Formation of Dense and High-Aspect-Ratio Iron Oxide Nanowires by Water-Vapor-Assisted Thermal Oxidation and their Cr(VI) Adsorption Properties

Faisal Budiman  
Telkom University

Wai Kian Tan (✉️ tan@las.tut.ac.jp )  
Toyohashi University of Technology: Toyohashi Gijutsu Kagaku Daigaku

Go Kawamura  
Toyohashi University of Technology: Toyohashi Gijutsu Kagaku Daigaku

Hiroyuki Muto  
Toyohashi University of Technology: Toyohashi Gijutsu Kagaku Daigaku

Atsunori Matsuda  
Toyohashi University of Technology: Toyohashi Gijutsu Kagaku Daigaku

Khairunisak Abdul Razak  
Universiti Sains Malaysia

ZAINOVIA LOCKMAN  
Universiti Sains Malaysia - Engineering Campus Seri Ampangan: Universiti Sains Malaysia - Kampus Kejuruteraan Seri Ampangan

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Formation of Dense and High-Aspect-Ratio Iron Oxide Nanowires by Water-Vapor-Assisted Thermal Oxidation and their Cr(VI) Adsorption Properties

Faisal Budiman1,2, Wai Kian Tan3*, Go Kawamura4, Hiroyuki Muto3,4, Atsunori Matsuda4, Khairunisak Abdul Razak1 and Zainovia Lockman1*

1Green Electronic Nanomaterials Group, School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
2Department of Electrical Engineering, School of Electrical Engineering, Telkom University, Jl. Telekomunikasi No. 1 Bandung 40257, Indonesia
3Institute of Liberal Arts & Sciences, Toyohashi University of Technology, Toyohashi, Aichi, 441-8580, Japan
4Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan
*E-mail: zainovia@usm.my

Abstract
In this work, highly crystalline and high aspect ratio $\alpha$-Fe$_2$O$_3$ nanowire (NWs) were successfully produced by thermal oxidation of iron in water vapor at 800 °C. The process was done for 2 h and the NWs were found to be covering the foil uniformly unlike when the oxidation environment was dry whereby the NWs formed were shorted and rather dispersed. The formation of NWs was proposed to be due to a stress-driven surface diffusion during thermal oxidation process. When oxidation was done at 700 °C, we observed coral-like nanostructures. The $\alpha$-Fe$_2$O$_3$ NWs were then used as adsorbent to remove Cr(VI) from stimulated wastewater. Removal efficiency of 97% in a 225 mg/L Cr(VI) solution was observed indicating very fast removal of Cr(VI) in the presence of the NWs. The kinetic characteristic of the adsorption was fitted to a pseudo-second-order kinetic model, and isothermal studies indicated that the $\alpha$-Fe$_2$O$_3$ NWs exhibited an adsorption capacity of 66.26 mg/g.

Keywords: Hexavalent Chromium, Adsorption, Hematite, Nanowires, Thermal Oxidation, Water Vapor

1. Introduction
Chromium has oxidation states from (II) to (VI), but is most stable in its trivalent (III) [Cr(III)] and hexavalent (VI) [Cr(VI)] forms; however, Cr(VI) rarely occurs naturally and is typically manufactured. Unlike Cr(III), Cr(VI) is toxic and carcinogenic (Guerin et al. 2016; Rahman and Singh 2019): excessive inhalation of Cr(VI) can lead to lung cancer (Lin et al. 2019); direct skin contact with it may result in dermatitis (Lejding et al. 2020); and when ingested, it can cause organ damage (Yu et al. 2020). Cr(VI) compounds are, nonetheless, extremely important for electroplating, steel manufacturing, leather tanning, and textile production (Rosli et al. 2021). Inevitably, wastewater from these processes contains large amounts of Cr(VI), and, unless properly treated, it can enter surface waters, causing harm to aquatic life and possibly entering the food chain. The World Health Organization has recommended that Cr(VI) concentrations in water should not exceed 0.05 mg/L (WHO, 2011); therefore, total removal of Cr(VI) from industrial wastewater is crucial to preventing surface water concentrations exceeding this level.
There are several accepted methods for removing Cr(VI), which typically exists as highly soluble and toxic chromate anions (HCrO$_4$ or Cr$_2$O$_7^{2-}$), from industrial wastewater: photocatalytic reduction (Rosli et al. 2021; Gao et al. 2020; BashiroM et al. 2020), chemical precipitation (Xie et al. 2017), electrokinetic remediation (Zheng et al. 2020), membrane filtration (Abdullah et al. 2019), and adsorption (Zhang et al. 2020; Rasheed et al. 2020). Among these methods, adsorption is especially appealing, as it is very effective at removing even minute amounts of Cr(VI) (Kumar et al. 2019). The adsorption process requires a solid surface (i.e., adsorbent) with a large surface area for the species to be adsorbed (i.e., adsorbate) to attach to, either by physical or chemical processes. Nanostructured materials present themselves as attractive large-surface-area adsorbents for this purpose, of which one-dimensional nanostructures, such as nanowires (NWs), are particularly effective.

Iron oxide is a compound material, largely found as hematite ($\alpha$-Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), wüstite (Fe$_{1-x}$O), and maghemite ($\gamma$-Fe$_2$O$_3$) (Cornell and Schwertmann 2003), which has attracted attention as an adsorbent due to its ability to remove various types of heavy-metal ions (Bahmani et al. 2019; Fayazi et al. 2019; Sruthi et al. 2018; Khan et al. 2020). Recent studies have demonstrated that $\alpha$-Fe$_2$O$_3$ has a high adsorption capability, which occurs through a chemisorption process involving the hydroxyl group on its surface (Singaraj et al. 2019). Ren et al. investigated using $\alpha$-Fe$_2$O$_3$ in fibrous form for Cr(VI) ion removal and reported that the porous fiber-like morphology of $\alpha$-Fe$_2$O$_3$ exhibited excellent adsorption of Cr(VI) from water, with rapid adsorption kinetics, high adsorption capacity, and good reusability (Ren et al. 2013). Kumar et al. used magnetic iron oxide nanoparticles for Cr(VI) removal and obtained an adsorption capacity of 1,052.63 mg/g (Kumar et al. 2019). In view of these results, we attempted to prepare $\alpha$-Fe$_2$O$_3$ NWs through thermal oxidation of iron foils and investigated the sample’s ability to remove Cr(VI) from aqueous solutions.

