

## Accepted Manuscript

Title: Removal of arsenic and mercury species from water by covalent triazine framework encapsulated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles

Authors: Karen Leus, Karel Folens, Nina Ricci Nicomel, Jeffrey Paulo H. Perez, Maria Filippousi, Maria Meledina, Marinela M. Dîrtu, Stuart Turner, Gustaaf Van Tendeloo, Yann Garcia, Gijs Du Laing, Pascal Van Der Voort



PII: S0304-3894(18)30259-0  
DOI: <https://doi.org/10.1016/j.jhazmat.2018.04.027>  
Reference: HAZMAT 19310

To appear in: *Journal of Hazardous Materials*

Received date: 12-12-2017  
Revised date: 12-4-2018  
Accepted date: 13-4-2018

Please cite this article as: Leus K, Folens K, Nicomel NR, Perez JPH, Filippousi M, Meledina M, Dîrtu MM, Turner S, Van Tendeloo G, Garcia Y, Du Laing G, Van Der Voort P, Removal of arsenic and mercury species from water by covalent triazine framework encapsulated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, *Journal of Hazardous Materials* (2010), <https://doi.org/10.1016/j.jhazmat.2018.04.027>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Removal of arsenic and mercury species from water by covalent triazine framework encapsulated $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles

Karen Leus<sup>1,†\*</sup>, Karel Folens<sup>2,†</sup>, Nina Ricci Nicomel<sup>2</sup>, Jeffrey Paulo H. Perez<sup>1,2,‡</sup>, Maria Filippousi<sup>3</sup>, Maria Meledina<sup>3</sup>, Marinela M. Dîrtu<sup>4</sup>, Stuart Turner<sup>3</sup>, Gustaaf Van Tendeloo<sup>3</sup>, Yann Garcia<sup>4</sup>, Gijs Du Laing<sup>2</sup>, Pascal Van Der Voort<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, Center for Ordered Materials, Organometallics and Catalysis (COMOC), Faculty of Sciences, Ghent University, Krijgslaan 281 (S3), 900 Ghent, Belgium. E-mail: Karen.Leus@UGent.be, Pascal.Vandervoort@UGent.be

<sup>2</sup> Laboratory of Analytical Chemistry and Applied Ecochemistry, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, 9000 Ghent, Belgium

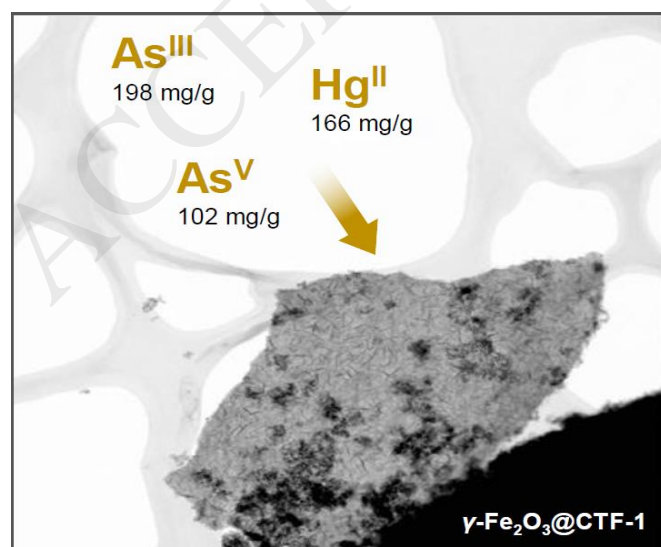
<sup>3</sup> EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen, Belgium

<sup>4</sup> Institute of Condensed Matter and Nanosciences, Molecules, Solids, Reactivity (IMCN/MOST) Université Catholique de Louvain, Place Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium

† Both authors contributed equally to this work.

‡ Present address: Helmholtz Centre Potsdam - GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany

## Graphical abstract



## Highlights

- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1 shows excellent removal efficiencies for As<sup>III</sup>, As<sup>V</sup> and Hg<sup>II</sup>
- No loss in removal efficiency is noted in the presence of Ca<sup>2+</sup>, Mg<sup>2+</sup> or NOM.
- An equilibrium for As and Hg is obtained after only a few minutes of contact time.
- No leaching of Fe and regeneration of the adsorbent can be achieved.

## Abstract

The covalent triazine framework, CTF-1, served as host material for the *in situ* synthesis of Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The composite material consisted of  $20 \pm 2$  m% iron, mainly in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase. The resulting  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1 was examined for the adsorption of As<sup>III</sup>, As<sup>V</sup> and Hg<sup>II</sup> from synthetic solutions and real surface-, ground- and wastewater. The material shows excellent removal efficiencies, independent from the presence of Ca<sup>2+</sup>, Mg<sup>2+</sup> or natural organic matter and only limited dependency on the presence of phosphate ions. Its adsorption capacity towards arsenite (198.0 mg g<sup>-1</sup>), arsenate (102.3 mg g<sup>-1</sup>) and divalent mercury (165.8 mg g<sup>-1</sup>) belongs amongst the best-known adsorbents, including many other iron-based materials. Regeneration of the adsorbent can be achieved for use over multiple cycles without a decrease in performance by elution at 70 °C with 0.1 M NaOH, followed by a stirring step in a 5 m% H<sub>2</sub>O<sub>2</sub> solution for As or 0.1 M thiourea and 0.001 M HCl for Hg. In highly contaminated water (100 µg L<sup>-1</sup>), the adsorbent polishes the water quality to well below the current WHO limits.

## Keywords

arsenic; mercury; covalent organic frameworks; iron oxide nanoparticles; water treatment

## 1. Introduction

Heavy metals and metalloids pose a widespread issue as they are persistent in the environment. Arsenic and mercury are highly toxic to all life forms. Remediation is challenging, in particular to achieve the very low standard in drinking water of  $10 \mu\text{g L}^{-1}$  As [1] and  $1 \mu\text{g L}^{-1}$  Hg [2]. Moreover, the elemental speciation complicates the treatment process since different forms of arsenic and mercury can exist simultaneously. Remediation requires a technique that is capable of removing all forms [3]. In aqueous media, arsenite ( $\text{As}^{\text{III}}$ ), arsenate ( $\text{As}^{\text{V}}$ ) and divalent mercury ( $\text{Hg}^{\text{II}}$ ) are the most common oxidation states. Among the available technologies for removal of inorganic arsenic and mercury from solution, adsorption is the most widely studied method [4].

Within this context, several metal-based engineered nanoparticles have been examined, especially  $\text{Fe}_x\text{O}_y$  based nanoparticles (NPs) [5, 6]. The oxidation state of iron is determinative in the removal mechanism, as it can contribute to oxidation/reduction reactions next to adsorption [7]. Although  $\text{Fe}_x\text{O}_y$  NPs demonstrated to be efficient and fast in arsenite and arsenate removal [8], the stability in water is rather limited due to oxidation and agglomeration processes, which will induce a decrease in the available surface area and therefore result in a reduced capacity and selectivity [9].

A way to circumvent this stability issue is to encapsulate these NPs into water-stable porous materials. A novel class of materials, covalent organic frameworks (COFs), is very promising for such application. COFs are porous aromatic polymers with pure organic groups connected via robust covalent bonds. Since their existence, a variety of COFs have been constructed by utilizing different linkages such as boronate, imine, hydrazone and triazine moieties [10]. The latter moiety is formed by a trimerization reaction of aromatic nitriles to triazine rings giving rise to the so called covalent triazine frameworks (CTFs). CTFs have been synthesized for the first time by Thomas and co-workers in 2008 by using an ionothermal synthesis route in which  $\text{ZnCl}_2$  acts as solvent and as catalyst [11]. Due to their promising features e.g. large surface area, high porosity, low density, facile synthesis and relatively cheap monomeric linkers, CTFs have been examined already in a wide range of interesting applications including gas adsorption or storage, supercapacitors and in catalysis [12-14]. A few pioneering studies appeared on environmental applications focusing mainly on the adsorption of organic dyes and aromatic compounds [15-19].

In this study, the embedding of  $\gamma\text{-Fe}_2\text{O}_3$  engineered nanoparticles in the CTF-1 material is presented. A thorough characterization of the material is realized by several (spectroscopic) methods, before evaluating it as novel adsorbent towards remediation of inorganic contaminants in water. Special attention is given to the kinetics, presence of other compounds, use of domestic wastewater and regeneration of the adsorbent, since the latter can successfully extend the adsorbent lifetime and hence suppress the associated costs of water purification.

