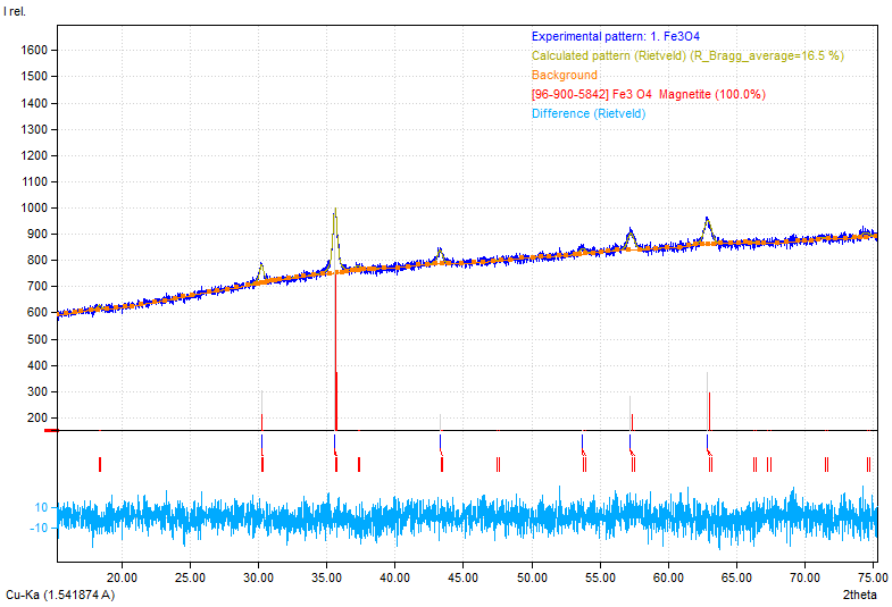
Electronic Supplementary Material (ESI) for RSC Advances.

Structural elucidation of hexavalent Cr-adsorbed on surfaces and bulks of Fe_3O_4 and α-FeOOH

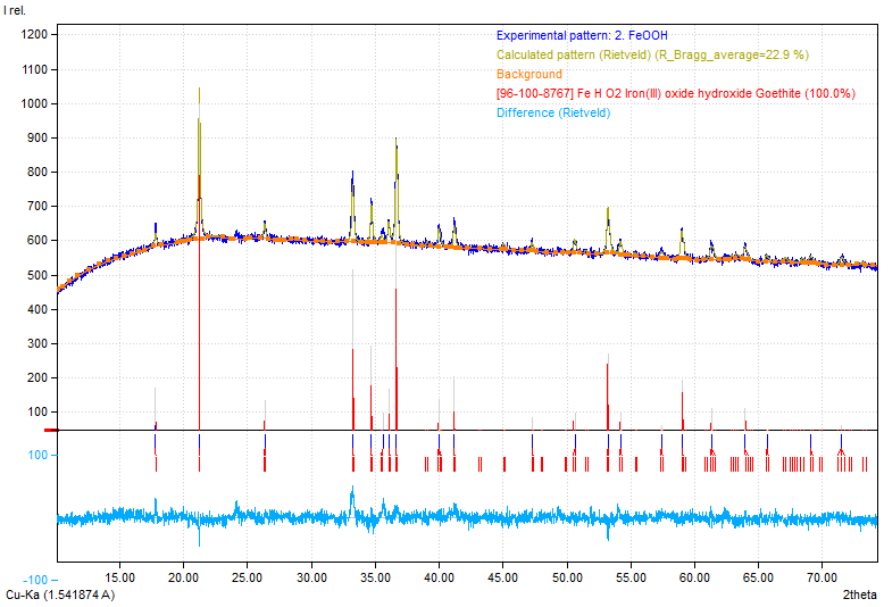
Nichapha Senamart,[a] Krittanun Deekamwong,[b] Jatuporn Wittayakun,[b] Sanchai Prayoonpokarach, [b] Narong Chanlek,[c] Yingyot Poo-arporn,[c] Suttipong Wannapaiboon,[c] Pinit Kidkhunthod[c] and Sirinuch Loiha*[a]

S1 Phase indexing of the obtained samples by employing Match! Software using Crystallography Open Database (COD) and their refined unit cell parameters obtained by the combined-package FullProf Software.

