Introduction

Hexavalent Cr\(^{6+}\) ions are toxic contaminants because of their mutagenicity, carcinogenicity, and teratogenicity.\(^{1–5}\) Toxic Cr\(^{6+}\) species generally exist in negatively charged forms, such as the ions of hydrogen chromate (HCrO\(_4\)), chromate (CrO\(_4^{2–}\)), and dichromate (Cr\(_2\)O\(_7^{2–}\)), depending on solution pH and concentration.\(^{6–9}\) However, no conclusive spectroscopic proof of structural changes in adsorbents and adsorbates is available.\(^{6–9}\) X-Ray absorption spectroscopy (XAS) is a powerful tool for the element-specific characterization of local structure and chemistry. The electronic and local structures or geometry of chromium species in water will be explored. Understanding the stability of Cr-species on the adsorbents is beneficial to the development of new materials from the waste treatment process. Wei et al.\(^{10}\) illustrated the determination of Cr-contamination in kitchen wastewater by XAS. The Cr-species distribution in the solution was estimated. Likewise, Meena and Arai\(^{11}\) could explore the Cr\(^{3+}\)/Cr\(^{6+}\) ratio and Cr-structures on surfaces and bulks of Fe\(_3\)O\(_4\) and α-FeOOH\(^{†}\).

Magnetite (Fe\(_3\)O\(_4\)) and goethite (α-FeOOH) were synthesized via a hydrothermal approach and utilized as adsorbents for Cr\(^{6+}\) removal in an aqueous medium. The typical crystal structures of the synthesized Fe\(_3\)O\(_4\) and α-FeOOH were confirmed by XRD and TEM. Fe\(_3\)O\(_4\) in a spherical shape with a surface area of 32 m\(^2\) g\(^{−1}\) was established. While α-FeOOH had a rod-like form with a larger surface area of 84 m\(^2\) g\(^{−1}\).

Cr\(^{6+}\) removal in an aqueous solution was studied in various conditions to evaluate thermodynamic and kinetic parameters. The adsorption isotherms on both adsorbents fit the Langmuir model indicating monolayer adsorption. Fe\(_3\)O\(_4\) showed a better adsorption ability than α-FeOOH even though it had a lower surface area. XAS and XPS analysis strongly evidenced the production of stable Cr\(^{3+}\) species of Fe\(_{3x}^{3−}α\)Cr\(_x\)OOH and Fe\(_{3x}^{3−}α\)Cr\(_x\)O\(_4\) by Cr\(^{6+}\) reduction and migration processes into the bulk structure. Thus, the existence of stable Cr-species in Fe\(_3\)O\(_4\) structure strongly affected Cr-adsorption ability rather than the surface area of the adsorbent. However, the precipitated Cr\(_2\)O\(_3\) and HCrO\(_4\) molecules electrostatically adsorbed on the outer surface of α-FeOOH without bulk transformation. The presence of physisorbed FeO–HCrO\(_4\) species on α-FeOOH led to low reducibility and adsorption capability of Cr\(^{6+}\).
because it has a suitable redox potential for Cr\textsuperscript{6+} reduction and excellent magnetic properties.\textsuperscript{27,28} It is widely known that Fe\textsuperscript{3+} in magnetite can reduce Cr\textsuperscript{6+} to Cr\textsuperscript{3+}, creating Cr\textsuperscript{3+}-hydroxide or mixed substances via an adsorption and reduction process, namely reductive precipitation.\textsuperscript{29,30} This adsorption behavior on the Fe\textsubscript{3}O\textsubscript{4} surface was explored and Cr\textsuperscript{3+} and Fe\textsuperscript{3+}-(oxy)hydroxides were passivated on the adsorbent surface.\textsuperscript{31} The adsorption ability and structural stability of Fe\textsubscript{3}O\textsubscript{4} are strongly affected by solution pH and the homogeneity of iron oxide particles. The effect of the passivation layer on bulk structure deserves our study. In addition, the relationship between adsorption ability and phase stability in bulk-iron oxides needs to be investigated. Understanding the stable Cr-forms on the ion-oxides is promising for catalyst applications.\textsuperscript{31}

In the present study, iron oxides of Fe\textsubscript{3}O\textsubscript{4} and α-FeOOH were synthesized by the hydrothermal method and used as Cr\textsuperscript{6+} adsorbents. The crystalline structure, morphology, and surface area of the bare and adsorbed materials were characterized. The Cr-adsorption ability and behavior were explored. The adsorbent surfaces and bulk structures were elucidated by XPS and XAS.

**Experimental**

**Materials and methods**

**Materials.** The chemicals including iron(III) nitrate nonahydrate (Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, 98%, Merck), iron(m) chloride (FeCl\textsubscript{3}, 98%, ACROS), potassium dichromate (K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}, 99.9%, LOBA), sodium acetate (NaOAc, 99.5%, LOBA), potassium hydroxide pellets (KOH, 85%, LOBA), hydrochloric acid (HCl, 37%, Q\textregistered{R}eC™), ethylene glycol (EG, AR grade, Q\textregistered{R}eC™), potassium hydroxide (KOH, 85%, LOBA), hydrochloric acid (HCl, 37%, Q\textregistered{R}eC™), ethylene glycol (EG, AR grade, Q\textregistered{R}eC™), and 1,5-diphenylcarbazone (50% diphenylcarbazide, ACS grade, Merck) were used in this work.

