

Review Paper

Chromium removal from water: a review

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ABSTRACT

Chromium is present in drinking water sources (naturally occurring or anthropogenic) in many countries throughout the world. Elevated concentrations of chromium in drinking water are carcinogenic to human beings. Different treatment methods such as coagulation followed by filtration, ion exchange, adsorption and membrane filtration are employed for the removal of chromium from water in producing drinking water. However, each of these treatment methods has some limitations and it is very often difficult to meet standards while applying these methods. This paper provides an overview of sources of chromium in water, its aqueous chemistry and health effects, as well as presenting a state-of-the-art review of the methods of chromium removal from water and discussion of their suitability under given conditions. A literature review revealed that coagulation–filtration (with and without prior reduction with iron(II)) is still the most commonly used and effective method of chromium removal from water. Adsorptive filtration and ion exchange are suitable for small-scale applications. Membrane technology is effective in removing both hexavalent and trivalent species of chromium: however, fouling of the membrane should be given due consideration and the removal process should be combined with removal of other contaminants to justify the associated costs.

Key words | adsorption, chromium removal, coagulation, drinking water, filtration, reduction

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INTRODUCTION

Chromium (Cr) is a steel-grey metallic element widely distributed in the Earth's crust. Chromium is an important industrial metal used in diverse products and processes (e.g. chromate is an antibiofoulant and anticorrosive agent). About 60% of the chromium produced goes into chromium-based alloys, 20% into chemical use including electroplating, and most of the remainder into furnace bricks and other refractory products (Brown & LeMay 1988; Slooff *et al.* 1990). At many locations, chromium has been released into the environment via leakage, poor storage or improper disposal practices. Sources of chromium waste include metal plating, steel fabrication, paint and pigment production, wood treatment, leather tanning, and chromium mining and milling. Chromate is also an important constituent of wastestreams from coal-burning power plants.

Groundwater is the major source of drinking water throughout the world. Chromium is present in elevated concentrations in many natural or polluted groundwater sources used for public water supply. Because of its carcinogenic effect on human health it is undesirable in water supplies. This paper provides an overview of sources of chromium in water, its aqueous chemistry and health implications, and discusses the suitability of the application of different treatment methods for the removal of chromium from water.

SOURCES OF CHROMIUM IN WATER

Chromium is naturally found and mined as double oxides, principally as chromite ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$) and, to a lesser

extent, as crocoite ($\text{PbO}\cdot\text{CrO}_3$) or chromic oxide (Cr_2O_3). Chromite is used almost exclusively for the production of chromium, its Cr_2O_3 content varying from 40–55% (Slooff *et al.* 1990).

The occurrence of chromium in natural groundwater has been found in many places around the globe. In the USA, hexavalent chromium contamination in groundwater has been found in California, Washington, Indiana, South Carolina, North Carolina and New Jersey (USEPA 2000; USGS 2004). Similarly the city of Leon in Mexico (Armienta-Hernandez & Rodriguez-Castilo 1995) and some cites in India, namely Ludhiyana, Kanpur and Lucknow (Bellander & Peterson 2001; Blacksmith Institute 2006) have reported contamination of water sources with hexavalent chromium. Other reported occurrences of contamination in groundwater are, namely, Ontario in Canada (Blowes 2001), Wuhan City in China (Li 2004), Glasgow in Scotland (Whalley *et al.* 1999), the Ljubljansko Polje aquifer in Slovenia (Brilly *et al.* 2003), La Spezia province in Italy (Fantoni *et al.* 2002) and Holon in Israel (EXACT 2003).

Naturally occurring chromium concentrations in groundwater are generally very low (less than $2\ \mu\text{g/L}$), although concentrations as high as $120\ \mu\text{g/L}$ have been reported (WHO 2006). In the USA, groundwater chromium levels up to $50\ \mu\text{g/L}$ have been reported; in shallow groundwater, median levels of $2\text{--}10\ \mu\text{g/L}$ have been found (USEPA 1987; Deverel & Millard 1988). In the Netherlands, a mean concentration of $0.7\ \mu\text{g/L}$ has been measured, with a maximum of $5\ \mu\text{g/L}$ (Fonds *et al.* 1987). A survey of Canadian drinking water supplies indicated an overall median level up to $14\ \mu\text{g/L}$ (raw water) and $9\ \mu\text{g/L}$ (treated water) (Meranger *et al.* 1979). In Italy, hexavalent chromium is found in groundwater with concentrations of $5\text{--}73\ \mu\text{g/L}$, which is associated with natural sources (Fantoni *et al.* 2002).

