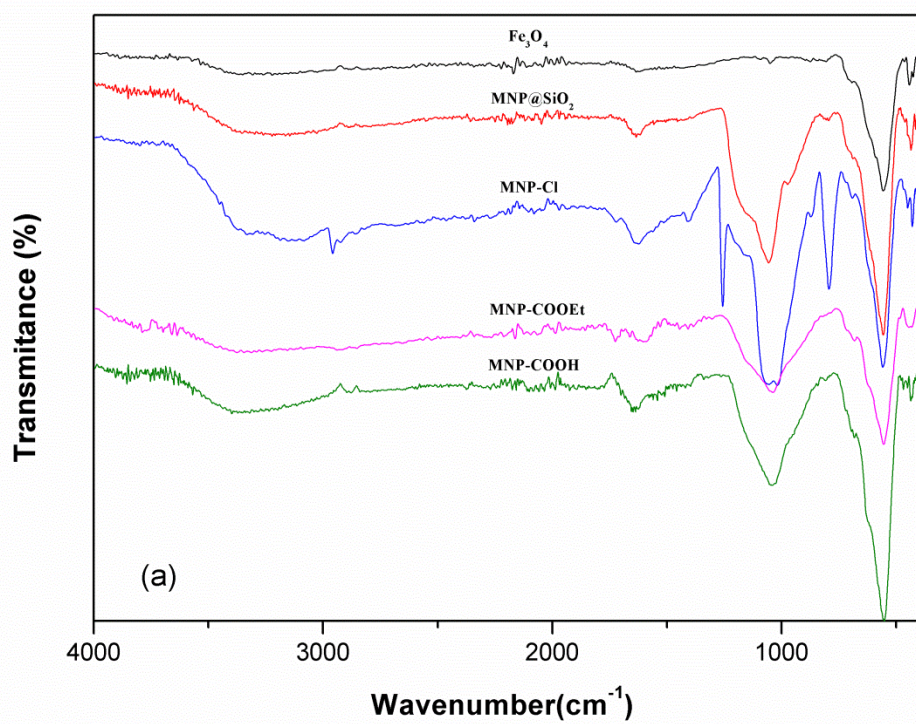
Two procedures have been then used to synthesize the ester-functionalized MNPs (MNP-COOEt). The first method “the step method” consists on the reaction of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  with 3-chloropropyltrimethoxysilane (CPTES) followed by the addition of the sodium salt of diethyl

malonate. In the second procedure, a one-pot condensation of CPTES with the diethyl malonate is carried out to give the diethylmalonic propyltrimethoxysilane derivative that was reacted *in situ*, without isolation, with Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles. Finally, the hydrolysis of MNP-COOEt nanoparticles affords to the acid-functionalized particles MNP-COOH.

The Fourier-transform infrared spectroscopy (FT-IR) was used to confirm the synthesis and the modification of MNPs during the different synthetic steps. FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, MNP-Cl and MNP-COOEt / MNP-COOH prepared by both methods are collected in figure 2. The characteristic peak of magnetite particles was observed at 556 cm<sup>-1</sup> and corresponds to the Fe-O bond vibration. The silica shell modification of the magnetic core was confirmed by the three strong absorption bands at around 794, 973 and 1056 cm<sup>-1</sup> related to the Si-OH, Si-O-Fe and Si-O-Si bands respectively [25].

