Preventing Uranium(VI) Redissolution in Water after Treatment with Zerovalent Iron Nanoparticles by Passivation with Chromium(VI)

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It has been proved that nanoscale zerovalent iron (nZVI) is efficient for a fast removal of U(VI) in the absence of dissolved oxygen. However, the reoxygenation of the system leads to the re-release of U(VI) to the solution. In this work, U(VI) removal by nZVI was studied and its redissolution was prevented by addition of Cr(VI) that produces the passivation of the nZVI surface. Starting at 0.25 mM of U(VI) under anoxic conditions, nZVI was added in a Fe(total):U(VI) molar ratio of 4 achieving a fast and complete U(VI) removal. After 0.5 h reaction, 0.33 mM Cr(VI) was added to the U(VI) system and reoxygenation of the system was allowed for 24 h. No re-release of U was observed, in contrast with the experiments performed in the absence of Cr(VI), where 16 % of U was redissolved after reoxygenation. Raman spectroscopy and X-ray diffraction analyses performed on the solids obtained after the experiments demonstrated the presence of magnetite, maghemite and Fe(0) in all the samples. X-ray photoelectron and energy disperse spectroscopies indicated that a larger amount of U was present in the nanoparticles coming from the experiment where Cr(VI) was added, compared with the experiments in the absence of Cr(VI). The proposed mechanism involves the reduction of U(VI) to U(IV) and its adsorption on the nanoparticles, followed by surface passivation produced by reduction of Cr(VI) to Cr(III), which prevents the reaction between oxygen and the adsorbed uranium.

1. Introduction

The presence of uranium in the environment is the consequence of leaching of natural mineral deposits and of industrial activities, mostly nuclear applications (Bhalara et al., 2014). Uranium chemical toxicity (WHO, 2012) is of concern for human health, as it can cause nephritis, high blood pressure and bone dysfunction. For this reason, the WHO (2012) has established a guideline value of 30 μg L^{-1} for uranium in drinking water. The speciation of uranium in water depends on pH and on the presence of dissolved oxygen (DO) and different anions in solution. Reported uranium remediation methods are ion exchange, reverse osmosis and ultrafiltration, adsorption (Zou et al., 2017), bioreduction and use of zerovalent iron (e.g., Quici et al., 2017 and references therein). Zerovalent iron nanoparticles (nZVI) are powerful materials for removal of a wide variety of pollutants (Sun et al., 2016). nZVI is composed by a core of α-Fe and an outer shell formed by a complex mixture of iron oxy(hydroxides) (Montesinos et al., 2014). Thus, the combination of a moderate reducing power (E^0 = -0.44 V) from the core and a high surface area from the shell gives rise to a versatile material useful for adsorbing and/or reducing water pollutants. In particular, removal of U(VI) using nZVI involves reduction to U(IV) followed by adsorption and coprecipitation during the formation of Fe(III) hydroxides (Li et al., 2013). Different works showed a fast (minutes) removal of U(VI) by reaction with nZVI both in laboratory

and in real waters (Crane et al., 2015; Crespi et al., 2016) with higher removal values obtained in the absence of DO. However, the reoxygenation of the solutions (in one to two days) leads, in all cases, to the re-release of U(VI) to the system. The reactivity of nZVI under oxic and anoxic conditions was compared, and it was found that, in the presence of DO, 40 % of U was released into the solution after 48 h, whereas under anoxic conditions, only 2 % of U release was found after the same time (Crane and Scott, 2014; Dickinson and Scott, 2010). Even when long term stability of U on iron nanoparticles is of great concern, strategies to avoid this reoxidation have not been proposed so far. Additionally, the provision of N_2 or Ar bubbling is not an economic approach for medium to large scale remediation technologies.

On the other hand, nZVI is a very good reagent to promote Cr(VI) removal from water (Zou et al., 2016). In a previous work of our group (Montesinos et al., 2014), the removal of aqueous Cr(VI) by nZVI was shown to be coupled with the passivation of the surface of the nanoparticles, and XPS analysis of the solids after the reaction showed that Cr(III) was the only Cr species incorporated in the external layer of the nanoparticles.

