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CHROMIUM IN A HIGHLY CONCENTRATED BRINE SOLUTION:

ASSESSMENT OF POTENTIAL IMPACT OF ENVIRONMENTAL DISCHARGE AND EVALUATION OF ION EXCHANGE PROCESSES AS TREATMENT OPTION

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Erwin Gil Alcasid
Studentnumber: 01801228

Academic promotor: Prof. dr. ir. Gijs Du Laing
Dr. ir. Marjolein Vanoppen

Non-academic supervisor: Nicolaas Van Belzen (The Dow Chemical Company)
Tutors: Amelia Parao and Bernd Mees

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The promoter(s), The author,

Prof. dr. ir. Gijs Du Laing *Erwin Gil Alcasid*

Dr. ir. Marjolein Vanoppen

The non-academic supervisor,

Nicolaas Van Belzen

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MASTER THESIS TOPIC

Preamble

This study was originally intended to focus on the feasibility of reducing the chromium content of a saturated brine solution using commercial ion exchange resins. The initial activities planned include batch tests, column experiments, and regeneration tests. By the 2nd of March 2020, the first round of batch experiments commenced according to schedule. However, due to the COVID-19 pandemic, Ghent University had to take precautionary measures and closed down all facilities including laboratory premises.

Due to this unfortunate event, the scope of the research has been severely impacted. More specifically, the following were not conducted:

1. Analysis of the batch test samples using electrochemical methods;
2. Column experiments; and
3. Regeneration tests

Therefore, the results and discussion within this study have been limited to the results of the batch experiments. To fulfill the requirements of the master thesis, a part of the dissertation has been reoriented towards a more extensive literature review that includes the *Fate of Chromium in the Environment*, and *Development of Hybrid Sorption-Based Techniques for Chromium Removal*.

This preamble was drawn up after consultation between the student and the supervisors, and is approved by all.

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When I take a restrospective view of the months that have passed, beyond the difficulties, stresses, and sleepless nights that it took to finish this master's degree, I will always look back at the smiles, support, trust, words of encouragement, and fond memories that I have shared with the people around me. It was not easy embarking on a journey alone in a completely unfamiliar place. However, as the days went by, it got a lot easier because of the people who believed in me and made this experience worth the anxiety of leaving my comfort zone. Truly, these past two years has been nothing but pushing my boundaries further.

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Lastly, to my family and friends in the Philippines. Thanks for sending your virtual love and support!

Erwin Alcasid

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List of Abbreviations

ASV	*Anodic Stripping Voltammetry*
BAT	*Best Available Technology*
CDPHE	*Colorado Department of Public Health and Environment*
COF	*Covalent Organic Framework*
COMOC	*Centre for Ordered Materials, Organometallics and Catalysis*
CSV	*Cathodic Stripping Voltammetry*
CTF	*Covalent Triazine Framework*
DOC	*Dissolved Organic Carbon*
ECOCHEM	*Analytical Chemistry and Applied Ecochemistry*
EPA	*Environmental Protection Agency*
FAO	*Food and Agriculture Organization*
FDA	*Food and Drug Authority*
FTIR	*Fourier-Transform Infrared Spectroscopy*
IARC	*International Agency for Research on Cancer*
ICP	*Inductively Coupled Plasma*
LOD	*Limits of Detection*
LOQ	*Limits of Quantification*
MOF	*Metal Organic Framework*
MS	*Mass Spectrometry*
NIOSH	*National Institute for Occupational Safety and Health*
NP	*Nanoparticle*
OEL	*Occupational Exposure Limits*
OES	*Optical Emission Spectrometry*
OMC	*Organic Mesoporous Carbon*
OMP	*Organic Mesoporous Polymer*
OSHA	*Occupational Safety and Health Administration*
PNS	*Pacific Northwest Snowfighters*
SAC	*Strong Acid Cation*
SBA	*Strong Base Cation*
TDS	*Total Dissolved Solids*
WAC	*Weak Acid Cation*
WBA	*Weak Base Cation*
WHO	*World Health Organization*
XPS	*X-ray Photoelectron Spectroscopy*

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Summary

The Dow Chemical Company (Dow) is a multinational company producing specialty materials and chemicals for various industries. In its manufacturing site in Terneuzen, one of the major processes generates huge volumes of salt by-products. Throughout the entire operation, various contaminants end up together with the salts, one of which is chromium. This limits the potential of the salts to be reused for different applications. While Dow was able to remove most of this trace impurity by washing the crystals with a saturated NaCl solution, the challenge now lies in searching for a practical purification technique that will permit the reuse of the contaminated brine for succeeding wash cycles.

Chromium (Cr) is an important heavy metal that is widely used in applications including chrome plating, metal alloying, pigmenting, and leather tanning. Among its different oxidation states, only two are commonly found in nature. While Cr(III) is considered to be an essential nutrient in trace amounts for humans and animals, Cr(VI) is known to cause adverse effects to living organisms. To make matters worse, Cr(VI) is more soluble and mobile compared to Cr(III), thereby increasing the bioavailability of the former.

Considering the hazards associated with Cr, this study first assessed the impacts of using these Cr-contaminated salts for deicing applications prior to any pre-treatment method (e.g. washing). Upon melting of ice and snow, it was estimated that surface runoffs containing 0.5 mg/L of total Cr could be mobilized into the environment. This is much higher than the provisional guideline set by WHO which limits the concentration of total Cr in drinking water to 50 μg/L. In the absence of adequate dilution, aquatic organisms in slow-flowing streams and small ponds are exposed to greater risks compared to larger surface waters. In contrast, the effect on groundwater is highly time-dependent due to the slow rate of percolation through the soil. In addition, plants, especially roadside vegetation, could potentially experience unfavorable alterations once a significant amount of Cr accumulates within their roots. While it is evident that there are risks associated with the mobilization of Cr from road salts, the release of high amounts of chlorides could still be considered as a bigger and more immediate threat to the environment.

The impacts of Cr release from deicing applications further emphasizes the need to purify the salt by-products prior to reuse. After Dow observed that most of the heavy metal could be removed through washing, the potential of commercial ion exchange resins to reduce the Cr content of the generated wash brine was evaluated. Batch experiments were conducted using different anion exchange resins (Amberlite PWA7, Amberlite PWA8, Amberlite HPR4800), amount of resin in g/mL (0.001, 0.01, 0.1), and pH levels (6, 11). With a full factorial experimental design, the best performing setup was determined after analyzing the residual total Cr concentrations of the samples using ICP-OES and ICP-MS.

Washing the salts produced a brine with a total Cr content of 0.59 ± 0.04 mg/L at pH 11. The student's t-test suggests that this value is not significantly different from the LOQ of the method. Therefore, the residual concentrations and removal efficiencies cannot be fully quantified within this study. Among all experimental setups, the highest removal efficiency of at least 27.3 ± 2.6% was measured using Amberlite PWA7 at a resin amount of 0.1 g/mL and pH 6. On the other hand, Amberlite PWA8 and Amberlite HPR4800 did not show any significant Cr removal at any of the tested conditions. The better performance of Amberlite PWA7 could be attributed to the secondary amines in its functional groups, macroporous matrix, and phenol-formaldehyde structure – qualities that give the resin higher affinity towards Cr(VI) species over chlorides. Surprisingly, this resin was also able to reduce the total Cr content of the brine at pH 11 by at least 25.4 ± 1.7%. For future studies, it is recommended to identify other analytical methods (e.g. electrochemical methods) that would fully measure the residual matrix concentration. Then, if high removal efficiencies are achieved after optimizing the conditions in the batch tests, column and regeneration experiments could be conducted. Similarly, it would be interesting to explore the potential of Amberlite PWA7 to remove Cr at pH 11 to avoid costs associated with pH adjustments.

Beyond the commercially available technologies for Cr removal, a new sorption-based strategy was proposed. This involves the development of a methodology that combines smart experimental approaches to selectively remove Cr using innovative, cheap, and stable ordered mesoporous polymers/carbon adsorbents with embedded iron oxide nanoparticles. Ultimately, this will lead to novel, cost-effective, and sustainable hybrid sorption-based technologies that could selectively reduce Cr concentrations in challenging (waste)waters to low or sub µg/L levels.

Introduction

The Dow Chemical Company (Dow) is an American multinational chemical company with headquarters in Midland, Michigan, United States. It is one of the largest chemical companies in the world with a diverse portfolio of advanced materials, industrial intermediates, and plastics that cater to different industrial sectors such as packaging, infrastructure, and consumer care. Out of its 113 manufacturing sites worldwide, Dow Terneuzen is the second largest production location of the company with 17 factories situated within the site [1].

One of the operation facilities at Terneuzen yields significant amounts of NaCl salt crystals as a by-product. After passing through several upstream processes, certain contaminants end up occluded within the salts which prevent the reuse or marketing of these by-products. While the company has made substantial progress in removing contaminants such as residual organics and nitrogen, chromium remains to be a potent impurity within the salt.

Chromium (Cr) naturally persists in the environment as either Cr(III) or Cr(VI). Due to the desirable properties that it imparts to different materials (e.g. corrosion and wear resistance, toughness, stability), Cr has found its way into various applications such as metal alloying, electroplating, leather tanning, etc. [2]. However, accompanying these benefits are the risks that it brings to living organisms. While Cr(III) is considered an essential element in humans and animals in trace concentrations, Cr(VI) is considered toxic when inhaled, ingested, or dermally exposed. In fact, there have been reports linking Cr(VI) to problems with the liver, kidney, gastrointestinal tract, and immune system when ingested. Moreover, it is considered carcinogenic once inhaled [3]. It can also cause huge alterations in aquatic life though the hazardous effects are mainly dependent on the concentration and exposure duration [4]. While some show tolerance to the heavy metal, plants can also be detrimentally affected by Cr through interference with various metabolic processes that are vital for growth and development [5]. Aside from their toxicity, the geochemistry of these two oxidation states also varies significantly. Cr(VI) is more soluble and mobile in aqueous systems, existing as an oxyanion within the entire pH range. On the other hand, Cr(III) is normally present as a cation under acidic conditions, which then precipitates out of the solution at $pH > 7$. In addition to the pH, the redox potential of the system greatly influences the predominant oxidation state of the metal [6].

As part of their conscious efforts to mitigate these potential hazards, Dow found that washing these crystals with saturated brine could remove up to 80% of its total Cr content. This, however, produces a highly alkaline, saturated brine solution with the removed Cr. Reusing this contaminated brine for succeeding washing steps would eventually accumulate the heavy metal within the system, hence necessitating the purification of the solution. Therefore, the company is now actively seeking for practical methods to remove Cr from the generated wash brine.

Various conventional techniques such as reduction/coagulation/filtration, adsorption, and ion exchange have already been applied in different studies for removing Cr. While these methods have shown high efficiencies in removing the heavy metal, ion exchange stands out due to its inherent advantages such as high selectivity and less sludge volume produced [7]. Despite these, studies have reported that the removal efficiency and selectivity of ion exchange resins towards Cr significantly decrease under the presence of competing ions (e.g. chlorides, sulfates) which are normally present at higher concentrations [8, 9, 10].

Within this context, three main goals have been established for this study. In Chapter 1, a base scenario was considered wherein the environmental impacts of using the Cr-contaminated salt by-products as deicing agents were assessed. Here, several assumptions were made to estimate the Cr concentration of surface runoffs resulting from deicing applications. The fate of the mobilized Cr was then evaluated by considering the general cycle of the metal in the environment, with emphasis on the potential risks upon uptake by living organisms.

In Chapter 2, considering the progress made by Dow Terneuzen in purifying the salt by-products, the feasibility of reducing the Cr content of the generated wash brine was evaluated. Batch ion exchange experiments were conducted to assess the performance of commercially available resins and factors affecting its performance (e.g. dosing and pH). Ultimately, the results of this study could serve as a basis for future optimization on the emerging best combination of parameters, and also support succeeding column and regeneration experiments.

After focusing on a readily available technology (i.e. ion exchange), new strategies for Cr removal was proposed in Chapter 3. This involves the development of a methodology to combine smart experimental approaches with the synthesis and application of novel, cheap, and stable adsorbents for Cr removal. Eventually, this will lead to the establishment of innovative, cost-effective, and sustainable hybrid sorption-based technologies that can selectively reduce the amount of Cr in complex or concentrated solutions.

Chapter 1

Chromium in the environment

1.1 Introduction to chromium

Chromium (Cr) is a grey, lustrous, hard metal abundant within the earth's crust as a crystalline solid [11]. Chromite (Cr_2O_3 or $FeCr_2O_4$ ± Mg) is the most significant mineral of Cr, with crocoite ($PbCrO_4$) occurring extremely rarely [12]. Approximately 80% of mined Cr is used for metallurgical applications, notably in stainless steel manufacturing and electroplating. About 15% is used to produce Cr-based chemicals, while the remainder is used in refractory applications [13]. Even in fractions as low as 10%, Cr provides high-corrosion resistance to alloys, making it an essential component of stainless steel. As chromic acid, it can be used in decorative plating (usually deposited on nickel) or hard plating due to its wear resistance and low coefficient of friction. Cr salts also find their way in wood preservatives as a chemical fixing agent on the cellulose and lignin of the timber, and in leather tanning as a cross-linking agent for the collagen fibers. Additionally, due to its high heat resistivity and high melting point, chromite and chromium(III) oxide are extensively used in combination with other refractory oxides of iron, aluminum, and magnesium for applications such as blast furnaces, cement kilns, and foundry sands for metal casting [14].

1.2 Chemistry and geochemistry

Chromium (atomic number 24) is a transition element with atomic weight 51.996u and a density of 7.19 g/mL which makes it a heavy metal [15]. Similar to other transition elements, it forms a number of salts that are brightly colored (e.g. Cr(III) chloride is violet, Cr(III) oxide is green), and is likely to be present as polyatomic ions when dissolved in water (e.g. CrO_4^{2-}) [6]. While Cr has 26 known isotopes, only four are stable: ^{50}Cr (4.4%), ^{52}Cr (83.8%), ^{53}Cr (9.5%), and ^{54}Cr (2.4%) [16]. Among its various oxidation states ranging from -2 to +6 [13], only three are found in nature: Cr(0), Cr(III) and Cr(VI) [6, 17]:

1. Cr(0) occurs in metallic or native Cr but is rarely found in the environment.
2. Cr(III) is often present in chromic compounds such as chromium(III) oxide (Cr_2O_3), chromium(III) hydroxide ($Cr(OH)_3$), or as soluble hydroxide cations $CrOH^{2+}$ and $Cr(OH)_2^+$.
3. Cr(VI) generally exists as soluble $Cr_2O_7^{2-}$ and CrO_4^{2-} anions in groundwater.

Both Cr(III) and Cr(VI) could be present in aqueous systems, the distribution of which is dependent on the redox potential and pH of the solution as illustrated by the Pourbaix diagram in Figure 1. Compared to Cr(VI), the stability zone of Cr(III) occurs over a wider range of E_h and pH. At extremely acidic conditions (< pH 4), Cr(III) is mainly present as soluble Cr^{3+}. As the pH of the solution increases from 4 to 7, Cr^{3+} is hydrolyzed to $Cr(OH)^{2+}$ and $Cr(OH)_2^+$. Then, as the pH increases, Cr is mainly precipitated as $Cr(OH)_{3(s)}$. Above pH 11.5, the solute redissolves, forming the $Cr(OH)_4^-$ complex. In contrast, Cr(VI) is generally present at highly oxidizing conditions. Under these conditions, Cr(VI) is extensively hydrolyzed to form $HCrO_4^-$ at acidic conditions. Above pH 6.5, only CrO_4^{2-} exists in the solution [18]. Additionally, $Cr_2O_7^{2-}$ ions could be present under extremely acidic conditions or when Cr(VI) concentrations are above 1000 mg/L [19].

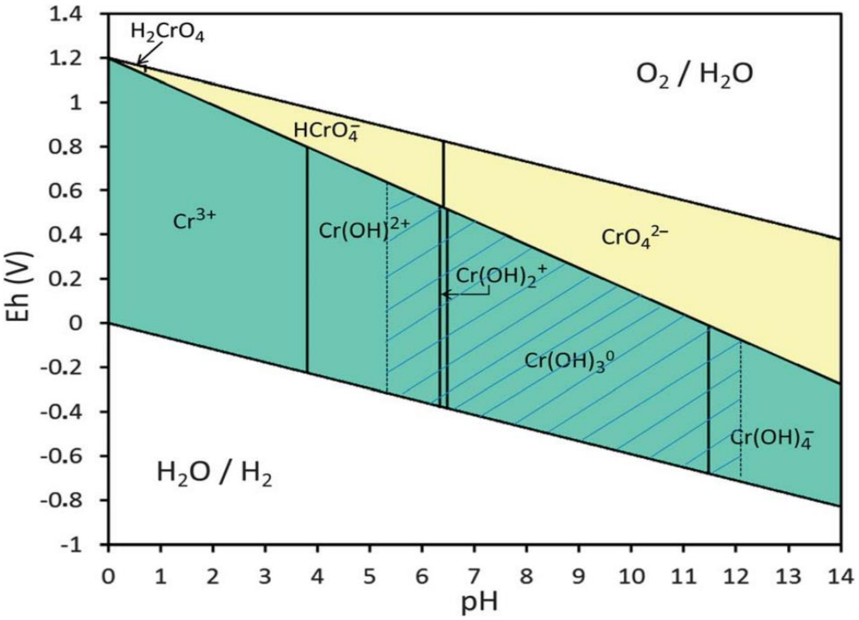

Figure 1. Pourbaix diagram for chromium in water [18].

Between the two oxidation states, Cr(VI) is more mobile in aqueous systems since it is present as an anion unlike Cr(III) which exists as a cation [20]. However, since the speciation of Cr is highly dependent on redox potential, it is expected that there would be an interconversion between Cr(III) and Cr(VI) due to naturally occurring redox agents. For example, Fe^{2+}, S^{2-}, microorganisms, and simple organic compounds such as amino, humic, and fulvic acids could quickly reduce Cr(VI) to Cr(III), which can then be easily precipitated or adsorbed [18, 21]. These reduction reactions occur faster at lower pH conditions. On the other hand, Mn(IV) oxides are the only oxidizing agents present in the environment that could oxidize Cr(III) to Cr(VI). Although at highly alkaline conditions, oxidation using dissolved oxygen could also occur [18].