Chromium and its salts are used in the leather tanning and textile dyeing industries, the manufacture of catalysts, laundry chemicals, pigments and paints, fungicides, the ceramics and glass industry, and in photography, and for chrome alloy and chromium metal production, chrome plating and corrosion control (Slooff *et al.* 1990). Uncontrolled emissions or waste discharges from industrial sites, landfills or roadways have great potential for contaminating the fresh waters with relatively toxic forms of chromium.

AQUEOUS CHEMISTRY OF CHROMIUM

Chromium is a transition metal with atomic number 24 and atomic weight 52, and which exhibits a complex chemistry. It exists in oxidation states ranging from +6 to –2: however, only the hexavalent Cr(VI) and trivalent Cr(III) are commonly encountered in the aquatic environment. The distribution of compounds containing Cr(III) and Cr(VI) depends on the redox potential, the pH, the presence of oxidizing or reducing compounds, the kinetics of the redox reactions, the formation of Cr(III) complexes or insoluble Cr(III) salts, and the total chromium concentration (Figure 1). In water, Cr(III) occurs as a cation that forms aqueous complexes and hydroxide precipitates. In surface waters, the ratio of Cr(III) to Cr(VI) varies widely, and relatively high concentrations of the latter can be found locally. In general, Cr(VI) salts are more soluble than those of Cr(III), making Cr(VI) relatively mobile (WHO 2003).

The dominant Cr(III) species occurring in water depends on pH, which include $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$ (aq) and $\text{Cr}(\text{OH})_4^-$. At high concentrations these ions impart a green colour to water. $\text{Cr}(\text{OH})_2^+$ is the dominant species in natural groundwater with a pH between 6 and 8 (Calder 1988). Under slightly acidic to alkaline conditions Cr(III) can precipitate as amorphous chromium hydroxide, $\text{Cr}(\text{OH})_3$ (s). Cr(III), being a positively charged ion, has

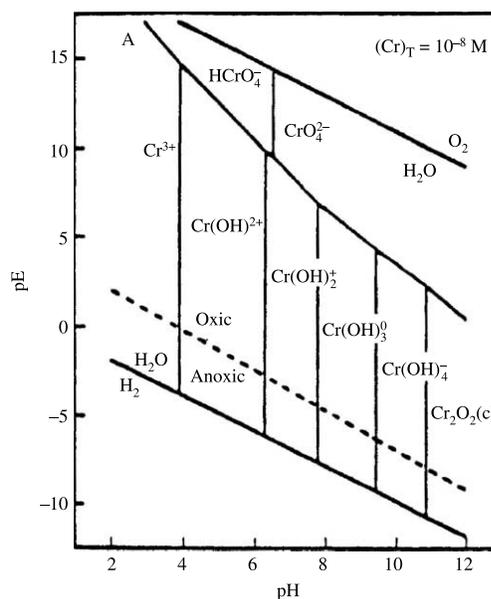


Figure 1 | pE–pH diagram of aqueous chromium (Source: AWWARF 2004).

a strong tendency to form very stable complexes with negatively charged organic or inorganic ligands. Hence, it is normally found in the form of complexes (Pichel *et al.* 1976).

The mobility of Cr(III) in the aquatic environment is expected to be low because of the low solubility of Cr(OH)₃(s) and (Cr,Fe)(OH)₃(s) precipitates and their strong adsorption onto solids under slightly acidic to basic conditions. Cr(III) attains its minimum solubility in the pH range of natural waters (i.e. pH = 7.5–8.5).

Cr(VI) exists in solution as monomeric species/ions: H₂CrO₄⁰, HCrO₄⁻ (hydrogen chromate) and CrO₄²⁻ (chromate); or as the dimeric ion Cr₂O₇²⁻ (dichromate—only exists in very strongly acidic solution). In the pH range (1–10) and at low concentrations, chromium is present in groundwater as either monovalent HCrO₄⁻ or divalent chromate CrO₄²⁻. The monovalent form predominates in acidic water while the divalent form predominates at neutral pH or above. The monomeric species (chromate and hydrogen chromate) impart a yellow colour to water when Cr(VI) concentration is greater than 1 mg/L. In dilute solutions (<1 mg/L), the predominant form is CrO₄²⁻ which, being negatively charged, does not complex with negatively charged surfaces (Pichel *et al.* 1976). However, Cr(VI) anions are adsorbed onto positively charged surfaces, such as the oxides and hydroxides of Fe, Mn and Al. Adsorption of Cr(VI) is usually limited, and decreases with increasing pH. Hence, Cr(VI) is more mobile than Cr(III) (Slooff *et al.* 1990; Faust & Aly 1998).