In view of these results, it was found opportune to study the U(VI) removal with nZVI adding Cr(VI) as a strategy to prevent the re-release of U(VI) during and after the treatment, taking profit of the passivation of the nZVI surface by the presence of Cr.

2. Materials and methods

2.1 Chemicals

U(VI) solutions were prepared using $UO_2(NO_3)_2 \cdot 6H_2O$ provided by May & Baker (now Sanofi-Aventis), while Cr(VI) solutions were prepared using $K_2Cr_2O_7$ (Mallinkrodt). Commercial nZVI (NANOFER 25, hereafter N25) were provided by NANO IRON s.r.o. as a suspension with a 274 g L^{-1} concentration of Fe(total) and 80-85 g Fe(0)/100 g Fe(total). The suspension was kept at low temperature (~4 °C) until used. o-Phenanthroline (Mallinckrodt), NaOH (Biopack), hydroquinone (Merck), 1,5-diphenylcarbazide (UCB) and phosphoric acid (Biopack) were of analytical reagent grade and used without further purification. In all experiments, Milli-Q water was used (resistivity = 18 MΩ cm). Nitrogen (purity 5.0) was provided by Linde.

2.2 Experimental setup for reactions with nZVI

Batch experiments were carried out in a 400 mL cylindrical jacketed Pyrex glass reactor closed to the atmosphere by means of a gas tight lid and a reaction volume of 200 mL. Temperature was controlled at 25 °C by recirculating water through the jacket using a Polystat® temperature controller (Cole-Parmer), and the suspensions were stirred by a vertical paddle agitator (Decalab).

100 mL of an N25 suspension with [Fe(total)] = 2 mM was prepared in N_2 purged water. For the U(VI) removal experiments, 100 mL of a 0.5 mM U(VI) solution were added to the N25 suspension, with $[U(VI)]_0$ = 0.25 mM and $[Fe(total)]_0$ = 1 mM as the initial concentrations in the experiments, i.e., a Fe(total):U(VI) molar ratio (MR) equal to 4. N_2 was bubbled in the reactor at 0.9 L min^{-1} for the first two hours to ensure anoxic conditions. The experiments with Cr(VI) (0.33 mM) were performed by addition of a Cr(VI) concentrated solution to the 200 mL of the uranyl system in two ways: (1) after 0.5 h of reaction and (2) at t = 0. In both cases, the Fe(total):Cr(VI) MR was 3. Blank experiments with only U(VI) and another experiment with only Cr(VI), respectively, were also performed under the same conditions. After two hours of anoxic experiment, the content of the reactor was separated in two equal portions. One of them was filtered through a 0.22 µm nylon membrane (Osmonics), and the other one was used to allow the reoxygenation of the system, i.e., leaving the reactor open to the atmosphere under agitation (using a Vicking orbital shaker); after 24 h, the suspension was also filtered. Initial pH was adjusted to 5.2 using 1 M NaOH in all cases. All experiments were performed at least by duplicate, and the results averaged. The solids obtained after filtration were dried in a vacuum desiccator for 24 h and then preserved in glass vials with the headspace purged with Ar until analysis.

2.3 Analytical methods

Samples (1.5 mL) were periodically withdrawn from the reactor and centrifuged using an Eppendorf MiniSpin® centrifuge. The concentration of total uranium in the supernatant was measured by Total Reflection X-ray Fluorescence (TXRF) using 1 mg L^{-1} Ga as internal standard (Custo et al., 2006), employing an S2 PICOFOX (Bruker) spectrometer. [Cr(VI)] was measured spectrophotometrically using the diphenylcarbazide method at 540 nm (ASTM, 2002), while [Fe(II)] and [Fe(total)] were measured with the o-phenanthroline method at 508 nm (Harvey et al., 1955). UV-Vis absorption measurements were performed employing a Hewlett Packard Agilent 8453UV-Vis spectrophotometer. For pH determinations, a pH-meter (Meterlab PH M210) was used. DO was measured with an oxygen sensor (Hach SensION 156 Multiparameter Meter) equipped with a Hach DO meter electrode.

