Physics and chemical properties of the volcanic ash material adsorbed with the hexavalent chromium by x-ray absorption spectroscopy

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Abstract

X-ray absorption spectroscopy (XAS) was used to characterize the volcanic ash (VA) materials as a low-cost and natural environmental adsorbent for the sorption of Cr(VI). The batch adsorption method was employed to synthesize the sample of chromium(VI) sorbed by VA. The results showed that the Cr-VA material is in the chromium oxidation state(III) and can be described as a composition of Cr2O3 (47.9%), FeCr2O7 (45.2%), and Na2Cr2O7 (6.9%). The promotion of the 1s Cr core electron implies the electronic transitions 1s→3d(t2g) and 1s→3d(eg). The first and second shells in the Cr-VA material were coordinated to the oxygen and chromium atoms in a distorted geometrical arrangement. The adsorption mechanism was associated with the chemical reduction of Cr(VI) to Cr(III) via an ion-exchange process. The XAS technique significantly contributes to the characterization of environmental VA, which can be proposed as an economical and alternative adsorbent for the sorption of Cr from contaminated wastewater.

1. Introduction

Heavy metal contamination has become one of the greatest concerns because metals can be released into the atmosphere, plants, soils, and water, implicating various environmental issues. Many of these metals, considered a major source of pollution, are inevitably released through waste products from industries such as mining, smelting, fishing, agriculture, leather tanning, alloys, metal refining, and electroplating (Parsons et al. 2002; Ming-Jan et al. 2004; Benaisa et al. 2016). The increase in these toxic elements is a considerable public risk to humans, animals, and plants because their inhalation and ingestion can be harmful. Dangerous diseases such as nasal septum, pneumonia, kidney damage, anemia, asthma, chronic bronchitis, and lung, tracheal, and nasal sinus cancers, are in most cases, the consequence of heavy metal contamination (Ming-Jan et al. 2004; Yang et al. 2015).

Chromium (Cr), among others is extensively used in the aforementioned industries. Cr can exist in different oxidation states. However, chromium is commonly found in the environment in the form of Cr(0), Cr(III) and Cr(VI). Trivalent Cr(III) is essential in humans because it plays an important role in glucose metabolism (Chiba et al. 1992; Peterson et al. 1997; Cuello et al. 2016). Its maximum recommended intake for humans is approximately 0.05 mg/L (Chiba et al. 1992). In contrast, hexavalent Cr(VI) is more toxic and can cause damage to organisms (Peterson et al. 1997). It is classified as carcinogenic to humans (Ming-Jan et al. 2004; Cuello et al. 2016). Thus, it is of great interest to investigate various methodologies and techniques for chromium environmental remediation, and especially water purification. The efficient remediation of different chromium-contaminated sites, such as waste industrial products, soils, plants, and water requires, knowledge of the chromium oxidation state, chromium sorption and precipitation modes. The development of novel technologies for chromium removal from aqueous solutions to preserve water quality has drawn particular attention from scientific community. Among other technologies, reduction onto metal oxy-hydroxides (Kaprara et al. 2016, Pinakidou et al. 2016, Kaprara et al. 2018), ion exchange (Dąbrowski et al. 2004), and chemical reduction (Mitrakas et al. 2011). In addition, it also exists the adsorption technology, which uses various adsorbent materials.
including biosorbants, and activated carbons (Mohan and Pittman 2006; Mohan et al. 2006), biomas (Parsons et al. 2002), plants (Aldrich et al. 2003; Howe et al. 2003), waste compost (Wei et al. 2005; Ghazy et al. 2010), rice husk (Ming-Jan et al. 2004; Bansal et al. 2008), activated fly ash and sawdust (Gupta and Babu 2008) and geopolymers (Al-Zboon et al. 2019). The volcanic ash (VA) material has also been proposed as low-cost adsorbents for removing iron (Thiodjio et al. 2021), lead and zinc (Esmaili et al. 2003; Bang et al. 2022a), chromium (Babel and Opiso 2007). In general, the lands around volcanoes are frequently subjected to the intermittent flow of lava and deposition of volcanic ash (VA) during the eruption of the volcano. Per month, small-scale explosive volcanic eruptions can emit more than a million cubic meters of ash into Earth's atmosphere (Simkin and Siebert 2000). These ashes can reach 600 km from the eruption point, depending on the wind speed and the height/eruption volume of volcano (Cai et al. 2016). Therefore, the VA can be affordable in any country that has a volcano.

The choice of adsorbent for the removal of pollutants is crucial because it may not have the same uptake to remove the same element. Another main challenge in overcoming the remediation issue through the adsorption process is to properly characterize the adsorbent materials. Therefore, various characterization techniques have been employed, such as scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS), inductively coupled plasma optical emission spectroscopy (ICP-OES), Fourier transform infrared (FTIR), x-ray diffraction (XRD), thermogravimetry (Cai et al. 2016; Lemougna et al. 2011; Jaafarzadeh et al. 2012; Botto et al. 2013; Medellin et al. 2014, 2016; Mem et al. 2016). These techniques can provide information related to elemental chemical speciation, morphology, functional groups, phase identification, crystallographic structure, and thermal stability, which are necessary for understanding the chemical, structural, and morphological properties of adsorbents. However, non-destructive X-ray absorption spectroscopy (XAS) is barely used, which is suitable for probing the local environment around the sorbed element in the adsorbents.

XAS comprises two complementary techniques: X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS). XANES is used to retrieve information on the oxidation state of the investigated central element and chemical speciation in the unknown material (Thiodjio et al. 2021; Koningsberger 1998). EXAFS probes the local structure, providing information about the coordination number, type of neighboring atoms, and bond length between the central element and its neighboring atoms (Koningsberger 1998). XAS has been widely used to investigate various compounds (Wu et al. 2017; Mastelaro and Zanotto 2018; Jianhong et al. 2019). However, to the best of our knowledge, few studies on XAS technique have been conducted on different environmental adsorbents employed for the sorption of chromium (Parsons et al. 2002; Ming-Jan et al. 2004; Peterson et al. 1997; Kaprara et al. 2018; Aldrich et al. 2003; Wei et al. 2005).

