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REVIEW ARTICLE

Hexavalent chromium in drinking water: Chemistry, challenges and future outlook on Sn(II)- and photocatalyst-based treatment

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HIGHLIGHTS

- Wide occurrence of Cr(VI) in US source drinking water.
- A strong dependence of occurrence on groundwater sources.
- Elucidate Redox and equilibrium chemistry of Cr (VI).
- Sn(II)-based and TiO_2-based reductive treatments hold extreme promise.
- Key challenges include residual waste, Cr(VI) re-generation and socioeconomic drivers.

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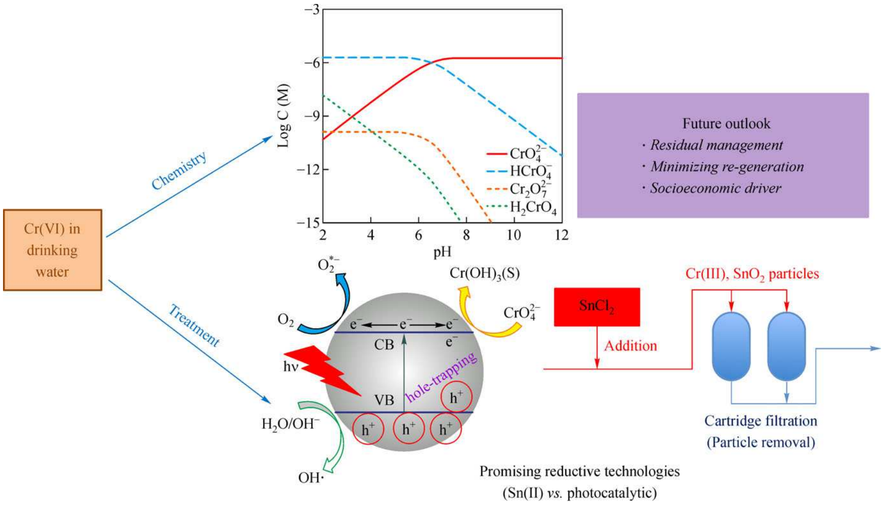
GRAPHIC ABSTRACT



ABSTRACT

Chromium (Cr) typically exists in either trivalent and hexavalent oxidation states in drinking water, *i.e.*, Cr(III) and Cr(VI), with Cr(VI) of particular concern in recent years due to its high toxicity and new regulatory standards. This Account presented a critical analysis of the sources and occurrence of Cr(VI) in drinking water in the United States, analyzed the equilibrium chemistry of Cr(VI) species, summarized important redox reaction relevant to the fate of Cr(VI) in drinking water, and critically reviewed emerging Cr(VI) treatment technologies. There is a wide occurrence of Cr(VI) in US source drinking water, with a strong dependence on groundwater sources, mainly due to naturally weathering of chromium-containing aquifers. Challenges regarding traditional Cr(VI) treatment include chemical cost, generation of secondary waste and inadvertent re-generation of Cr(VI) after treatment. To overcome these challenges, reductive Cr(VI) treatment technologies based on the application of stannous tin or electron-releasing titanium dioxide photocatalyst hold extreme promise in the future. To moving forward in the right direction, three key questions need further exploration for the technology implementation, including effective management of residual waste, minimizing the risks of Cr(VI) re-occurrence downstream of drinking water treatment plant, and promote the socioeconomic drivers for Cr(VI) control in the future.

1 Sources and occurrences of hexavalent chromium

Hexavalent chromium, Cr(VI), is a contaminant of emerging concern in drinking water due to its toxicity and possibly more tightening drinking water standards in

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the future. Exposure to Cr(VI) through respiratory, oral and dermal pathways induces cancers and other terminal illnesses. Chromium mainly existing as hexavalent Cr (VI) and trivalent Cr(III) are the two stable forms in the aquatic environment. At circumneutral pHs, Cr(VI) exists as an oxyanion, *i.e.*, chromate CrO_4^{2-}, whereas Cr(III) exists as different low-soluble solids depending on the co-existing constituents such as hydroxide, iron and copper. Cr(III) is considered non-toxic, a micro-nutrient in mammalian diets and aids in the metabolism of glucose and lipids.