2.4 Characterization of the solids after the removal experiments

X-ray diffraction (XRD) patterns, Raman, X-ray photoelectron (XPS) and energy dispersive X-ray (EDS) spectroscopies analyses were carried out to characterize the iron nanoparticles after exposure to U(VI) and Cr(VI). XRD patterns were obtained with a PanAnalytical Empirean X-ray diffractometer with PIXcel 3D detector, using Cu-Kα radiation, over a range in 2θ of 10 to 100° with step of 0.026° and 97 seconds by step. Raman spectra were recorded on a LabRAM HR Raman system (Horiba Jobin Yvon), equipped with two monochromator gratings and a charge coupled device detector. The Ar laser line at 514.5 nm was used as excitation source. Measurements were taken in a backscattering geometry, with 100× magnification.

XPS spectra were obtained with a Phoibos 150 electron energy analyser using monochromatic Al Kα radiation (hv = 1486.71 eV). All spectra were measured with a constant pass energy of 30 eV, what yields an overall energy resolution of 0.9 eV. EDS spectra were obtained in a SEM Supra 40 with an EDS detector, Oxford Instruments, model INCA x-act, operating at a voltage of 20 kV.

3. Results and discussion

3.1 U(VI) and Cr(VI) removal with zerovalent iron nanoparticles

Table 1 shows the results of the removal of U(VI) and Cr(VI) with N25, in the four different experiments: (1) U(VI) alone, (2) U(VI) with the addition of Cr(VI) after 0.5 h of reaction, (3) U(VI) and Cr(VI) added simultaneously and (4) Cr(VI) alone, under two hours of anoxic conditions followed by 24 hours of oxic conditions.

Table 1: Percentage of U(VI) and Cr(VI) removal during the experiments

Experiment	Removal of U(VI)		Removal of Cr(VI)	
	2 h	26 h	2 h	26 h
(1) U(VI) alone	99 %	83 %	-	-
(2) U(VI) + Cr(VI) added at t = 0.5 h	100 %	98 %	59 %	61 %
(3) U(VI) + Cr(VI) added simultaneously	31 %	28 %	36 %	40 %
(4) Cr(VI) alone	-	-	27 %	28 %

In experiments (1) and (2), an almost complete removal of U(VI) was achieved after two hours of anoxic conditions. In experiment (2), the Cr(VI) aliquot was added after 0.5 h of reaction in order to assure a complete U(VI) removal before Cr(VI) addition. After the two hours of anoxic conditions, in both cases, the reactor was opened to the atmosphere to evaluate the effect of the reoxygenation of the system during a time span of 24 hours. As expected, in the experiment performed only with U(VI), a re-release of 16 % of uranium was observed. On the contrary, the addition of Cr(VI) to the system at t = 0.5 h prevented this partial U(VI) re-release. On the other hand, when Cr(VI) was added at t = 0 (experiment (3)), only 31 % of the initial U(VI) was removed but still prevented the re-release of U(VI) into the solution.

Concerning Cr(VI) removal, in the absence of U(VI) (experiment (4)), 27 % of the initial Cr(VI) was removed at the end of the anoxic experiment, whereas in the presence of U(VI), the Cr(VI) removal was increased to 36 % when the addition is simultaneous (experiment (3)) and to 59 % if Cr(VI) was added after the almost complete removal of U(VI) (experiment (2)). At the same time, the concentration of Cr(VI) present after the anoxic period remained constant during the 24 h under oxic conditions, in accordance with previous results indicating that chromium removal with nZVI is not affected by dissolved oxygen (Montesinos et al., 2014).

