Adsorption of Cr(VI) on Al-substituted hematites and its reduction and retention in the presence of Fe2+ under conditions similar to subsurface soil environments

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Abstract: Aluminum substitution is common in iron (hydr)oxides in subsurface environments, and can significantly modify mineral interactions with contaminants. However, few studies investigate Cr(VI) adsorption and its subsequent mobility on Al-substituted iron (hydr)oxide surfaces. Here shows that Al substitution gradually modifies hematite crystals from {101}, {12}, {110} and {104} faceted rhombohedra to {001} faceted plates, resulting in a general decrease in Cr(VI) adsorption density and favoring of monodentate mononuclear over bidentate binuclear Cr(VI) adsorption complexes. Consequently, the mobility of Cr(VI) might be increased in environments with an abundance of Al-containing iron (hydr)oxides. However, pre-adsorption of Fe2+ on hematite promotes Cr(VI) adsorption, reduction and fixation, and Al-substituted hematite removes more Cr(VI) than pure hematite. Similarly, although addition of Fe2+ to Cr(VI)-adsorbed hematite remobilizes a small proportion of Cr, it greatly increases the proportion of Cr fixed. As the coexistence of Fe2+ and iron (hydr)oxides is common in subsurface environments, Al-containing iron (hydr)oxides will promote Cr(VI) uptake and retention, with a significant proportion fixed as Cr(III), limiting Cr mobility and toxicity. These results offer new insights into how iron (hydr)oxides might control the behaviors of other high-valence redox-sensitive contaminants, and provide a platform for modeling such processes in complex soil and sediment systems.

**Keywords:** Iron oxide, Al substitution, Cr(VI), Fe2+, adsorption

**1.Introduction**

Iron hydroxide minerals are ubiquitous in terrestrial and aquatic environments, and in atmospheric aerosols [1, 2]. They are of fundamental importance in a series of geochemical reactions that control metal mobility and fate, such as sorption, coprecipitation and dissolution, and are strongly involved in redox reactions [1, 3]. These processes play a controlling role in the cycling, transformation and bioavailability of both bioessential elements, and inorganic and organic contaminants [1, 4, 5]. In particular, hematite, α-Fe2O3, is often the most thermodynamically stable phase for iron (hydr)oxides in highly weathered soils, such as red soil, brick red soil and dry red soil, that cover significant areas of the terrestrial surface, especially those that were not glaciated during the Pleistocene epoch [1, 2]. It is isostructural with corundum and consists of hexagonal close-packed oxygen ions with Fe atoms occupying 2/3 of the available octahedral cavities. Polyhedral nanocrystals of hematite expose a number of facets and thus exhibit a variety of crystal morphologies, depending on the thermodynamic and chemical conditions during mineral formation [6]. Hematite morphology can not only be used as an indicator of contemporaneous environmental conditions [6], but morphology also determines the reactivity of these minerals. In particular, different morphologies can exhibit different crystallographic faces with different atomic arrangements, and thus unique charging and adsorbent characteristics [7] and electrical resistivities [3]. In turn, different facets can have different adsorption mechanisms, densities and affinities for different contaminants, such as chromate [8], arsenate [9] and lead [10, 11].

Whilst much is known about the morphology and reactivity of hematite, in natural soils, iron (hydr)oxide minerals commonly contain a significant amount of impurities. Aluminum is the most common substituent, through the coprecipitation of Al3+ with Fe3+/2+ during (hydr)oxide nucleation and/or mineral transformation [1, 12, 13]. The contents of Al in hematite can be as high as 16 mol% [22]. Due to the different chemical and physical properties of Al and Fe, including radius, electronic structure, ion potential, bond stability and so on, replacement of Al for lattice Fe in an iron (hydr)oxide structure can greatly modify the physicochemical properties of the host mineral [12, 14, 15]. Aluminum substitution for Fe in hematite can lead to changes in the color, morphology, structure, transformation and reactivity of hematite, and ultimately the mechanisms by which hematite interacts with other inorganic and organic soil constituents. For example, experimental studies show that hematite crystal morphology changes from pseudocubic to platey with increasing Al substitution [15, 16], and can result in activation of the inert {001} facets by the creation of Fe vacancies, which greatly increases charge density and Pb2+ adsorption capacity [15]. In natural hematite minerals this morphology change is reflected by an increase in the diameter to thickness ratio of the crystals [12, 17], and as a result of these morphological changes, phosphate adsorption is decreased [12, 18]. Similarly, arsenite adsorption affinity and density on Al-substituted iron (hydr)oxides is also gradually decreased with increasing Al content [19], while chromate, selenate, and sulfate adsorption mechanisms on Al-substituted ferrihydrite are modified, in that these anions form both outer-sphere complexes and inner-sphere monodentate and bidentate complexes at the mineral surfaces, but the relative fraction of outer-sphere complexes significantly increases for all anions, and chromate inner-sphere bidentate complexes are disproportionately suppressed over monodentate complexes, with increasing Al substitution [20].

Hexavalent chromium (Cr(VI)) is a widely found anthropogenic metal pollutant released from a variety of different industrial processes, including electroplating, wood treatment, leather tanning, textile industries, and chromite ore processing. Due to its high toxicity, carcinogenicity, and mutagenicity, Cr(VI) receives significant attention in the literature [8, 20-22]. Common pathways for Cr(VI) removal from soil porewater involve Cr(VI) complexation to soil minerals, formation of insoluble Cr(VI) salts, and reduction of Cr(VI) to Cr(III) by various reductant substances (e.g. Fe2+), which reduce the toxicity and mobility of Cr(VI) [8, 20, 22]. In subsurface environments, the fate of Cr(VI) is primarily controlled by its transformation on iron (hydr)oxide surfaces [23]. Because of this, several studies have investigated Cr(VI) adsorption and transformation mechanisms on iron (hydr)oxides, including hematite. Chromate can form both outer-sphere and inner-sphere complexes on hematite surfaces, the latter occurring as monodentate mononuclear (MM) and bidentate binuclear (BB) complexes, among which MM complexes were dominant above pH 6 and BB complexes are dominant below pH6 [22]. Recently it was found that the MM complexes were formed on hematite {001} facets while BB complexes are formed on {110} facets, and Cr(VI) adsorption density on the {110} facets was estimated to be 2 times that on {001} facets [8]. However, despite the significant substitution of Al for Fe in natural soil hematites, no studies have investigated the adsorption behaviors of Cr(VI) on Al-substituted hematite minerals.