In-depth studies characterizing such environmental adsorbents using XAS are lacking. The main problem in the investigation of the local electronic and structural environment of the metal sorbed element in VA by XAS is that these materials are a mixture of various pollutants and compounds (Thiodjio et al. 2021; Bang et al. 2022a,b). The present study registers in the same line as the previous (Thiodjio et al. 2021; Bang et al. 2022a,b), which focused on the investigation of the VA from Cameroon volcanic line (CVL)
probing for the removal of some pollutants. The XAS technique was utilized to study the chemical composition and electronic properties of VA used to sorb iron and lead metals (Thiodjio et al. 2021; Bang et al. 2022a,b). The results showed that the main components present in the Fe-sorbed VA were iron(II) oxide-FeO, hematite Fe$_2$O$_3$, iron(II) sulfate FeSO$_4$, and magnetite Fe$_3$O$_4$. Whereas those in the Pb-sorbed VA were Pb-goethite Pb-α-FeOOH, lead monoxide PbO, Pb acetate Pb(C$_2$H$_3$O$_2$)$_2$, and Pb cerussite PbCO$_3$.

Our main objective is to document a prominent XAS analysis technique addressing on the one hand, the oxidation state and chemical composition of Cr(VI) sorbed onto VA, on the other hand, the electronic properties and local structure around the Cr(VI) in the VA adsorbent. The insights gained from this study will contribute to water purification application by expanding the characterization methods for the environmental adsorbents.

2. Experimental Details

2.1. Raw materials

Raw VA samples were collected in the Mounogo zone inside the CVL. This site is located in Djourou, approximately 6 km from the main road joining Littoral to West Cameroon. The collected samples consisted of large scoop particles in gray color, sampled at 04°35’09” North, 09°37’37” East and 134 ± 3 m altitude. Samples were taken at the center of the CIMENCAM quarry at depth of approximately 30 cm. All collected samples were air-dried for 24 h and sieved.

2.2. Sample preparation by batch adsorption

An initial volume $V_0$ of 60 mL with an initial concentration $C_0$ of 100 mg/L of Cr(VI) was prepared from Na$_2$Cr$_2$O$_7$, reagent grade and deionized water. The solution was then placed in a centrifuge vial and adjusted to a pH of 3. VA (0.2 g) was mixed with 40 ml of the prepared Cr(VI) solution in a conical vial and immersed in a bath at 25°C. The pH was periodically adjusted until equilibrium was reached after three days. The Cr(VI)-sorbed VA sample retrieved from the mixed solution was labeled Cr-SVA (Cr sorbed by VA) and dried in an oven at a moderate temperature (50°C) for two hours for XAS measurements. Details concerning the batch adsorption experiments on VA samples can be found in Refs. (Thiodjio et al. 2021; Bang et al. 2022a,b).

2.3. XAS data measurements

XAS measurements were performed at the Cr K-edge on the pellets prepared from Cr-SVA samples and the predicted standards. These pellets were obtained by mixing 100 mg of the sample with 50 mg of polyvinylpyrrolidone. XAS data of Cr-SVA were collected at the XAFS beamline (ELETTRA, Trieste) (Di Cicco et al. 2009) in fluorescence mode because of the low concentration of chromium in the sample whereas those of standards were performed in transmission mode. Spectra of ten model compounds FeCrO$_7$, Cr$_2$S$_3$, Cr(NO$_3$)$_3$, K$_2$CrO$_4$, K$_2$Cr$_2$O$_7$, Cr(OH)$_3$, CrCl$_3$, Na$_2$Cr$_2$O$_7$, Cr$_2$O$_3$, and CrO$_3$ were also collected. All model compounds were also of reagent grade.
The storage ring was operated at 2 GeV yielding a current of 310 mA. A double crystal silicon Si (111) monochromator was used with a detuning of 0.5. The first inflection point of the Cr K-edge XANES spectrum was assigned as 5989 eV for the monochromator calibration. Ion chambers $I_0$, $I_1$, and $I_2$ were filled with a mixture of Ar, N$_2$, and He at 6000 eV and, an absorption of 10% $I_0$, 70% $I_1$, and 95% $I_2$, respectively. The X-ray absorption data were collected in the energy range of [5695–7073] eV and a wave vector range of [0–14] Å$^{-1}$. Six scans for Cr-SVA and two scans for the standards were collected at room temperature using Cr foil as a reference.

2.4. XAS data analysis

The spectra of the absorption coefficient ($\mu$) collected for each sample were averaged to improve the statistical noise and then normalised to one absorption event using the ATHENA program (Ravel and Newville 2005). The normalisation process consisted of subtracting the pre-edge, post-edge and background signals from the experimental absorption coefficient $\mu$. Three methods of XAS data analysis were employed in this study: the linear combination fitting (LCF) of the XANES signal consisting of reconstructing the experimental spectrum of the unknown material Cr-SVA using the selected model spectra for the chemical speciation; the peak fitting method to find a deconvolution of the existing components in the XANES pre-edge features (pre-peaks); and the EXAFS modelling to reproduce the FT experimental spectra from the theoretical backscattering amplitudes and phase shift parameters to describe the local structure around the central (core) atom.

2.4.1. Linear combination fitting (LCF)

LCF was performed in ATHENA (Ravel and Newville 2005) in an energy range of −20 eV below to +35 eV above the edge using at least four model compounds. The ten model compounds FeCrO$_7$, Cr$_2$S$_3$, Cr(NO$_3$)$_3$, K$_2$CrO$_4$, K$_2$Cr$_2$O$_7$, Cr(OH)$_3$, CrCl$_3$, Na$_2$Cr$_2$O$_7$, Cr$_2$O$_3$, and CrO$_3$ were used as standards for fitting. Subsequently, they were compared and combined to obtain a suitable combination. The XANES spectra of Cr(0) foil, Cr$_2$O$_3$(III), and CrO$_3$(VI) in different oxidation states (values in parentheses) were compared to the Cr-SVA spectrum to determine the oxidation state and guess suitable standards. This method is accurate if the chosen standards are sufficient for the investigated samples (Ravel and Newville 2005). The choice of the suitable components is guided by $R_{\text{factor}}$ parameter, which indicates the most likely combination that results in the best fit (Thiodjio et al. 2021).