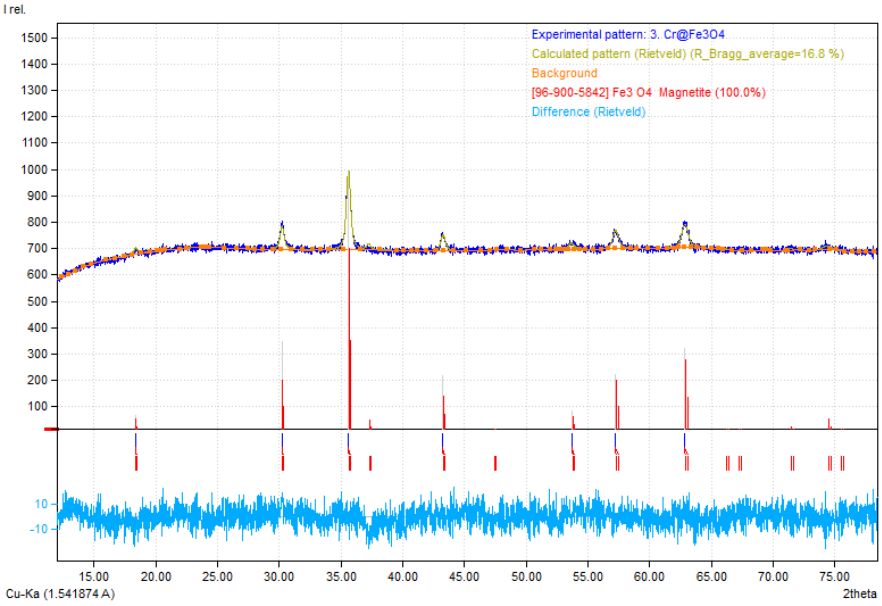
Data /Samples	**Fe_3O_4**	**FeOOH**	**Cr@Fe_3O_4**	**Cr@FeOOH**
Indexed phase	Fe_3O_4 Magnetite	FeOOH Iron(III) oxide hydroxide Goethite	Fe_3O_4 Magnetite	FeOOH Iron(III) oxide hydroxide Goethite
COD Entry number	96-900-5842	96-100-8767	96-900-5842	96-100-8767
Figure of Merit (FoM)	0.8516	0.9064	0.8736	0.9073
Crystal system	cubic	orthorhombic	cubic	orthorhombic
Space group	Fd-3m	Pbnm	Fd-3m	Pbnm
Database unit cell parameters (Å)	a = b = c = 8.3440 Å	a = 4.6188 Å, b = 9.9528 Å, c = 3.0236 Å	a = b = c = 8.3440 Å	a = 4.6188 Å, b = 9.9528 Å, c = 3.0236 Å
Refined unit cell parameters				
a	8.36375	4.61080	8.36239	4.60876
b	8.36375	9.96234	8.36239	9.95935
c	8.36375	3.02355	8.36239	3.02265
α	90.0	90.0	90.0	90.0
β	90.0	90.0	90.0	90.0
γ	120.0	90.0	90.0	90.0
Chi^2	0.774	1.15	0.862	1.21



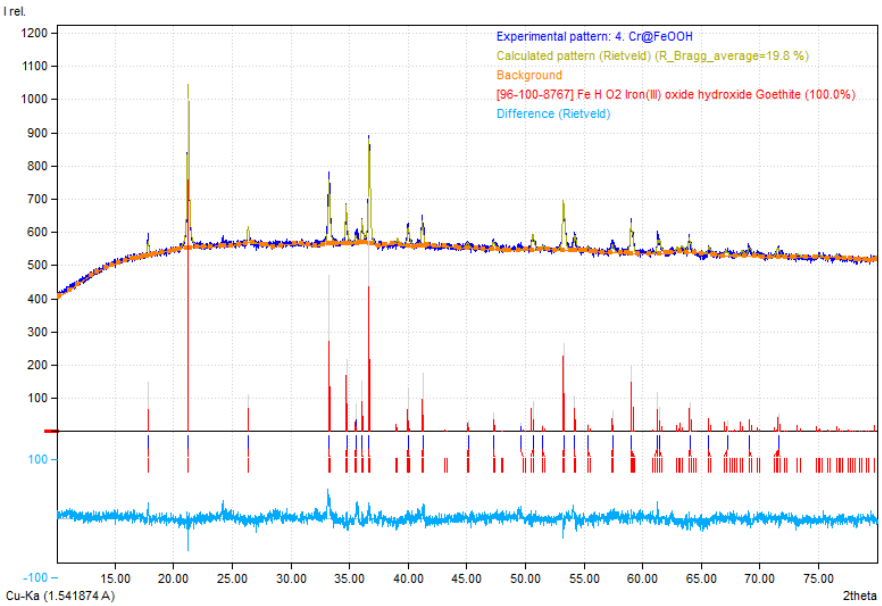
S2 XRD pattern indexing and Rietveld refinement of the sample Fe_3O_4 showing the refined phase as Magnetite Fe_3O_4 (COD, Entry Number 96-900-5842).