Additionally, it is also widely acknowledged that, whilst a significant fraction of heavy metal contaminants associates with iron (hydr)oxides in contaminated soil environments (e.g. [37]), these minerals might not provide a permanent sink for these toxins. Environmental conditions, such as temperature, pH, ionic strength and redox conditions (reflected in and influenced by the presence of reductants, e.g., aqueous Fe2+ and organic matter, and the occurrence of ﬂooding and so on), change frequently, making soils highly dynamic environments. These often oscillating conditions result in the dissolution, reduction and/or transformation of these iron (hydr)oxide minerals, and thus can impact the retention and cycling of associated metals [24]. In particular, Fe2+ plays an important role in iron (hydr)oxide stability. After being produced biotically or abiotically, Fe2+ usually coexists with (hydr)oxides under anoxic soil conditions, and the reactions between them occur readily, such as interfacial electron transfer and atom exchange [3, 24, 25]. Of particular relevance, it is reported that the reduction potential (EH) of Fe2+ associated with (hydr)oxide surfaces is lower than that of aqueous Fe2+ in the same aqueous system, and Fe2+ associated with iron (hydr)oxide surfaces can reduce oxidized contaminants much faster than aqueous Fe2+ alone [26-28]. This is important because it suggests that the reduction of Cr(VI) to less toxic and less mobile Cr(III) might be facilitated by Fe2+ at the hematite surfaces. However, the reactions of Fe2+ with hematite are surface-specific [3, 29] and are inﬂuenced by particle size, pH, and Fe2+ concentration [30]. As Al doping not only modifies the hematite morphology and thus particle size [12, 16] but can also enhance cation adsorption [15], the interactions of Fe2+ with hematite and associated metal pollutants are likely significantly complicated by Al substitution for lattice Fe in the hematite structure, and are in need of focused study.

To address the gaps in knowledge around Cr(VI) adsorption on Al-substituted hematite, and the effect of aqueous Fe2+ on Al-substituted hematite stability and retention of Cr(VI), a series of Al-substituted hematite samples were synthesized and characterized by powder X-ray diffraction (XRD), high-resolution transmission electron microscope (HRTEM), spherical aberration-corrected scanning transmission electron microscopy (Cs-STEM), and X-ray photoelectron spectroscopy (XPS). Then the adsorption behaviors of Cr(VI) on these Al-substituted hematites were investigated. The reacted solids were analyzed by Fourier transform infrared spectroscopy (FTIR), and XPS. Following this, to represent dynamic soil conditions where iron (hydr)oxides can become exposed to Fe2+ either before or after adsorption of Cr(VI), we performed hematite-Fe2+-Cr(VI) experiments by firstly exposing Al-hematite to Fe2+ before Cr(VI) adsorption, and secondly by exposing Cr(VI)-loaded mineral to Fe2+. These results improve our understanding of the physicochemical properties of Al-substituted hematites, the effects of Al impurity on the mineral reactivity towards Cr(VI), and the transformation, mobility and fate of adsorbed Cr(VI) during exposure to Fe2+. Consequently, our results can be used to provide insights into the role of Al-substituted hematites in controlling the mobility and fates of Cr(VI) and similar metal pollutants in soils, which in turn can provide guidance for exploring innovative management, remediation and utilization strategies for moderately heavy metal contaminated soils.

**2.Materials and methods**

**2.1 Preparation of Al-substituted hematite samples**

Aluminum-substituted hematite samples were synthesized according to the method used in our previous study [16]. Certain amounts of mixtures of Fe(NO3)3·9H2O and Al(NO3)3·9H2O salts (the molar ratios of Al/(Al+Fe) were 0, 0.03, 0.07, 0.09, 0.13) were dissolved into 500 mL of deionized water (the resistivity was greater than 18 MΩ·cm) preheated at 90 °C, followed by addition of KOH solution (1 mol·L-1, 300 mL) preheated at 90 °C and NaHCO3 solution (1 mol·L-1, 50 mL). The mixture was stored in an oven at 90 °C for 4 d. Then, a certain amount of nitric acid (2 mol·L-1) was added to the above suspensions to remove the amorphous components and impurities. The obtained samples were washed several times with deionized water and dried at 60 °C for several days. Finally, the samples were ground carefully in an agate mortar to particle sizes below 100 mesh, and stored in polyethylene plastic tubes at room temperature. The obtained samples at Al/(Al+Fe) molar ratios of 0, 0.03, 0.07, 0.09 and 0.13 were labeled as Hem, AlH3, AlH7, AlH9, and AlH13, respectively.

**2.2 Solid characterizations**

Powder X-ray diffraction analysis of the obtained samples was carried out on a Bruker D8 Advance diffractometer equipped with a LynxEye detector using Ni-filtered Cu Kα radiation (λ = 0.15418 nm). The diffractometer was operated at a tube voltage of 40 kV and a current of 40 mA, with a step size of 0.02o and a scan rate of 1or 10 o·min-1 in the range of 15-85o 2θ. Rietveld structure refinement was carried out by using the TOPAS software, based on the structure model (ICSD 82137) [31].The specific surface area (SSA) was measured with an Autosorb-1 standard physical adsorption analyzer (Quantachrome, USA). The samples were degassed at 150 oC for 5 h in vacuum to remove water and adsorbates. The multi-point BET method was used to calculate the SSA. FTIR spectra of the mineral sample were collected at room temperature using a VERTEX 70 Fourier transform infrared spectrometer (Bruker, Germany). 0.001 g of the dried sample was ground and mixed in an agate mortar at a mass ratio of 1:100 with dry KBr powder, and analyzed after tableting. The resolution was 4 cm-1, and the number of scans per sample was 128.The Raman spectroscopy was observed on a laser confocal micro-Raman spectrometer (LabRAM HR Evolution, France) with a 633 nm laser excitation source. The morphologies of the samples were observed on a JSM 6700F scanning electron microscope (JEOL, Japan) and a JEM-2100F high-resolution transmission electron microscope (JEOL, Japan). The phase lattice and selected-area electron diffraction of typical samples were also collected on a high-resolution transmission electron microscope (HRTEM, JEM-2100F). STEM-EDS mapping of a typical Cr(VI) adsorbed AlH13 crystal was conducted on Talos F200S (FEI, USA). Spherical aberration-corrected scanning transmission electron microscopy (Cs-STEM) analysis was carried out on a Titan Cubed Themis G2300 operated at 200 kV (FEI, USA). High angular annular dark-ﬁeld (HAADF) images were collected for typical samples. The X-ray photoelectron spectroscopy (XPS) experiments were carried out on a VG Multilab2000 X-ray photoelectron spectrometer (Thermo VG, UK) with an Al Kα X-ray source (1486 eV). The charge effect was corrected by adjusting the binding energy (BE) of adventitious C (1s) to 284.80 eV. The spectra were analyzed using the Avantage software. The Shirley-type background was subtracted before deconvolution and ﬁtting.

The chemical compositions of the samples were determined as follows: 0.01 g of sample was dissolved in 10 mL of 6 mol·L-1 HCl solution and heated in a 40 oC oven until the mineral was completely dissolved. Inductively coupled plasma atomic emission spectroscopy (Varian, USA) was used to determine the contents of Fe and Al in the minerals. Triplicate measurements were made. The zeta potential (ζ) of typical samples, Hem and AlH13, were measured at different pH conditions ranging from 3 to 10 using a Malvern Zetasizer ZEN 3600 zeta potential analyzer (Malvern, U.K.). The pH of the mineral suspension was firstly adjusted to predetermined pH before measurement. At least 3 measurements were conducted for each sample. The average values and stand errors are reported.

