*Supporting Information*

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

Shuqi Jianga,b,c**#**, Xinran Yana,b, c**#**, Caroline L. Peacockd, Shuang Zhanga,b,c, Wei Lia,b,c, Jing Zhange, Xionghan Fenga,b,c, Fan Liua,b,c, Hui Yina,b,c\*

aCollege of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China.

bKey Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtze River) Ministry of Agriculture, Wuhan 430070, China.

cHubei Key Laboratory of Soil Environment and Pollution Remediation Wuhan 430070, China.

dSchool of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

eBeijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China

#Thefirst two authors contributed equally.

\*Corresponding author. Tel./fax: +86 27 87280271. Email: [yinhui666@mail.hzau.edu.cn](mailto:yinhui666@mail.hzau.edu.cn) (H. Yin).

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**1. Powder XRD analysis**

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**Figure S1.** Powder XRD patterns of Al-substituted hematite samples over a range of (a) 5-85 o 2 theta (Blue lines are experiment data, red lines are calculated patterns, and gray lines are difference patterns), and (b) 30-40 o 2 theta, in which the gray dotted lines show the right shifts of the (104) and (110) peaks upon increasing the Al dopant level.

**Table S1**. The elemental analysis, specific surface area (SSA), lattice parameters, cell volume, calculated crystal density, coherent scattering domain (CSD) sizes of these Al-substituted hematite samples.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Al(Al+Fe) (mol%) | SSA  (m2·g-1) | Lattice parameters | | Cell volume (Å3) | Crystal density  (g·cm-3) | CSD  (nm) | RWP% |
| a (Å) | c (Å) |
| Hem | 0 | 29 | 5.0381(12) | 13.7642(34) | 302.56(17) | 5.2587(29) | 44.62(37) | 3.94 |
| AlH3 | 2.85(10) | 27 | 5.0311(18) | 13.7515(49) | 301.44(24) | 5.2237(41) | 68.90(15) | 6.01 |
| AlH7 | 6.70(7) | 21 | 5.0253 (9) | 13.7403(25) | 300.51(12) | 5.1662(21) | 71.36(79) | 4.21 |
| AlH9 | 9.05(15) | 28 | 5.0231(12) | 13.7397(34) | 300.22(17) | 5.1261(28) | 59.38(66) | 4.28 |
| AlH13 | 12.86(21) | 50 | 5.0193(70) | 13.7340(19) | 299.65(94) | 5.0630(16) | 19.03(24) | 5.75 |

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**Figure. S2** Variations of lattice parameters *a* (a), *c* (b), cell volume (c) and crystal density (d) of these hematite samples with the increase of ﬁnal Al concentrations. Blue squares are experimental data, and red lines are the best linear ﬁt.

### 2. Thermal gravimetric analysis

Hematite samples are quite stable upon heating in N2 atmosphere from room temperature to 800 oC. However compared to the pure hematite, Hem, the stability of Al-substituted hematite is generally reduced with the increase of Al substitution for Fe.

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**Figure S3.** The thermal gravimetric analysis profiles of Al-substituted hematites.

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**Figure S4**. The zeta potentials of Hem and AlH13 at different pHs from 3 to 10.

**3. SEM images and particle sizes analysis**

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**Figure S5.** FESEM images and corresponding size distribution histograms of Al-substituted hematite crystals. (a) and (f), Hem; (b) and (g), AlH3; (c) and (h), AlH7; (d) and (i), AlH9; (e) and (j), AlH13.

### 5. STEM-EDS mapping and HAADF image of AlH13.

### STEM-EDS mapping of a typical Cr3+ adsorbed AlH13 crystal was conducted on Talos F200S. The High angle annular dark-field (HAADF) image (a) shows the typical disk-shape of AlH13. The EDS spectrum (b) shows the existence of Fe, Al and O in the crystal however no Cr signal is observed owing to its low concentration. Elemental mapping of Fe (c), Al (d) and O (e) distribution demonstrate that Al3+ is evenly distributed in the crystal.

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**Figure S6.** High angle annular dark-field (HAADF) image (a) and EDS spectrum (b) and elemental mapping of Fe (c), Al (d) and O (e) distribution on a typical Cr(VI) adsorbed AlH13 crystal. In panel (b), Si and Cu signals are from the background.

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**Figure S7**. A typical raw HAADF image of AlH13.

### 6. X-ray photoelectron spectroscopy analysis (XPS)

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**Figure S8**. XPS broad scans of Al-doped hematites before and after Cr(VI) adsorption. A, Hem; b, AlH3; c, AlH7; d, AlH9; e, AlH13 and f, Cr(VI) adsorbed Hem.

