Functionalised Magnetic Nanoparticles for Uranium Adsorption with Ultra-High Capacity and Selectivity

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1 Abstract

Removal of radioactive contaminants from the environment for safe and efficient waste disposal is a critical challenge, requiring the development of novel selective and high-capacity sequestering materials. In this paper the design of superparamagnetic iron oxide nanoparticles (SPIONs) as highly efficient magnetic-sorbent structures for uranium (U(VI)) separation is described. The nanosorbent was developed by surface functionalisation of single crystalline magnetite (Fe\textsubscript{3}O\textsubscript{4}) nanoparticles with a phosphate-based complex coating. This new design allowed for the development of a magnetically-separable ultra-effective sorbent, with a measured U(VI) sorption capacity of \( \sim 2333 \text{ mg U/g Fe} \) (1690 mg U/g Fe\textsubscript{3}O\textsubscript{4} NP); significantly higher than everything previously reported. Based on TEM analysis, it is proposed that these properties are the result of a multi-layer ligand structure, which enables high degree of U-incorporation compared to conventional surface-ligand systems. Moreover, the phosphate-NP construct \((\text{PO})\times\text{Fe}_3\text{O}_4\) shows exceptionally high specificity for the sequestration of U(VI) in solution at pH 7. Adsorption tests in the presence of competing ions, such as Sr(II), Ca(II) and Mg(II), showed high selectivity of the nanoparticles for U(VI) and extremely rapid kinetics of contaminant removal from solution, with the total
amount of uranyl ions removed after only 60 seconds of contact with the NPs. The results presented in this paper highlight the potential for such phosphate-functionalised magnetic nanosorbent as a highly effective material for the remediation of U(VI) from contaminated water and industrial scenarios.

2 Introduction

Whilst the development of the nuclear power industry offers a feasible alternative to fossil fuels for greenhouse-gas free power generation, the toxic waste associated with the nuclear fuel cycle is a potential barrier to growth and an ongoing environmental legacy. Uranium is the most common radionuclide involved in the nuclear power production, and therefore the highest proportion of waste. It is highly toxic and carcinogenic in nature, and so increasing efforts are being employed to avoid environmental contamination when dealing with fuel cycle wastewater. For this reason, the establishment of a highly effective and sensitive radionuclide detection, separation and sequestration approach is an important challenge, which is yet to be solved.

Recent years has seen the development of nanotechnologies that have potential to be used for this application, as nanoparticles offer advantages as nanosensors in rapid and high-throughput detection methods [1]. Specifically, magnetite (Fe$_3$O$_4$) nanoparticles, given their capability of showing superparamagnetic behaviour in a specific size range (1-100 nm) and their easy manipulation with even low magnetic fields, can be a potential tool in separation technologies, when compared to other nanomaterials. Their intrinsic magnetic properties allow for their easy separation from the matrix, with subsequent concentration of the sequestered radionuclide in a small volume. Moreover, due to their low cost and ease of preparation the particles are readily up-scalable, and due to their biocompatibility and low toxicity magnetic nanoparticles (MNPS) have been widely applied in the biotechnological and biomedical field [2-4]. More recent studies investigate the use of magnetic nanoparticles for the removal of aqueous metal pollutants through adsorption on the nanomaterials' surface [5-7]. However, given their high surface to volume ratio, uncoated magnetite nanoparticles readily oxidise in air and aggregate. Moreover, bare nanoparticles do not show selectivity nor high loading capacity for the adsorption of radionuclides and heavy metal ions [8-10]. Functionalisation of the nanoparticles’ surface with a ligand that would show specificity for the contaminant of interest provides a solution. Numerous studies have established the advantage of grafting Fe$_3$O$_4$ NPs with molecules showing affinity for uranyl ions, such as quercetin [11], aminopropyl groups [12], dihydroimidazole [12], polypropyleneimine (PPI) dendrimer [12], amidoxime [13], polyoxime [14], oleyl-phosphate [15], oley acid bilayer [16], trybutyl phosphate [17] or sodium dodecyl phosphate [18]. The ultimate goal is to develop a sorbent exhibiting the highest sorption capacity and selectivity for uranyl ions in aqueous systems, and with the potential characteristic of facile removal from the aqueous medium.
Phosphate molecules have been shown to form complexes with uranium (VI) when exposed to a particular pH environment \cite{19, 20} and organo-phosphorous ligands have been applied for U(VI) bonding in solvent extraction (SX) since 1900 \cite{21, 24}. Previous investigations have applied P-O-functionalised nanomaterials to water remediation from U(VI) \cite{12, 17, 18, 25, 29, 30}, and shown a capacity ranging from 166.7 mg/g \cite{17} to as high as 1250 mg/g (pH 7) \cite{29}, with sorption equilibrium reached in 3 hours \cite{17} and 24 hours \cite{29}, respectively. Faster U(VI) removal kinetics have been observed for SiO$_2$ coated Fe$_3$O$_4$ NPs functionalised with quercetin \cite{11}, however a capacity of 12.3 mg/g was reported in this work. Nevertheless, an outstanding sorption capacity combined with extremely fast kinetics is continuously researched, and an optimum material combining both the characteristics is not reported yet.