**2.3** **Cr (VI) adsorption experiments**

The Cr (VI) adsorption experiments were conducted at a constant supporting electrolyte concentration (NaNO3, I = 0.1 mol·L−1). Since the pH of heavy metal polluted soils with relatively high contents of iron (hydr)oxide is about 4 [32], in this study pH4, was chosen to investigate the Cr (VI) adsorption behaviors on the Al-doped hematite samples. The mineral concentration was 0.75 g·L-1. Typically, 0, 0.2, 1, 2, 3, 4, 6 and 8 mL of 0.1 g·L-1 Cr(VI) at pH4±0.05 was added into the mineral suspensions which were pre-adjusted to pH4±0.05, and thus the Cr(VI) concentration in the reaction system was 0.5, 2.5, 5.0 7.5, 10, 15, 20 mg·L-1,respectively. Then the reaction was carried out in a shaker at a rate of 250 r·min-1 at 25 °C for 4 h. After the reaction, the mixture was centrifuged at 10,000 r·min-1 for 10 min. The residual Cr(VI) in the supernatant was determined by the 1,5-diphenylcarbazide spectrophotometric method [33], and the solid was collected and washed several times, and then dried in an oven at 40 oC for further analysis.

**2.4 Effect of Fe2+ on Cr(VI) transformation on Hematite**

Theseexperiments were conducted in an anaerobic chamber. All solutions were made by dilution of stock solutions using deoxygenated deionized water. Fe2+ ((NH4)2Fe(SO4)2·6H2O) was added before or after Cr(VI) adsorption. During the first approach, 0.5 g of hematite sample was suspended in 0.1 mol·L-1 NaNO3 solution, and the pH was adjusted to pH4±0.05. An aliquot of Fe2+ was added and then stirred for 15 min. Then 3.9 mL of 1 g·L-1 Cr(VI) was added. The total volume of the reaction system was 100 mL. The molar ratio of Fe2+ to Cr(VI) at 1:1 or 3:1 (the Fe2+ concentration was 0.75 or 2.25 mmol·L-1 correspondingly) was investigated. After reaction for 4 h, the suspensions were filtered through a 0.22 μm membrane, and the content of Cr(VI) in the filtrate was determined by the colorimetric method [33] while the total Cr was determined by ICP-AES. For the second approach, Cr(VI) pre-adsorbed hematite was firstly prepared. Cr(VI) solution was added into the Hem suspension to make a mineral concentration of 5 g·L-1 and Cr(VI) concentration of 20 mg·L-1 in a total volume of 100 mL. The adsorption was conducted at pH4 ± 0.05 in 0.1 mol·L-1 NaNO3 solution for 12 h being shaken at a rate of 250 r·min-1 at 25 °C. After centrifugation, Cr(VI) in the supernatant was determined and the solid was rinsed several times before drying at 40 oC for several days. Then 0.5 g of Cr(VI) pre-adsorbed hematite sample was re-suspended. Fe2+ was then added to obtain Fe2+/Cr(VI) molar ratio of 1:1 or 3:1 (the Fe2+ concentration was 0.14 or 0.42 mmol·L-1 correspondingly). Other details were the same as those in the first approach.

A certain amount of the residual solid from the hematite, Fe2+, Cr(VI) system was firstly desorbed with 10 mL of 0.1 mol·L-1 NaOH solution for 4 h, and then the mixture was centrifuged at 10,000 r·min-1 for 10 min to separate the solid and supernatant solution. A further 10 mL of 1 mol·L-1 NaOH solution was added to the solid, and then the mixtures were shaken for another 4 h before centrifugation. This desorption step was repeated twice, and thus in total desorption steps were performed 3 times. The contents of Cr(VI) and Cr(III) in the supernatant after each desorption step were determined and used for mass balance calculation.

Samples retaining enough Cr after desorption were chosen for further analysis by X-ray absorption near edge structure (XANES) spectroscopy. Cr K-edge XANES data were collected at room temperature on the 1W1B beamline at the Beijing Synchrotron Radiation Facility (BSRF) [34]. Fluorescence-yield spectra of the samples were obtained over an energy range of 5788-6523 eV, while the spectra of reference materials Cr2O3 and CrO3 were collected in transmission mode. Cr metal foil (E0 = 5989 eV) was collected for calibrating the monochromator before each sample run. Data processing was conducted by using the Ifeffit/Athena program, which allows the user to perform energy calibration, averaging, background removal, and normalization of the XANES data [35].

In order to investigate the possible mineral phase transformation of hematite with Fe2+, the reaction of Fe2+ with Hem was also monitored by powder XRD analysis. Firstly, 0.15 g Hem was suspended in 30 mL deionized water and the pH was adjusted to pH4±0.05. After purging N2 for 1 h to remove O2, the suspension was placed in an anaerobic glove chamber. 0.3375 mol·L-1 Fe2+ solution was prepared in the anaerobic glove chamber by dissolving (NH4)2Fe(SO4)2·6H2O salt in deoxygenated water. Then 67 or 200 µL of the above Fe2+ solution (the corresponding Fe2+ concentration in the system was 0.75 or 2.24 mmol·L-1) was added into the mineral suspension to start the reaction under continuous stirring. At the end of the reaction, the suspension was filtered through a 0.22 μm membrane. The obtained solid was immediately washed thoroughly and then for XRD analysis.

**3. Results and discussion**

**3.1 Characterization of as-prepared Al-doped hematite crystals**

**3.1.1 Physicochemical properties**

When the initial Al/(Al+Fe) molar ratios are 0, 0.03, 0.07, 0.09 and 0.13, the final Al/(Al+Fe) ratios in the obtained samples, Hem, AlH3, AlH7, AlH9, and AlH13, are 0, 0.029±0.001, 0.067±0.001, 0.091±0.002, and 0.129±0.002 respectively (Table S1). This suggests that almost all Al3+ are incorporated into the hematite structure. The highest Al substitution level is 13 mol% (Table 1), similar to that in natural hematite samples [12, 17, 32]. The XRD patterns of these samples match quite well with that of hematite standard (JCPDS 33-0664), confirming that all the samples are pure hematite crystals without any impurities (Figure S1a). With an increase in Al substitution level, the diffraction peaks gradually shift to higher angles, especially the (104) and (110) peaks (Figure S1b). This indicates the d-spacings of these planes are decreased after Al doping, suggesting lattice contraction induced by Al substitution for lattice Fe in the hematite crystals [12, 16, 36]. Rietveld structure refinement of these samples is also conducted and the results are presented in Figure. S1, Figure. S2 and Table S1. It demonstrates that, lattice parameter *a* of hematite has a significant negative linear relationship with the content of Al in the sample (Figure S2a; R2=0.9608, n=5, α=0.01), while lattice parameter *c* is also gradually decreased with increasing Al content (Figure S2b; R2=0.9101, n=5, α=0.05). Consequently, cell volume has a negative linear relationship with the Al content (Figure S2c; R2=0.9514, n=5, α=0.05). These changes are mainly caused by the substitution of lattice Fe in hematite structure by Al, owing to the smaller radius of Al3+ than Fe3+ [17, 37]. The calculated crystal density of the obtained hematite sample is also found to have a significant negative linear relationship with the final Al/(Al+Fe) molar ratio (Figure S2d; R2=0.9967, n=5, α=0.01). Further, it is found that with increasing Al content, the intensity of the diffraction peaks initially increases and then decreases. This is consistent with the changes in the coherent scattering domain (CSD) sizes of these samples. The CSD sizes of Hem, AlH3, AlH7, AlH9, and AlH13 are 45, 69, 71, 59 and 19 nm respectively (Table S1). What’s more, the relative ratios of the (104) to (110) peak intensities gradually change. This suggests a modification of the morphologies of these hematite crystals after Al doping [12, 15, 16, 36].

