

# **SPIONs nano-devices based on Fe<sub>3</sub>O<sub>4</sub> coated by megluminic ligands for the adsorption of metal anions from water**

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## **ABSTRACT**

The uptake ability towards arsenic (V), chromium (VI) and boron (III) ions of *ad hoc* functionalized magnetic nanostructured devices has been investigated. To this purpose, ligands based on meglumine, have been synthesized and used to coat magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) obtained by co-precipitation methodology. The as-prepared hybrid material was characterized by Infrared Spectroscopy (IR), X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy combined with Energy Dispersive X-ray Analysis (SEM-EDX). Moreover, its magnetic hysteresis properties were measured to evaluate their magnetic properties, as well the adsorption kinetics and– isothermal models were applied to discern between the different adsorption phenomena. Specifically, the better fitting was observed by Langmuir isotherm model for all metal ions tested, highlighting a higher uptake in arsenic (28.2 mg/g), chromium (12.3 mg/g) and boron (23.7 mg/g) sorption values if compared with other magnetic nanostructured materials. After adsorption, an external magnetic stimulus can be used to efficiently

remove nanomaterials from the water. Finally the nanomaterial can be reused up to five cycles and regenerated for other three cycles.

## INTRODUCTION

In light of the increasing issues related to exhausted water resources, global warming and environmental pollution, in the last years, water decontamination represents one of the main goal to achieve. In this scenario, the water control intended for human consumption derived from underground aquifers or surface reservoirs represents an achievement of crucial importance. Indeed, the prolonged contact of water with the surround causes the dissolution or the float of compounds derived from the earth background or anthropogenic activities.<sup>1-4</sup> In particular, harmful and toxic metal ions present in water have become a global critical issue and the severe environmental pollution represent a danger to human health and aquatic life.<sup>5</sup> Moreover, the non-biodegradability of these pollutants ensures the tendence to accumulate in living organisms.<sup>6,7</sup> Generally, metal ions are not removed even after the wastewater treatments by sewage treatment plants, increasing the risk of soil contamination and subsequently of the food chain.<sup>8-10</sup> Intake of them by the food chain has been widely reported and as a consequence several pathologies have been observed deriving from pollutants bio-accumulation.<sup>11-14</sup>

To protect the aquatic and the human life, it is now urgent to develop industrially scalable and easy applicable strategies in existing plants to treat contaminated water prior to its discharge into the environment. Various chemical and physical processes have been used for wastewater treatment in order to reduce the pollutant amount values under the law limit.<sup>15-19</sup> Although, most of the existing metal anions removal technologies have exhibited high efficiency in the lab scale, several issues are arisen due to their high cost, complex procedures and pre-treatment processes. Among various techniques for removing toxic metal ions from wastewater, adsorption is found to be one of the most effective and feasible due to simplicity of design, initial cost, to reduce operation and insensitivity to harmful pollutants.<sup>20,21</sup> Additionally, adsorbing materials are able to guarantee flexibility in design and operation but are also characterized by reversibility in order to regenerate them for multiple use through suitable desorption method bearing to low maintenance cost.<sup>22-24</sup> In this optic, meglumine (MEG) functionalized materials have represented a solution for the metal ions uptake due to its high efficiency and selectivity towards metal ions such us Chromium,

Arsenic, and Boron.<sup>25–27</sup> Firstly, this ligand is used for a selective boron removal from the water constituting the chelating moiety of different ions exchange commercial products based on polymeric resins.<sup>27–32</sup>

However, it was demonstrated that it exhibited excellent sorption capability also for other metals anions such as arsenic, chromium, antimony and germanium, although in the presence of antagonist anions.<sup>25,27,29</sup> Regarding this topic, the employ of high-gradient magnetic separation (HGMS) based technologies combined with the adsorption approach by the use of magnetic stimuli responsive materials represents an efficient strategy to water treatment.<sup>21,33–37</sup> Moreover, in the recent years proof of concept as well as prototype technologies, showed that magnetic nanosized metal oxide (MNO) can be proficiently used for environmental purposes.<sup>31,38–42</sup> Indeed, by the application of external magnetic stimulus, the devices can be easily removed from the water, refreshed, and reused. Especially, the application of super-paramagnetic iron oxide nanoparticles (SPIONs) has been extensively studied to prepare functional magnetic nano-sorbent.<sup>43,44</sup> Recent works have proposed a series of the functionalized nanostructured materials in order to enhance adsorption capacity and/or selectivity against specific pollutants by tuning their surface chemistry and physical properties. Alam et al. have prepared  $\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-NH}_2$  magnetic core-shell amino adsorbents by multi-step sol-gel methodology able to uptake heavy metal cations such as Zn, Pb and Cu, where the magnetic element was used like a support and the adsorbent phase was bonded onto metal surface by click chemistry.<sup>45</sup>

An other approach is the direct use of SPIONs like adsorbent materials before their deposition onto support, Das's group have employed nano-magnetic particles to decorate graphene oxide (GO) in order to obtain high efficient iron-graphene oxide nano-hybrid materials in terms of adsorption capability against As(III) and As(V).<sup>46</sup> The same strategy has been used to Yuan et al. to immobilized SPIONs onto montmorillonite to enhance the Cr(VI) adsorption with respect to unsupported nanoparticles.<sup>47</sup> In addition, magnetic nanocomposites with a range of organic coatings were prepared by Guivar and co-workers in order to investigate the correlation between the ligands and surface properties, as well as the adsorption capability against copper and lead.<sup>48</sup> A strictly dependence between the ligands chemistry and the materials uptake properties has been observed, this open to the possibility to tune the SPIONs features with specific functionalized ligands in order to improve their adsorption efficiency and selectivity.

In this view, we have exploited the synergistic effects of both high surface area and magnetic properties of SPIONs and the huge affinity of MEG moiety versus toxic oxyanions to formulate a smart magnetic nano-device for water remediation. Specifically, a novel approach was herein performed to cover SPIONs nanoparticles testing its efficiency in removing As(V), Cr(VI) and B(III) from the water medium by batch experiments setup

## **EXPERIMENTAL PART**

### **2.1 Materials**

Meglumine (MEG), 4-vinyl-benzyl chloride, ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), sodium arsenate heptahydrate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), boric acid (H<sub>3</sub>BO<sub>3</sub>), poly-ethylene oxide (PEO), iron(III) chloride (FeCl<sub>3</sub>) and ammonium iron(II) sulfate hexahydrate ((NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>) were purchased from Sigma Aldrich and directly used. The solvents were used without further processes of purification. The monomer and the related polymer were previously synthesized and characterized as described below.

### **2.2 Synthesis of (4-vinyl-benzyl)-meglumine (VbMEG)**

The monomer was synthesized follow the experimental methodology described by Mecca et al. MEG was suspended (1 g, 5 mmol) in 30 mL of CH<sub>3</sub>OH and an equimolar amount of 4-vinyl-benzyl chloride (0.70 mL, 5 mmol) was added to the suspension in the presence of anhydrous Na<sub>2</sub>CO<sub>3</sub>.<sup>29</sup> The reaction mixture was stirred at room temperature controlling the reaction progress by Thin Layer Chromatography (TLC). Then, the mixture was filtered and the methanol evaporated. The product was washed several times with cold CHCl<sub>3</sub> and dried under vacuum. The monomer was characterized by Nuclear Magnetic Resonance (NMR) and Infrared (IR) Spectroscopy (see Figure S1-2).

### **2.3 Synthesis of poly-(4-vinyl-benzyl)-meglumine (pVbMEG)**

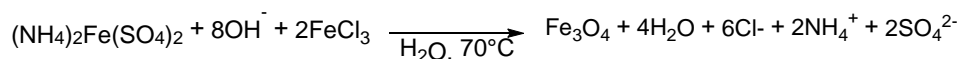
The polymerization of pVbMEG was carried out in a three-necked flask under nitrogen atmosphere. The polymer was synthesized by dissolving 1 g of monomer in 10 mL of water. Ammonium persulfate was added as initiator (1% mol/mol). The stirred solution was heated up to 60° C for 72h. After cooling the mixture to room temperature, it was dropped in methanol.

Then, the product was filtered and washed with methanol up to three times. The pVbMEG was characterized by Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy (IR) and Thermogravimetric Analysis (TGA) (see Figure S3-5).

## 2.4 Synthesis of functionalised magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles

### 2.4.1 Synthesis of Fe<sub>3</sub>O<sub>4</sub> NPs

The nanostructured materials were prepared by co-precipitation methods. FeCl<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Mohr's salt) have been chosen like nanoparticles precursors.