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**Figure S9**. O 1s spectra of Al-doped hematite samples. (The circles are the experimental

data, the thick, solid curve is the best fit of the spectral data, the solid, dash, and dash-dot

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

**Table S2**. Parameters used for fitting O (1s) spectra of Al-doped hematites before and after Cr(VI) adsorption

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | Species | BE(eV) | FWHM(eV) | Percentage (at.%) |
| Hem | O2- | 530.16 | 1.50 | 53.17 |
| OH- | 531.89 | 2.20 | 30.57 |
| H2O | 533.70 | 2.60 | 16.26 |
| AlH3 | O2- | 530.33 | 1.50 | 50.44 |
| OH- | 532.11 | 2.20 | 38.08 |
| H2O | 533.97 | 2.60 | 11.47 |
| AlH7 | O2- | 530.24 | 1.50 | 41.54 |
| OH- | 532.03 | 2.20 | 43.65 |
| H2O | 533.68 | 2.60 | 14.81 |
| AlH9 | O2- | 530.24 | 1.50 | 44.80 |
| OH- | 532.07 | 2.20 | 45.14 |
| H2O | 537.79 | 2.60 | 10.06 |
| AlH13 | O2- | 530.34 | 1.50 | 42.21 |
| OH- | 532.05 | 2.20 | 47.28 |
| H2O | 534.05 | 2.60 | 10.51 |
| Cr(VI) adsorbed Hem | O2- | 529.70 | 1.50 | 56.54 |
| OH- | 530.58 | 2.20 | 19.77 |
| H2O | 532.16 | 2.60 | 23.69 |

### 7. Chromate adsorption experiments

### 7.1 Adsorption kinetics

Hematite (0.15 g) was added in 195 mL of 0.1 mol·L-1 NaNO3 solution, and the pH of the suspension was adjusted to pH4±0.05 by 0.1 mol·L-1 HNO3 or NaOH solution. Then 5 mL of 0.1 g·L-1 Cr(Ⅵ) solution was added to the above mineral suspension, followed by re-adjust the mixture pH to pH4±0.05. The adsorption reaction started by shaking at a speed of 250 r·min-1 at 25 oC. At the pre-determined time interval, a certain volume of the suspension was withdrawn and immediately filtrated through a 0.22 μm membrane. The Cr(VI) content in the filtrate was determined by chromium-1,5-Diphenylcarbazide (DPCI) spectrophotometric method [1].

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**Figure S10.** Adsorptionkinetics of Cr(Ⅵ) on Hem.

**7.2** **Isothermal curve fitting parameters.**

**Table S3.** Langmuir fitting parameters of the isothermal adsorption curves of Cr(Ⅵ) on these Al-substituted hematite samples.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | Parametersa | | |
| Amax (μmol·m-2) | K | R2 |
| Hem | 2.01 | 0.1352 | 0.9685 |
| AlH3 | 1.54 | 0.1189 | 0.9631 |
| AlH7 | 1.55 | 0.2608 | 0.9479 |
| AlH9 | 1.21 | 0.4288 | 0.9742 |
| AlH13 | 1.47 | 0.1398 | 0.9888 |

a The Langmuir equation is as *Y*=AmaxK*C*/(1+K*C*), where *Y* is the amount of Me2+ adsorbed (μmol·m-2), Amax the maximum capacity (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 [2].

**Table S4.** The relative proportions of various Cr species during the transformation of Cr(Ⅵ) on Hem and AlH13 surfaces with the addition of Fe2+.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | Solution | | Mineral surface | | | Removal rate | |
| Cr(Ⅵ) | Cr(III) | Cr(Ⅵ) | Cr(III) | fixed | Exp. | theory |
| Hem+Cr | 64%a | — | 36% | — | — | 36% | 36% |
| AH13+Cr | 53% | — | 47% | — | — | 47% | 47% |
| Fe2++Cr(1:1) | 64% | 36% | — | — | — | 36% | 35% |
| Fe2++Cr(3:1) | 0% | 100% | — | — | — | 100% | 100% |
| Hem+ Fe2++Cr(1:1) | 37% | 21% | 32% | 3% | 7% | 63% | 72% |
| AlH13+ Fe2++Cr(1:1) | 24% | 8% | 39% | 4% | 25% | 76% | 83% |
| Hem+Cr+ Fe2+(1:1)b | 9% | 11% | 45% | 8% | 27% | 91% | 100% |
| Hem+ Fe2++Cr(3:1) | 0% | 29% | 1% | 1% | 69% | 100% | 100% |
| AlH13+ Fe2++Cr(3:1) | 0% | 17% | 2% | 1% | 80% | 100% | 100% |
| Hem+Cr+ Fe2+(1:3)b | 0% | 11% | 2% | 2% | 85% | 100% | 100% |

aThese valueswere calculated based on the unit mass of Hem or AlH13.

bThe proportions of various Cr species are calculated based on the total amount of Cr(Ⅵ) adsorbed on the Hem surfaces.

**References**

[1] Bartlett, R., James, B., 1979. Behavior of chromium in soils: Iii. Oxidation1. Journal of Environmental Quality 8, 31-35.

[2] Kinniburgh, D.G., 1986. General purpose adsorption isotherms. Environ. Sci. Technol. 20, 895-904.