S3 XRD pattern indexing and Rietveld refinement of the sample FeOOH showing the refined phase as iron(III) oxide hydroxide goethite (COD, Entry Number 96-100-8767)

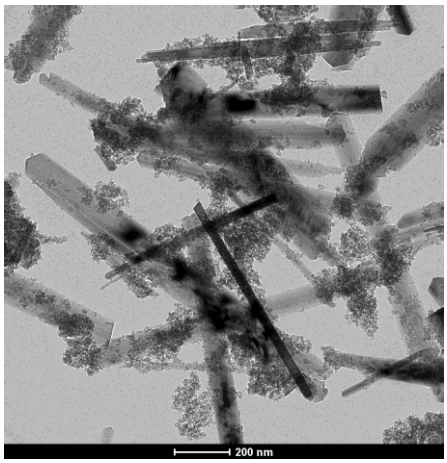


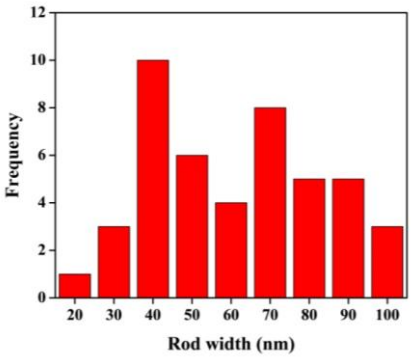
S4 XRD pattern indexing and Rietveld refinement of the sample Cr@Fe_3O_4 showing the refined phase as Magnetite Fe_3O_4 (COD, Entry Number 96-900-5842)

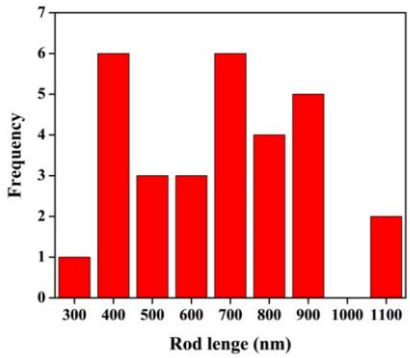


S5 XRD pattern indexing and Rietveld refinement of Cr@FeOOH showing the refined phase as iron(III) oxide hydroxide goethite (COD, Entry Number 96-100-8767)