1.3 Sources of chromium in the environment

Chromium is highly ubiquitous in the air, soil, and water, the concentration of which greatly varies depending on the source and geochemical conditions. Moreover, its distribution is highly governed by redox reactions, sorption-desorption, and precipitation-dissolution [22, 23]. Although there are natural sources of Cr in the environment, due to its wide application, the majority of the metal found in the environment, especially Cr(VI), could be traced back to different industrial activities.

1.3.1 Natural sources of chromium

The concentration of Cr in soils and sediments varies greatly as it is strongly influenced by the composition of the parent rock. For example, serpentine soils formed on ultramafic rocks could contain as much as 200 mg/kg of Cr, the source of which is mainly chromite ($FeCr_2O_4$). Due to the natural weathering of the mineral, Cr(III) is released and is mainly adsorbed on clay minerals or precipitates with Al(III) or Fe(III)-hydroxides. On the other hand, naturally occurring Cr(VI) is rarely found in the environment, except in highly oxidizing conditions. Upon contact with naturally occurring oxidizing agents such as Mn(IV) oxides (commonly birnessite), Cr(VI) can be formed on the surface of soil minerals under pH 9 [23, 24].

Different bodies of water also serve as a natural sink of Cr due to weathering of Cr-containing rocks, deposition from air, and leaching from soil [25]. Typically, rainwater contains 0.2 to 1.0 μg/L of total Cr, surface water 0.5 to 2.0 μg/L, groundwater 1.0 μg/L, and seawater 0.3 μg/L. However, it should be noted that these concentrations will highly be dependent on the media that it occurs in [6, 26]. Depending on the pH, Cr(III) could either precipitate out (i.e. neutral to alkaline pH) or remain solubilized (acidic pH). Moreover, unlike in soils and sediments, aqueous environments normally do not contain oxidizing agents such as Mn(IV) oxides in high concentrations to yield a significant amount of Cr(VI). Even if oxidation of Cr(III) could proceed (i.e. using dissolved oxygen), various studies have indicated that this will only be in insignificant amounts as the process will be greatly inhibited by competing species in natural waters [23]. Also, any Cr(VI) that might end up in aquatic media can easily be reduced by organic matter into Cr(III) [25].

Gaseous Cr does not occur in nature due to its extremely high boiling point (2676 ºC). Hence, most of the Cr suspended in the atmosphere are aerosols that are either particle-bound or dissolved in droplets [23]. Total Cr concentrations in most non-industrialized areas are typically below 10 ng/m^3. Worldwide, the biggest sources of Cr in the atmosphere are wind-borne soil particles and volcanoes, while other sources such as sea salt spray and wild forest fires have also been recorded in other studies. Yearly, a global fallout of as much as 3.4×10^4 ton/y of Cr is deposited into the soil [27]. Cr entrained in aerosols could be removed from the atmosphere either through dry deposition or wet deposition, although studies suggest that it could remain suspended in the air for 14 days [6, 23].

Food is the source of essential Cr(III) by humans and animals. Typically, these sources contain Cr(III) within the range of < 10 to 1,300 μg/kg, with meat, fish, fruits, and vegetables bearing the highest concentrations (Table 1) [11, 28].

Table 1. Chromium content of common food sources [28].

Food	Cr(III) Content, μg/100g
Mussels	128
Oyster	57
Pear	27
Tomato	20
Broccoli	16
Egg yolk	6
Beef	3
Herring	2

1.3.2 Anthropogenic sources of chromium

Various anthropogenic activities contribute to the emissions of Cr to the environment. Due to the numerous industrial applications of Cr, it is expected that vast amounts of the metal in the environment would be coming from industrial discharges. According to Choppala et al. [22], soil and groundwater can become contaminated with Cr due to the following: leachate from landfills, sewage, or sewage sludge; leachate from mining wastes; seepage from industrial lagoons; and, spills and leaks from industrial processes.

Worldwide, up to 1.18 x 10^6 tons/y of Cr has been estimated to be added to the soil due to agricultural fertilizers [29]. In particular, the amount of Cr from using phosphates and limestone typically exceeds the Cr concentration in the soil. Phosphate fertilizers contain 30 to 3,000 mg/kg of Cr while limestone contains 1 to 120 mg/kg Cr [30]. However, the largest amount of Cr directly applied to the soil is through the disposal of trapped and bottom fly ash. Huge amounts of Cr are emitted in burning coal and bituminous coal which contains 15 mg/kg and 172 mg/kg of Cr, respectively [29, 31].

Almost 170,000 tons of Cr are being discharged annually by various industries into the environment worldwide [32]. Cr(III) and Cr(VI) could be released from the effluent of smelters, metal plating, tanning, wood preservation, corrosion inhibitors in cooling water, and oxidation of stainless steel [23, 33]. Current practice is to treat the effluent on-site to reduce its Cr content or at sewage treatment facilities [34]. Cr derived from various raw materials can also concentrate on the sludge at sewage treatment facilities. In Europe, five Cr(VI) substances (chromium trioxide, sodium chromate, sodium dichromate, ammonium dichromate, and potassium dichromate) are considered to have significant releases to the environment [35]. The estimated emissions of these compounds to the aquatic environment are listed in the following table:

Table 2. Chromium emissions from the five priority Cr(VI) compounds in the EU. Adapted from Vaiopoulou & Gikas [36].

Process	**Cr emissions, ton / y**
Pigment Production	5.6
Chromium (III) oxide production	22
Chrome tanning salt production	38
Wood preservative formulation	8.2
Wood preservative application	6.2
Metal treatment formulation	12
Metal treatment use	2.342

Cement-producing plants significantly contribute to the Cr in the atmosphere, with Portland cement containing 41.2 mg/kg of Cr, 2.9 mg/kg of which is Cr(VI). Other anthropogenic sources of Cr in the air include fuel combustion and catalytic converters in automobiles. The wearing of vehicular brake linings that contain asbestos could also be a source of atmospheric Cr since asbestos may contain up to 1,500 mg/kg of Cr [11]. The release of bubbles in electroplating baths containing chromic acid could also carry entrained Cr(VI) into the air. Additionally, the firebrick linings of glass furnaces could contribute to Cr(VI) emissions into the air [22].

The total concentration of Cr in the biosphere could be greatly enhanced due to the contribution from these anthropogenic sources. In urban areas, the amount of Cr in the air is 2 to 4 times higher than in regional background concentrations [3]. In Europe, the air was found to contain between 4 to 70 ng/m^3 of Cr, while industrial areas were in the range of 5 to 200 ng/m^3 [37]. Indoors, this could go as high as 400 times greater than outdoor concentrations (up to approximately 1 μg/m^3) due to smoking. While no specific information is available regarding the form of Cr in the air, it is approximated that one-third of anthropogenic releases in the air is Cr(VI) [11]. In some European countries, workplace Cr(VI) concentration in the air was measured to be as high as 1 μg/m^3 (France) and 5 μg/m^3 (Sweden, Lithuania, and Denmark) [25].

The extent of industrial activity is reflected in the Cr content of surface waters. In the US, the total Cr content of surface waters could reach as high as 84 μg/L, 40 times greater than the average natural concentration. In Canada, this ranges from 0.2 to 44 μg/L [3]. In Europe, Cr concentration ranges from <0.01 to 43 μg/L [38]. Shallow groundwater in the US contains Cr concentrations between 2 to 10 μg/L, although cases with 50 μg/L of Cr have also been reported [3]. In Europe, the geochemistry of groundwater has been studied by evaluating the total Cr content of bottled drinking water in different areas, which was found to vary between < 0.2 to 27.2 μg/L (Figure 2) [38]. While this range sits comfortably below the 50 μg/L total Cr provisional guideline set by the World Health Organization (WHO) and the EU, drinking water companies are now confronted by new challenges brought by the impending implementation of stricter threshold values for total Cr and Cr(VI) content [16, 39].

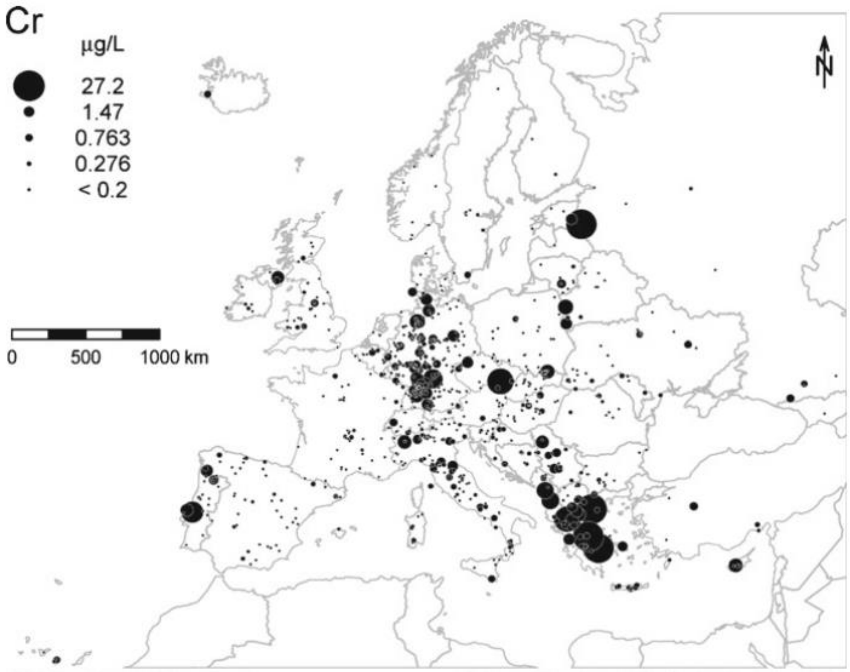

Figure 2. Distribution of total Cr in bottled drinking water across Europe [38].

1.4 The chromium cycle

The atmosphere is a major pathway for long-distance transport of Cr into different ecosystems. The mobility of the metal in the air is largely influenced by the particle size, meteorological factors, topography, and vegetation – the oxidation state of Cr is not important. Cr(III) is likely to be the abundant form in atmospheric conditions due to the abundance of reducing agents in the air (i.e. V^{2+}, Fe^{2+}, H_2S, HSO_3^-, NO_2^-, and organic matter); oxidation of Cr(III) to Cr(VI) due to ozone is considered insignificant due to its low concentration [40].

On the other hand, the mobility of Cr within the soil and water systems is affected by its hydrogeochemistry: redox transformations, precipitation/dissolution, and adsorption/desorption processes [2]. In natural water systems, three main important types of Cr exist: soluble Cr(III), insoluble Cr (III), and soluble Cr(VI). Insoluble forms of Cr(VI) are only soluble in strong acids, hence, they are not important sources of Cr(VI) in water [23]. Under neutral to alkaline conditions, Cr(III) forms hydroxides of varying solubilities and could also co-precipitate with $Fe(OH)_3$, while under acidic conditions, Cr(III) will tend to solubilize. In contrast, Cr(VI) is mainly solubilized at all pH levels [40].

Soluble forms of Cr(VI) formed or disposed into soil and water systems will remain highly available unless it is removed by leaching, adsorption, precipitation, uptake by living cells, or by reduction to Cr(III). The reduction of Cr(VI) could spontaneously occur at the same time with the oxidation of Cr(III) (Figure 3) [41, 42]. As it is a strong oxidizing agent, Cr(VI) is easily reduced to Cr(III) under acidic conditions by widely abundant reducing agents such as Fe^{2+} ions (equation 1), S^{2-} ions (equation 2), and organic matter. Similarly, significant amounts of oxidizing agents such as dissolved oxygen and Mn(IV) oxides (equation 3) are available in aqueous systems to oxidize Cr(III) to Cr(VI) [43, 40]. Just as Fe^{3+} can be reduced by sunlight to Fe^{2+}, Mn^{2+} can be reoxidized by sunlight and oxygen, replenishing the oxidizing agent within the system [23]. Due to its solubility, Cr(VI) can migrate in aqueous systems in its soluble form, while both Cr(III) and Cr(VI) can migrate bound to dissolved organic carbon (DOC) or suspended particles. As Cr compounds cannot volatilize from water, transport from water to the atmosphere is only through windblown sea sprays. Hence, most of the Cr in water bodies will be deposited in the sediment [11].

$$3Fe^{2+} + HCrO_4^- + 8H_2O \rightleftharpoons 3Fe(OH)_{3(s)} + Cr(OH)_{3(s)} + 5H^+ \quad \text{[Equation 1]}$$

$$2CrO_4^{2-} + 3S^{2-} + 4H^+ \rightleftharpoons 2Cr(OH)_{3(s)} + 3S_{(s)} + 2OH^- \quad \text{[Equation 2]}$$

$$2Cr^{3+} + 3MnO_2 + 2H_2O \rightleftharpoons 2HCrO_4^- + 3Mn^{2+} + 2H^+ \quad \text{[Equation 3]}$$

Likewise, the hydrogeochemistry of Cr dictates the speciation of both oxidation states present in soil systems. Due to its mobility, Cr(VI) can easily be taken up by plants or leached out into deeper layers, causing potential groundwater contamination. Such risks become more preeminent as the adsorption of these oxyanions onto soil surfaces (i.e. iron and aluminum oxide) decreases with increasing soil pH. On the other hand, most Cr(III) species in soil systems are naturally insoluble and immobile, preventing it from leaching or being assimilated by plants. In fact, it is strongly and rapidly adsorbed by iron oxides, clay minerals, and sand [40]. However, under the presence of organic ligands such as citric, gallic, and oxalic acid, Cr(III) forms organic complexes with considerable mobility. This permits the transport of Cr(III) towards the Mn(IV) oxide surfaces, facilitating the oxidation of Cr(III) to Cr(VI) [18]. Similar to aqueous systems, naturally occurring reducing agents such as Fe^{2+}, S^{2-}, and organic matter are present in soil systems which allows simultaneous reduction of Cr(VI) to Cr(III). This can, however, be inhibited by the sorption of Cr(VI) onto soil surfaces at acidic conditions, rendering it unavailable for reduction [40].

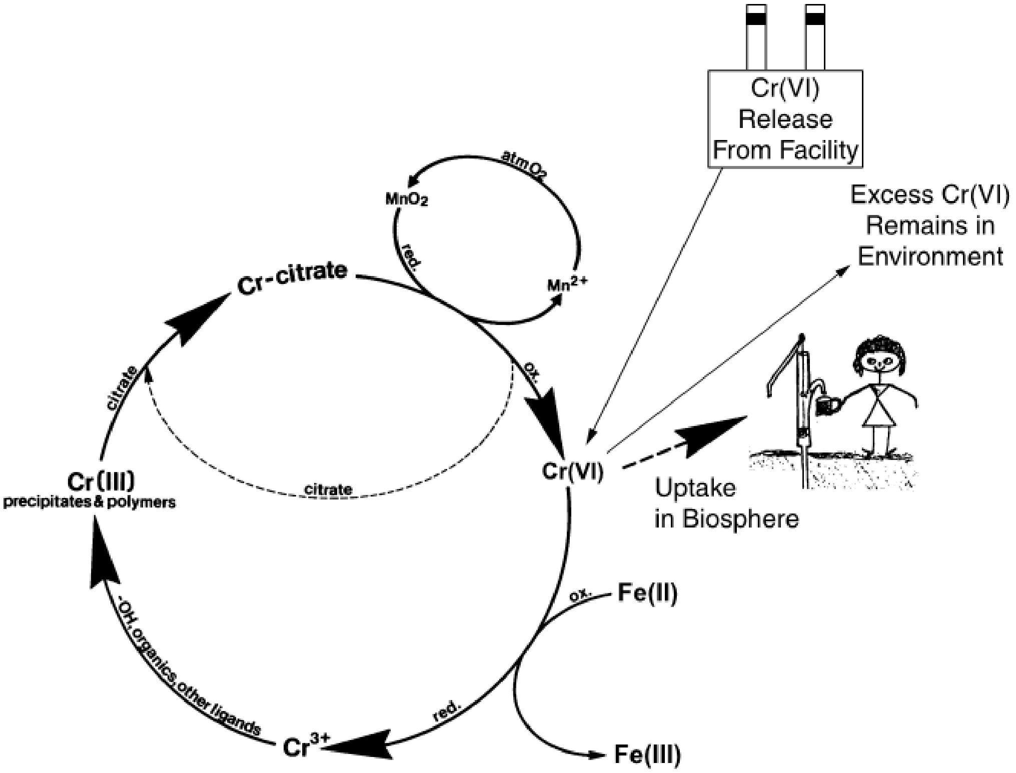

Figure 3. Chromium cycle in the environment. Adapted from Bartlett [42] and Testa [27].

1.5 Chromium toxicity and uptake into the biosphere

1.5.1 Effect on humans and animals

The health effects of Cr are significantly different between its two predominant oxidation states. Cr(III) is generally considered as an essential nutrient for humans and animals, while Cr(VI) is classified as a Group 1 carcinogen by the International Research Agency fo Cancer (IARC). In its biologically active form, Cr(III) helps facilitate the interaction of insulin with its receptor site, thus improving glucose, protein, and lipid metabolism [44]. While there is no evidence yet of Cr deficiencies in humans, severe Cr deficiency in animals could cause hyperglycemia, decreased weight, elevated serum cholesterol levels, corneal opacities, impaired fertility, and death [11]. On the other hand, sufficient evidence has been recorded to link Cr(VI) compounds to cancer in humans and animals [45].

WHO indicated that the daily Cr requirement for adults is estimated to be between 2 to 8 μg of Cr(III) per kg of body weight per day, with daily supplementation not exceeding 250 μg/day. On the other hand, ingestion of 1 to 5 g of Cr(VI) compounds can cause severe acute health problems which could be lethal due to risks of cardiovascular shock [46, 26, 47, 48].

There are three possible ways that chromium could enter the body and cause physiological damage: through *ingestion*, *skin contact*, and *inhalation*.