**Methods.** The crystal structures of α-FeOOH and Fe\textsubscript{3}O\textsubscript{4} were revealed by powder X-ray diffraction (XRD; PANalytical, EMPYREAN). The XRD patterns were indexed by Match! Software using the Crystallography Open Database (COD), which was available at Beamline 1.1 W (Multiple X-ray Techniques), Synchrotron Light Research Institute, Thailand, SLRI. The unit cell parameters are refined by using FullProf Software. Morphologies were detected by transmission electron microscopy (TEM; Tecnai G\textsuperscript{2}). The oxidation states of the samples before and after adsorption were determined by X-ray absorption spectroscopy (XAS) under the 3.2 and 5.2 beamlines (SLRI) in the intermediate photon energy ranges of Cr K-edge (5.7–6.7 keV), Fe K-edge (7.0–8.0 keV), Fe L\textsubscript{3}-edge (0.7–0.73 keV) and O K-edge (5.2–5.5 keV), respectively. The chemical states of Fe, Cr and O were analyzed by X-ray photoelectron spectroscopy (XPS; PHI5000 Versa Probe II, ULVAC-PHI, Japan) at the SUT-NANOTEC-SLRI Joint Research Facility, 5.2 beamline.

**Synthetic procedures**

**Synthesis of α-FeOOH.** Goethite (α-FeOOH) was synthesized by the following hydrothermal route.\textsuperscript{31} Iron solution was prepared by dissolving 4.85 g of Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O into 10 mL of deionized (DI) water. The solution was then slowly dropped into 10 mL of 4.8 M KOH solution. The mixture was transferred to a Teflon-lined autoclave and crystallized at 100 °C for 6 h. The crystallized sample was then washed with DI water and ethanol several times, and the resultant brown powder of goethite was dried overnight at 50 °C.

**Synthesis of Fe\textsubscript{3}O\textsubscript{4}.** Magnetite (Fe\textsubscript{3}O\textsubscript{4}) was synthesized by the following route.\textsuperscript{31} 1.94 g of FeCl\textsubscript{3} solution was dissolved into 40 mL of EG in a two-necked round-bottom flask under N\textsubscript{2} atmosphere. The solution mixture was stirred for 30 min and then 10 mL of 1.35 M NaOAc in EG was then added. After 3 h, the mixture was transferred to a Teflon-lined autoclave and heated to 190 °C for 24 h. The obtained powder was separated by a magnetic bar. The resultant black powder of Fe\textsubscript{3}O\textsubscript{4} was washed with DI water and ethanol several times and dried overnight at 50 °C.

**Cr\textsuperscript{6+} adsorption analysis.** A stock solution of 100 ppm Cr\textsuperscript{6+} was prepared from K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}. Working solutions with desired concentrations were prepared by diluting the stock solution with DI water. Adsorption experiments were carried out by adding each adsorbent to 50 mL of Cr\textsuperscript{6+} solution and stirring vigorously. After adsorption, the adsorbents were separated from the solution by centrifugation for α-FeOOH and using a magnet for Fe\textsubscript{3}O\textsubscript{4}. Cr\textsuperscript{6+} concentrations were determined by the colorimetric method. Each sampling solution was added to 1,5-diphenylcarbazide ligand with 10% (v/v) of H\textsubscript{2}SO\textsubscript{4} (pH = 2) to form chromium complex. The absorbance of this complex was collected by using UV-Vis spectrophotometry at λ\textsubscript{max} = 540 nm.\textsuperscript{34,35} The Cr adsorption capacity of the absorbents (mg g\textsuperscript{-1}) was calculated as:

\[
q_e = \frac{(C_0 - C_e)}{W},
\]

where \(C_0\) (mg L\textsuperscript{-1}) and \(C_e\) (mg L\textsuperscript{-1}) are the initial and equilibrium metal concentrations, respectively, \(V\) (L) is the solution volume, and \(W\) (g) is the adsorbent weight.

Adsorption isotherms were detected by the Langmuir (eqn (1)) Freundlich (eqn (2) and (3)), Dubinin–Raduskevich–Kananger (eqn (4)–(6)) and Temkin (eqn (7)) models.\textsuperscript{36}

\[
\begin{align*}
C_e &= \frac{1}{bQ_m} + \frac{C_e}{Q_m}, \\
q_e &= K_f C_e^{1/n}, \\
\log q_e &= \log K_f + \frac{1}{n} \log C_e, \\
\ln q_e &= \ln q_O + \kappa (e^{-\beta C_e}), \\
\varepsilon &= RT \ln \left( 1 + \frac{1}{C_e} \right), \\
E &= \frac{1}{\sqrt{2b}}, \\
q_e &= k_1 \ln(k_2) + k_1 \ln C_e,
\end{align*}
\]

where \(q_e\) is the amount of adsorbed Cr\textsuperscript{6+} (mg g\textsuperscript{-1}), \(C_e\) is the equilibrium concentration (mg L\textsuperscript{-1}), \(b\) is the adsorption equilibrium constant (L mg\textsuperscript{-1}), \(Q_m\) (mg g\textsuperscript{-1}) is the maximum adsorption capacity of the adsorbent.
adsorption capacity for the Langmuir model, \( K_L \) is Freundlich constants \( (\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}) \) and \( n \) is heterogeneity factor, representing the adsorption capacity and the adsorption intensity, respectively. \( q(e) \) is the theoretical adsorption capacity \( (\text{mg g}^{-1}) \), \( \beta \) is a constant related to adsorption energy for a mole of the adsorbate \( (\text{mol}^2 \text{kJ}^{-2}) \), \( R \) is the ideal gas constant \( (0.008314 \text{kJ K}^{-1} \text{mol}^{-1}) \), \( T \) is the absolute temperature \( (K) \), \( E \) \( (\text{kJ mol}^{-1}) \) is the mean free energy per molecule of adsorbate when it transfers from the bulk of the solution (infinity) to the adsorbent surface, \( k_1 \) and \( k_2 \) are Temkin constants, where \( k_1 \) is related to the heat of adsorption \( (\text{J mol}^{-1}) \) and \( k_2 \) is the equilibrium binding constant \( (\text{L g}^{-1}) \).