In this work, superparamagnetic iron oxide (Fe$_3$O$_4$) nanoparticles have been synthesised through a thermal decomposition method and functionalised with phosphate via a ligand exchange reaction. The exchange led to water dispersible nanoparticles grafted with phosphate functionalities arranged in a complex multilayer structure. The NPs application as a uranyl ion sorbent in water was explored at two different pH conditions, neutral (pH 7) and alkaline (pH 11), in batch tests and the NP capacity was also calculated. The choice of the parameters was based on the conditions characterising natural waters, and some waste forms and effluents in fuel temporary storage ponds in the UK. Investigation of the NPs sorption behaviour in solutions containing competing ions commonly found in industrial waste waters, such as Mg(II), Ca(II) and Sr(II), was also performed. The (PO)$_x$-Fe$_3$O$_4$ NPs were found to be extremely effective in selectively targeting and sequestering uranyl ions in solution, at pH 7, with 100% of U(VI) removed from water after just 60 seconds of contact time when a 20 mg L$^{-1}$ uranyl ions solution was tested. The extremely high capacity (2.33 g U/g Fe) revealed by the nanoparticle sorbent, in addition to the rapidity of the sequestration process and the selectivity towards U(VI), suggests the possible application of the (PO)$_x$-Fe$_3$O$_4$ nanosorbent as a powerful tool to be used in the remediation of uranium in groundwater and the clean-up of industrial wastewater.

3 Experimental

3.1 12 nm Fe$_3$O$_4$ nanoparticles synthesis and surface activation through ligand exchange

12 nm magnetite (Fe$_3$O$_4$) nanoparticles were synthesised following a thermal decomposition method as proposed by Park et al. \cite{31}. An iron-oleate complex was obtained by dissolving 10.8 g of iron chloride (FeCl$_3$•6H$_2$O, 40 mmol, Aldrich, 98%) and 36.5 g of sodium oleate (120 mmol, TCI, 95%) in a mixture of 80 mL ethanol (≥99.8 %, ACS reagent, VWR), 60 mL DI water and 140 mL hexane (anhydrous, 95 %, Sigma-Aldrich). The solution was heated until it reached 70°C, where it was kept for 4 h until the reaction’s completion. The iron-oleate complex was washed several times with ethanol in order to remove the
organic layer from the waxy solid product. To form 12 nm magnetite nanoparticles, 36 g of the iron-oleate precursor were mixed with 5.7 g of oleic acid and 200 g of 1-octadecene (90 % technical grade, Sigma-Aldrich). The reaction mixture was heated at a controlled heating rate of 3.3°C per minute up to 320°C, where it was kept for 30 minutes. The final product was cooled to room temperature and washed with ethanol at least three times. After centrifuging the nanocrystals (4500 rpm, 18°C), the particles were redispersed in hexane, where they remained stable for over 14 months.

The oleic acid functionalised Fe₃O₄ nanoparticles, dispersible in organic solvent solely, underwent a phase transfer in order to render the particles hydrophilic. Moreover, the ligand exchange method allowed for the realisation of Fe₃O₄ NPs specific for uranyl ions capture. Phosphate functionalised magnetite NPs were obtained by using a modified version of the procedure described by Li et al. In a typical batch reaction, 10 mg of oleic acid functionalised Fe₃O₄ nanoparticles were added drop-wise to 5 mL of a solution containing a mixture of Na₂HPO₄ (ACS reagent, anhydrous, ≥99.0 %, Sigma-Aldrich) and KH₂PO₄ (ACS reagent, anhydrous, ≥99.0 %, Sigma-Aldrich). In order for the reaction to be favourable towards the exchange, hexane was added to the mixture to obtain a 5:1 ratio with the water phase. The mixture was subsequently stirred for 17 hours at room temperature and the product was washed at least twice with ethanol. The phosphated-NPs were ultimately dispersed in DI water, where they remained stable for over 14 months.