Ingestion. Cr could easily be ingested once food or drinking water becomes contaminated with the metal. Studies have shown that Cr(VI) is more efficiently absorbed by the gastrointestinal tract compared to Cr(III), although the absorption of Cr(VI) is estimated to be only less than 5%. This low absorption efficiency is attributed to the rapid reduction of Cr(VI) to Cr(III) due to the action of the gastric juices. This significantly reduces the hazards associated with Cr ingestion [49, 44]. Despite the lower risk associated with ingesting Cr, a number of cases of ulcers, diarrhea, abdominal pain, vomiting, indigestion, leukocytosis, and presence of immature neutrophils have been recorded due to Cr(VI) contamination in drinking water [50, 44]. On the other hand, accidental poisoning from ingesting Cr(VI) compounds (i.e. chromic acid) could lead to acute tubular necrosis, kidney failure, and death [51, 44].

Skin contact. While a less common mode of exposure, Cr could enter the body once liquids or dust particles containing the metal gets in contact with the skin. Due to its higher solubility in water, Cr(VI) compounds penetrate the skin faster than Cr(III) compounds [11, 52]. However, their relative rates become equal once the metal enters through skin lesions [11, 53]. Cr(VI) compounds are very corrosive, thus causing severe burns and possibly systemic toxicity [11, 54].

Inhalation. Inhalation of Cr in airborne particles is a major concern as the bronchial tree is the primary target for the carcinogenic effects of this metal. While inhalation of Cr(VI) causes nasal damage, no irritation is caused by Cr(III). Similarly, due to its higher solubility, Cr(VI) is more readily absorbed by the lungs than Cr(III) as observed from the Cr transferred to the blood from particles from the lungs. However, around 15% to 47% of Cr(VI) remains in the lungs which could be associated with its carcinogenic effects [11, 55]. A study on production workers with occupational exposure to Cr(VI) has shown a significant association with cancer from inhalation. On the contrary, those exposed to Cr(III) have shown no signs of adverse health effects [11].

1.5.2 Effect on aquatic species

Due to its mobility in water systems, Cr(VI) is considered to be the main form of Cr that causes great threats to aquatic species. However, certain species show more sensitivity to Cr(VI) than others [56]. Among the different freshwater invertebrates, *Daphnia magna* is considered to be one of the most sensitive species to Cr. Water bodies with 10 μg/L of Cr(VI) could affect the fertility of these species, while 44 μg/L of Cr(III) is considered lethal. On the other hand, the growth of *Salmo gairdneri,* a species of fish, is negatively affected in environments with 16 μg/L of Cr(VI) [57]. The major pathway for Cr(VI) to penetrate bodies of fish is through passive diffusion to the gill membrane. Other major tissues that experience major alterations include the kidney, intestines, liver, and muscles. Acute exposure could cause fish to lose body balance, lower breathing rate, and increase the rate of mucus secretion. Chronic effects to fishes include significant changes in total glycogen, protein, and lipid concentrations in various tissues, while genotoxicological effects include breakage of DNA and presence of micronucleated and binucleated red blood cells [4].

1.5.3 Effect on plants

There is no clear consensus as to whether Cr is an essential element in plants [58, 59, 40]. Still, several studies observed that plants grown in environments with high total Cr content have shown impairments at various stages of growth and development (Table 3). Moreover, some important physiological activities of plants are highly disrupted by the presence of Cr (Table 4). Although some crops have shown tolerance to Cr at low concentrations, the metal is considered detrimental to most plants at total Cr concentrations above 5.2 mg/L per kg dry weight [59].

Table 3. Effect of chromium on plant growth and development [59].

	Effects
Germination	Reduced germination percentage and bud sprouting
Root Growth	Decrease in root length and dry weight Increase in root diameter and root hairs
Shoot Growth	Reduction in plant height
Leaf Growth	Reduction in leaf number, leaf area, and biomass Scorching of leaf tip
Yield and dry matter production	Up to 50% reduction in yield Reduced number of flowers per plant Reduced grain weight Increased seed deformity Reduced pod weight

Table 4. Effect of chromium on plant physiology [59].

	Effects
Photosynthesis	Electron transport inhibition Calvin cycle enzyme inactivation Reduced CO_2 fixation Chloroplast disorganization
Water Relations	Decreased water potential Increased transpiration rate Wilting
Mineral Nutrition	Uptake of N, P, K, Fe, Mg, Mn, Mo, Zn, Cu, Ca, B affected
Enzymes and other compounds	Inhibition of assimilatory enzymes

1.5.4 Bioaccumulation and biomagnification of chromium

There is little evidence regarding the biomagnification of Cr in either aquatic or terrestrial food chains. In fact, studies suggest that in many instances, “biominification” exists where Cr substantially decreases with increasing position in the food chain. Within the aquatic ecosystem, markedly lower concentrations of Cr were observed in primary and secondary consumer fish (mackerel, dogfish, monkfish) compared to the species in the lower trophic levels (mussels, tunicate worms, lugworms). Likewise, the Cr content within various body organs of seabirds was considerably lower compared to their prey species (mussels, limpets, crabs, various fishes) [57]. In the terrestrial ecosystem, it is possible that due to the poor absorption of Cr from the gastrointestinal tract, the Cr concentration in animals is either lower or similar to those in soils and vegetation. [11, 40, 57]. On the other hand, while studies have reported that plants growing in soils with high Cr concentration have a higher uptake of the metal compared to those grown in normal soils, most of the metal has only been retained in the roots. Therefore, the bioaccumulation of Cr from the soil to the edible parts (aboveground) is considered unlikely [11]. Moreso, plants and most invertebrates are reported to become stunted and die before accumulating sufficient amounts of Cr that could be toxic to predators [57].

1.6 Regulatory status

Due to the threats associated with excessive exposure to this heavy metal, different international and national regulatory bodies have set guidelines on the threshold concentration of Cr in various media, particularly in air and water. No international guidelines, however, are set by bodies such as WHO or FAO on the maximum permissible concentration of Cr in food [60]. Likewise, the US EPA and FDA do not have guidelines on the limit of Cr in food other than its recommended daily intake for adults [11]. Similarly, no such guidelines are present here in Europe on the assumption that Cr(VI) will readily be reduced to Cr(III) in food, thereby eliminating imminent concerns due to its poor absorption efficiency in the body at this oxidation state. Moreover, no standardized methods are available to accurately measure Cr(VI) concentration in food [61].

Very limited information is available regarding the state and bioavailability of Cr in ambient air. In fact, most available data are derived from studies regarding the exposure of people being the most susceptible to the metal (e.g. production workers for Cr(VI) compounds). Despite this, WHO has noted that at a Cr concentration of 1 $\mu g/m^3$ in the air, the lifetime risk for a person, that is, the likelihood to develop or die from cancer during his lifetime, is 4×10^{-2} [37].

The Occupational Exposure Limits (OEL) for Cr which are based on an 8-hour time-weighted average, vary from country to country and depend on the type of compound. Currently, no general OEL is in place for EU member states, but a Cr(VI) concentration of 25 $\mu g/m^3$ is currently being proposed regardless of the compound. This value is more stringent compared to the existing standards in other countries such as Japan, Australia, and Canada (Table 5). Once approved, this OEL will give greater protection to approximately 83% of the total exposed workers who are located in EU member states without a governing OEL or one that is less stringent (Figure 4).

Table 5. Exposure limit values for Cr(VI) in different countries [62].

	Cr(VI) OEL, μg/m^3
EU (Proposed)	25
US	
NIOSH	1
OSHA	5
Japan	50
Australia	50
Canada	50
China	not regulated

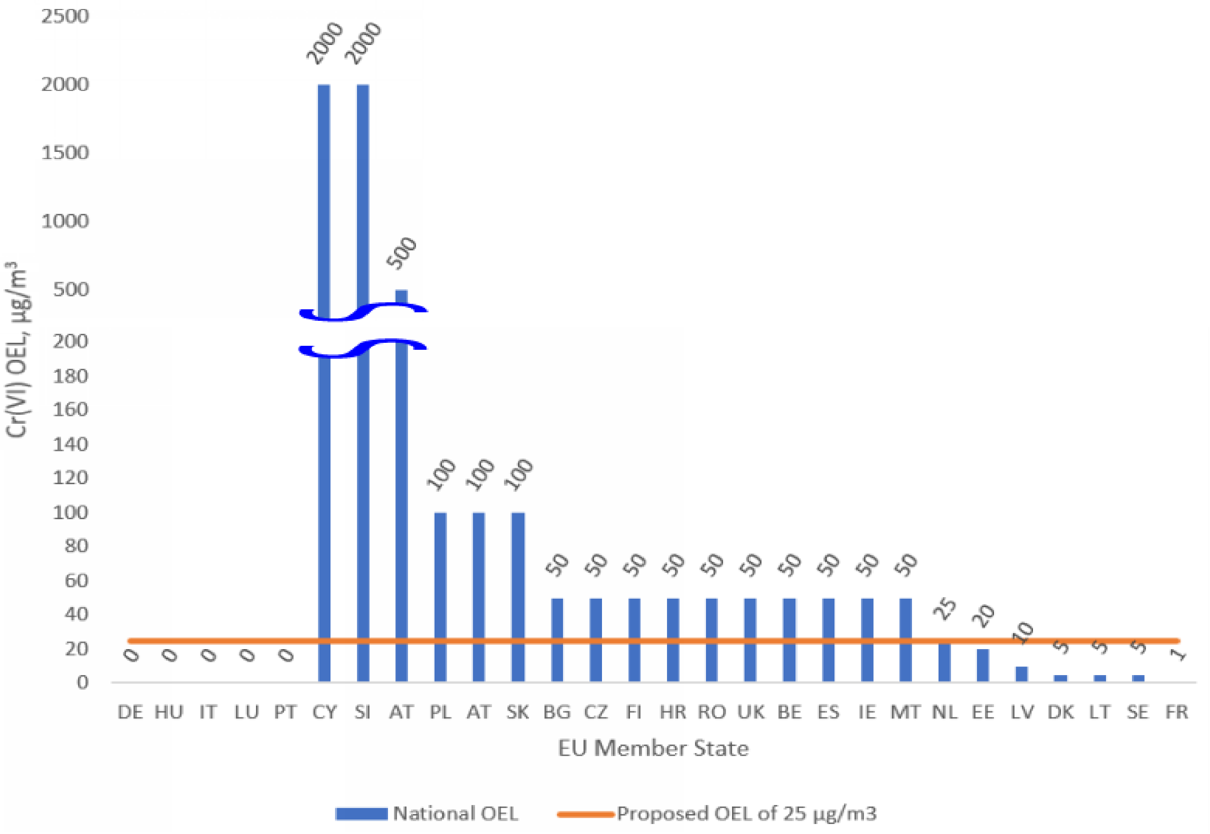

Figure 4. Current Cr(VI) OEL in EU member states vs. proposed EU OEL. For countries with OEL ranges, the upper limit is depicted [62].

When it comes to drinking water, WHO set a provisional guideline to limit the concentration of total Cr to 50 μg/L. Although this raised a number of concerns due to the carcinogenicity of Cr(VI) when inhaled, uncertainties in the available toxicological data do not support any amendments to the current value, thus considering it provisional [3]. As seen in Table 6, other regulatory bodies such as Health Canada and the EU Drinking Water Directive recommend the same guideline as the WHO for total Cr in drinking water [16, 63].

Table 6. Limits for total chromium content in drinking water in different countries [63, 36].

	Total Cr Limit, µg/L
WHO	50
EU	50
US	100
Canada	50
Australia	50
Japan	50

In 2014, the California EPA imposed a separate limit of 10 µg/L for the Cr(VI) content of drinking water due to concerns on the adverse effects of the metal. However, in 2017, the Sacramento Superior Court ordered the State Water Board to withdraw this guideline and set a new one after concerns about the economic feasibility of reaching this target were raised, particularly by small water systems operators [64]. In China, the guideline of 50 µg/L is applied for Cr(VI) instead of total Cr [36, 65]. Meanwhile, although their current guidelines are still aligned with the EU Drinking Water Directive, Germany and The Netherlands are already considering limiting the Cr(VI) content of drinking water to 0.3 µg/L and 0.2 µg/L, respectively [16, 63].

In the same way, the Cr content of various industrial effluents is being controlled to avoid possible contamination to different bodies of water, the limits of which depends on the type of industrial application. For example, the Code of Federal Regulations in the US regulates the total Cr content of effluents from the metal plating industry to 2.77 mg/L. For the leather tanning and finishing industry, the discharge limits are set at 240 mg/kg and 90 mg/kg of raw material, respectively [66]. In Europe, each member state has its own set of discharge quality limits depending on the source (i.e. tanning, metal plating) and sink (i.e. surface waters, sewers), but these generally range from 0.05 to 0.5 mg/L for Cr(VI) and from 0.2 to 5 mg/L for total Cr [36].

1.7 Fate of chromium from road salts

Safe driving conditions during winter are of primary importance for areas located in cold regions. Until the 1960s, highway maintenance groups relied heavily on abrasives such as cinders, sand, washed stone, and slag screenings for snow and ice control. However, due to its inherent disadvantages such as easy dispersion through wind and traffic conditions, greater application volumes, and high costs of usage and cleanup, abrasives have slowly been replaced by deicing agents such as road salts. These are commonly made from rock salts, although some manufacturers include additives such as ferric and sodium ferrocyanide as an anti-caking agent, and chromate or phosphate as corrosion inhibitors [67, 68]. Since then, numerous studies have been conducted regarding the fate of road salts in the environment and its subsequent impact on the biosphere. However, these environmental assessments focused more on the impacts of sodium and chloride, and less on other components such as Cr [67, 68, 69, 70].

Road salts, together with the associated contaminants, can be mobilized into the environment via different transport mechanisms and pathways (Figure 5). Even before these deicing agents are applied to roads and highways, contamination to nearby streams within the holding facility can occur if these salts are not properly stored. Previously, shipments of rock salt are typically stored outdoors with or without a covering and stockpiled directly on the ground. However, it is now a common practice to store these salts in enclosed structures provided with drainage ditches to prevent contamination of local groundwater and surface waters [67]. Once the road salts are dosed in roads and highways, these can then be dissolved in melted snow and runoff directly to the roadside or drainage systems. Moreover, a fraction of these runoffs may infiltrate the road surface and reach the road internals. Vehicular traffic could cause the salts or salt solution to splash into the adjacent roadside soil, making it amenable for ground percolation and plant uptake. Road salts could also be transported during clearing operations of snow and ice [70].

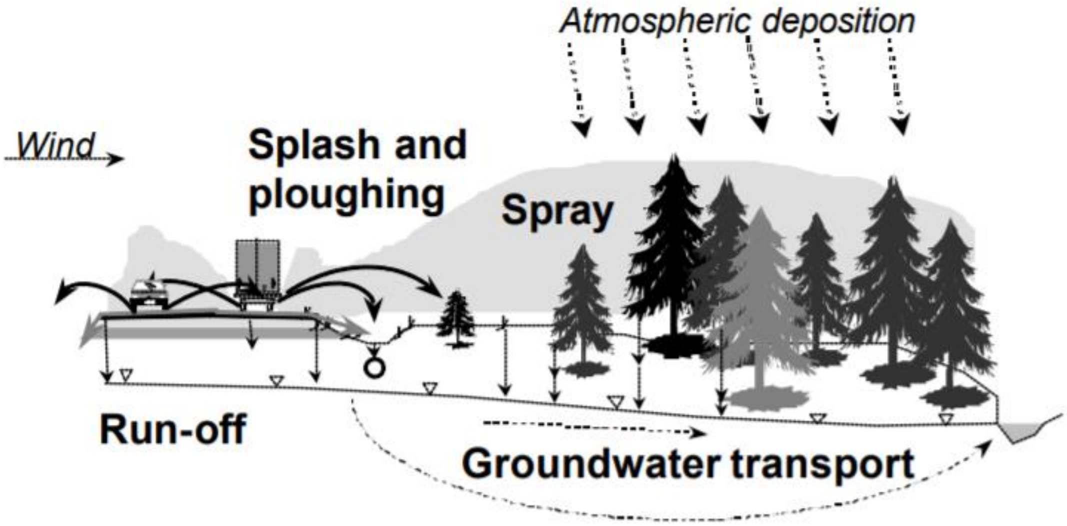

Figure 5. Transport mechanisms of deicing agents along a road network [71].

While it was believed that the use of Cr as a corrosion inhibitor in deicing agents has been significant in the previous decades [72], limited studies are available regarding the release of this heavy metal from the road salts into the environment. This is likely due to the decision of some companies to cease the sales of this type of deicing agents because the cost of adding Cr overshadows its use as a corrosion inhibitor [67]. On the other hand, the Michigan Department of Transport prohibited the use of road salts with Cr within the state due to the toxicity of this heavy metal [73]. Still, prior to the discontinuation of such deicing agents, Cargill, after employing Carguard salt in Minneapolis, reported that samples from street runoff and sewers collected in the area during one winter season contained 24 mg/L of Na_2CrO_4 and 3.9 mg/L of Cr, respectively. While these are considerably above the desired levels of Cr in public water supplies, Cargill reported that no samples in surface waters exceeded 50 µg/L of total Cr. Even if deicing agents with Cr have already been obsolete, the EPA noted that the effects of past use of Cr additives may still be present in soils and groundwaters [67].

Commercial deicing agents in various US states can still contain Cr in trace concentrations as long as it is below the 0.5 mg/kg threshold limit set by the Pacific Northwest Snowfighters (PNS). A study by the Colorado Department of Public Health and Environment (CDPHE) aimed to assess the impacts of the trace elements in these deicing agents once these chemicals become airborne due to vehicular movements. Results showed that long-term exposure of 8 hours/day and 6 months/year to these commercial deicing agents containing Cr corresponded to a risk factor above 1×10^{-6}, meaning that the chance of a human to develop cancer due to continuous exposure to the deicing agent is above 1 out of 1,000,000. The source of Cr in this particular study cannot, however, be attributed to a specific source. Hence, CDPHE recommended conducting a more precise quantitative analysis on the effect of the trace elements in these deicing agents [68].