High Al doping generally decreases the thermal stability of these samples. After heating to 800 oC in an N2 atmosphere, the weight losses for Hem, AlH3, AlH7, AlH9, and AlH13 are 4.2%, 4.1%, 5.2%, 5.6% and 9.6%, respectively (Figure S3). The specific surface areas of these Al-substituted hematites are 29, 27, 21, 28 and 50 m2·g-1, respectively. The zeta potentials (ζ) of Hem and AlH13 are presented in Figure S4. With an increase in pH, the ζ of Hem or AlH13 gradually decreases and changes its sign at 8-8.5. At any given pH, the mineral surface positive or negative charge of AlH13 is smaller than that of Hem.

**3.1.2 Raman spectra**

The Raman spectra of these Al-doped hematite samples are shown in Figure 1. The main peaks of Hem are located at 226, 244, 291, 407, 495 and 611 cm-1. This further confirms that the obtained sample is pure hematite [38]. With the increase of the Al content, the peaks of Al-doped hematite samples are redshifted. Insertion in the hematite lattice of the lighter Al cations lowers the average reduced mass. Further, as Al3+ is much smaller than Fe3+ in the octahedral crystal field [37], replacement of lattice Fe by Al will induce crystal strain due to the formation of shorter Al-O bonds with respect to Fe-O bonds. The shortening of the interionic distance is known to be correlated to an increase of the force constants between pairs of ions. All these lead to an increase in the Raman vibrational wavenumbers [38]. It is also observed that the full widths at half-maxima (FWHMs) of these Raman active peaks are gradually increased with the increase of Al content. This is in accordance with reduced crystallinity of these hematite samples with high Al contents, caused by substitutional defects.

What is more, a new peak appears at 670-678 cm-1. Raman studies of different aluminum hydroxides show that the hydroxy deformation peak of boehmite (γ-AlOOH) is located at 674 cm-1 [39]. This indicates that the peaks at 670-678 cm-1 in the spectra of these Al-substituted hematite samples correspond to the deformation vibration of Al-OH in the structure [39, 40]. With the increase of Al content, the intensity of this peak gradually increases, indicating more Al-OH groups exist in the mineral structure. This is consistent with the results obtained by XPS O 1s spectra analysis of similar samples [15]. However, the appearance of this peak might also be related to structural disorder [38]. In a Raman study of a series of Al-doped hematite samples with particle sizes of 5-20 µm, an additional peak located at ~425-434 cm-1 was observed and assigned to a vibrational mode involving the [AlO6] octahedra. This peak was not observed in the present study probably because of the nano-dimension features of the hematite particles.

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**Figure 1.** The Raman spectra of these Al-substituted hematites.

**3.1.3 Morphology**

Almost uniform Al-doped hematite nanoparticles with various morphologies, including rhombohedral and plates, are obtained as shown in Figure 2 and Figure S5. As expected, the morphologies of these α-Fe2O3 particles change with different Al doping levels. The pure hematite, Hem, is rhombohedral (upper inset in Figure 2a, Figure S5a). These images conﬁrm the well-deﬁned single-crystalline structure. The size distribution histogram (Figure S5f) shows an average size of 43 ± 8 nm. In a typical HRTEM image (Figure 2a), interplanar distances of 0.411, 0.367 and 0.246 nm are observed. As shown in the corresponding SAED pattern (Figure 2e) with the incident electron beam along the [11] zone axis, these interplanar distances can be indexed to the (101), (12) and (110) facets, respectively. The angles between (12) with (101) and (110) facets are 55.6° and 90° respectively, which agree well with the theoretical angles. Another HRTEM image is also taken with the incident electron beam along the [41] zone axis, which shows that the (110) plane and (104) plane have an angle of 57.6o (bottom inset in Figure 2a). It seems that the {101}, {12}, {110} and {104} facets are the predominantly exposed facets of the rhombohedral hematite crystals.

With increasing Al content to 2.9 ± 0.1%, the AlH3 obtained crystals are also rhombohedral, but the edges become rougher (upper inset in Figure 2b, Figure S5b). The average crystal size of AlH3 is 66 ± 12 nm (Figure S5g). With the incident electron beam along the [11] zone axis the obtained lattice distances are the same as that of Hem (Figure 2b and f). However, along the [41] zone axis, no lattice corresponding to (110) planes is observed. This may suggest that {101}, {12}, {110} and {104} facets are the mainly exposed facets of AlH3 crystals, but the proportion of the total facets contributed by the {110} facets is reduced, and thus the area of the {110} facets is decreased, compared to the Hem crystals.

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**Figure** **2**. (a-d) Typical HRTEM images of individual Al-doped hematite samples (Hem, AlH3, AlH7, and AlH13). Corresponding typical low-magniﬁcation TEM image is displayed in the upper-left inset of each panel while another typical HRTEM image is presented in the lower right inset of each panel. (e−h) corresponding SAED patterns.

With further increase in Al content, the morphologies of the hematite crystals change to plates (upper insets in Figure 2c and d, Figure S5c-e). The typical HRTEM images show lattice fringes with an interplanar distance of ~0.250 nm and rotated with respect to each other by 60o. They match well with the (110), (20), and (20) facets with the incident electron beam along the [001] zone axis. This indicates that the basal planes of these high Al-containing hematite crystals are mainly {001} facets and the lateral planes include {110}, {20}, and {20} facets. It can also be observed that with increasing the Al doping level, the thickness of the disk-shaped crystals decreases but the diameter gradually increases to 150 ± 7 nm, 210 ± 13 nm and 295 ± 23 nm for AlH7, AlH9 and AlH13, respectively (Figure S5h-j). A comparison of the actual physical size with the CSD size of the Al-doped hematite sample shows that the two are almost the same for the sample with a small amount of Al (Hem and AlH3), but the physical size is much larger than the CSD size for the sample with high Al content (AlH7, AlH9 and AlH13). As the CSD size is the average size of crystals along diﬀerent axes, it can be greatly aﬀected by the crystal morphologies (e.g., length to width ratio) and structural defects in the structure [41, 42]. The big difference of the physical size and CSD size of the sample with high Al content further confirms the morphology change and/or creation of structural defects after insertion of a high amount of Al. Further, the edges of the plate crystals become rougher for samples with higher Al content than those with no or lower Al content. Conclusively, with increasing Al doping level, the growth rate of α-Fe2O3 along the [001] direction slows and the surface area of the {001} facet increases. Analysis of the SEM and TEM images reveals that the {001} facet areas are 48 ± 7%, 49 ± 6%, 77 ± 9%, 88 ± 15%, and 94 ± 20 % of the total areas of Hem, AlH3, AlH7, AlH9, and AlH13, respectively. However, the {001} facet area proportions of the samples with high Al contents, especially AlH13, must be overestimated, as the rough edges of these samples are assumed to be smooth cylindrical surfaces during the calculation. Modification of the hematite morphologies and an increase in the {001} facet areas probably arise because Al doping changes the atom densities along the different crystallographic directions, as proposed in our previous study [16]. It is noteworthy that most exposed facets of these Al-doped hematite crystals are observed by HRTEM here for the first time. In previous studies only lattice fringes corresponding to the (104) crystallographic plane [23] or (012) and {01} planes [43] are observed.