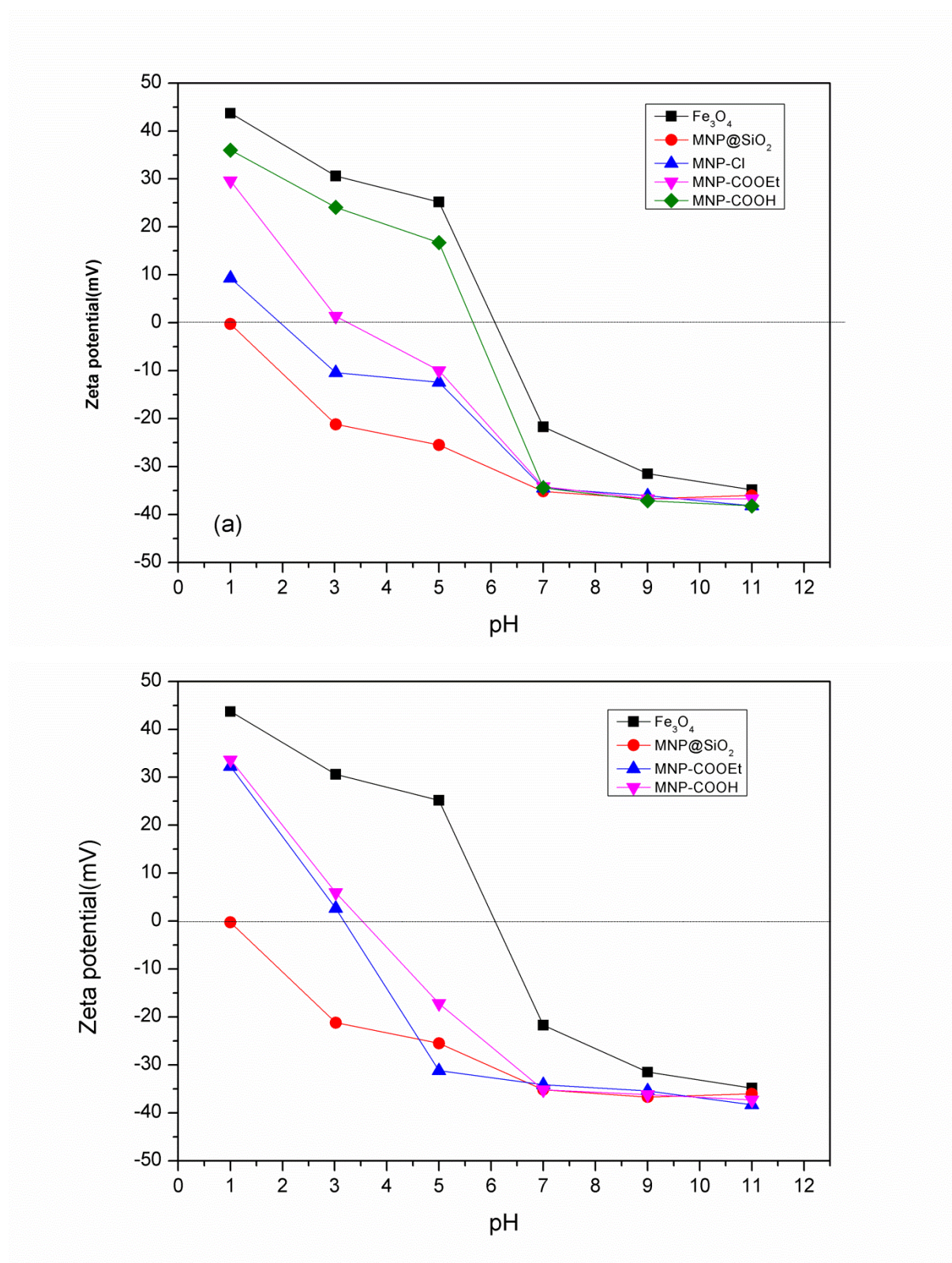
Successful chloropropyl functionalization of the silica layer of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> through the step method was evidenced by the C-H stretching vibrations of the propyl spacer at 2975 cm<sup>-1</sup> and 2852 cm<sup>-1</sup> and the strong stretching vibration of the terminal C-Cl bond at 793 cm<sup>-1</sup> (Fig 2a, MNP-Cl). This vibration disappears in the spectra of malonic condensation intermediate MNP-COOEt (Fig 2a, MNP-COOEt) at the benefit of novel bands at 1725 cm<sup>-1</sup> and in the region of 1210 - 1260 cm<sup>-1</sup> related to C=O and C-O vibrations, respectively.