## 2. Materials and methods

### 2.1 Material synthesis

The synthesis of CTF-1 was based on the procedure reported by Thomas et al. [11]. Under an inert atmosphere, 10 g  $\text{ZnCl}_2$  and 2 g 1,4-dicyanobenzene were mixed in a pyrex ampoule, sealed and heated to 400 °C for 4 h and kept at this temperature for 40 h. In order to remove  $\text{ZnCl}_2$ , the obtained black powder was stirred subsequently in water and 1 M HCl at room temperature for 24 h. Afterwards, the black powder was filtered and dried under vacuum at 120 °C prior to analysis. The  $\text{Fe}_2\text{O}_3$  nanoparticles were synthesized *in situ* by adding 406.9 mg of  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  and 152.6 mg of  $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$  into a 100 mL aqueous suspension containing 0.5 g CTF-1. The resulting mixture was stirred for 2 h under an inert atmosphere, followed by the addition of 15 mL  $\text{NH}_3$  solution. After stirring for 10 min, the  $\gamma\text{-Fe}_2\text{O}_3\text{@CTF-1}$  material was filtered and washed thoroughly with water and acetone. Hereafter, the material was dried under vacuum at 90 °C for 12 h.

### 2.2 Material characterization

Nitrogen sorption isotherms were measured on a Belsorp-mini II apparatus at 77 K. The samples were activated under vacuum overnight at 120 °C prior to surface area analysis to remove adsorbed water. Elemental analysis of the material's Fe content was determined in triplicate ( $N = 3$ ) by Inductively Coupled Plasma – Optical Emission Spectroscopy (Varian MPX, Palo Alto, CA) at  $\lambda$  238.204 nm. The As and Hg concentrations were determined by Inductively Coupled Plasma – Mass Spectrometry (Elan DRCe II, Perkin Elmer SCIEX, Waltham, MA) at  $m/z$  91 ( $\text{AsO}^+$ ) and  $m/z$  202, respectively. As reacted with  $\text{O}_2$  gas that was added at a flow rate of 0.4 mL  $\text{min}^{-1}$  to the reaction cell.

A combination of angular dark field scanning electron microscopy (ADF-STEM) imaging with energy-dispersive X-ray spectroscopy (EDX) spectroscopy, electron energy loss spectroscopy (EELS) and  $^{57}\text{Fe}$  Mössbauer spectroscopy was used to provide the information on the resulting morphology and to determine the valency of iron in the iron oxide nanoparticles. Transmission electron microscopy (TEM) micrographs, HAADF-STEM images and EDX spectra were recorded using a FEI Tecnai Osiris electron microscope operated at 200 kV, equipped with a ChemiSTEM system. STEM-EELS experiments were carried out on a Titan “cubed” microscope, equipped with an aberration corrector, a monochromator and a high-resolution GIF QUANTUM energy filter. For STEM-EELS experiments, the microscope was operated at 120 kV. The electron monochromator was excited to provide an estimated EELS energy resolution of 150 meV. The convergence angle used in the STEM-EELS experiments was 18 mrad, while the acceptance angles for EELS analyses were 160 and 85 mrad, respectively.  $^{57}\text{Fe}$  Mössbauer spectra were recorded in transmission geometry with a conventional Mössbauer spectrometer equipped with a  $^{57}\text{Co(Rh)}$  radioactive source operating at room temperature. The samples were sealed in aluminum foil and mounted on a nitrogen Oxford bath cryostat. The spectra were fitted to the sum of

Lorentzians by a least-squares refinement using or Recoil 1.05 Mössbauer Analysis Software [20]. All isomer shifts refer to  $\alpha$ -Fe at room temperature.

### 2.3 Adsorption experiments

A quantity of 40 mg  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1 is brought in contact for 24 h at room temperature with 10 mL of 10.0 mg L<sup>-1</sup> As<sup>III</sup>, As<sup>V</sup> and Hg<sup>II</sup> solution using the respective metal salts NaAsO<sub>2</sub>, Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O and Hg(NO<sub>3</sub>)<sub>2</sub>. Phase separation is done by centrifugation at 9,000 rpm and subsequent filtration using a membrane filter of 0.45  $\mu$ m pore size. Finally, the As and Hg concentrations in the filtrate are measured by ICP-MS. The kinetics are studied and fitted to the pseudo-second order model according Equation 1.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$$

Desorption experiments were carried out in triplicate ( $N = 3$ ) with 0.1 M NaOH solution for As and 0.1 M thiourea with 0.001 M HCl for Hg, at 70 °C for 30 min per run ( $N = 8$ ), followed by identical phase separation and monitoring of As and Fe concentrations. After desorption of As, the material is stirred an additional 2 h at room temperature in a 5 m% H<sub>2</sub>O<sub>2</sub> solution and regularly opened for release of pressure generated by O<sub>2</sub> gas. Microfiltration of the product, whereby the filtrate was analysed for Fe leaching, proceeded and the solid was dried under vacuum overnight at 90 °C.

## 3. Results and discussion

### 3.1 Material characterization

The obtained Fe<sub>2</sub>O<sub>3</sub>@CTF-1 material has a pore volume of 0.46 cm<sup>3</sup> g<sup>-1</sup>. The Langmuir surface area after introduction of 20  $\pm$  2 m% Fe in form of engineered nanoparticles is 1049 m<sup>2</sup> g<sup>-1</sup>, which is about 10% lower than the pristine CTF-1, as is seen in Figure 1. After the introduction of the nanoparticles, some additional intraparticle porosity can be observed in the high pressure regime of the isotherm.

In Figure 2,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1 is visualized by means of electron microscopy. High resolution transmission electron microscopy (HR-TEM) depicts the CTF-1 structure (Figure 2a). Bright contrast features decorating the bigger CTF-1 particles after the loading procedure correspond to the iron oxide nanoparticles. The ADF-STEM image, shown in Figure 2b confirms that the nanoparticles (ca. 5 to 7 nm) are distributed throughout the CTF-1. EDX elemental map of Fe of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1 (Figure 2c) reveal the equal distribution of Fe throughout the CTF particles. No significant surface enrichment is observed.

EELS is known to be a direct technique for “fingerprinting” the oxidation state and coordination of transition metals and was exploited to identify the phase of the iron oxide nanoparticles. Figure 3 contains EEL spectra of the Fe<sub>2</sub>O<sub>3</sub>@CTF-1. Looking at the recorded EEL spectrum, one can clearly

observe a small pre-peak in the Fe L<sub>3</sub>-edge, and a post-peak in the Fe L<sub>2</sub>-edge (Figure 3b). These features in the Fe 2p L-edge are indicative of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> [21]. Moreover, the iron sites in the material were quantitatively evaluated from the corresponding <sup>57</sup>Fe Mössbauer lines presented in Table S1. The iron phase has 88% of Fe<sup>III</sup> species present within the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1 form which are preserved during the multiple cycles of adsorption and desorption (see Figure 4).

### 3.2 *Dependence of adsorption on pH*

The influence of the pH on arsenic removal by our novel adsorbent was investigated since this is known to have a significant impact on the removal of arsenic from water [17]. In Figure 5, the uptake of  $\text{As}^{\text{III}}$ ,  $\text{As}^{\text{V}}$  and  $\text{Hg}^{\text{II}}$  by  $\gamma\text{-Fe}_2\text{O}_3\text{@CTF-1}$  is presented at different pH values. The optimal removal of all species is observed in the neutral pH domain, which is the pH level that corresponds very well to natural waters. The removal of Hg decreases only at the pH of 11, presumably due to the formation of stable hydroxide complexes, withdrawing free ions from solution. Overall, the embedding of  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles allows for high removal efficiencies under environmentally relevant conditions.

### 3.3 *Adsorption uptake and isotherms*

The maximum adsorption capacities of  $\gamma\text{-Fe}_2\text{O}_3\text{@CTF-1}$  for  $\text{As}^{\text{III}}$ ,  $\text{As}^{\text{V}}$  and  $\text{Hg}^{\text{II}}$  were assessed using the Langmuir isotherms presented in Figure S1 and Table S2. These values are shown in Table 1 and 2 in comparison to those of pure iron oxide nanoparticles, other Fe-based adsorbents supported on (carbon-based) porous frameworks and surface-modified iron oxide nanoparticles. Most of the adsorbents were tested at near-neutral pH values, which can be a good basis for comparison, considering that the solution pH is an important parameter affecting the adsorption process.