The HAADF image of AlH13 was collected to investigate the atomic-scale structure of these Al-doped hematite samples. Elemental mapping of Fe, Al, and O in a typical AlH13 crystal shows a uniform distribution of Al in the crystal (Figure S6). The HAADF image confirms the rough edges of the AlH13 crystals (Figure S6a and Figure S7). Further, this image shows that there are some dark areas in the background. This can probably be ascribed to the roughness of the {001} facets, resulting in the different thickness of the local domains in the crystals upon illumination by the electron beam [44, 45] and/or the existence of structural defects [15]. The observed atom arrangements (Figure 3a and Figure S7) match well with those of theoretical hematite crystals (Figure 3b). As the Cs-STEM images are Z-contrast images, where atomic brightness is typically proportional to Z1.6, the observed atoms are probably Fe and Al, and not O [15, 45]. The atomic image for AlH3 is also calculated based on the hematite model (ICSD 82137), with 0.13 Al(III) substituted for lattice Fe per octahedron (Figure 3c). It shows that the brightness of all atoms is equal, consistent with the experimental data (Figure 3a). This is mainly ascribed to the uniform distribution of Al and almost the same total number of Fe and Al below each position that electrons attack.

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**Figure 3**. (a) HAADF-STEM image of AlH13 in the [001] zone axis. (b) Fe (Al) atomic arrangements in the (001) facets (the yellow balls are Fe atoms while the light gray balls are Al atoms; the locations of Al cations are arbitrary while the Al/Fe atomic ratios are close to that in the sample). (c) Calculated atomic image for AlH13 based on the hematite model (ICSD 82137), by substituting 0.13 Al(III) at the position (12c) for Fe(III) per octahedron. The calculation was done with a thickness of 104.4 Å.

**3.1.4 X-ray photoelectron spectroscopy (XPS)**

X-ray photoelectron spectroscopy is a useful analytical technique to investigate the abundance and chemical state of elements of interest in the uppermost few atomic layers of solid sample surfaces. In the survey scans of these Al-doped hematite samples (Figure S8), the peak intensity of Al 2p is gradually increased with increased Al doping. Analysis of high-resolution Fe 2p and Al 2p spectra show that, with increasing Al doping, the binding energy (BE) of Fe 2p slightly shifts to lower BE while that of Al 2p shifts to higher BE (Figure 4 A and B). With the increase of Al content, there are an increasing amount of Fe-O-Al and Al-O-Al pairs. Compared with Fe-O-Fe pairs, in Fe-O-Al pairs the electron density around Fe is increased owing to the fact that the negativity of Al(III) (χ=1.5149) is much lower than that of Fe(III) (χ=1.7053), and thus an Al-O pair has more of an ionic bond character and the Fe-O pair has more of a covalent bond character [37, 46]. This leads to a right shift of Fe 2p. Compared with Fe-O-Al pairs, the electron density around Al in Al-O-Al pairs is decreased, leading to an increase in BE. The O 1s spectra on the mineral surfaces are not symmetrical, indicating the coexistence of lattice O, and O in hydroxyl groups and water molecules [47]. Deconvolution and fitting of the O 1s spectra of these hematite samples demonstrate that the proportions of hydroxyl O gradually increase with increasing Al dopant level, i.e., from ~31 % on the surface of Hem to ~47% on the surface of AlH13 (Figure 4C, Figure S9, and Table S2). This is commonly observed in Al-substituted metal oxides [1, 48, 49]. Owing to the high ionic potential resulting from smaller ionic radius [37, 50], Al3+ more strongly retains coordinated hydroxyl units, rendering Al-OH with a higher bond dissociation energy (BDE) than Fe-OH [51], and thus Al3+ can combine more strongly with hydroxyl groups.

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**Figure 4**. High-resolution X-ray photoelectron spectroscopy (XPS) scans of (A) Fe 2p

and (B) Al 2p for Hem and Al-doped samples (a, Hem, b, AlH3, c, AlH7, d, AlH9, e,

AlH13 and f, Cr(VI) adsorbed Hem), and the O 1s spectra of Hem before (C) and

after (D) Cr(VI) adsorption. (The circles are the experimental data, the thick, solid

curve is the best fit to the spectral data, the solid, dash and dash-dot curves represent

photopeak contributions from O2-, OH- and H2O, respectively.)

**3.2** **Cr(VI) adsorption**

**3.2.1 Isothermal adsorption**

A preliminary adsorption kinetic study shows that, during the first 30 min of adsorption, the adsorption of Cr(VI) from solution is very fast, after which it slows down. After reaction for 4 h, an adsorption equilibrium is achieved (Figure S9).  The results of isothermal adsorption experiments of Cr(VI) on the Al-substituted hematites are shown in Figure 5. When the initial concentration of Cr(VI) is low, the adsorbed concentration of Cr(VI) on hematite increases rapidly; with increasing concentration of Cr(VI), the adsorption rate becomes slower; and finally, the reaction reaches equilibrium. The isothermal adsorption curves of hematite samples with different Al contents are similar to that of Hem, and all conform to the L-type isotherm curve [52]. However, with an increase of Al substitution up to 9%, the maximum adsorption density generally decreases with increasing Al doping, compared to Hem, except for when the Al content is at its maximum of 13%, at which point the adsorption density is inversely increased above that for AlH9. All the adsorption isotherms are well fitted using the Langmuir equation, Y = AmaxKC/(1 + KC), where Y is the amount of Cr(VI) adsorbed (µmol·m-2), Amax the maximum adsorption density (µmol·m-2), C the equilibrium concentration of the adsorbate (µmol·L-1), and K a constant related to the adsorption energy as function of temperature and adsorption enthalpy [53]. The fitting results are shown in Figure 5 and Table S3. The Amax for Hem, AlH3, AlH7, AlH9, and AlH13 are 2.01, 1.54, 1.55, 1.21 and 1.47 µmol·m-2, respectively.

