Iron oxide submicron wires are successfully synthesized via a microwave irradiation method within a short period of 20 s. Upon reduction, this material shows orders of magnitude faster Cr(VI) removal rate than conventional adsorbents. A redox reaction based removal mechanism is revealed instead of adsorption.

Chromium, one of the toxic heavy metals, is generated from a wide range of anthropogenic sources and industrial processes. Inhaled Cr(VI), a human carcinogen, is able to transport into cells via the sulfate transport mechanism taking advantage of the similarity of sulfate and chromate with respect to their structure and charge. The national toxicology program has concluded that Cr(VI) in drinking water shows “clear evidence of carcinogenic activity” in laboratory animals. In 2010, the U.S. Environmental Protection Agency (EPA) found that Cr(VI) in tap water is “likely to be carcinogenic to humans.” Even though US EPA has recommended the maximum permissible limit of the total Cr in drinking water as 100 ppb, a much lower Cr(VI) concentration of 0.06 ppb has been proposed by California regulators. Recent laboratory tests committed by the environmental working group have detected carcinogenic Cr(VI) in tap water from 31 out of 35 sampled US cities. Among the 31 US cities, water samples from 25 cities contained Cr(VI) at concentrations above the safe maximum limit of 0.06 ppb. At least 74 million Americans in 42 states drink chromium-polluted tap water, most of which are likely in the cancer-causing Cr(VI) form.

The present technologies to eliminate or reduce the Cr(VI) from water include cyanide treatment, electrochemical precipitation, reverse osmosis (RO), ion exchange (IE) and adsorption. Among these methods, adsorption seems the most promising technique in practical applications unless highly efficient adsorbents can be developed. Recently, iron containing nanomaterials have demonstrated efficient heavy metal removal property due to their large surface area, easy binding with chemicals, easy separation by the extracting magnetic field, and reusability. Major attention is paid to zero-valent nano iron, and polymorphic forms of iron oxides and FeOOH. The preparation of iron containing nanostructures can be roughly divided into physical, chemical, and biological approaches. Among them, the chemical approach is the most accepted and used method including chemical co-precipitation, thermal decomposition, sol–gel, and electrochemical method. However, the disadvantages of wet-chemical synthesis should be addressed, such as relatively complex procedure, extra chemicals, and tentative aggregation in aqueous systems. The microwave method has advantages of facile process, simple operation and high efficiency, which is demonstrated to be effective in manufacturing structure defined nano- and submicron materials.

Here, iron oxide submicron-wires (MWs) are manufactured by a microwave method and their reduced form (r-MWs) is used for heavy metal removal test. Upon 20 s microwave irradiation on a graphite–Fe(CO)₅ mixture at 1250 W power level, reddish MWs were formed without any pre-treatment, additives or gas protection. Refer to ESI† for experimental details. This microwave approach presents a facile, cost-effective and ultrafast way to synthesize structure controlled iron oxide materials and these materials will play important roles in chemical, biological and electrochemical applications.

Fig. 1(a) shows the growth mechanism of MWs with graphite powders. In the ideal case, liquid Fe(CO)₅ fully contacts with graphite (heating source). The surface layer of Fe(CO)₅ converts to nanoparticles upon microwave irradiation and the as-formed nanoparticles further served as active sites for growth of the wire structure. Within a short reaction time of 20 s, the MW...
network is formed as observed in Fig. 1(b) and Fig. S1 (ESI†). An enlarged SEM image, Fig. 1(c), shows the uniform size distribution of MWs. This is further evidenced by the statistical analysis in the inset figure where the diameter of MWs majorly distributes in a narrow range of 0.4–0.6 μm (average: 0.49 μm). The as-synthesized MWs show reddish color, indicating the major component of Fe₂O₃. These MWs are then reduced in 5% H₂/Ar at 600 °C for 2 hours to obtain black r-MWs. The reduction process has two major benefits, one is to obtain more active species of iron for effective Cr(vi) removal. HRTEM confirms the existence of pure Fe species in r-MWs, Fig. S2 (ESI†). The other is to increase magnetization for fast separation with magnet after water treatment, Fig. S3 and S4 (ESI†).