Adsorption of  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  has already been studied on different iron oxides nanoparticles [44]. In the work done by Lin et al. [22], magnetic  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles achieved maximum adsorption capacities of  $67.0 \text{ mg g}^{-1}$  and  $95.4 \text{ mg g}^{-1}$  for  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$ , respectively (Table 1 entry 1). These values are relatively high compared to other Fe-based adsorbents reported in literature. However, the adsorption capacity of this material is limited by the occurrence of some agglomeration, which is also the reason why its regeneration process is inhibited [22]. In a similar study performed by Kilianová et al. [23], ultrafine superparamagnetic  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles were also used to remove arsenic from water (Table 1 entry 2). In this study, the adsorbent was only examined for arsenate, which is a drawback taking into account that arsenite is more harmful than arsenate as the former is more cytotoxic, genotoxic, mobile, and soluble [45]. The same is true for the work done by Faria et al. [24], in which  $\delta\text{-FeOOH}$  nanoparticles were used (Table 1 entry 3).

The maximum adsorption capacities of some Fe-based adsorbents supported by a carbon-based framework were also included in Table 1. In the work of Reed et al. [26],  $\text{Fe}^{\text{III}}$  impregnated activated carbon was investigated for  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  removal. This adsorbent showed  $q$  values of  $4.67$  and  $4.50 \text{ mg g}^{-1}$  for  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$ , respectively (Table 1 entry 5), whereas in the study of Zhang et al. [27], a magnetite-impregnated activated carbon fiber (MACF) was synthesized (Table 1 entry 6) exhibiting a similar uptake for  $\text{As}^{\text{V}}$ . Magnetite nanoparticles were also supported on multiwalled carbon nanotubes (Table 1 entry 10) demonstrating a simultaneous removal of  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  from aqueous solutions with a capacity of  $53.2$  and  $39.1 \text{ mg g}^{-1}$ , respectively [31].

Besides the evaluation of  $\text{Fe}_x\text{O}_y$ -based adsorbents, zero-valent iron (nZVI) adsorbents were also examined. For instance, in the work of Zhu et al. [29], nZVI was supported onto activated carbon (Table 1 entry 8). Relatively fast kinetics for the removal of arsenic was observed, however, both arsenite and arsenate removal were largely affected by the presence of anions and humic acid, with silicate and phosphate showing the most significant effect. In contrast to this work, Wang et al. [34] obtained a more effective adsorbent operating at a lower dose by using reduced graphite oxide (RGO) as support to anchor the nZVI (Table 1 entry 13). In comparison to these previous studies, much higher adsorption capacities were obtained for  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  by using  $\text{Fe}_2\text{O}_3\text{@CTF-1}$  as adsorbent. At pH 7, adsorption capacities of  $198$  and  $102.3 \text{ mg g}^{-1}$  were obtained for  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$ , respectively (Table 1 entry 16). These values are significantly higher than the pristine CTF-1 material having a maximum adsorption capacity for  $\text{As}^{\text{V}}$  of only  $28.60 \text{ mg g}^{-1}$  (Table 1 entry 15). These results are in correspondence to the work of Shang et al. [46] in which also higher adsorption capacities for  $\text{As}^{\text{III}}$  than for  $\text{As}^{\text{V}}$  were observed. The authors addressed this observation to the difference in surface charge of  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  below pH 9.2.

Iron oxide nanoparticles have also shown good performance for the adsorption of mercury. Etale et al. [36] tested  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles and achieved a maximum adsorption capacity of  $8.9 \text{ mg g}^{-1}$  for  $\text{Hg}^{\text{II}}$ .

(Table 2 entry 1). This value is similar to the maximum adsorption study obtained for  $\text{Fe}_3\text{O}_4$  nanoparticles (Table 2 entry 2) [37]. However, pristine iron oxide nanoparticles are chemically unstable under ambient conditions, usually easily oxidized in air or easily dissolved in acidic medium [47, 48]. In addition, they also exhibit low affinity for mercury species.

In order to increase their stability and affinity for mercury, surface modification is usually employed on iron oxide nanoparticles using polymers and functionalized chemical coatings. Liu and co-workers [38] coated  $\text{Fe}_3\text{O}_4$  NPs with humic acid (HA) in order to reduce aggregation, and improve its affinity for mercury due to the carboxylic, phenolic and quinone functional moieties attached to it (Table 2 entry 3). The maximum metal uptake was found to be  $97.7 \text{ mg Hg}^{\text{II}} \text{ g}^{-1}$  adsorbent, which is five times higher than the pristine  $\text{Fe}_3\text{O}_4$ . Aside from HA, another commonly used surface coating for iron NPs is silica. It acts both as a stabilizer and an inorganic shell wherein specific functionalities can be grafted through silanization. Zhang et al. [37] utilized 3-mercaptopropyltrimethoxysilane (MPTS) as the thiol precursor for the silanization reaction at the surface of silica-coated  $\text{Fe}_3\text{O}_4$  (Table 2 entry 4).  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$  has a maximum adsorption capacity of  $148.8 \text{ mg g}^{-1}$ , which is significantly higher compared to that of pristine and silica-coated  $\text{Fe}_3\text{O}_4$  nanoparticles.

Porous framework-supported iron oxide nanoparticles have also been examined for the removal of mercury. Huang et al. [42] designed a thiol-functionalized core-shell magnetic metal organic framework (MOF) composite,  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{HKUST-1}$  which was evaluated for  $\text{Hg}^{2+}$  adsorption, resulting in a maximum adsorption capacity of  $264 \text{ mg g}^{-1}$  (Table 2 entry 8). Despite its excellent performance in Hg removal, it was chemically unstable and transformed after exposure to acidic condition for less than 30 minutes. Furthermore, significant leaching of  $\text{Cu}^{2+}$  was also observed from the MOF composite, which is not favorable for water treatment as it releases a secondary pollutant. The same group also prepared a thiol-functionalized  $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{UiO-66}$ , which is more chemically stable and has a maximum adsorption capacity of  $282 \text{ mg g}^{-1}$  (Table 2 entry 9) [43].

In addition to its excellent adsorption capacity,  $\gamma\text{-Fe}_2\text{O}_3@\text{CTF-1}$  can also remove arsenic and mercury species at low contaminant concentration range (Table 3). At an initial element concentration of  $100 \mu\text{g L}^{-1}$ , the equilibrium concentrations after adsorption onto  $\gamma\text{-Fe}_2\text{O}_3@\text{CTF-1}$  were able to meet the stringent standard limits for As and Hg in drinking water of  $10 \mu\text{g L}^{-1}$  and  $1 \mu\text{g L}^{-1}$ , respectively.

### 3.4 Influence of competing ions

The presence of other compounds, such as calcium, magnesium, phosphate or natural organic matter (NOM), can affect the removal behavior due to competition for the binding sites at the adsorbent [49]. The effects were evaluated by separately spiking excess amounts of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  ions and NOM to solutions of arsenite and arsenate. Moreover, the arsenic and mercury removal was evaluated in real water bodies of surface-, ground- and domestic wastewater of which the chemical composition is given

in Table 4. Figure 6 illustrates that no significant decrease in the efficiency of  $\gamma\text{-Fe}_2\text{O}_3\text{@CTF-1}$  towards arsenic and mercury species was observed under the described conditions. Even if both species ( $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  and  $\text{Hg}^{\text{II}}$ ) were present no loss in the removal efficiency was noted demonstrating the potential use of this CTF material as multifunctional adsorbent. The presence of NOM or  $\text{Ca}^{2+}$  can contribute to the binding of inorganic contaminants by, respectively, a direct binding to amine functional groups on NOM or through cation bridges [50]. Only negatively charged phosphate ions re

The kinetics of the adsorption process was studied for the inorganic contaminants. The resulting data were plotted according to the pseudo-second order kinetic model. Figure 7 and Table 5 clearly show that the kinetics of As and Hg adsorption are obviously very fast, reaching equilibrium already after a few minutes.

