Metal (Hydr)oxides for the removal of Cr(VI) from drinking water: a XAFS study

F Pinakidou*, E Kaprara*, M Katsikini, E C Paloura, K Simeonidis, M Mitrakas*

*Aristotle University of Thessaloniki, School of Chemical Engineering, Analytical Chemistry Laboratory, 54124, Thessaloniki, Greece
Aristotle University of Thessaloniki, School of Physics, Department of Solid State Physics, 54124, Thessaloniki, Greece,
E-mail: fpina@physics.auth.gr

Abstract. The reduction mechanism and adsorption behaviour of Cr(VI) onto Sn(II) oxy-hydroxides are investigated using Cr-K edge X-ray absorption fine structure (XAFS) spectroscopies. The synthesis of the Sn oxy-hydroxide proceeds via hydrolysis of SnSO4. The successful reduction of Cr(VI) was identified by the analysis of the Cr-K edge XANES spectra where only Cr(III) species in octahedral sites are detected. According to the Cr-K edge EXAFS analysis results, Cr(III) forms bidentate inner sphere (binuclear (2C) and mononuclear (2E)) complexes. However, the surface coverage of Cr affects the type of Cr(III)-complexes formed: as the Cr-loading increases, Cr(III)-oxy-anions preferentially sorb in a “combined” 2C and 1V configuration, at the expense of the existing 2E sorption geometry.

1. Introduction
Chromium is a naturally occurring element, commonly present in the environment, as trivalent Cr(III) and hexavalent Cr(VI). Cr(VI) is a well-established carcinogen and can enter groundwater from both anthropogenic activities and natural sources, e.g. by underground water contact with ultramafic rocks [1]. Considering the severe health effects of Cr(VI) and its natural occurrence in groundwater, it becomes crucial to develop technologies that can both efficiently remove Cr(VI) from water to concentrations of low μg/L and efficiently scale-up to large-scale treatment. Among the several methods developed to remove Cr(VI) from water, the use of materials that can combine reductive and adsorptive capacity became a very promising solution. For example, solid materials such as Cu-Zn alloys [2], Fe3O4 nanoparticles [3], zero-valent Fe [4] have been extensively used in water treatment technology, because they act as electron donors that reduce the highly mobile Cr(VI) to Cr(III) which exhibits significantly low water solubility. Recently, the feasibility of using Sn(IV)-compounds for heavy metal-removal from wastewater has been under investigation, mainly due to their low cost and safe disposal. [5,6] However, the effectiveness of Sn(II)-compounds for reduction/adsorption of Cr(VI) from drinking water has not been evaluated yet.

The understanding of chromium adsorption under realistic water treatment can promote the design of optimum adsorbents in respect of their efficiency and environmental impact after their disposal. Therefore, this study attempts to explain the reduction and adsorption behavior of Cr(VI) onto Sn(II) oxy-hydroxides by means of Extended (EXAFS) and Near Edge (XANES) X-ray Absorption Structure
spectroscopies, since these techniques are sensitive to the bonding environment of Cr, yielding direct information on the oxidation state, distances and number of atoms bonded to Cr-oxy-anions.

2. Experimental details
A Sn(II) oxy-hydroxide (Sn$_6$O$_4$(OH)$_4$) was prepared by the hydrolysis of SnSO$_4$ at neutral pH. The collected solid suspension was washed, centrifuged, dried at 100 °C, ground and sieved to obtain either a fine powder form (<45 μm) used for batch adsorption experiments or granules (0.25-0.50 mm) for column tests. For batch adsorption experiments, 250 mg of fine powder were dispersed in 1L of 5 mg/L Cr(VI) solution in NSF water matrix and stirred at 20 °C for 24 h. Adsorption tests were performed at pH-values 5, 7 and 7.5 and at the end of the experiments the suspensions were filtered through a 0.45 μm pore-size membrane. Rapid small scale column tests (RSSCTs) were designed for an empty bed contact time (EBCT) 2 min and a particle size 0.25-0.50 mm, using glass columns of 1.1 cm diameter with PTFE valves and caps and a glass frit in the bottom, which was fed from the top with 100 μg/L Cr(VI) in NSF water matrix at pH=7. Initial and residual Cr(VI) concentration was determined by the diphenyl-carbazide method. Details on the Cr(VI) adsorption experiments are listed in table 1.