The initial tests indicate that the Cr(vi) removal of r-MWs is significantly better than in MWs. Therefore, a systematic study is performed on r-MWs in this work. Fig. 2(a) shows the standard curve of Cr(vi) concentration (50–1500 ppb) with UV-Vis spectra intensity at a wavelength of 540 nm. The inset figure shows a highly linear increase of the peak intensity with increasing Cr(vi) concentration. Refer to ESI† for experimental details. With this standard curve, the Cr(vi) concentration in solution can be precisely quantified using a UV-Vis spectrometer. Obviously, the original Cr(vi) concentration and r-MWs concentration affect the final Cr(vi) removal percentage, Fig. 2(b). By fixing the [r-MWs] = 2.0 g L⁻¹, Cr(vi) can be completely removed when the concentration is below 400 ppb. Upon increasing the [Cr(vi)] to 1000 ppb, only 82% of the Cr(vi) can be removed. By fixing the [Cr(vi)] at 500 ppb, the minimum [r-MWs] is 2.0 g L⁻¹ for complete removal. To quantify the removal capacitance and rate performance of the r-MWs, a kinetic study has been performed at different temperatures, 20, 30, 40 and 60 °C with fixed [r-MWs] = 2.0 g L⁻¹ and [Cr(vi)] = 1000 ppb, respectively. Meanwhile, two mixing approaches, sonication and mechanical stirring, are comparatively investigated at 20 °C to evaluate the process effect, Fig. 2(c). It is observed that the Cr(vi) can be completely removed within 30 min, which is much faster than conventional adsorbents such as activated carbon and biomass those require hours or even days of adsorption to reach better removal percentage.¹⁴ The Cr(vi) removal with sonication mixing at 20 °C is slightly better than that through mechanical stirring due to the better dispersion quality of r-MWs. However, mechanical mixing is widely adopted in industry. Therefore, the kinetic study of Cr(vi) removal is performed with mechanical stirring at different temperatures. It is observed that the removal rate is significantly enhanced with increasing temperature. The complete removal time decreases from 30 min (20 °C) to 5 min (30 °C), 3 min (40 °C) and 1 min (60 °C), respectively. To quantify the removal rate and capacity, different kinetic models including pseudo-first-order, pseudo-second-order,¹⁵ elovich,¹⁶ and interaparticle diffusion¹⁷ have been used to fit the kinetic results and the correlation coefficient (R²) is used to evaluate the suitability of each model. The higher R² value indicates a more applicable model. Among these models, the pseudo-second order acquires the highest correlation coefficient of R² = 0.999 at different temperatures, Fig. 2(d), which can be expressed in eqn (1):

$$\frac{t}{q_t} = \frac{1}{k_{ad}q_e} + \frac{t}{q_e}$$  

(1)

where qᵣ (mg g⁻¹) is the solid-phase loading of Cr(vi) in the r-MWs at time t (min), qₑ (mg g⁻¹) is the adsorption capacity at equilibrium, kₑ (g (mg⁻¹ min⁻¹)) is the rate constant of adsorption and h (mg (g⁻¹ min⁻¹)) is the initial adsorption rate at t approaching zero, h = kₑqₑ. The qₑ falls in the range of 0.50–0.52 mg g⁻¹ at different temperatures, which is similar to commercial α-Fe₂O₃ (0.68 mg g⁻¹)¹⁸ and CeO₂ (0.37 mg g⁻¹)¹⁹ but relatively lower than graphene nanocomposites (1.03 mg g⁻¹)²⁰ and carbon coated magnetic nanoparticles (1.52 mg g⁻¹).²¹ The uniqueness of this material is the ultrafast removal rate. The rate constant kₑ at 20 °C is 1.2 g (mg⁻¹ min⁻¹). Upon increasing the temperature to 30, 40 and 60 °C, kₑ increases dramatically to 18.2, 58.2 and 1502.3 g (mg⁻¹ min⁻¹), respectively. The typical rate constant for most of the existing materials is less than...
0.5 g (mg⁻¹ min⁻¹). Therefore, r-MWs show unprecedented properties in fast Cr(vi) removal.