The adsorption thermodynamics of \( \alpha \)-FeOOH and Fe\(_3\)O\(_4\) was determined at the temperatures of 25 °C, 40 °C and 60 °C using 1 ppm Cr\(_{6+}\) solution and 0.02 g of each adsorbent. The effects of different initial Cr\(_{6+}\) concentrations \( (1–20 \text{ ppm}) \), adsorbent doses \( (0.02–0.1 \text{ g}) \), and contact times \( (10–90 \text{ min}) \) in the Cr adsorption efficiency were investigated. The optimization of pH for Cr\(_{6+}\) removal was conducted in the range of 1–7, which covers the point of zero charges (PZC) of both absorbents.

The stability and adsorption behavior of Cr species on adsorbent surfaces were investigated by performing a reusability test. Each adsorbent was separated from the solution and dried overnight at 50 °C before starting a new cycle.

**Results and discussion**

**Structures of \( \alpha \)-FeOOH and Fe\(_3\)O\(_4\)**

The crystal structures of as-synthesized and Cr-adsorbed Fe\(_3\)O\(_4\) and \( \alpha \)-FeOOH were determined by XRD as shown in Fig. 1a and b, respectively. The XRD pattern of \( \alpha \)-FeOOH indicated its orthorhombic structure. The lattice constants of \( \alpha \)-FeOOH structure were calculated as \( a = 4.611 \text{ Å}, \) \( b = 9.962 \text{ Å}, \) \( c = 3.024 \text{ Å} \) (JCPDS no. 29-0713).\(^{37,38}\) The diffraction pattern of Fe\(_3\)O\(_4\) indicated its cubic structure (JCPDS no. 19-0629)\(^{39,40}\) with a lattice constant of \( a = b = c = 8.364 \text{ Å} \). The phase indexing and the refined unit cell parameters were reported in ESI data S1\(^\dagger\) and their corresponding XRD refinement in S2–S5.\(^\dagger\) Specifically, the Fe\(_3\)O\(_4\) and Cr@Fe\(_3\)O\(_4\) samples were indexed as magnetite Fe\(_3\)O\(_4\) phase (cubic, space group \( \text{Fd3m} \)), while the \( \alpha \)-FeOOH and Cr@FeOOH samples were indexed as iron (\( m \)) oxide hydroxide goethite phase (orthorhombic, space group \( \text{Pbnm} \)).

A closer inspection of the refinement results, the addition of chromium species into the materials led to a slight shrinkage of the unit cell parameters compared to the pristine materials. This observation suggested the incorporation of Cr\(_{3+}\) into the material matrix of Fe\(_3\)O\(_4\) (or FeOOH) without the presence of an additional crystalline impurity phase. In these cases, the atomic site occupancy could not be precisely defined. In addition, XAS was used to propose the local structures of Cr and Fe species in the obtained materials.

The TEM images and lattice parameters of \( \alpha \)-FeOOH and Fe\(_3\)O\(_4\) are displayed in Fig. 2. The \( \alpha \)-FeOOH exhibited short-range-order and rod-like structures (Fig. 2a). The selected area electron diffraction (SAED) pattern of rod-like particles confirmed the orthorhombic structure of \( \alpha \)-FeOOH with the (130) and (061) characteristic planes. Its particle size was in the range of 620 (\( \pm 219 \)) × 55 (\( \pm 21 \)) nm as shown in S6.\(^\dagger\) The TEM image of Fe\(_3\)O\(_4\) in Fig. 2b revealed spherical particles of 400 ± 124 nm with characteristic planes of (311) and (422).\(^{31}\) The BET surface areas of \( \alpha \)-FeOOH and Fe\(_3\)O\(_4\) were 84 m\(^2\) g\(^{-1}\) and 32 m\(^2\) g\(^{-1}\), respectively. The larger particle size of Fe\(_3\)O\(_4\) led to a lower surface area.

**Cr-adsorption ability**

**Effect of pH.** The PZC values of Fe\(_3\)O\(_4\) and \( \alpha \)-FeOOH were 5.95 ± 0.04 and 3.95 ± 0.06, respectively (S7\(^\dagger\)). The Cr-adsorption dependency on pH is shown in Fig. 3. When pH < PZC, surfaces of Fe\(_3\)O\(_4\) and \( \alpha \)-FeOOH are protonated to a positive charge. Thus, the adsorption behavior of Fe\(_3\)O\(_4\) and \( \alpha \)-FeOOH is facilitated by an electrostatic mechanism with negative Cr-compounds \( (\text{HCrO}_4^-) \), \( \text{CrO}_4^{2-} \), and \( \text{Cr}_2\text{O}_7^{2-} \).\(^{40}\) The adsorbent surface does not favor Cr\(_{6+}\) adsorption with a pH increase.\(^{41}\) The highest Cr-adsorption ability of both adsorbents was detected at pH = 3.