Cr(VI) is easily reduced by Fe(II), dissolved sulfides and certain organic compounds with sulfhydryl groups. In contrast, Cr(III) is oxidized rapidly by a large excess of MnO₂ and slowly by oxygen under conditions similar to natural waters. Based on these trends of inter-conversions, it is desirable that water quality standards should be based on total chromium concentration as well as the concentration of the more toxic species Cr(VI).

PROBLEMS WITH CHROMIUM IN WATER SUPPLIES, AND STANDARDS

Health effects of chromium

Chromium toxicity is dependent on chemical speciation and thus associated health effects are influenced by chemical

forms of exposure (Calder 1988). Cr(VI) compounds are much more soluble than Cr(III) and are much more toxic (mutagenic and carcinogenic) to microorganisms, plants, animals and humans (NTP 2007). In contrast, Cr(III) has relatively low toxicity and is immobile under moderately alkaline to slightly acidic conditions (Zobuboulis *et al.* 1995).

Cr(III) is a nutritionally essential trace element, non-toxic and poorly absorbed. Its deficiency results in glucose intolerance, inability to use glucose and other metabolic disorders. The daily chromium requirement is estimated to be 0.5–2 µg of adsorbable Cr(III). However, an excess quantity of chromium above the recommended value may be toxic to human health. Ingestion of 1–5 g of chromate results in severe acute effects and death may occur following cardiovascular shock (WHO 2003, 2006).

Cr(VI) is toxic, producing liver and kidney damage, internal hemorrhage and respiratory disorders. An oral dose of 2–5 g of a soluble hexavalent chromium compound can be fatal to an adult human. Ingesting less than 2 g of hexavalent chromium compound can result in kidney and liver damage after 1–4 days of exposure (Katz & Salem 1994). Sub-chronic and chronic effects include dermatitis and skin ulceration. Cr(VI) has been shown to cause cancer in humans and animals through inhalation exposure, but has not been shown to be carcinogenic through ingestion exposure. Cr(VI) compounds have been associated with lung cancer in factory workers.

Standards/guideline values for drinking water

Due to human toxicity, the World Health Organization (WHO) recommends the provisional guideline value of 50 µg/L for total chromium (WHO 2006). The USEPA classifies chromium as human carcinogen (group A) with a maximum contaminant level (MCL) for total chromium of 100 µg/L (USEPA 1987). The EC water directives as well as Canadian and Australian drinking water quality guidelines have also set the maximum allowable concentration of total chromium in water as 50 µg/L (EC 1998; HC 2007; NHMRC 2004).

The following conclusion is made by WHO concerning the health effects and the guideline value for chromium in drinking water. “In principle, because the health effects are determined largely by the oxidation state, different guideline

values for chromium(III) and chromium(VI) should be derived. However, current analytical methods and the variable speciation of chromium in water favour a guideline value for total chromium. Because of the carcinogenicity of chromium(VI) by the inhalation route and its genotoxicity, the current guideline value of 0.05 mg/L has been questioned, but the available toxicological data do not support the derivation of a new value. As a practical measure, 0.05 mg/L, which is considered to be unlikely to give rise to significant risks to health, has been retained as a provisional guideline value until additional information becomes available and chromium can be re-evaluated" (WHO 2003).

REMOVAL METHODS, THEIR SUITABILITY AND LIMITATIONS

Treatment methods available for the removal of chromium from water can be classified into five main groups:

- (i) Coagulation–precipitation–filtration (including redox assisted coagulation).
- (ii) Adsorption onto different media.
- (iii) Ion exchange.
- (iv) Membrane technology and electro dialysis.
- (v) Biological removal.

Most of these methods are suitable for the removal of chromium in high concentrations. Traditional methods of chromium removal from (waste)water are specially aimed at recovery and reuse of chromium. However, in ground-water environments, the chromium concentration levels are much lower; therefore the aim is to remove them to below the level specified by the drinking water quality standards and guidelines. These treatment methods, suitable for chromium removal from water sources, are elaborated in the following paragraphs. Table 1 summarizes the processes as well as the advantages and disadvantages of the main methods for chromium removal from water.