The [Fe(total)] in solution was strongly dependent on the presence or the absence of Cr(VI) in the system. In the case of the experiment with U(VI) alone, [Fe(total)] rapidly reached a maximum final value of 5 mg L^{-1}, similarly to that obtained in a previous work (Crespi et al., 2016). When Cr(VI) was added to the U(VI) system at the beginning of the experiment, iron was not found in solution at any time of the reaction. Consistently, the addition of Cr(VI) after 0.5 h of U(VI) reaction with N25 triggered the immediate disappearance of Fe from the solution.

3.2 Characterization of the solids

3.2.1 XRD patterns and Raman results

Figure 1(a) compares the diffractogram of the initial N25 sample with those corresponding to the solids obtained after the oxic and anoxic experiments in the presence and in the absence of Cr(VI) (added at t = 0.5 h). All the samples (before and after removal experiments) exhibit the peaks corresponding to zerovalent iron (around 44.7°) and to magnetite and/or maghemite (M,m), that cannot be differentiate by XRD. The presence of iron oxides has been reported by aqueous corrosion of nZVI in less than a day (Pullin et al., 2017). The

diffractograms of the solids obtained in the experiments with chromium addition were less intense than the ones obtained in its absence, indicating a higher number of amorphous compounds in the sample after chromium addition.

The presence of magnetite and maghemite was confirmed by Raman analysis. In all the samples (with and without chromium), characteristic peaks of $UO_2(OH)_2 \cdot H_2O$ were also found.
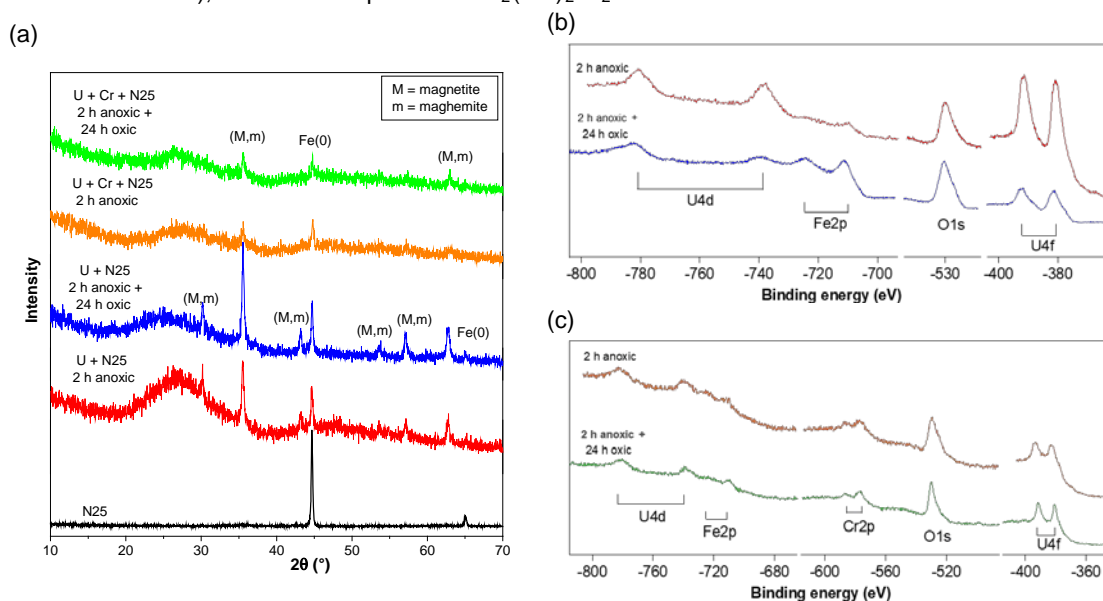

Figure 1: (a) XRD patterns, (b) XPS spectra for U(VI) alone, (c) XPS spectra for U(VI) + Cr(VI) added at t = 0.5 h.