Thermal oxidation can be used to produce thin-film oxides composed of NWs (Tan et al. 2011). Although there are various other ways of producing $\alpha$-Fe$_2$O$_3$ NWs, such as electrospinning (Deng et al. 2018; Ponti et al. 2020), hydrothermal (Sun et al. 2020), and nanocasting methods (Azeez et al. 2021), which produce NWs with a uniform diameter and length, they are known to be time consuming, and post-annealing treatments are required for crystalline oxide formation. Thermal oxidation presents a simpler approach to forming surface oxide layers, and, through careful control of the oxidation parameters, e.g., oxidation temperature (Rahmat et al. 2018a; Rahmat et al. 2018b; Srivastava et al. 2016; Budiman et al. 2016), unique nanostructures can be produced. Apart from temperature, oxidation time and environment also affect the growth of NWs (Rahmat et al. 2020). Our previous work explored the formation of iron oxide NWs by thermal oxidation in water-vapor-assisted conditions (Rahmat et al. 2018b; Budiman et al. 2016). The presence of water vapor during oxidation induced more densely packed nanostructures with a uniform distribution compared with those under dry-air conditions; however, this work was performed at lower temperatures (400°C–500°C). When iron is oxidized at high temperatures, it grows an oxide scale containing multilayered oxides, which are markedly different to the oxide phases formed below 570°C (Yu et al. 2003; Aquino et al. 2020); therefore, investigating these high-temperature oxidations further may result in novel and potentially useful nanostructures for various applications, including adsorption.

Our previous work on the synthesis of iron oxide NWs using thermal oxidation focused on a low-temperature oxidation regime (Budiman et al. 2016). In this study, we investigated the formation of iron oxide nanostructures by thermal oxidation under water-vapor-assisted conditions at high temperatures (i.e., 700°C and 800°C) to assess the Cr(VI) removal capability of the samples. This study makes a number of important contributions relating to the growth of iron oxide NWs at temperatures > 570°C under water vapor, proposing a mechanism of the NW
formation and exploring the Cr(VI) adsorption properties of the NWs, which were also evaluated by kinetic and equilibrium studies.

2. Experimental procedure

The 1 × 1 cm iron foils (99.9%, Nilaco Corporation) were polished with a 2,000-grit silicon carbide paper, ultrasonically cleaned in acetone, rinsed using deionized water, and then dried. Then, they were placed in an alumina crucible and positioned in the hot zone of a horizontal furnace. The furnace was progressively heated by 5°C/min until the desired oxidation temperature was reached, which was either 700°C or 800°C. Once this temperature was reached, the furnace was purged with water vapor generated using a nebulizer (Omron NE-C801). The evolution of the surface oxide was monitored using a field-emission electron microscope (FESEM) (Zeiss Supra 35 VP), and higher magnification images were obtained using a high-resolution transmission electron microscope (HR-TEM) (Tecnai G2 20 S-TWIN). Crystal structures were examined by taking X-ray diffraction (XRD) patterns (Bruker D8 Advance diffractometer) with a Cu Kα radiation source (λ = 0.154 nm). A Raman spectrometer (Renishaw RL633) was used for phase identification, and an X-ray photoelectron spectrophotometer (XPS) (Kratos Axis Ultra XPS Spectroscopy) with an Al X-ray radiation source was used for surface and elemental analysis.

To evaluate the Cr(VI) removal ability of the nanostructures, oxidized iron with α-Fe₂O₃ NWs was placed in Cr(VI) solutions of various concentrations between 225–300 mg/L. The pH of the solutions was adjusted to pH 2 by adding H₂SO₄. The assessment of Cr(VI) content was performed using a diphenyl-carbazide (DPC) colorimetry method. DPC solution was prepared by diluting 0.25 g of 1,5-diphenylcarbazide in 50 ml acetone, and a droplet was added into the Cr(VI) solutions. A colour change in the solution to purple indicated the existence of Cr(VI). UV-Visible (UV-Vis) measurements were taken with a UV-Vis spectrophotometer (Perkin Elmer Lambda 35), and absorption values were recorded at a wavelength of 540 nm to detect Cr(VI) (Onchoke et al. 2016). The adsorption study was divided into two parts: equilibrium and kinetic. First, 50 ml solutions of Cr(VI) with concentrations ranging from 225 to 300 mg/L were prepared. The α-Fe₂O₃ NWs were then immersed in the Cr(VI) solution. During this adsorption process, bubbles, which were supplied by an air pump (Super X Classica) with an output of 250 L/h, were used for stirring the Cr(VI) solution. The amount of Cr(VI) adsorbed at the equilibrium condition (qₑ) was calculated using Eq. 1:

\[ qₑ = \frac{(C₀ - Cₑ)V}{m}, \quad (1) \]

where \( C₀ \) and \( Cₑ \) are the initial and equilibrium concentrations of Cr(VI) (mg/L), respectively; \( V \) is the volume of solution used (L); and \( m \) is the mass of the adsorbent (g). For the kinetic study, the amount of Cr(VI) adsorbed at time \( t \) (qₜ) was calculated using Eq. 2:

\[ qₜ = \frac{(C₀ - Cₜ)V}{m}, \quad (2) \]

where \( Cₜ \) is the concentration of Cr(VI) at time \( t \).

3. Results and discussion

3.1 Morphology observations
FESEM images of the surface morphologies of the foils oxidized in dry air and water vapor are presented in Figs. 1 (a) and (b), respectively. At 700°C, the surface oxidation exhibited a coral-like structure, which was larger on the water-vapor-oxidized sample than on the air-oxidized sample. Micrographs of the foils oxidized at 800°C in dry air and water vapor are presented in Figs. 1 (c) and (d), respectively, and they show that the NWs formed on these foils were finer and longer (up to 20 μm) when oxidized in water vapor. This demonstrated that water-vapor-assisted thermal oxidation strongly influenced the aspect ratio of the NWs.

![FESEM images of iron foils oxidized for 2 h in (a) 700 °C air, (b) 700 °C water vapor, (c) 800 °C air, and (d) 800 °C water vapor.](image)

To further investigate the effect of water vapor on the growth of the NWs, various oxidation durations were applied at 800°C, and the resulting surface morphologies are illustrated in Fig. 2. Interestingly, the NWs were formed after only 5 min of oxidation, as illustrated in Fig. 2 (a), but the areal density was initially low with only sparse NWs formed on the foil surface. Here areal density was defined as the number of NWs per measured area in an FESEM image. Extending the oxidation time to 15, 30, and 60 min increased the areal density of the NWs, as illustrated in Figs. 2 (b–d), respectively, and oxidation for 120 min resulted in the formation of a dense, homogenous NW surface, as illustrated in Fig. 2 (e); therefore, we concluded that both the length and diameter of the NWs increased with increasing oxidation time. A summary of the morphological observations at 800°C, including those of the length, aspect ratio, and areal density as a function of oxidation time, is presented in Fig. 3. These results indicate that controlled formation of α-Fe$_2$O$_3$ NWs can be achieved by controlling the oxidation time during water-vapor-assisted thermal oxidation.
Fig. 2. FESEM images of the oxidized iron at 800°C in water vapor for (a) 5, (b) 15, (c) 30, (d) 60, and (e) 120 min.