Dow considers Belgium as one of the possible markets once their salt by-products are to be sold as a deicing agent. According to Dow, without any pretreatment, these road salts could contain approximately 7 mg/kg of total Cr. During the winter season of 1986, approximately 200,000 tons of road salt has been applied on roads and highways throughout the country [69]. To assess the potential impact of using these salt by-products as deicing agents without any prior purification, it is assumed that this same amount of salt is used yearly to decrease the freezing point of snow/ice by 5 ºC. This results to surface runoffs with an estimated chloride content of 48 g/L and a total Cr content of 0.5 mg/L. This total Cr concentration is considerably higher than the 50 µg/L total Cr limit for drinking water. Likewise, it is higher than the average total Cr concentration in Flemish surface waters and groundwater wells of 10.5 µg/L and 2 µg/L, respectively [74, 75].

Although the calculated total Cr concentration of the runoff is higher than the levels present in the environment, it should be noted that such concentrations would typically be observed at locations close to the roads and highways. Therefore, roadside vegetation would be the ones that are highly susceptible to these high Cr concentrations. As mentioned in Section 1.5.3, Cr is typically accumulated within the roots of plants. Even if the concentration of this heavy metal is below the levels to cause immediate detrimental effects, it is possible that succeeding deicing operations would eventually accrue sufficient amounts of Cr within the roots to cause severe plant damage. On the other hand, the threats of Cr in these runoffs are expected to be low in surface waters as the concentration of the heavy metal is expected to be diluted within a range of 100 to 500 folds, except in slow-flowing streams and small ponds where the risks to aquatic organisms would be greater (see Section 1.5.2) [68]. Unlike surface waters, a water table is characterized by a clearly defined volume. Therefore, rather than dilution, the extent of groundwater contamination would be more defined by the nature of the soil, its permeability, existing plant cover, depth of the water table [70], and ground components that could affect the adsorption and conversion between Cr(III) and Cr(VI). Also, if the ground is covered by a layer of frost, the runoff could move further laterally away from the roadside, thus allowing infiltration at greater distances [67]. Although the effect on groundwater might not be immediately seen due to the slow rate of percolation, the possibility of increased total Cr concentration of the water table, in the long run, cannot be discarded [67, 70]. Aside from the Cr in snowmelts, the heavy metal within in the salt crystals could be ingested by birds and mammals that are typically attracted to road salts [68], although, as discussed in Section

1.5.1, the hazards associated with Cr ingestion is low due to its poor absorption by the gastrointestinal tract. Therefore, while there are risks associated with the release of Cr from these road salts, these are rather minimal and rely on possible accumulation of the metal over time. Ultimately, the biggest threats from road salts would still be coming from the high concentrations of sodium and chloride [67].

Chapter 2

Chromium removal through ion exchange

2.1 Introduction

In the previous chapter, the fate of Cr in the salt by-products of Dow has been discussed. While immediate risks seem to be low, the long-term effects of the heavy metal could be very detrimental to the ecosystem. Hence, it is within the best interest of the company to purify these salts before marketing it for deicing applications. At present, Dow has made substantial progress in removing up to 80% of the total nitrogen and Cr by washing the salts with a saturated NaCl solution. However, appreciable amounts of contaminated brine are now generated through this technique. To ensure the sustainability of the process, the company is now looking at practical methods to purify this brine and reuse it for succeeding washing steps.

At present, a diverse set of techniques have been employed in removing Cr from (waste)water streams. Among the available technologies present, *reduction/coagulation/filtration (RCF)*, *adsorption,* and *ion exchange* are considered as the most common ones. In the first method, electron donors such as Fe(0) and Fe(II) are used to reduce Cr(VI) to Cr(III) before precipitating the metal as $Cr(OH)_{3(s)}$ or as $Fe_xCr_y(OH)_{3(s)}$ complexes [76]. Meanwhile, in adsorption, Cr is transferred from the liquid phase onto the surface of a solid phase (i.e. iron oxide). This is different from ion exchange wherein Cr is taken out of the liquid phase by exchanging it with a counter ion from the solid phase [77].

The main advantage of ion exchange is its high selectivity and small amounts of sludge generated [20]. In addition, it is a simple and reliable process suitable for small and large installations. In fact, ion exchange is considered as one of the best available technologies (BAT) for Cr removal [78, 39]. In a comprehensive study conducted by the City of Glendale in California, ion exchange emerged as one of the leading techniques that could achieve Cr(VI) removal efficiencies greater than 90%. This was achieved for groundwater containing trace amounts of Cr(VI) at neutral pH, with competing ions such as chlorides and sulfates at concentrations 1000 times greater than Cr(VI). Compared to other investigated methods such as adsorption and RCF, ion exchange using Amberlite PWA7, a weak base anion exchange resin (WBA), showed a consistent performance at high capacities [79]. Using the same ion exchange resin at neutral pH, an excellent Cr(VI) removal efficiency of as high as 97% was observed by SMAT, a drinking water company in Italy. Even at trace amounts of Cr(VI), the method was found to be highly selective as the major competing ions that were present at concentrations 2000 times greater than Cr(VI) such as nitrates and sulfates were completely retained in the effluent [80]. In tannery wastewater where chlorides and sulfates are also present at levels 1000 times greater than Cr(VI), Kabir and Ogbeide [81] observed 99% Cr(VI) removal at pH 4 using IR-45, another commercially available WBA. The excellent performance of various ion exchange resins warrants its potential use in removing Cr(VI) in more challenging solutions.

Therefore, within this research, particular interest is given to the feasibility of removing trace amounts of Cr from a concentrated brine solution through commercially available ion exchange resins. While this method has already been proven to efficiently and selectively remove trace amounts of Cr in various (waste)water streams [76], its performance in concentrated saline solutions, such as in this study, is still limited.

2.1.1 Principles of ion exchange

Ion exchange is a process wherein dissolved ions are removed from the solution through electrostatic sorption onto an ion exchange material. Due to the higher affinity of these dissolved ions towards the functional groups (or *fixed ions*) in the resin, previously bound ions (called *counter-ions*) are displaced from the solid surface and released in the solution [82]. Ion exchange is widely used in water softening (removal of Ca^{2+} and Mg^{2+}) and demineralization of water, although it has also found other applications such as in the recovery of precious metals [83]. Figure 6 illustrates the exchange in water softening between one Ca^{2+} ion from the solution and two Na^+ ions on the exchanger.

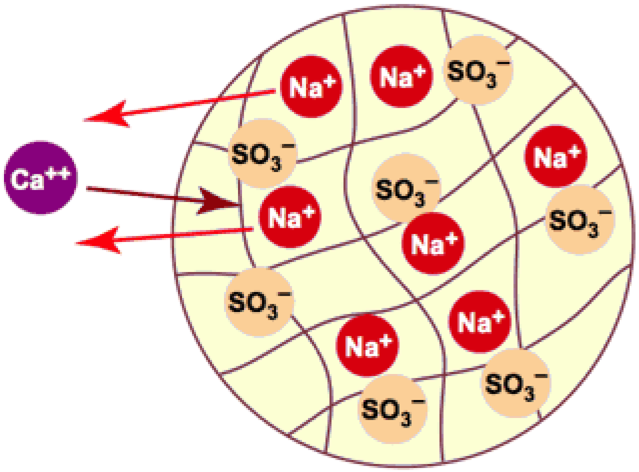

Figure 6. Schematic diagram of the principle of ion exchange in water softening [84].

2.1.2 Classification of ion exchange resins

2.1.2.1 Based on functional groups

Ion exchange resins can be classified according to their functional groups: strong acid cation (SAC), weak acid cation (WAC), strong base anion (SBA), and weak base anion (WBA) exchange resins. The following table shows the functional groups of different ion exchange resins.

Table 7. Functional groups of typical ion exchange resins [82].

Cation exchangers		Anion exchangers	
Type	**Functional Group**	**Type**	**Functional Group**
Sulfonic acid	$-SO_3^-$	Quaternary amine	$-N(CH_3)_3^+$
Carboxylic acid	$-COO^-$	Quaternary amine	$-N(CH_3)_2(EtOH)^+$
Phosphonic acid	$-PO_3H^-$	Tertiary amine	$-NH(CH_3)_2^+$
Phosphinic	$-PO_2H^-$	Secondary amine	$-NH_2(CH_3)^+$
Phenolic acid	$-O^-$	Primary amine	$-NH_3^+$
Arsonic acid	$-AsO_3H^-$		
Selenonic acid	$-SeO_3H^-$		

**shaded groups refer to strong acid / base resins*

Cation exchange resins have cationic counter-ions which are typically H^+ or Na^+. Na^+ is typically the preferred ionic form of cation exchange resins since these have relatively low affinity for sodium, thus facilitating favorable adsorption of other metals [85]. SAC exchange resins have functional groups that are fully ionized over the entire pH range. As these groups behave like strong acids, these can neutralize strong bases and convert metal salts into their corresponding acid. On the other hand, WAC exchange resins are only typically ionized at higher pH values (e.g. above pH 7) [86, 87].

Likewise, anion exchange resins have anionic counter-ions which are typically OH^- or Cl^-. Having quaternary amine functional groups, SBA exchange resins can function over the entire pH range whereas the less substituted amines of WBA exchange resins are only ionized at lower pH values (e.g. below pH 7). Similarly, SBA exchange resins can neutralize an acid solution into water, while WBA exchange resins cannot split salts [86, 87].

A number of studies have already been made in evaluating the performance of SBA and WBA exchange resins in removing metal anions under different operating conditions [88]. Because of its complete dissociation over the entire pH range, SBA exchange resins are commonly used in the removal of various anion complexes. While this allows SBA exchange resins to have higher sorption rates, its high strength greatly reduces the selectivity of the resin in multi-ionic solutions. For this reason, SBA exchange resins remain less desirable for purification processes [89, 90]. Nevertheless, to a minimal extent, the geometrical configuration of quaternary ammonium groups provides SBA exchange resins with selectivity towards complexes having linear geometry over those with trigonal planar or tetrahedral configurations [91]. In contrast, WBA exchange resins with tertiary and secondary amine groups are more suited for selective metal removal due to their limited range of protonation. In fact, the dissociation constant (pK_a) of these resins can be modified to ensure ionization at the solution pH [83]. While these resins are generally used at pH levels below its pK_a, Cortina et al. [92] suggested that WBA exchange resins are still able to remove low amounts of target ions due to possible chelating interaction between the metal complex and free electron pair of the nitrogen in the amines.

The type of alkyl group present has a big impact on the selectivity towards multivalent ions. According to Clifford [93], the *distance-of-charge separation* is the primary factor dictating selectivity towards divalent ions. As the functional groups become larger, so is the space between the active sites, thereby making it difficult for divalent ions to attach to two fixed ions. Recently, modifications on the functional groups have been shown to improve the selectivity of resins towards Cr(VI). This was further supported by the findings of Guter [94] wherein NO_3^- ions were preferentially adsorbed over SO_4^{2-} ions by resins with large quaternary ammonium groups, -$RN(CH_2CH_3)_3^+$ and -$RN(CH_2CH_2CH_3)_3^+$. Kusku et al. [95] observed that the removal of Cr(VI) is enhanced when the methyl groups of quaternary ammonium resins are substituted by one or more carbonyl-amide groups. Wójcik et al. [96] found out that Cr(VI) removal is enhanced when ketone groups were included in quaternary ammonium and tertiary amine groups.

2.1.2.2 Based on matrix

Ion exchange resins can also be classified according to their three-dimensional polymeric structure (also called *matrix* network). The structure of these matrices is illustrated in Figure 7.

1. *Polystyrene* matrices are common in ion exchange resins. These are made from copolymers of styrene, cross-linked by divinylbenzene. In the case of SAC exchange resins, 8 to 10 $–SO_3H$ groups are introduced in the matrix for every 10 benzene rings through sulfonation [86].
2. *Polyacrylic* matrices are made from copolymers of acrylic or methacrylic acid, cross-linked by divinylbenzene. This results in weak acid ion-exchange resin with –COOH groups [86]. Due to their open-chain aliphatic structure with carbonyl groups, polyacrylic matrices are more hydrophilic than polystyrene matrices [8]. In other words, this type of matrix holds a greater amounts of water inside the resin.
3. *Phenolic* matrices exist in various kinds. Matrices manufactured through the condensation of phenol and formaldehyde are very weak acid exchangers with phenolic –OH fixed ionic groups. In this type of matrix, formaldehyde acts as the cross-linking agent [86].

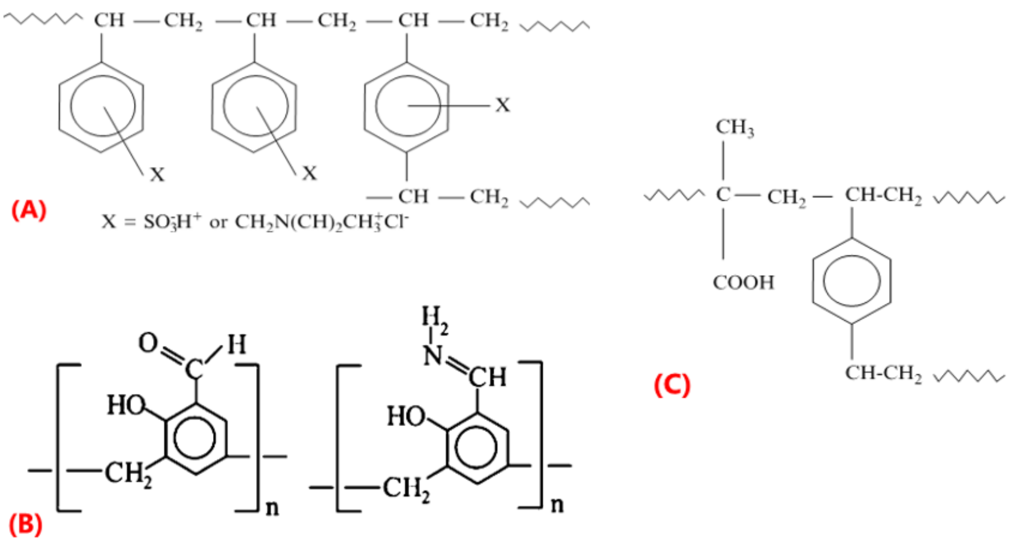

Figure 7. Different resin matrices: (A) polystyrene divinylbenzene; (B) phenol-formaldehyde; (C) polymethylmethacrylate divinyl copolymer resins [97].

The degree of crosslinking in polystyrene and polyacrylic matrices is determined by the amount of divinylbenzene present (e.g. 5% mol divinylbenzene corresponds to 5% degree of cross-linking). This is an important characteristic of ion exchange resins as the degree of cross-linking determines many resin properties. For instance, a higher degree of cross-linking leads to a harder, less porous resin that has a higher resistance to mechanical degradation. Additionally, the cross-linking of hydrocarbon chains renders the resin insoluble and less susceptible to swelling [86].

The type of resin matrix has previously been associated with the affinity of anion exchange resins towards Cr(VI) species. The low charge density of $HCrO_4^-$ and $Cr_2O_4^{2-}$ (1 and 2 negative charges, respectively, to 6 atoms) gives these ions their hydrophobic character, and, therefore, they are not easily attracted to polar solvents (e.g. not easily hydrated). Hence, Cr(VI) is more selectively removed by resins with a polystyrene-divinylbenzene matrix due to their hydrophobicity [98] [99].

Aside from its ability to imbibe polar water molecules, the resin matrix also contributes to the distance-of-charge separation concept introduced earlier. SenGupta et al. [98] noted that while resins IRA-458 (polyacrylic) and IRA-900 (polystyrene) both have quaternary ammonium groups and equal wet volume exchange capacities, IRA-458 holds substantially higher moisture than IRA-900. Hence, IRA-458 is more compact than IRA-900. This allows the amino-functional groups of polyacrylic IRA-458 to be closer to each other, giving higher selectivity towards divalent ions over monovalent ions. Considering the proximity of its functional groups and its hydrophilic nature, the polyacrylic resin still has overall lower selectivity towards Cr(VI) than polystyrene resin [98]. In another study, Tung [100] suggested that while phenol-formaldehyde resins have high nitrogen content, these functional groups are very closely spaced, rendering some of the sites unusable.

2.1.2.3 Based on internal structure

Resins with minimal discrete pores (0.5 to 20 nm) are called *gel (microporous)* resins, while those with larger pores (20 to 200 nm) with a multi-channeled structure are called *macroporous (macroreticular)* resins (Figure 8) [97]. Hence, the main difference between the two is the presence of a pore phase in the macroporous resin in addition to its gel phase. This makes the gel phase of the macroporous resin more cross-linked than a gel resin even with the same amount of divinylbenzene present [98]. This gives macroporous resins higher osmotic shock resistance, less swelling, and higher oxidation resistance. Still, gel resins are widely used for most water applications due to their higher capacity [100].

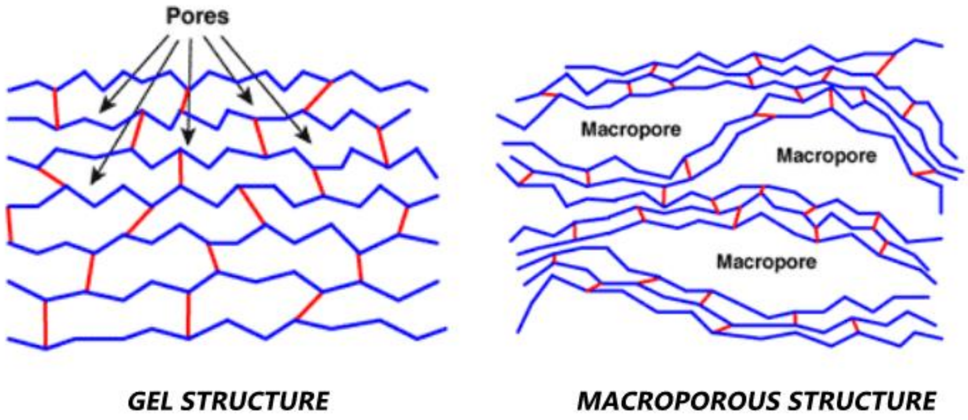

Figure 8. Internal structure of ion exchange resins. Polymeric chains are represented in blue while divinylbenzene is in red [101].

Some studies suggest that pore size contributes to the higher selectivity of macroporous resins compared to gel resins towards large ions [102, 103]. However, SenGupta et al. [98] noted that the pore sizes generally do not affect the selectivity of resins due to the relatively small sizes of inorganic ions. Instead, it is the hydrophobic nature of the internal structure that affects selectivity. Due to the higher cross-linking in the gel phase of the macroporous resin, less moisture reaches the ionogenic groups, contributing to its hydrophobicity. Hence, macroporous resins exhibit higher selectivity compared to gel resins towards less hydrated ions such as chromates.