Both anthropogenic activity and natural occurrence lead to Cr(VI) in the aquatic environment, and natural occurrence plays a more substantial contribution. The occurrence of Cr(VI) in the aquatic environment was historically driven by anthropogenic release from chemical and manufacturing industries, including paints, pigments, paper, electroplating and leather tanning (Jacobs and Testa, 2005). One notable example is the disastrous Cr(VI) release from an industrial site in Hinkley, Calif. between 1950s and 1960s, which garnered an international attention four decades later through the blockbuster Oscar-winning movie *Erin Broachvich* (Izbicki and Groover, 2018). However, as the manufacturing industry sets more stringent standards on wastewater treatment in recent decades, the contribution of industrial wastewater discharge to Cr(VI) occurrence becomes less of a routine concern. In contrast, natural release of Cr(VI) driven by geochemical sources makes a more substantial contribution to the wide occurrence of Cr(VI) in drinking water (Coyte et al., 2020; Oze et al., 2007; Vengosh et al., 2016). One major source of natural-occurring Cr(VI) is from groundwater and aquifer materials. Chromium is widely embedded in aquifer minerals as the 21st most abundant element in the earth's crust (Oze et al., 2004). The naturally geological weathering of aquifer materials releases Cr(VI) via a slow oxidation of Cr(III)-containing iron minerals $Fe_xCr_{(1-x)}(OH)_{3(s)}$ in the aquifer by co-existing manganese (IV) minerals (Eary and Rai, 1987; Pan et al., 2017):

$$\begin{aligned} &Fe_xCr_{(1\text{-}x)}(OH)_{3(s)}+\frac{3}{2}(1-x)MnO_{2(s)}+(1-x)H^+ \\ &\rightarrow(1-x)CrO_4^{2-}+\frac{3}{2}(1-x)Mn^{2+}+xFe(OH)_3 \\ &\quad +2(1-x)H_2O \qquad (1) \end{aligned}$$

where x is the molar fraction of chromium in the mixed phase of iron-chromium hydroxide solid, and its value varies between 0 and 1.

An analysis of a recent US EPA database on chromium – Unregulated Contaminant Monitoring Rule Round 3 (UCMR3) showed that hexavalent chromium is widely present in drinking water sources across the US (Chebeir et al., 2016). Drinking water systems using groundwater as the main source water report much higher percentages of Cr(VI) occurrence than those using surface water as the main source, especially for cases with elevated levels of Cr (VI) higher than 10 μg/L (Fig. 1A). This dependence clearly indicates the strong influence of naturally geological weathering process in the natural occurrence of Cr(VI) in source waters, which preferentially impacts groundwater sources.

Furthermore, chromium accumulated in urban drinking water infrastructure, namely the drinking water distribution systems risks to become another geochemical source of hexavalent chromium. Recent surveys have discovered that chromium accumulates in the corrosion scales of

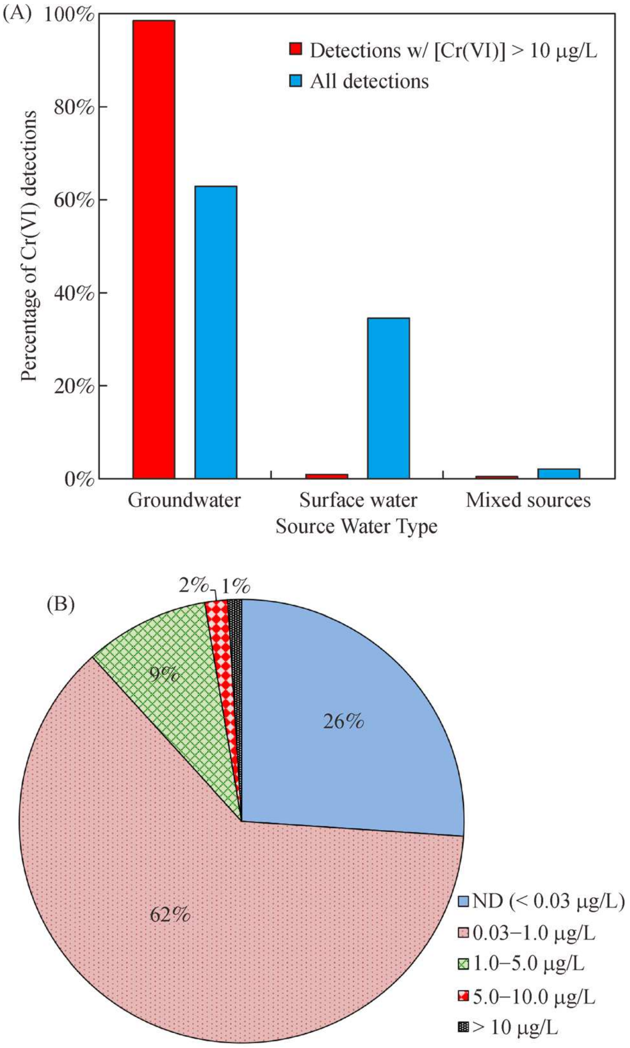

Fig. 1 Distributions of Cr(VI) concentrations in source drinking water and at the exit point of the drinking water distribution systems in the United States. This analysis is based on data from 4,583 water utilities and 22,734 drinking water samples in the USPEA UCMR3 database. (A) Cr(VI) distribution at the entry point to the water distribution systems based on 22,734 detections. (B) Cr(VI) distribution at the maximum residence time of the exist to the distribution systems based on 4583 public water utilities.