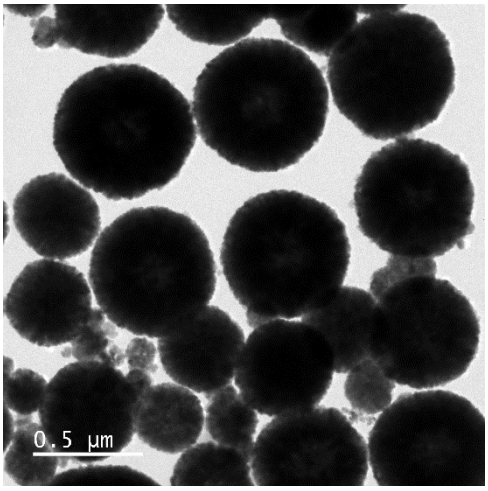
α-FeOOH

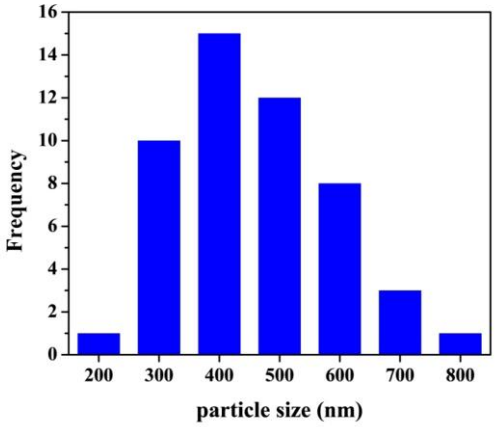




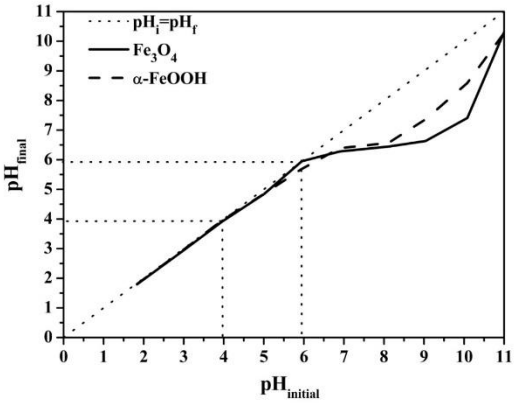


Fe_3O_4

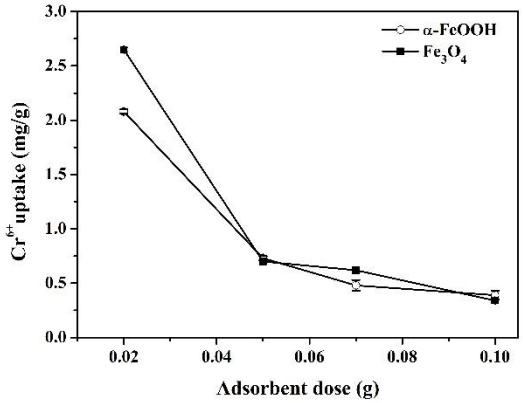




S6 Particle size distribution of Fe_3O_4 and α-FeOOH calculated by TEM images.

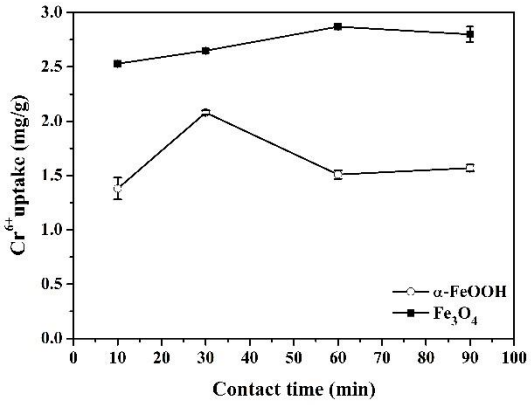


S7 Point of zero charges (PZC) of as-synthesized Fe_3O_4 and α-FeOOH adsorbents.



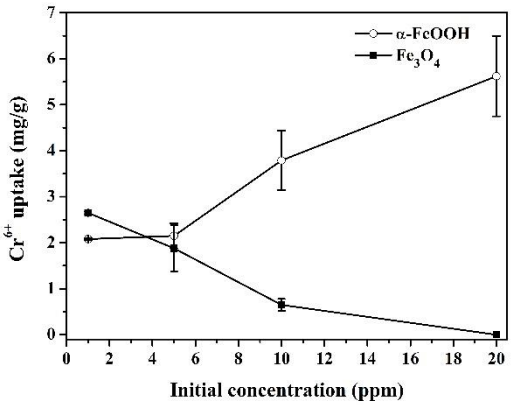
S8 Effect of adsorbent dose on the Cr^{6+} uptake by the Fe_3O_4 and α-FeOOH, adsorption condition: Cr^{6+} initial concentration = 1 ppm, volume 50 mL, pH = 3, time = 30 min.

The effect of the adsorbent dose on Cr^{6+}-adsorption is described in Fig. S8. The maximum Cr^{6+} uptakes on α-FeOOH and Fe_3O_4 are 2.08 and 2.65 mg/g, respectively, at the adsorbent dose of 0.02 mg. The Cr^{6+} uptakes on both adsorbents decreased with increasing adsorbent doses. The results might be attributable to a decrease in the adsorbent-surface area by particle agglomeration when the dosing was increased.[1, 2] Each particle could strongly induce magnetism facilitating the particle accumulation of Fe_3O_4. Meanwhile, the suspended α-FeOOH also aggregates to large particles in water due to the high electrostatic attraction of the particles.