Fig. 3. Quantitative analysis of the (a) length, (b) aspect ratio, and (c) areal density of the iron foils oxidized at 800°C for 5–120 min.
To gain an insight into the crystallinity of the NWs, we performed HR-TEM observations of a single α-Fe₂O₃ NW obtained through water-vapor-assisted thermal oxidation at 800°C for 2 h. The subsequent HR-TEM image is presented Fig. 4 (a), which indicates that the diameters of the bottom and tip of the nanowire were approximately 60 and 5 nm, respectively. The image also shows that the measured d-spacing was approximately 0.25 nm, which is in accordance with the (110) plane of α-Fe₂O₃. The tapered structure of the NWs was confirmed by the FESEM image in Fig. 4 (b).

Fig. 4. (a) HR-TEM image of a single α-Fe₂O₃ NW and (b) FESEM image of iron foil oxidized at 800°C for 2 h in water vapor.

3.2 Crystal phase of the α-Fe₂O₃ NWs

Fig. 5 (a) presents XRD patterns of the iron foils oxidized at 800°C for 2 h in air and water vapor. The XRD results indicated that the NWs consisted of crystalline structures with peaks indexed to hematite (α-Fe₂O₃) (ICDD #98-001-2733) and magnetite (Fe₃O₄) (ICDD #98-001-7319). It has been previously reported that following the thermal oxidation of iron, the outermost oxide layer is α-Fe₂O₃, and the underlying oxide is Fe₃O₄ (Yuan et al. 2012). To verify this, we performed Raman spectroscopy. The Raman results are presented in Fig. 5 (b) and include bands at 227, 245, 293, 412, 499, and 612 cm⁻¹, which correspond to the α-Fe₂O₃ phase (Taniguchi et al. 2020). Owing to the low penetration depth of a Raman laser compared with XRD, we concluded that the outermost oxide layer was α-Fe₂O₃. Also, although the water-vapor-assisted oxidation resulted in a denser formation of NWs, the outer α-Fe₂O₃ phase oxide layer was observed in the air-oxidized samples.
The surface elemental compositions of the foils oxidized at 800°C for 2 h in water vapor were confirmed using XPS measurements. The obtained XPS spectrum is presented Fig. 6 and indicates the presence of Fe, O, and C in the α-Fe$_2$O$_3$ NWs, as shown in the wide scan spectrum in Fig. 6 (a). Fig. 6 (b) presents a high-resolution spectrum of Fe 2p, including two peaks at 724.4 and 709.9 eV, which correspond to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, respectively. A binding energy difference of 14.5 eV and the absence of a peak at 719.0 eV suggested a predominant Fe$^{3+}$ oxidation state, which further verified the presence of the α-Fe$_2$O$_3$ phase (Ma et al. 2021). The O 1s peak, shown in Fig. 6 (c), with a binding energy of 530 eV corresponds to the O$^{2-}$ oxidation state in the oxide, and the second broad peak at 531.5 eV corresponds to the adsorbed oxygen or hydroxyl ion (Ma et al. 2021). These XPS results further indicated that the outermost layer generated on the surface of the oxidized foils consisted of α-Fe$_2$O$_3$. 

Fig. 5. (a) XRD patterns and (b) Raman spectra of the iron foils oxidized at 800 °C for 2 h in air and water vapor.

Fig. 6. (a) Wide scan, (b) Fe 2p, and (c) O 1s XPS spectra of iron foils oxidized at 800°C in water vapor for 2 h.
3.3 Growth mechanism of the NWs

3.3.1 Initial oxidation stage

During dry-air thermal oxidation, the diffusion process is initiated by the chemisorption of oxygen onto the surface of the iron foil, forming a chemisorbed layer, which is then followed by the ionization of oxygen, forming O\(^-\) (Eq. 3). The ionization of oxygen generates an electric field on the surface of the foil and triggers the oxidation of Fe (Eq. 4). Overall, the reciprocal diffusion of oxygen and iron promotes the buildup of the oxide layer and forms a thin layer of iron oxide.

\[
O_2(g) \rightarrow O_2(ads) \rightarrow 2O(ads) = 2O^- (chem) + 2h^+ \rightarrow 2O^-(latt) + 4h^+ \tag{3}
\]

\[
Fe \rightarrow Fe^{2+} + 2e^- \tag{4}
\]

During water-vapor-assisted thermal oxidation, the previously stable (Khanna 2002) (Eq. 5) adsorbed water molecule dissociates as vapor (Eq. 5 and 6).

\[
H_2O(g) \rightarrow H_2O(ads) \tag{5}
\]

\[
H_2O(ads) \rightarrow HO^- + H_3^+ \tag{8}
\]

It has been reported that oxidation under water-vapor conditions is accelerated compared with in dry air [36], which may be due to the incorporation of a proton, accompanied by electrons, within the oxide scale during oxide growth. Fujii and Meussner reported that during oxidation in water vapor, the desorption of hydrogen from the oxide surface occurred (Eq. 7); this resulted in partial dissolution in the oxide (Eq. 8) (Fujii and Meussner 1964). The small ionic radius of H atoms compared with those of Fe and O (Lange 1985) means H can interstitially bind with O as OH\(_o\) in the oxide. The creation of such defects, compensated by electron deficiency, metal vacancies, and oxygen interstitials, may in turn increase the oxidation rate, resulting in the increased rate of NW formation observed in this study.

\[
2h^+ + 2e^- \rightarrow H_2 \tag{7}
\]

\[
H_2O(ads) \rightarrow HO^- + H_3^+ \tag{8}
\]

3.3.2 Formation of the oxide scale

The interaction of iron with reactive oxidative gases at high temperatures resulted in the formation of an oxide scale on the foil surface, as illustrated in the cross-sectional FESEM image in Fig. 7. This scale was composed of multiple layers of oxides, an outer layer of \(\alpha\)-Fe\(_2\)O\(_3\) and an inner layer of Fe\(_{1-x}\)O and Fe\(_3\)O\(_4\), depending on the oxidation temperature. Fe\(_{1-x}\)O is thermodynamically unstable below 570°C; thus, it was likely to be present during oxidation at the temperatures used in this study. The cross-sectional FESEM image in Fig. 7 indicates that the Fe\(_{1-x}\)O layer was thicker than the Fe\(_3\)O\(_4\) and \(\alpha\)-Fe\(_2\)O\(_3\) layers after oxidation at 800°C for 2 h under water-vapor-assisted conditions. Fe\(_{1-x}\)O is a non-stoichiometric compound with rich metal vacancies, which, through phase transformation, aids the growth of other phases during oxidation. Phase formation is thought to follow Eq. 9, with Fe\(_{1-x}\)O being transformed first to Fe\(_3\)O\(_4\) and then to \(\alpha\)-Fe\(_2\)O\(_3\). The phase transformations during oxidation in dry air and water vapor are presented in Table 1.