drinking water distribution systems. The level of chromium observed in the corrosion scales has exceeded the level observed in earth crust (Peng et al., 2012). Under oxidative conditions in drinking water and in scenarios with abrupt changes of source water and associated water chemistry, the accumulated chromium can release back into drinking water and increased Cr(VI) level at the tap. For example, an analysis of the US EPA UCMR3 database showed that the hexavalent chromium level at the exit point of the drinking water distribution systems was statistically higher than the level at the entrance to the distribution system (Chebeir et al., 2016). A synthesis of the database also showed that a considerable percentage of public water utilities in the US detects Cr(VI) at the exist point to the drinking water distribution systems, range from sub-μg/L to higher than 10 μg/L (Fig. 1B).

US EPA currently regulates total chromium, *i.e.*, a combination of Cr(III) and Cr(VI), at 100 μg/L in treated drinking water. A new standard specifically for Cr(VI) was established at 10 μg/L in California in 2013 but was subsequently withdrawn (US EPA, 2015). Considering the public health risks of Cr(VI) and a tightening regulatory perspective in the future, it is urgent and important to understand chromium chemistry that drives Cr(VI) occurrence in drinking water, and develop efficient treatment technologies to minimize risks.

2 Redox chemistry of hexavalent chromium

Because Cr(VI) is redox reactive, its redox chemistry drives the fate of Cr(VI) in drinking water, and dictates the development of effective treatment processes. Consequently, it is imperative to examine the redox chemistry of chromium in typical drinking water conditions. From a chemical speciation perspective, Cr(VI) can undergo protonation and bimolecular combination via chronic acid H_2CrO_4, and exists in different soluble species depending on the solution pH (Fig. 2). Within the typical pH range of drinking water, *i.e.*, neutral to slightly basic (pH of 7–8), Cr(VI) predominately exists as the deprotonated oxyanion chromate CrO_4^{2-}, the protonated $HCrO_4^-$ only accounts for a small fraction, and other soluble species including $Cr_2O_7^{2-}$ are negligible.

In contrast, trivalent Cr(III) exists as different solid phases with a low ^{low} solubility in typical drinking water chemical conditions. For example, various Cr(III) minerals exist in corrosion products in drinking water distribution systems (Chebeir and Liu, 2016, 2018; Choi et al., 2004). The redox potential of these Cr(III) solids coupled with CrO_4^{2-} ranged between −0.57 and 0.57 V in typical drinking water chemical condition (Fig. 3). Meanwhile, common disinfectants used in drinking water, e.g., free chlorine (HOCl), possess a higher redox potential (E = 1.23V) than any of the CrO_4^{2-}/Cr(III) solid couple; therefore, chlorine can oxidize Cr(III) and affect the mobility of Cr in drinking water (Chebeir and Liu, 2016, 2018). Taking $Cr(OH)_{3(s)}$ as an example:

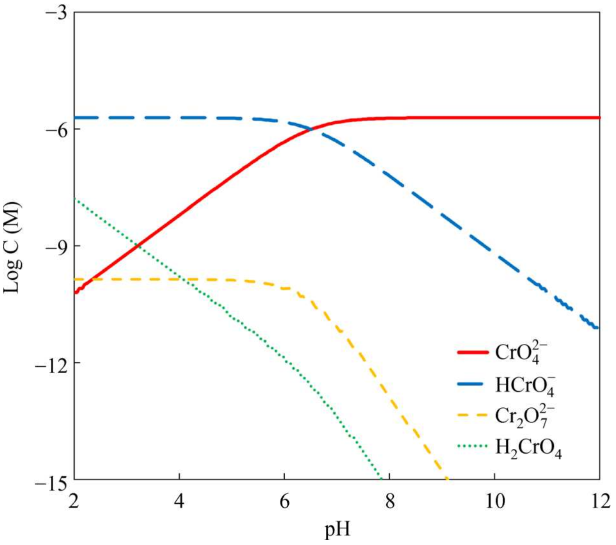

Fig. 2 Speciation of hexavalent chromium as a function of drinking water pH. The total Cr(VI) level is modeled at 100 μg/L, *i.e.*, the US EPA drinking water maximum contaminant level for total chromium. T = 25°C.

$$Cr(OH)_{3(s)} + 3HOCl \rightarrow 2CrO_4^{2-} + 3Cl^- + 7H^+ \qquad (2)$$

The reactions of Cr(III) solids oxidation by free chlorine residuals can take place in drinking water distribution systems, as supported by statistical analysis of EPA UCMR3 database. The accumulation of even non-toxic Cr(III) in water distribution systems may be inadvertently converted to Cr(VI) by residual chlorine in the distribution systems. This transformation could seriously jeopardize the benefits of upstream treatment.