XAFS measurements were conducted at the BAM beamline at the synchrotron radiation facility BESSY-II in Berlin.[7] Both EXAFS and XANES spectra were recorded in the fluorescence yield mode using an energy dispersive (Bruker X-Flash) detector. The Cr-K edge XANES data were normalized with the intensity of the impinging beam ($I_0$) recorded with an ionization chamber positioned in front of the sample and were subjected to linear background subtraction and normalization to the edge jump. In the EXAFS spectra, after subtraction of the atomic absorption, the theoretical phase and amplitude functions for the scattering paths were calculated by FEFF8.2 [8] and curve fitting was carried out using FEFFIT.[9] The spectra of Cr(OH)$_3$ and K$_2$CrO$_4$ powder samples were used as references and were recorded in the transmission mode.

| Table 1. Cr-adsorption configuration, sorption pH and Cr content |
|---------------------------------------------------------------|
| Configuration | Sorption pH | Cr (wt%) |
|----------------|-------------|----------|
| Batch          | 5           | 0.42     |
| Batch          | 5           | 1.24     |
| Batch          | 7.5         | 1.17     |
| Column         | 7           | 0.77     |

3. Results and Discussion

3.1. Cr-K edge XANES
The effective reduction of Cr(VI) to Cr(III), using Sn$_6$O$_4$(OH)$_4$ at batch and dynamic conditions and after exposure to different Cr-loading was investigated using Cr-K edge XANES spectroscopy. As in all 3d-transition metals, a pre-edge absorption exists in the Cr-K edge XANES spectra, the characteristics of which are modulated by the Cr-valence: a prominent pre-edge peak is present in Cr(VI) compounds, which is related to 1s transitions to empty 3d states. This transition is dipole forbidden in octahedral Cr(III); nevertheless, a weak pre-edge peak is detected, due to the loss in centrosymmetry in Cr(III)O$_6$ compounds, which is attributed to 1s transitions to 3d(t$_{2g}$) and 3d(e$_g$) electronic states, respectively [10]. The characteristics (energy position and area) of the pre-edge peak were determined using Voigt functions (blue lines at the inset of Figure 1(a)) and the position of the absorption edge (E$_{ab}$) was determined using a sigmoidal function which simulates transitions to the continuum (red line at the inset of figure 1(a)). In the XANES spectra of all studied samples, shown in Figure 1(a), a weak pre-edge absorption is detected and its characteristics (intensity and energy position) are identical to the respective in reference Cr(OH)$_3$: the two Voigt functions used are located at 5989.5-5989.8 and 5991.9-5992.1 (±0.25) eV respectively, as in Cr(OH)$_3$ (5989.8 and 5992.1
where Cr(III) forms CrO₆ octahedra. This finding verifies the presence of Cr(III) in octahedral sites while Cr(VI) is not detected. Thus the reduction of Cr(VI) to Cr(III) at the tin oxy-hydroxide surface takes place successfully and independently of Cr-loading. The presence of Cr(III) species is further supported by the position of the E_{abs}; in all studied samples, it is located at 6001.1-6001.5 eV (±0.25), i.e. as in the case of reference Cr(OH)₃ (6001.3 eV).

3.2. Cr-K edge EXAFS

In an effort to determine whether Cr(III) is adsorbed onto the tin oxy-hydroxide surface or precipitates as Cr(OH)₃, Cr-K edge EXAFS spectroscopy was applied and the Fourier Transforms (FT) of the k²χ(k) EXAFS spectra are shown in figure 1(b). The unsuccessful fitting attempts to simulate the EXAFS spectra assuming the formation of Cr(III)-precipitates suggests that Cr(III) must form inner sphere surface complexes. Thus, the EXAFS spectra were fitted assuming that Cr forms mononuclear and binuclear inner sphere complexes. More specifically, the fitting proceeds assuming bidentate mononuclear (2E) and binuclear (2C) contributions of the Cr(III) oxy-anions. In the 1st nearest neighbor (nn) shell, the coordination number (CN) was kept fixed to six while the Debye-Waller (σ²) factor was iterated. In the next, Sn-comprised, nn shells, the σ² factors were constrained to be equal, although allowed to vary during the fitting. Finally, a Cr-Sn-O multiple-scattering (MS) path, accounting for scattering at four adjacent Sn atoms around the CrO₆ octahedron in the 2C geometry, was used. The fitting analysis results are listed in table 2.