Coagulation–precipitation–filtration

In the conventional water treatment process, coagulation using alum and ferric (Fe(III)) coagulants has been

used for Cr(III) removal, in which the removal is due to precipitation as $\text{Cr}(\text{OH})_3$ and co-precipitation with $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$. Fatoki & Ogunfowokan (2002) studied the removal of chromium from river water (initial concentration = 0.46 mg/L) and reported that removal efficiency was 85.4% and 89.6%, respectively, for alum (pH = 7.7, dosage = 10 mg/L) and Fe(III) sulfate (pH = 7.4, dosage = 13 mg/L). However, the two above-mentioned coagulants are ineffective for Cr(VI) removal. Alternatively, chemical reduction of Cr(VI) to Cr(III) using Fe(II) sulfate, zero valent iron, sulfur dioxide or sodium bisulfite followed by precipitation of $\text{Cr}(\text{OH})_3$, has long been applied for Cr(VI) removal.

It has been observed that, when Fe(II) sulfate is used, Cr(VI) removal is nearly 100%. The reason for this is Cr(VI) reduction by the Fe(II) ion, with subsequent precipitation as $\text{Cr}(\text{OH})_3$. (Faust & Aly 1998; Lee & Hering 2003; Qin *et al.* 2005). The reduction of Cr(VI) to Cr(III) is fast (of the orders of minutes to hours) and effective over the pH range 5.0–9.0. Required Fe(II) dosage is 3–5 times the Cr(VI) concentration (Beukes *et al.* 1999; Lee & Hering 2003). Barrera-Diaz *et al.* (2003) reported that it is required to add an excess (50%) of the stoichiometric quantity of reducing agent to achieve the Cr(VI) removal that meets environmental standards after precipitation of the resulting Cr(III). In a variation of this method, Fe(II) is added electrochemically to the Cr(VI) containing water. From a pure iron electrode, Fe^{2+} ions are released into the solution and bring forth the reduction of Cr(VI) (Mukhopadhyay *et al.* 2007).

A possible explanation for the effectiveness of Fe(II) salts is that, while reducing the Cr(VI) compounds, Fe(II) ions are oxidized to Fe(III) compounds. *In situ* produced Fe(III) compounds are excellent coagulating agents. The Fe(III) hydroxides formed in the simultaneous oxidation–reduction processes cause the resulting poorly water-soluble Cr(III) compounds to coagulate, so that the Fe(III)-hydroxide–Cr(III)-hydroxide aggregations become amenable to conventional solid–liquid phase separation treatment (Zotter & Licsko 1992).

At pH > 6.5, the redox reaction between Cr(VI) and Fe(II) can be written as (Lee & Hering 2003)



Table 1 | Comparison of chromium removal methods

Technology	Process	Advantages	Disadvantages	References
Coagulation – precipitation/ redox-assisted coagulation	<p>Conventional Coagulation – Precipitation</p> <ul style="list-style-type: none"> Coagulation with alum and Fe(III) salts Precipitation with lime, caustic soda and sodium carbonate (to increase the pH) Two-stage process for Cr(VI) removal: reduction of Cr (VI) to Cr (III) and precipitation/ filtration of Cr(III) Reduction proceeds rapidly at low pH Reducing agents most commonly employed are sulfur dioxide, sodium sulfite and Fe(II) sulfate 	<ul style="list-style-type: none"> Low capital and O&M costs Low pretreatment requirement Effective for Cr(III) removal Recovery of chromium for recycling Reaction time is short 	<ul style="list-style-type: none"> Two-stage process for Cr(VI) removal Precipitation is often ineffective if metals are complexed or if they are present as anions Removal of the microflocs formed is often difficult and critical for process efficiency Produces high volume of sludge 	<p>Beszedits (1988), Calder (1988) and USBR(2001)</p>
	<p>Redox-assisted coagulation with Fe(II)</p> <ul style="list-style-type: none"> Cr (VI) is reduced to Cr(III) by Fe(II), which in turn oxidised to Fe(III). The reduced Cr (III) is then sorbed and/or co-precipitated with Fe(III) hydroxides Also known as RCF process (reduction – coagulation – filtration) 	<ul style="list-style-type: none"> Very effective for removal of Cr (VI) Excellent Cr(VI) removal (>99%) can be achieved with excess Fe(II) 	<ul style="list-style-type: none"> Settleability of floc and filterability of the precipitated solids affects the performance of redox-assisted coagulation Polishing treatment using microfiltration or ultrafiltration may be required for the removal of colloidal flocs formed 	<p>Lee & Hering (2003) and Qin <i>et al.</i> (2005)</p>
	<p>Electro-chemical reduction</p> <ul style="list-style-type: none"> Uses consumable iron electrodes and an electric current to generate Fe(II) ions which reacts with Cr(VI) to give Cr(III) 	<ul style="list-style-type: none"> Reaction occurs rapidly and requires minimum retention time 	<ul style="list-style-type: none"> Increased quantity of sludge due to additional precipitation of iron hydroxide 	<p>Calder (1988) and Mukhopadhyay <i>et al.</i> (2007)</p>
	<p>Sulfide precipitation</p> <p>Soluble sulfide precipitation process (SSP) in which sulfide is added in the form of water soluble reagent</p> <ul style="list-style-type: none"> Reduction of Cr (VI) to Cr(III) and precipitation of Cr(III) as metal – chromium – sulfide 	<ul style="list-style-type: none"> Potentially reduce Cr(VI) and precipitate chromium in one step Provide lower metal residue concentration than hydroxide precipitation Metal sulfides settle faster and can be dewatered more readily 	<ul style="list-style-type: none"> Relatively expensive and not suitable for drinking water treatment applications 	<p>Calder (1988)</p>