Meanwhile, several reductants exists a redox potential lowered than that of Cr(VI)/Cr(III) couple and can serve as a reductive reagent to convert toxic Cr(VI) to benign Cr (III) end products. For example, ferrous ion with the $Fe(OH)_{3(s)}/Fe^{2+}$ redox couple has a redox potential of 0.02 V, and divalent tin Sn(II) with the $SnO_{2(s)}/Sn^{2+}$ redox couple also has a very low redox potential of −1.43 V in typical drinking water conditions (Fig. 3). These reductants provides possibilities for reductive treatment of Cr(VI) in drinking water.

3 Cr(VI) drinking water treatment technologies

3.1 Traditional drinking water treatment technologies

Traditional Cr(VI) treatment technologies that have been applied at full scale drinking water treatment plants include ion exchange and ferrous iron Fe(II)-based reduction

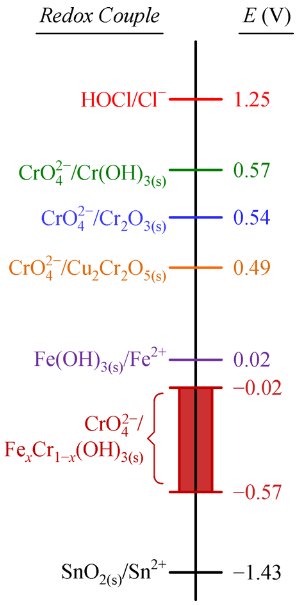

Fig. 3 Redox potentials of different redox couples in typical drinking water chemical conditions. The calculation is based on the following condition: [HOCl] = 1 mg/L as Cl_2; [Cl^-] = 3.5 mg/L; [CrO_4^{2-}] = 100 μg/L; [Fe^{2+}] = 2 mg/L; [Sn^{2+}] = 0.5 mg/L, pH = 7, T = 25°C. The actual redox potentials are calculated based on the standard redox potential values obtained from Benjamin, 2004.

coagulation (Seidel et al., 2013). The treatment principle of ion exchange is based on the physical separation of Cr(VI) anions using quaternary amino functionalized ion exchange resins, and has been employed in small drinking water treatment systems – mostly groundwater based systems. The handling and disposal of concentrated Cr (VI)-containing ion exchange brine is very challenging and costly, which hinders the wide application of ion exchange to large-scale drinking water treatment. In addition, the application of effective ion exchange treatment needs to avoid the competitive exchange in co-existing anion in the source drinking water sources, including sulfate, nitrate, arsenic and radioactive uranium, which can potentially decrease the Cr(VI) treatment efficiency or increases the operational complexity (Plummer et al., 2018).

Fe(II)-based reductive Cr(VI) removal is another existing technology that has been applied at pilot-scale for Cr (VI) drinking water treatment in California (Blute et al., 2014). This process applies ferrous chloride as a reductant to convert Cr(VI) to non-toxic Cr(III) particles, followed by a coagulation step to promote the formation of Cr(III) and Fe(III) particles, and a final filtration step to remove the particles, therefore achieving a total chromium removal. This technology is proven viable at full-scale; however, it also brings operational challenges to deal with, including a long treatment time, high chemical dosage requirement and large secondary solid waste. For example, to ensure a complete conversion of Cr(VI) to Cr(III) particles via Fe(II) reduction, this process requires a large over-stoichiometric molar ratio of Fe(II)-to-Cr(VI) (between 20 and 30) to achieve a desirable reaction kinetics in a continuous treatment mode. The long reaction time for reductive reaction requires 30 min or more. In addition, the over-stoichiometric dosage of Fe(II) requires a subsequent re-oxidation step – achieved by either aeration or chlorination – to convert residual Fe(II) to Fe (III) particles prior to filtration step. This results in the formation of a large quantity of iron sludge waste that is operationally complicated to handle (Seidel et al., 2013).

Redox-driven Cr(VI) treatment technologies are more promising and cost-effective than physical separation technologies (for example, ion exchange), because Cr (VI) is chemically reduced to non-toxic Cr(III) solids in the presence of a reductant and subsequently removed as Cr (III) particles, eliminating the need for additional brine disposal (Eary and Rai, 1988). The challenges to overcome for a full-scale application in drinking water treatment include operational complexity, high chemical dosage requirement and secondary waste generation.