### 3.6 Desorption and adsorbent regeneration

To study the regeneration potential of  $\gamma\text{-Fe}_2\text{O}_3\text{@CTF-1}$ , desorption experiments were performed. Full desorption of As and reactivation of the adsorbent was established by washing it with 0.1 M NaOH at 70 °C and 5 m%  $\text{H}_2\text{O}_2$  solution. The loaded Hg could be desorbed by washing with a solution of 0.1 M thiourea in 0.001 % HCl, having a pH of 3.2, also at 70 °C. Figure 8 shows that a same removal performance for  $\text{As}^{\text{III}}$  and  $\text{Hg}^{\text{II}}$  can be achieved in additional cycles. For  $\text{As}^{\text{V}}$ , a slightly decreased performance is observed in the third and fourth cycle of adsorption. This decrease might be attributed to the mobility of the  $\text{Fe}_2\text{O}_3$  nanoparticles, which tend to migrate to the surface of the material to form  $\text{Fe}_2\text{O}_3$  aggregates. The latter hypothesis was supported by EDX-STEM images obtained after the adsorption of 5 m%  $\text{As}^{\text{V}}$ , showing the formation of  $\text{Fe}_2\text{O}_3$  aggregates at the surface (see Figure S2). The cumulative leaching of Fe from the adsorbent was minimized to < 0.2 % after 4 cycles.

#### 4. Conclusions

The use of Fe<sub>2</sub>O<sub>3</sub> nanoparticles encapsulated in the CTF-1 was presented as first for the abatement of two major inorganic pollutants in aqueous media. Characterization by Mössbauer spectroscopy and EELS revealed the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase of iron oxide nanoparticles. The corresponding paramagnetic properties of maghemite can be exploited during phase separation. The adsorption capacity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1 reached 198.0 mg g<sup>-1</sup> for As<sup>III</sup>, 102.3 mg g<sup>-1</sup> for As<sup>V</sup> and 165.8 mg g<sup>-1</sup> for Hg<sup>II</sup>, which is higher in comparison to the pristine CTF-1 and other state-of-the-art adsorbents, including other iron-based materials. The presence of potentially interfering compounds, such as Ca<sup>2+</sup>, Mg<sup>2+</sup> and NOM, did not affected the adsorption performance of As. In natural water bodies, high removal efficiencies were maintained for As and Hg, demonstrating its applicability in real-life situations. Moreover, the material could be reused over multiple cycles while maintaining good adsorption performance.

#### Acknowledgments

Karen Leus acknowledges financial support from Ghent University. Nina Ricci Nicomel and Jeffrey Paulo H. Perez thank the funding of the VLIR-UOS. Marinela M. Dîrtu acknowledges F.R.S.-FNRS for a Chargé de recherches position. Stuart Turner gratefully acknowledges the FWO Vlaanderen for a post-doctoral scholarship. The Titan microscope used for this investigation was partially funded by the Hercules foundation of the Flemish government. This work was supported by the Belgian IAP-PAI network.

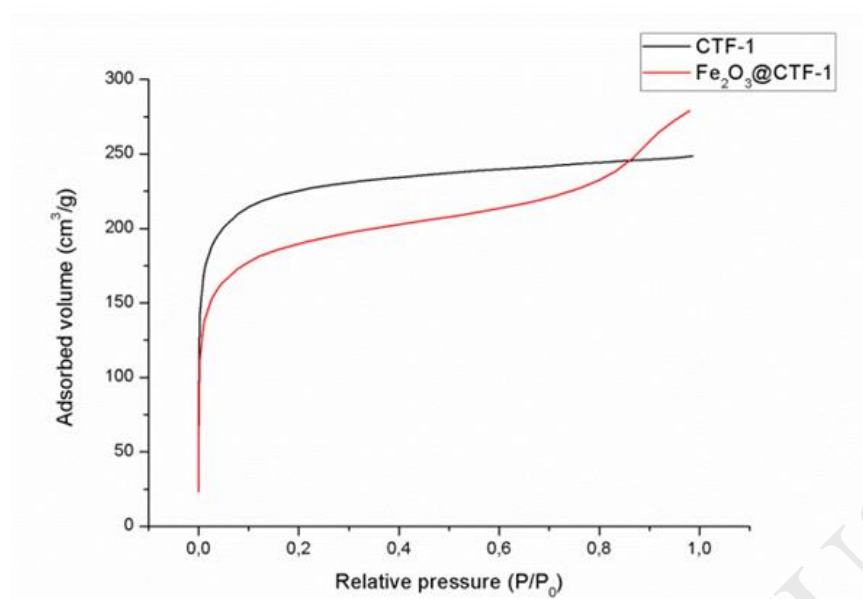
## References

- [1] WHO, Arsenic in drinking water, in: W.H. Organisation (Ed.), Geneva, Switzerland, 2011.
- [2] European Commission, Council Directive 98/83/EC, in: Quality of water intended for human consumption, 2015.
- [3] K. Folens, K. Leus, N.R. Nicomel, M. Meledina, S. Turner, G. Van Tendeloo, G.D. Laing, P. Van Der Voort, Fe<sub>3</sub>O<sub>4</sub>@MIL-101 – A Selective and Regenerable Adsorbent for the Removal of As Species from Water, *European Journal of Inorganic Chemistry*, 27 (2016) 4395-4401.
- [4] D. Mohan, C.U. Pittman, Arsenic removal from water/wastewater using adsorbents - A critical review, *J Hazard Mater*, 142 (2007) 1-53.
- [5] M. Habuda-Stanic, M. Nujic, Arsenic removal by nanoparticles: a review, *Environ Sci Pollut R*, 22 (2015) 8094-8123.
- [6] J.F. Liu, Z.S. Zhao, G.B. Jiang, Coating Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water, *Environmental science & technology*, 42 (2008) 6949-6954.
- [7] S. Tang, I. Lo, Magnetic nanoparticles: essential factors for sustainable environmental applications, *Water Research*, 47 (2013) 2613-2632.
- [8] P. Dave, L. Chopda, Application of iron oxide nanomaterials for the removal of heavy metals, *Journal of Nanotechnology*, 246 (2014) 572-574.
- [9] N.R. Nicomel, K. Leus, K. Folens, P. Van der Voort, G. Du Laing, Technologies for Arsenic Removal from Water: Current Status and Future Perspectives, *Int J Env Res Pub He*, 13 (2016).
- [10] S.Y. Ding, W. Wang, Covalent organic frameworks (COFs): from design to applications, *Chem Soc Rev*, 42 (2013) 548-568.
- [11] P. Kuhn, M. Antonietti, A. Thomas, Porous, covalent triazine-based frameworks prepared by ionothermal synthesis, *Angew Chem Int Edit*, 47 (2008) 3450-3453.
- [12] K. Kamiya, R. Kamai, K. Hashimoto, S. Nakanishi, Platinum-modified covalent triazine frameworks hybridized with carbon nanoparticles as methanol-tolerant oxygen reduction electrocatalysts, *Nat Commun*, 5 (2014).
- [13] R. Gomes, P. Bhanja, A. Bhaumik, A triazine-based covalent organic polymer for efficient CO<sub>2</sub> adsorption, *Chem Commun*, 51 (2015) 10050-10053.
- [14] L. Hao, J. Ning, B. Luo, B. Wang, Y.B. Zhang, Z.H. Tang, J.H. Yang, A. Thomas, L.J. Zhi, Structural Evolution of 2D Microporous Covalent Triazine-Based Framework toward the Study of High-Performance Supercapacitors, *J Am Chem Soc*, 137 (2015) 219-225.
- [15] J.L. Liu, E.M. Zong, H.Y. Fu, S.R. Zheng, Z.Y. Xu, D.Q. Zhu, Adsorption of aromatic compounds on porous covalent triazine-based framework, *J Colloid Interf Sci*, 372 (2012) 99-107.
- [16] A. Bhunia, S. Dey, M. Bous, C.Y. Zhang, W. von Rybinski, C. Janiak, High adsorptive properties of covalent triazine-based frameworks (CTFs) for surfactants from aqueous solution, *Chem Commun*, 51 (2015) 484-486.
- [17] M.P. Jian, B. Liu, G.S. Zhang, R.P. Liu, X.W. Zhang, Adsorptive removal of arsenic from aqueous solution by zeolitic imidazolate framework-8 (ZIF-8) nanoparticles, *Colloid Surface A*, 465 (2015) 67-76.
- [18] T. Wang, K. Kailasam, P. Xiao, G.S. Chen, L.Q. Chen, L.H. Wang, J.L. Li, J.J. Zhu, Adsorption removal of organic dyes on covalent triazine framework (CTF), *Micropor Mesopor Mat*, 187 (2014) 63-70.
- [19] W. Zhang, F. Liang, C. Li, L.-G. Qiu, Y.-P. Yuan, F.-M. Peng, X. Jiang, A.-J. Xie, Y.-H. Shen, J.-F. Zhu, Microwave-enhanced synthesis of magnetic porous covalent triazine-based framework composites for fast separation of organic dye from aqueous solution, *J Hazard Mater*, 186 (2011) 984-990.
- [20] L. K., R. D., Recoil-Mössbauer spectral analysis software for Windows, University of Ottawa, in, 1998.
- [21] T.P. Almeida, A.R. Muxworthy, T. Kasama, W. Williams, C. Damsgaard, C. Frandsen, T.J. Pennycook, R.E. Dunin-Borkowski, Effect of maghemization on the magnetic properties of nonstoichiometric pseudo-single-domain magnetite particles, *Geochem Geophy Geosy*, 16 (2015) 2969-2979.
- [22] S. Lin, D.N. Lu, Z. Liu, Removal of arsenic contaminants with magnetic gamma-Fe<sub>2</sub>O<sub>3</sub> nanoparticles, *Chem Eng J*, 211 (2012) 46-52.