3.2 Batch Adsorption Tests

The (PO)x-Fe₃O₄ NP construct was tested for uranium adsorption at several starting radionuclide concentrations (20 mgL⁻¹, 50 mgL⁻¹ and 100 mgL⁻¹) at pH 7, and at 0.4 mgL⁻¹ U (VI) concentration at pH 11. The sorption studies were conducted into 15 mL Fisherbrand centrifuge tubes. All the solutions used in the experiments were prepared with degassed DI water and the tests were carried in a Braun glove box to ensure absence of CO₂. The adsorption capacity of the (PO)x-Fe₃O₄ nanoparticles was studied by adding different amounts of NPs to different concentrations of uranyl nitrate solution followed by agitation on a flatbed orbital shaker. After U(VI) was added to the NPs suspensions, the solutions were equilibrated for 1 min, 5 min, 30 min, 60 min, 90 min, 120 min and 240 min. The maximum adsorption capacity was evaluated by mixing of a 0.02 gL⁻¹ (PO)x-Fe₃O₄ NP suspension with a 100 mgL⁻¹ uranyl nitrate solution equilibrated for 60 min. The (PO)x-Fe₃O₄ specificity for U(VI) was evaluated by testing the adsorptive capacity of the competitive ions Mg(II), Ca(II), and Sr(II) on the particles at pH 7, and K(I), Ca(II), Sr(II) at pH 11. Prior to adsorption tests, NP and metal ion solutions were purged with N₂ for at least 2 hours to ensure a carbon dioxide-free reaction, to avoid competing U(VI)-carbonate complexation, usually occurring at the investigated pHs [19][35][36]. The particles were separated out of the solution by ultracentrifugation at 6000 rpm for 30 minutes. The supernatant was collected and filtered a first time through a 0.22µm syringe filter and then using Amicon Ultra centrifugal filter units (Ultra-15, MWCO 30 kDa). The resul-
tant double filtered liquid was prepared for Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analyses. ICP-OES and ICP-MS were used to measure the amount of cations remaining in the solution after the different mixing times. The reacted materials (U-NPs) collected after centrifugation were redispersed in DI water and prepared for TEM analysis. Copper grids with a holey carbon film (3.05 mm Diam. 300 mesh, TAAB) were baked in a vacuum oven for 2 hours to remove residual contamination prior to deposition of the liquid sample, and blot-dried before analysis. High Resolution TEM (Transmission Electron Microscopy, JEOL JEM 2100F) imaging and EDS (Energy Dispersive X-Ray Spectroscopy, Oxford Instruments) were performed on the samples prior and after adsorption. The adsorption density value expressed as mg of metal ion adsorbed/g of Fe\(_3\)O\(_4\) nanoparticles was calculated with the formula:

\[
qe = (C_0 - C_e)V/m
\]

where \(q_e\) is the amount of adsorbed ion (mg/g), \(C_0\) and \(C_e\) are the ion initial and equilibrium concentration respectively (mg/L), \(V\) is the final volume in which the tests were undertaken (L), and \(m\) is the mass of the adsorptive material ((PO)\(_x\)-Fe\(_3\)O\(_4\) NPs) (g).

### 3.3 Fe\(_3\)O\(_4\) Nanoparticle Characterisation

The morphology and the size of the nanocrystals were determined by a JEOL JEM-2100F and a JEOL JEM 2100Plus TEMs, operating at a 200 kV voltage. Infrared spectroscopy (FT-IR) was operated in the attenuated total reflectance mode (ATR) to investigate the surface properties of oleic acid coated-NPs and of phosphate coated-NPs (Thermo Scientific Nicolet iS10 FTIR with Smart Golden Gate for Single-Reflection Diamond ATR). Thermogravimetric analysis (TGA, TG 449 F1 Jupiter Thermo-Nanobalance (NETZSCH)) was used to quantify the Fe\(_3\)O\(_4\) NPs surface coverage. The hydrodynamic diameter of the particles in suspension was evaluated by Dynamic Light Scattering (DLS, Malvern Zetasizer Nano). XRD patterns were acquired over \(2\theta\) range from 20° to 80° to show the nanocrystalline nature of the Fe\(_3\)O\(_4\) NPs (PANalytical X-Ray diffractometer, Cu k\(\alpha\) source). Magnetic measurements were performed using the vibrating sample magnetometer (VSM) option in a Quantum Design Physical Property Measurement System (PPMS-9T).

### 3.4 ICP-OES and ICP-MS

Samples were prepared for ICP-OES analysis through two subsequent filtering processes on the liquids. The double filtering was carried out in order to ensure the contribution to the resulting signal was only due to the U and/or metal ions present in solution and not from the ions adsorbed on the solid sample (NPs). All the samples were diluted with 2% HNO\(_3\) solution and the tests were run on a Thermo Scientific iCAP 6000 ICP Spectrometer.
with a CETAC ASX-520 autosampler. For detection of concentrations in the ppb levels an Agilent Technologies 7700 ICP-MS was used, given the instrument’s lower detection limits.

4 Results

4.1 Magnetite NP characterisation

The magnetite nanoparticles obtained via thermal decomposition of iron oleate precursor in 1-octadecene were monodisperse and homogeneous in size, with a distribution of 11.9 ± 1.5 nm. The crystals were dispersible in several organic solvents, such as hexane and cyclohexane, and remained stable for several months. The successful formation of monodisperse 12 nm iron oxide NPs depended on the separation of the nucleation and growth processes. Firstly, the iron oleate complex was decomposed at 200-240 °C to generate nuclei, the growth of which starts at ~300°C. Then, ageing the NPs at 320 °C for 30 minutes, as first suggested by Park et al. [31], ensured a monodisperse production of 12 nm Fe$_3$O$_4$ nanocrystals. The particles characterization was conducted by TEM, XRD, ATR-FTIR, DLS and VSM analyses. Electron Microscopy images (Figure S1) show a homogeneous size distribution and no aggregation of the sample, which were also confirmed by DLS measurements (Figure S1). ATR-FTIR spectroscopy found a high surface coverage in oleic acid molecules, which was calculated to be ~80%. The signals at ~583 and 630 cm$^{-1}$, in Figure 1 (a) (blue line) correspond to the Fe-O bonds in the spinel structured iron oxides [38]. At higher wavenumbers two intense signals at 2850 and 2920 cm$^{-1}$ can be found, due to -CH$_2$- stretching vibrations from the acid carbon chain [39]. The crystalline structure of the 12 nm MNPs is confirmed by the XRD patterns, with comparison of the acquired data with reference patterns suggesting magnetite as the only iron oxide phase present in the analysed samples (Figure S1, JCPDS Card 75-1610). The particles exhibited superparamagnetic behaviour at room temperature and at 5 K, with a saturation magnetisation of 73.2 emu/g (Figure S1).