Table 1 | (continued)

Technology	Process	Advantages	Disadvantages	References
Adsorption	<p>Iron-oxide-coated media or iron oxides Commercial iron-oxide-coated adsorbents, natural or artificially prepared iron oxides like GFH or GFO</p>	<ul style="list-style-type: none"> Media can adsorb either cationic and anionic Cr species (depending upon pH) Can produce much lower levels of chromium than precipitation Considerably less sludge production Regenerable adsorbent 	<ul style="list-style-type: none"> Difficult to adjust pH for removal of both cation and anion species Disposal of the exhausted media The media should be such that it could be used as a throwaway spent adsorbent (for sanitary landfill) after passing TCLP Limited /low capacity 	Bailey <i>et al.</i> (1992) and Das (2004)
	<p>Activated carbon Adsorption of chromium onto filter media</p>	<ul style="list-style-type: none"> Effective for removal of both Cr(III) and Cr(VI) Could be combined with the removal of other heavy metals and organic micro-pollutants 	<ul style="list-style-type: none"> More efficient for chromium recovery applications Recovery of micropores high surface area (HSA) of activated carbon after regeneration is low which limits the service life 	Hu <i>et al.</i> (2003); Mohan & Pittman (2006) and Selomulya <i>et al.</i> (1999)
Ion exchange	<p>Ions in resin bed are replaced with ions of similar charge in water. Anions resin to remove Cr(VI) and cations resin to remove Cr(III)</p>	<ul style="list-style-type: none"> Ease of operation Highly reliable and effective Suitable for small and large installations Variety of specific resins are available for removing specific contaminants 	<ul style="list-style-type: none"> Regular regeneration Concentrate disposal Pre-treatment required for excess TSS Resin fouling Removal efficiency is affected by the presence of other ions in water 	Sengupta <i>et al.</i> (1986); Sengupta & Clifford (1986); USBR (2001); Rengaraj <i>et al.</i> (2001); Gode & Pehlivan <i>et al.</i> (2005)
Membrane technology	<p>Reverse osmosis All forms of chromium (inorganic ions as well as complexes) are retained by the reverse osmosis membranes</p>	<ul style="list-style-type: none"> One of the best available technology for chromium removal Good (60–90%) to excellent (90–100%) removal for Cr(VI) and Cr(III) Can effectively remove wide range of contaminants simultaneously 	<ul style="list-style-type: none"> High investment and operational costs Fouling of membrane Brine disposal 	Faust & Aly (1998) and USBR (2001)

or



The removal of chromium by coagulation–precipitation is pH-dependent. In general, the reduction of Cr(VI) to Cr(III) is done under acidic conditions and then precipitation of hydrated chromium oxide is achieved by raising the pH with the addition of NaOH or lime. Sometimes, when chromium is present as Cr(III) only, its removal is achieved simply by raising the pH with the addition of NaOH. Addition of NaOH or lime softening (addition of $\text{Ca}(\text{OH})_2$) can effectively remove Cr(III) by promoting its precipitation (Sorg 1979; USBR 2001). Besides conventional coagulation–precipitation–filtration, chromium removal is also feasible with direct filtration.