2.1.3 Characteristics of ion exchange resins

2.1.3.1 Ion exchange capacity

Ion exchange capacity is usually expressed as the milliequivalents (of charge) per gram of dry resin or liter of wet resin. This usually reflects the number of functional groups available for exchange per unit weight of the resin [82].

For Cr(VI) removal, the exchange capacity of a resin is often maximized at lower pH values (i.e. 3 to 6) where $HCrO_4^-$ is the predominant species present. In contrast to higher pH values wherein Cr is mainly present as CrO_4^{2-}, only one exchange site is necessary to remove one molecule of Cr in its $HCrO_4^-$ form [10].

2.1.3.2 Swelling

Swelling refers to the water uptake of the resins when immersed in the solution. Hydration of the fixed ionic group takes place and the randomly arranged polymer chains unfold due to the increase in the size of the solvated ions. As the internal space within the resin becomes concentrated with a solution of fixed ions and counter-ions, the mobile counter-ions tend to diffuse out of the resin. In turn, water molecules are forced into the resin phase to reduce the strength of the ionic solution [82]. In more concentrated external solutions, less water uptake is observed due to osmotic pressure [104].

2.1.3.3 Selectivity

During an ion exchange process, equilibrium is reached when the concentration of the target ion A^- and counter-ion E^- in the solution and the resin remains constant. Selectivity coefficients can then be defined using the ratio of ions in the solution and the resin. These values depict the preference of the resin for a particular ion. Considering the stoichiometric exchange of y moles of A^{x-} with x moles of E^{y-}, the equilibrium established could be shown as [82]:

$$yA_m^{x-} + xE_r^{y-} \rightleftharpoons yA_r^{x-} + xE_m^{y-} \qquad \text{[Equation 4]}$$

where m denotes the mobile (solution) phase and r denotes the stationary (resin) phase. The corresponding selectivity coefficient ($K_{A,E}$) can then be written as:

$$K_{A,E} = \frac{[A_r^{x-}]^y [E_m^{y-}]^x}{[A_m^{x-}]^y [E_r^{y-}]^x} \qquad \text{[Equation 5]}$$

Various sources are available showing the relative affinities of resins towards different ions (with respect to H^+ or OH^-), but the general affinity of SAC exchange resins for cations follow the series [82, 105, 106]:

$$Cr^{3+} > Pb^{2+} > Ca^{2+} > Mg^{2+} > Na^+ > H^+$$

Similarly, the affinity of SBA exchange resins for anions follows the following series [82]:

$$CrO_4^{2-} > SO_4^{2-} > NO_3^- > Cl^- > OH^-$$

The same affinity series applies for WAC and WBA resins with the exception for H^+ and OH^-, for which WAC and WBA exchange resins show very high affinities, respectively [107].

As a general rule, the selectivity of an ion exchange resin depends on its *electroselectivity*. That is, multivalent ions have higher affinities towards the functional groups compared to monovalent ions through increased coulombic interactions [82]. This degree of electrostatic interaction is similarly affected by the closest distance the ion can approach the functional group [108]. However, it should be noted that at high concentrations, the exchange potential of ions becomes negligible, and in some cases becomes reversed [109].

In a solution with ions of similar charges, the selectivity of an ion exchange resin is significantly affected by the size of the hydrated ion wherein the highly hydrated ion will be held most weakly. This is directly related to swelling as smaller ions would be more easily accommodated within the pores of the resin. Hence, as mentioned earlier, resins with a higher degree of cross-linking (i.e. macroporous over gel) would have a higher affinity towards smaller solute ions [82].

Extensive literature is available discussing the effect of competing ions that are normally present in (waste)water streams on the ion exchange performance of resins for Cr(VI) removal. In their study on tannery wastewater, Kabir & Ogbeide [81] observed no significant effect on the removal of Cr(VI) using WBA exchange resin IR-45 in the presence of chloride and sulfate ions which are present at concentrations 100 folds greater than Cr(VI) at pH 4. However, at this same pH, SenGupta et al. [98] observed that chlorides, present at concentrations 400 times greater than Cr(VI) in cooling water, significantly reduced the selectivity of anion exchange resins towards Cr(VI). Furthermore, the authors added that an increase in sulfate concentration at pH 4 causes an increase in the selectivity of anion exchange resins towards the trace Cr(VI) ions. This selectivity reversal was attributed to the lesser degree of hydration of $HCrO_4^-$ compared to sulfates. As the sulfate concentration increases, the selectivity towards Cr(VI) slightly increases due to the decrease in hydration of the ion exchange resin. At pH 9, however, the selectivity of the studied resins towards Cr(VI) was virtually independent of sulfate ions [110]. In another study, Bahowick et al. [9] observed a significant reduction in the performance of SBA exchange resins in Cr(VI) removal under the presence of even greater concentrations of sulfate ions (i.e. 1000 times greater than chromate). Aside from chlorides and sulfates, Jianwei et al. [10] observed an even more significant reduction in Cr(VI) removal using surfactant-modified zeolites due to the presence of bicarbonates at high concentrations.

Aside from inhibitory effects, the complexation of Cr(VI) with other existing ions was found to cause a significant reduction in ion exchange performance. Terry et al. [111] observed that the ion exchange of Cr(VI) in hydrotalcite is reduced under the presence of Zn(II) and Cd(II) in binary systems and ternary systems. Similarly, a ternary system of Pb(II), Cd(II), and Cr(VI) showed reduced ion exchange removal efficiencies using clinoptilolite due to the formation of metal complexes among these ions [112].

2.1.4 Exhaustion and regeneration

Ion exchange can be operated in either batch or continuous mode. In a batch method, the resins and solution are mixed in a continuously stirred tank until the exchange reaction reaches equilibrium, upon which the resins are separated from the solution. On the other hand, in a continuous method, the resins are placed in a vertical column to form a bed. Then, the solution flows through this bed until the target effluent concentration is attained [97, 113]. While both are easy to operate, the former suffers from inefficient regeneration and also requires an additional operation to separate the liquid from the ion exchange resins [97]. Therefore, it is more common to encounter ion exchange columns in industrial applications. Figure 9 shows a typical cyclic operation for an ion exchange process.

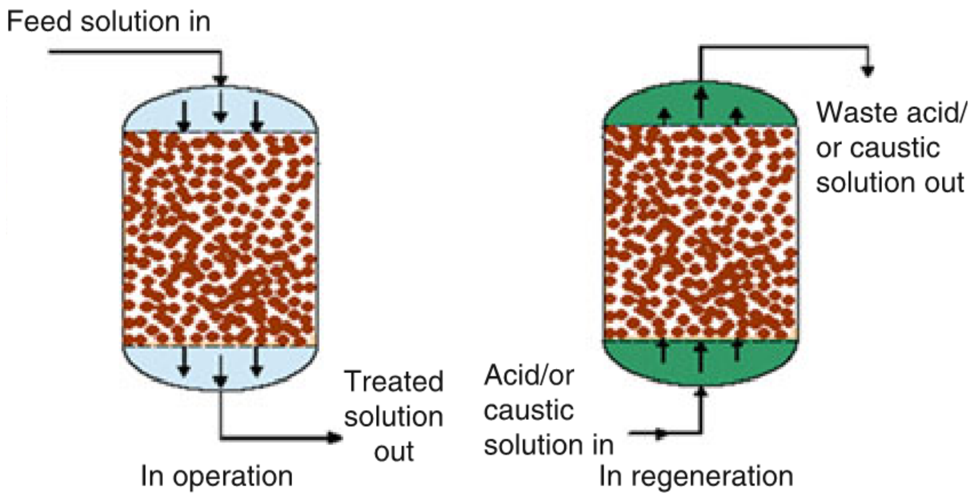

Figure 9. Operation cycle of an ion exchange process [97].

1. **Exhaustion**: During operation, the solution to be treated is passed over a column filled with the ion exchange resins. The resins at the topmost section of the column will be depleted first and this depletion zone will steadily move downwards until it reaches the bottom of the column. At this point, a *breakthrough* is said to have occurred wherein the target effluent concentration is reached as observed through the leakage of the target ions at the discharge [85].

2. **Regeneration**: After the exhaustion step, the resins are already loaded with ions having a higher affinity towards the fixed groups compared to the original ions. Hence, to regenerate these resins, SAC exchange resins are treated with either a strong acid such as HCl or a highly concentrated NaCl solution to reverse the selectivity of the resins and bring it back to either H^+ or Na^+ form, respectively. WAC exchange resins need a lower concentration of acid regenerant compared to SAC exchange resins due to the higher affinity of the former towards H^+ ions. Similarly, SBA exchange resins can be treated with a strong base such as NaOH or concentrated NaCl solution to return it to its OH^- or Cl^- forms, respectively, and WBA exchange resins using NaOH [86].

2.2 Materials and methods

2.2.1 Ion exchange resins

Three commercially available anion exchange resins (one SBA, two WBA) with varying properties were evaluated for their performance in removing Cr from a highly concentrated brine solution. These resins were all recommended by Dow and DuPont based on their previous experiences in heavy metal removal under various conditions. WBA exchange resins, Amberlite PWA7 and Amberlite PWA8 were provided by Dow while SBA exchange resin, Amberlite HPR4800, was provided by DuPont. Amberlite PWA7 is specifically designed to remove chromate from drinking water whereas Amberlite PWA8 is more commonly applied for uranium removal [114, 115]. On the other hand, Amberlite HPR4800 is typically used for industrial demineralization applications [116]. Summarized in Table 8 are some of the physical and chemical properties of the resins as stated in their product datasheets.

Table 8. Properties of the ion exchange resins [115, 116, 114].

	PWA7	**PWA8**	**HPR4800**
Type	WBA	WBA	SBA, Type I
Structure	Porous	Gel	Gel
Matrix	crosslinked phenol-formaldehyde polycondensate	crosslinked acrylic	styrene-divinylbenzene
Functional group	Secondary amine	Tertiary amine	Trimethylammonium
Physical form	Cream, opaque, granules	White, translucent, spherical beads	Amber, translucent, spherical beads
Particle diameter	550 - 700 μm	500 - 750 μm	575 ± 50 μm
Ionic Form	Free Base	Free Base	Cl^-
Total exchange capacity per liter of wet resin	≥ 1.9 eq/L	≥ 1.6 eq/L	≥ 1.3 eq/L
Operating pH Range	5 - 6.5	0 - 6	1 - 14

2.2.2 Preparation of wash brine solutions

The schematic diagram of the conducted experiment is shown in Figure 10. Salt samples were provided by Dow in the form of crystals. While the composition of the salts has not been analyzed, as previously mentioned, it was expected that aside from Cr, other residual organics and nitrogen might be present with the samples. In two separate 2L glass bottles, 587 g of the salt was washed by mixing it with 815 mL of saturated NaCl solution prepared from analytical grade NaCl salts and distilled water. To ensure maximum contact between the salts and the solution, these bottles were allowed to be shaken in the rotary shaker for 24 hours. The glass bottles were positioned horizontally on the surface of the shaker to ensure that the salts were homogenously washed within each setup. After 24 hours, the mixture was filtered, and the combined filtrate from the two setups was collected as the wash brine solution.

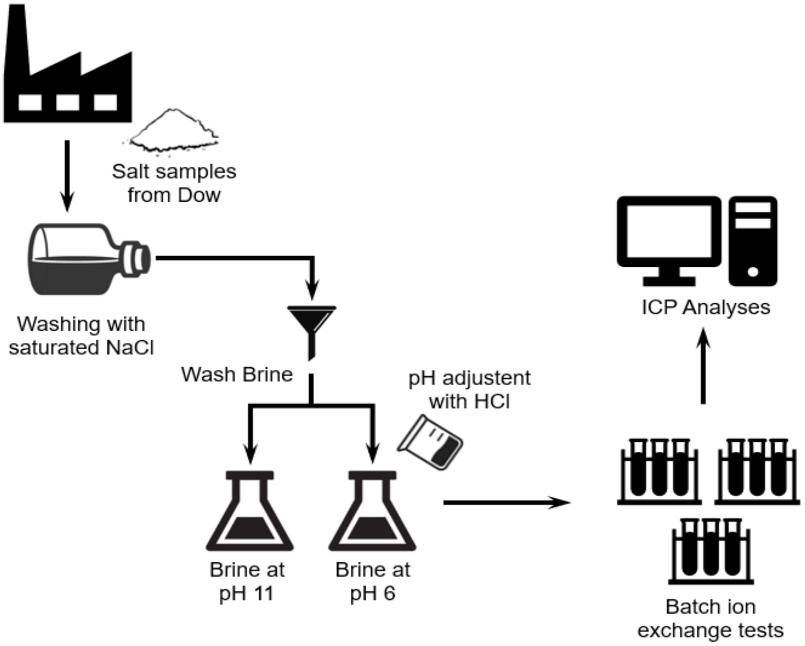

Figure 10. Schematic diagram of the ion exchange experiment.

The collected wash brine had a pH of 11. Hence, to investigate the Cr removal at the optimum pH of the WBA exchange resins, another set of wash brine at pH 6 was prepared. A titration curve was first prepared using 50 mL of the wash brine and 0.01 M of HCl. Due to its high buffering capacity, 53 mL of the acid was used to reduce the pH of the wash brine from 11 to 6 (Figure 11). Hence, to prepare 500 mL of wash brine at pH 6, 0.4 mL of 37% (or 12M) HCl solution was added.

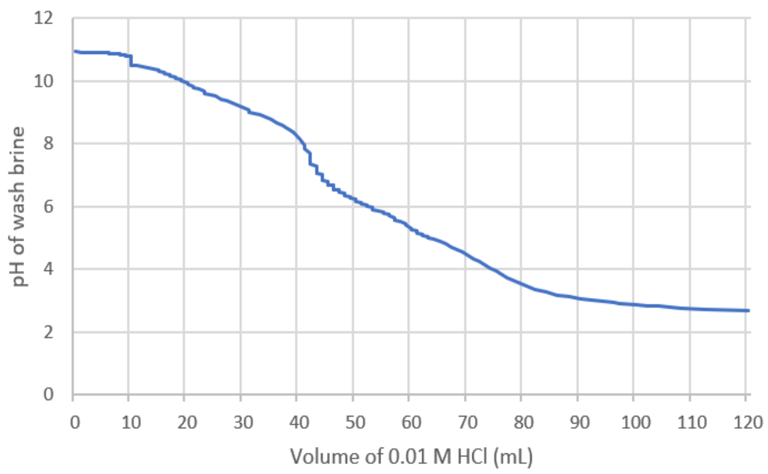

Figure 11. Titration curve for a 50mL wash brine.

2.2.3 Batch ion exchange experiments

Three different parameters were tested for their effect on chromium removal: type of resin (Amberlite PWA7, Amberlite PWA8, Amberlite HPR4800), amount of resin in g/mL (0.001, 0.01, 0.1), and pH (6, 11). This was done using a full factorial experimental design, with each setup performed in three replicates (Table 9). The tests were carried out in sterile 12mL round-bottom tubes and shaken overhead in the 360º vertical rotator for 24h.

Table 9. Batch ion exchange setups using a full factorial experimental design.

Setup	Type of resin	Amount of resin (g/mL)	pH
1	Amberlite PWA7	0.001	6
2		0.001	11
3		0.01	6
4		0.01	11
5		0.1	6
6		0.1	11
7	Amberlite PWA8	0.001	6
8		0.001	11
9		0.01	6
10		0.01	11
11		0.1	6
12		0.1	11
13	Amberlite HPR4800	0.001	6
14		0.001	11
15		0.01	6
16		0.01	11
17		0.1	6
18		0.1	11

2.2.4 Analysis using ICP-OES and ICP-MS

The total Cr analyses were performed after the batch tests using Thermo Scientific™ iCAP™ 7400 ICP-OES and PerkinElmer NexION® 350S ICP-MS. Likewise, the Cr content of the original salt crystals was determined by dissolving 5 g of the solid in 50 mL of distilled water, which was then subjected to the same analytical procedure. Due to the high NaCl content, each sample was diluted 10 times for the ICP-OES and 1000 times for the ICP-MS using 1% v/v HNO_3. Calibration standards were prepared by adding a single element Cr standard in a solution with 1% v/v HNO_3 and 36 g/L of NaCl to match the sample matrix.

2.2.5 Statistical analysis

The standard deviation for each setup was calculated using the sample standard and is presented as error bars in Section 2.3. Moreover, the Data Analysis function of MS Excel was used to perform an unequal variance t-test to determine whether the equilibrium concentration of each setup is significantly different from the initial concentration. On the other hand, a multi-way ANOVA was performed using SPSS Statistics 26 to determine whether the tested variables cause a significant effect on the Cr removal efficiency and whether there is significant interaction among the three variables.

2.3 Results and discussion

2.3.1 Analytical methods: ICP-OES vs ICP-MS

Analysis of the samples using ICP-OES showed limits of detection (LOD) at 20 μg/L total Cr and limits of quantification (LOQ) at 60 μg/L total Cr. Considering a dilution factor of 10, this means that ICP-OES would be able to detect the presence of Cr at concentrations higher than 0.2 mg/L. While the initial and residual concentrations of Cr within all samples were above the LOD, these are, however, either equal or below the LOQ. Hence, to get a better insight on the removal efficiencies of each setup, all samples were reanalyzed using the more sensitive ICP-MS. This method exhibited an LOD and LOQ of 1 μg/L and 2 μg/L, respectively. Considering a dilution factor of 1000, this means that within this matrix, ICP-MS would only be able to detect chromium concentrations higher than 1 mg/L – a value considerably higher than ICP-OES. Figure 12 shows that the measured values using ICP-OES are very different from those measured using ICP-MS. Therefore, the succeeding values that are presented will refer to those measured using ICP-OES. For both methods, dilution was highly necessary since ICP-OES can only handle total dissolved solids (TDS) up to 30% m/m while ICP-MS can only tolerate TDS up to 0.2% m/m [117].