4.2 (PO)$_x$-Fe$_3$O$_4$ NP construct characterisation

The ligand-exchange reaction between the oleic acid capped-MNPs and phosphate ligands successfully formed water dispersible nanoparticles, and as shown in the ATR-FTIR spectrum reported in Figure 1 (a) (orange line) the phosphate ligand has replaced oleic acid as surface functional group. Specifically, the presence of Fe-O signals suggests that the magnetite core structure has not changed, despite shifted towards lower wavenumbers (from 583 and 630 cm$^{-1}$ to 525 and 553 cm$^{-1}$) due to influence of the different species bonded to the Fe-O core. The signals at 944 and 997 cm$^{-1}$ can be attributed to the P-O-Fe and the P-O stretching vibrations, respectively. The shoulder at 1080 cm$^{-1}$ is typical of a P=O stretching signal [40]. Dynamic light scattering (DLS) and ζ-potential measurements were carried out to ensure the particles stability in water (Figure 1 (b) and (c)). DLS analysis
Figure 1: (a) ATR-FTIR spectra obtained for oleic acid capped-MNPs (green dashed line) and phosphate capped-MNPs (orange line). The spectra are normalised with respect to the Fe-O stretching peaks to give a quantitative comparison of the two samples signals intensities; (b) DLS measurement of the hydrodynamic diameter for the \((\text{PO})_x\text{-Fe}_3\text{O}_4\) NPs at pH 7; (c) \(\zeta\)-potential negative value obtained on the \((\text{PO})_x\text{-Fe}_3\text{O}_4\) NPs at pH 7; (d), (e), (f) HR-TEM images depicting the \((\text{PO})_x\text{-Fe}_3\text{O}_4\) NPs. The arrows in the figure highlight the new ligand construct surrounding the magnetite core (lighter amorphous layer). (g) EDS spectrum acquired in TEM mode on a \((\text{PO})_x\text{-Fe}_3\text{O}_4\) NPs sample. The orange boxes highlight the contributions from contamination on the sample grid, whereas the green box the signal generated by the phosphate coating; (h) DLS measurement of the hydrodynamic diameter for the \((\text{PO})_x\text{-Fe}_3\text{O}_4\) NPs at pH 11; (i) \(\zeta\)-potential negative value obtained on the \((\text{PO})_x\text{-Fe}_3\text{O}_4\) NPs at pH 11.
showed a hydrodynamic diameter of the phosphate capped MNPs of $\sim 44$ nm, although TEM imaging did not show any increase in the Fe$_3$O$_4$ core size, with retainment of spherical shape (Figure 1 (d)) and of the crystalline nature of the magnetite NPs (Figure 1 (e)). The particles remained dispersible in suspension for over a year, with no detectable sedimentation or aggregation. Some agglomeration was evidenced during TEM imaging, as visible from Figure 1 (f). Nevertheless, the presence of an amorphous layer surrounding the exchanged-NPs is evident in the micrographs, which was not visible on the oleic acid functionalised-MNPs (Figure S1). TEM-EDS analysis on the exchanged-NPs confirmed the presence of phosphorous as main component of the coating (Figure 1 (g)). Zeta potential results showed a negative surface charge, suggesting that the phosphate coated-MNPs are deprotonated at pH 7, with a $\zeta$-potential value of -36 mV (Figure 1 (c)). Due to DLS and TEM results suggesting possible partial agglomeration of the new NPs construct, the nature of the inter-particle interactions was, therefore, investigated. The phenomenon can partially be explained by H-bonding between water molecules and the phosphate moieties at neutral pH [41], consequently generating a greater solvation layer [33], as also observed by others [42]. The hydrodynamic diameter detection might also be influenced by the nature of the technique, as the thicker double layer of charged particles in a low conductivity medium causes a slower diffusion speed of the NPs in the liquid, with a consequent increased $H_d$ measured. As confirmation of the hypothesis, DLS and $\zeta$-potential measurements were carried out on the (PO)$_x$-Fe$_3$O$_4$ NPs after increasing the pH of the suspension at a value of 11. The recorded $H_d$ of 32 nm (Figure 1 (h)) with a more negative $\zeta$-potential value of -44 mV (Figure 1 (i)) can be explained by the higher density of negative charges as consequence of further deprotonation of the phosphate species. The lower $H_d$ value recorded for the NPs in alkaline conditions confirms the presence of weakly associated agglomerates in suspension, as the presence of covalent inter-particle interactions would have resulted in the same $H_d$. The still higher $H_d$ value compared to the one recorded for the oleic acid functionalised NPs (Figure S1 (e)) can be explained by the contribution of the sorbed water molecules to the phosphate layer generating the greater solvation shell.