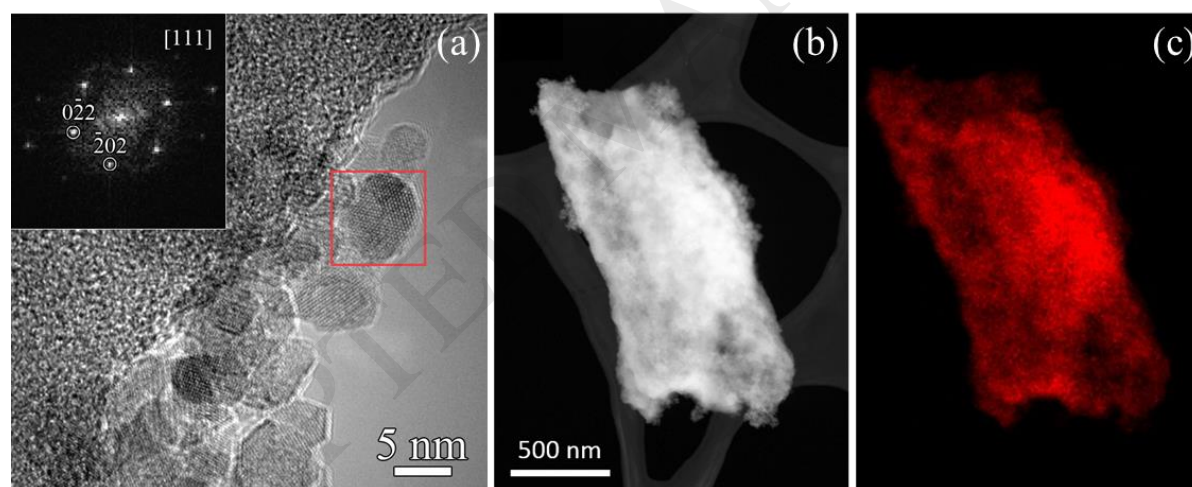
- [23] M. Kilianova, R. Prucek, J. Filip, J. Kolarik, L. Kvitek, A. Panacek, J. Tucek, R. Zboril, Remarkable efficiency of ultrafine superparamagnetic iron(III) oxide nanoparticles toward arsenate removal from aqueous environment, *Chemosphere*, 93 (2013) 2690-2697.
- [24] M.C.S. Faria, R.S. Rosemberg, C.A. Bomfeti, D.S. Monteiro, F. Barbosa, L.C.A. Oliveira, M. Rodriguez, M.C. Pereira, J.L. Rodrigues, Arsenic removal from contaminated water by ultrafine delta-FeOOH adsorbents, *Chem Eng J*, 237 (2014) 47-54.
- [25] P. Mondal, C.B. Majumder, B. Mohanty, Effects of adsorbent dose, its particle size and initial arsenic concentration on the removal of arsenic, iron and manganese from simulated ground water by Fe<sup>3+</sup> impregnated activated carbon, *J Hazard Mater*, 150 (2008) 695-702.
- [26] B.E. Reed, R. Vaughan, L.Q. Jiang, As(III), As(V), Hg, and Pb removal by Fe-oxide impregnated activated carbon, *J Environ Eng-Asce*, 126 (2000) 869-873.
- [27] S.J. Zhang, X.Y. Li, J.P. Chen, Preparation and evaluation of a magnetite-doped activated carbon fiber for enhanced arsenic removal, *Carbon*, 48 (2010) 60-67.
- [28] W.F. Chen, R. Parette, J.Y. Zou, F.S. Cannon, B.A. Dempsey, Arsenic removal by iron-modified activated carbon, *Water Research*, 41 (2007) 1851-1858.
- [29] H.J. Zhu, Y.F. Jia, X. Wu, H. Wang, Removal of arsenic from water by supported nano zero-valent iron on activated carbon, *J Hazard Mater*, 172 (2009) 1591-1596.
- [30] L. Lorenzen, J.S.J. Vandeventer, W.M. Landi, Factors Affecting the Mechanism of the Adsorption of Arsenic Species on Activated Carbon, *Miner Eng*, 8 (1995) 557-569.
- [31] A.K. Mishra, S. Ramaprabhu, Magnetite Decorated Multiwalled Carbon Nanotube Based Supercapacitor for Arsenic Removal and Desalination of Seawater, *J Phys Chem C*, 114 (2010) 2583-2590.
- [32] Z. Velickovic, G.D. Vukovic, A.D. Marinkovic, M.S. Moldovan, A.A. Peric-Grujic, P.S. Uskokovic, M.D. Ristic, Adsorption of arsenate on iron(III) oxide coated ethylenediamine functionalized multiwall carbon nanotubes, *Chem Eng J*, 181 (2012) 174-181.
- [33] E. Pehlivan, T.H. Tran, W.K.I. Ouédraogo, C. Schmidt, D. Zachmann, M. Bahadir, Removal of As(V) from aqueous solutions by iron coated rice husk, *Fuel Processing Technology*, 106 (2013) 511-517.
- [34] C. Wang, H.J. Luo, Z.L. Zhang, Y. Wu, J. Zhang, S.W. Chen, Removal of As(III) and As(V) from aqueous solutions using nanoscale zero valent iron-reduced graphite oxide modified composites, *J Hazard Mater*, 268 (2014) 124-131.
- [35] X. Hu, Z.H. Ding, A.R. Zimmerman, S.S. Wang, B. Gao, Batch and column sorption of arsenic onto iron-impregnated biochar synthesized through hydrolysis, *Water Research*, 68 (2015) 206-216.
- [36] A. Etale, B. Yalala, H. Tutu, D.C. Drake, Adsorptive removal of mercury from acid mine drainage: a comparison of silica and maghemite nanoparticles, *Toxicological & Environmental Chemistry*, 96 (2014) 542-554.
- [37] S. Zhang, Y. Zhang, J. Liu, Q. Xu, H. Xiao, X. Wang, H. Xu, J. Zhou, Thiol modified Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> as a robust, high effective, and recycling magnetic sorbent for mercury removal, *Chem Eng J*, 226 (2013) 30-38.
- [38] J.-f. Liu, Z.-s. Zhao, G.-b. Jiang, Coating Fe<sub>3</sub>O<sub>4</sub> Magnetic Nanoparticles with Humic Acid for High Efficient Removal of Heavy Metals in Water, *Environmental science & technology*, 42 (2008) 6949-6954.
- [39] X. Zhang, T. Wu, Y. Zhang, D.H.L. Ng, H. Zhao, G. Wang, Adsorption of Hg<sub>2</sub><sup>+</sup> by thiol functionalized hollow mesoporous silica microspheres with magnetic cores, *RSC Advances*, 5 (2015) 51446-51453.
- [40] P.N. Diagboya, B.I. Olu-Owolabi, K.O. Adebawale, Synthesis of covalently bonded graphene oxide-iron magnetic nanoparticles and the kinetics of mercury removal, *RSC Advances*, 5 (2015) 2536-2542.
- [41] L. Cui, X. Guo, Q. Wei, Y. Wang, L. Gao, L. Yan, T. Yan, B. Du, Removal of mercury and methylene blue from aqueous solution by xanthate functionalized magnetic graphene oxide: Sorption kinetic and uptake mechanism, *J Colloid Interf Sci*, 439 (2015) 112-120.
- [42] L. Huang, M. He, B. Chen, B. Hu, A designable magnetic MOF composite and facile coordination-based post-synthetic strategy for the enhanced removal of Hg<sub>2</sub><sup>+</sup> from water, *Journal of Materials Chemistry A*, 3 (2015) 11587-11595.