Fe\(_3\)O\(_4\) had a higher Cr-adsorption ability than \( \alpha \)-FeOOH, indicating its stronger attraction to the negative compounds of Cr\(_{6+}\). Thus, pH = 3 was selected as the optimized value to reach the maximum capacity of the adsorbents. The maximum Cr\(_{6+}\) uptakes by \( \alpha \)-FeOOH and Fe\(_3\)O\(_4\) were determined as about 2.08 mg g\(^{-1}\) and 2.87 mg g\(^{-1}\), respectively. In addition, the effects of adsorbent dose, initial concentration and contact time of Cr-adsorption were discussed in S8–S10.\(^\dagger\)

**Adsorption behavior of Fe\(_3\)O\(_4\) and \( \alpha \)-FeOOH**

**Adsorption kinetics.** The kinetic parameters of Cr\(_{6+}\) adsorption on \( \alpha \)-FeOOH and Fe\(_3\)O\(_4\) are summarized in S13.\(^\dagger\) The given
correlation coefficient ($R^2$) of the adsorbents obeyed the pseudo-second order model. The model implies that the rate law for adsorption is described in terms of an initial concentration of Cr rather than in terms of adsorbent concentration. In addition, the chemisorption process is implicated in a rate-determining step of Cr on both ion-oxides. 45,46

**Adsorption thermodynamics.** Adsorption isotherms were fitted based on the Langmuir and Freundlich, Dubinin–Raduskevich–Kanager and Temkin models (S11†), and the corresponding fitting parameters and correlation coefficients are listed in S12.† The Cr$^{6+}$ adsorption behaviors of α-FeOOH and Fe$_3$O$_4$ obeyed the Langmuir model (higher regression coefficient ($R^2$)) indicating that adsorption takes place at a specific homogeneous site, and monolayer coverage was formed on the adsorbent surface. 42–44 A low $b$ value implied a strong binding ability. 28 Therefore, the lower $b$ value of Fe$_3$O$_4$ indicated its stronger Cr$^{6+}$ adsorption ability than that of α-FeOOH.

The thermodynamic parameters of α-FeOOH and Fe$_3$O$_4$ are listed in S14.† Gibbs’s free energy changes ($\Delta G^\circ$) for both adsorbents had negative values, confirming a spontaneous nature of adsorption. 34 An α-FeOOH had a negative standard enthalpy change ($\Delta H^\circ$) implying an exothermic process. 47 α-FeOOH had a negative entropy change ($\Delta S^\circ$) indicating the decreased randomness at the solid/solution interface. 48 In contrast, Fe$_3$O$_4$ showed an endothermic process from a positive $\Delta H^\circ$ value indicating that an ion-exchange on the adsorbent surface might occur. 49 The positive $\Delta S^\circ$ of Fe$_3$O$_4$ implied randomness at the solid–solution interface during the adsorption process due to adsorption and subsequent desorption. 48

The reusability of both adsorbents for five cycles is shown in Fig. 4 to support the thermodynamic hypothesis of α-FeOOH and Fe$_3$O$_4$. Different adsorption behaviors of the adsorbents were exhibited. The Cr$^{6+}$ uptake of Fe$_3$O$_4$ dramatically decreased (90–95%) in the subsequent cycles. On the other hand, the Cr$^{6+}$ uptake of α-FeOOH slowly decreased by 55–60% in the subsequent cycles. These results implied that the Fe$_3$O$_4$ surface was completely adsorbed by Cr-species and it was difficult to detach from the surface. In contrast, the α-FeOOH surface was weakly adsorbed by the adsorbent due to a weak interaction (physical adsorption) which probably detached from the surface.

**Analysis of the adsorbed species on adsorbents**

**Surface analysis of α-FeOOH and Fe$_3$O$_4$ by XPS.** The oxidation states of surface elements in the pristine and Cr-adsorbed adsorbents were analyzed by XPS (Fig. 5). The C 1s peak at 284.8 eV was used as a reference to correct electrostatic charging. The binding energies of Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ in Fig. 5a and b corresponded to Fe$_3$O$_4$ and α-FeOOH. The peaks of octahedral Fe$^{3+}$, octahedral Fe$^{2+}$, and tetrahedral Fe$^{3+}$ at 710.7 eV, 711.7 eV, and 714.1 eV were determined in the pristine Fe$_3$O$_4$ sample corresponded to the typical Fe$_3$O$_4$ structure. The corresponding energies of Cr@Fe$_3$O$_4$ were found at 710.3 eV, 711.7 eV, and 713.9 eV, respectively, which were slightly lower

---

**Fig. 2** TEM images of (a) α-FeOOH and (b) Fe$_3$O$_4$.

**Fig. 3** Effect of pH on Cr$^{6+}$ uptake by the Fe$_3$O$_4$ and α-FeOOH adsorption condition: Cr$^{6+}$ initial concentration = 1 ppm, adsorbent dose = 0.4 g L$^{-1}$, time = 30 min.

**Fig. 4** Reusability for Cr$^{6+}$ removal of Fe$_3$O$_4$ and α-FeOOH adsorbents with Cr$^{6+}$ initial concentration = 1 ppm, adsorbent dose = 0.4 g L$^{-1}$, pH = 3, time = 30 min.
than those of the pristine Fe$_3$O$_4$. In addition, the area ratio of Fe$_{2+}$/Fe$_{3+}$ in Cr@Fe$_3$O$_4$ was higher than the pristine Fe$_3$O$_4$. The result indicated a decrease of Fe$_{3+}$ in Fe$_3$O$_4$ after Cr-adsorption. The Fe 2p energies at 710.7 eV and 712.3 eV corresponding to Fe$_2$O$_3$ and $\alpha$-FeOOH components, respectively, were observed on both the pristine $\alpha$-FeOOH and Cr@FeOOH.