\[
Fe \rightarrow FeO \rightarrow Fe_3O_4 \rightarrow \alpha - Fe_2O_3 \tag{9}
\]
Table 1. Oxidation reactions of iron in dry and water-vapor-assisted conditions.

| Oxidation reaction in dry air          | Oxidation reaction in water vapor          |
|---------------------------------------|-------------------------------------------|
| $O_2 + 4e^- \rightarrow 2O^{2-}$      | $H_2O \rightarrow OH^- + H^+$             |
| $2Fe^{3+} + 3O^{2-} \rightarrow Fe_2O_3$ | $2Fe^{3+} + 3OH^- \rightarrow Fe_2O_3 + 3H^+$ |
| $2Fe^{3+} + Fe^{2+} + 4O^{2-} \rightarrow Fe_3O_4$ | $2Fe^{3+} + Fe^{2+} + 4OH^- \rightarrow Fe_3O_4 + 4H^+$ |
| $Fe^{2+} + O^{2-} \rightarrow FeO$     | $Fe^{2+} + OH^- \rightarrow FeO + H^+$     |
| $Fe \rightarrow Fe^{2+} + 2e^-$        | $Fe \rightarrow Fe^{2+} + 2e^-$            |

3.3.3. Oxidation growth stress

The cross-sectional FESEM images in Fig. 7 indicate that the surface region of the iron was composed of layered oxides in various phases, the presence of which generated stress within the oxide scale. During oxidation, thermal expansion leads to an increase in volume, which also contributes to oxide growth; however, this expansion resulted in a volume discrepancy of the iron and iron oxide, which induced a stress region at the metal–oxide interface. This caused the surface scale to be either in high compressive or tensile stress, especially at the interface regions; if the expansion of outer oxide layer is larger than that of the oxide layer underneath, a compressive stress develops (Pilling–Bedworth ratio > 1) in the upper oxide, and a tensile stress develops in the underlying oxide. This discrepancy alters the diffusion rate of the growing species, leading to preferential growth of the oxide at the oxide–air interface in the c-axis direction (Yuan et al. 2012).

The relaxation of the generated stresses resulted in the growth of NWs at the surface by a mechanism illustrated in Fig. 8. During the thermal oxidation process, Fe species diffuse and are accelerated across the oxide layer before nucleating on $\alpha$-Fe$_2$O$_3$ grains through surface diffusion. This continuous and fast diffusion led to NW growth along the c-axis, which generated elongated oxide nanostructures, i.e., NWs. Observations under FESEM
evidenced this phenomena, with the nucleation and surface diffusion processes clearly seen in Figs. 9 (a) and (b), respectively.

![Schematic illustration of the NW growth mechanism through thermal oxidation on an iron foil.](image)

Fig. 8. Schematic illustration of the NW growth mechanism through thermal oxidation on an iron foil.

![FESEM image showing (a) the initial growth of NWs on α-Fe₂O₃ grains and (b) formation of NWs through surface diffusion.](image)

Fig. 9. FESEM image showing (a) the initial growth of NWs on α-Fe₂O₃ grains and (b) formation of NWs through surface diffusion.

3.4 Evaluation of Cr(VI) adsorption using the α-Fe₂O₃ NWs

We then evaluated the Cr(VI) adsorption properties of the NWs using the α-Fe₂O₃ NWs formed through thermal oxidation at 800°C for 2 h in water vapor, using various initial concentrations of Cr(VI) between 225 and 300 mg/L. The results are illustrated in Fig. 10. The kinetic and equilibrium dynamics of the adsorption behavior were also obtained and evaluated. An equilibrium was reached after 90 min of contact between the NWs and the Cr(VI) solution, and the α-Fe₂O₃ NWs adsorbed of around 200 mg/L of Cr(VI) in a 50 ml solution. The adsorption profiles exhibited similar patterns across the various Cr(VI) solutions. A bare iron foil was used as a control using 200 mg/L Cr(VI) solution, and the result is shown in the inset of Fig. 10. This demonstrated that the α-Fe₂O₃ NWs were required for more effective adsorption of Cr(VI).
As chromate ions exist as negative ions (HCrO$_4^-$) at pH 2 (Park et al. 2008), the surface charge of α-Fe$_2$O$_3$ NWs must be positively charged for electrostatic attraction to happen. The immersion of the α-Fe$_2$O$_3$ NWs in a Cr(VI) solution starts a hydroxylation process, and the surfaces of the oxides are covered with hydroxyl ions (OH$^-$). The pH of the point of zero charge of α-Fe$_2$O$_3$ has been reported to be between pH 7.2 and pH 9.5 (Aredes et al. 2012), and because the pH used was below this, the surface of the NWs was protonated with H$^+$ ions, as shown in Eq. 10:

$$S - OH + H^+ \rightarrow S - OH_2^+ ,$$

where S is the surface of the hydroxylated α-Fe$_2$O$_3$ NWs. Electrostatic interactions between Cr(VI) species and the positively charged α-Fe$_2$O$_3$ NW surfaces drove the adsorption process and the removal of Cr(VI) species from the solution (Nalbandian et al. 2016; Zhou et al. 2020).

### 3.5 Determination of adsorption kinetics

By knowing the rate of adsorption, we were able to investigate an appropriate kinetic model by fitting the data to several kinetic adsorption models: (1) pseudo-first-order, (2) pseudo-second-order, and (3) intraparticle diffusion, which are illustrated in Fig. 11. The validity of the predicted models with the experimental data was
determined using values of $R^2$, which are presented in Table 2 along with the corresponding correlation coefficients; the closer the value of $R^2$ to 1, the better the model fitted the adsorption kinetics of Cr(VI) in the tested system. The details of the fitting of each model are described below.

3.5.1. Pseudo-first-order kinetic model

The linear fit of Cr(VI) adsorption on $\alpha$-Fe$_2$O$_3$ NWs in accordance with a pseudo-first-order kinetic model is presented in Fig. 11 (a). The pseudo-first-order model follows an adsorption process according to Eq. 11 (Largitte et al. 2016):

$$\frac{dq_t}{dt} = k(q_e - q_t).$$

(11)

By applying the initial condition, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the integration of the pseudo-first-order model can be expressed as Eq. 12:

$$\log(q_e - q_t) = \log q_e - 0.434k_1t,$$

(12)

where $q_e$ and $q_t$ are the total adsorbed Cr(VI) at equilibrium and at time $t$ (mg/g$^{-1}$), respectively, and $k_1$ is the pseudo-first-order kinetic constant (min$^{-1}$). The $R^2$ values for the pseudo-first-order kinetic model in Table 2 are below 0.8, indicating that the experimental data deviated from the theoretical data; therefore, this model was unsuitable.