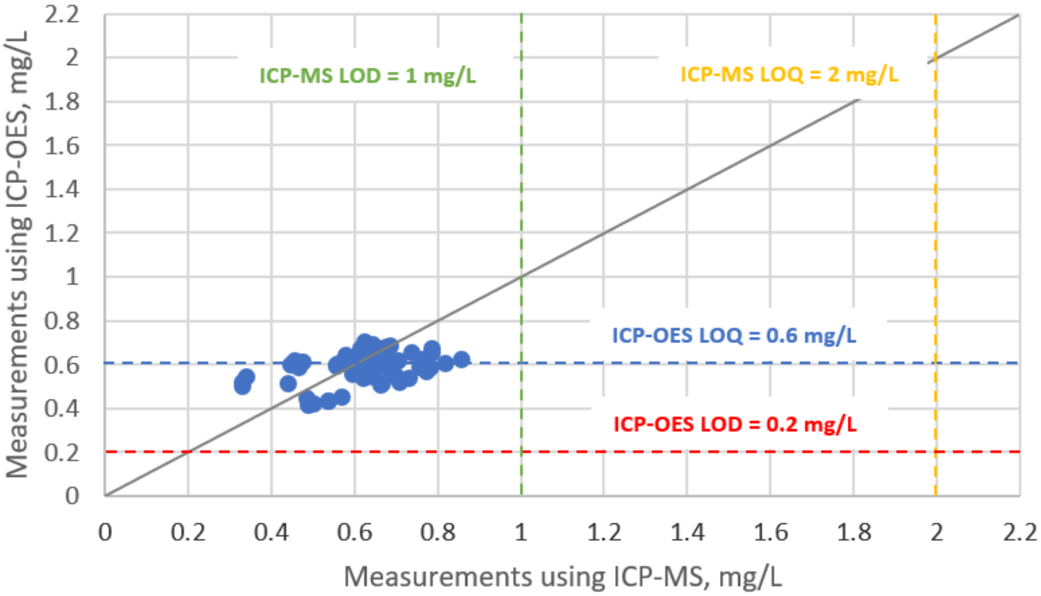

Figure 12. Relationship between the measured values using ICP-OES and ICP-MS.

Both methods are highly limited in measuring the Cr content of the salt solutions. Several studies have also experienced difficulties in determining the concentrations of trace elements in highly saline solutions (i.e. seawater) using ICP-OES and ICP-MS. Dehouck et al. [118] noted that such solutions can cause salt precipitation and build-up at the torch top and orifice of the cone on ICP-MS. Additionally, Violante et al. [119] observed that chlorine can combine with H and O in the matrix to create polyatomic ions $^{35}Cl^{17}O$ and $^{35}Cl^{16}O^{1}H$ that cause severe interference with ^{52}Cr in ICP-MS. While the most common method to overcome the effect of high salinity is to dilute the samples prior to analysis, it is not advisable in this case as this would further decrease the concentration of chromium below the LOQ and LOD of the equipment. Hence, for future analyses, it is suggested to investigate the feasibility of pre-treating the samples (e.g. preconcentration, coprecipitation, derivatization of chromium) before using ICP-OES or ICP-MS [120, 121]. Moreover, the potential of electrochemical methods such as anodic stripping voltammetry (ASV) could also be an interesting technique to explore [122, 123, 124, 125].

2.3.2 Characterization of the salt sample and brine solution

To reduce the amount of Cr occluded within the crystals, salt samples were washed with a saturated NaCl solution. This produced a highly alkaline brine with a pH of 11 and a total Cr concentration of 0.59 ± 0.04 mg/L. As supported by a student’s t-test (Table A.4), this initial brine concentration is not significantly different from the LOQ of the ICP-OES. Thus, as will be discussed in the following section, the resulting residual concentrations are below the LOQ which prohibits the full quantification of the ion exchange performance.

The amount of Cr leached into the brine solution corresponds to a 17% reduction in the total chromium content of the salt samples as seen in Figure 13. This is a lot lower compared to the expected chromium reduction through washing as reported by Dow which reached up to 80% removal. For future studies, it is suggested to increase the ratio of the saturated NaCl solution with the salt samples to enhance solid-liquid contact and shift the equilibrium towards having the Cr in the solution. Furthermore, it might be interesting to test if continuous washing would yield a better Cr removal compared to a batch setup.

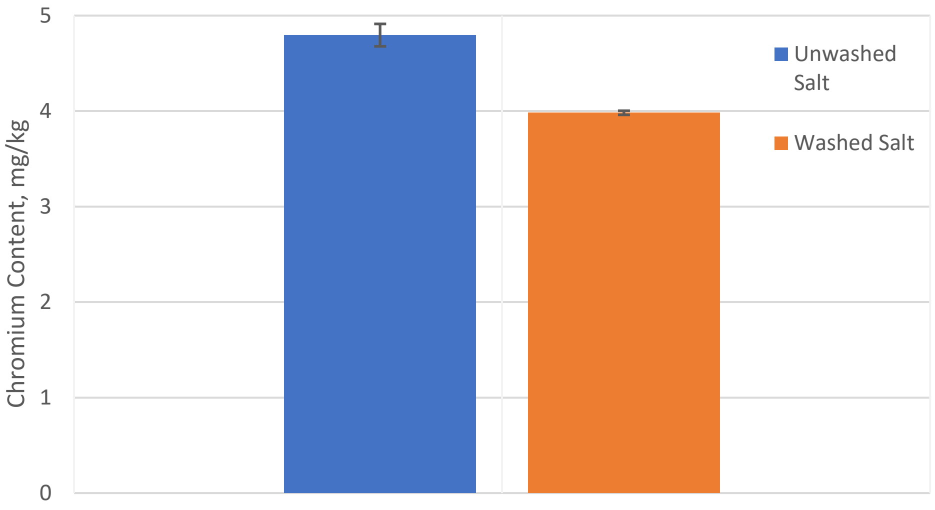

Figure 13. Chromium content of the salt samples before and after washing with saturated NaCl.

2.3.3 Batch adsorption Tests

The speciation of 5 mg/L of Cr in a saturated NaCl solution at 25ºC is shown in Figure 14. From this Pourbaix diagram, it can be expected that Cr(VI) is mostly present as chromate (CrO_4^{2-}) in the wash brine at pH 11 while a mix of chromate and bichromate ($HCrO_4^{-}$) is in the brine solution at pH 6. On the other hand, any Cr(III) released to the brine solution after washing is expected to precipitate as CrO(OH) at both pH levels. As Cr(III) hydroxides are expected to be removed using a filter paper [126], only Cr(VI) is expected to be in the wash brine. These are exchanged onto the resins according to the following reactions [7]:

$$RCl + HCrO_4{}^{-} \rightleftharpoons RHCrO_4 + Cl^{-} \qquad \text{[Equation 6]}$$

$$2RCl + CrO_4{}^{2-} \rightleftharpoons R_2CrO_4 + 2Cl^{-} \qquad \text{[Equation 7]}$$

where R indicates the resin with Cl^- as the mobile portion of the active group. One resin site is needed for bichromate while two are required for chromate to maintain electroneutrality.

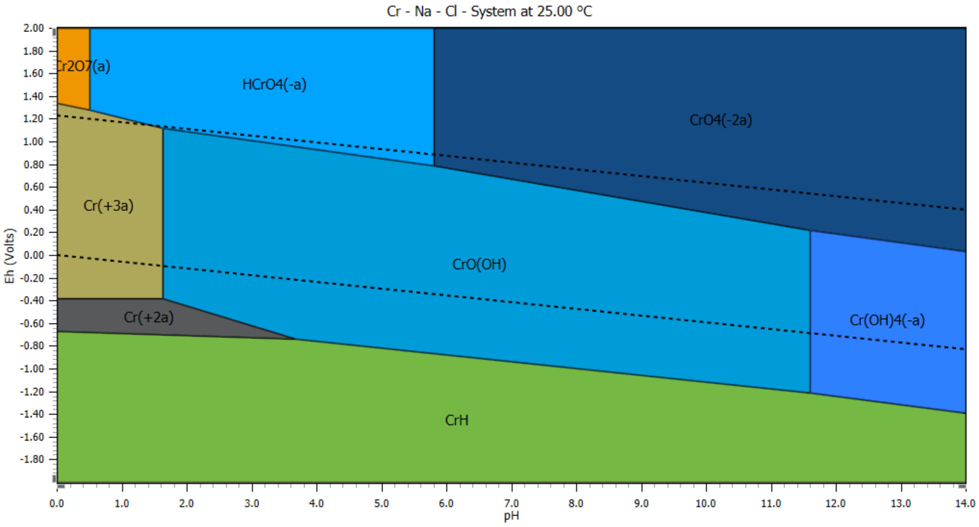

Figure 14. Pourbaix diagram of the contaminated brine solution.

The results of the batch ion exchange tests as a function of the type of resin, amount of resin, and pH are shown in Figure 15 and Figure 16, with error bars showing the standard deviation (n=3) for these values. In general, the measured values within each setup is highly variable. A multi-way ANOVA test suggests that there is a statistically significant interaction between the type of resin and resin load ratio in removing Cr. For brine solutions at pH 6 and pH 11, the highest total Cr removal of *at least* 27.3 ± 2.6% and 25.4 ± 1.7%, respectively, was observed using PWA7 with 0.1 g of resin / mL of brine. These were the only setups that exhibited significant removal of Cr from the brine solutions. As previously mentioned, since the initial Cr concentration of the brine is equal to the LOQ, it should be emphasized that the exact removal efficiencies cannot be fully quantified as any reduction in the total Cr of the initial brine solution would result in a concentration that is below the LOQ. Hence, these removal efficiencies were reported as a *minimum value* and that using these values as a measure of good or poor performance cannot be established. On the other hand, several setups exhibited a residual concentration higher than the initial concentration, thereby causing apparent negative removal efficiencies. While these further highlight the uncertainties of working with concentrations that are clustered towards the LOQ of the analytical method employed, these negative values were interpreted as zero removal efficiency.

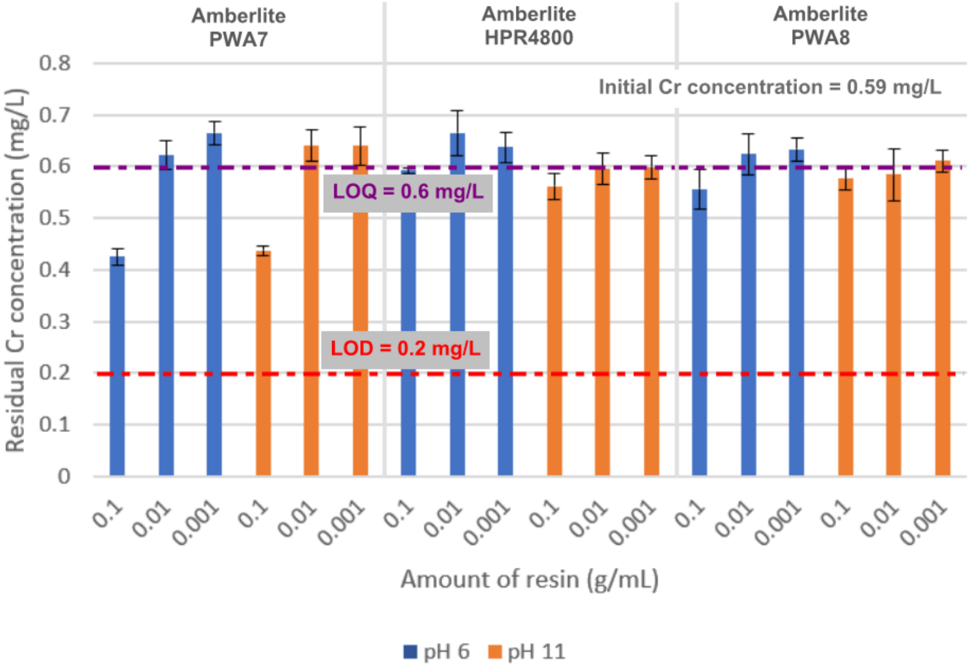

Figure 15. Residual total chromium concentrations at different combinations of resin type, resin amount, and pH.

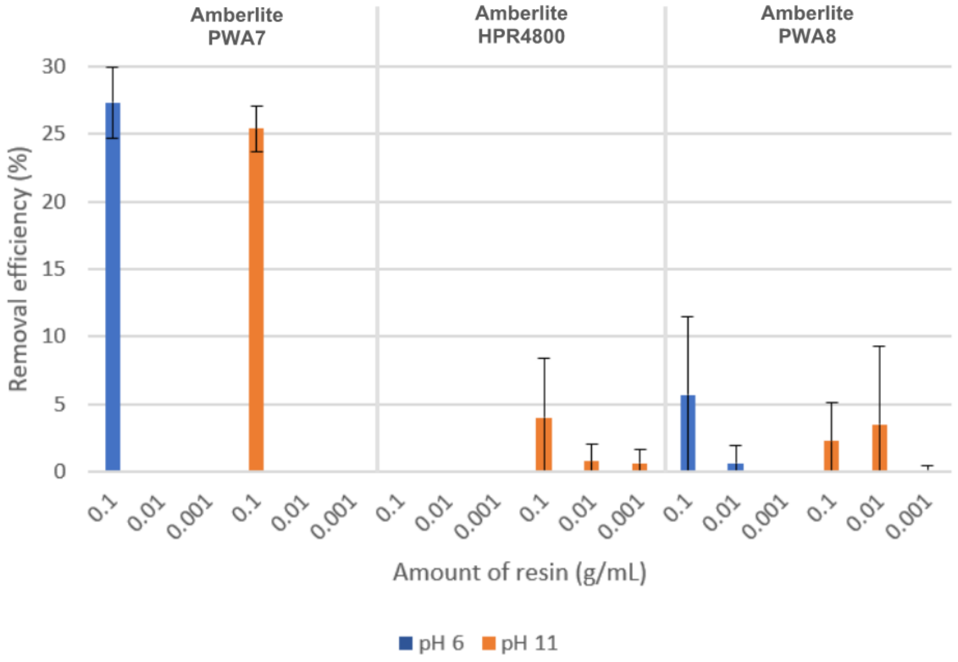

Figure 16. Total chromium removal at different combinations of resin type, resin amount, and pH.

Qualitatively, the electroselectivity of anion exchangers would suggest that these resins would preferentially adsorb the divalent chromate ions over chlorides due to its higher ionic charge density [127]. However, as expected, low removal efficiencies were observed even if the optimal pH for these resins were used. This could be attributed to the extremely high amount of chloride ions present in the solution that is competing with Cr for the same exchange site. Additionally, any Cr adsorbed onto the binding site could be displaced by the chlorides due to their higher concentration, even if it has a weaker force of attraction towards the ionic groups. In fact, this *selectivity reversal phenomenon* between chloride and chromate is leveraged in the highly efficient regeneration of strong base anion (SBA) exchange resins loaded with chromate [128]. Considering their relative concentrations in the studied solutions, resins (or methods) that are approximately 160,000 times more selective towards chromate would be needed to remove Cr ions as much as the chlorides.

2.3.3.1 Effect of resin type

The results for these setups at a resin amount of 0.1 g/mL and pH 6 (where all resins are ionized) are summarized in Figure 17. Among the three resins tested, only Amberlite PWA7 showed significant Cr removal efficiency at least 27.3 ± 2.6%. On the other hand, the student’s t-test suggests that the residual concentrations for the setups using Amberlite PWA8 and Amberlite HPR4800 are not significantly different from the initial brine concentration, hence these statistically have zero removal efficiencies (Table A.8 and Table A.10). The differences among the observed behaviors show that the type of resin significantly affects Cr removal – this is supported by the results of the multi-way ANOVA test in Table A.11.

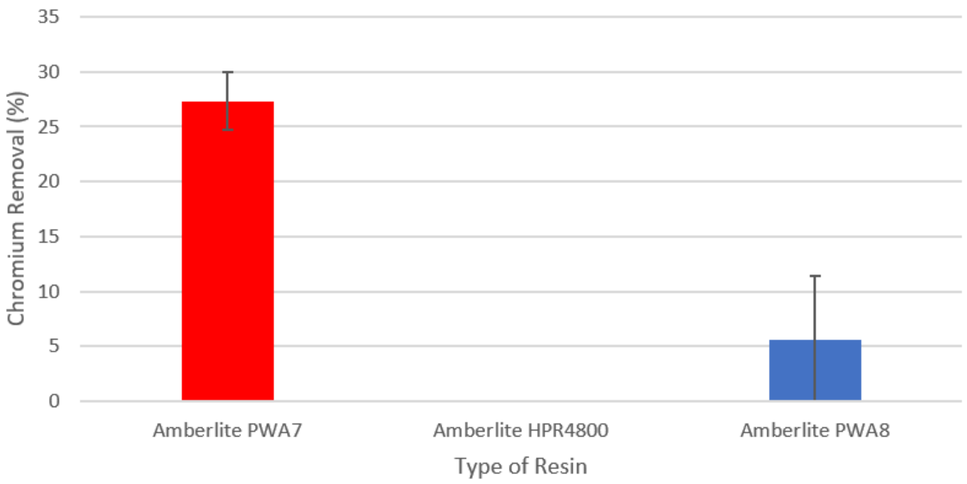

Figure 17. Removal efficiencies of different resins at pH of 6 and resin amount of 0.1 g/mL.

The relative performance of each resin against each other in this concentrated solution is as expected. The physicochemical properties of Amberlite PWA7 make it an ideal resin for the selective removal of chromate due to its functional group and polymer matrix. First, the secondary amines in Amberlite PWA7 make the active sites more accessible for the divalent chromate ion compared to the tertiary and quaternary amines. In other words, the absence of a higher number of alkyl groups decreased the spacing between the active sites. This could be related to the concept of *distance-of-charge* used in other studies to correlate the separation of sulfate/nitrate and nitrate/chloride with the nature of the alkyl groups present [93, 94]. In contrast, no removal of Cr was observed using Amberlite HPR4800 as quaternary amine groups have very high adsorption rates for all anions but very low selectivity. Second, only Amberlite PWA7 has a macroporous structure out of all the resins tested. Due to their higher degree of cross-linking, macroporous resins have lower moisture around their ionogenic groups, making them selective towards less hydrated anions. Within the matrix, chromate and bichromate are less hydrated because of their polyatomic tetrahedral structure in contrast to chlorides with a monatomic spherical structure [8]. Hence, Amberlite PWA7 has a higher affinity towards these ions. This corresponds well to the findings of Sengupta et al. [8] wherein the selectivity of removing bichromate over the less hydrated sulfate and chloride in cooling water blowdown was higher for resins with a macroporous structure compared to those with a gel structure. Third, Amberlite PWA7 has the highest theoretical exchange capacity among the resins studied. This could be attributed to its phenol-formaldehyde polymer structure which can typically achieve higher nitrogen content than other matrices [100]. This translates to more active sites and contributes to the previously discussed effect of the spacing of the functional groups, facilitating the easier adsorption of divalent chromate ions.