It was implied that surface species of $\alpha$-FeOOH were not changed after Cr-adsorption. The O 1s peaks of pristine Fe$_3$O$_4$ at 530.5 eV, 531.8 eV, and 533.1 eV appeared from lattice oxygen (O$_{\text{lattice}}$), oxygen in the adsorbed-hydroxyl group (OH$_{\text{ads}}$), and oxygen in water-adsorbed molecules (H$_2$O$_{\text{ads}}$), respectively (Fig. 5c and d). After Cr adsorption, the binding energies of O$_{\text{lattice}}$ and OH$_{\text{ads}}$ slightly decreased to 530.1 eV and 530.9 eV, respectively, indicating a presence of O$_{\text{lattice}}$ in CrO(OH) over the Fe$_3$O$_4$ surface. The O 1s peaks of Cr@Fe$_3$O$_4$ at 530.5 eV, 530.5 and 531.5 eV corresponded to O$_{\text{lattice}}$, OH$_{\text{ads}}$ and adsorbed H$_2$O species, respectively. The adsorbed H$_2$O was not determined on Cr@FeOOH. In addition, the binding energy of O$_{\text{lattice}}$ in Cr@FeOOH was slightly higher than that in $\alpha$-FeOOH. These results possibly indicate the presence of precipitate oxide form of Cr$_2$O$_3$ on the $\alpha$-FeOOH surface.

The binding energies of Cr 2p$_{3/2}$ and Cr 2p$_{1/2}$ in Cr@Fe$_3$O$_4$ and Cr@$\alpha$-FeOOH are shown in Fig. 6. The Cr 2p$_{3/2}$ to Cr 2p$_{1/2}$ splitting energies of both samples were about 10 eV which was typically found in a Cr$^{3+}$/Cr$^{6+}$ mixture. The Cr 2p$_{3/2}$ exhibited the characteristics of Cr$^{3+}$ in Cr$_2$O$_3$ (576.6 eV), CrO(OH)/Cr(OH)$_3$ (577.7 eV) and Cr$^{6+}$ in CrO$_x$ (579.9 eV). Those characters were similarly found in Cr@Fe$_3$O$_4$ and Cr@FeOOH. However, the area ratio of Cr$_2$O$_3$/CrO(OH) in Cr@FeOOH was higher than that in Cr@Fe$_3$O$_4$. The finding correlated with the enhancement of O$_{\text{lattice}}$ species of Cr@FeOOH in O 1s spectrum. This result revealed the presence of precipitated Cr$_2$O$_3$ species on the $\alpha$-FeOOH surface at pH 3.

It was noticeable that a high CrO(OH) content in Cr@Fe$_3$O$_4$ might proceed through Cr$^{3+}$ migration on the Fe$_3$O$_4$ surface.

### Bulk analysis of $\alpha$-FeOOH and Fe$_3$O$_4$ by XAS

**XANES of Fe K-edge and L$_3$-edge.** The Fe K-edge spectra of Fe$_3$O$_4$ and $\alpha$-FeOOH compared with the iron oxide standards are shown in Fig. 7. The Fe K-edge energy of the pristine Fe$_3$O$_4$ was calculated as 7120.7 eV while the energy of Cr@Fe$_3$O$_4$ slightly shifted to a lower value of 7120.5 eV. This result indicated that ferrous specie (Fe$^{2+}$) in Fe$_3$O$_4$ increased after Cr-adsorption. On the other hand, the Fe K-edge energies of the pristine $\alpha$-FeOOH and Cr@FeOOH were similar (Fig. 7b). Thus, the bulk structure of $\alpha$-FeOOH was not affected by Cr-adsorption process.

In principle, Fe L$_3$-edge has a better resolution for fine structures and manifests a lower intrinsic lifetime broadening than Fe K-edge. Thus, the local geometry of Fe$_3$O$_4$ was further investigated by Fe L$_3$-edge. The spectra of Fe$_3$O$_4$ and Cr@Fe$_3$O$_4$ are presented in Fig. 7c. The $I_a/I_b$ intensity ratio in the Fe L$_3$-edge spectrum was used to determine the mixed valence state. The Cr@Fe$_3$O$_4$ had $I_a/I_b$ ratio of 0.59 which was higher than that of pristine Fe$_3$O$_4$ (0.53). The higher $I_a/I_b$ intensity ratio...
corresponded to the lower Fe²⁺ content in the tetrahedral site of Fe₃O₄.

XANES of Cr K-edge. A comparison of Cr K-edge in the Cr-adsorbed samples with CrCl₃ (Cr³⁺) and K₂Cr₂O₇ (Cr⁶⁺) standards are shown in Fig. 8. The Cr⁶⁺ (4-fold Cr–O) character was exhibited by a strong pre-edge intensity at 5999 eV. Besides, a weak pre-edge intensity was found in Cr³⁺ (6-fold Cr–O). XANES profile of Cr@Fe₃O₄ explored a reduction of pre-edge intensity compared with the Cr⁶⁺ standard. Thus, the Fe₃O₄ could partially reduce Cr⁶⁺-species (HCrO₄⁻/CrO₄²⁻/Cr₂O₇²⁻) to Cr³⁺ on the surface under aqueous solution at pH 3. This behavior was also observed on Cr@FeOOH. However, a decrease in pre-edge intensity of Cr@FeOOH was much lower than that of Cr@Fe₃O₄. Furthermore, Cr⁶⁺ was a major species in the solution after adsorption (S15†).