3.5.2. Pseudo-second-order kinetic model

The linear fit of Cr(VI) adsorption on $\alpha$-Fe$_2$O$_3$ NWs according to the pseudo-second-order kinetic model is presented in Fig. 11 (b). The pseudo-second-order kinetic model follows an adsorption process according to Eq. 13, which describes a kinetic rate driven by chemisorption (Largitte et al. 2016):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2.$$

(13)

By applying the initial condition, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the integration of the pseudo-second-order kinetic model can be expressed by Eq. 14:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t,$$

(14)

where $q_e$ and $q_t$ are the total adsorbed chromium at equilibrium and at time $t$ (mg/g$^{-1}$), respectively. The value of $k_2$ is the rate constant of pseudo-second-order adsorption (g/mg$^{-1}$/min). The $R^2$ values obtained for all the concentrations investigated were higher than 0.98 for the pseudo-second-order model, as shown in Table 2, indicating that it is appropriate to describe the dynamic behavior of Cr(VI) adsorption onto $\alpha$-Fe$_2$O$_3$ NWs.

3.5.3. Intraparticle diffusion model

The linear fit of Cr(VI) adsorption on $\alpha$-Fe$_2$O$_3$ NWs according to the intraparticle diffusion model is presented in Fig. 11 (c). The intraparticle diffusion model describes an adsorption process that occurs in multiple stages (Largitte et al. 2016). First, a sharp Cr(VI) concentration reduction indicates a spontaneous adsorption process. Second, a gradual adsorption is driven by a controlled diffusion phenomenon. Finally, the low concentration of the remaining adsorbate results in a slow adsorption process. The intraparticle diffusion model can be expressed using Eq. 15:
\[ q_t = k_{ad} (t)^{1/2} + c, \quad (15) \]

where \( q_t (\text{mg/g}) \) is the amount of Cr(VI) adsorbed, \( k_{ad} \) is the rate factor (\( \text{mg/g/min}^{1/2} \)), and \( c \) (\( \text{mg/g} \)) represents the boundary layer thickness. The \( R^2 \) values for the intraparticle diffusion model, presented in Table 2, were close to 0.9, which is even lower than the values obtained for the pseudo-second-order kinetic model. This indicated that the intraparticle diffusion model was unsuitable.

![Fig. 11. Linear fit of α-Fe2O3 NWs kinetics to (a) pseudo-first-order kinetic, (b) pseudo-second-order kinetic, and (c) intraparticle diffusion models.](image)

| Method               | Sample | \( R^2 \) | Kinetic rate constant |
|----------------------|--------|-----------|----------------------|
| Pseudo-First Order   | 225 mg/L | 0.77800   | \( k_1 = 0.03576 \) |
|                      | 250 mg/L | 0.88960   | \( k_1 = 0.03304 \) |
|                      | 275 mg/L | 0.80328   | \( k_1 = 0.03719 \) |
|                      | 300 mg/L | 0.78220   | \( k_1 = 0.00443 \) |
| Pseudo-Second Order  | 225 mg/L | **0.99159** | \( k_2 = 0.00214 \) |
|                      | 250 mg/L | **0.98664** | \( k_2 = 0.00111 \) |
|                      | 275 mg/L | **0.99300** | \( k_2 = 0.00194 \) |
|                      | 300 mg/L | **0.99692** | \( k_2 = 0.00027 \) |

Table 2. Comparison of the kinetic models fitted for Cr(VI) adsorption.
Intra-Particle Diffusion  

| Concentration (mg/L) | $k_{id}$ |
|----------------------|--------|
| 225                  | 0.93541 |
| 250                  | 0.91151 |
| 275                  | 0.92915 |
| 300                  | 0.91090 |

3.6 Investigation on the adsorption equilibrium

To determine the loading capacity of the adsorbent, we continued investigating the equilibrium. The adsorption data were fitted to Langmuir and Freundlich models, and the obtained plots are presented in Fig. 12. Similarly to the kinetics study, the validity was determined by $R^2$ values, i.e., the closer $R^2$ was to 1, the better the fit of the model. The correlation coefficient and $R^2$ value for each model are presented in Table 3. Each model is described below.

3.6.1. Langmuir model

The linear fit of Cr(VI) adsorption on $\alpha$-Fe$_2$O$_3$ NWs according to the Langmuir model is presented in Fig. 12 (a). The Langmuir model describes an adsorption process that occurs across a homogeneous adsorbent surface (Foo et al. 2010), which can be described by Eq. 16:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e,$$  \hspace{1cm} (16)

where $K_L$ (L/mg$^{-1}$) is the Langmuir equilibrium constant, and $q_m$ (mg/g$^{-1}$) is the monolayer capacity, which indicates the available active sites per mass of sample where Cr(VI) could be adsorbed. The $R^2$ value for the Langmuir model was close to 0.99, indicating that it fitted the equilibrium behavior of Cr(VI) adsorption onto $\alpha$-Fe$_2$O$_3$ NWs well. The calculated adsorption capacity of $\alpha$-Fe$_2$O$_3$ NWs for Cr(VI) using the Langmuir model was approximately 66.2690 mg/g.

3.6.2. Freundlich model

The linear fit of Cr(VI) adsorption on $\alpha$-Fe$_2$O$_3$ NWs according to the Freundlich model is presented in Fig. 12 (b). The Freundlich model describes an adsorption process that occurs across a heterogeneous adsorbent surface (Foo et al. 2010), which can be described by Eq. 17:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e,$$  \hspace{1cm} (17)