The Cr(VI) adsorption densities on the Al-doped samples generally decrease after Al doping. This can be ascribed to several phenomena. Firstly, with increasing dopant concentration there is significant variation in crystal morphology which likely results in a decrease in the densities of active adsorption sites. It is commonly known that different crystallographic faces exhibit unique charging and thus reaction characteristics [7, 8, 10, 11, 54]. The (001) face is the most stable crystalline plane on natural hematite surface, but, over the pH range of most natural and contaminated environments, the oxygen atoms on the {001} facets are doubly protonated (≡Fe2OH0), rendering the surface charge neutral and these sites relatively inert [7, 55, 56]. On the other hand, the oxygen atoms on the {12} surfaces are both singly (≡FeOH-0.5) and triply (≡Fe3O-0.5) coordinated, leading to variable charge depending on pH [57], while the {110} surfaces are composed of equal numbers of singly, doubly and triply coordinated surface oxygen groups [55]. Consequently, the adsorption densities of metals on {12} and/or {110} facets are typically higher than those on {001} facets, and indeed, Cr(VI) adsorption density on hematite nanoplates with exposed {001} facets is reported to be only 59% of that on hematite nanorods with exposed {001} and {110} facets [8]. Similarly, a study of Pb2+ adsorption on hematite single crystal surfaces by a combination of extended X-ray absorption ﬁne structure (EXAFS) spectroscopy and resonant anomalous X-ray reﬂectivity (RAXR) demonstrated that Pb2+ uptake was higher and pH dependence was greater on the {012} and {110} surfaces than on the {001} surface [10]. In the present study, pure hematite (Hem) crystals are rhombohedra with {101}, {12}, {110} and {104} facets exposed. Upon Al doping, the hematite particles change to platy crystals with increasing diameter and decreasing thickness. For these high Al-containing hematite crystals the basal planes are mainly {001} facets, and the lateral planes, including {110}, {120}, and {210} facets, account for only a small contribution to the total surface area. Consequently, the decline of the proportions of the active facets ({12}, {110}) and the increase of the inactive ({001}) facets act to decrease the Cr(VI) adsorption density.

Secondly, the substitution of Fe sites by Al sites might also result in a reduced Cr(VI) adsorption density, owing to the different acid-base properties of Al and Fe sites and their reactions with background electrolyte anions. The surface complexation constant for the dominant Cr(VI) species, HCrO4-, on iron (hydr)oxides is ~3 orders of magnitude greater than that on Al oxides [58-60]. Thus in Al doped samples the Cr(VI) is predominantly adsorbed on active Fe sites, and substitution of these Fe sites by relatively inactive Al sites likely results in reduced Cr(VI) adsorption density. This can also explain why the proportions of hydroxyl groups on the Al-substituted hematite surfaces increase but the Cr(VI) adsorption densities decrease with increasing Al doping. Furthermore, although the stability constant for protonation of Al sites is ~2 orders of magnitude greater than that for Fe sites, because Cr(VI) adsorption occurs in 0.1 M NaNO3 solution, the screening of the Al sites by NO3- is also likely a significant factor in reducing the Cr(VI) adsorption density on the Al-doped hematites [60]. Lastly, Al-substitution results in more vacancies on the hematite (001) facets which carry a large amount of negative charge, confirmed by acid-base titration experiment [15]. This increase in negative charge, and resulting electrostatic repulsion of HCrO4- likely also lead to a reduction of the Cr(VI) adsorption density. These factors were used to rationalize the effects of Al substitution on Cr(VI) adsorption on goethite [60].

These effects, however, do not account for the inversely increased Cr(VI) adsorption density on AlH13, above that for AlH9 (adsorption density on AlH13 inversely increased by ~21% compared to AlH9). This phenomenon might be explained by the fact that the edges of the platy crystals of AlH13 have many cracks, as shown in the SEM and TEM images (Figure 2, Figure S6 and Figure S7). This increases the areas of exposed edge faces, e.g. including {110}, {120}, and {210} facets, which probably provide an increased number of active sites for Cr(VI) adsorption, compared to AlH9.

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**Figure 5.** Isothermal adsorption curves of Cr(VI) adsorption on the Al-substituted hematite samples at pH4±0.05.

**3.2.2** **Characterization of Cr(VI) adsorbed hematite**

**3.2.2.1** **FTIR**

After Cr(VI) adsorption by Hem, new spectral peaks appear at 803, 836, 900 and 942 cm-1 (Figure 6). These peaks indicate the formation of Cr(VI) inner-sphere complexes, of which 803 and 836 cm-1 are assigned to monodentate mononuclear (MM) complexes and 900 and 942 cm-1 to bidentate binuclear (BB) complexes [8, 22, 61, 62]. With increased Al doping, the 803 cm-1, 900 cm-1, and 942 cm-1 peaks gradually disappear while the 836 cm-1 peak remains, indicating that with increasing Al content, the formation of MM complexes are favored over BB complexes, and thus Al doping suppresses the formation of BB complexes. This is consistent with a previous study of chromate adsorption on Al-substituted ferrihydrite, which demonstrates that the effect of Al substitution is mechanism-speciﬁc, with bidentate complexes disproportionately suppressed over monodentate [20]. For AlH13 the 942 cm-1 peak is inversely increased and a tiny peak appears at 948 cm-1. This suggests that more BB complexes and outer-sphere complexes are formed on AlH13 compared to the other Al-containing samples [8]. As is clearly observed in the TEM and SEM images (Figure 1 and Figure S3), the edges of the AlH13 disks are dentiform meaning that more {110} planes are exposed, on which Cr(VI) BB complexes form [8]. However, it is noteworthy that the Cr(VI) binding modes on the hematite surfaces may change upon drying [63]. The Cr(VI) outer-sphere complexes on the hematites, especially those with high Al contents, might be underestimated by the powder FTIR analysis of Cr(VI) adsorbed minerals, since drying favors inner-sphere complexation.

Adsorption of Cr(VI) also modifies the shape of the 637-659 cm-1 peak. This peak is related to the longitudinal lattice vibration on the mineral surfaces, which is parallel to the c-direction [64]. The peak intensity is decreased after Cr(VI) adsorption, especially for the Al-containing samples. This suggests that the corresponding Fe-O atoms are on the {104} and/or {001} facets, and that they also bind hydroxyl groups [65] to balance the surface charge before Cr(VI) adsorption. Increasing Cr(VI) is adsorbed by exchanging hydroxyl groups on these facets to form monodentate complexes [8, 22, 62], resulting in the attenuation of Fe-O vibration.

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**Figure 6.** FTIR spectra of the Al-substituted hematite samples before (black lines) and after (red lines) Cr(VI) adsorption.

**3.2.2.2 XPS analysis**

Surveyscans and high-resolution spectra of a typical Cr(VI) adsorbed hematite sample are shown in Figure S8 and Figure 4. High-resolution Fe 2p and O 1s spectra show that the binding energies of these atoms shift to lower energy after Cr(VI) adsorption (Figure 4). Further, the intensity of the peak corresponding to hydroxyl groups in the O 1s spectrum is greatly reduced (Figure 4d), compared to that in the pristine spectrum (Figure 4c). Results of fitting of the O 1s spectrum demonstrate that after Cr(VI) adsorption, the concentration of hydroxyl groups decreases from ~32 % before Cr(VI) adsorption to ~20 % after Cr(VI) adsorption. This suggests that hydroxyl groups on the mineral surface are exchanged with HCrO4− species [8, 62]. Generally, inner-sphere complexes might be formed on hematite surfaces by this kind of ligand exchange mechanism between hydroxyl groups and oxyanions [66, 67] and therefore, XPS confirms that Cr(VI) is adsorbed onto the hematite surface to form inner-sphere complexes via a ligand exchange mechanism. However, there are still some free hydroxyl groups on the Cr(VI) adsorbed hematite surfaces, the presence of which may be ascribed to the low reactivity of these remaining sites. Quantification of various O species on the Al-doped hematite surfaces demonstrates that with increasing Al dopant level the relative proportions of hydroxyl groups gradually increase (Figure 4, Figure S9 and Table S2). However, the corresponding Cr(VI) adsorption densities are inversely decreased. This may be related to the low affinity of Al-OH sites to Cr(VI) anions, in addition to the inert Fe-OH sites. Owing to the higher bond dissociation energy (BDE) of Al-OH (502 ± 11 kJ·mol−1) compared to Fe-OH (407 ± 1 kJ·mol−1) [51], Al3+ can bind more strongly with hydroxyl groups. Consequently, hydroxyl groups in Al-OH are harder to exchange with anions.