3.2.2 XPS and EDS results

XPS spectra were obtained for the solids obtained after the removal of U(VI) alone and U(VI) + Cr(VI) added at t = 0.5 h in both cases after 2 h of anoxic conditions and after the 2 h of anoxic followed by 24 h of oxic conditions. For each spectrum, the relative height of the U, Cr and Fe peaks were compared with the height of the O1s peak, set as reference. In the absence of Cr(VI), the U4f and U4d peaks were more intense when the removal experiment was performed in the absence of oxygen, whereas the Fe2p peaks were weaker. This suggests that the presence of oxygen leads to a lower amount of U retained in the solids surface (Figure 1(b)). On the other hand, the presence of Cr(VI) the spectra obtained under oxic and anoxic conditions were similar indicating that the amounts of Cr and U retained on the solids surface might remain invariable after using oxic conditions (Figure 1(c)). EDS analysis performed in solids obtained in the absence of Cr(VI) showed a higher amount of U when the removal was done under anoxic conditions than under oxic conditions, in agreement with the redissolution found in the latter case. On the other hand, the content of U found in the solids obtained with Cr(VI) addition at 0.5 h, was similar both under anoxic and oxic conditions, in agreement with XPS results.

3.3 Proposed mechanisms

The mechanism of U(VI) removal with nZVI under anoxic conditions has been described as a sequence of adsorption/reduction and coprecipitation steps (Li et al., 2015; Quici et al., 2017 and reference therein). The main equations involved were included in table 2. After U(VI) adsorption on the nZVI surface, electron transfer from Fe(0) or surface bound Fe(II) to U(VI) takes place (Eq(1) and (2)), being the formed U(IV) immobilized on the nanoparticle surface as UO_2. Another possible mechanism under anoxic conditions includes the adsorption of UO_2^{2+} on the oxide layer of the nanoparticles through proton exchange (Eq(3)) (Li et al., 2015). The adsorbed uranyl ion would be later reduced by reaction with Fe(0) (Eq(1)). Hydrolysis of U(VI) with $UO_2(OH)_2$ precipitation on the surface can also occur (Eq(4)) at pH values between 5 and 9 (Grenthe et al., 1992).

After reoxygenation of the system, oxidation of UO_2 to UO_2^{2+} is thermodynamically favored leading to the re-release of U(VI) into the solution, putting at risk the intended long-term isolation of uranium over the nZVI material (Eq(5)).

Table 2: Reactions involved in the mechanism for U(VI) removal by nZVI

Condition	Equation	Description	Reaction
	(1)	Reduction of U(VI) by Fe^0	$\equiv UO_2^{2+} + Fe^0 (s) \rightarrow UO_2 (s) + Fe^{2+}$
Anoxic	(2)	Reduction of U(VI) by Fe^{2+}	$\equiv UO_2^{2+} + 2 \equiv Fe^{2+} \rightarrow UO_2 (s) + 2 Fe^{3+}$
environment	(3)	Adsorption of UO_2^{2+}	$2 \equiv Fe{-}OH + UO_2^{2+} \rightarrow [(\equiv Fe{-}O)_2 UO_2] + 2 H^+$
	(4)	$UO_2(OH)_2$ precipitation	$UO_2^{2+} + 2 OH{-} \rightarrow UO_2(OH)_2 (s)$
Oxic environment	(5)	Oxidation of UO_2 to UO_2^{2+}	$UO_2 + \frac{1}{2} O_2 + 2 H^+ \rightarrow UO_2^{2+} + H_2O$
	(6)	Cr(VI) reduction	$HCrO_4^- + Fe^0 (s) + 7 H^+ \rightarrow Cr^{3+} + Fe^{3+} + 4 H_2O$
	(7)		$HCrO_4^- + 3 Fe^{2+} (dissolved) + 7 H^+ \rightarrow Cr^{3+} + 3 Fe^{3+} + 4 H_2O$
Oxic or	(8)		$Cr^{3+} + 3 H_2O \rightarrow Cr(OH)_3 (s) \downarrow + 3 H^+$
anoxic	(9)	Surface passivation	$x Cr^{3+} + (1{-} x) Fe^{3+} + 3 H_2O \rightarrow (Cr_xFe_{1-x})(OH)_3 (s) \downarrow + 3 H^+$
	(10)		$x Cr^{3+} + (1{-} x) Fe^{3+} + 2 H_2O \rightarrow Cr_xFe_{1-x}OOH (s) \downarrow + 3 H^+$