The same bands were observed on MNP-COOEt spectrum prepared by the one-pot method (Fig 2b, MNP-COOEt) but with lower intensity suggesting that the grafting ratio on the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles was less important. The shift of this band to 1637 cm<sup>-1</sup> in the acid-functionalized nanoparticles MNP-COOH (Figures 2a and 2-b) was assigned to C=O vibration of the formed carboxylic acid function.



**Fig 2.** FT-IR spectra of silica coated magnetic nanoparticles prepared by a) the step method, b) the one-pot method

## Electrokinetic study:



**Fig 3.** Zeta potential of silica coated magnetic nanoparticles prepared by a) the step method, b) the one-pot method as function of pH

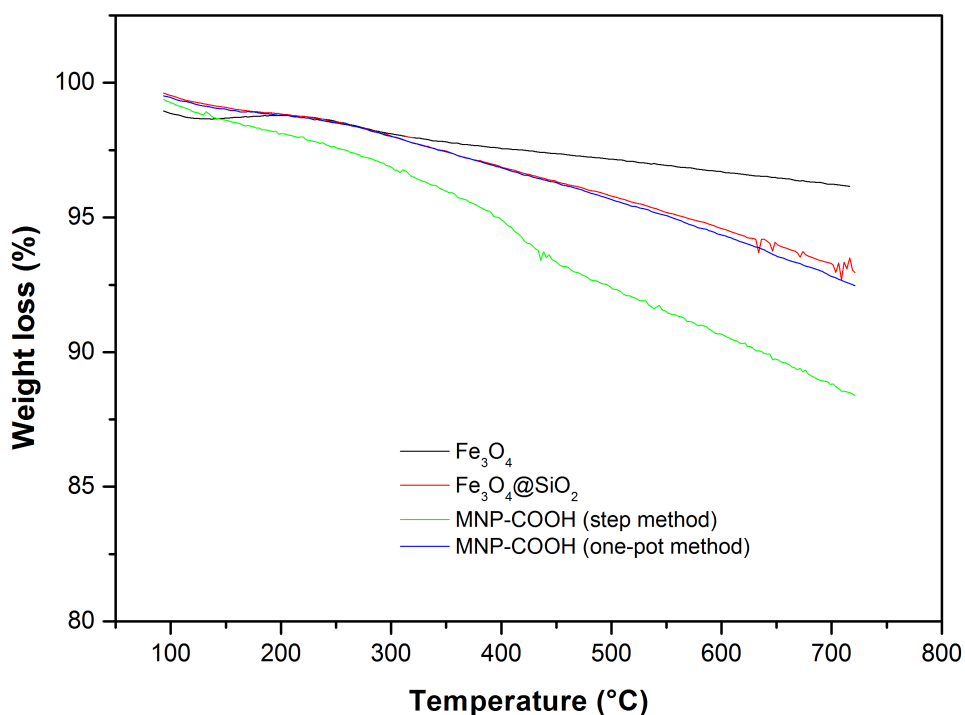
The surface charge and isoelectric point of magnetite NPs and intermediates were studied by zeta potential measurements. The Zeta potential ( $\zeta$ ) allows to predict the stability of the colloidal magnetic nanoparticle and the extent of surface functionalization. For these measurements MNPs were dispersed in 1 mM NaCl aqueous solution. The pH of the solution was then varied from 1 to 11 by titration with NaOH and HCl.

Figure 3 show the variation of zeta potential values of MNPs synthesized by both procedures as a function of pH value. One can see that zeta potential curve of magnetite evolved from positive values at low pH to negative value at higher pH with an isoelectric point (IEP) at pH =6.1 consistent with the values reported in the literature [26-27] The  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  sample showed an IEP of 1.1 which is nearly identical to that of amorphous silica [9], indicating successful wrapping of the  $\text{Fe}_3\text{O}_4$  core by the formation of a fully covered silica layer [17] The low isoelectric point and the higher negative charge of silica coated magnetic nanoparticles suggest a better stability and dispersability.