3.2 Sn(II)-based reductive Cr(VI) treatment

To overcome the disadvantages of over-stoichiometric addition of chemicals and secondary waste generation, a new chemical reductive treatment has recently been developed based on divalent tin Sn(II) addition as the chemical of stannous chloride $SnCl_2$. The following redox reaction takes place (Henrie et al., 2019; Kennedy et al., 2020):

$$3Sn^{2+} + 2CrO_4^{2-} + 4H_2O$$
$$\rightarrow 2Cr(OH)_{3(s)} + 3SnO_{2(s)} + 2H^+ \qquad (3)$$

Upon the completion of reaction, divalent tin is oxidized to tetravalent tin solid $SnO_{2(s)}$ and removed together with Cr(III) solids by a filtration unit. Compared to Fe(II), using Sn(II) as the reductant is advantageous in multi-fold. First, the reaction kinetics between Sn(II) and Cr(VI) is extremely fast, *i.e.*, reaction in typical drinking water condition typically completes within seconds, whereas the reaction kinetics between Fe(II) and Cr(VI) is much slower and takes more than 30 min to completion. This inherent advantage of fast reaction kinetics enhanced the easiness of continuous Sn(II)-based treatment operation. Second, stannous addition requires a much lower stoichiometric molar ratio of Sn(II)-to-Cr(VI) compared to Fe(II)-to-Cr (VI) in ferrous-based approach (2–5 *vs.* 20–30). Therefore, the formation of solid residual waste is minimized and the secondary waste generation is not a concern when Sn(II) is employed as the reductant. Due to the small amount of solid formation as the end product, additional coagulation and flocculation are not required. Instead, a simple treatment step utilizing cartridge filtration or porousmedium sand filtration typically follows the addition of Sn (II) to remove residual particles (Fig. 4A). For example, a pilot-testing conducted in Coachella Valley, Calif. showed that the cost of Sn(II) reductive treatment would substantially decrease capital and operation/maintenance costs, as well as minimizing waste residuals, compared to Fe(II) reductive treatment. Third, residual tin in the treated drinking water acts as a corrosion inhibitor and benefits drinking water distribution systems. A recent study has demonstrated that residual tin is sequestered in the corrosion scales of distribution systems. Cr(III) solids – the end products of Sn(II) reductive treatment – also exhibited a low risk in re-oxidation to Cr(VI) when the treated drinking water enters a distribution system in the presence of chlorine as the residual disinfectant.

3.3 Photocatalytic Cr(VI) treatment

Another promising reductive treatment technology harnesses electrons as a strong reductant for Cr(VI) removal via photocatalysis. Differing from other chemical reductive treatment technologies, photocatalytic reduction does not require consumable chemicals, and converts photon energy to reactive electrons via catalysts to drive the reduction of Cr(VI) to Cr(III). Titanium dioxide (TiO_2) photocatalysts are popular materials because of its high stability, low toxicity, low cost, large surface areas and good optical properties (Loeb et al., 2019). Upon UV irradiation by photons with energy equal or greater than its bandgap, TiO_2 undergoes a hole-electron separation process, generated holes on the valence band (VB) and electrons on the conduction band (CB), and induces reductive conversion of Cr(VI) when electrons migrate to the surface of TiO_2 catalyst (Fig. 5A).

Thermodynamically, CB-associated electrons ($E = -0.29$ V) can be utilized to reduce Cr(VI) to Cr(III). However, with conventional TiO_2 (e.g., commercial P25 TiO_2), the holes on the valence band quickly oxidize surface adsorbed H_2O to hydroxyl radicals ($HO^\bullet$) and creates a highly oxidative environmental that is detrimental to reductive Cr(VI) treatment. In addition, the migration of the electrons takes random pathway, which make it a high probability for electrons to recombine with holes, and interfacial electron transfer is much slower than hole-electron recombination rate and interfacial hole transfer. These facts make electrons from conventional TiO_2 materials unavailable for Cr(VI) reduction.

To fully utilize photogenerated electrons and make TiO_2 reductively reactive, polyol molecules as hole scavengers are applied to covalently bond onto the TiO_2 surface via bridged O atoms is a promising strategy (Fig. 5B). This surface modification can be realized simply via thermal hydrolysis, which induces the occupied energy state inside the TiO_2 band gap, and significantly improve the hole