After addition of chromium to the system, the Cr(VI) removal by zerovalent iron reactions occur via a heterogeneous reduction by Fe(0) or Fe(II) (structural or dissolved), the overall reaction can be represented by Eq(6) (Montesinos et al., 2014). The produced Cr(III) can then precipitate as amorphous $Cr(OH)_3$, $(Cr_xFe_{1-x})(OH)_3$ and $Cr_xFe_{1-x}OOH$ (Eqs(8)-(10)), which has been associated with the passivation of the surface of nZVI (Montesinos et al., 2014, Zou et al., 2016). The improvement of Cr(VI) removal when it is added to the U(VI)/nZVI system after 0.5 h can be explained by reaction of Cr(VI) with Fe(II) (Eq(7)), already in solution generated by Eqs(1), which is not present in solution in the case of the reaction of Cr(VI) alone. This reduction is followed by the passivation of the nanoparticles (Eqs(9)-(10)), in agreement with the absence of Fe in solution.

Thus, the effect of the addition of Cr(VI) to the U(VI)-nZVI system should be carefully analyzed taking into account whether Cr(VI) is added either simultaneously or sequentially to the uranium system. In the first case, there will be a competition between Cr(VI) and U(VI) to react with the nanoparticles, and Cr(VI) would quickly passivate the surface, hindering U(VI) reduction. However, if Cr(VI) is added after the complete removal of U(VI), it will produce the passivation of the surface, preventing the access of oxygen and the subsequent reoxidation of U(IV) to U(VI) (together with the re-release of uranium to the solution). Therefore, the sequential addition is crucial to obtain complete U removal and avoid reoxidation.

Last, ways to get complete Cr(VI) removal at the end of the treatment should be searched to avoid leaving an additional contaminant in the system. As Cr(VI) has a high toxicity, solubility and mobility, the maximum recommended concentration of Cr(VI) in drinking water is 0.05 mg L^{-1} (WHO, 2012). In this work, a much higher Cr(VI) concentration remains in water after the treatment. However, the concentration of iron nanoparticles tested here was extremely low (1 mM = 0,056 g L^{-1}). Iron concentrations up to 0.5 (Crane and Scott, 2014), 1 (Klimkova et al., 2011) and 2 g L^{-1} (Yuan and Chen, 2103) was reported in literature in both laboratory and field applications of nZVI for uranium remediation. With a higher excess of iron, a complete removal of U(VI) and Cr(VI) is expected.

4. Conclusions

The addition of Cr(VI) to the U(VI)-nZVI system after reaching the total removal of U(VI) has been proven to be an efficient solution to avoid the reoxidation of U(IV) to U(VI) and its subsequent redissolution. A higher concentration of iron in solution, as a consequence of the previous reaction between Fe(0) and U(VI), leads also to an improvement of the Cr(VI) removal, compared with the reaction of Cr(VI) with nZVI in the absence of U(VI). In contrast, the simultaneous addition of U(VI) and Cr(VI) in the system showed poor removal percentages for both species, indicating that the sequential addition is crucial to obtain complete U removal. It is important to note that, after the simultaneous addition of U(VI) and Cr(VI), the re-release of U(VI) is also prevented. In the case of Cr(VI), the same removal degree was found under oxic and anoxic conditions.

XPS and EDS analysis of the solids obtained after the removal showed a larger incorporation of U when Cr was present in the experiments, in agreement with the hypothesis that Cr(VI) addition improves the U retention in the nanoparticles. Also, XRD analysis showed the presence of Fe(0), maghemite and/or magnetite after the removal. These oxides could also be detected by Raman analysis, together with $UO_2(OH)_2 \cdot H_2O$ observed in the anoxic experiments.

The strategy presented in this paper can be useful for improving uranium removal from water avoiding the detrimental redissolution of uranium in oxidizing environments. Nevertheless, the design should contemplate that a complete Cr(VI) removal must be achieved to not add an additional contaminant to the system.

Acknowledgments

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