To reveal the Cr(vi) removal mechanism by r-MWs, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to characterize the crystalline structure and surface element before and after water treatment. Fig. 3(A) shows the XRD pattern of MWs, r-MWs and r-MWs after water treatment. All the peaks from MWs correspond well to the Fe₂O₃ crystal planes, 43.1° (400), 44.4° (410), 49.3° (421), 54.1° (422), 57.7° (511), 62.9° (440) and 64.5° (530) according to PDF#39-1346. After reduction in hydrogen at 500 °C, two more iron species, pure iron and iron carbide, were formed as evidenced by the crystalline peaks at 44.6° (110), 65.8° (200) for iron (PDF#00-06-0696) and 41.6° (200), 63.6° (222) for Fe₃C (PDF#00-003-0411). The newly formed crystal phases are the key components for efficient Cr(vi) removal since a significantly enhanced removal capacity and rate have been observed after reduction. Iron and iron oxide nanostructures have been reported to remove Cr(vi) due to the spontaneous redox reaction between reductive zero-valent Fe and oxidative heavy metals. A similar redox reaction mechanism is expected since pure iron in r-MWs is highly reductive that is able to convert Cr(vi) to less-toxic Cr(III). At the same time, pure iron will be oxidized to iron oxide. Therefore, a reaction based removal mechanism can be determined once the iron and iron oxide species can be quantified before and after water treatment. However, identical crystalline peaks are observed before and after Cr(vi) removal, especially the iron peak is retained, Fig. 3(A), indicating that either the pure iron is not completely reacted or the Cr(vi) removal is based on adsorption. To further confirm the reaction mechanism, XPS was performed and the spectrum of r-MWs after water treatment is shown in Fig. 3(B); for the XPS spectrum of MWs and r-MWs refer to ESI† Fig. S5. The complete scan within 0–800 eV identifies the C 1s at 285 eV, which is used as a reference for other peaks in this work. Besides, different iron elemental species including Fe2p, Fe(LMM), Fe3s, Fe3p and oxygen species such as O(KVV) and O1s have been determined. The detected weak Cr peaks, Cr(LMM) and Cr2p, confirms the existence of Cr element on the r-MW surface after water treatment. However, the removal mechanism cannot be determined unless quantitative results are obtained. The fraction of surface elements is summarized in Table 1. The Fe/O ratio increases from 0.10 (MWs) to 0.33 (r-MWs) due to the partial reduction by annealing in a H₂/Ar atmosphere. After water treatment, the Fe/O ratio decreases to 0.26 indicating the oxidation of iron species at the surface, which suggests a reaction-based removal mechanism. Moreover, only 1% of Cr has been detected on the r-MW surface, which further confirms that most of the Cr(vi) has been reduced to Cr(III) rather than adsorption on the r-MW surface. The 1% Cr detected on the surface may be attributed to the adsorption on the low surface area r-MWs, Fig. S6 (ESI†).

In conclusion, iron oxide submicron wires have been successfully manufactured via an ultrafast microwave method. The uniqueness of this material has been demonstrated in toxic Cr(vi) removal from polluted water with orders of magnitude faster rate performance at elevated temperatures. The kinetic study reveals that the removal behaviour follows a pseudo-second order model. The removal mechanism is based on a redox reaction between reductive iron species in r-MWs and oxidative Cr(vi) rather than adsorption.

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Notes and references

Table 1  XPS analysis results of samples

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<th>Sample</th>
<th>Fe</th>
<th>O</th>
<th>C</th>
<th>Cr</th>
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<td>39</td>
<td>57</td>
<td>—</td>
<td>0.10</td>
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<tr>
<td>r-MWs</td>
<td>11</td>
<td>33</td>
<td>56</td>
<td>—</td>
<td>0.33</td>
</tr>
<tr>
<td>r-MWs†</td>
<td>10</td>
<td>42</td>
<td>47</td>
<td>1</td>
<td>0.26</td>
</tr>
</tbody>
</table>

* Indicates the sample after water treatment.
Communication