where $K_F$ (mg/g$^{-1}$) is the Freundlich constant, which describes the adsorption capacity, and $1/n$ is the heterogeneity factor. It can be seen from Table 3 that the $R^2$ value for Freundlich model was below 0.95, indicating that the experimental data deviated from the theoretical data; therefore, the Freundlich model was unsuitable.
Finally, to demonstrate the impact of our findings, we compiled and compared previously reported Cr(VI) adsorption properties of iron oxide, presented in Table 4. This demonstrated that iron oxides can be used for Cr(VI) adsorption but that their adsorption properties differ depending on their morphologies. As previously mentioned, the adsorption capacity of Cr(VI) onto iron oxide is influenced by the pH of the solution, with a low pH being preferable to promote a higher adsorption capacity (Adegoke et al. 2013). Another factor that affects Cr(VI) adsorption is the specific surface area that is available for adsorption. Nalbandian et al. achieved an improved adsorption capacity of 90.9 mg/g using small-diameter (i.e., higher surface area) α-Fe$_2$O$_3$ nanofibers (Nalbandian et al. 2016). The TEM and SEM images in Figs. 2 and 4 allowed us to estimate the surface area provided by one NW to be approximately 204.28 $\times$ $10^{-15}$ m$^2$. On a 1 cm $\times$ 1 cm oxidized iron foil, we estimated there to be approximately 3 $\times$ $10^{10}$ NWs on the surface, assuming a homogeneous distribution; therefore, we consider our Cr(VI) adsorption capacity of 66.26 mg/g to be rather good. Although this is lower than the 1052.63 mg/g and 90.9 mg/g values reported by Kumar et al. (2019) and Nalbandian et al. (2016), respectively, the use of α-Fe$_2$O$_3$ NWs on iron foils enables their simple removal from the target solution and improved recyclability. This indicates that the formation of α-Fe$_2$O$_3$ NWs by the water-vapor-assisted surface oxidation of iron has an excellent potential for the removal of harmful Cr(VI) from wastewater.

| Iron oxide adsorbent material | pH | T (°C) | Adsorption capacity (mg/g) | References |
|------------------------------|----|--------|---------------------------|------------|
| Maghemite nanoparticles      | 2.5| 25     | 19.2                      | (Hu et al. 2005) |
4. Conclusions

We investigated the high-temperature (700°C and 800°C) formation of iron oxide nanostructures through thermal oxidation in dry-air- and water-vapor-assisted conditions. Oxidation at 700 °C led to the formation of coral-like nanostructures, whereas α-Fe₂O₃ NWs were obtained from oxidation at 800 °C. Water-vapor-assisted thermal oxidation resulted in an increased rate of oxide formation and larger or denser coral-like or NW structures with high aspect ratios at 700 °C and 800 °C, respectively. Through systematically observing the oxidation process, we were able to describe the formation mechanism of the α-Fe₂O₃ NWs, which was a stress-driven mechanism through surface diffusion. Notably, NWs were produced after 5 min of oxidation, but the densest NWs with the highest aspect ratio were obtained only after 2 h. We then evaluated the Cr(VI) adsorption property of α-Fe₂O₃ NWs obtained from water-vapor-assisted thermal oxidation at 800 °C for 2 h. A removal efficiency of 97% was achieved within 90 min using an aqueous Cr(VI) solution with a concentration of 225 mg/L. Finally, we investigated the adsorption equilibrium and kinetic models, which were in agreement with the Langmuir and pseudo-second-order kinetic models, respectively. The adsorption capacity of these α-Fe₂O₃ NWs was calculated to be 66.26 mg/g. This simple methodology for forming high-aspect-ratio α-Fe₂O₃ NWs through surface oxidation has a great potential for producing large-surface-area adsorbents to enable the simple removal of Cr ions from aqueous systems. The findings of this study will be beneficial and useful for the removal and mitigation of harmful Cr(VI) ions from wastewater.

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Ethical Approval

Not applicable.

Consent to Participate

Not applicable.

Consent for Publication
Not applicable.

Authors Contributions

Faisal Budiman: Investigation, Methodology, Writing-original draft. Wai Kian Tan: Investigation, Visualization, Validation, Writing-Review and Editing, Funding acquisition. Go Kawamura: Validation. Hiroyuki Muto: Validation. Atsunori Matsuda: Validation, Khairunisak Abdul Razak: Validation. Zainovia Lockman: Conceptualization, Supervision, Writing-Review and Editing, Project Administration, Funding acquisition.

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Competing interests

The authors declare that they have no completing interests.

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

REFERENCES

Abdullah N, Yusof N, Shah MHA, Ikhsan SNW, Ng ZC, Maji S, Lau WJ, Jaafar J, Ismail AF, Ariga K (2019) Hydrous ferric oxide nanoparticles hosted porous polyethersulfone adsorptive membrane: chromium (VI) adsorptive studies and its applicability for water/wastewater treatment. Environ Sci Pollut Res 26:20386-20399. https://doi.org/10.1007/s11356-019-05208-9.

Adegoke HI, AmooAdekola F, Fatoki OS, Ximba BJ (2014) Adsorption of Cr (VI) on synthetic hematite (α-Fe₂O₃) nanoparticles of different morphologies. Korean J Chem Eng 31:142-154. https://doi.org/10.1007/s11814-013-0204-7.

Aquino CL, Balela MD (2020) Thermally grown Zn-doped hematite (α-Fe₂O₃) nanostructures for efficient adsorption of Cr (VI) and Fenton-assisted degradation of methyl orange. SN Appl. Sci. 2:1-6. https://doi.org/10.1007/s42452-020-03950-1.

Aredes S, Klein B, Pawlik M (2013) The removal of arsenic from water using natural iron oxide minerals. J. Clean. Prod. 60:71-6. https://doi.org/10.1016/j.jclepro.2012.10.035.

Azeez NA, Dash SS, Gummadi SN, Deepa VS (2020) Nano-remediation of toxic heavy metal contamination: Hexavalent chromium [Cr (VI)]. Chemosphere. 5:129204.

Bahmani P, Maleki A, Daraei H, Rezaee R, Khamforoush M, Athar SD, Gharibi F, Ziaee AH, McKay G (2019) Application of modified electrospun nanofiber membranes with α-Fe₂O₃ nanoparticles in arsenate removal from aqueous media. Environ Sci Pollut Res 26:21993-22009. https://doi.org/10.1007/s11356-019-05228-5.

Bashirom N, Tan WK, Kawamura G, Matsuda A, Lockman Z. Comparison of ZrO₂, TiO₂, and α-Fe₂O₃ nanotube arrays on Cr (VI) photoreduction fabricated by anodization of Zr, Ti, and Fe foils. Mater Res Express 7:055013.
Bertrand N, Desgranges C, Poquillon D, Lafont MC, Monceau D (2010) Iron oxidation at low temperature (260–500 °C) in air and the effect of water vapor. Oxid Met 73:139-162. https://doi.org/10.1007/s11085-009-9171-0.

Budiman F, Bashir N, Tan WK, Razak KA, Matsuda A, Lockman Z (2016) Rapid nanosheets and nanowires formation by thermal oxidation of iron in water vapour and their applications as Cr (VI) adsorbent. Appl Surf Sci 380:172-177. https://doi.org/10.1016/j.apsusc.2016.01.209.