EXAFS of Fe and Cr K-edge

EXAFS analysis of Cr K-edge. The EXAFS of Fe K-edge XANES analysis. The EXAFS analysis is reported in Table 1 and S16.† The 4-fold and 2-fold Fe–O bonds with distances of 1.61 Å and 1.89 Å, respectively, were observed in bare Fe₃O₄. The bond length of 1.61 Å was shorter than the typical tetrahedral Fe–O bond length in Fe₃O₄ (1.88 Å) due to the existence of oxygen vacancies. The second shell of the Fe₃O₄ structure consisted of Fe–O in Fe₂O₃ or tetrahedral Fe–O in FeOOH. For α-FeOOH, the first shell consisted of tetrahedral Fe–O bonds with an average bond distance of 1.97 Å (Table 1). Moreover, 3-fold Fe–Fe bonds with bond distances of 3.00 Å and 3.30 Å were also displayed. Octahedral Fe–O (1.98 Å) and Fe–Fe (3.47 Å) bonds. After Cr adsorption, the first shell represented 2-fold (1.97 Å) and 4-fold (2.40 Å) of Fe–O bonds. The bond distances fitted well with octahedral Fe–O in Fe₂O₃ or tetrahedral Fe–O in α-FeOOH. For α-FeOOH, the first shell consisted of tetrahedral Fe–O bonds with an average bond distance of 1.97 Å (Table 1). Moreover, 3-fold Fe–Fe bonds with bond distances of 3.00 Å and 3.30 Å were also displayed. Octahedral Fe–O (1.98 Å) and Fe–Fe (3.00 Å) bonds in Cr@FeOOH were similar to α-FeOOH. Thus, the bulk structure of α-FeOOH did not change after Cr adsorption.
bond distances of 1.33 Å and solution pH 2.0 in Fig. 10b and Table S17. (Cr\(^{3+}\)) and CrO\(_3\) (Cr\(^{6+}\)) were formed on Cr@Fe\(_3\)O\(_4\). Moreover, 2-(1.87 Å) adsorbed on the surface of both adsorbents. Some Cr\(^{6+}\) was a predominant form of HCrO\(_4\) in an aqueous solution at pH 3. Removal mechanism of Cr\(^{6+}\) on Fe\(_3\)O\(_4\) and \(\alpha\)-FeOOH. In the solution pH 2.0–6.5, Cr\(^{6+}\) in an aqueous solution existed as a predominant form of HCrO\(_4\)\(^−\) (eqn (8)). This species moved and adsorbed on the surface of both adsorbents. Some Cr\(^{6+}\) was reduced to Cr\(^{3+}\) or precipitated on surfaces which confirmed by the existence of Cr\(_2\)O\(_3\), CrO(OH)/Cr(OH)\(_3\) and CrO\(_3\) from XPS surface analysis. Compared with \(\alpha\)-FeOOH, the lower Cr\(_2\)O\(_3\)/CrO(OH) ratio in Cr@Fe\(_3\)O\(_4\) implied the Cr-ion migration into the bulk structure of Fe\(_3\)O\(_4\). XANES and EXAFS as bulk analysis further revealed this behavior. The contained Fe\(^{2+}\) species inside Fe\(_3\)O\(_4\) could reduce Cr\(^{6+}\) in HCrO\(_4\)\(^−\) to Cr\(^{3+}\) (eqn (9)) with a relatively slow reaction rate due to the limited electron transfer rate in the maghemite (Fe\(_2\)O\(_3\)) passivation layer. Then, Cr\(^{3+}\) species migrated to bulk Fe\(_3\)O\(_4\) and formed Fe\(_{1−x}\)Cr\(_x\)OOH containing Fe\(^{3+}\) and Cr\(^{3+}\) in between FeOOH lattice (eqn (10)). These dissolved octahedral Cr\(^{3+}\)-O sites could prevent the bulk structure of Fe\(_3\)O\(_4\) from collapsing.

\[
\text{H}_2\text{CrO}_4 → \text{HCrO}_4^- + \text{H}^+ \quad (8)
\]

\[
2\text{HCrO}_4^- + 2\text{Fe}^{2+} + 10\text{H}^+ → 2\text{Fe}^{3+} + 2\text{Cr}^{3+} + 6\text{H}_2\text{O} + \text{O}_2 \quad (9)
\]

\[
(1−x)\text{Fe}^{3+} + (x)\text{Cr}^{3+} + 2\text{H}_2\text{O} → \text{Fe}_{1−x}\text{Cr}_x\text{OOH(s)} + 3\text{H}^+ \quad (10)
\]

Additionally, the XPS and XAS results revealed the increase of FeO species in Fe\(_3\)O\(_4\) after Cr-adsorption. Thus, the most likely form was a Fe\(_{1−x}\)Cr\(_x\)O\(_3\) solid solution containing Fe\(^{2+}\) and Cr\(^{3+}\) in forms of FeO and Cr\(_2\)O\(_3\). The presented species might be created through Cr\(^{6+}\) reduction mechanism by FeO in Fe\(_3\)O\(_4\) (or FeO–Fe\(_2\)O\(_3\)) structure as expressed by eqn (11).

\[
2\text{Fe}^{2+} + 4\text{HCrO}_4^- + 4\text{H}^+ → 2\text{Fe}_{1−x}\text{Cr}_x\text{O}_4 + 4\text{H}_2\text{O} + 3\text{O}_2 \quad (11)
\]