**3.3 Effects of Fe2+ on the transformation of Cr(VI) at hematite-water interfaces**

**3.3.1 Reaction of Fe2+ with hematite**

To investigate whether Fe2+ causes hematite transformation in the hematite, Fe2+, and Cr(VI) ternary systems, the reaction products of different concentrations of Fe2+ (0.75 or 2.24 mmol·L-1) with hematite were checked by powder XRD analysis. After the reaction of 0.75 or 2.24 mmol·L-1 Fe2+ with hematite for 4 h under anoxic conditions at pH4 ± 0.05, no obvious change in the hematite mineralogy is observed (Figure 7). Under these conditions, magnetite (JCPDS 19-0629) or maghemite (JCPDS 25-1402) are the most likely phases to form. It should be noted that in order to detect the possible appearance and growth of magnetite or maghemite, the ~0.30 nm peak (2 θ ≈ 29.6 o, Cu Kα) of these minerals, instead of the strong ~0.25 nm and ~0.15 nm peaks, should be monitored because the latter two peaks overlap with the corresponding strong peaks of hematite (JCPDS 89-0599). After carefully investigating the 28-32 o 2θ region of the XRD patterns, no peaks are observed (indicated by the light gray rectangle in Figure 7). A lack of phase transformation of the hematite is to be expected as the reaction of Fe2+ with hematite can induce some changes in the mineral structure, but not the formation of a new phase. Overall, at acidic conditions, Fe2+ tends to be be oxidatively adsorbed on hematite surfaces, with one electron transferred to a more oxidizing Fe(III) surface site, which is then reduced and desorbed as a newly formed Fe2+, such that there is little net adsorption [3, 29].

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**Figure 7**. Powder XRD analysis of the reaction products of Fe2+ with hematite under stirring for 4 h under anoxic conditions at 25 oC with different concentrations of Fe2+ (0.75 or 2.24 mmol·L-1), over a range of 5-85 degree (2 theta, Cu Kα). The reaction conditions: hematite = 1 g·L-1 and pH = 4±0.05.

**3.3.2 Cr species**

Aqueous Fe2+ in the absence of hematite can directly reduce Cr(VI), where increasing Fe2+ concentration compared to Cr(VI) results in increased Cr(VI) reduction: specifically, an equal molarity of Fe2+ to Cr(VI) reduces 33% of the Cr(VI), whereas Fe2+ with a concentration 3 times that of Cr(VI) reduces 100% of the Cr(VI) to Cr3+ (Figure 8 and Table S4). This effect is investigated in the hematite systems, by adding an equal or triple molar ratio of Fe2+ to Cr(VI), either pre or post Cr(VI) addition. Regardless of the order of Fe2+ addition, the presence of an equal molarity of Fe2+ significantly increases Cr removal from solution and results in some Cr(VI) reduction, while the presence of a triple molarity of Fe2+ almost completely removes Cr(VI) from solution and results in almost complete Cr(VI) reduction. For example, in the Fe2+ free Hem and AlH13 systems, Hem can remove 36% Cr(VI) from solution while AlH13 can remove 47% Cr(VI) from solution per unit mass of mineral (Figure 8 and Table S4). However, after the addition of an equal molarity of Fe2+ prior to Cr(VI) addition, there is a similarly increased Cr removal with increased Al doping, but the absolute proportions of Cr removed are increased in the presence of Fe2+: specifically, there is 42% removal of Cr by Fe2+-Hem, and 68% removal of Cr by Fe2+-AlH13. Furthermore, after the addition of a triple molarity of Fe2+ prior to Cr(VI) addition, again there is a similarly increased Cr removal with increased Al doping, but the absolute proportions of Cr removed are further increased in the presence of increased concentration of Fe2+: specifically, there is 71% removal of Cr by Fe2+-Hem, and 83% removal of Cr by Fe2+-AlH13. Overall the most efficient Cr removal is achieved with a Fe2+: Cr(VI) molar ratio of 3:1, where the Fe2+ is added after Cr(VI) adsorption, with 89% Cr removal from solution to the mineral surface. These results clearly show that the removal of Cr(VI) by hematite is enhanced in the presence of Fe2+, and is enhanced further still for Al-doped hematites in the presence of Fe2+. This is unlike the adsorption of As(V) species on hematite which is reported not to be substantially affected by Fe2+ [25].

In the first instance enhanced adsorption may be attributable to the influence of adsorbed Fe2+ on the hematite surface charge, in that Fe2+ adsorption should substantially shift the mineral surface potential to be more positive, such that the Cr(VI) surface complex electrostatic activity coefficient is reduced and Cr(VI) adsorption is increased [25]. In addition, enhanced adsorption may also be attributed to the reduction of Cr(VI) to Cr(III), explored further with XANES spectroscopy described below. In comparison with Hem, AlH13 adsorbs more and also reduces more Cr(VI) per unit mass of mineral. This can be explained by considering the effect of Al substitution on hematite crystals. It was reported recently that Al-substitution in hematite results in more Fe vacancies on the mineral (001) facets, forming new singly (≡FeOH−0.5) and triply (≡Fe3O−0.5) coordinated hydroxyl sites. This greatly enhanced the Pb2+ adsorption capacity [15]. Thus in the present study, it is likely that Fe2+ is more favorably adsorbed on AlH13 than Hem. As the reduction potential of Fe2+ adsorbed on iron (hydr)oxide surfaces is much lower than that of aqueous Fe2+/Fe3+ redox couples, the (hydr)oxide-associated Fe2+ has enhanced reduction capacity towards oxidized contaminants [26, 27]. Thus an enhanced adsorption of Fe2+ on AlH13 likely results in the higher total removal of aqueous Cr(VI) and its reduction and fixation at the mineral surfaces.

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**Figure 8**. Proportions of various Cr species at the end of reaction in various reaction systems involving a unit mass of Hem or AlH13, Cr(VI), with Fe2+ addition before or after Cr(VI) adsorption. The molar ratios of Fe2+ to Cr(VI) is 1:1 or 3:1.