The reaction was carried out in a three-neck flask under nitrogen atmosphere by dissolving the precursors in a Fe<sup>2+</sup>: Fe<sup>3+</sup> molar ratio of 1:2 in 100 mL of water. Sodium hydroxide was added as a base to promote the formation of mixed oxide. The solution was stirred for 30 min at 70°C.

The obtained functionalized magnetic nanoparticles were filtered using a Buchner funnel and washed several times with distilled water to remove ionic species. The synthesized nanomaterials was characterized by Infrared spectroscopy (IR), thermogravimetric analysis (TGA), X-Ray diffraction (XRD) and vibrating-sample magnetometry (VSM).

### 2.4.2 Preparation of Fe<sub>3</sub>O<sub>4</sub>@MEG NPs

The functionalization of magnetite nanoparticles with meglumine was carried out follow the same procedure describe before but adding a freshly prepared 5% w/w aqueous solution of meglumine after the base adding. The mixture was stirred for 30 min at 70°C. The obtained MNPs were filtered using a Buchner funnel and washed several times with distilled water to remove ionic species.

### 2.4.3 Preparation of Fe<sub>3</sub>O<sub>4</sub>@ VbMEG NPs

A commercial poly-ethylene oxide (PEO) has been chosen to prepare a freshly 5% w/w aqueous solution and used to covering the MNPs as described above obtaining the MNPs@PEO. After then, 1 g of as prepared MNPs was added in a round bottom flask in the presence of 5% w/w aqueous solution of VbMEG. The exchange process between the two ligands was carried out under vigorous stirring at room temperature for 48h. The product was filtered and washed several times.<sup>50</sup>

#### 2.4.4 Preparation of Fe<sub>3</sub>O<sub>4</sub>@ pVbMEG NPs

The functionalization of magnetite nanoparticles with p-VbMEG was carried out adding a freshly prepared 5% w/w aqueous solution of polymeric ligands after the base addition during the as-reported magnetite nanoparticles preparation. The mixture was stirred for 30 min at 70°C.

The obtained MNPs were filtered using a Buchner funnel and washed several times with distilled water to remove ionic species.

### 2.5 Characterization methods

The synthesized monomer and the polymer were accurately characterized. Their structures were confirmed by <sup>1</sup>H-NMR spectroscopy, by using a Varian “Mercury 400”, operating at 400 MHz. TMS was used as an internal reference standard. The compounds were characterized by Fourier Transform-Infrared Spectroscopy (FT-IR), the spectra were acquired through an ATR-IR Bruker Alpha I spectrometer. Thermal behaviour was analysed by thermogravimetric analyses (TGA) using a thermogravimetric apparatus (TA Instruments Q500) under nitrogen atmosphere (flow rate 60 mL/min) and air atmosphere at 10 °C/min heating rate, from 20 °C to 600 °C. TGA sensitivity is 0.1 µg with a weighting precision of ± 0.01%. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X’PertPRO X-ray diffractometer. A Cu radiation source ( $\lambda = 1.54 \text{ \AA}$ ) was utilized, and diffraction patterns were recorded between 10–80 2 $\theta$  over a scan time of 10 min. The synthesized nanostructured devices were characterized by Scanning Electric Microscopy Thermo Phenom Prox desktop SEM combined with a fully integrated Energy Dispersive X-ray detector (Silicon Drift Detector) to evaluate size, morphology and elemental composition of the samples. To further confirm the nanometric size of the prepared materials, Dynamic Light Scattering (DLS) analysis were carried out by Malvern Zetasizer Nano ZS instrument setting the experimental temperature at 25°C and recording three set of 25 scan to minimize the experimental error. Moreover, poly dispersity-index (PDI) has been evaluated on a scale from 0 to 1, where value of 0 represented the mono-dispersity condition. The magnetic properties of nanostructured materials were investigated by means of hysteresis loops and first order reversal curves by a Lakeshore 8604 vibrating sample magnetometer. Magnetic particles were placed into pharmaceutical gel caps #4 for their characterizations: the coercive force ( $B_c$ ), the saturation remanent magnetization by mass ( $M_{rs}$ , or SIRM) and the saturation magnetization by mass ( $M_s$ ) were measured at a maximum field of 1.0 T. Concentration dependent hysteresis parameters were

calculated subtracting the high field paramagnetic linear trend before dividing the magnetic moments for the net weight of the samples. The coercivity of remanence ( $B_{cr}$ ) values were extrapolated from backfield re-magnetization curves up to  $-1.0$  T, after saturating at  $1.0$  T field. FORCs were measured in steps of  $2.5$  mT, with  $100$  ms averaging time and maximum applied field being  $0.5$  T using a Lakeshore 8604 VSM the Micromag operating software: FORC diagrams were processed, smoothed by Variforc and drawn with the FORCINEL 3.05 Igor Pro routine<sup>49</sup>. The amount of metal anions in solution after the treatment with the synthesized nanomaterials, was determined by an ICP-MS Nexion 300X (Perkin Elmer Inc. Waltham, Massachusetts, U.S.A.) using the kinetic energy discrimination mode (KED) for interference suppression.

## 2.6 Adsorption test

The amount of metal anions in solution after the treatment with the synthesized nanomaterials, was determined by an ICP-MS Nexion 300X (Perkin Elmer Inc. Waltham, Massachusetts, U.S.A.) using the kinetic energy discrimination mode (KED) for interference suppression. To evaluate the equilibrium retention capacity ( $Q_e$ ) values and the metal ions removal percentage a series of batch setup equilibrium tests were carried out.

In general, a specific amount of functionalized nanoparticles ( $5$  mg) were dipped in  $2.5$  mL of each solution ( $\text{pH}=6$ ) containing metal anions at different initial concentration, ranging from  $500$  to  $16500$   $\mu\text{g/L}$  as metal concentration. The experiments were carried out at  $25$  °C under constant stirring ( $180$  rpm) for  $24$  h. Several withdraws of  $100$   $\mu\text{L}$  at different time intervals were fulfilled to investigate the kinetic behaviour. By ICP-MS measurements the residual concentrations of metal anions were evaluated. The kinetic phenomena were investigated by employing three different semi-empirical adsorption kinetic: pseudo-first order, pseudo-second order, and intraparticle diffusion models.<sup>51-53</sup> The mathematical approach and the related equations applied were reported in the supplementary information (SI). In addition, several non-linear isotherm models have been used in order to investigate the adsorption equilibrium of the  $\text{Fe}_3\text{O}_4\text{-pVbMEG}$  nanostructured material. In particular Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isothermal adsorption models have been employed to understand the interactions adsorbent-adsorbate.<sup>54-58</sup> In the SI (see Figure S10-12) the adsorption models and the physical parameters used to fit and correlate the observed adsorption process have been described.

## RESULTS AND DISCUSSION

With the aim to cover SPIONs with a polymeric ligands able to chelate metal ions, pVbMEG were synthesised by starting from VbMEG. The reactions to produce the monomer, has been already reported in literature.<sup>29</sup> In light of this, the synthetic procedures to obtain it and related NMR, IR and TGA characterizations, were presented in the supplementary materials (Figure S1-S5).

The meglumine ligand and related based-monomer were used to functionalize the SPIONs by different approaches. Specifically, as described in the experimental section, the Fe<sub>3</sub>O<sub>4</sub>@meglumine NPs were prepared by a one-pot synthesis. Conversely, due to the high reactivity of vinyl-benzyl monomer, whose can react at 70°C forming the polymer into the aqueous solution, the one-pot methodology was not used, preferring a top-down strategy for the formulation of Fe<sub>3</sub>O<sub>4</sub>@VbMEG NPs. To this purpose, (see experimental section) a novel strategy consisting in the introduction of a preliminary coating agent, based on PEO was tested. Subsequently, ligands exchange reaction was carried out in order to introduce the monomer VbMEG like a coating agent. (Figure S8) In this view, the chemistry of the coated has been preserved, avoiding the polymerization reaction. As a follows, a whole characterization of the as-prepared materials was described including also their adsorption properties versus the selected metal ions targets.