2.4.2. Peak fitting method

The peak fitting method is a powerful tool to find a deconvolution of the main pre-edge peaks. Pseudo-Voigt line shapes including the Gaussian function were utilised to model the pre-edge peaks. The energy position, full width at half-maximum (FWHM) and peak height were varied during fitting. Energy ranges of 5976–5984 eV, 5986–5996 eV, 5988–5992 eV, 5982–5994 eV were used for Cr-SVA, Cr$_2$O$_3$, FeCr$_2$O$_7$, and Na$_2$Cr$_2$O$_7$, respectively.

2.4.3. EXAFS modelling
The EXAFS oscillations were extracted using the formula 
\[ E = \frac{\mu - \mu_0}{\mu_0} \] where \( \mu_0 \) is a smooth spline representing the embedded-atom absorption background. The \( k \) range of 3–11 Å\(^{-1}\) and a sine window were used for the Fourier transform (FT) functions. For the EXAFS modelling, least-square fitting based on multiple scattering approximation was employed. The EXAFS theoretical signals for all the samples were generated using the FEFF6 code from the backscattering amplitudes and phase shift parameters (Ravel and Newville 2005). Knowledge of the space group and crystal structure of the compound to be modelled is required to generate EXAFS theoretical signals. Table 1 shows the space group and crystal system of the predicted model compounds used in this study. Artemis program (Ravel and Newville 2005) was used to fit the EXAFS spectra under the conditions listed in Table 1. The \( R_{\text{factor}} \) parameter which evaluates the difference between the experimental and modelled functions, describes the reliability of the best fit.

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Space group</th>
<th>Crystal system</th>
<th>K range (Å(^{-1}))</th>
<th>R range (Å)</th>
<th>dk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(_2)S(_3)</td>
<td>R-3</td>
<td>Trigonal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(NO(_3))(_3)</td>
<td>P 1</td>
<td>Triclinic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(_2)CrO(_4)</td>
<td>Pnma</td>
<td>Orthorhombic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(_2)Cr(_2)O(_7)</td>
<td>P 1</td>
<td>Triclinic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(OH)(_3)</td>
<td>P 1</td>
<td>Triclinic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrO(_3)</td>
<td>C2cm</td>
<td>Orthorhombic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrCl(_3)</td>
<td>C2/m</td>
<td>Monoclinic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-SVA</td>
<td>UN</td>
<td>UN</td>
<td>3–11</td>
<td>1.25–3.0</td>
<td>0</td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>R-3c</td>
<td>Trigonal</td>
<td>3–10</td>
<td>1.00–2.2</td>
<td>1</td>
</tr>
<tr>
<td>FeCr(_2)O(_4)</td>
<td>Fd-3m</td>
<td>Cubic</td>
<td>3–12</td>
<td>1.00–2.0</td>
<td>1</td>
</tr>
<tr>
<td>Na(_2)Cr(_2)O(_7)</td>
<td>P 1</td>
<td>Triclinic</td>
<td>3–10</td>
<td>1.00–2.0</td>
<td>0</td>
</tr>
</tbody>
</table>

3. Results And Discussion
3.1. Oxidation state

In Fig. 1, we present the normalized XANES absorption spectrum at the Cr K edge of the Cr-SVA sample compared with those of the standards at different Cr oxidation state (0), (III) and (VI). The energy shift (E₀) of each spectrum is indicated by arrows. The insert highlights the pre-edge features. The Cr-SVA spectrum showed a clear XANES signal, confirming the presence of chromium in the sample. It was shown that the energy position could be correlated with the oxidation state with respect to the position of E₀ (Wong et al. 1984; Huggins et al. 1999). Different spectral features can be seen for each compound starting from Cr-SVA where the vertical lines show two pre-peaks at 5990 eV and 5993.7 eV with low intensities compared to those of chromium metal in the oxidation state (0) and chromium trioxide (CrO₃) in the oxidation state (VI), in contrast to that of chromium(III) oxide (Cr₂O₃) in the oxidation state (III). The edge energy and pre-peaks of Cr-SVA sample are similar to those of chromium(III) oxide (Cr₂O₃) with the oxidation state (III), therefore, one can consider that Cr-SVA is in an oxidation state (III). In addition, the XANES spectra of chromium samples with the oxidation state (VI) generally exhibit high intensities in their pre-peaks, while those of chromium (III) have pre-peaks with low intensities (Parsons et al. 2002; Peterson et al. 1997; Cuello et al. 2016; Wei et al. 2005; Huggins et al. 1999). The pre-peaks in Cr-SVA indicate that the most likely Cr species present in our sample is Cr(III) and the lack of pre-peak associated with Cr(VI) might suggest the absence or presence of a very small amount of Cr(VI). Knowing that the samples were prepared from reactive Cr(VI), these observations suggest that Cr(VI) was reduced to Cr(III) species which agrees with the results of Parsons et al. (2002), Cuello et al. (2016), Aldrich et al. (2003), Wei et al. (2005) and Zayed et al. (1998) reported from different samples such as: waste compost, biomass, tobacco, smoke cigarettes, and plants.

3.2. Chemical speciation

We used the LCF method for the chemical speciation of unknown Cr-SVA material. Ten standards were chosen to proceed with the LCF analysis (see sections 2.2. and 2.3.). The choice of these standards was motivated by the elements described below.