- [43] L. Huang, M. He, B. Chen, B. Hu, A mercapto functionalized magnetic Zr-MOF by solvent-assisted ligand exchange for Hg<sup>2+</sup> removal from water, *Journal of Materials Chemistry A*, 4 (2016) 5159-5166.
- [44] D.E. Giles, M. Mohapatra, T.B. Issa, S. Anand, P. Singh, Iron and aluminium based adsorption strategies for removing arsenic from water, *J Environ Manage*, 92 (2011) 3011-3022.
- [45] R. Singh, S. Singh, P. Parihar, V.P. Singh, S.M. Prasad, Arsenic contamination, consequences and remediation techniques: A review, *Ecotox Environ Safe*, 112 (2015) 247-270.
- [46] W.S. Tang, Q. Li, S.A. Gao, J.K. Shang, Arsenic (III,V) removal from aqueous solution by ultrafine alpha-Fe<sub>2</sub>O<sub>3</sub> nanoparticles synthesized from solvent thermal method, *J Hazard Mater*, 192 (2011) 131-138.
- [47] D. Maity, D.C. Agrawal, Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media, *Journal of Magnetism and Magnetic Materials*, 308 (2007) 46-55.
- [48] A.-H. Lu, E.L. Salabas, F. Schüth, Magnetic nanoparticles: Synthesis, protection, functionalization, and application, *Angewandte Chemie International Edition*, 46 (2007) 1222-1244.
- [49] P. Sharma, A. Kappler, Desorption of arsenic from clay and humic acid-coated clay by dissolved phosphate and silicate, *J Contam Hydrol*, 126 (2011) 216-225.
- [50] P. Sharma, A. Kappler, Desorption of arsenic from clay and humic acid-coated clay by dissolved phosphate and silicate, *Journal of Contaminant Hydrology*, 126 (2011) 216-225.

# Figures captions

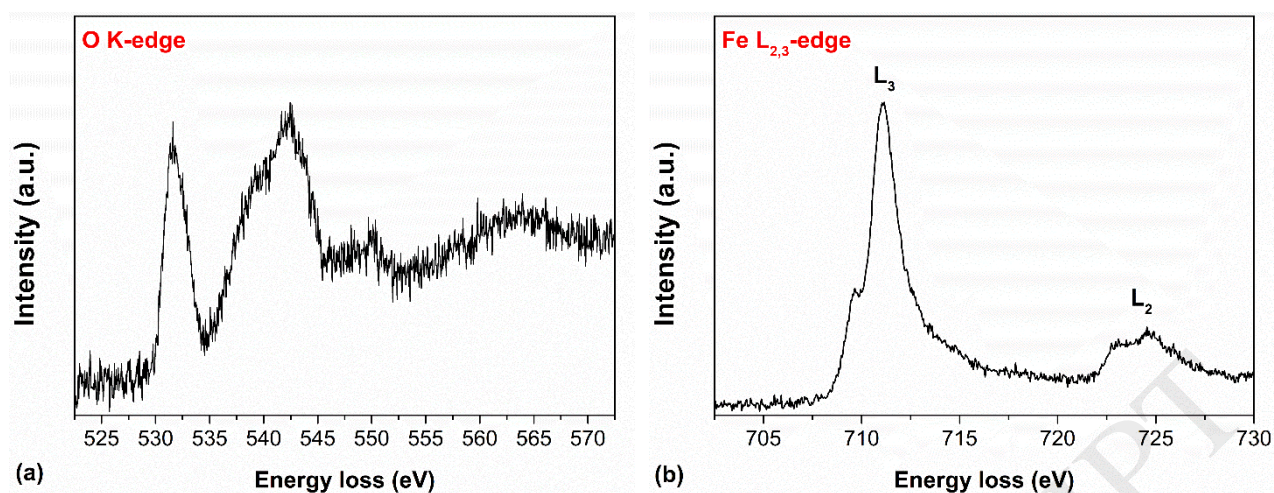


**Figure 1.** N<sub>2</sub> adsorption isotherms of CTF-1 and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1.

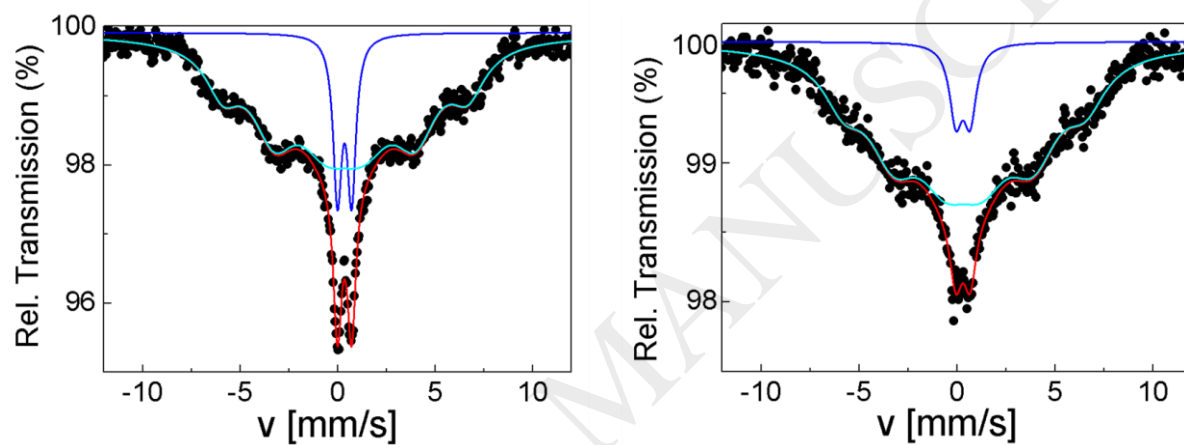


**Figure 2.** Visualisation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1 by (a) HR-TEM (Inset: FFT pattern along the [111] zone axis, taken from the area marked with red revealing the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase of iron oxide nanoparticles (JCPDS 39-1346)), (b) ADF-STEM image and (c) EDX elemental map, revealing the presence of Fe (red) in the material.