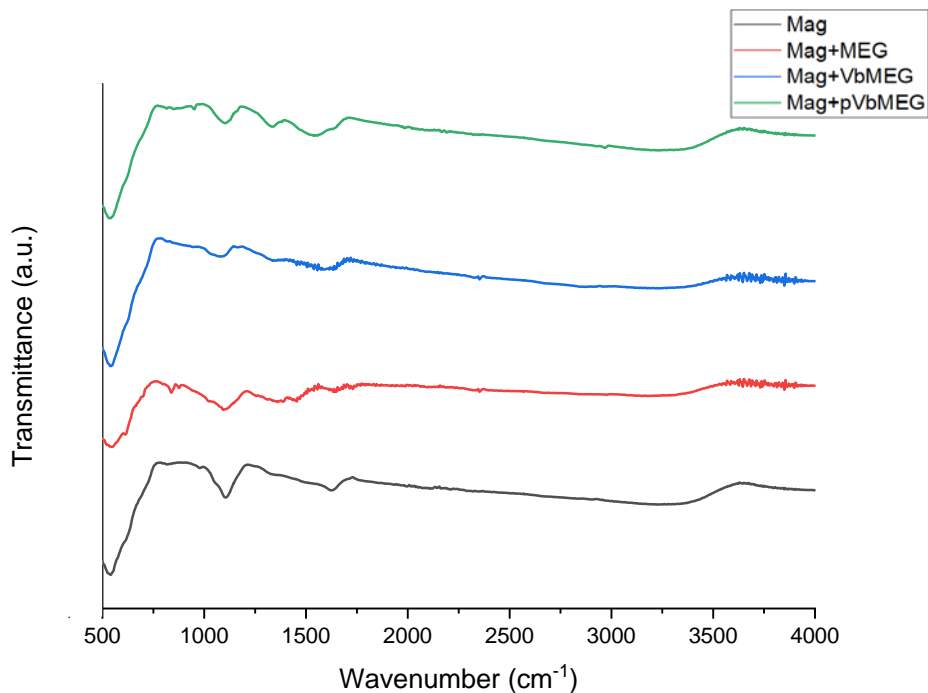
### 3.1 Fe<sub>3</sub>O<sub>4</sub> nanostructured materials characterization

The FT-IR spectra of functionalized magnetite nanoparticles with meglumine, VbMEG and pVbMEG are shown in Fig.1 and compared to the reference Fe<sub>3</sub>O<sub>4</sub> NPs. Typical band at 580 cm<sup>-1</sup> corresponding to the Fe-O bonds stretching was observed. Moreover, the peak at 1100 cm<sup>-1</sup> can be attributed to the stretching vibration of the Fe-OH formed during the synthetic route.<sup>59</sup>

The spectra of the Fe<sub>3</sub>O<sub>4</sub>@glucamine NPs, evidenced the appearance of new band at 1300 cm<sup>-1</sup>, assigned to the C-N stretching of related amine group. The signals emerged with a little intensity and are more evident in the system Fe<sub>3</sub>O<sub>4</sub>@pVbMEG. Lastly, a wide band at 1600 cm<sup>-1</sup> corresponding to the aromatic moiety was observed in the samples synthesized by monomer and polymer.



Despite, the absence of defined signals, IR spectra confirmed the correct functionalization of the magnetite nanoparticles compared to the bare nanomaterial.

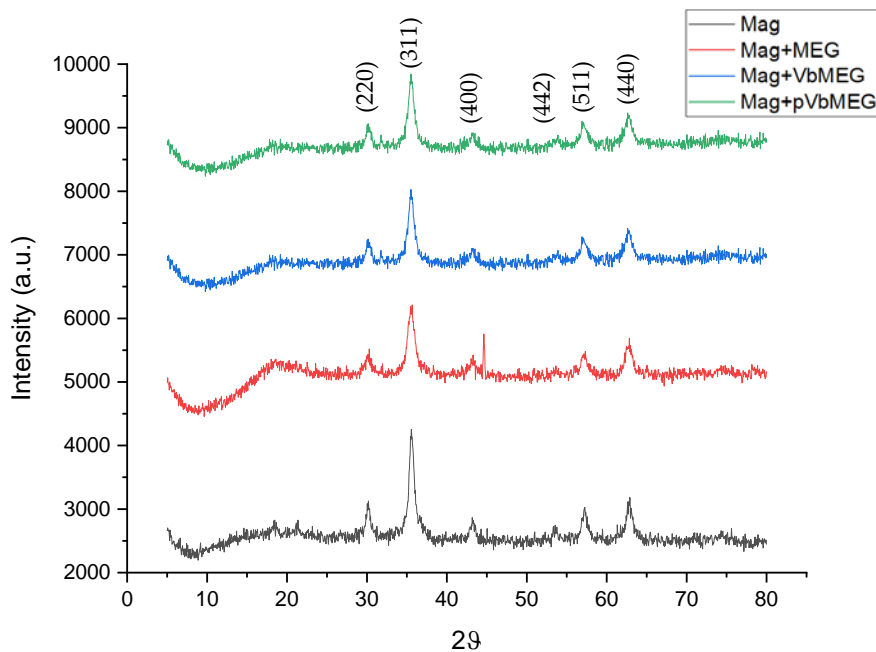


**Figure 1:** FT-IR spectra of the bare magnetite nanoparticles (black); MEG loaded on Fe<sub>3</sub>O<sub>4</sub> (red); VbMEG loaded on Fe<sub>3</sub>O<sub>4</sub> (blue) and poly-VbMEG loaded on Fe<sub>3</sub>O<sub>4</sub> (green)

The successful coating of Fe<sub>3</sub>O<sub>4</sub> nanostructured materials is further confirmed by XRD. The unit cell of cubic spinel structure can be described with the follow structural formula by of (Fe<sup>3+</sup>)<sub>A</sub>[Fe<sup>2+</sup>Fe<sup>3+</sup>]<sub>B</sub>O<sub>4</sub>, where the A and B represent if the ferrous and/or ferric ions are located in tetrahedral sites and octahedral sites, respectively.<sup>60</sup> Typically, magnetite can be easily oxidized in air at temperature between 110 and 230°C to form the maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) and when the temperature rise up above 250°C it can be further transformed to the hematite (α-Fe<sub>2</sub>O<sub>3</sub>). However, typical magnetite inverse spinel structure can be observed in Fig.2 diffractograms, where it can be seen the main peaks at 2θ values of 30.1°, 35.4°, 43.1°, 53.5°, 57.9°, and 63.0° corresponding to (220), (311), (400), (442), (511), and (440) Bragg reflection respectively.<sup>59</sup> Characteristic diffraction peaks related to the other iron oxide structure are not revealed in the XRD pattern in Figure 2. Therefore no other iron based compounds are present into the as prepared magnetite. Comparing the uncoated magnetite nanoparticles with the coated one, the XRD spectra exhibit similar diffraction peaks; this indicates a not significantly affect of the coating agent on the crystal

structure of the magnetite nanoparticles. In addition, the decrease of nanoparticles size was observed due to the presence of organic coating.

The crystalline size of nanostructured materials were calculated by Debye-Scherrer equation: 12.4, 7.3, 9.2 and 9.7 nm are the size for the bare  $\text{Fe}_3\text{O}_4$ , MEG, VbMEG and pVbMEG loaded on  $\text{Fe}_3\text{O}_4$ , respectively. The presence of coating agents plays an important role to reduce magnetite nanoparticles size.

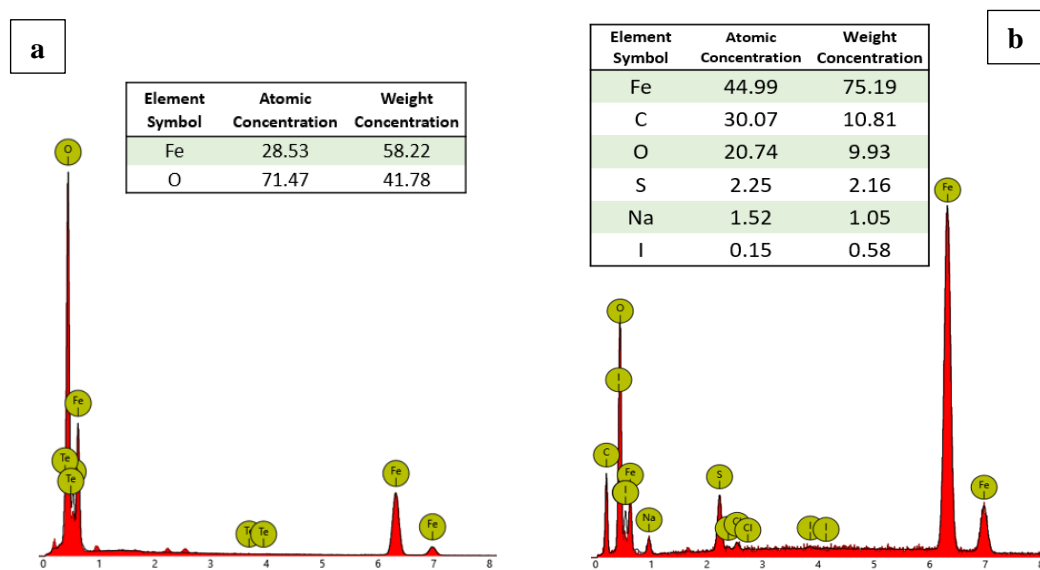


**Figure 2:** XRD pattern for the bare magnetite nanoparticles (black); MEG loaded on  $\text{Fe}_3\text{O}_4$  (red); VbMEG loaded on  $\text{Fe}_3\text{O}_4$  (blue) and poly-VbMEG loaded on  $\text{Fe}_3\text{O}_4$  (green)