### 4.3 Uranium adsorption onto phosphated-Fe$_3$O$_4$ NPs

The aim of the sorption experiments was to evaluate the maximum capacity of the (PO)$_x$-Fe$_3$O$_4$ NPs for U(VI) and the possible uptake of competing ions. Metal cations commonly found in natural and waste water, such as Sr(II), Mg(II), and Ca(II), may compete for the negatively charged binding ligand on the NPs’ surface. ICP-OES results of preliminary adsorption tests with a starting U(VI) concentration of 20 mgL$^{-1}$ on 2.5 mg phosphated-Fe$_3$O$_4$ MNPs are reported in Figure 2 (a). It is evident that for all different adsorption times (1 min, 5 min, 10 min and 30 min) the particles were extremely effective in sequestering uranyl ions. Specifically, the analysed supernatants after adsorption showed an extremely rapid uranium uptake, with 100% of the U(VI) present in solution removed.
after a contact time of 1 min. By increasing the concentration of U(VI) in solution to 100 mgL$^{-1}$, the nanoparticles capacity was found to amount to 2333 mg g$^{-1}$ (mg of U g$^{-1}$ Fe in (PO)$_x$- Fe$_3$O$_4$ NPs). The sorption capability of the phosphated-Fe$_3$O$_4$ NPs for U(VI) was subsequently tested with three possible interfering ions, Sr$^{2+}$, Ca$^{2+}$, and Mg$^{2+}$, and, as shown from the ICP-OES results in Figure 2 (b), these ions were found to have no appreciable competing effect at mixing times of 1 min, 1 h and 24 h. Desorption tests carried out using DI H$_2$O as eluent were performed on the (PO)$_x$- Fe$_3$O$_4$ particles post-adsorption, in order to evaluate the stability of the complex formed between the adsorbent and the adsorbate. ICP-OES data obtained from the water collected after three washings of the samples are reported in Figure 2 (c). Interestingly, no appreciable uranium detachment can be observed, suggesting the formation of an extremely stable U-NPs complex after adsorption.

To further confirm adsorption of uranium on the NPs surface, ICP-OES was performed on the U-sorbed (PO)$_x$-Fe$_3$O$_4$ samples after digested in 2% HNO$_3$. Results obtained on the analysis of a ~0.1 mg of magnetite NPs after agitation with a 100 ppm U(VI) solution are reported in Figure 4. As shown, upon saturation of the NPs a 34.53 ± 0.06 ppm U(VI) concentration was detected in the digested sorbed-samples. TEM images and EDS analysis on the same samples also confirmed the presence of uranium uniformly distributed on the MNPs’ surface (Figure 3). Due to U(VI) known complexation with carbon dioxide in water when at pH≥8 [19,20], the (PO)$_x$-Fe$_3$O$_4$ NPs efficiency in adsorbing U(VI) was tested when exposed to open atmosphere conditions. Results reported in Fig. S3 show a retained excellent removal capacity after exposure of the (PO)$_x$-Fe$_3$O$_4$ NPs and the U(VI) stock solution to air, with an 85 % uranium uptake upon equilibration for 1 minute.

Sorption studies were also undertaken at pH 11 to investigate the NPs selectivity in simulated alkaline repository water conditions. Due to the low solubility of the uranyl ion at this pH the issue of capacity is less critical - but there is potential for use in sensor technology. Because of this lower solubility at pH 11, uranium concentration had to be limited to 0.04 ppm. In addition, Ca (0.60 mgL$^{-1}$), K (0.46 mgL$^{-1}$) and Sr (2.43 mgL$^{-1}$) were added to the test solutions, as typical ionic concentrations in repository water. After equilibration of the NPs with test solutions for different contact times (5 min, 60 min, 24 h, and 48 h), analysis of the supernatants showed no affinity of the NPS for any of the additional cations tested with, again, sorption of uranium only. In comparison with the previously achieved results at pH 7, lower sorption values were measured in alkaline conditions. Figure S2 exhibits the sorption results for all the ions in the mixed solutions, from which a decrease of 7 ppb in U(VI) concentration after the longest contact time (48 h) is evident, and a negligible variation of competing ion concentrations.
Figure 2: (a) ICP-OES data acquired on the supernatants collected after U(VI) adsorption on (PO)$_x$-Fe$_3$O$_4$ NPs. The results show the rapidity of the sorption process, with the U(VI) concentration dropping to zero after only 1 minute of contact between the sample and the contaminant at an initial U(VI) concentration of $\sim$18.5 ppm. (b) Graph obtained from ICP-OES tests after Sr(II), Ca (II), Mg(II) and U(VI) adsorption on the phosphated-MNPs over a range of contact time (1 min, 1 h, 24 h). The concentration variations observed for the competing ions is negligible, whereas U(VI) is completely removed from the mixing solution after 1 minute of contact with the (PO)$_x$-Fe$_3$O$_4$ NPs. (c) Water analysed at ICP-OES after three subsequent washings of the adsorbed NPs. The washings were carried on 0.11 mg of (PO)$_x$-Fe$_3$O$_4$ NPs after sorption of 172.5 µg of U(VI). No uranium release was observed after the second and third washings, suggesting a strong interaction with the NPs.
Figure 3: STEM-EDS elemental maps and spectrum of (PO)$_x$-$\text{Fe}_3\text{O}_4$ NPs after adsorption with U(VI) (20 mgL$^{-1}$ solution). The technique allows to map the position and the intensity of the elements in the sample. Intense uranium signals are highlighted in red in the spectrum (bottom left).
Figure 4: Elemental concentration ICP-OES results obtained on the analysis of 0.11 mg of uranium sorbed-(PO)$_x$-Fe$_3$O$_4$ NPs after overnight digestion in HNO$_3$. The sample underwent three subsequent washings with DI H$_2$O prior to digestion.