After grafting with CPTES (pathway 1) the IEP shifts to pH=1.9. Further functionalization with diethylmalonate (Fig 3a) induced a substantial increase of pH value of zero point charge ( $\text{pH}_{\text{IEP}}=3.1$ ). Thus, the MNP-COOEt nanoparticles have positive surface charge at  $\text{pH} < \text{pH}_{\text{IEP}}$  and negative surface charge at  $\text{pH} > \text{pH}_{\text{IEP}}$ . This difference in their charge properties may be attributed to the ionization of functional groups (COOEt) at different pH. The isoelectric point after the hydrolysis (MNP-COOH) was observed in the region of pH 5.65 (figure 3a) which is close to the pKA value of dianionic salt of malonic acid ( $\text{pKA} (\text{CH}_2\text{COO}^- = 5.7)$ ). This acidic character prohibits the aggregation of MNP-COOH particles and benefits the sorption of positively charged substance. The difference of isoelectric point before and after the hydrolysis reveals a good hydrolysis of the ester on the surface of MNP.

No marked difference in Zeta potential profile was observed for MNP-COOEt and MNP-COOH prepared by the one-pot procedure (figure 2b). The slightly higher IEP values obtained for MNP-COOH ( $\text{pH}_{\text{IEP}}=3.57$ ) indicates lower surface functionalization of the silica coated magnetic nanoparticles or the formation partial dissociated malonic function ( $\text{pKA} (\text{CH}_2(\text{COOH})\text{COO}^- = 2.8)$ )

### **Thermogravimetry analysis**



**Fig 4.** TGA thermograms of Fe<sub>3</sub>O<sub>4</sub> and MNP-COOH MNPs prepared by the step method and the one-pot method.

Thermogravimetry analysis was used to estimate the degree of modification of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles. The TGA curves of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and MNP-COOH NPs prepared by both methods are collected in figure 4. The relative comparison between weight losses of MNP-COOH with that of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> indicates the extent of organic functionalization.

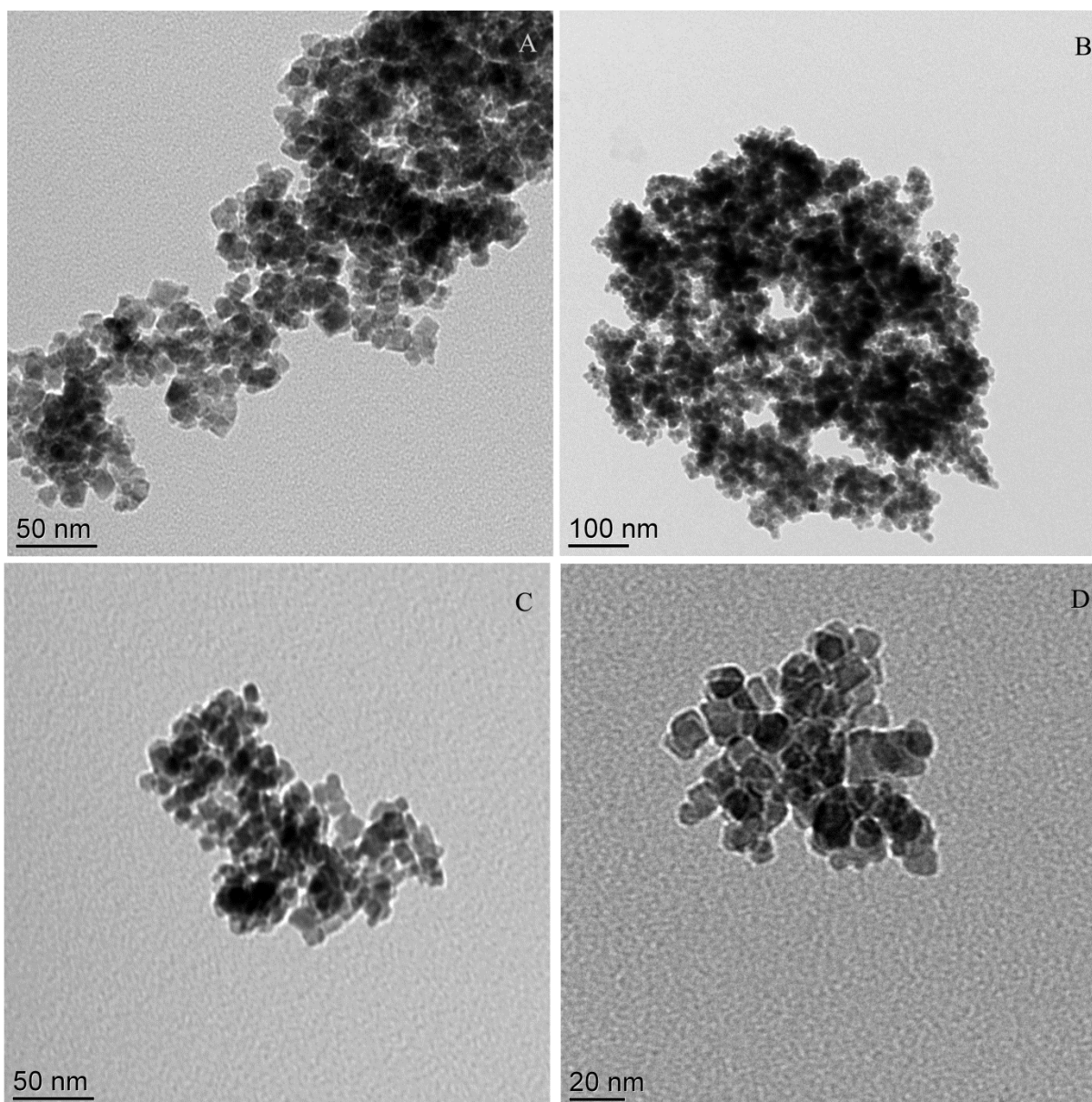
Less than 3.8% weight loss for the whole temperature range was obtained for Fe<sub>3</sub>O<sub>4</sub> due the high thermal stability of the iron oxide nanoparticles. This weigh loss is related to evaporation of physical and chemical adsorbed water. The quantity of silica shell grafted on Fe<sub>3</sub>O<sub>4</sub> core was estimated to 3.81 wt.%.