FeCrO₇, Cr₂S₃, Cr(NO₃)₃, K₂CrO₄, K₂Cr₂O₇, Cr(OH)₃ and CrCl₃, were used because the volcanic ash samples were initially rich in iron (23.33 mg/kg) and sulfur (127 mg/kg) (Bang et al. 2022b). They also contained a non-negligible amount of potassium (5.36 mg/kg) (Bang et al. 2022b). Na₂Cr₂O₇ is among the standards because it is chemically reactive for adsorption experiments, and it exists approximately 8.19 mg/kg of Na in the VA samples as shown ICP-OES results (Bang et al. 2022b). In solution, it can be reduced by the oxidation-reduction (redox) reaction, in which Cr(VI) is transformed into Cr(III) with a Cr(OH)₃ precipitate. Thus, we decided to use Cr(OH)₃ as the standard. In addition, Cr(VI) is chemically reduced by organic substances (Wei et al. 2005). Moreover, it has been reported that metal elements can be bound to organic substances through carboxylic groups (Wei et al. 2005). Therefore, it is understandable that there is a high probability of Cr ions being bound to these elements. The infrared spectrum of the unsorbed VA sample was described in our previous studies, which showed the presence of peaks suggesting the deformation of metal-OH functional groups (P-OH, Si-OH, or Al-OH) (Bang et al. 2022b).
Therefore, it is possible that these groups can interact and form chromium oxide phases such as \(\text{Cr}_2\text{O}_3\), \(\text{CrO}_3\) during the adsorption process. More to that, \(\text{Cr}_2\text{O}_3\) occurs naturally as a rare chromium oxide mineral, eskolaite, and can be found in the VA products of volcanic eruptions (Eskolaite 2022). It can be produced at high temperatures by the reduction of \(\text{Na}_2\text{Cr}_2\text{O}_7\) with sulfur (Anger et al. 2005). In addition, \(\text{CrO}_3\) was obtained by mixing \(\text{Na}_2\text{Cr}_2\text{O}_7\) with sulfuric acid (e.g., \(\text{H}_2\text{SO}_4\)) (AroKor 2022). Sulfur is present in the VA sample at an important concentration (127 mg/kg) (Bang et al. 2022). Thus, \(\text{Cr}_2\text{O}_3\) and \(\text{CrO}_3\) were also considered among the standards. It is worth noting that the choice of these compounds is evidenced by the fact that XANES spectrum is principally associated with electronic structures and multiple scattering diffusions of the target standards. Motivated by the above-mentioned reasons, LCF was performed using all available standards with different combinations. Some were discarded because they could not provide satisfactory fit and results. The best fit was obtained with a good \(R_{\text{factor}}\) of 0.002 and reasonable uncertainty.

Figure 2 shows the superimposed XANES experimental and theoretical curves of the Cr-SVA sample obtained by LCF using chromium(III) oxide \(\text{Cr}_2\text{O}_3\), iron(II) chromite \(\text{FeCr}_2\text{O}_7\), and sodium dichromate \(\text{Na}_2\text{Cr}_2\text{O}_7\) standards. This set of standards allowed us to obtain the best fit for the experimental curve. The use of other standards was not satisfactory during the fit. The LCF is indicated by the open blue circles, whereas the experimental data are indicated by the black solid line. The results of the best fit are shown in Table 2, with the agreement parameter \(R_{\text{factor}}\). It can be observed that the XANES signature of Cr-SVA can be principally explained by the contribution of chromium(III) oxide \(\text{Cr}_2\text{O}_3\) (47.9%), iron(II) chromite \(\text{FeCr}_2\text{O}_7\) (45.2%), sodium dichromate \(\text{Na}_2\text{Cr}_2\text{O}_7\) (6.9%).

<table>
<thead>
<tr>
<th>Standards</th>
<th>Weight (w%)</th>
<th>(\Delta E_0) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cr}_2\text{O}_3)</td>
<td>47.9(3)</td>
<td>0.068(0.004)</td>
</tr>
<tr>
<td>(\text{FeCr}_2\text{O}_7)</td>
<td>45.2(3)</td>
<td>0.068(0.004)</td>
</tr>
<tr>
<td>(\text{Na}_2\text{Cr}_2\text{O}_7)</td>
<td>6.90(5)</td>
<td>0.068(0.004)</td>
</tr>
</tbody>
</table>

The presence of \(\text{FeCr}_2\text{O}_7\) is not surprising since it was expected because it was expected that the high content of iron present in the VA sample could participate in the reduction of Cr(VI). Thus, iron electrons
can be bind to $\text{Cr}_2\text{O}_7^{2-}$ ions through electrostatic attraction to form an iron chromite complex. This statement is supported by the works on biochar adsorbents presented by Liu et al. (2020), who described the role of Fe in the reduction of Cr(VI) during the adsorption of Cr(VI) onto biochar with a positive charge at its surface. Na$_2$Cr$_2$O$_7$ was initially used as a reactive reagent for contaminating water for adsorption experiments and could be expected to be present or not. Its presence might be justified by the fact that the sorption time was insufficient to reduce the total Cr(VI) ions. In this case, chromium compounds should not be expected to exist in the oxidation state (VI) for a longer sorption time. The Cr$_2$O$_3$ present in the sample might suggest that it existed in the mineral form or was produced by the reduction of Na$_2$Cr$_2$O$_7$ with sulfur. This can be clarified using x-ray diffraction for the phase identification of Cr-SVA. However, further investigations in this study related to the electronic and local structural properties would provide insight into it.

In contrast, Cr(OH)$_3$ which was also expected because of the reasons given earlier (see Section 3.2.) was not detected in the LCF results, suggesting that there was no precipitation of chromium hydroxide. In other words, the adsorption mechanism did not involve the Cr(OH)$_3$ precipitate. It should be noted that the Cr(OH)$_3$ standard was ruled out to derive the best fitting curve with a good agreement factor and uncertainties. The use of this standard makes the LCF simulation very poor.

Overall, the LCF results showed that the chromium species were distributed in weight percentages of 47.9% Cr$_2$O$_3$ + 45.2% FeCr$_2$O$_4$ + 6.9% Na$_2$Cr$_2$O$_7$. It is noted that Cr species are shared Cr(III) in 93.1% and Cr(VI) in 6.9%. This suggests that Cr(VI) in solution is mostly reduced to Cr(III) leading to the presence of compounds with Cr in an oxidation state (III) which is supported by the absence of the characteristic Cr(VI) pre-edge strong peak. However, the small amount of Cr(VI) present in the sample can be justified by assuming that the sorption time (three days) is insufficient for the complete reduction of Cr(VI). This suggests that the sorption time should be an important factor to consider when sorbing VA materials using Cr(VI). These results demonstrate that VA materials can reduce Cr(VI) to Cr(III), which is of great importance because Cr(VI) is one of the most toxic elements and Cr(III) is essential for human life. Wei et al. (2005) investigated Cr sorption by kitchen waste compost and found that Cr(VI) was reduced to Cr(III), with the remaining weight percent of Cr(VI). Their studies performed as a function of time showed that the Cr(VI) amount decreased as the time increased from 27.5% for 0.5 h to 6.1% for 48 h, and that of Cr(III) increases reversibly. Parsons et al. (2002) and Adrich et al. (2003) also showed that Cr(VI) after reacting with hops biomass, and plants is reduced to Cr(III). The same trend was observed for cigarette smoke, tobacco (Cuello et al. 2016), and rice husk (Ming-Jan et al. 2004). The reduction of Cr(VI) to Cr(III) in the adsorption mechanism has also been proven in various studies on biochar material (Liu et al. 2020; Zhou et al. 2016; Choudhary et al. 2017; Rajapaksha et al. 2018). Based on these observations, we hypothesised that the sorption of Cr(VI) by VA could be explained by the chemical reduction of Cr(VI) to Cr(III).