5 Discussion

The maximum uranium sorption capacity experienced for the phosphated-Fe$_3$O$_4$ nanoparticles (2333 mg g$^{-1}$) is above that reported in literature so far: specifically, our value is a factor of 10 times higher than the majority of studies using iron oxide based nanoparticles and phosphate-functionalised sorbent materials [11][16][17][28][29]. This result can in part be explained by consideration of the NPs construct. From Figure 1 ((c), (d) and (e)), presence of an irregular amorphous layer of $\sim$1.5 nm thickness, surrounding the magnetite NPs, is shown. The elemental analysis performed by TEM-EDS and by ICP-OES on the exchanged-NPs reported an atomic averaged Fe:P ratio of 3.5 $\pm$ 2.1 Fe atoms per P atom. Considering a 0.24 nm$^2$ surface area [40] occupied by every phosphate molecule on a 12 nm Fe$_3$O$_4$ NP, the estimation of the Fe:P ratio for a monolayer coating can be calculated:

$$N_{phosphate} = \frac{S_A \text{Fe}_3\text{O}_4}{\text{theoretical } S_A \text{ bi-PO}_4}$$  \hspace{1cm} (1)

Where $S_A$ is the surface area of an Fe$_3$O$_4$ NP with a 12 nm diameter ($S_A$ Fe$_3$O$_4$), and theoretical $S_A$ bi-PO$_4$ the one occupied by a bidentate phosphate molecule on the NP surface [40]. Estimating the number of Fe atoms per 12 nm Fe$_3$O$_4$ NP ($N_{Fe}$) the Fe:P ratio can subsequently be obtained. Considering the measured mean diameter obtained by TEM analysis of 11.9 $\pm$ 1.5 nm, $N_{Fe}$ is obtained from Equation 2:

$$N_{Fe} = \frac{V_{NP}}{V_{unit \ cell}} \times N_{(Fe/unit \ cell)} = \frac{4/3\pi r^3}{(8.39 \text{ Å})^3} \times 24 = 36773$$  \hspace{1cm} (2)
Where $V_{NP}$ is the estimated NP volume, $r$ the NP radius, $V_{\text{unit cell}}$ is the unit cell volume for Fe$_3$O$_4$, calculated from magnetite unit cell parameters ($a=b=c=8.39$ Å), and 24 the number of Fe atoms per unit cell ($N_{(Fe/\text{unit cell})}$).

A Fe:P ratio of $\sim$20:1 is expected for a simple monolayer of phosphate. Here, our nanoparticles exhibit a phosphate moieties number at least 3.5 times greater than the monolayer estimation, which, together with the direct high resolution TEM imaging evidence, demonstrates the presence of a multilayer coating structure. The ATR-FTIR characterisation reported in Figure 1 further support the multilayer hypothesis, with signals typical of both protonated phosphate complex and of polyphosphates. The FTIR-ATR broad peak between 950-1200 cm$^{-1}$ if fitted by a linear background and a Gaussian profile, as firstly proposed by Daou et al. [40], suggests the presence of a monoprotonated binuclear phosphate structure, (FeO)$_2$(PO)(OH). On the other hand, a contribution at 1160 cm$^{-1}$ is also present in the analysed sample: such a high wavenumber peak, according to Daou et al., would be generated by the influence of two hydroxyl groups onto the P=O peak’s position, and hence attributed to a bihydroxylated phosphate complex [40]. The shift of this peak in our spectrum at lower frequencies (1160 cm$^{-1}$) is possibly due to deprotonation of the complex, as encountered in the H$_2$PO$_4^-$ spectrum (P=O band at 1159 cm$^{-1}$) [43]. Moreover, a broad peak between 1350 and 1220 cm$^{-1}$ is visible, characterised by others as typical of polyphosphate chains (Poly-P) [44–46]. These ATR-FTIR findings support the presence of different phosphate-based species functionalising the Fe$_3$O$_4$ NPs. The amorphous layer visible from Figure 1 on the surface of the ligand exchanged-NPs, and estimations from ICP-OES and EDX results, suggest a multilayer shell, hence providing a higher number of U(VI)-bonding sites. The predominant uranium species present in water at the considered neutral conditions, such as UO$_2^{2+}$, UO$_2$OH$^+$, and (UO$_2$)$_3$(OH)$_5$$^+$ [15, 19, 35, 47], explain the strong affinity towards the negatively charged (PO)$_x$-Fe$_3$O$_4$ NPs (Fig. 1 (c)), with formation of stable uranyl-phosphate complexes, as previously discussed by others [19,48,49].