Moreover, heavy metal removal by coagulation–precipitation has some practical limitations: (i) precipitation is often ineffective if metals are complexed or they are present as anions (e.g. CrO_4^{2-}), (ii) the lowest metal concentration achievable is limited by the solubility product and (iii) precipitated metals may form small particles that do not settle readily. As a result, a large settling basin may be required to collect metal precipitates, usually followed by a large filtration unit. Under such conditions, the solid–liquid separation is fairly difficult (Benjamin *et al.* 1996). Furthermore, this method produces a large amount of chromium-rich sludge that must be disposed of.

Adsorption onto different media

In addition to effective removal of dissolved metals, adsorption processes can often remove inorganically and organically complexed metals, as well as as oxyanionic metals such as CrO_4^{2-} and SeO_3^{2-} that would not be removed by conventional treatment methods (Benjamin *et al.* 1996). Adsorption onto iron oxide has higher removal efficiency than precipitation-based processes for reducing the levels of many metals in solutions. Ferrihydrite (amorphous iron oxide) has been one of the most commonly used adsorbents in metal removal processes. Iron-oxide-coated sand (IOCS), produced by coating quartz sand with ferric nitrate, has proven to be effective for removal of chromium from wastewater effluent (Edwards &

Benjamin 1989; Bailey *et al.* 1992). Previous studies by the authors also showed that adsorption of heavy metals onto IOCS is a promising method, with high potential for heavy metals (including chromium) removal from drinking water (Das 2004).

Apart from IOCS, activated carbon is widely used for adsorptive removal of different contaminants including heavy metals. Since activated carbon also possesses an affinity for heavy metals, several laboratory-scale studies has been conducted on the effectiveness of activated carbon for the removal of both Cr(III) and Cr(VI) (Sorg 1979; Beszedits 1988; Selomulya *et al.* 1999; Hu *et al.* 2003; Mohan & Pittman 2006). So far, however, there is no evidence on application and efficiency of activated carbon in removing low chromium concentrations from drinking water sources.

Different researchers have studied the effectiveness of various other adsorbents for the removal of Cr(VI) from (waste)water in batch, fixed bed and fluidised bed processes. Some of the adsorbents include: pyrite fines, calcined Mg– AlCO_3 hydrotalcite (Zouboulis *et al.* 1995; Lazaridis & Asouhidou 2003), coal (Lakatos *et al.* 2002), bone charcoal (Dahbi *et al.* 1999) and manganese-oxide-coated sand (MnOCS) (Guha *et al.* 2001). However, most of these studies were conducted at laboratory scale only and there are very few systems like zero-valent iron media (mostly in a permeable reactive barrier, *in situ* contaminated groundwater treatment process) that have been used in practice (USEPA 2000; Melitas *et al.* 2001).

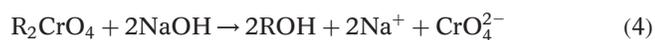
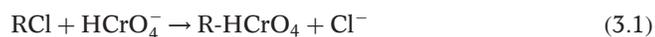
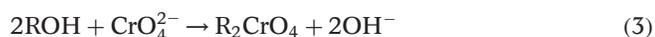
Ion exchange

Ion exchange is one of the “best available technologies” as per the USEPA recommendation for the removal of chromium (USEPA 2003). It is a proven technology for small systems for the removal of low concentrations of chromium. Removal of chromium by ion exchange has been extensively studied (Sengupta *et al.* 1986; Sengupta & Clifford 1986; Rengaraj *et al.* 2001; Korngold *et al.* 2003; Galan *et al.* 2005). Cation exchangers are effective for Cr(III), while anion exchangers are appropriate for Cr(VI) removal. For removal of Cr(VI), strong-basic anion exchangers, with an exchangeable counter ion of Cl^- , are commonly used. Theoretically, anion exchange with synthetic resins is considered an ideal process for chromium

removal because chromate is the most preferred of the common anions present in water (Galan *et al.* 2005).