Meanwhile, \(\alpha\)-FeOOH surface changed to positive [FeO–OH\(_2\)]\(^{2+}\) species at pH = 3.0 (eqn (12)). These [FeO–OH\(_2\)]\(^{2+}\) molecules could react with the presented negative HCrO\(_4\)\(^−\) species by an electrostatic force (physiosorption) and created FeO–HCrO\(_4\) species (eqn (13)). This adsorption behavior did not change the local geometry and oxidation state of iron atoms in \(\alpha\)-FeOOH.

\[
\text{FeOOH} + \text{H}^+ → \text{FeO}–\text{OH}_2^+ \quad (12)
\]

\[
\text{FeO}–\text{OH}_2^+ + \text{HCrO}_4^- → \text{FeO}–\text{HCrO}_4 + \text{H}_2\text{O} \quad (13)
\]

**Conclusions**

Fe\(_3\)O\(_4\) (magnetite) and \(\alpha\)-FeOOH (goethite) synthesized by the hydrothermal method were mainly in cubic and orthorhombic structures, respectively. The Cr adsorption isotherms of Fe\(_3\)O\(_4\) and \(\alpha\)-FeOOH fitted well with the Langmuir model, indicating a monolayer adsorption process. The maximum Cr\(^{6+}\) uptake of 2.87 mg g\(^−1\) was found by Fe\(_3\)O\(_4\). After Cr-adsorption, the Cr\(^{3+}\)-doped forms of Fe\(_{1−x}\)Cr\(_x\)OOH and Fe\(_{3−x}\)Cr\(_x\)O\(_3\) solid solution was observed in bulk Fe\(_3\)O\(_4\) resulting in a high Cr-adsorption capacity. Besides, an electrostatic attraction of FeO–HCrO\(_4\) occurred only on the \(\alpha\)-FeOOH surface leading to a low Cr-adsorption capacity. The Cr-adsorption ability and behavior in an aqueous solution of the adsorbents were strongly influenced by an adsorbed species stabilized on their structures. The discovered Cr-solid solution in Fe\(_3\)O\(_4\) could be a promising catalyst preparation through water treatment process.
Author contributions
Nichapha Senamart-data curation, formal analysis, writing-original draft, writing-review & editing; Krittanan Deekamwong-writing-review & editing; Jatuporn Wittayakun-supervision & editing; Sanchai Prayoonpokarach-review & editing; Narong Chanlek-data analysis; Yingyot Poo-arpon-review & editing; Suttipong Wannapaiboon-data curation, formal analysis, writing; Pinit Kidkhunthod-data analysis and Sirinuch Loiha-conceptualization, funding acquisition, supervision, writing-review & editing.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
This work was supported by the Science Achievement Scholarship of Thailand (SAST), Center for Innovation in Chemistry (PERCH-CIC), Materials Chemistry Research Center (MCRC), Thailand. Department of Chemistry, Faculty of Science, Khon Kaen University. Khon Kaen, Thailand. Research and Graduate Studies Department, KKU (Research Program, grant number RP64-6/001), fiscal year 2021. Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand (BL1.1W, BL2.2, BL3.2Ua, BL5.2 and BL5.3). Suranaree University of Technology (SUR), Thailand Science Research and Innovation (TSRI), and National Science, Research and Innovation Fund (NSRF) (90464/project code 90464).