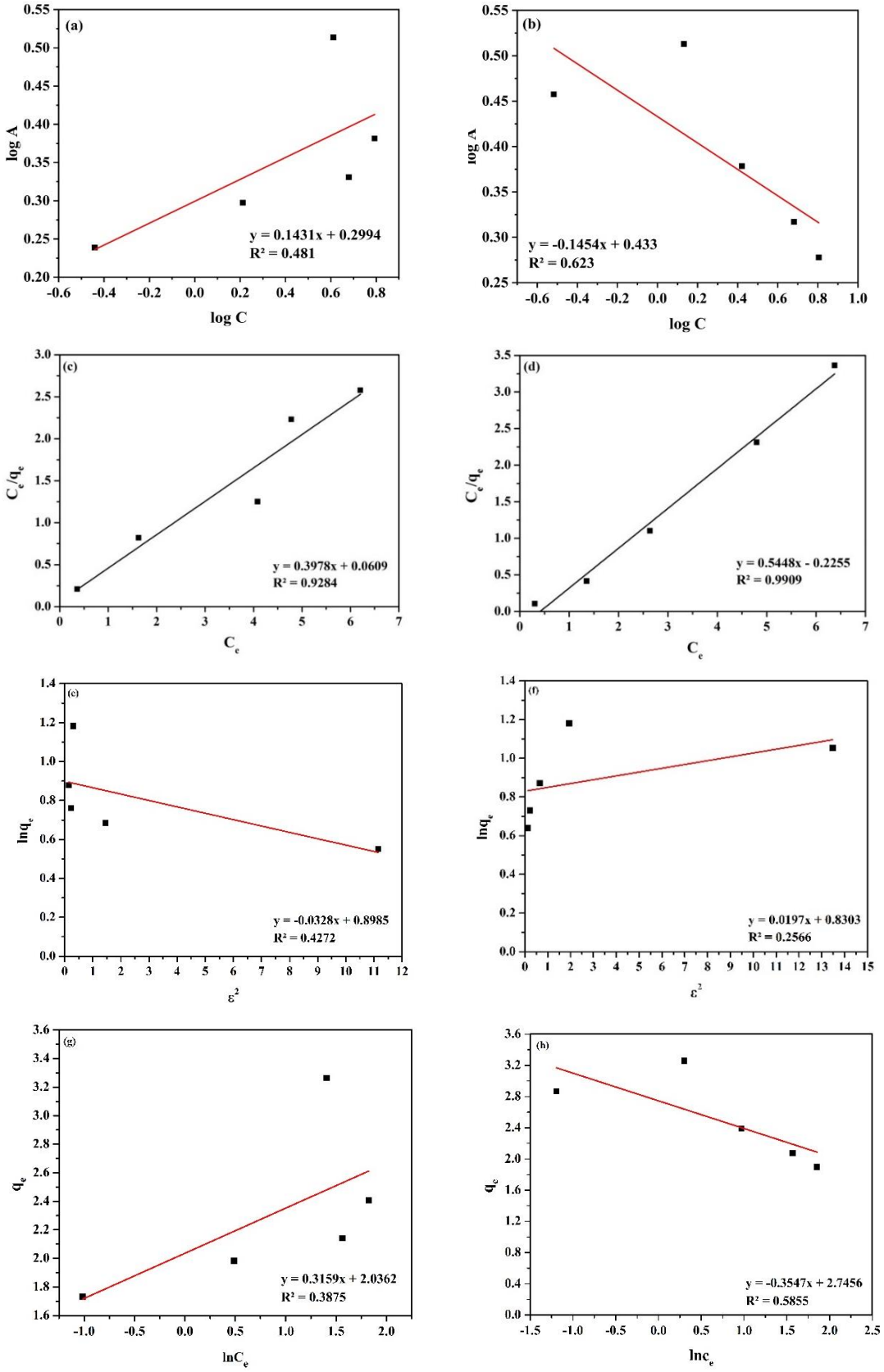
S9 Effect of contact time on the Cr^{6+} uptake by the Fe_3O_4 and α-FeOOH, adsorption condition: Cr^{6+} initial concentration = 1 ppm, volume 50 mL, pH = 3, adsorbent dose 0.4 g/L.

The effect of contact time on the Cr^{6+} removal was investigated from 10 to 90 min. Time-dependences of Cr^{6+} uptake on α-FeOOH and Fe_3O_4 are shown in Fig. S9. The adsorption saturation time of the materials was rapidly achieved at about 30 min and 60 min for α-FeOOH and Fe_3O_4, respectively. The decrease of Cr-uptake from α-FeOOH after 30 min might be due to a spontaneous change in adsorption conditions such as pH. The maximum Cr-uptake of 2.87 mg/g was observed by Fe_3O_4.