The thermograms related to the SPIONs functionalized materials are results complex due to the presence of different degradation steps from 25°C to 600°C (Figure S6). The nanomaterials show a first stage around 200-220°C related to the transformation from magnetite to maghemite. For the functionalized nanomaterials, in the second stage from 250°C to 320 °C, weight loss occurred due to the thermal decomposition of meglumine moiety. In this stage, the samples  $\text{Fe}_3\text{O}_4$ -VbMEG shows two distinct degradation temperatures, whereas the nanostructured material obtained by the use of polymer-like coating agent have a single step in which both degradative phenomena occurred. The third stage from 400 to 500°C is presented only for the sample  $\text{Fe}_3\text{O}_4$ -pVbMEG, this weight loss is attributed to the final decomposition of the polymeric structure by breakage of

its chain. Thermogravimetric analysis in oxidative atmosphere was carried out in order to evaluate the functionalization degree of coated nanomaterials. The thermograms registered in oxidative atmosphere show more degradative steps than the same samples analysed under nitrogen. The degree of functionalization was calculated evaluating the amount of residue at the end of the analysis. The values obtained were 13, 11 e 10 % of functionalization for meglumine loaded on  $\text{Fe}_3\text{O}_4$ ; VbMEG loaded on  $\text{Fe}_3\text{O}_4$  and pVbMEG loaded on  $\text{Fe}_3\text{O}_4$ , respectively. (Figure S7)

Morphological data were obtained by using a SEM (see experimental part) up a magnification of 25k Images (Figure S9) revealed a sub-micrometre size of the nanomaterials. In addition, by EDX probe analysis the correct functionalization of magnetite nanoparticles have been confirmed to the presence of elements like carbon e oxygen related to the polymeric ligands in the sample  $\text{Fe}_3\text{O}_4@\text{pVbMEG}$ . By images of not functionalized magnetite nanoparticles can be observed the absence of carbon than the polymer coated SPIONs system. (Figure 3)



**Figure 3:** EDX spectra related to bare  $\text{Fe}_3\text{O}_4$  (a) and  $\text{Fe}_3\text{O}_4@\text{pVbMEG}$  nanoparticles (b)

The DLS analysis were carried out to evaluate the nanometric size of prepared SPION's devices and to confirm the outcomes observed with the other characterization techniques. The samples Mag+MEG and Mag+VbMEG have been easily dispersed in water since the superficial functionalization has change the solubility properties of the materials. On the other hand the bare

magnetite and Mag+pVbMEG were insoluble, for this reason the materials were dispersed in a meglumine solution for 24h in order to change the surface properties improving the solubility. In particular, a post-synthesis approach has been employed to anchor the meglumine ligands on the bare nano-oxides. Instead, ligands exchange reaction has been involved to change the polymeric ligands with the meglumine. Despite a partially aggregation in solution was observed due to SPION magnetic behaviour, the results obtained confirmed the nano size of the materials prepared, nearby 45 nm was the hydrodynamic volumes for all samples in agreement with the other analysis. (Figure S10) In addition, slight poly-dispersity was observed with values around 0.5 of PDI. The average size and the related PDI values were reported in Table 1.

**Table 1: DLS diameters and PDI values related to the SPION prepared.**

	<b>Mag</b>	<b>Mag+MEG</b>	<b>Mag+VbMEG</b>	<b>Mag+PVbMEG</b>
<b>d<sub>DLS</sub> (nm)</b>	<b>46</b>	<b>46</b>	<b>44</b>	<b>44</b>
<b>PDI</b>	<b>0.5</b>	<b>0.3</b>	<b>0.5</b>	<b>0.6</b>

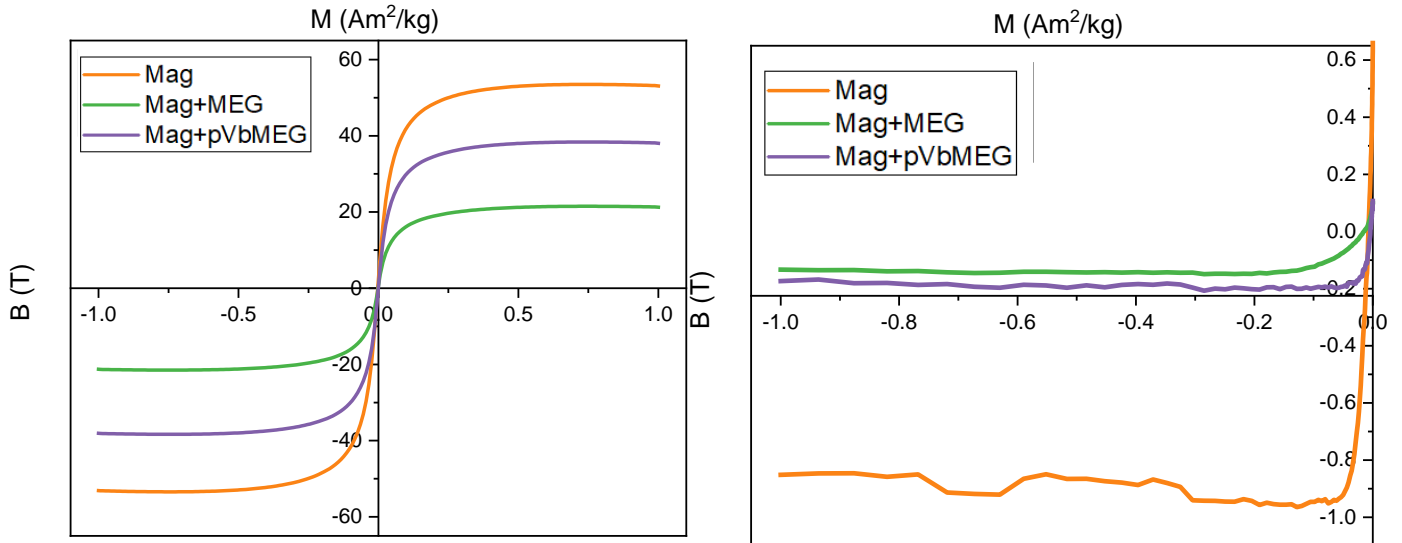
### **3.1.1 Magnetic analysis**

The magnetic properties of the synthesized materials were investigated. The magnetic hysteresis properties of Fe<sub>3</sub>O<sub>4</sub>, meglumine loaded on Fe<sub>3</sub>O<sub>4</sub>, poly-VbMEG loaded on Fe<sub>3</sub>O<sub>4</sub> have been measured to evaluate the contribution of different ligands on the magnetic power. In addition, FORC diagrams have been used for distinguishing between SP (superparamagnetic), SD (single domain), MD (multidomain) and PSD (pseudo single domain) behaviours according to the distributions of the interaction field ( $B_u$ ) and the coercivity in samples. The hysteresis parameters and coercivity values are reported in Tab. 2. As revealed from the left part of Figure 4, hysteresis loops were very narrow for all samples, well saturated before 1T, with almost null  $B_c$  and, as highlighted in the right part of Figure 4, very low values for both  $B_{cr}$  and saturation remanence field. This set of data are typical for magnetic mineralogizes dominated by ultrafine superparamagnetic particles (Figure 4 left), that should theoretically have zero remanence and coercivity when measured at room temperature adopting standard averaging times  $\geq 100$  ms.  $M_s$  was always lower than the bulk value for magnetite, that is 90-92 Am<sup>2</sup>/kg. The decrease of  $M_s$  values with the reduction of particle size for magnetite can be explained in several ways, including