Several ion exchange resins including strong anionic resins (e.g. Amberlite IR and IRA-900, DOWEX 1), weak anionic resins (e.g. Amberlite IR 67RF and IRA-94, DOWEX MA43 and MAC3) and cation exchange resins (e.g. Amberlite IR-120, IRN77 and SKN1) have been used for removal of chromium from water (Rengaraj *et al.* 2001; Galan *et al.* 2005; Rees-Novak *et al.* 2005). Because of the positive charge of Cr(III) and the negative charge of Cr(VI), a two-step ion exchange process in which use of a cation resin for Cr(III) removal followed by use of an anion resin for Cr(VI) removal could be effective if both species were present. In the ion exchange treatment system installed on the chrome-plating line of an Illinois firm, the wastewater first passes through a column containing Amberlite IR-120 cation exchange resin to remove iron, nickel, trivalent chromium and various other cations and then through a second column packed with Amberlite IRA-402 anion exchange resin, which removes hexavalent chromium, fluoride and other anions (Beszedits 1988).

Equations (3) and (4) show the ion-exchange and regeneration reactions for chromate ion (Korngold *et al.* 2003):



For removing chromates from water under acidic pH values, weak-base anion exchange resins are generally used. The resins are regenerated with a stoichiometric ratio of sodium hydroxide. For removing traces of chromate from tap water at neutral pH, only strong-base anion exchange resins may be used. These resins are regenerated with concentrated (5–8%) sodium chloride solution. The efficiency of the regeneration can be improved by adding sodium hydroxide to the regeneration solution, which transforms the resin from the HCrO_4^- form to the CrO_4^{2-} form. The main limitations of this method are

requirements for regular regeneration and concentrate disposal, potential fouling of the resins and the effect of other ions present in the water on removal efficiency.

Membrane technology and electro dialysis

Membrane technology, specifically reverse osmosis, is also considered as one of the best available technologies for chromium removal (Faust & Aly 1998; Hafiane *et al.* 2000; USEPA 2003). Reverse osmosis is effective in removal of all forms of chromium. According to Hamann *et al.* (1990) the effectiveness of reverse osmosis for the treatment of chromium is rated as good (60–90% removal) to excellent (90–100% removal) for Cr(VI), and excellent (90–100% removal) for Cr(III). Reverse osmosis has been used for the removal of chromium and other heavy metals from different wastewater effluents (Beszedits 1988).

Though it is anticipated that nanofiltration will effectively remove Cr(VI), little has been published in the literature on this subject (Hafiane *et al.* 2000). Furthermore, different modifications of membrane technology have been examined for their effectiveness in chromium removal. These include, among others, (i) micellar-enhanced ultra-filtration using cationic surfactants (Gzara & Dhahbi 2001), (ii) use of polymer inclusion membranes (Kozłowski & Walkowiak 2002) and (iii) ion-exchange membranes (Tor *et al.* 2004). Some researchers have also reported on the effectiveness of electro dialysis for the removal of Cr(III) from water and wastewater (AWWARF 2004; Mohammadi *et al.* 2005; Lambert *et al.* 2006).

Even though reverse osmosis is one of the options that can remove both species of chromium for drinking water production, the process of keeping the membrane from fouling is quite an important consideration that could incur investment and operational costs. It is important to avoid corrosion of well casings and entrapment of air that could cause oxidation of iron and sulfur compounds, causing severe fouling of membranes. Therefore, non-corrosive materials such as stainless steel, polyvinyl chloride and fibreglass should be used for pipings. In addition, vertical turbine pumps with mechanical seals or submersible pumps should be used, so that an airtight system is virtually ensured (Conlon 1990).

Biological removal

Based on the results of laboratory-scale studies, several researchers have reported the biological removal of chromium from wastewater using different types of bacteria (biological reduction and precipitation) or biomass (biosorption). However, there is little information available on the biological removal of chromium from water sources used for the production of drinking water. Furthermore, these biological removal methods are more effective at lower pH (<6), which may not be suitable for drinking water treatment applications.

Microbial Cr(VI) reduction is one of the potential methods currently drawing increasing attention (Chen & Hao 1997; Michel et al. 2003). A wide variety of bacteria have been utilised in Cr(VI) reduction under aerobic or anaerobic conditions, e.g. *Pseudomonas fluorescens* LB300 (Bopp & Ehrlich 1988), *Enterobacter cloacae* HO1 (Wang et al. 1989) and *Bacillus* sp. (Wang & Xiao, 1995).

Dokken et al. (1999) reported the high potential of alfalfa biomass for the removal of both species of chromium. The biomass of the marine alga *Sargassum* sp. has also demonstrated a good capacity of chromium biosorption, highlighting its potential for effluent treatment processes (Kratovichil et al. 1998). Bai & Abraham (2003) and Srivastava & Thakur (2006) have reported the effectiveness of fungal biomasses in the removal of chromium from water.