For MNP-COOH, an initial weight loss stage was observed bellow 200°C in the range of 1.19-1.96 % attributable to the evaporation of adsorbed water in the samples. The second stage of decomposition between 200-721°C was due to the decomposition of the organic component. The resulted organic contents of MNP-COOH prepared by the step method and the one-pot method was found to be 5.02 and 0.96%, respectively

This result confirm the successful grafting of malonic acid functions onto the silica coated magnetic surface and the higher functionalization yield of the step method discussed previously.

### **Morphology study**

Transmission electron microscopy (TEM) was used to visualize the morphology of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  particles before and after functionalization with carboxylic acid groups and to determine their size. Some typical TEM images are shown in Figure 5a-c. Results show that spherical shaped particles are obtained with an average particle size in the range of  $10 \pm 2$  nm. The mean particle sizes are almost the same for crude and functionalized silica coated magnetic particles regardless the used synthetic procedure (step or one-pot method). The obtained particles exhibit however, a noticeable trend for aggregation, particularly in the dried state that prevented the determination of their size by dynamic light scattering analysis.



**Fig 5.** TEM images of a)  $\text{Fe}_3\text{O}_4$ , b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , c) MNP-COOH(step method) and d) MNP-COOH (one-pot method) MNPs

### **Magnetic properties:**

The magnetic properties of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and of the corresponding acid functionalized nanoparticles MNP-COOH were characterized at room temperature by vibrating sample magnetometer (VSM). The saturation magnetization values ( $M_s$ ) of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and MNP-COOH prepared by the step and one-pot methods are 59.07, 55.29, 58.16 and 57.71 emu/g, respectively. One can see that the magnetic properties of the acid based nanoparticles are almost constant whatever the investigated synthetic mode.