The increased site density cannot be the only factor explaining the high capacity shown by the (PO)$_2$-Fe$_3$O$_4$ NPs. Batch experiments using a starting U(VI) concentrations of 100 mg L$^{-1}$ showed an OES-measured sorption of 34.5 mg L$^{-1}$ when using 0.11 mg of functionalised nanoparticles, which corresponds to an estimated U:P molar ratio of $\sim$3:1. On the other hand, when analysing results on the same samples from EDS atomic %, a U:P ratio of 1.5:1 is calculated. Disagreement between the two sets of results might originate from the difference in the amount of sorbed-sample analysed through ICP-OES, where the whole U-NPs solid is digested in HNO$_3$ and analysed, and EDS data, which were instead obtained on a smaller number of sampled regions imaged through TEM. As visible in Figure 3, formation of aggregates of $\sim$150-500 nm in size was observed after U(VI) adsorption onto the NPs. The same phenomenon was noticed by Lee et al. after adsorption of uranium onto octadecylphosphonic acid coated MnFe$_2$O$_4$ NPs [29]. Aggregation of the phosphated NPs after high loading with uranyl species in solution through adsorption, which would shield the charge effect previously stabilising the phosphated-NPs in suspension, might be a possible explanation [15,29]. Finally, the structural differences in the various phosphate-
based complexes forming the NPs shell would result in binding interactions involving a different number of uranium moieties and (PO)$_x$-functionalities. 2:1 and 1:1 phosphate-uranium interactions were observed by Vazquez et al. at pH 7 [50]. Lee et al. explained their enhanced uranium sorption capacity shown by bilayered ODP-MnFe$_2$O$_4$ NPs as due to complexation by the phosphate ligand as well as U(VI) reduction occurring at the Fe$^{2+}$ and Mn$^{2+}$ interphase of the NPs surface [29]; the double-effect mechanism proposed by Lee et al. supports the observations of our work. Specifically, as Lee’s et al. work’s bilayer functionalising structures did not seem to restrict the redox reaction, a similar behaviour would be expected in our work.

Table 1: Comparison of U(VI) sorption capacities reported for published work’s sorbents and this work’s material.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Max. Sorption Capacity (mg/g)</th>
<th>Eq. Time</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$ NPs (50-100 nm)</td>
<td>5 (pH 7.0)</td>
<td>4-6 h</td>
<td>8</td>
</tr>
<tr>
<td>Quercetin-SiO$_2$@Fe$_3$O$_4$ NPs</td>
<td>12.3 (pH 3.7)</td>
<td>30 min</td>
<td>11</td>
</tr>
<tr>
<td>SiO$_2$@Fe$_3$O$_4$ NPs</td>
<td>52 (pH 6.0)</td>
<td>3 h</td>
<td>51</td>
</tr>
<tr>
<td>Graphene/Fe$_3$O$_4$ NPs</td>
<td>69.5 (pH 5.5)</td>
<td>4 h</td>
<td>47</td>
</tr>
<tr>
<td>Amidoxime-SiO$_2$@Fe$_3$O$_4$ NPs</td>
<td>105 (pH 5.0)</td>
<td>2 h</td>
<td>13</td>
</tr>
<tr>
<td>Tributyl PO$_4$-C nanotubes</td>
<td>166.7 (pH 5.0)</td>
<td>3 h</td>
<td>17</td>
</tr>
<tr>
<td>Oleic acid bilayer@Mn$_2$FeO$_4$ NPs</td>
<td>312.5 (pH 5.6)</td>
<td>24h</td>
<td>15</td>
</tr>
<tr>
<td>Oleic acid bilayer@Fe$_3$O$_4$ NPs</td>
<td>344.8 (pH 5.6)</td>
<td>24 h</td>
<td>16</td>
</tr>
<tr>
<td>PO$_4$-C spheres</td>
<td>434.8 (pH 6.0)</td>
<td>2 h</td>
<td>27</td>
</tr>
<tr>
<td>Oleic acid bilayer@Fe$_3$O$_4$ NPs</td>
<td>635 (pH 5.6)</td>
<td>24 h</td>
<td>18</td>
</tr>
<tr>
<td>Monododecyl Phosphate-OA bilayer@Fe$_3$O$_4$ NPs</td>
<td>657 (pH 5.6)</td>
<td>24 h</td>
<td>18</td>
</tr>
<tr>
<td>Oleic acid bilayer@MnFe$_2$O$_4$ NPs</td>
<td>666.7 (pH 7.0)</td>
<td>24 h</td>
<td>29</td>
</tr>
<tr>
<td>Octadecylphosphonic acid bilayer@MnFe$_2$O$_4$ NPs</td>
<td>1000 (pH 7.0)</td>
<td>24h</td>
<td>29</td>
</tr>
<tr>
<td>Oleyl phosphate bilayer@MnFe$_2$O$_4$ NPs</td>
<td>1667 (pH 5.6)</td>
<td>24h</td>
<td>29</td>
</tr>
<tr>
<td>Phosphated-Fe$_3$O$_4$ NPs</td>
<td>1690 (pH 7.0)</td>
<td>1 min</td>
<td>This work</td>
</tr>
</tbody>
</table>
The capability of phosphorous species/compounds in binding U(VI) in aqueous systems was observed in several studies, as reported in Table 1. Yu et al. [27] in particular reported extremely high selectivity of o-phosphoethanolamine for U(VI) when mixed with co-existing ions, such as Mg(II), Sr(II) and Na(I) at pH 5-6. However, the reason of such a high selectivity compared to other 2+ cations was not investigated in [27]. Lee et al. [29] experienced slightly reduced sorption of uranium due to Ca(II) and Na(I) competition, if the three ions were added in solution simultaneously, with almost complete release of the competing cations through displacement when uranium was subsequently added [29].