![Figure 1](attachment:figure1.png)

**Figure 1.** (a) Cr-K edge XANES spectra and (b) Fourier Transforms (FT) of the k²-weighted χ(k) Cr-K edge EXAFS spectra, of the studied SnO₆(OH)₄ and reference Cr(OH)₃ and K₂CrO₄. The experimental data and the fitting are shown in black and colored lines, respectively. The pre-edge absorption region and the functions used for the simulation of the XANES spectra are shown in the inset of figure 1(a).

![Figure 2](attachment:figure2.png)

**Figure 2.** The ratio of bidentate ²E vs ²C complexes as a function of the weight percentage of Cr uptake.

The EXAFS analysis reveal that the Cr-O bond-length is equal to 1.94-1.97Å (±0.01), i.e. characteristic of the presence of Cr(III)O₆ species [11]. The Cr-Sn-O length in the MS path is found equal to 3.72-3.75 Å (± 0.05 Å) in all studied samples. Furthermore, as listed in table 2, even though the total number of Cr(III) that participate in the ²E and ²C configurations does not change, we detect a difference in the type of sorption geometry as a function of the Cr content. More specifically, the total
number of inner sphere complexes (sum of $^2E$ and $^2C$) is approximately equal to 3.0 – 4.7 ($\pm 0.8-1.3$). However, as shown in Figure 2, the number of the Cr(III) complexes in the $^2E$ geometry versus the number in the $^2C$ configuration ($^2E^2C$ ratio) decreases as the Cr-loading increases. Thus, it can be stated that the Cr-sorption mechanism changes as a result of increasing surface coverage: as the Cr-uptake increases more Cr(III)-oxy-anions prefer to link via corners with the Sn-octahedra of SnO$_2$. As Cr(VI) approaches Sn$_6$O$_4$(OH)$_4$, the latter oxidizes to SnO$_2$ through the hexavalent chromium reduction to Cr(III).

Table 2. Cr-K edge EXAFS results of the studied samples.

| Cr (wt%) | $R_{Cr-O}$ (Å) ($\pm 0.01$) | $\sigma^2$ ($\times 10^{-3}$Å$^2$) (±0.01) | $R_{Cr-Sn}$ (Å) ($\pm 0.02$) | $\sigma^2$ ($\times 10^{-3}$Å$^2$) (±0.03) | $R_{Cr-Sn}$ (Å) (±0.03) | $\sigma^2$ ($\times 10^{-3}$Å$^2$) (±0.03) |
|----------|---------------------------|--------------------------------------|-----------------------------|--------------------------------------|-----------------------------|--------------------------------------|
| 0.42     | 6* 1.96                   | 2.2                                  | 1.5                         | 3.06                                 | 1.6                         | 3.60                                 | 3.4*                                  |
| 0.77     | 6* 1.94                   | 2.3                                  | 1.5                         | 3.03                                 | 3.2                         | 3.55                                 | 2.9*                                  |
| 1.17     | 6* 1.97                   | 2.9                                  | 1.1                         | 3.10                                 | 3.6                         | 3.53                                 | 3.2*                                  |
| 1.24     | 6* 1.97                   | 2.0                                  | 1.0                         | 3.10                                 | 3.4                         | 3.54                                 | 3.6*                                  |

$R$ is the nearest neighbour distance and $\sigma^2$ is the Debye-Waller factor

* Values kept fixed during the fitting

4. Conclusions

The feasibility of implementing Sn$_6$O$_4$(OH)$_4$ for the reduction and adsorption of Cr(VI) in water treatment was investigated using XAFS spectroscopies at the Cr-K-edge. The analysis of the Cr-K edge XANES and EXAFS spectra confirmed the effective use of Sn$_6$O$_4$(OH)$_4$ for Cr(VI) removal from drinking water through its oxidation to SnO$_2$. Indeed, only Cr(III) species that form CrO$_6$ octahedra are detected. No Cr(OH)$_3$ precipitates are formed, on the contrary Cr(III)-oxy-anions sorb onto the SnO$_2$ surface. However, changes in the type of inner sphere complexes formed is observed due to increased surface coverage: Cr(III)-oxy-anions preferentially sorb in the $^2C$ geometry at the expense of the present $^2E$ inner sphere complexes.

Acknowledgments

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