3.3. Electronic properties
Table 3
Main parameters fitted on the deconvolution of Cr K-edge pre-peaks in Cr-SVA, FeCr_2O_4, Cr_2O_3 and Na_2Cr_2O_7 corresponding to the fits shown in Fig. 3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak Energy (eV)</th>
<th>Intensity (u. a.)</th>
<th>FWHM</th>
<th>Red-$\chi^2$</th>
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</thead>
<tbody>
<tr>
<td>Cr-SVA</td>
<td>5977.867±1.084</td>
<td>0.083±0.010</td>
<td>1.894±0.125</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5978.722±0.556</td>
<td>0.025±0.001</td>
<td>1.894±0.154</td>
<td>4.23 x 10^{-05}</td>
</tr>
<tr>
<td></td>
<td>5979.922±0.342</td>
<td>0.039±0.002</td>
<td>1.372±0.392</td>
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</tr>
<tr>
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<td>5981.005±0.904</td>
<td>0.073±0.002</td>
<td>1.696±0.341</td>
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</tr>
<tr>
<td>Cr_2O_3</td>
<td>5989.932±4.862</td>
<td>0.027±0.005</td>
<td>1.437±0.431</td>
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<td></td>
<td>5990.351±5.384</td>
<td>0.024±0.008</td>
<td>1.278±0.080</td>
<td>1.25 x 10^{-06}</td>
</tr>
<tr>
<td></td>
<td>5992.584±0.989</td>
<td>0.042±0.002</td>
<td>1.909±0.065</td>
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<tr>
<td></td>
<td>5993.612±0.613</td>
<td>0.042±0.003</td>
<td>1.464±0.065</td>
<td></td>
</tr>
<tr>
<td>FeCr_2O_4</td>
<td>5989.810±0.988</td>
<td>0.019±0.005</td>
<td>1.053±0.082</td>
<td>2.68 x 10^{-06}</td>
</tr>
<tr>
<td></td>
<td>5990.402±0.588</td>
<td>0.014±0.009</td>
<td>2.565±0.008</td>
<td></td>
</tr>
<tr>
<td>Na_2Cr_2O_7</td>
<td>5988.021±0.051</td>
<td>1.371±0.015</td>
<td>1.354±0.120</td>
<td>2.817 x 10^{-05}</td>
</tr>
</tbody>
</table>

To understand the electronic properties corresponding to the behaviour of Cr-SVA, the pre-peak features of all the standards were fitted using the peak fitting method described in section 2.4. The pre-peaks P1 and P2 in Cr-SVA, and those of Cr_2O_3, FeCr_2O_4, and Na_2Cr_2O_7 (suitable standards suggested by LCF) were considered. The superimposed curves of the experimental and theoretical spectra of the pre-peaks along with the different deconvoluted components are shown in Fig. 4. Table 3 presents the results.

It is observed that the position of the energy and the intensity of the individual components depend on the type of sample. The samples with Cr in oxidation state (III) have at least two well-resolved peaks, whereas those in oxidation state (VI) only have a strong peak. A good similarity in the behaviour of the pre-edge features can be observed between the Cr-SVA sample and the Cr_2O_3 standard with four deconvoluted peaks. However, the energy positions and heights of these peaks are slightly different. The difference can be explained by the type and crystal structure of the samples, which affect their electronic properties. It is reminiscent that the Cr-SVA sample is an unknown compound compared with Cr_2O_3 standard which has a defined crystal structure (Table 1). The similarity between both samples suggests that the Cr-SVA sample can adopt the electronic properties of Cr_2O_3. These results are consistent with the LCF results, which showed Cr_2O_3 and FeCrO_4 as the most suitable components likely present in the Cr-SVA sample. However, the different behaviour in the pre-edge observed between Cr-SVA and FeCrO_4 may suggest that our VA sample cannot be fitted to the crystal structure of FeCrO_4. The results of the pre-
peaks can complement the LCF by suggesting that Cr$_2$O$_3$ is the most suitable for the local electronic properties around Cr in such a VA complex.

In general, the pre-peak features observed in the XANES pre-edge region of the metal element with d$^n$ (n = 1,...,9) electronic configuration are characteristic of the transition to bound states quadrupolar $1s \rightarrow 3d$ and/or dipolar $1s \rightarrow 4p$ (Berry et al. 2008). It has been shown that the intensity and energy of pre-edge features are highly sensitive to 3d orbitals (Guo 2016). Therefore, the two energy positions of the pre-peaks have distinct final state orbital. Thus, it can be understood that the VA sample comprises the pre-edge region, the quadrupolar transition $1s \rightarrow 3d$, corresponding respectively to the energy states of t$_{2g}$ (5990 eV) and e$_g$ (5993.7 eV) orbitals. As we have previously seen that the Cr-SVA compound is in the oxidation state of Cr(III) and can be fitted in the Cr$_2$O$_3$ structure, we attempted to assign the electronic transitions with respect to the rule used in the Cr(III) structure.

We sketch the XAS experimental process in Cr-SVA when a core electron is excited as shown in Fig. 4. In the ground state configuration of Cr(III), the three lowest d-orbitals are occupied by three spin-up electrons. The lowest orbitals correspond to the t$_{2g}$ level. The t$_{2g}$ and e$_g$ levels of the d-orbitals are unsaturated, as shown in Fig. 4. The e$_g$ is empty and t$_{2g}$ is half-filled. When the sample is irradiated with X-ray light at a sufficient 1s Cr core energy, a 1s electron can be expelled to the $1s$ level, leading to an excited state $(t_{2g})^3 (e_g)^3$ or to the t$_{2g}$ state corresponding to an excited state $(t_{2g})^2 (e_g)^4$. In the former configuration, two possible situations can be derived, the promoted electron can be in its spin-down or spin-up state (cases A and B). The latter configuration leads to the promotion of electrons in its spin-down state (case C). These results show that the promotion of the 1s electron in Cr-SVA implies the excited states of the 3d orbitals $(t_{2g})^3 (e_g)^3$ and $(t_{2g})^2 (e_g)^4$.