The energies of formation of metal-ligand complexes may help to explain such selectivity. Several groups modelled the affinity of phosphate compounds towards Mg(II) [52,53], Ca(II) [53] and U(VI). DFT calculations performed by Mayaan et al. [52] reported the formation of the H₃PO₄-Mg(II) complex to be unfavourable, whereas the phosphate anion-Mg(II) complex was found to be favourable, but small in magnitude (ΔH of formation ~ -6 kcal/mol). Petrov et al. modelled the binding affinities of Ca(II) and Mg(II) to a dimethyl phosphate anion (DMP⁻), and found the process to be unfavourable (positive ΔH of complex formation in the monodentate and bidentate geometry) [53]. In both papers the results were explained in terms of the high affinity of the divalent cations towards the water molecules, which need to be displaced by the new ligand (phosphate-) for complex formation [52, 53], due to the unfavourable energetics involved in the removal of water molecules from the first solvation shell [54]. To the best of our knowledge, a computational comparison of the three complexes’ formation energies is not available, however, Shvareva et al. [55] reviewed thermodynamics properties experimentally obtained for several uranyl phosphates. The enthalpies (ΔH) of formation were found to be highly favourable (~60 kcal/mol) for U(VI)-phosphate complexes [55]. Even though a consistent comparison between the enthalpies of formation for the Mg(II)-, Ca(II)-, and U(VI)-phosphates is not possible, due to lack of studies where all systems are explored experimentally or simulated using the same method, the data discussed above report a difference in the ΔH of U(VI)-phosphate complex ten times higher than those reported for Mg(II)-phosphate. Moreover, we note that the studies performed here are only short term and so there may be further kinetic effects that require longer contact time to evaluate the possible formation of Mg(II)-, Ca(II)-, Sr(II)-(PO)ₓFe₃O₄ NPs complexes.

Interestingly, to date, the reported adsorption capacity by Lee’s group [29] is most similar to the one reported in our work (Table 1), being the only other characterised by the same order of magnitude [29]. The group experienced the highest sorption capacity at pH 5.6 (1667 mg U/g nanocrystal), with decrease to 1250 mg U/g nanocrystal when the same system was tested at pH 7. The increased capacity at slightly acidic pH can be explained by UO₂²⁺ ion being the main species at pH 5 [15,16,29,35,17], hence increasing the performance of the negatively charged sorbent material.

Sorption tests at pH 11 did not show an appreciable uranium loading on the (PO)ₓFe₃O₄ NPs. This is not unexpected, given the radionuclide speciation in water at alkaline pH. Specifically, presence of anionic species, such as (UO₂)₃(OH)₈²⁻ and (UO₂)(OH)₃⁻, is
extensively documented for U(VI) speciation in solution at pH 11 [16, 28, 35, 36, 47]. The anionic uranium oxides will, hence, repel the negatively charged (PO)_x-Fe_3O_4 NPs, preventing the formation of the U(VI)-NP complex. The trend is consistent with all reported similar studies [8, 13, 16, 17, 27, 47].

6 Conclusion

In this paper we have reported the development of Fe_3O_4 nanoparticle constructs for extremely rapid and enhanced uranium sorption in water at neutral pH and shown the efficacy in relevant competing ions environments. The NPs produced in this work showed the highest adsorption capacity reported to date, ~ 1700 mg U/g Fe_3O_4 NP, high specificity, and selectivity for U(VI) when coexisting with divalent cations such as Mg(II), Sr(II) and Ca(II). Kinetic studies showed reach of equilibrium after 60 seconds of contact of the (PO)_x-Fe_3O_4 NPs with the radionuclide in solution. The extremely high sorption capacity was explained by the presence of a multilayer shell of negatively charged phosphate species surrounding the Fe_3O_4 core, binding to the positively charged uranium species in solution. Overall, the optimal performances exhibited by the (PO)_x-Fe_3O_4 sorbent described here show the promises for our NPs application in sensing, detection and separation of uranium in water.

7 Acknowledgements

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8 Supporting Information

Supporting Information: Characterisation of as-synthesised 12 nm Fe_3O_4 NPs including TEM micrographs, size-distribution, DLS measurements, VSM hysteresis loop and XRD data; results of adsorption tests at pH 11; results of adsorption test in oxic conditions.
References