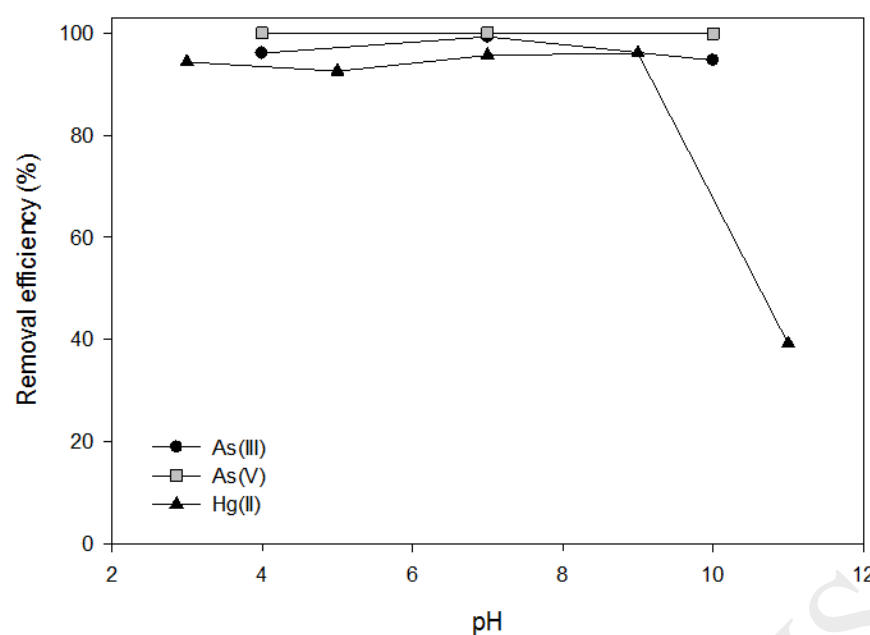




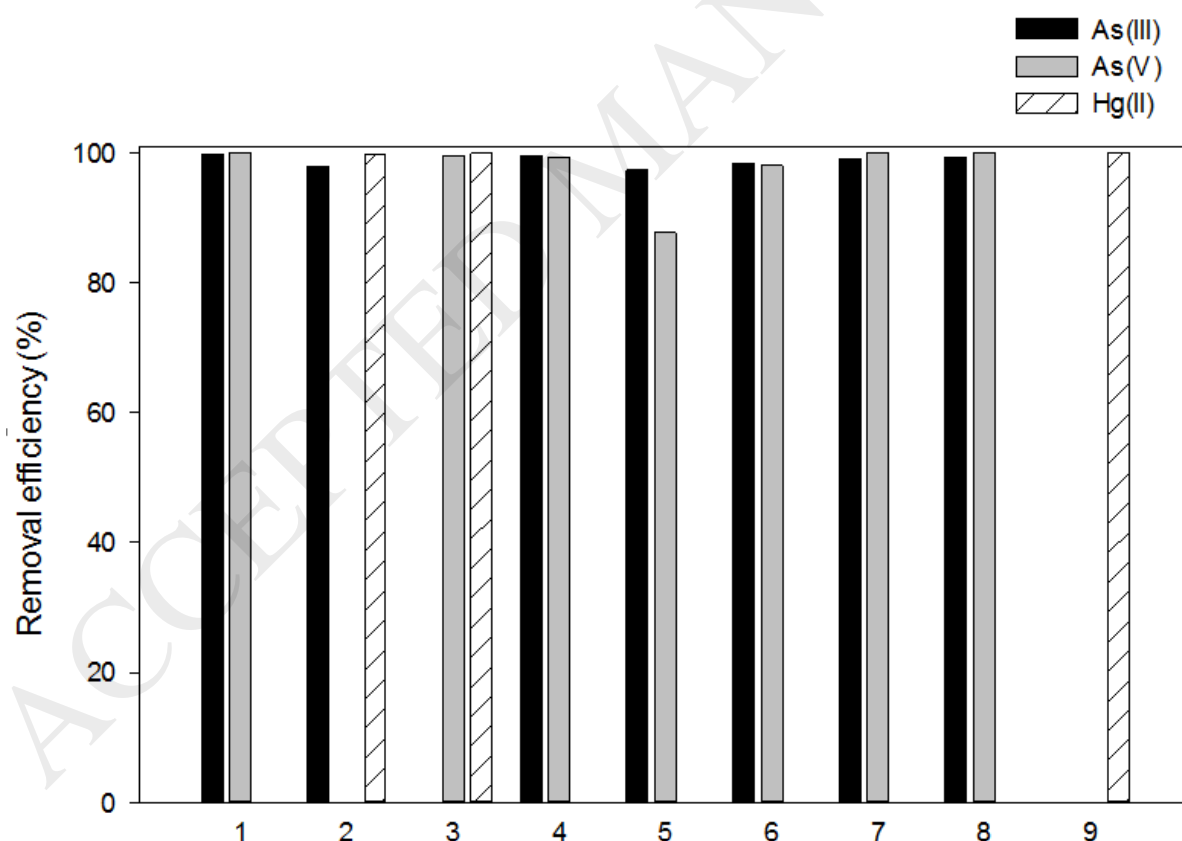
**Figure 3.** EEL spectra of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1 showing (a) O K- and (b) Fe L<sub>2,3</sub>-edges.



**Figure 4.** Mössbauer spectra of the pristine Fe<sub>2</sub>O<sub>3</sub>@CTF-1 (left) and after washing with 5 m% H<sub>2</sub>O<sub>2</sub> solution after As desorption (right).

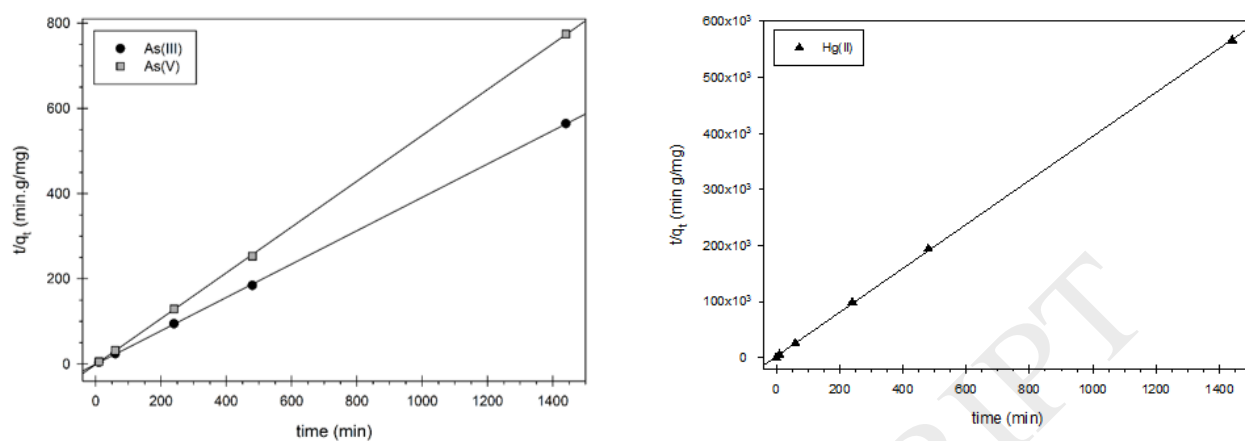


**Figure 5.** Dependence of the removal efficiency on the solution pH for removal of arsenic (100 µg L<sup>-1</sup>) and mercury (10 µg L<sup>-1</sup>) species by  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1