S10 Effect of initial concentration on the Cr Cr^{6+} uptake by the Fe_3O_4 and α-FeOOH, adsorption condition: Cr^{6+} solution volume 50 mL, pH = 3, adsorbent dose 0.4 g/L, time = 30 min.

The effect of initial concentration Cr^{6+} solution was carried out from 1-20 ppm. The adsorption capacities of the adsorbents are shown in Fig. S10. The adsorption capacity of α-FeOOH increased with increasing initial concentration according to the surface area of the α-FeOOH. In contrast, the adsorption capacity of Fe_3O_4 decreased with increasing initial concentration. The adsorption saturation is reached at the beginning of the adsorption process indicating low surface binding of the adsorbents. [3, 4]



S11 Adsorption isotherms fitted with models of Freundlich (a-b), Langmuir (c-d), Dubinin-Raduscke visch-Kanager (e-f) and Temkin (g-h) isotherms of α-FeOOH and Fe_3O_4, respectively.

S12 Adsorption parameters calculated from Freundlich, Langmuir, Dubinin-Radusckevisch-Kanager (DRK) and Temkin adsorption models of Cr^{6+} adsorption by α-FeOOH and Fe_3O_4.

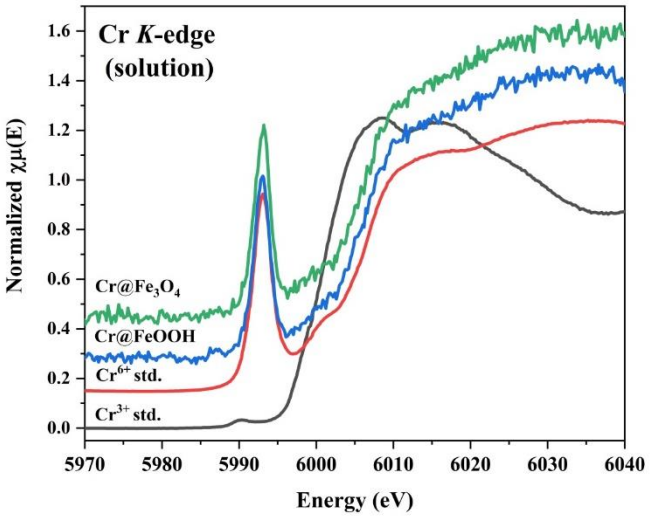
Isotherm	Isotherm parameter	Materials	
		α-FeOOH	**Fe_3O_4**
Freundlich	K_f (mg/g)	1.35	1.54
	n	6.99	-6.88
	R^2	0.4810	0.6237
Langmuir	Q_m (mg/g)	2.51	1.84
	b	6.53	-2.42
	R^2	0.9284	0.9909
DRK	$q_{(D-R)}$ (mg/g)	2.4559	2.2940
	E (kJ/mol)	3.904	n.a.
	R^2	0.4272	0.2940
Temkin	k_1 (J/mol)	0.3159	-0.3547
	k_2 (L/g)	629.9875	4.3455×10^{-4}
	R^2	0.3875	0.5855