The peak energy difference (splitting $\Delta E$) between the higher-energy peak component and the lower one is a direct probe of the 10 $Dq$ parameter in crystalline field theory (Tchana et al. 2021). In Cr-SVA, two pre-peaks at 5990 eV (P1) and 5993.7 eV (P2) (see Fig. 1) are deconvoluted to determine $\Delta E$ which is 3.13 eV. This value slightly agrees with that (2–3 eV) obtained for octahedral crystal field splitting between the t$_{2g}$ and e$_g$ levels in several Cr(III) compounds (Burns 1970). According to Peterson et al. (1997), the two pre-edge features in octahedral Cr(III) are attributed to the $1s \rightarrow 3d (t_{2g})$ and $1s \rightarrow 3d (e_g)$ electronic transitions. The peaks at low and high energies correspond to the transitions towards t$_{2g}$ and e$_g$. Thus, one can assign the $1s \rightarrow 3d (t_{2g})$ and $1s \rightarrow 3d (e_g)$ electronic transitions to those involved in the Cr-SVA compound which is consistent with previous studies (Peterson et al. 1997; Burns 1970; Cabaret et al. 2010). The deconvolution of pre-peaks P1 and P2 in Cr-SVA showed two components for each pre-peak. Peak P1, corresponding to t$_{2g}$ exhibited a minor and dominant component, suggesting the promotion of a spin-down electron to the t$_{2g}$ level, as shown in Fig. 4 (case C). The two components from peak P2, which corresponds to e$_g$ are well resolved, suggesting the promotion of spin-down and spin-up electrons to the e$_g$ level (cases A and B). These results are in line with the results of Cabaret et al. (2010), who...
demonstrated that one peak is expected for the $t_{2g}$ component, while two are expected for the $e_g$ component.

3.4. Local structural properties

Table 4
Theoretical structural parameters for various scattering paths of all model compounds derived from FEFF6 calculation at Cr-K edges (Ravel and Newville 2005). $R_{\text{eff}}$ stands for theoretical bond distances and $\text{CN}_{\text{th}}$ for the theoretical coordination number.

<table>
<thead>
<tr>
<th>Standards</th>
<th>Atoms</th>
<th>Paths</th>
<th>$\text{CN}_{\text{th}}$</th>
<th>$R_{\text{eff}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_2$O$_3$</td>
<td>O1</td>
<td>Cr1-O1</td>
<td>3</td>
<td>1.736</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>Cr1-O2</td>
<td>3</td>
<td>2.568</td>
</tr>
<tr>
<td></td>
<td>Cr1</td>
<td>Cr1-Cr1</td>
<td>1</td>
<td>2.652</td>
</tr>
<tr>
<td></td>
<td>Cr2</td>
<td>Cr1-Cr2</td>
<td>3</td>
<td>2.889</td>
</tr>
<tr>
<td>FeCr$_2$O$_4$</td>
<td>O1</td>
<td>Cr1-O1</td>
<td>6</td>
<td>1.993</td>
</tr>
<tr>
<td></td>
<td>Cr1</td>
<td>Cr1-Cr1</td>
<td>6</td>
<td>2.961</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>Cr1-O2</td>
<td>2</td>
<td>3.443</td>
</tr>
<tr>
<td>Na2Cr$_2$O$_7$</td>
<td>O41.1</td>
<td>Cr8-O41.1</td>
<td>3</td>
<td>1.636</td>
</tr>
<tr>
<td></td>
<td>O37.1</td>
<td>Cr8-O37.1</td>
<td>1</td>
<td>1.793</td>
</tr>
<tr>
<td></td>
<td>Cr10.1</td>
<td>Cr8-Cr10.1</td>
<td>1</td>
<td>3.277</td>
</tr>
</tbody>
</table>
Table 5
Fitted structural parameters for Cr-SVA and model compounds derived from EXAFS modelling at Cr K edges. * symbol corresponds to the coordination number fixed to its theoretical value (Table 4). CN stands for the coordination number and R for the bond distance. The energy shift is $\Delta E_0$ and the Debye-Waller factor $\sigma^2$. $S_0$ parameter was equal to 1 for all samples except for FeCr$_2$O$_4$ fixed at 0.7.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Interaction</th>
<th>$\Delta E_0$ (eV)</th>
<th>CN</th>
<th>R(Å)</th>
<th>$\sigma^2$(Å$^2$)</th>
<th>R$_{factor}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-SVA</td>
<td>Cr-O1</td>
<td>3.23(10)</td>
<td>3.26(42)</td>
<td>1.69(2)</td>
<td>0.0014(3)</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>Cr-O2</td>
<td>2.30(71)</td>
<td>2.59(2)</td>
<td>0.0009(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr-Cr1</td>
<td>1*</td>
<td>2.54(2)</td>
<td>0.0023(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>Cr-O1</td>
<td>-2.62(6)</td>
<td>4.02(21)</td>
<td>1.79(2)</td>
<td>0.0017(8)</td>
<td>0.011</td>
</tr>
<tr>
<td>FeCr$_2$O$_4$</td>
<td>Cr-O1</td>
<td>-4.72(8)</td>
<td>5.73(58)</td>
<td>1.99(0.7)</td>
<td>0.0004(0.1)</td>
<td>0.009</td>
</tr>
<tr>
<td>Na$_2$Cr$_2$O$_7$</td>
<td>Cr-O41.1</td>
<td>6.94(7)</td>
<td>3.15(52)</td>
<td>1.67 (3)</td>
<td>0.0065(1)</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>Cr-O37.1</td>
<td>1*</td>
<td>1.82(4)</td>
<td>0.0110(3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The LCF XANES investigation revealed in the decreasing order the presence of Cr$_2$O$_3$, FeCr$_2$O$_7$, and Na$_2$Cr$_2$O$_7$ as the main components of the Cr-SVA material. The qualitative analysis was based on the comparison of the FT of Cr-SVA and the theoretical paths corresponding to the first shells of the suitable components. Table 4 lists the theoretical contribution of some paths and atoms with their coordination numbers and bond distances of the standards used. Atoms with the distances greater than 5 Å are not shown.