Cao CY, Qu J, Yan WS, Zhu JF, Wu ZY, Song WG (2012). Low-cost synthesis of flowerlike α-Fe$_2$O$_3$ nanostructures for heavy metal ion removal: adsorption property and mechanism. Langmuir 28:4573-4579. https://doi.org/10.1021/la300097y.

Cornell RM, Schwertmann U (2003) The iron oxides: structure, properties, reactions, occurrences and uses. John Wiley & Sons, New Jersey.

Deng J, Liu J, Dai H, Wang W (2018) Preparation of α-Fe$_2$O$_3$ nanowires through electrospinning and their Ag$_3$PO$_4$ heterojunction composites with enhanced visible light photocatalytic activity. Ferroelectrics 528:58-65. https://doi.org/10.1080/00150193.2018.1448625.

Fayazi M, Afzali D, Ghanei-Motlagh R, Iraji A (2019) Synthesis of novel sepiolite–iron oxide–manganese dioxide nanocomposite and application for lead (II) removal from aqueous solutions. Environ Sci Pollut Res 26:18893-18903. https://doi.org/10.1007/s11356-019-05119-9.

Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. Chem Eng J 156:2-10. https://doi.org/10.1016/j.cej.2009.09.013.

Fu YY, Wang RM, Xu J, Chen J, Yan Y, Narlikar AV, Zhang H (2003) Synthesis of large arrays of aligned α-Fe$_2$O$_3$ nanowires. Chem. Phys. Lett. 379:373-9. https://doi.org/10.1016/j.cplett.2003.08.061.

Fujii CT, Meussner RA (1964) The Mechanism of the High · Temperature Oxidation of Iron · Chromium Alloys in Water Vapor. J Electrochem 111:1215. https://doi.org/10.1149/1.2425963.

Gao Z, Yang H, Fu X, Jin Q, Wu Q, Kang L, Wu J (2019) Efficient photoreduction of Cr (VI) on TiO$_2$/functionalized activated carbon (TiO$_2$/AC-AEMP): improved adsorption of Cr (VI) and induced transfer of electrons. Environ Sci Pollut Res 1-12. https://doi.org/10.1007/s11356-019-05374-w.

Guerton J, Avakian CP, Jacobs JA (2016) Chromium (VI) handbook. CRC press. Florida.

Gusain D, Srivastava V, Sillanpää M, Sharma YC (2016) Kinetics and isotherm study on adsorption of chromium on nano crystalline iron oxide/hydroxide: linear and nonlinear analysis of isotherm and kinetic parameters. Res Chem Intermediat 42:7133-7151. https://doi.org/10.1007/s11164-016-2523-x.

Hu J, Chen G, Lo IM (2005) Removal and recovery of Cr (VI) from wastewater by maghemite nanoparticles. Water Res 39:4528-4536. https://doi.org/10.1016/j.watres.2005.05.051.

Jia Z, Wang Q, Ren D, Zhu R (2013) Fabrication of one-dimensional mesoporous α-Fe$_2$O$_3$ nanostructure via self-sacrificial template and its enhanced Cr (VI) adsorption capacity. Appl Surf Sci 264:255-260. https://doi.org/10.1016/j.apsusc.2012.09.179.

Khan FSA, Mubarak NM, Khalid M, Walvekar R, Abdullah EC, Mazari SA, Nizamuddin S, Karri RR (2020) Magnetic nanoadsorbents’ potential route for heavy metals removal—a review. Environ Sci Pollut Res 1-15. https://doi.org/10.1007/s11356-020-08711-6.

Khanna AS (2002) Introduction to high temperature oxidation and corrosion. ASM international, Delhi.
Kumar H, Sinha SK, Goud VV, Das S (2019) Removal of Cr (VI) by magnetic iron oxide nanoparticles synthesized from extracellular polymeric substances of chromium resistant acid-tolerant bacterium Lysinibacillus sphaericus RTA-01. J Environ Health Sci 17:1-16. https://doi.org/10.1007/s40201-019-00415-5.

Lange NA D (1985) Lange’s Handbook of Chemistry. McGraw-Hill, New York.

Largitte L, Pasquier R (2016) A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. Chem Eng Res Des 109:495-504. https://doi.org/10.1016/j.cherd.2016.02.006.

Lejdjing T, Engfeldt M, Bruze M, Isaksson M, Svedman C, Zimerson E, Verma K, Mowitz M (2020) Skin application of glutathione and iron sulfate can inhibit elicitation of allergic contact dermatitis from hexavalent chromium. Contact dermatitis 82:45-53. https://doi.org/10.1111/cod.13409

Lin CH, Lai CH, Peng YP, Wu PC, Chuang KY, Yen TY, Xiang YK (2019) Comparative health risk of inhaled exposure to organic solvents, toxic metals, and hexavalent chromium from the use of spray paints in Taiwan. Environ Sci Pollut Res 26:33906-33916. https://doi.org/10.1007/s11356-018-2669-8.

Liu Z, Yu R, Dong Y, Li W, Lv B (2017) The adsorption behavior and mechanism of Cr (VI) on 3D hierarchical α-Fe₂O₃ structures exposed by (0 0 1) and non-(0 0 1) planes. Chem Eng J 309:815-823. https://doi.org/10.1016/j.cej.2016.10.108.

Ma H, Hwang JB, Chae WS, Chung HS, Choi SH, Mahadik MA, Lee HH, Jang JS (2021). Magnetron sputtering strategy for Zr-Fe₂O₃ nanorod photoanode fabricated from ZrOₓ/β-FeOOH nanorods for photoelectrochemical water splitting. Appl. Surf. Sci 30:149233. https://doi.org/10.1016/j.apsusc.2021.149233.

Nalbandian MJ, Zhang M, Sanchez J, Choa YH, Nam J, Cwiertny DM, Myung NV (2016) Synthesis and optimization of Fe₂O₃ nanofibers for chromate adsorption from contaminated water sources. Chemosphere 144:975-981. https://doi.org/10.1016/j.chemosphere.2015.08.056.

Onchoke KK Sasu SA (2016) Determination of Hexavalent Chromium (Cr (VI)) concentrations via ion chromatography and UV-Vis spectrophotometry in samples collected from nacogdoches wastewater treatment plant, East Texas (USA). Adv Environ Chem 2016: 3468635. https://doi.org/10.1155/2016/3468635.

Park HJ, Tavlarides LL (2008) Adsorption of chromium (VI) from aqueous solutions using an imidazole functionalized adsorbent. Ind Eng Chem Res 47:3401-3409. https://doi.org/10.1021/ie7017096.

Ponti A, Raza MH, Pantò F, Ferretti AM, Triolo C, Patanè S, Pinna N, Santangelo S (2020) Structure, Defects, and Magnetism of Electrospun Hematite Nanofibers Silica-Coated by Atomic Layer Deposition. Langmuir 36:1305-1319. https://doi.org/10.1021/acs.langmuir.9b03587.