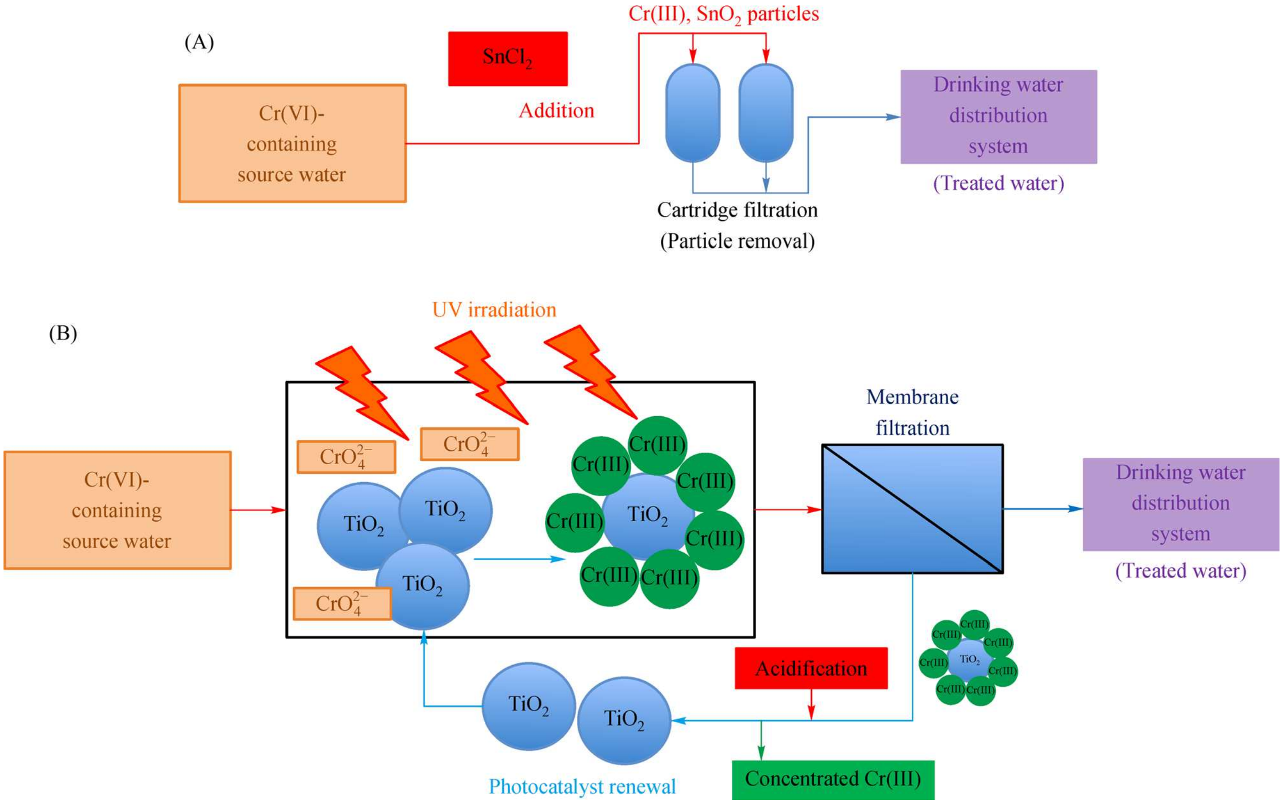

Fig. 4 Promising treatment technologies for hexavalent chromium in drinking water. (A) A schematic illustration of Sn(II)-based reductive treatment for hexavalent chromium in drinking water. (B) The molecular structure of a DEG-capped TiO_2 catalyst.

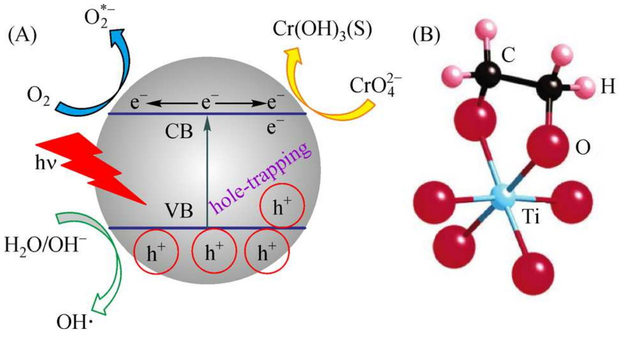

Fig. 5 (A) Reaction mechanism for photocatalytic reduction of Cr(VI) in aqueous suspension of TiO_2 nanocrystals. (B) The molecular structure of a diethylene glycol (DEG)-capped TiO_2 catalyst.

trapping efficiency (Chen et al., 2017). Polyols reacts with holes, prevents $HO^{\bullet}$ generation and effectively releases electrons for Cr(VI) reduction. A recent study has shown that using diethylene glycol (DEG) as the polyol molecule, the surface modified TiO_2 photocatalyst exhibited a much faster kinetics on reductive Cr(VI) conversion in comparison to the non-reactive conventional TiO_2 material (Chen et al., 2017). The TiO_2-based photocatalytic Cr(VI) treatment process is also cost-effective and safe. Conventional TiO_2 photocatalysts such as Degussa P25$^{@}$ is widely available, and food-grade TiO_2 has been frequently used as a pigment for food production. These low-cost traditional TiO_2 materials can undergo a simple surface fabrication with polyols and convert into reductive TiO_2 tailored for Cr(VI) treatment. In addition, the modified TiO_2 can be recycled for multiple rounds of treatment without losing its reductive capacity. Pilot-scale photocatalytic water treatment reactors are already available in the market (e.g., PhotoCat system$^{@}$) and a full-scale application is possible.