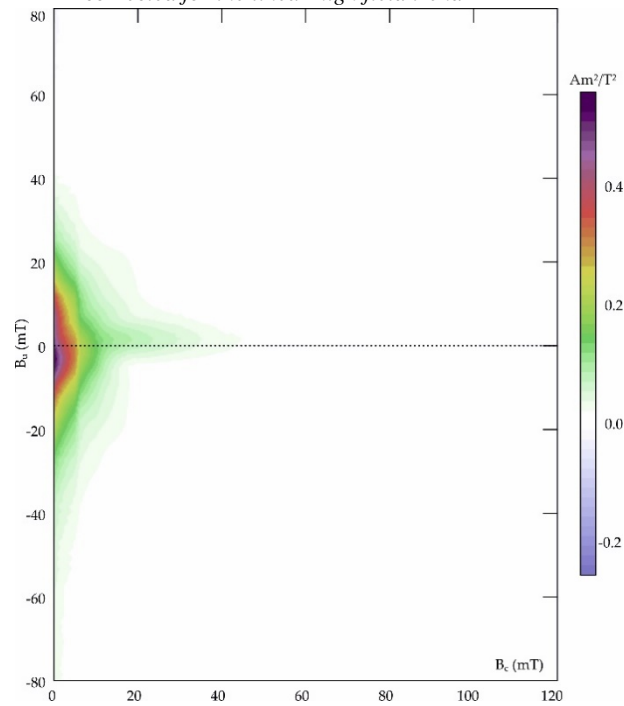
spin disorder layer, which increases with the decrease in crystallite size, and dipolar interaction between magnetite nanoparticles. Moreover, the value of  $M_s$  can be influenced by the irregular morphology of magnetite particles, due to surface anisotropy and incomplete crystallization after the reaction synthesis.<sup>61,62</sup> As observed from Mascolo and co-workers, the slope of the linear correlation between  $M_s$  and the particle size of magnetite decreased for the 6.5–8.0 nm grain-size range, with respect to the 9-12 nm interval.<sup>63</sup> In this sense, it is possible to confirm the trend observed by XRD spectra: according to the  $M_s$  values, the grainsize of Mag+MEG is lower than Mag+pVbMEG lower than bare magnetite nanoparticles. In Figure 5, the FORC diagram confirms the superparamagnetic ultrafine nature of magnetite particles. Indeed, the FORC diagrams of SP grains with relaxation times between 100 ms and 250 ms resemble those of MD grains, with distinguishable asymmetry and lower coercivity features. The FORC diagrams reported for Mag+MEG and Mag+pVbMEG were similar but noisier, if compared to the pure magnetite, thus validating the grainsize trend discussed above, and recalling that smaller superparamagnetic grains are unstable due to thermal agitation, so that the interaction field associated with such particles is not constant during the time it takes for a neighbouring interacting magnetic moment to flip.<sup>64</sup> Independently from the nature of our samples, it is possible to conclude that the magnetic properties of the analysed materials were dominated by ultrafine superparamagnetic features that, for magnetite, are carried by particles whose grainsize is < 35 nm.

**Table 2:** Hysteresis parameters for the bare magnetite, MAG loaded on  $Fe_3O_4$  and poly-VbMAG loaded on  $Fe_3O_4$ : values are mass specific

	$M_s$ ( $Am^2/kg$ )	$M_{rs}$ ( $Am^2/kg$ )	$B_c$ (mT)	$B_{cr}$ (mT)
Mag	53.4	1.46	1.50	7.3
Mag+MEG	21.4	0.12	0.44	4.1
Mag+pVbMEG	38.3	0.36	0.25	4.1



**Figure 4:** Hysteresis loops (left) and backfield applications after saturating at 1T magnetic field (right) for the bare magnetite, meglumine loaded on  $\text{Fe}_3\text{O}_4$  and poly-VbMEG loaded on  $\text{Fe}_3\text{O}_4$ ; the reported values are mass specific, hysteresis loops were corrected for the linear high field trend



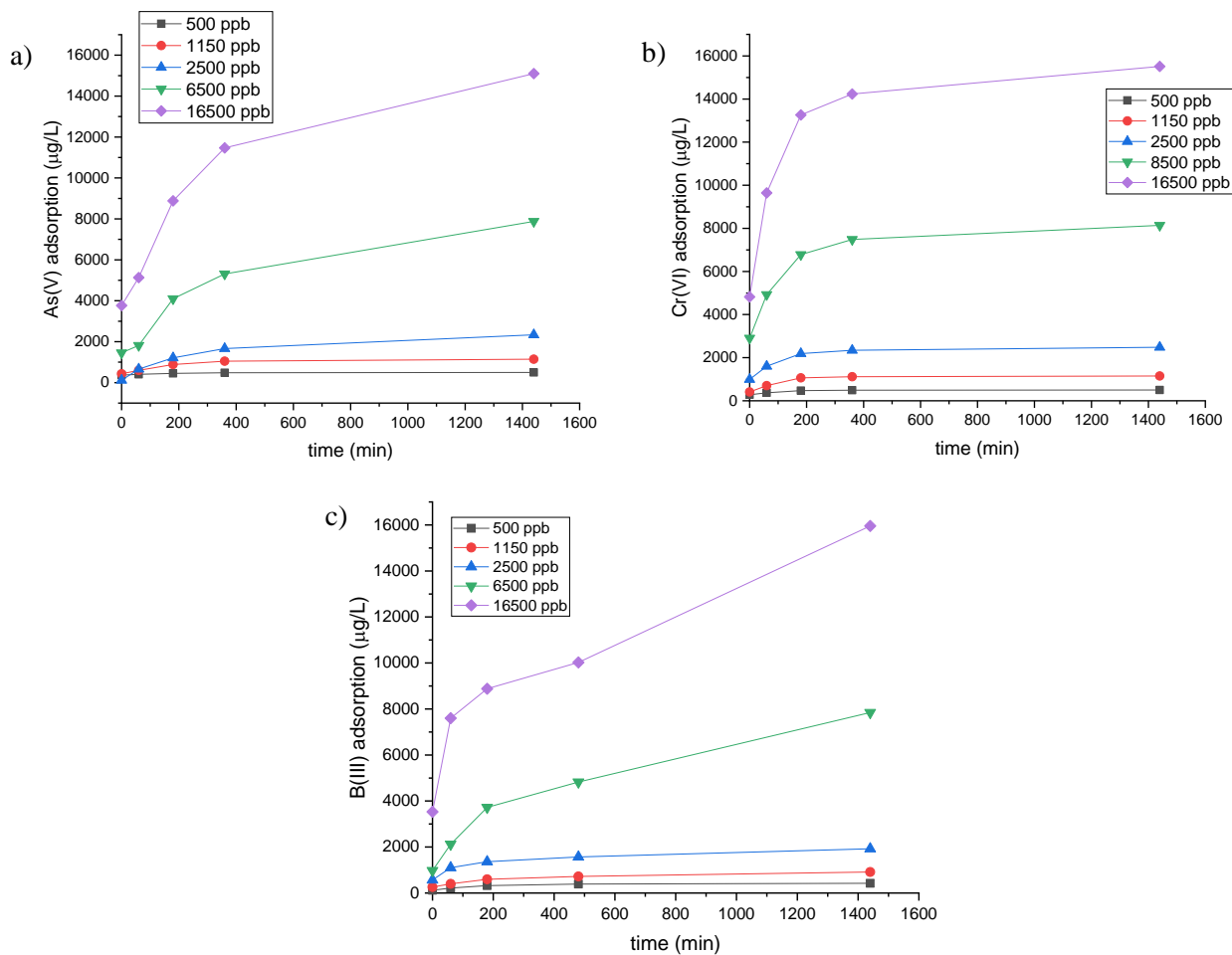
**Figure 5 :** FORC diagram of pure magnetite sample, with asymmetric and low coercivity features typical for superparamagnetic particles; smoothing factor was 3 for the vertical and horizontal ridge, 5 for the background

## 3.2 Adsorption study

In a first stage, to evaluate the adsorption ability of the intrinsically magnetic nanostructured materials versus the selected metal anions preliminary tests were carried out taking in contact ~5 mg of each sample in a metal ions solutions with a 500 ppb concentration of As(V). Only the Fe<sub>3</sub>O<sub>4</sub> functionalized with pVbMEG was able to reduce the metal ions concentration. The other samples have showed high solubility in water due to the high hydro-solubility of the coating agent, as a consequence the materials taken in contact with the pollutant solution have been solubilized themselves. Specifically, after 24 h of contact time, pVbMEG-Fe<sub>3</sub>O<sub>4</sub> nanomaterials showed the best performance in terms of metal ions uptake. Considering the results obtained, the effect of concentration as well as the kinetic and adsorption phenomena were widely investigated using pVbMEG-Fe<sub>3</sub>O<sub>4</sub>.