Figure 5 shows the modulus of the FT of the experimental data for Cr-SVA and some theoretical paths related to the Cr$_2$O$_3$, FeCr$_2$O$_7$, and Na$_2$Cr$_2$O$_7$ structure in a), and the FT functions of these samples along with their theoretical EXAFS fitting curves in b). Paths with lengths up to 2.6 Å were used in Fig. 5 because the FT in Cr-SVA could be better described at a distance below 3 Å. As shown in Fig. 5b, the FT function of Cr-SVA shows features similar to those of Cr$_2$O$_3$ and FeCr$_2$O$_7$. However, the height of the outer peaks makes a slight difference between them, especially for the standard FeCr$_2$O$_7$ (height too high). The FT behaviour of the Na$_2$Cr$_2$O$_7$ standard is completely different in its FT behaviour suggesting that the Cr-SVA local structure cannot be described within this compound. This analysis was consistent with the results obtained from the pre-edge fitting investigation which showed that the electronic properties and structure of Cr-SVA could not be assigned to that of Na$_2$Cr$_2$O$_7$. In addition, the Cr-SVA compound was found to have the oxidation state of Cr(III) instead of Cr(VI) in the Na$_2$Cr$_2$O$_7$ compound. Because of the similarity observed in the FT behaviour between Cr-SVA, Cr$_2$O$_3$ and FeCr$_2$O$_7$, it might be possible to use
one or other theoretical structures to perform EXAFS fitting. In addition, the closed weight percentage obtained from LCF for both (47.9% Cr$_2$O$_3$ and 45.2% FeCr$_2$O$_7$) may lead to the confusion. To have a clear vision, we decided to compare the first theoretical paths of the three suitable standards and the Cr-SVA experimental FT function, as shown in Fig. 5a. The paths O1, O2, and Cr1 of Cr$_2$O$_3$ match perfectly in the first two peaks in the Cr-SVA experimental FT while O1 of FeCr$_2$O$_7$ and 041.1 and 037.1 of Na$_2$Cr$_2$O$_7$ do not match. This implies that Cr$_2$O$_3$ is the most suitable crystal structure which can be adopted for EXAFS modelling (fitting) of the Cr-SVA data. We then used the paths of Cr$_2$O$_3$ to model the Cr-SVA data. In addition, the experimental data of the three suitable standards were modelled for comparison. The fitted results are listed in Table 5.

The first shell of Na$_2$Cr$_2$O$_7$ was successfully reproduced using the first shorter oxygen atoms suggesting that this model component shows a distorted O atoms closely bound to the central Cr(VI) at the Cr-O bond distances of 1.67 Å and 1.82 Å in the coordination numbers of 3.15 and 1 respectively (the coordination number for the second O was kept fix at 1). In addition, the first shells of FeCr$_2$O$_7$ and Cr$_2$O$_3$ were successfully reproduced using their first oxygen atoms. This explains why the Cr(III) central atom is coordinated to oxygen at a Cr-O bond distance of 1.99 Å with a coordination number of 5.73, in the first shell of FeCr$_2$O$_7$. On the other hand, in the first shell of Cr$_2$O$_3$ model compound, Cr(III) central atom is coordinated to oxygen at a Cr-O bond distance of 1.79 Å with the coordination number of 4.02.

For EXAFS modelling of the Cr-SVA sample, the first and second overlapped shells were perfectly fitted using the first two oxygen and first chromium atoms from the theoretical paths of Cr$_2$O$_3$. This is based on the preceding results, which show a good match with the Cr$_2$O$_3$ model compound. The first two shells of Cr-SVA compound can be described by two distorted oxygen atoms at a Cr-O bond distances 1.69 Å and 2.59 Å respectively with the coordination numbers of 3.26 and 2.3, in addition to one Cr atom coordinated at Cr-Cr bond distance of 2.54 Å. It is worth noting that during the fitting process, using only the first two oxygen atoms and excluding the first chromium atom made the fit very poor, and the results were not reasonable. Thus, the best option was to include the first chromium in the fitting and to keep its coordination number fixed to obtain the best fit with reasonable results. It can be observed that the bonding distances of Cr(III) with oxygen and chromium atoms in Cr-SVA are similar to those in Cr$_2$O$_3$. The methodology employed in this study was also used elsewhere to describe the local structure around the Cr central atom in plants and natural soils rich in silicon and oxides (Parsons et al. 2002; Peterson et al. 1997; Aldrich et al. 2003).

Finally, the EXAFS results indicate that Cr$_2$O$_3$ is the only standard in this study, which is similar in coordination and binding in the first two shells of the Cr-SVA. This suggests that the atomic structure of Cr in Cr-SVA is the same as that of Cr$_2$O$_3$ with a geometrical arrangement of distorted O atoms and Cr atoms in the first and second shells. The results from EXAFS and XANES (LCF + pre-peak fitting) coincide and strengthen the argument that in the Cr-SVA material, Cr(III) is bounded to oxygen and chromium atoms in the first two coordination shells in geometrical coordination of Cr$_2$O$_3$ model. This reinforces the idea that Cr$_2$O$_3$ is the main component of the Cr-SVA. Thus, the adsorption mechanism assigned to the
reduction of Cr(VI) followed by ion exchange was proven. In contrast to Cr-SVA, Cr(OH)$_3$ precipitates were found in various biochar materials after adsorption of Cr(VI) (Liu et al. 2020; Rajapaksha et al. 2018). In addition, Wei et al. (2005) showed that the reduction of Cr(VI) by waste compost is followed by the formation of Cr(OH)$_3$ precipitates. In contrast, they did not find Cr(OH)$_3$ precipitate for the sorption of Cr(III) by the compost. Fang et al. (2021) also demonstrated that Cr(OH)$_3$ precipitates predominantly occurred at pH values greater than 6.4. The Cr-SVA sample was synthesised at a pH of 3. Our results conclusively demonstrate the sorption of VA materials using Cr(VI), which is of great interest in water purification applications.