4 Challenges and future outlook

Both Sn(II)-based and photocatalytic reductive Cr(VI) treatments hold extreme promise as well as challenges in the future. Future research focused on solving these challenges is necessary. To moving forward in the right direction to minimize the occurrence of chromium in drinking water, the following three important questions needs to be considered: 1) What are the challenges on residual waste management during treatment? 2) Are there hidden risks of Cr(VI) re-occurrence downstream of drinking water treatment plant? 3) What are the socio-economic drivers for Cr(VI) control in the future?

4.1 What are the challenges on secondary waste management during treatment?

All reductive Cr(VI) treatment inevitably generates Cr(III) solids as the end product of chromium. Because Cr(III) is also redox reactive and can participate in an oxidative reaction to re-generate hexavalent chromium, the handling of Cr(III) residual is a major challenge that dictates the success of the treatment. Although Cr(III) itself is non-toxic at low dose, an excessive presence of Cr(III) in the treated water can violate total chromium regulatory standard in the US at 100 µg/L. The presence of dissolved oxygen does not pose the risk of re-oxidizing Cr(III) solids. Instead, the addition of a secondary disinfectant (e.g., free chlorine) in the treated water can induce the oxidation. Therefore, the removal of Cr(III) solids as a subsequent treatment step should be integrated into the Cr(VI) treatment train. During the Sn(II)-based treatment, Cr(III) solids are precipitated out together with $SnO_{2(s)}$ and generate a mixed phase solid product. A cartridge filtration unit with pore sizes of 0.45 µm has been demonstrated to successfully remove Cr(III) residual solids. In the final treated drinking water coming out the filtration unit, the addition of free chlorine with a contact time of 15 days did not generate Cr(VI), indicating the combination of Sn(II) reductive treatment and subsequent microfiltration or porous media filtration is effective in removing Cr(VI) and total chromium (Henrie et al., 2019).

Regarding the photocatalytic Cr(VI) treatment option, the separation of Cr(III) solids and regeneration of TiO_2 photocatalysts are critical to the success of the technology. The reductive TiO_2 photocatalysts are typically in nano- to micro- size range. As Cr(III) solids are generated, they deposited on the surface TiO_2 particles and results in a composite particle size in the range of 25-220 nm (Chen et al., 2017). Accordingly, a membrane ultrafiltration unit can be added to remove TiO_2 and Cr(III), and produce Cr-free drinking water (Fig. 4B). The combination of a photochemical reactor and an ultrafiltration unit as a treatment train has been commercialized (e.g., PhotoCat$^{@}$ system by Purifics), and the process can be readily scaled up into the design of future full-scale treatment. Furthermore, the reductive TiO_2 recovered by membrane separation can undergo mild acid washing to dissolve Cr(III) solids and renew its surface (Fig. 4B). Although the polyols coated on the catalyst surface are eventually consumed during the Cr(VI) reduction, the catalysts can be re-dispersed in polyol solutions, subsequently heated to replenish the hole scavengers, and regenerated for the next cycle of treatment.

4.2 Are there Cr(VI) re-occurrence risks downstream of drinking water treatment plant?

In addition to the implementation of treatment technologies, any risks involving a potential release of Cr(VI) downstream of the treatment needs to be considered and minimized. The average residence time of water staying in the downstream distribution systems can be up to several days compared to hours in the upstream treatment facility, thus providing ample time for reactions. As an in situ source, Cr can potentially be leached from plumbing materials (e.g., cast iron and stainless steel) in water distribution systems (Choi et al., 2004; Gonzalez, et al., 2013; Percival, et al., 1998). In addition, pipe corrosion scales can accumulated chromium from its trace level in drinking water over decades (Hering and Harmon, 2004; Peng et al., 2012), thus creating in situ sources of chromium in drinking water distribution systems.