### 3.2.1 Concentration effect

Batch equilibrium experiments were employed in order to investigate the concentration effect and quantify the adsorption capacity of pVbMEG loaded on magnetite nanoparticles in function of As(V), Cr(VI) and B(III) concentration. For this reason, five different metal ions solutions were prepared with a concentration significantly higher than the permitted World Health Organization (WHO) limits (10 µg/L, 50 µg/L, 2.4 mg/L for As(V), Cr(VI) and B(III) respectively).<sup>65</sup> A defined amount of nanomaterials (5 mg) was used for each batch experiment. In Table 3 were reported the initial concentrations of metal ion ( $C_0$ ), the measured concentration at the equilibrium ( $C_e$ ), the normalized equilibrium capacity ( $Q_e$ ), and the calculated percentage of metal ion retention after 24 h of contact time at room temperature and pH=6. The batch experiments showed an efficient removal higher than 90% for As(V) and Cr(VI) ions for all the concentration analysed. Instead, for the boron ions a minor removal percentage was observed. Despite this the B(III) equilibrium concentration values were lower of the WHO limit for the first concentrations tested (500, 1150, 2500 ppb).



**Figure 6:** Amount of metal ion adsorbed as a function of time for (a) As(V), (b) Cr(VI) and (c) B(III) for different metal ion concentrations

**Table 3:** Initial concentration of metal ions ( $C_0$ ), at the equilibrium ( $C_e$ ), equilibrium removal capacity ( $Q_e$ ), and percentage of metal ions removal after 24 h of contact ( $R\%$ )

As(V)				Cr(VI)				B(III)			
$C_0(\mu\text{g/L}^{-1})$	$C_e(\mu\text{g/L}^{-1})$	$Q_e(\text{mg/g})$	$R\%$	$C_0(\mu\text{g/L}^{-1})$	$C_e(\mu\text{g/L}^{-1})$	$Q_e(\text{mg/g})$	$R\%$	$C_0(\mu\text{g/L}^{-1})$	$C_e(\mu\text{g/L}^{-1})$	$Q_e(\text{mg/g})$	$R\%$
500	1.7	0.58	99.7	500	1.1	0.25	99.8	500	77.4	0.21	84.5
1150	7.1	0.85	99.4	1150	2.5	0.57	99.8	1150	190.3	0.48	83.5
2500	162.9	1.30	93.5	2500	18.6	1.16	99.2	2500	354.4	1.1	85.8
8500	621.8	4.30	92.7	8500	358.8	4.07	95.8	8500	3022.5	2.7	64.4
16500	1398.6	8.25	91.5	16500	1488.1	7.50	90.9	16500	5928.2	5.3	64.1



### 3.2.2 Adsorption kinetic profiles

Adsorption kinetic profiles were investigated in order to determine the adsorption equilibrium time. Different initial concentrations were employed for all experiments conducted and similar adsorption trends can be observed: firstly we have a significant increment for the first 3 h that level off at 6 h, reaching the equilibrium. In order to rationalize the kinetic behaviour, three different models were used (Fig. S11-13). In particular, the better fitting for all metal ions analysed in terms of  $R^2$  values was obtained by applying the pseudo-second order kinetic model. Moreover, to confirm the results observed the theoretical adsorption capacity values ( $Q_{et}$ ) and the experimental data were compared with each other. (Table 4). Specifically,  $Q_{et}$  derived from the following equation reported in supplementary materials (eq.3)

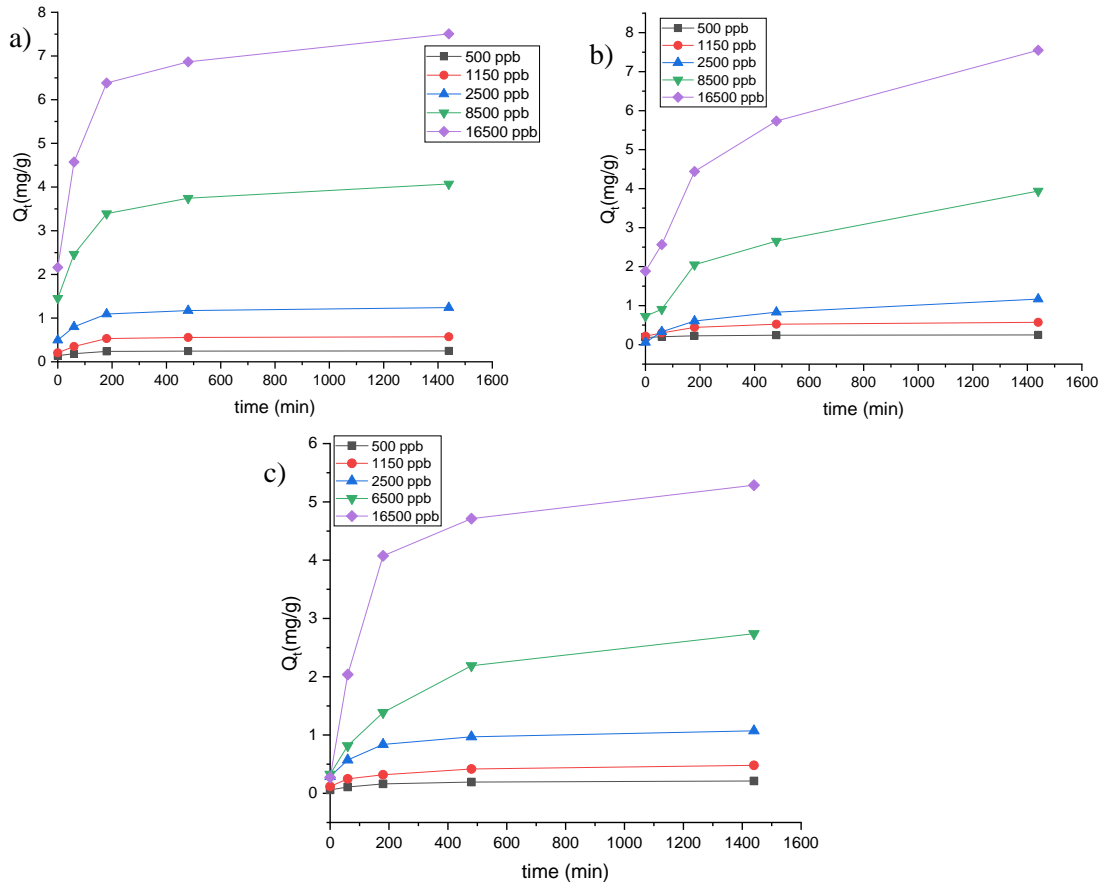
$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

showed a good match with the experimental values ( $Q_{exp}$ ), conversely to those derived from equation 4 (in SI) obtained by an interparticle diffusion model.

$$Q_t = k_i \sqrt{t} + C \quad (4)$$

By the trend extracted from the experimental data a deviance from the linearity was observed applying the pseudo-first order model probably derived to an intense adsorption during the initial phase of the process. Instead, the pseudo-second order model data fitting allowed to identify the surface adsorption of metal ions as rate-limiting step in chemisorption. According to the literature, the pH represented a crucial parameter for the adsorption of metal anions. In particular, at the pH value employed ( $\sim 6$ ) the electrostatic attraction deriving from protonated tertiary amine and the hydrogen bonds between the oxydrylic moieties of megluminic ligands control the adsorption process.<sup>55,56,66</sup> Moreover, the decreased of the kinetic constant values with increasing of initial metal ions concentrations suggested a surface saturation when an high concentrations of metal ions were used, in agreement with the pseudo first and second kinetic models (see Table 4) (Figure S11-13).

Instead, deviation from the linearity of the intraparticle diffusion was observed by kinetic profiles and therefore it's possible to not consider it as a rate-limiting step.