While the other resins also have high theoretical exchange capacities and hydrophobic structures (e.g. polystyrene), their overall removal efficiencies were still negligible. This likely shows that beyond these properties, the nature of the functional group plays the biggest part in overcoming the effect of high chloride concentration.

2.3.3.2 Effect of resin amount

The effect of varying the resin amount is shown in Figure 18. Initially, it was planned to construct adsorption isotherms to have better insights on the amount of Cr ions removed by each resin as a function of varying adsorbate-to-resin ratios. However, due to the observed limitations of the analytical methods employed, the fitted curves showed very poor correlation coefficients and negative isotherm constants which were deemed unmeaningful for the research.

The results of the multi-way ANOVA test suggest that the effect of the resin amount in Cr removal is statistically significant (Table A.11). The performance of Amberlite PWA7 clearly shows that the increase in the amount of resin improves Cr removal efficiency. This was expected as the increase in the amount of resin provides more active sites for the Cr to attach. Given the limited tests done in the study, the maximum amount of resin that can be added to the system before observing a plateau in the removal efficiency cannot be identified. On the other hand, as supported by the student’s t-test, Amberlite PWA8 and Amberlite HPR4800 did not show any significant Cr removal at the tested resin amounts (Table A.8 and Table A.10). As discussed in the previous section, the physical and chemical properties of these two resins are not ideal for the selective removal of Cr in a saturated chloride solution which limits their performance even at high amounts.

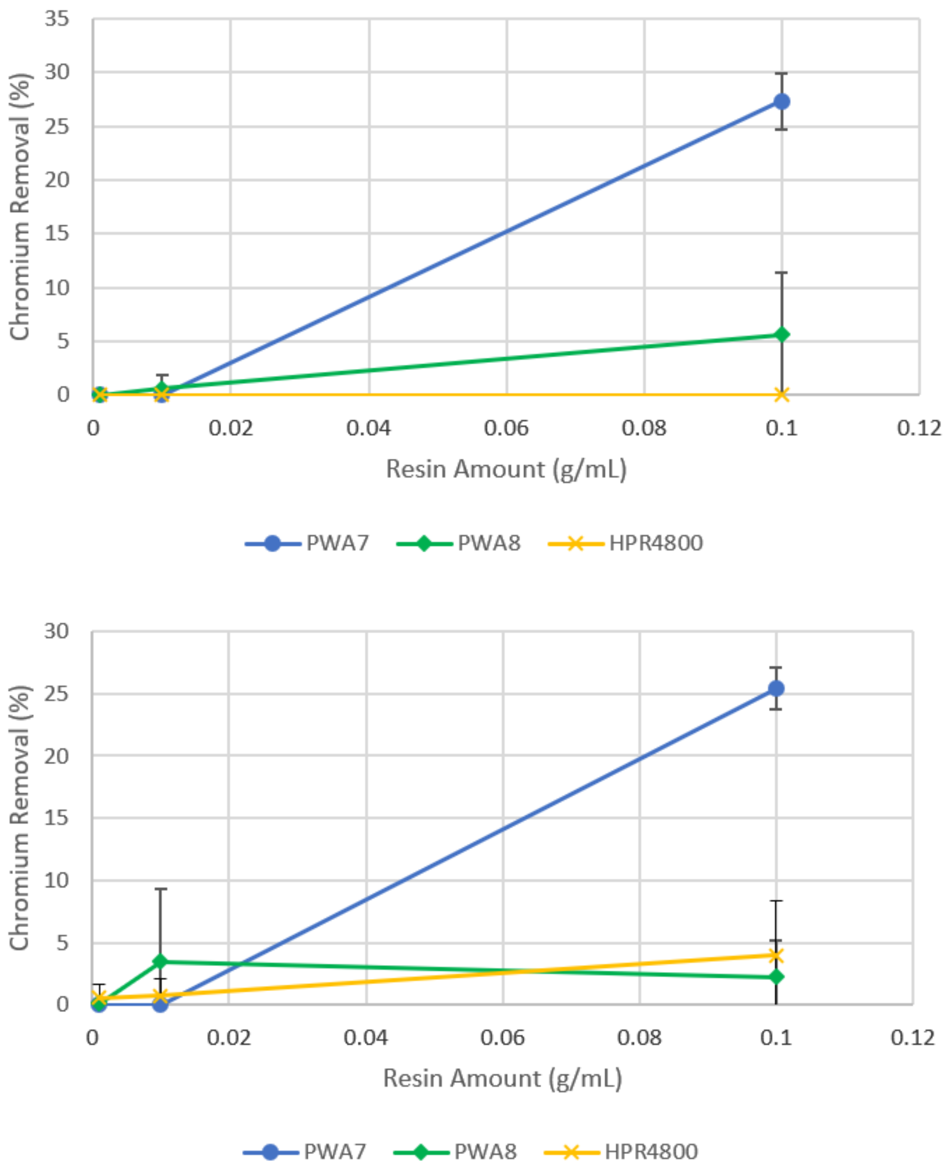

Figure 18. Removal efficiencies of different resins at varying resin amount and constant pH of 6 (above) and pH of 11 (below).

2.3.3.3 Effect of pH

The effect of pH on the removal efficiencies of the different resins at a fixed resin amount of 0.1 g/mL is shown in Figure 19. As previously mentioned, Amberlite PWA7 performed best at both pH levels compared to the other resins. On the other hand, as supported by the student's t-test, no significant removal on Cr was observed in both pH levels using Amberlite PWA8 and Amberlite

HPR4800. The multi-way ANOVA test suggests that within the tested conditions, pH has no statistically significant effect on Cr removal, nor does it have any between-variable effect with the type of resin or resin amount (Table A.11).

Amberlite PWA7 and Amberlite PWA8 should perform better in mildly acidic conditions than in alkaline conditions since these WBA exchange resins have functional groups that are only ionized at pH below 7. At alkaline conditions, the surface of these resins gets a partial negative charge due to the surrounding OH^- ions, thereby repelling the Cr anions. On the other hand, as an SBA exchange resin, Amberlite HPR4800 should be able to remove Cr under both pH levels as its functional groups remain highly dissociated over the entire pH range. However, these behaviors were not observed for Amberlite PWA8 and Amberlite HPR4800 as the high concentration of chlorides could have prevented these resins from exchanging any significant amount of Cr due to the selectivity reversal effect. While the same behavior also affects the removal efficiency of the Amberlite PWA7, the limitations of the analytical methods make it difficult to clearly show if there is any difference between the performance of this resin under the two pH levels.

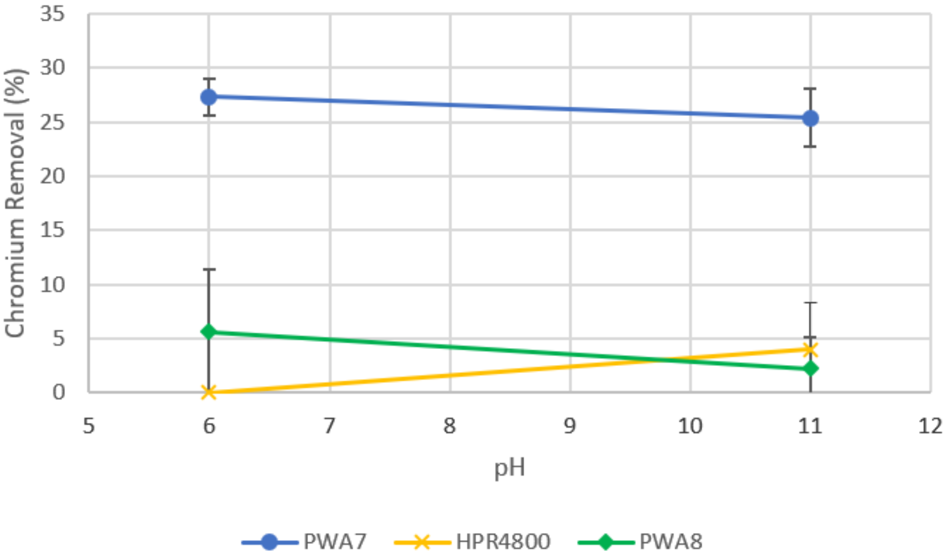

Figure 19. Removal efficiencies of different resins at pH 6 and pH 11 at a resin amount of 0.1g/mL.

While WBA exchange resins are only ionized at acidic conditions, at least 25.4 ± 1.7% of Cr has been removed from the wash brine at pH 11. However, without any protonated groups at pH 11, it is very unlikely for Amberlite PWA7 to remove anions from the solution. In a study by Cortina et al. [92], different WBA exchange resins were still able to extract 75% of gold from a cyanide leach solution even at pH 14. It was suggested that $Au(CN)^{2-}$ was extracted by a ligand substitution reaction of the CN^- of the gold-cyanide complex with the electron pair of the nitrogen in the amine group. However, in the case of chromate, the bond between Cr(VI) and oxide ions are too strong to be broken that such substitution reaction might be difficult to achieve [129]. Therefore, for future studies, if other analytical techniques would be able to verify that Amberlite PWA7 could indeed remove Cr at pH 11, it would be beneficial to examine the exchange mechanism through methods such as X-ray photoelectron spectroscopy (XPS) or IR spectroscopy (FTIR). These would give better insights on whether Cr was removed as a chromate ion and if the removal mechanism was only through a simple ion-exchange process or a ligand substitution reaction.

2.4 Conclusions

Ion exchange is known to be one of the most effective methods to selectively remove heavy metals such as Cr from an aqueous solution. Several studies have already proven that the efficiency of anion exchange resins in removing Cr could reach greater than 90% without sacrificing selectivity. However, this is only often observed in simple (waste)water streams where the competing ions such as chlorides and sulfates are at concentrations 100 times higher than the trace element. Hence, when confronted with solutions containing high amounts of competing ions such as in this concentrated wash brine, *would commercial ion exchange resins still be able to reduce the amount of Cr?* This is the fundamental question that this Chapter wanted to address.

Two analytical methods, ICP-OES and ICP-MS, were used in the study. As both methods were sensitive to very high TDS concentrations, all samples were diluted 10 times for the ICP-OES and 1000 times for the ICP-MS prior to analysis. Subsequently, the LOD values were determined to be 0.2 mg/L and 1 mg/L of total Cr for ICP-OES and ICP-MS, respectively. Due to the lower LOD, the measurements using ICP-OES were used for data analysis.

Washing the salts with a saturated NaCl solution removed 17% of their total Cr content. This generated a wash brine at pH 11 containing 0.59 ± 0.04 mg/L of total Cr. According to the Pourbaix diagram, at this pH level, Cr(III) should form hydroxides that would easily precipitate out of the solution whereas Cr(VI) should be present as chromate and bichromate ions. On the other hand, the measured total Cr concentration of the wash brine is not significantly different from the LOQ. This suggests that analysis using ICP-OES is highly limited in this particular case. In fact, any subsequent reduction in the amount of Cr through ion exchange would result in a residual concentration that is below the LOQ. Therefore, the removal efficiencies reported in this research only represent minimum values and does not fully quantify the extent of Cr removal.

Batch ion exchange experiments suggested that the type and amount of resin tested significantly affect Cr removal efficiency. In contrast, pH was not found to significantly affect Cr removal, nor does it have significant interaction with the two other variables. The highest total Cr removal efficiency of at least 27.3 ± 2.6% was observed using Amberlite PWA7 at a resin amount of 0.1 g/mL and pH of 6. On the other hand, Amberlite PWA8 and Amberlite HPR4800 did not remove any significant amount of Cr at any of the tested conditions. This is likely to be caused by the high concentration of chlorides competing against Cr for the same exchange sites. The better performance of Amberlite PWA7 under this concentrated solution could be attributed to its physical and chemical properties (i.e. secondary amines, macroporous matrix, phenol-formaldehyde structure) that are better tailored towards Cr(VI) species than chlorides.

As a WBA exchange resin, Amberlite PWA7 is only ionized at acidic conditions. Still, the resin was able to reduce the total Cr concentration of the wash brine by at least 25.4 ± 1.7% at a resin amount of 0.1 g/mL and a pH of 11. While the removal of anionic complexes using WBA exchange resins has been described by other studies as a ligand substitution reaction rather than a simple ion exchange process at high pH values, the findings of this research are insufficient to conclude that the same phenomenon exists for Cr oxyanions.

Therefore, to answer the research question, the results of this study suggest that ion exchange could reduce the trace amounts of Cr in highly concentrated brine solutions. However, the extent of Cr removal cannot be fully quantified due to the limitations encountered in the study. While these findings could serve as a basis for future validation and optimization tests using Amberlite PWA7, it should be emphasized that this only serves as a short-term solution for the Cr contamination of the salts. Hence, it would still be best to identify and address the source of contamination to provide a long-term and sustainable solution.

2.5 Recommendations

One of the biggest limitations of the research was on fully quantifying the amount of Cr removed in the solution through ion exchange. Therefore, prior to any optimization studies, it is important to identify a suitable analytical method with enough sensitivity to determine trace amounts of Cr in the presence of high concentrations of competing ions. Aside from measuring total Cr, it would be better to also quantify the amounts of Cr(III) and Cr(VI) in the solution. While it was assumed that the precipitates of Cr(III) were removed using a filter paper, some particles might have passed through the filter and transferred to the wash brine. This would inadvertently reduce the removal efficiencies of anion exchange resins if only total Cr is measured. If the current circumstances would have permitted, electrochemical methods such as anodic and cathodic stripping voltammetry (ASV and CSV) would have been explored to determine the concentrations of Cr(III) and Cr(VI) in the presence of competing ions [124, 125, 130].

Although it has not been done in the experiment, it would be helpful to measure the final pH of the solution (especially when starting at pH 6) as the change in pH during the process could greatly reduce the performance of the resins, especially for the WBA exchange resins. Maintaining the pH of the solution below 7 would ensure that the amine groups of the anion exchange resins remain protonated.

It is also highly recommended to fully quantify and further study the Cr removal of Amberlite PWA7 at pH 11. Employing methods such as XPS and FTIR could shed light on the possible removal mechanism of Cr using WBA exchange resins at high pH values. If the analytical methods could verify that the resin indeed removes significant amounts of Cr at the original brine pH, then the process would be more attractive since the need for pH adjustment could be avoided. Likewise, optimization studies might also be interesting to explore by varying both pH and resin amount.

It is only recommended to proceed with the column experiments if conditions for high removal efficiencies are achieved in the batch tests to prevent an early breakthrough. Additional experiments and simulation of the whole washing and purification loop would also be useful in defining the target effluent concentration in the column. Also, regeneration tests (i.e. using 1M NaOH [113]) should be conducted to assess the sustainability of the process. This also includes studies for subsequent handling of the regenerant solution containing the removed Cr ions.

Chapter 3

Developing hybrid sorption-based techniques for chromium removal

It was previously mentioned that many technologies have already been investigated and applied for the removal of Cr including oxidation-reduction, coagulation-flocculation, membrane filtration, adsorption, and ion exchange [131]. However, these current technologies are often employed to remove these trace elements in the g/L or mg/L range. Moreover, the lack of selectivity of these conventional processes in the presence of competing ions such as chlorides and sulfates that often exist at higher concentrations (i.e. at least 1000x higher [8]) in (waste)waters is also an important issue to be addressed. These issues clearly show that the available conventional methods can no longer meet the increasingly stringent standards in drinking water and (waste)waters [16, 63]. In other words, there is a strong need to develop novel techniques through ground-breaking new approaches that could selectively remove Cr. While Chapter 2 focused on the performance evaluation of commercial ion exchange resins for removing Cr, in this chapter, adsorption, which is a highly related technique, will be proposed as a possible strategy for efficiently and selectively removing trace amounts of Cr.

In contrast to ion exchange which involves a transfer of ions between a solid and liquid phase, in adsorption, the mass transfer happens through the attraction of an ion in the liquid phase towards the surface of the solid phase [77]. These two processes are highly related as some adsorbents also involve ion exchange, aside from electrostatic attraction, redox process, and surface complexation, for their adsorption mechanism [132]. Extensive literature is available regarding the use of adsorptive media to remove Cr, most of which are highly successful in removing the bulk of this heavy metal down to the acceptable limits [133]. Similarly, a wide variety of materials have been extensively studied in this field (e.g. activated carbon, biosorbents, clays, polymers) [133], with iron-based adsorbents gaining increased interest due to their low costs and high efficiencies [132]. Most conventional adsorbents suffer from low adsorption capacities for their irregular pore structures and/or low specific surface areas, as well as poor regeneration. While there has been substantial progress in developing adsorbents with improved adsorption capacities, these were only assessed on pure (synthetic) streams of Cr, often without considering selectivity [131]. Hence, their applicability on real (waste)water is not well understood. Thorough understanding of the kinetics of (de)sorption processes for different species, its dependence on process parameters (e.g. pH), adsorbent (i.e. functionalized or not), and behavior in the presence of competing species may be used to further improve selectivity. Moreover, changing the matrix composition of the (waste)water to increase the ratio of the trace elements against the competing compounds using methods such as selective complexation or precipitation while varying pH and redox potential can render the adsorption of the target element more favorable.

Within this context, the ECHOCHEM and COMOC research groups of Ghent University recently immobilized iron oxide nanoparticles within a porous metal-organic framework (MOF) and covalent-triazine framework (CTF), denoted as MIL-101 and CTF-1, respectively [134, 135]. Although the resulting composite materials exhibited high adsorption capacities and excellent removal efficiencies (>95%) for oxyanions such as As(III) and As(V), they possessed some inherent disadvantages. First, their high cost and difficulties to scale-up set huge restrictions for their wide industrial applicability. Second, the MOF-based adsorbent showed limited durability. Even the hydrolytically more stable CTF exhibited a slow diffusion of the nanoparticles (NPs) out of the pores, which consequently resulted in a decrease of the adsorption capacity [134, 135].