The effect of Fe2+ on the fate of Cr(VI) adsorbed on the Al-doped hematite surfaces is also investigated via desorption experiments, where Cr that cannot be desorbed by 0.1 M NaOH solution is operationally defined as fixed Cr. For Hem the addition of an equal molarity of Fe2+ prior to Cr(VI) addition fixes 7% Cr on the mineral surfaces, whereas the addition of an equal molarity of Fe2+ after Cr(VI) addition fixes 27% Cr on the mineral surfaces. Similarly, for Hem with the addition of a triple molarity of Fe2+ prior to or after Cr(VI) addition, almost all the Cr(VI) is reduced to Cr(III), and 69% or 85% Cr was fixed on the mineral surfaces, respectively. This suggests that the addition sequence of Fe2+ affects the final partition of various Cr species between solutions and mineral surfaces, where overall, the addition of Fe2+ after Cr(VI) adsorption greatly increases the proportions of Cr fixed, independent of the molar ratios of Fe2+ to Cr(VI). In turn this suggests that adding Fe2+ to heavy metal adsorbed iron (hydr)oxide-based adsorbents or heavy metal polluted soils that are enriched in iron (hydr)oxide minerals could enhance Cr fixation and thus reduce Cr mobility, and as such could be a promising strategy for contaminant control and remediation. According to previous studies, the desorbable Cr(VI) is likely bonded to the surface hydroxyl groups [28], and thus can be exchanged by OH- anions, whereas the non-desorbable Cr(VI) is probably complexed with Fe(III) active sites by forming small irreversible Cr atom clusters [68], and/or incorporated into the micro-pores of the minerals, and/or into the mineral new surfaces or the surface layers [69-71].

**3.3.3 Valence of fixed Cr species on mineral surfaces**

Figure 9 depicts Cr K-edge XANES spectra of the fixed Cr on mineral surfaces in the Hem+Fe+Cr(1:1), Hem+Fe+Cr(3:1) and AlH13+Fe+Cr(3:1) systems along with the +3 and +6 Cr standards. Owing to the tetrahedral coordination of Cr6+ in CrO3, a large pre-edge feature appears at 5996.5 eV. This peak corresponds to the 1s to 3d orbital transition [72, 73]. However, in compounds where Cr has a valence of 3+ and has octahedral coordination, this pre-edge feature is very weak, such as in Cr2O3. In the spectrum for Hem+Fe2++Cr(1:1) an obvious pre-edge peak appears, indicative of the existence of some Cr(VI) fixed on the mineral surfaces. This part of Cr(VI) is possibly retained in nano-pores in the hematite crystals [74], which is not extractable by NaOH solution. However, in the spectra of Hem+Fe2++Cr(3:1) and AlH13+Fe2++Cr(3:1), no such a pre-edge peak can be observed. This indicates that Cr species fixed in these systems are almost entirely Cr3+.

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**Figure 9.** The Cr K-edge XANES spectra of Cr adsorbed on these Al substituted hematites. (a) Cr2O3, (b) CrO3, (c) Hem+Fe2++Cr(1:1), (d) Hem+Fe2++Cr(3:1), and (e) AlH13+Fe2++Cr(3:1).

# **4. Conclusions and environmental implications**

Owing to extremely small particle sizes, large surface areas, unique surface charge and redox-sensitive properties, iron (hydr)oxides in subsurface environments play a pivotal role in controlling the mobility, bioavailability and toxicity of various inorganic and organic contaminants in polluted soil and water systems [1, 24]. Hematite has received significant attention among the various types of iron (hydr)oxides because of its thermodynamic stability and prevalent occurrence in many soil and sediment environments, but also because it can display wide variations in particle size, morphology and reactivity [1, 2, 30]. Previous studies however have mainly focused on pure hematite minerals [8, 22], whereas in natural and contaminated environments Al substitution for lattice Fe is a common feature of iron (hydr)oxides. Indeed, the Al contents in natural hematite can be as high as 16 mol% [1, 32]. It is known that Al substitution in hematite minerals modifies their morphology, specifically modifying the relative proportions of different exposed facets, and that this can cause different affinity and reactivity towards contaminants [3, 8, 10, 11, 29, 54], but it is also known that Al sites have different reactivity from that of Fe sites, and this can result in changes in the mechanisms of uptake and release of these contaminants [20, 60]. Because of this behaviour the present study investigates the effect of Al doping and exposure to Fe2+ on Cr(VI) adsorption and retention under conditions similar to subsurface soil environments.

The present study shows that Al substitution in hematite reduces the proportions of exposed facets with high active site densities, resulting in a decrease in Cr(VI) adsorption density. Aluminum sites also weaken the chemical interactions of Cr(VI) with hematite surfaces, changing Cr(VI) inner-sphere complexes from binuclear bidentate to mononuclear monodentate. Consequently, the mobility of Cr(VI) is likely increased in soils with an abundance of Al-containing iron (hydr)oxide phases. However, the coexistence of Fe2+ and Fe (hydr)oxides is common in soil environments, where Fe2+ can be generated during the reduction of Fe (hydr)oxide minerals by small organic molecules and biomolecules produced by plants and microorganisms, weathering of Fe2+-bearing primary rocks, and microbial respiration and so on [24]. Importantly, the coexistence of Fe2+ with Fe (hydr)oxides and pollutants can modify the fate of these pollutants [24, 25, 28]. The present study shows that the presence of Fe2+ promotes the adsorption of Cr(VI) on hematite surfaces and also reduces part of the Cr(VI) to Cr(III)and firmly fixes a certain proportion of the Cr species. Furthermore, the coexistence of Fe2+ with Al-substituted hematite removes more Cr(VI) from solution than that removed with pure hematite. Even though adding Fe2+ to Cr(VI) adsorbed hematite remobilizes a small proportion of the Cr species, Fe2+ addition could be an efficient way to fix pollutants on the mineral surfaces. The effect of Fe2+ addition to increasing Cr adsorption and retention is potentially similar for other high-valence toxic metalloids, such as arsenate, arsenite, urinate, tungstate, antimonite and so on, and deserves further study. Nonetheless, the characteristics of Al-substituted hematite minerals in soil environments are much more complicated than the synthesized analogs used here. Natural iron (hydr)oxide minerals in soils and sediments commonly contain other impurities, such as Co and Ni [1, 13], and coexist with clay minerals or Mn oxides [21]. And naturally formed Fe (hydr)oxides may have higher reactivities than synthetic Fe (hydr)oxides [75]. Overall, however, the results demonstrated here provide important information on, and offer insights into, how iron (hydr)oxide minerals in subsurface environments help control the mobility and toxicity of contaminants, and provide a platform for extending the study of such processes in more complex soil and sediment systems.

**Associated content**

**Supporting information**

Powder XRD patterns, Rietveld refinement results, SEM images and particle size analysis, thermal gravimetric analysis, zeta potentials of Hem and AlH13 at different pHs from 3 to 10, STEM-EDS mapping and HAADF image of AlH13, X-ray photoelectron spectroscopy analysis of survey scan and O 1s spectra of Al-substituted hematite samples before and after Cr(VI) adsorption, Cr(VI) adsorption kinetics, fitting parameters of adsorption isothermal curves, and the relative proportions of various Cr species during the transformation of Cr(Ⅵ) on Hem and AlH13 surfaces by addition of Fe2+.

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**Conflicts of interest**

The authors declare no competing ﬁnancial interest.

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