Table S13 Kinetic parameters for Cr^{6+} adsorption of α-FeOOH and Fe_3O_4

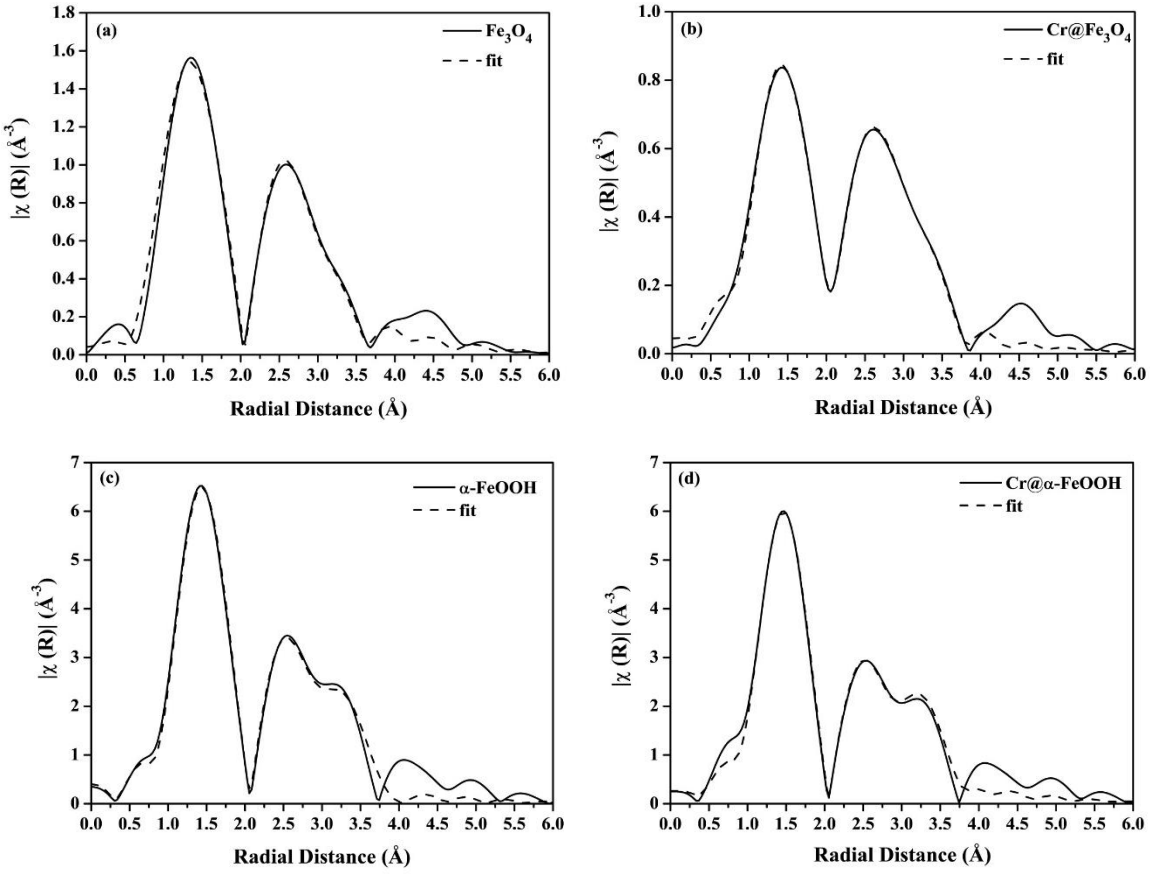
Materials	Pseudo-first order			Pseudo-second order		
	q_e	**k_1**	**R^2**	**q**	**k_2**	**R^2**
α-FeOOH	2.90	2.48	0.2369	3.19	0.02	0.9663
Fe_3O_4	2.42	5.53	0.9965	2.52	0.05	0.9987

S14 Thermodynamic parameters of α-FeOOH and Fe_3O_4 for Cr^{6+} adsorption.

Materials	ΔH° (kJ/mol)	ΔS° (J/mol•K)	$\Delta G°_{298}$ (kJ/mol)	$\Delta G°_{313}$ (kJ/mol)	$\Delta G°_{333}$ (kJ/mol)
α-FeOOH	-4.42	-2.09	-3.85	-3.76	-3.72
Fe_3O_4	10.48	49.79	-4.35	-5.10	-6.09



S15 Cr *K*-edge XANES spectra of $Cr@Fe_3O_4$ and Cr@FeOOH compared with Cr-standards.



S16 Fourier transforms of the $k^3(\chi)$-weighted in Fe *K*-edge of EXAFS data collected from the Fe_3O_4 (a) $Cr@Fe_3O_4$ (b) α-FeOOH (c) and Cr@α-FeOOH (d).

S17 EXAFS fitting parameters of k^3 (χ) weight of Cr *K*-edge on $Cr@Fe_3O_4$ and Cr@FeOOH.

Sample	Bond	Distance (Å)	Coordination number (CN)	Debye-Waller factor (σ^2)
$Cr@Fe_3O_4$	Cr-O	1.22	1.1	0.013
	Cr-O	1.56	2.0	0.008
	Cr-O	1.87	2.0	0.010
	Cr-Cr	2.41	2.0	0.018
	Cr-Cr	3.62	1.4	0.005
Cr@FeOOH	Cr-O	1.33	2.2	0.006
	Cr-O	1.59	1.9	0.018
	Cr-Cr	3.17	2.0	0.022

References

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