References
1 A. Chiu, X. L. Shi, W. K. P. Lee, R. Hill, T. P. Wakeman, A. Katz, B. Xu, N. S. Dalal, J. D. Robertson, C. Chen, N. Chiu and L. Donehower, J. Environ. Sci. Health, Part C: Environ. Carcinog. Ecotoxicol. Rev., 2010, 28, 188–230.
2 M. Narayani and K. V. Shetty, Crit. Rev. Environ. Sci. Technol., 2012, 43, 955–1009.
3 R. Rakhunde, L. Deshpande and H. D. Juneja, Crit. Rev. Environ. Sci. Technol., 2011, 42, 776–810.
4 E. J. Tomaszewski, S. Lee, J. Rudolph, H. Xu and M. Ginder-Vogel, Chem. Geol., 2017, 464, 101–109.
5 L. Li, Y. Li, L. Cao and C. Yang, Carbohydr. Polym., 2015, 125, 206–213.
6 P. Lazo, J. Int. Environ. Appl. Sci., 2009, 4, 207–213.
7 S. Wu, J. Lu, Z. Ding, N. Li, F. Fu and B. Tang, RSC Adv., 2016, 6, 82118–82130.
8 S. R. Chowdhury, E. K. Yanful and A. R. Pratt, J. Hazard. Mater., 2012, 235–236, 246–256.
9 X. Lv, J. Xu, G. Jiang, J. Tang and X. Xu, J. Colloid Interface Sci., 2012, 369, 460–469.
10 Y. L. Wei, Y. C. Lee and H. F. Hsieh, Chemosphere, 2005, 61, 1051–1060.
11 A. H. Meena and Y. Arai, Geochem. Trans., 2016, 17, 1.
12 M. Gheju and I. Balcu, J. Hazard. Mater., 2011, 196, 131–138.
13 A. Maleki, B. Hayati, M. Naghizadeh and S. W. Joo, J. Ind. Eng. Chem., 2015, 28, 211–216.
14 M. Gheju, Water, Air, Soil Pollut., 2011, 222, 103–148.
15 S. M. El-Sheikh, A. B. Azzam, R. A. Geioushy, F. M. El Dars and B. A. Salah, J. Alloys Compd., 2021, 857, 157513.
16 R. A. Geioushy, S. M. El-Sheikh, A. B. Azzam, B. A. Salah and F. M. El-Dars, J. Hazard. Mater., 2020, 381, 120955.
17 F. Di Natale, A. Erto, A. Lancia and D. Musmarra, J. Hazard. Mater., 2015, 281, 47–55.
18 S. M. Lee, L. Lalchhingpuii and D. Tiwari, Chem. Eng. J., 2016, 296, 35–44.
19 Q. Liu, Q. Liu, W. Ma, W. Liu, X. Cai and J. Yao, Colloids Surf., A, 2016, 511, 8–16.
20 E. I. Basaldella, P. G. Vázquez, F. Iucolano and D. Caputo, J. Colloid Interface Sci., 2007, 313, 574–578.
21 L. N. Dossing, K. Dideriksen, S. L. S. Stipp and R. Frei, Chem. Geol., 2011, 285, 157–166.
22 D. I. Sedlak and P. G. Chan, Geochim. Cosmochim. Acta, 1997, 61, 2185–2192.
23 A. E. Gleason, R. J. Meanz and M. Kunz, Am. Mineral., 2008, 93, 1882–1885.
24 H. Abdel-Samad and P. R. Watson, Appl. Surf. Sci., 1997, 108, 371–377.
25 T. Mineno and M. Okazaki, Soil Sci. Plant Nutr., 2004, 50, 1043–1046.
26 V. D. Nguyen, J. Kynicky, P. Ambrozova and V. Adam, Materials, 2017, 10, 783.
27 M. Kumari, C. U. Pittman Jr and D. Mohan, J. Colloid Interface Sci., 2014, 442, 120–132.
28 S. Rajput, C. U. Pittman and D. Mohan, J. Colloid Interface Sci., 2016, 468, 334–346.
29 A. H. Meena and Y. Arai, Geochem. Trans., 2016, 17, 1.
30 J. Chang, H. Wang, J. Zhang, Q. Xue and H. Chen, Colloids Surf., A, 2021, 611, 125784.
31 N. Senamart, J. Watcharakitti, K. Athawalai, K. Phedluen, P. Nasomjai and S. Loiha, Suranaree J. Sci. Technol., 2018, 25, 445–454.
32 P. Ou, G. Xu, Z. Ren, X. Hou and G. Han, Mater. Lett., 2008, 62, 914–917.
33 U. Pal, S. Uribe Madrid and F. Sanchez De-jesus, Adv. Nano. Res., 2014, 2, 187–198.
34 G. Du, Z. Li, L. Liao, R. Hanson, S. Leick, N. Hoeppner and W. T. Jiang, J. Hazard. Mater., 2012, 221–222, 118–123.
35 M. Kazemi, M. Jahanshahi and M. Peyravi, J. Hazard. Mater., 2018, 344, 12–22.
36 O. Ali and S. K. Mohamed, Turk. J. Chem., 2017, 41, 967–986.
37 F. Geng, Z. Zhao, J. Geng, H. Cong and H.-M. Cheng, Mater. Lett., 2007, 61, 4794–4796.
38 A. R. Amani-Ghadim, S. Alizadeh, F. Khodam and Z. Rezvani, J. Mol. Catal. A: Chem., 2015, 408, 60–68.
39 S. Alibeigi and M. R. Vaezi, Chem. Eng. Technol., 2008, 31, 1591–1596.
40 Y. F. Shen, J. Tang, Z. H. Nie, Y. D. Wang, Y. Ren and L. Zuo, Sep. Purif. Technol., 2009, 68, 312–319.
41 N. Guo, X. Lv, Q. Li, T. Ren, H. Song and Q. Yang, Microporous Mesoporous Mater., 2020, 299, 110101.

© 2022 The Author(s). Published by the Royal Society of Chemistry
42. Z. Liu, G. Chen, L. Xu, F. Hu and X. Duan, *ChemistrySelect*, 2019, 4, 13817–13827.
43. M. Bhaumik, A. Maity, V. V. Srinivasu and M. S. Onyango, *J. Hazard. Mater.*, 2011, 190, 381–390.
44. S. U. N. Zhenya, Z. H. U. Chunshui, H. Jiangbo, G. Wenhui, C. Hesheng and M. U. Shanbin, *Acta Geol. Sin.*, 2006, 80, 597–603.
45. X. Q. Zhang, Y. Guo and W.-C. Li, *RSC Adv.*, 2015, 5, 25896–25903.
46. M. Ahmaruzzaman, *Adv. Colloid Interface Sci.*, 2011, 166, 36–59.
47. G. Vijayakumar, R. Tamilarasan and M. Dharmaendiranakumar, *J. Mater. Environ. Sci.*, 2012, 3, 157–170.
48. M. Hasanpour and M. Hatami, *Adv. Colloid Interface Sci.*, 2020, 284, 102247.
49. Y. H. Li, Z. Di, J. Ding, D. Wu, Z. Luan and Y. Zhu, *Water Res.*, 2005, 39, 605–609.
50. A. P. Grosvenor, B. A. Kobe, M. C. Biesinger and N. S. McIntyre, *Surf. Interface Anal.*, 2004, 36, 1564–1574.
51. X. Zhang, W. G. Sloof, A. Hovestad, E. P. M. van Westing, H. Terryn and J. H. W. de Wit, *Surf. Coat. Technol.*, 2005, 197, 168–176.
52. Z. Wen, J. Ke, J. Xu, S. Guo, Y. Zhang and R. Chen, *Chem. Eng. J.*, 2018, 343, 416–426.