Recently, ordered mesoporous polymers/carbons (OMP/OMCs) have attracted significant interest due to their structural regularity, large specific surface area, thermal stability, chemical inertness, biocompatibility, and many potential applications in the fields of adsorption, hydrogen storage, catalyst supports, bioengineering, and energy storage [136]. Iron oxide NPs, on the other hand, have been widely used in environmental applications and have shown promising performance in pollutant removal or toxicity mitigation [137]. Among the most widely used NPs, zero-valent iron, magnetite (Fe_3O4) and maghemite (γ-Fe_2O_3) have sparked immense interest in the treatment of polluted waters. Because of their extremely small particle size and high surface-to-volume ratio, these NPs have a large removal capacity, fast kinetics, and high reactivity for contaminant removal. However, because of their small size, there is a high tendency for these to aggregate. This reduces their overall removal capacity and reactivity. An attractive approach is to stabilize them within the OMP/OMC, thereby combining ‘best of both worlds’.

It would be very advantageous to set up, test, and optimize a methodology for the development of sorption-based techniques for selective removal of toxic trace elements such as Cr to the low or sub µg/L range in presence of high concentrations of competing compounds, i.e. from different complex solutions. This will ideally comprise two stages: bulk removal of the target metal, and polishing. In the bulk removal stage, smart experimental approaches could be combined focused on exploiting all options to increase the ratio between the trace element and the competing compounds (different combinations of pH levels, complexing agent, precipitating agent) before removing the trace elements using different types of adsorbents. Afterwards, in the polishing stage, novel, cost-effective adsorbents (i.e. iron oxide nanoparticles within OMP/OMCs) can be used to reduce the trace element concentration to low or sub µg/L levels. This will ultimately lead to a set of hybrid sorption-based techniques with optimum selectivity and efficiency for the target element in a specific (waste)water stream.

Conclusions

Large quantities of salt by-products are produced from one of the operations in Dow Terneuzen. Throughout the process, different contaminants such as Cr end up within these salts, thereby limiting their reuse and possible marketing as road salts. One method that has been tested to reduce the Cr content of the salts is through washing with a saturated NaCl solution. This, however, generates a Cr-contaminated wash brine which needs to be purified prior to reuse for succeeding wash cycles. Therefore, for this dissertation, three main goals have been established: to assess the environmental impact of using a Cr-contaminated road salt; to evaluate the feasibility of using commercial ion exchange resins for the purification of the wash brine; and, to propose a novel strategy for Cr removal in aqueous streams.

Chromium is highly ubiquitous in nature. While it can be present in various oxidation states, only two commonly persists in the environment, Cr(III) and Cr(VI). The distribution of these two oxidation states in the environment is highly dependent on the pH and redox potential of the system. Cr(III) is normally present as a precipitate above pH 7 while Cr(VI) generally exists as an oxyanion in the entire pH range, thus making the latter more mobile and available for uptake. Cr(III) is also considered an essential element for humans and animals in trace amounts. In contrast, Cr(VI) is known to cause adverse health effects to all living organisms. To mitigate the health risks associated with Cr, the WHO imposed a provisional guideline value of 50 μg/L of total Cr in drinking water.

Road salts and their contaminants can be mobilized into the environment via melted snow runoff, vehicular traffic splashing, and snow hauling and disposal. Snowmelt runoffs could find their way into surface water bodies, while groundwater can become contaminated through soil percolation of the salt solution. It was estimated that if unpurified road salts were to be employed as deicing agents, snowmelt runoffs would contain 0.5 mg/L of total Cr. This concentration is considerably higher than the prevailing safety standards for drinking water. Still, this is not expected to cause detrimental effects to aquatic organisms in large surface waters where adequate dilution is available, in contrast to slow-flowing streams and small ponds where immediate risks could be significant. On the other hand, a substantial effect on groundwater might only be seen after a longer period since soil percolation is considered to be a slow process. Similarly, it might take a longer period before detrimental amounts of Cr accumulate in the roots of plants. Ultimately, while risks associated with Cr are present, it is expected that the high amounts of sodium and chloride would persist as a bigger and more immediate environmental concern.

The results of the ion exchange experiment in purifying the wash brine were largely limited by the analytical methods employed. Therefore, since the removal efficiencies cannot be fully quantified, the feasibility of removing Cr using the tested setups cannot be completely evaluated. Still, only Amberlite PWA7 showed significant Cr removal of at least 27.3 ± 2.6% at a resin amount of 0.1 g/mL at a pH of 6. Its physical and chemical properties (i.e. secondary amines, macroporous matrix, phenol-formaldehyde structure) allowed for selective Cr removal even under high concentrations of chlorides. Surprisingly, this WBA exchange resin was also able to remove significant amounts of Cr of at least 25.4 ± 1.7% even at pH 11 where amines are not protonated. It is suggested to further validate the performance of this setup and understand the mechanism (e.g. ligand substitution) associated with the removal of Cr as this could eventually eliminate the necessity for pH adjustment. Moreover, it is recommended to explore other analytical methods (e.g. ASV, CSV) that can fully quantify the amounts of Cr(III) and Cr(VI) present in the solution. Only if promising removal efficiencies are achieved in the batch tests would it be beneficial to proceed with column tests and regeneration tests.

Another highly promising technique for Cr removal is adsorption. It could remove Cr from the solution through ion exchange, electrostatic attraction, redox process, and surface complexation. While there has been substantial progress in developing adsorbents with improved adsorption capacities, these are often insufficiently selective, making them unusable when interfering compounds are present in the (waste)water at elevated concentrations. Nevertheless, selective adsorption of the trace elements could still be accomplished by manipulating parameters such as type of adsorbent, pH, and redox conditions, and by the addition of complexing/precipitating agents. Therefore, it is proposed to develop, apply, and optimize a methodology that combines smart experimental approaches to selectively remove Cr using a novel, cheap, and stable OMP/OMC adsorbents with embedded iron oxide NPs. This will ultimately lead to novel cost-effective and sustainable hybrid sorption-based technologies that can selectively reduce Cr concentrations in challenging (waste)waters to low or sub µg/L levels.

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Appendices

Table A.1. Determination of LOD and LOQ for ICP-OES and ICP-MS.

Blanks	Cr Conc (ICP-OES), mg/L	Cr Conc (ICP-MS), mg/L
1	0.02	0.001
2	0.01	0.001
3	0.01	0.001
4	0.01	0.001
5	0.01	0.001
6	0.01	0.001
7	0.01	0.001
8	0.01	0.001
9	0.01	0.001
Mean	0.01	0.001
Standard Deviation	0.00	0.0001
LOD	**0.02**	**0.001**
LOQ	**0.06**	**0.002**

Table A.2. Total chromium content of the salt crystals.

Sample	Cr Conc, mg/L	Undiluted Cr, mg/L	Mass Cr, mg/kg
1	0.05	0.50	4.59
2	0.05	0.52	4.79
3	0.05	0.54	5.00
Average		0.52	**4.80**

Table A.3. Total chromium content of the initial brine.

Sample	Cr Conc, mg/L	Undiluted Cr, mg/L	Mass Cr leached, mg/kg
1	0.05	0.51	0.71
2	0.06	0.61	0.85
3	0.06	0.59	0.82
4	0.06	0.61	0.85
5	0.06	0.59	0.82
6	0.06	0.60	0.84
Average		**0.59**	**0.813**

Table A.4. Student's t-test for comparing the total chromium content of the dissolved salt and brine solution against the LOQ of ICP-OES at 95% confidence.

	Dissolved Salt	***Brine***
count	3	6
Mean	0.052	0.059
SD	0.002	0.004
Std Err	0.001	0.002
Hypothesized Mean	0.06	0.06
Alpha	0.05	0.05
tails	1	1
df	2	5
t stat	-4.1	1.1
p value	1.0	0.2
t Critical	2.9	2.0
Reject Hypothesis	no	no

Table A.5. Results of the ion exchange tests using PWA7.

pH	Resin Load, g/10mL	Sample	Cr Conc, mg/L	Undiluted Conc, mg/L	Standard Deviation	Cr adsorbed, mg/L	% Removal	% Removal (adjusted)	Mean	Standard Deviation
6	1	1	0.04	0.42	0.02	0.16	28.1	28.1	27.3	2.6
		2	0.04	0.41		0.17	29.5	29.5		
		3	0.04	0.44		0.14	24.4	24.4		
	0.1	1	0.07	0.65	0.03	-0.07	-11.8	0.0	0.0	0.0
		2	0.06	0.61		-0.02	-3.9	0.0		
		3	0.06	0.60		-0.02	-2.9	0.0		
	0.01	1	0.07	0.69	0.02	-0.10	-17.1	0.0	0.0	0.0
		2	0.07	0.67		-0.08	-14.2	0.0		
		3	0.06	0.64		-0.06	-9.6	0.0		
11	1	1	0.04	0.45	0.01	0.14	23.5	23.5	25.4	1.7
		2	0.04	0.43		0.16	26.5	26.5		
		3	0.04	0.43		0.15	26.2	26.2		
	0.1	1	0.06	0.63	0.03	-0.05	-8.2	0.0	0.0	0.0
		2	0.07	0.67		-0.09	-15.2	0.0		
		3	0.06	0.61		-0.03	-4.8	0.0		
	0.01	1	0.07	0.67	0.04	-0.09	-14.7	0.0	0.0	0.0
		2	0.06	0.60		-0.01	-2.3	0.0		
		3	0.06	0.65		-0.06	-11.0	0.0		

Table A.6. Student's t-test comparing the mean of the equilibrium concentration of each PWA7 setup and the initial brine concentration.

	Brine	**Acidic**			**Basic**		
		1 g	**0.1 g**	**0.01 g**	**1 g**	**0.1 g**	**0.01 g**
Mean	0.06	0.04	0.06	0.07	0.04	0.06	0.06
Variance	1.45E-05	2.4E-06	8.1E-06	5.0E-06	9.7E-07	9.6E-06	1.4E-05
Observations	6	3	3	3	3	3	3
Hypothesized Mean Difference		0	0	0	0	0	0
t Stat		-8.9	1.6	4.0	-9.0	2.3	2.1
P(T<=t) two-tail		0.00004	0.2	0.01	0.0001	0.1	0.1
t Critical two-tail		2.36	2.57	2.36	2.45	2.57	2.78
Reject Hypothesis		yes	no	yes	yes	no	no

Table A.7. Results of the ion exchange tests using HPR4800.

pH	Resin Load, g/10mL	Sample	Cr Conc, mg/L	Undiluted Conc, mg/L	Standard Deviation	Cr adsorbed, mg/L	% Removal	% Removal (adjusted)	Mean	Standard Deviation
6	1	1	0.06	0.60	0.01	-0.01	-2.3	0.0	0.0	0.0
		2	0.06	0.59		-0.01	-0.9	0.0		
		3	0.06	0.59		0.00	-0.4	0.0		
	0.1	1	0.07	0.70	0.04	-0.11	-19.3	0.0	0.0	0.0
		2	0.07	0.68		-0.10	-16.4	0.0		
		3	0.06	0.61		-0.03	-5.0	0.0		
	0.01	1	0.07	0.67	0.03	-0.09	-14.7	0.0	0.0	0.0
		2	0.06	0.62		-0.04	-6.4	0.0		
		3	0.06	0.62		-0.03	-5.8	0.0		
11	1	1	0.06	0.58	0.03	0.00	0.6	0.6	4.0	4.3
		2	0.06	0.57		0.01	2.5	2.5		
		3	0.05	0.53		0.05	8.9	8.9		
	0.1	1	0.06	0.57	0.03	0.01	2.3	2.3	0.8	1.3
		2	0.06	0.63		-0.04	-7.6	0.0		
		3	0.06	0.59		0.00	-0.2	0.0		
	0.01	1	0.06	0.62	0.02	-0.03	-5.9	0.0	0.6	1.0
		2	0.06	0.60		-0.02	-2.9	0.0		
		3	0.06	0.58		0.01	1.8	1.8		

Table A.8. Student's t-test comparing the mean of the equilibrium concentration of each HPR4800 setup and the initial brine concentration.

	Brine	Acidic			Basic		
		1 g	**0.1 g**	**0.01 g**	**1 g**	**0.1 g**	**0.01 g**
Mean	0.06	0.06	0.07	0.06	0.06	0.06	0.06
Variance	1.5E-05	3.3E-07	2E-05	8.4E-06	6.5E-06	8.9E-06	5.1E-06
Observations	6	3	3	3	3	3	3
Hypothesized Mean Difference		0	0	0	0	0	0
t Stat		0.5	2.6	2.3	-1.1	0.5	0.7
P(T<=t) two-tail		0.7	0.1	0.1	0.3	0.7	0.5
t Critical two-tail		2.6	2.8	2.6	2.5	2.6	2.5
Reject Hypothesis		no	no	no	no	no	no

Table A.9. Results of the ion exchange tests using PWA8.

	Resin Load, g/10mL	Sample	Cr Conc, mg/L	Undiluted Conc, mg/L	Standard Deviation	Cr adsorbed, mg/L	% Removal	% Removal (adjusted)	Mean	Standard Deviation
Acidic	1	1	0.05	0.54	0.04	0.05	8.4	8.4	5.7	5.8
		2	0.05	0.51		0.07	12.4	12.4		
		3	0.05	0.52		0.07	11.5	11.5		
		4	0.06	0.60		-0.02	-3.1	0.0		
		5	0.06	0.59		0.00	-0.8	0.0		
		6	0.06	0.58		0.01	1.6	1.6		
	0.1	1	0.06	0.57	0.02	0.02	3.2	3.2	0.6	1.3
		2	0.06	0.58		0.00	0.5	0.5		
		3	0.06	0.65		-0.06	-10.9	0.0		
		4	0.06	0.63		-0.05	-8.1	0.0		
		5	0.07	0.67		-0.08	-13.7	0.0		
		6	0.06	0.65		-0.06	-10.8	0.0		
	0.01	1	0.06	0.61	0.02	-0.02	-4.0	0.0	0.0	0.0
		2	0.06	0.61		-0.03	-5.0	0.0		
		3	0.07	0.65		-0.07	-11.3	0.0		
		4	0.07	0.67		-0.08	-14.0	0.0		
		5	0.06	0.64		-0.05	-9.4	0.0		
		6	0.06	0.62		-0.03	-5.7	0.0		

	Resin Load, g/10mL	Sample	Cr Conc, mg/L	Undiluted Conc, mg/L	Standard Error	Cr adsorbed, mg/L	% Removal	% Removal (adjusted)	Mean	Standard Deviation
Basic	1	1	0.06	0.60	0.02	-0.02	-2.9	0.0	2.2	2.9
		2	0.06	0.58		0.01	0.9	0.9		
		3	0.05	0.55		0.04	6.1	6.1		
		4	0.06	0.58		0.00	0.6	0.6		
		5	0.06	0.55		0.03	5.8	5.8		
		6	0.06	0.60		-0.01	-2.1	0.0		
	0.1	1	0.06	0.60	0.05	-0.01	-1.9	0.0	3.5	5.8
		2	0.06	0.60		-0.02	-3.0	0.0		
		3	0.05	0.50		0.08	13.8	13.8		
		4	0.05	0.54		0.04	7.1	7.1		
		5	0.06	0.62		-0.04	-6.5	0.0		
		6	0.06	0.64		-0.05	-8.6	0.0		
	0.01	1	0.06	0.60	0.02	-0.02	-3.2	0.0	0.1	0.3
		2	0.06	0.62		-0.04	-6.6	0.0		
		3	0.06	0.58		0.00	0.7	0.7		
		4	0.06	0.64		-0.06	-10.0	0.0		
		5	0.06	0.61		-0.02	-4.2	0.0		
		6	0.06	0.60		-0.02	-3.1	0.0		

Table A.10. Student's t-test comparing the mean of the equilibrium concentration of each PWA8 setup and the initial brine concentration.

	Brine	Acidic			Basic		
		1 g	**0.1 g**	**0.01 g**	**1 g**	**0.1 g**	**0.01 g**
Mean	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Variance	1.5E-05	1.5E-05	1.6E-05	5.4E-06	5.0E-06	2.5E-05	4.5E-06
Observations	6	6	6	6	6	6	6
Hypothesized Mean Difference		0	0	0	0	0	0
t Stat		-1.3	1.7	2.6	-0.5	0.0	1.4
P(T<=t) two-tail		0.2	0.1	0.03	0.7	1.0	0.2
t Critical two-tail		2.2	2.2	2.3	2.3	2.3	2.3
Reject Hypothesis		no	no	yes	no	no	no

Table A.11. Multi-way ANOVA Test for all the ion exchange setups.

Source of Variation	df	Sum of Squares	Mean Square	F-value	P-Value
Resin	2	704.6	352.3	42.3	8.7E-12
Ratio	2	1,534.1	767.1	92.2	3.9E-18
pH	1	1.8	1.8	0.2	0.6
Resin * Ratio	4	1,727.5	431.9	51.9	7.0E-18
Resin * pH	2	15.6	7.8	0.9	0.4
Ratio * pH	2	7.5	3.8	0.5	0.6
Resin * Ratio * pH	4	50.5	12.6	1.5	0.2
Error	54	449.2	8.3		

Estimation of runoff Cr concentration

The calculation for the Cr content of the runoff is based on the formula for freezing point depression:

$$\Delta T_f = iK_f m$$

Where ΔT_f = change in freezing temperature;

i = van’t Hoff factor (for NaCl, i = 2)

K_f = freezing point depression constant (for water, K_f = 1.86 ºC/kg-mol)

m = molality of the solution

Table A. 12. Determination of the Cr content of snowmelt runoff.

Parameter	Value
Road Salt Usage in Belgium (1985), tons [69]	200,000
Freezing Temperature Depression, ºC	5
Concentration of Cr in the salts, mg/kg	7
Mass of water, g	2.5E12
Volume of water, L	2.5E9
Concentration of NaCl, g/L	78.5
Concentration of Cl^-, g/L	47.6
Concentration of Cr, g/L	0.5