Rahman Z, Singh VP (2019) The relative impact of toxic heavy metals (THMs)(arsenic (As), cadmium (Cd), chromium (Cr)(VI), mercury (Hg), and lead (Pb)) on the total environment: an overview. Environ Monit Assess 191:419. https://doi.org/10.1007/s10661-019-7528-7.

Rahmat ST, Chin OY, Tan WK, Kawamura G, Matsuda A, Lockman Z (2018) Hierarchical Porous α-Fe₂O₃ Formation by Thermal Oxidation of Iron as Catalyst for Cr (VI) Reduction. IOP Conf Series: J Phys Conf Series 1082:012044. doi:10.1088/1742-6596/1082/1/012044.

Rahmat ST, Hong CY, Budiman F, Tan WK, Kawamura G, Matsuda A and Lockman Z (2018) Tailoring Parameters to Produce Nanowires on Metal Surface via Surface Oxidation Process. IOP Conf Series: J Phys Conf Series 1082: 012052. doi:10.1088/1742-6596/1082/1/012052.

Rahmat ST, Tan WK, Kawamura G, Matsuda A, Lockman Z (2020) Synthesis of rutile TiO₂ nanowires by thermal oxidation of titanium in the presence of KOH and their ability to photoreduce Cr (VI) ions. J Alloys Compd 812:152094. https://doi.org/10.1016/j.jallcom.2019.152094.
Rasheed A, Carvalho AAC, de Carvalho GGA, Ghaus T, Nomura CS, Esposito, BP (2020) Chromium removal from aqueous solutions using new silica gel conjugates of desferrioxamine or diethylenetriaminepentaacetic acid. Environ Sci Pollut Res 27:1-10. https://doi.org/10.1007/s11356-020-08097-5.

Ren T, He P, Niu W, Wu Y, Ai L, Gou X (2013) Synthesis of α-Fe₂O₃ nanofibers for applications in removal and recovery of Cr (VI) from wastewater. Environ Sci Pollut Res 20:155-162. https://doi.org/10.1007/s11356-012-0842-z

Rosli SA, Alias N, Bashirnom N, Ismail S, Tan WK, Kawamura G, Matsuda A, Lockman Z (2021) Hexavalent Chromium Removal via Photoreduction by Sunlight on Titanium–Dioxide Nanotubes Formed by Anodization with a Fluorinated Glycerol–Water Electrolyte. Catalysts 11:376. https://doi.org/10.3390/catal11030376.

Singaraj SG, Mahanty B, Balachandran D, Padmaprabha A (2019) Adsorption and desorption of chromium with humic acid coated iron oxide nanoparticles. Environ Sci Pollut Res 26:30044-30054. https://doi.org/10.1007/s11356-019-06164-0.

Srivastava H, Srivastava AK, Babu M, Rai S, Ganguli T (2016) Topotaxial growth of α-Fe₂O₃ nanowires on iron substrate in thermal annealing method. J Appl Phys 119:244311. https://doi.org/10.1063/1.4954975.

Sruthi PD, Sahithya CS, Justin C, SaiPriya C, Bhavya KS, Senthilkumar P, Samrot AV (2019) Utilization of Chemically Synthesized Super Paramagnetic Iron Oxide Nanoparticles in Drug Delivery, Imaging and Heavy Metal Removal. J Clust Sci 30:11-24. https://doi.org/10.1007/s10876-018-1454-7.

Sun X, Sun X, Liu X, Liu R, Li S, Shen M, Li Q (2020) One-dimensional Mg²⁺-induced α-Fe₂O₃ nanowires for high-performance supercapacitor. Results Mater 5:100052. https://doi.org/10.1016/j.rinma.2019.100052.

Tan WK, Razak KA, Ibrahim K, Lockman Z (2011) Oxidation of etched Zn foil for the formation of ZnO nanostructure. J Alloys Compd 509:6806-11. https://doi.org/10.1016/j.jallcom.2011.03.055.

Taniguchi K, Kitazawa N (2020) Characterization of α-Fe₂O₃ nanorod arrays prepared by a quasi-topotactic transformation of solvothermal derived β-FeOOH nanowire-like arrays. J Phys Chem Solids 147:109632. https://doi.org/10.1016/j.jpcs.2020.109632.

WHO G (2011) Guidelines for drinking-water quality. World Health Organization, Geneva.

Xie B, Shan C, Xu Z, Li X, Zhang X, Chen J, Pan B (2017) One-step removal of Cr (VI) at alkaline pH by UV/sulfite process: reduction to Cr (III) and in situ Cr (III) precipitation. Chem Eng J 308:791-797. https://doi.org/10.1016/j.cej.2016.09.123.

Yu JH, Lu JX, Smollin C, Cheng HT, Seak CJ, Chen HY (2020) N-acetylcyesteine and ascorbic acid therapy for acute hepatic injury after hexavalent chromium ingestion. J Clin Pharm Ther 45:208-210. https://doi.org/10.1111/jcpt.13044.

Yuan L, Wang Y, Cai R, Jiang Q, Wang J, Li B, Sharma A, Zhou G (2012) The origin of hematite nanowire growth during the thermal oxidation of iron. Mat Sci Eng B 177: 327-336. https://doi.org/10.1016/j.mseb.2011.12.034.

Zelmanov G, Semiat R (2011) Iron (Fe⁺³) oxide/hydroxide nanoparticles-based agglomerates suspension as adsorbent for chromium (Cr⁺⁶) removal from water and recovery. Sep Purif Technol 80:330-337. https://doi.org/10.1016/j.seppur.2011.05.016.

Zhang R, Zeng Q, Guo P, Cui Y, Sun Y (2020) Efficient capture of Cr (VI) by carbon hollow fibers with window-like structure. Environ Sci Pollut Res 27:1-11. https://doi.org/10.1007/s11356-020-07939-6.
Zheng Y, Yan Y, Yu L, Li H, Jiao B, Shiau Y, Li D (2020) Synergism of citric acid and zero-valent iron on Cr (VI) removal from real contaminated soil by electrokinetic remediation. Environ Sci Pollut Res 27:5572-5583. https://doi.org/10.1007/s11356-019-06820-5.

Zhou N, Gong K, Hu Q, Cheng X, Zhou J, Dong M, Wang N, Ding T, Qiu B, Guo Z (2020). Optimizing nanocarbon shell in zero-valent iron nanoparticles for improved electron utilization in Cr (VI) reduction. Chemosphere 42:125235. https://doi.org/10.1016/j.chemosphere.2019.125235.