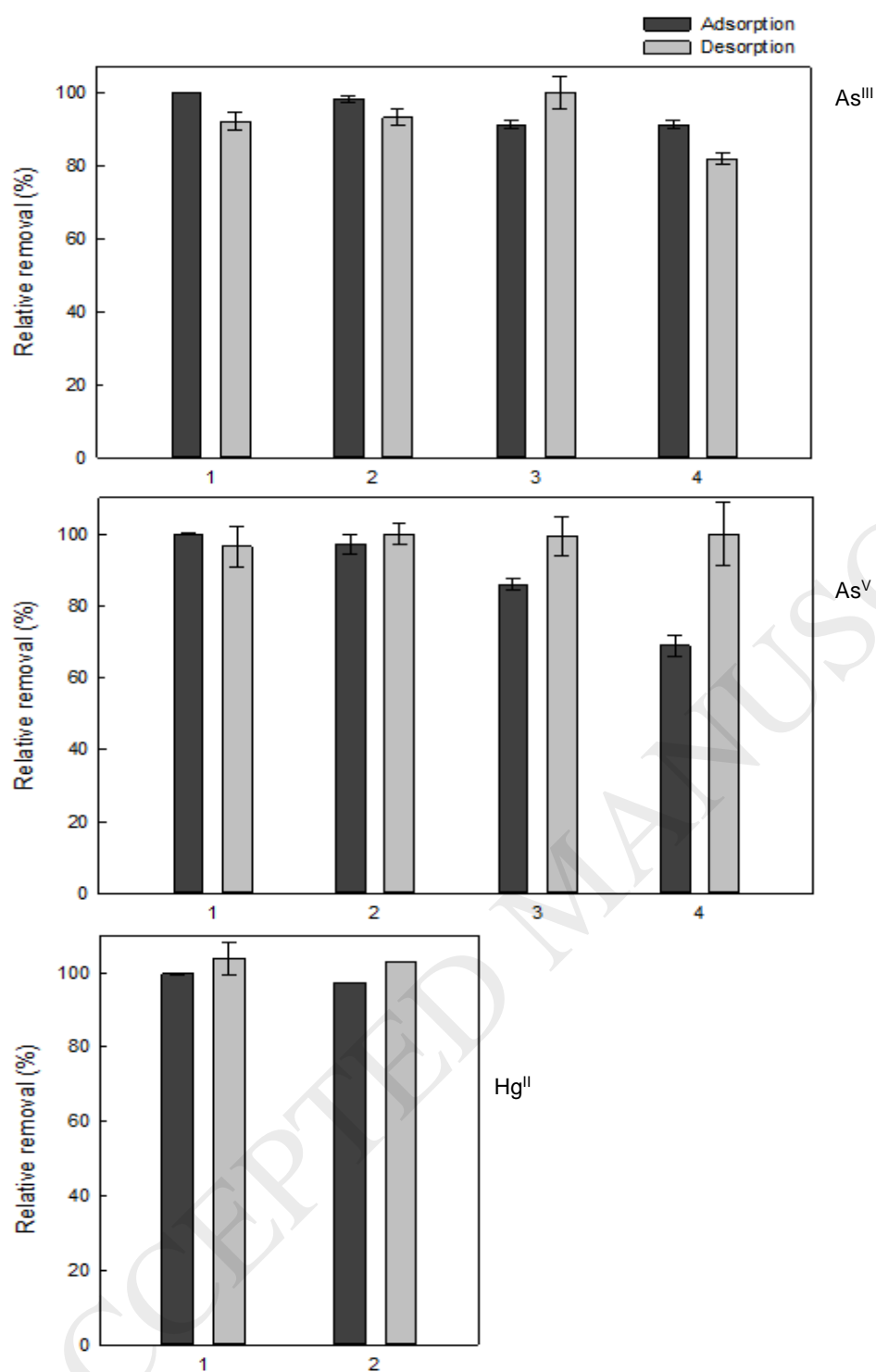


**Figure 6.** Removal efficiency (%) of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@CTF-1 for As<sup>III</sup> (black), As<sup>V</sup> (grey) and Hg<sup>II</sup> (white dashed) in the presence of potentially interfering compounds: (1) control, (2) As<sup>III</sup> and Hg<sup>II</sup> together (10 mg L<sup>-1</sup> of each component), (3) As<sup>V</sup> and Hg<sup>II</sup> together (10 mg L<sup>-1</sup> of each component), (4) 25 mg L<sup>-1</sup> Ca<sup>2+</sup> and 25 mg L<sup>-1</sup> Mg<sup>2+</sup>, (5) 25 mg L<sup>-1</sup> phosphate, (6) 25 mg L<sup>-1</sup> NOM, (7) surface water, (8) groundwater and (9) domestic wastewater

### 3.5 Kinetics of arsenic and mercury adsorption



**Figure 7.** Kinetics of As<sup>III</sup>, As<sup>V</sup> (left) and Hg<sup>II</sup> (right) adsorption on  $\gamma\text{-Fe}_2\text{O}_3\text{@CTF-1}$  according to the pseudo-second order model



**Figure 8.** Performance of  $\gamma\text{-Fe}_2\text{O}_3\text{@CTF-1}$  during consecutive cycles of  $\text{As}^{\text{III}}$  (top),  $\text{As}^{\text{V}}$  (middle) and  $\text{Hg}^{\text{II}}$  (bottom) adsorption and desorption using 0.1 M NaOH for As and 0.1 M thiourea with 0.001 M HCl for Hg, both at 70 °C, illustrating the regenerability of the adsorbent. The error bars represent the standard deviation of  $N = 3$  replicates.

## Tables

**Table 1.** Adsorption capacities and experimental conditions of different iron-impregnated carbon-based adsorbents towards arsenic species in water at room temperature

Entry	Adsorbent	pH	Contact time (h)	Adsorption capacity (mg g <sup>-1</sup> )		Reference
				As <sup>III</sup>	As <sup>V</sup>	
1	Magnetic $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> nanoparticles	6 (As <sup>III</sup> ) 3 (As <sup>V</sup> )	*	67.0	95.4	[22]
2	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> nanoparticles	7	*	*	45.0	[23]
3	$\delta$ -FeOOH nanoparticles	7	24	*	37.3	[24]
4	GAC-Fe	7	72	0.0231	0.0248	[25]
5	Fe <sub>x</sub> O <sub>y</sub> AC	7	48	4.67	4.50	[26]
6	MACF	4	24	*	4.16	[27]
7	FeAC	6	24	38.8	51.3	[28]
8	nZVI/AC	6.5	72	18.2	12.0	[29]
9	Coconut-shell carbon pretreated with Fe(III)	5	24	*	4.53	[30]
10	Fe <sub>3</sub> O <sub>4</sub> -MWNTs	*	*	53.2	39.1	[31]
11	e-MWCNT/Fe <sup>2+</sup>	4	*	*	23.47	[32]
12	RH-FeOOH	4	6	*	2.50	[33]
13	nZVI-RGO	7	4	35.8	29.0	[34]
14	Fe-impregnated biochar	5.8	*	*	2.16	[35]
15	CTF-1	8	24	*	28.6	This study
16	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @CTF-1	7	24	198.0	102.3	This study

**Table 2.** Adsorption capacities and experimental conditions of different modified and encapsulated iron oxide adsorbents towards mercury species in water at room temperature

Entry	Adsorbent	pH	Contact time (h)	Adsorption capacity (mg g <sup>-1</sup> )	Reference
1	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> nanoparticles	3	0.5	8.9	[36]
2	Fe <sub>3</sub> O <sub>4</sub> nanoparticles	6.5	4	20.0	[37]
3	Humic acid-coated Fe <sub>3</sub> O <sub>4</sub>	6.0	0.5	97.7	[38]
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -SH	6.5	4	148.8	[37]

5	MPTS-mesoporous Fe <sub>3</sub> O <sub>4</sub> /C@SiO <sub>2</sub>	6.5	8	118.6	[39]
6	GO-Fe <sub>3</sub> O <sub>4</sub>	5.0	3	16.6	[40]
7	Fe <sub>3</sub> O <sub>4</sub> -rGO	7.0	3	118.6	[41]
8	Bi-I-functionalized Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @HKUST-1	3.0	0.33	264	[42]
9	SH-Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /UiO-66	3.0	1	282	[43]
10	CTF-1	3-5	24	32.8	This study
11	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @CTF-1	3-5	24	165.8	This study

**Table 3.** Equilibrium concentration and removal efficiency after adsorption of 100  $\mu\text{g L}^{-1}$  onto  $\gamma\text{-Fe}_2\text{O}_3\text{@CTF-1}$ .

Species	$C_e$ ( $\mu\text{g L}^{-1}$ )	Drinking water standard ( $\mu\text{g L}^{-1}$ )	Removal efficiency (%)
As(III)	3.3	10	97.1
As(V)	3.7	10	96.6
Hg(II)	1.0	1	99.0

duce the removal efficiency of  $\text{As}^{\text{V}}$  by 12.3% due to the similar tetrahedral chemical structure they possess.

**Table 4.** Chemical composition of surface-, ground- and domestic wastewater used to evaluate the adsorption of  $\text{As}^{\text{III}}$ ,  $\text{As}^{\text{V}}$  and  $\text{Hg}^{\text{II}}$  on  $\gamma\text{-Fe}_2\text{O}_3\text{@CTF-1}$ 

Parameter	Unit	Surface water	Groundwater	Domestic wastewater
pH		7.9	8.0	7.4
$\text{EC}_{25\text{ }^\circ\text{C}}$	$\mu\text{S cm}^{-1}$	142	939	1094
TOC	$\text{mg L}^{-1}$	NA	8.5	11.2
$\text{Ca}^{2+}$	$\text{mg L}^{-1}$	1.1	78.0	
$\text{Mg}^{2+}$	$\text{mg L}^{-1}$	0.1	10.4	
$\text{Cl}^-$	$\text{mg L}^{-1}$	1.4	63.1	
$\text{NO}_2^-$	$\text{mg L}^{-1}$	1.1	0.5	
$\text{NO}_3^-$	$\text{mg L}^{-1}$	5.3	22.1	
$\text{PO}_4^{3-}$	$\text{mg L}^{-1}$	1.0	< 2.0	
$\text{SO}_4^{2-}$	$\text{mg L}^{-1}$	3.4	77.0	

**Table 5.** Parameters of the pseudo-second order equation model describing the kinetics of  $\text{As}^{\text{III}}$ ,  $\text{As}^{\text{V}}$  and  $\text{Hg}^{\text{II}}$  adsorption on  $\gamma\text{-Fe}_2\text{O}_3\text{@CTF-1}$ 

Model	Constant	$\text{As}^{\text{III}}$	$\text{As}^{\text{V}}$	$\text{Hg}^{\text{II}}$
Pseudo-second order	$Q$ ( $\text{mg g}^{-1}$ )	2.554	1.859	2.54
	$1/k_2$ ( $\text{mg min g}^{-1}$ )	-2.688	-3.709	0.013
	$R^2$	0.99994	0.99994	0.9999