DISCUSSION

Table 2 summarises the main methods used for the removal of Cr(III) and Cr(VI) from water. In general, the removal of

Cr(III) from water is relatively easier than removal of Cr(VI). Two types of chemical treatment are currently used for Cr(VI) removal: the first type removes Cr(VI) anions directly while the second type relies on the reduction of Cr(VI) to Cr(III). Zero or divalent iron, sulfur dioxide and sulfides are applicable only for reduction. Often a reducing agent can act as a sorbent for the resultant Cr(III) ion. Iron-oxide-coated sand, activated carbon, modified clays and zeolites have been found to be effective for both reduction and removal of Cr(VI). Additionally, a number of naturally occurring organic materials including agricultural wastes and biomass, peat and coals have also been investigated for this purpose.

Among the existing methods of chromium removal, some methods like coagulation followed by filtration, chemical reduction followed by precipitation (redox-assisted coagulation) and ion exchange are well established, while others like adsorption of chromium by IOCS, MnOCS, electrolytic reduction of Cr(VI) to Cr(III) and subsequent precipitation, and biological removal methods are new and innovative. A literature review revealed that most of these innovative methods of chromium removal have been tested so far only in the laboratory (at bench and/or pilot scale). Furthermore, most of the methods are suitable for the removal of chromium from industrial effluents containing relatively high concentrations of chromium, which may not be effective for the application to drinking water supply due to the effectiveness of these treatment methods at low/high pH, which is not suitable for drinking water.

The conventional chemical reduction of Cr(VI) to Cr(III) and subsequent Cr(OH)₃ precipitation is expensive due to the use of large amounts of chemicals and the

Table 2 | Summary of the removal methods for two main chromium species

	Cr(III)	Cr(VI)
Removal methods	Coagulation/filtration	Anion exchange
	Softening through addition of NaOH or Ca(OH) ₂	Adsorption onto natural zeolites or iron-oxide-based media
	Cation exchange	Membrane technology (reverse osmosis, nanofiltration)
	Membrane technology (reverse osmosis)	Reduction to Cr(III) (with Fe(II), Na ₂ S ₂ O ₃ , Na ₂ SO ₃) followed by coagulation/precipitation and filtration

generation of chemical sludges (precipitates). Adsorption-based processes also produce chromium-rich adsorbents and spent regenerant which must be disposed in an environmentally acceptable way. Adsorbent used in chromium removal should either be regenerable or its characteristics should be such that it could be used as throwaway spent sorbent (for landfills) after passing the Toxic Characteristics Leaching Protocols (TCLP) test. Therefore, the search for process-efficient and cost-effective alternative treatment methods for chromium removal from water is still underway worldwide.

Since chromium is widely used in industrial processes, it is becoming one of the most widely occurring contaminants in water sources used for drinking water production, including groundwater. Even if some of the above-mentioned methods for removing chromium are technically feasible, there is a need to look for a more effective and economically affordable treatment method that could be used at different treatment scales.

SUMMARY/CONCLUSIONS

Based on the literature review the following conclusions can be drawn:

- (i) Chromium contamination of water sources (natural or anthropogenic) has been reported in many countries. Toxicity and carcinogenicity due to the presence of chromium in drinking water sources is well documented and standards for drinking water have been set by regulatory agencies world-wide.
- (ii) Chromium removal from water is affected by the species of the chromium present and their concentrations, pH and the concentrations of other cations and anions in the water. As Cr(III) is insoluble at neutral and higher pH, its removal is relatively easy compared to Cr(VI) removal.
- (iii) Coagulation followed by filtration, adsorption, ion-exchange and membrane filtration has been applied for the removal of chromium from water. Of the different methods, coagulation–precipitation (including redox-assisted coagulation) is the most effective method of chromium removal from water, with adsorption processes the second most effective. The

main problem associated with coagulation–filtration and adsorption-based methods is the disposal of the chromium-rich sludge, adsorbent and regenerant after the treatment.

- (iv) Ion exchange is a proven technology for removal of low concentration of chromium for small systems. It has the potential for application in larger water treatment systems. However, different types of exchange resins need to be used for the removal of Cr(III) and Cr(VI).
- (v) Reverse osmosis, and probably nanofiltration, are effective in removing both species of chromium. However, fouling of the membrane, generation of large volumes of concentrated liquid toxic waste and high costs are associated limitations of this method.
- (vi) There is still a need for a process-efficient and cost-effective treatment method for chromium removal from drinking water supply sources that could be used at different treatment scales.

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