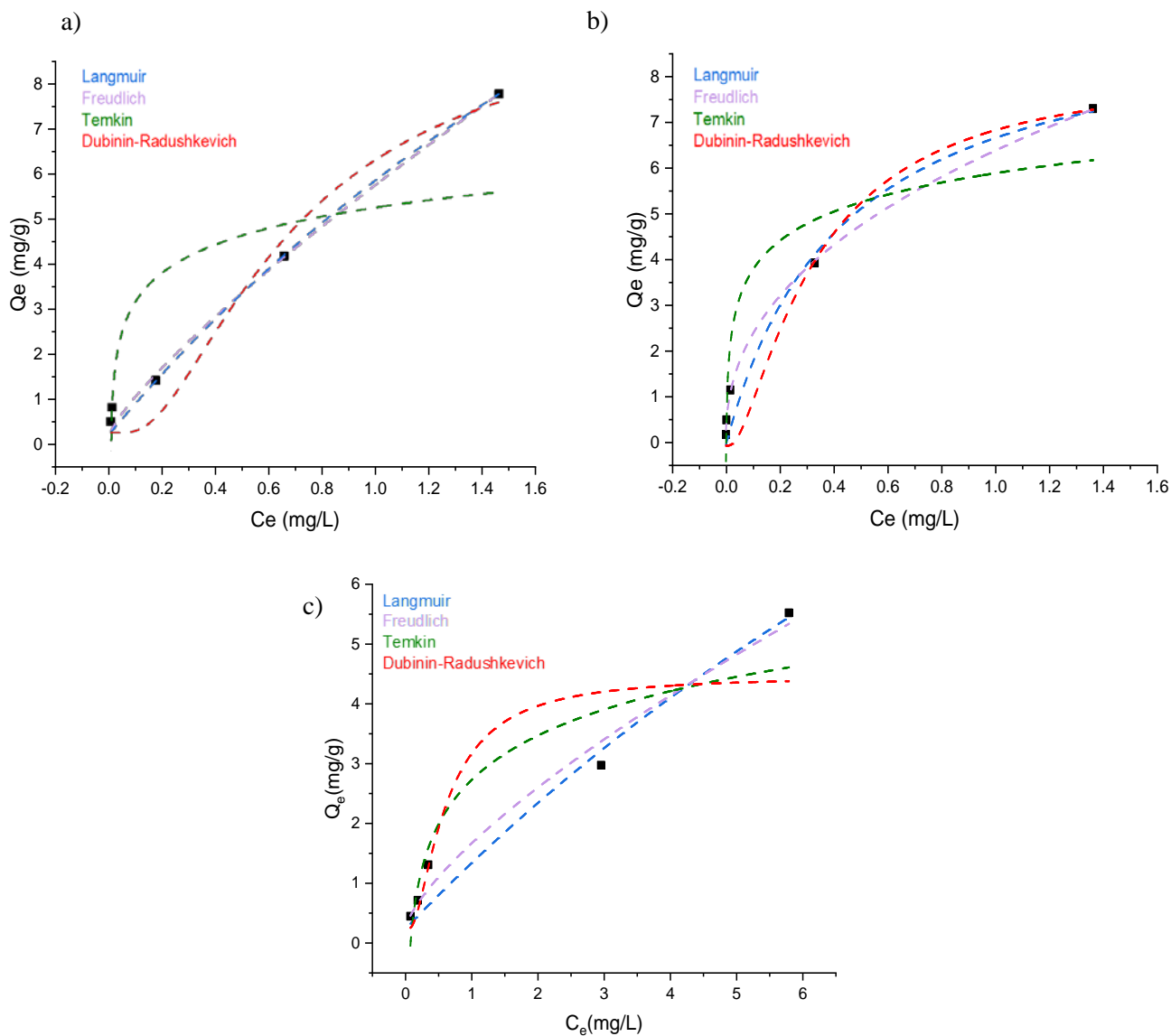
**Figure 7:** Kinetic profiles collected at room temperature of (a) As(V), (b) Cr(VI) and (c) B(III) adsorption calculated for different metal ion concentrations

**Table 4:** Adsorption kinetic models of As(V), Cr(VI) and B(III) for poly-VbMEG loaded on Fe<sub>3</sub>O<sub>4</sub> fitted with the pseudo-first order, the pseudo-second order and the intraparticle diffusion models

	<b>As (V)</b>					<b>Cr(VI)</b>					<b>B(III)</b>				
<b>C<sub>0</sub> (μg/L)</b>	500	1150	2500	8500	16500	500	1150	2500	8500	16500	500	1150	2500	8500	16500
<b>Q<sub>exp</sub> (mg/g)</b>	0.3	0.6	1.2	3.9	7.6	0.3	0.6	1.2	4.1	7.5	0.2	0.5	1.1	2.7	5.3
<b>Pseudo I-order</b>															
<b>K<sub>1</sub> (min<sup>-1</sup>)</b>	4.6	4.1	2.4	2.0	2.4	6.2	6.3	4.8	4.1	4.1	4.4	3.0	3.1	3.5	4.4
<b>R<sup>2</sup></b>	0.99	0.98	0.95	0.94	0.97	0.88	0.88	0.89	0.92	0.86	0.91	0.99	0.94	0.98	0.97
<b>Q<sub>et</sub> (mg/g)</b>	0.1	0.3	1.0	3.1	5.5	0.1	0.3	1.8	2.1	3.9	0.1	0.3	1.5	2.4	4.0
<b>Pseudo II-order</b>															
<b>K<sub>2</sub> (min<sup>-1</sup>)</b>	3.98	1.71	0.80	0.24	0.13	3.98	1.72	0.80	0.24	0.13	4.62	2.02	0.91	0.34	0.18
<b>R<sup>2</sup></b>	0.99	0.97	0.98	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.98	0.99	0.99	0.99
<b>Q<sub>et</sub> (mg/g)</b>	0.3	0.6	1.2	4.2	7.9	0.3	0.6	1.2	4.1	7.6	0.2	0.5	1.1	2.9	5.5
<b>Intraparticle diffusion</b>															
<b>K<sub>ip</sub></b>	0.002	0.01	0.03	0.09	0.16	0.003	0.01	0.02	0.07	0.14	0.004	0.01	0.02	0.07	0.13
<b>R<sub>2</sub></b>	0.87	0.87	0.97	0.97	0.97	0.71	0.71	0.77	0.82	0.78	0.85	0.91	0.84	0.96	0.80

### 3.2.3 Adsorption isothermal models

To investigate the adsorption equilibrium, different isothermal models were employed. In Figure 8 and in Table 5 were reported the isothermal trends and the relative parameters for the adsorption of As(V), Cr(VI) and B(III). By analysing the R<sup>2</sup> values, Langmuir and Freundlich models are the most corrected to describe adsorption process of pVbMEG-Fe<sub>3</sub>O<sub>4</sub> nanomaterials. Based on Langmuir model, the maximum adsorption capacities (q<sub>m</sub>) for As(V), Cr(VI) and B(III) are respectively 28.2, 12.3 and 23.7 (mg g<sup>-1</sup>). These values are higher than the maximum capacity calculated by Dubinin-Radushkevich model. Moreover, an other parameters useful to analysed the adsorption efficiency is represented of separation factor (R<sub>L</sub>), for the values derived from Langmuir model being in the range of 0-1 the efficiency of the adsorption process is facilitated. Furthermore, the free energy of adsorption (E<sub>D-R</sub>) obtained from the application of Dublin-Radushkevich model described the nature of metal ion/adsorbent interaction (e.g. physical, ion exchange, or chemisorption). As reported in the supplementary material, when the E<sub>D-R</sub> is lower than 8 kJ/mol physical adsorption of metal anions was suggested.



**Figure 8:** Equilibrium adsorption isotherms collected at room temperature by plotting  $Q_e$  versus  $C_e$  experimental data for (a) As(V), (b) Cr(VI) and (c) B(III) for  $Fe_2O_3$ -pVbMEG

**Table 5:** Isothermal parameters obtained by applying Langmuir, Freundlich, Temkin and Dubinin-Reduschkevich models for As(V), Cr(VI) and B(III) testing their adsorption at room temperature

		<i>Langmuir</i>				<i>Freundlich</i>		
Metal ion	$q_m$ (mg/g)	$K_L$ (L/mg)	$R_L$	$R^2$	$K_F$ (mg/g)	$n_F$	$R^2$	
As(V)	28.2	0.26	0.96-0.23	0.99	5.76	1.23	0.99	
Cr(VI)	12.3	1.09	0.64-0.052	0.97	6.34	2.38	0.99	
B(III)	23.7	0.04	0.99-0.65	0.96	1.40	1.39	0.98	
		<i>Temkin</i>			<i>Dubinin-Radushkevich</i>			
Metal ion	$B_T$ (kJ/mol)	$K_T$ (L/mg)	$R^2$	$q_m$ (mg/g)	$E_{D-R}$ (kJ/mol)	$R^2$		
As(V)	0.89	0.29	0.70	9.47	1.9	0.96		
Cr(VI)	0.93	0.60	0.87	8.31	2.80	0.93		
B(III)	1.06	0.01	0.88	4.21	1.98	0.84		