The relatively slighter  $M_s$  value of MNPs in comparison with bulk magnetite (92 emu/g) [29-30] is due to the rather small size of the magnetite-based nanoparticles prepared by co-



precipitation method and to the presence of the adsorbed or covalently attached nonmagnetic layer on the magnetic core as adsorbed water molecules and hydroxyl and acid functions. However, this reduction of saturation magnetization does not affect the application of these MNPs at room temperature since they possess an excellent magnetic response and redispersibility. In fact, they can be easily and quickly manipulated, attracted and separated by an external magnet.

### Adsorption behavior

Methylene blue (MB) was used as a cationic organic dye model for the preliminary evaluation of the adsorption capacity of MNP-COOH nanoparticles. For this purpose, batch equilibrium technique was used by mixing 2 mg of the magnetic adsorbent MNP-COOH, obtained by the step method, with 1 mL of MB aqueous solution of a concentration 500 ppm. After 2h30 of stirring at 250 rpm and 25°C, the adsorption equilibrium was reached. The amount of residual dye in the solution was measured by UV-visible spectrophotometer at 664 nm wavelength after magnetic separation of MNP-COOH particles from the supernatant.

The adsorption capacity  $q_e$  (mg.g<sup>-1</sup>) was calculated according to the equation (3):

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (3)$$

where  $C_0$  (mg.L<sup>-1</sup>) is the initial dye concentration,  $C_e$  (mg.L<sup>-1</sup>) is the equilibrium concentration in solution,  $V$  (L) is the total volume of solution, and  $M$  (g) is the adsorbent mass.

Adsorption capacity of 142.45 mg/g was reached by MNP-COOH particles which are much higher than those previously reported for several adsorbents as shown in table 1. The high adsorption of MB by acid functionalized magnetic particles could be attributed to electrostatic interactions between the surface COO<sup>-</sup> groups and the cationic methylene blue molecules.

**Table 1.** Comparison of adsorption capacities of various magnetic adsorbents

Adsorbent	$q_m$ (mg/g)	Reference
Zeolite	55	[31]
Tea waste	85	[32]
Fe(III)/Cr(III) hydroxide	22	[33]
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> nanocomposite	116	[34]
Fe <sub>3</sub> O <sub>4</sub> @C	44	[35]
Magnetite-loaded multi-walled carbon nanotubes	48	[35]

## Conclusion

In this study, we developed a new soft-synthetic approach for the preparation of Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub> silica-coated magnetic nanoparticles with a core-shell structure functionalized by dicarboxylic acid groups. These nanoparticles exhibit superparamagnetic properties that allow their easy and fast separation by an external magnetic field

The strategy is a three steps synthesis based on the grafting of (3-chloropropyl)-trimethoxysilane reagent on of Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>NPS followed by the covalent binding of malonic ester and the hydrolysis of the ester functions. The corresponding one-pot method using the same chemical reagents was found less efficient for the surface modification of silica-coated magnetic nanoparticles

The extent of functionalization was evidenced by FTIR, TGA and zeta potential measurements. Such materials showed a high adsorption affinity for methylene blue and could thus be used as promising adsorbents for the remove cationic organic pollutants, especially, cationic dye, from polluted water.

## Acknowledgments

The authors thank Geraldine Agausti for TEM and TGA help analysis and thanks to Quentin Lelong magnetization measurement.

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## Figure and table captions

**Figure 1.** Powder X-ray diffractogram of magnetite  $\text{Fe}_3\text{O}_4$ .

**Figure 2.** FT-IR spectra of silica coated magnetic nanoparticles prepared by a) the step method, b) the one-pot method.

**Figure 3.** Zeta potential of silica coated magnetic nanoparticles prepared by a) the step method, b) the one-pot method as function of pH.

**Figure 4.** TGA thermograms of  $\text{Fe}_3\text{O}_4$  and MNP-COOH MNPs prepared by the step method and the one-pot method.

**Figure 5.** TEM images of a)  $\text{Fe}_3\text{O}_4$ , b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , c) MNP-COOH (step method) and d) MNP-COOH (one-pot method) MNPs.

**Table 1.** Comparison of adsorption capacities of various magnetic adsorbents.