3.5. Adsorption mechanism

The value of the zero-point charge pH (pH$_{ZPC}$) is 7.64 for the VA material (Thiodjio et al. 2021). The pH$_{ZPC}$ is required to understand the adsorption mechanism on the VA. The surface of the adsorbent is positively charged at pH < pH$_{ZPC}$ (Medellin et al. 2014, 2016), favoring electrostatic attraction with anions onto the adsorbent surface. Thus, the adsorption mechanism cannot be attributed to the electrostatic attraction between the VA sample and chromium ions which are positively charged. Otherwise, ion exchange can be involved in the reduction process of Cr(VI) (Thiodjio et al. 2021), while competing Ca$^{2+}$, Mg$^{2+}$, H$^+$, etc, can be replaced by Cr(III) on some available sites. Therefore, we hypothesized that the sorption of Cr(VI) by VA may be explained by the reduction of Cr(VI) to Cr(III), followed by ion exchange onto the Cr-SVA surface. These conclusions are in line with the results of Kaprara et al. (2018), who showed the reduction of Cr(VI) to Cr(III) by physisorption and chemisorption onto the FeOOH surface for the removal of Cr(VI) in drinking water. Based on the XAS results, the adsorption mechanism proposed for Cr sorption by VA can be described as follows: First, Cr$_2$O$_7^{2-}$ charges were adsorbed to the positive charges on the VA surface by a physisorption process involving electrostatic attraction. Second, Cr(VI) was reduced owing to the absence of Cr(III) in aqueous solutions at the beginning of the adsorption experiment. Cr(III) is then distributed at the VA surface until equilibrium is reached with a small accumulation of Cr(VI) (6.9%). Third, sufficient Cr(VI) was attracted to the VA surface and reduced to Cr(III). The amount of Cr(III) (93.1%) on the VA surface was considerable. This is because the exchangeable H$^+$ ions from the metal-OH functional groups (Bang et al. 2022) could have been replaced by Cr(III), which is involved in the ion exchange process. Finally, it can be concluded that the mechanism for chromium sorption by the VA material from CVL is associated with Cr(VI) reduction followed by ion exchange. This mechanism was consistent with that proposed by Liu et al. (2020) for biochar.

4. Conclusion

In summary, we have shown that the electronic and structural properties of environmental adsorbents can be investigated using X-ray absorption spectroscopy (XAS) through chromium sorption by volcanic ash (VA). Linear combination fitting (LCF) and pre-peak fitting methods of XANES gave details of the oxidation state, chemical composition of Cr(VI)-VA, and the possible electronic transition states in the VA compound. The results showed that the oxidation state of chromium after sorption by VA changed from
(VI) to (III) during the reduction process. The chromium-sorbed VA contained chromium species in 93.1% Cr(III) and 6.9% Cr(VI), distributed as Cr$_2$O$_3$ (47.9%) + FeCr$_2$O$_7$ (45.2%) + Na$_2$Cr$_2$O$_7$ (6.9%). It was observed that chromium-sorbed VA compounds were more likely to be described in the Cr$_2$O$_3$ structure. The electronic transitions $1s \to 3d(t_{2g})$ and $1s \to 3d(e_g)$ were assigned to chromium-sorbed VA material, suggesting the promotion of 1s electron to the excited states of the 3d orbitals $(t_{2g})^3(e_g)^3$ or $(t_{2g})^2(e_g)^4$. The EXAFS modelling of the first two shells of the chromium-sorbed VA compound showed good agreement with the theoretical values of the Cr$_2$O$_3$, complex confirming the XANES results. The first and second shells of the sorbed VA compound can be described by two distorted oxygen atoms at Cr-O bond distances of 1.69 Å and 2.59 Å respectively with the coordination numbers of 3.26 and 2.3 and one Cr atom coordinated at Cr-Cr bond distance of 2.54 Å. The proposed mechanism for chromium sorption by VA material is associated with Cr(VI) reduction, followed by ion exchange. The overall results prove that XAS technique is efficient to provide the chemical, electronic and structural properties of sorbed metal in the environmental adsorbents which is one of today main concerns. This XAS technique might be reproduced for any other materials which can be efficient for the sorption of heavy metals as demonstrated as well in the literature.

**Declarations**

**Acknowledgments**

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**Conflict of interests** The authors declare that they have no conflict of interest.

**Ethical Approval** Not applicable.

**Authors’ contributions**

Gristianho Lontin Lontin: XANES and EXAFS data analysis, writing original draft; Bridinette Thiodjio Sendja: design of the experiment, performed the experiment, XANES and EXAFS data analysis and interpretation, writing original draft; Duclair Tchana Kamgne: XANES data analysis and interpretation, manuscript reviewing; Giuliana Aquilanti: supervision, performed the experiment, manuscript reviewing; Germain Ben-Bolie: supervision, manuscript reviewing.

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Availability of data and materials Data will be made available under request.

References


Figures
Figure 1

Cr K-edge XANES spectra of Cr-SVA and some reference compounds at different oxidation states: Chromium metal (Cr; (0)), Chromium(III) oxide (Cr₂O₃; (III)), Chromium trioxide (CrO₃; (VI)). Each arrow indicates the E₀ of the corresponding standard and the insert indicates the pre-edge features with the values of their energies in Cr-SVA spectrum. The numbers in parentheses are the oxidation states. The plots are done with various y-offset for clarity.
Figure 2

Linear combination analysis of Cr-K XANES spectrum of sample Cr-SVA using Cr$_2$O$_3$, iron(II) chromite FeCr$_2$O$_7$, and sodium dichromate Na$_2$Cr$_2$O$_7$ standards.
Figure 3

Fit of the pre-peaks of Cr K-edge in Cr-SVA (top left panel) and standard components FeCr$_2$O$_7$ (bottom left panel), Cr$_2$O$_3$ (top right panel), Na$_2$Cr$_2$O$_7$ (bottom right panel). A deconvolution of one, two and four components related to the quadrupolar transitions are also shown.
Figure 4

Scheme for the analysis of XANES measurements of Cr-SVA with $t2g$ state unsaturated for the ground state and the possible final states. After absorption of the X-ray, the transitions can be assigned to $1s \rightarrow 3d(t2g)$ and $1s \rightarrow 3d(e_g)$. 
Figure 5

a) Comparison of the FT of Cr-SVA and the theoretical paths corresponding to the first shells of Cr2O3, FeCr2O7, and Na2Cr2O7 suitable components; b) The best fit of FT functions of the experimental data and the theoretical curves of Cr K-edge for samples Cr-SVA; and Cr2O3, FeCr2O7, and Na2Cr2O7 models.