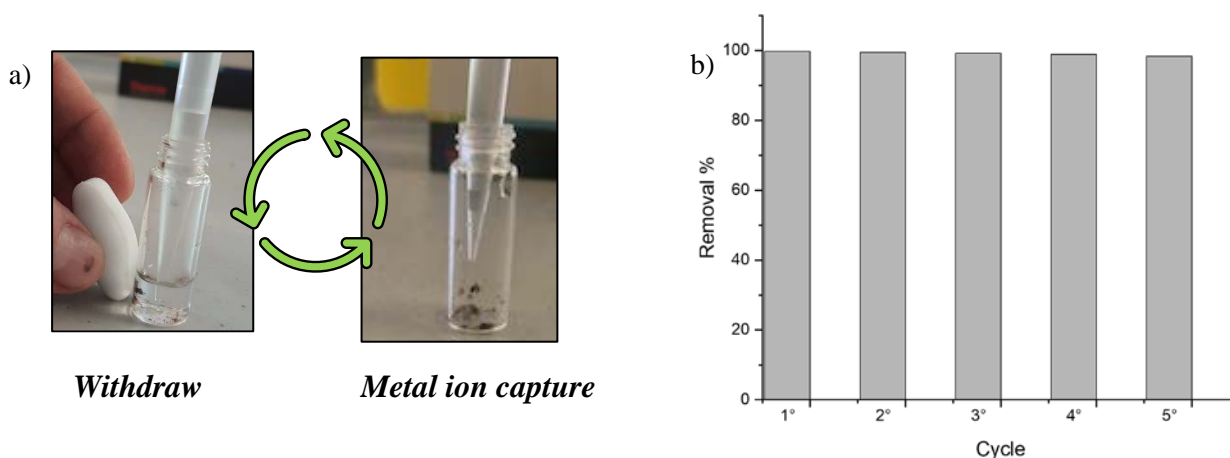
**Table 6:** Comparison of  $q_m$  values of different adsorbent materials reported in the most recent literature with the as synthesized pVbMEG-Fe<sub>3</sub>O<sub>4</sub>

Year	Adsorbent materials	As(V) $q_m$ (mg g <sup>-1</sup> )	Cr(VI) $q_m$ (mg g <sup>-1</sup> )	B(III) $q_m$ (mg g <sup>-1</sup> )	pH	Time of contact	Reference
2021	pVbMEG-Fe <sub>3</sub> O <sub>4</sub>	28.2	12.3	23.7	6	24h	this work
2021	Waste foundry dust	12.6	2.42	-	3	24-48h	67
2020	pVbNMG cryogel	76.3	130.9		6	24h	29
2020	Bare Magnetite	-	-	6.9	6	10h	68
2020	Magnetic thiourea-formaldehyde resin	1.6	3.7	-	1-9	3h	69
2019	NMDG@chitosan	-	-	19.9	7	10h	70
2019	Magnetite Char	19.9	-	-	6	1h	71
2010	IRA-743	14.7	-	-	6	3d	72
2004	IRA-743	-	29.3	-	6	1h	66

To evaluate the adsorption ability of different materials the maximum adsorption capability parameter ( $q_m$ ) can be used. In Table 5, the  $q_m$  values related to the synthesized nanostructured materials and analogue systems was reported and compared. In general pVbMEG-Fe<sub>3</sub>O<sub>4</sub> shows better performance in terms of  $q_m$  value if compared with the other materials reported in literature and therefore present highly competitive ability versus As(V), Cr(VI) and B(III) sorption. Commercially available IRA-743 showed Cr(VI) maximum adsorption of 29.3 mg/g due to its cross-linked structure the materials has high amount of megluminic groups able to adsorb the metal ions. The same behaviour was observed considering a polymeric cryogel formed on meglumine functionalized units with a adsorption capability of 76.3 mg/g and 130.9 mg/f for As(V) and Cr(VI), respectively. However, our nanostructured material is a combination of inorganic and organic part and the amount of MEG's moieties is necessarily lower in terms of total weight of adsorbent material rather than the corresponding amount present into a whole polymeric system. For this reason, the adsorption uptake observed is minor than the value reported for the organic resins. Moreover, a wide range of applicability in terms of kind of metals anions absorbed was noted for the materials synthesized in this work than the other reported in Table 6.

### 3.2.4 Reusability test and regeneration cycles

The reusability of the synthesized nanomaterials have been evaluated by five successive absorption/separation cycles. The tests were carried out on the chromium solution in light of best adsorption data observed against this pollutant. The material was dipped in a dichromate solution containing 1150 ppb of chromium VI, then separated by using of a magnet to facilitate the removal of the solution after each subsequent reuse test. The treated solution was analyzed by ICP-MS to evaluate the remaining Cr(VI) after each purification step. In Figure 9a-b was showed the purification method adopted as well as the absorption efficiency of the material up to tested five cycles. As it is possible to appreciate from the histogram (Figure 9b) the removal efficiency remained almost unchanged for all the tested cycles. To further exploit the potential of our material in terms of sustainability, together with the reusability, we also carried out the regeneration tests. Specifically, the material (5 mg) was immersed overnight in a solution of Cr(VI) (17000 ppb). Then, regeneration of nanoparticles was achieved by washing with 3M NaOH solution, determining the Cr (VI) content in the eluted solution. After then, the sample was washed with water and reactivated by HCl 0.1M. The regenerated material was retested with the same procedure for other 3 cycles showing good results (Figure 10).



**Figure 9:** (a) Scheme of the purification process repeated up to 5 cycles. After 15 min of contact time, the Cr(VI) solution (1.15 mg/L) was removed as depicted. (b) ICP-MS of the withdrawn Cr(VI) solutions showed removal of ~99% up to 5 repeated cycles performed at room temperature

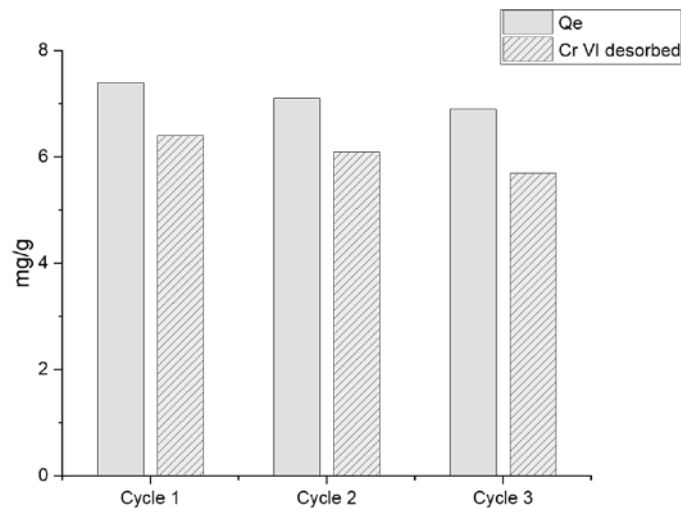


Figure 10. Regeneration experiment repeated up 3 cycles at room temperature. ( $C_0=17$  mg/L, material = 5 mg)

## CONCLUSION

A magnetic nano-device based on magnetite nanoparticles coated by polymeric megluminic ligands, able to absorb As(V), Cr(VI) and B(III) from water matrix has been prepared. Functionalized nanostructured materials obtained by co-precipitation in water showed good uptake properties versus the metal anions analysed even if present in low concentrations. Different spectroscopic and thermal analyses were carried out in order to investigate the composition of synthesized nanomaterials. Moreover, magnetic experiments were performed to confirm magnetic grain size and domain state of the synthesized particles. Regarding the uptake process, pVbMEG-Fe<sub>3</sub>O<sub>4</sub> sorption was well described by the Langmuir isotherm, the maximum adsorption capability ( $q_m$ ) observed is 28.2, 12.3 and 23.7 mg/g for arsenic, chromium and boron, respectively. In addition, the pseudo-second order model best represents sorption kinetics, therefore it's possible identify the surface adsorption of ions as the rate-limiting step during the chemisorption. If compared with other similar materials present in literature, pVbMEG-Fe<sub>3</sub>O<sub>4</sub> exhibits good sequestering performances and a wide range of application in terms of kind of anions adsorbed. In addition, the synthesized nanomaterials have exhibited a good reusability after five cycles and an efficient strategy was developed to regenerate the materials by changing the pH value of the solution. The results obtained are the combination between the high superficial area derived from magnetite nanostructure and the selectivity in the removal of the above metals due to meglumine

group that have allowed to develop novel magnetic device for the adsorption of metal anions from water.

## **ASSOCIATED CONTENT**

**Supporting information:**  $^1\text{H}$ -NMR and IR spectra for the synthesised monomer and polymer; thermogravimetric analysis for the synthesised polymer as well as the nanostructured materials prepared; SEM images of nanostructured materials; mathematic approach of adsorption and kinetic models and As(V), Cr(VI) and B(III) adsorption kinetic profiles

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