Theoretical redox potential calculation suggests the oxidation of common Cr(III) solids, including chromium oxides, copper chromite and iron chromite by free chlorine are all thermodynamically favorable (Fig. 3). Recent kinetics model also predicts that Cr(III) oxidation by free chlorine can result in a Cr(VI) concentration at the tap (*i.e.*, the exit of the distribution system) exceeding 10 µg/L, a possible benchmark for future Cr(VI) regulatory standard (Henrie et al., 2019). In addition, the kinetics of Cr(III) oxidation process driven by free chlorine is catalyzed by bromide, a conservative anion typically existing in source water originated from seawater desalination, water reuse or impacted by wastewater discharge from hydraulic fracking. Water utilities need to incorporate source water protection and distribution system corrosion control as part of the mitigation strategy for Cr(VI) control in drinking water.

4.3 What are the socioeconomic drivers for Cr(VI) treatment in the future?

The incentive for future Cr(VI) treatment and control will first comes from regulatory perspective. Currently only total chromium in drinking water was regulated in the US without differentiating Cr(III) and Cr(VI); therefore, no mandate to specifically treat Cr(VI) exists in the US In the State of California, a recent drinking water standard specifically targeting Cr(VI) at 10 µg/L was established in 2013 but was subsequently challenged in the court and invalidated in 2017. The withdrawal of the new Cr(VI) regulation was partially driven by the huge economic cost of upgrading treatment to comply with the new regulation. However, the economic cost calculation was based on traditional Cr(VI) treatment options available back then, *i.e.*, ferrous reductive treatment or ion exchange treatment. In contrast, the newly developed Sn(II)-based or photocatalytic treatment would significantly reduce the cost of water utilities and become economically feasible. Combined with the convincing evidence of the toxicological effects of Cr(VI), it is reasonable to expect that a new Cr (VI) regulatory standard specifically on Cr(VI) will be reintroduced in the future.

Furthermore, the importance of redox processes taking place in drinking water distribution systems should be considered when establishing new Cr(VI) standards in drinking water. In the future, climate change adaptation strategies (including water reuse, desalination and water conservation) and associated changes on water chemistry including bromide enhancement will pose challenges for water distribution systems, alter redox chemistry at the pipe-water interface, affect the corrosion behaviors of piping materials, and change the stability of Cr-containing corrosion scales. To address this cascade of changes on water distribution infrastructure, future regulatory standards on Cr(VI) should incorporate drinking water distribution systems into considerations. For example, in an approach similar to the US EPA Lead and Copper Rule, samplings of Cr(VI) at the tap should be considered and distribution system corrosion control strategies – especially for water systems with cast iron pipes and using groundwater as the source water – should be part of the mitigation. More broadly speaking, more cities in the future will deal with aging water infrastructure. Although distribution systems might be functional when operating as they have been for decades, the risks are going to come when source waters are abruptly switched in response to droughts or a decision to use a new water supply. These universal challenges needs to be addressed and to prevent another Flint crisis with hexavalent chromium from distribution systems.

4.4 What is the future outlook of Cr(VI) drinking water treatment technologies?

Sn(II)-based reductive technology can offer immediate benefit to water systems that are experiencing elevated Cr (VI) levels in their source water, and an implementation of this technology will be a cost-effective and easy retrofitting to the existing water treatment infrastructure. Although questions regarding the stability of Sn and Cr residual products need to be better understood through more careful laboratory-scale research and pilot-scale testing, this technology is expected to be a widely considered candidate in the future when new Cr(VI) drinking water regulatory standard is established, and used as a benchmark to compare against other new technologies. Meanwhile, recent advances in nanotechnology lead to the development of new photocatalysts with tailored surface reactivity for Cr(VI) treatment. New photocatalysts that are based on semiconductor materials exhibited a high reduction efficiency for Cr(VI). There are ample promising opportunities to further optimize these photocatalysts in areas including enhanced stability, materials longevity, and ease to separate and recover catalysts. In addition, advancement in Cr(VI) removal technologies tested at laboratory-scale or tailored for industrial wastewater treatment and environmental remediation, including electrochemistry, nanomaterials and photochemistry can guide the future design for drinking water treatment (Chen and Liu, 2020; Pan et al., 2016; Pan et al., 2019). For example, the introduction of magnetic property and doping of co-catalyst can offer enhanced catalytic capacity and easy reuse after treatment. However, challenges need to be overcome prior to their wide application associated with cost, complex fabrication process and release of nanomaterials to the environment. Despite the unresolved issues, these nanomaterial based Cr(VI) treatment technologies are promising next-generation technologies for Cr(VI) removal in drinking water treatment.

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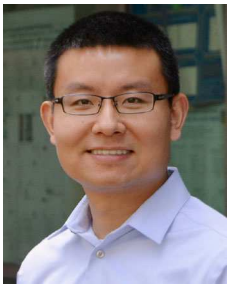

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