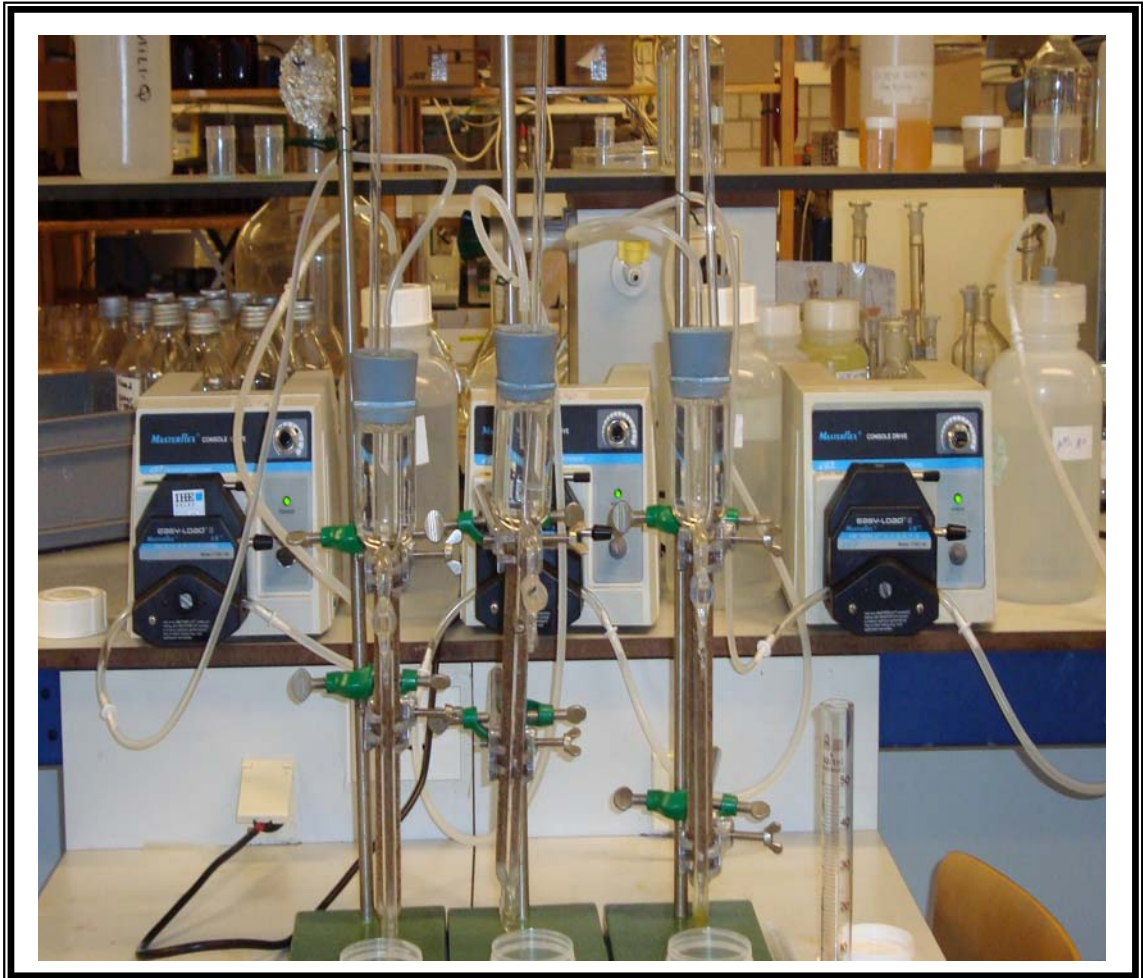


UNESCO-IHE INSTITUTE FOR WATER EDUCATION



Effect of Water Quality Matrix on Chromium Removal

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Institute for Water Education



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Abstract

The removal of heavy metals from urban runoff has become important due to environmental pollution concerns and environmental protection rules and regulations in recent time. Chromium is an important industrial metal used in diverse products and processes. Cr (VI) compounds are highly toxic and considered as health hazards. Therefore, the World Health Organization (WHO) has set maximum concentration level for total chromium in drinking water as 0.05 mg/L. Chromium is removed from drinking water by chemical precipitation, ion exchange, and reverse osmosis. However, these methods have technical and economical limitations. Therefore, it is a priority to investigate an effective and affordable treatment method. A very few research has been carried out on the extent of heavy metal removal by sand filtration.

Stability experiments were performed to assess the Cr(III) stability depending on pH, HCO_3^- and Ca^{2+} concentration in model water. This study focused on understanding of the stability of Cr species under different model water composition and chromium precipitates removal rapid sand filtration. The model water (500 ml) was placed in PE (Polyethylene) bottle and shaken speed at 100 rpm. Unfiltered and filtered samples were taken at specified time and analyzed for total Cr(III) and dissolved Cr(III). Cr(III) was found to be unstable under slightly acidic and basic conditions. Longer the contact time and higher the Cr(III) concentration greater the precipitation was found. The Phreeqc interactive program showed that above pH 6.0 the Cr(III) precipitation took place as chromium hydroxide, and chromium oxide.

Removal of Cr(III) and Cr(VI) were investigated in batch adsorption and rapid sand filtration experiments. In this case of Cr(VI) removal was based on chemical reduction was employed by dosing Fe(II) and rapid sand filtration. Batch adsorption experiments were conducted to assess the adsorptive capacity of IOCS and quartz sand for Cr(III) and Cr(VI) removal as function of pH. IOCS proved to be a good adsorbent for Cr(III). Cr(III) removal rate was more at higher pH due to both adsorption and precipitation of Cr(III). However the, adsorption capacity of IOCS for Cr(VI) decreased with the increase pH. Virgin quartz sand showed the adsorptive capacity for the removal of Cr(III).

The filtration experiments, were conducted at initial Cr(III) concentration 100 $\mu\text{g/L}$, filtration rate 5 m/hr, sand size 0.5 to 1.0 mm, media depth of 20 cm showed that Cr(III) can be removed efficiently through filtration and adsorption at pH 6, 7 and 8. The rapid sand filter removed the precipitate Cr(III) through filtration and adsorption. The removal efficiencies of Cr(III) was higher at pH 7 and 8 compared to pH 6. Similarly, the filtration experiment was conducted with initial concentration Cr(III) 50 $\mu\text{g/L}$ and Cr(VI) 50 $\mu\text{g/L}$. The chemical reduction of Cr(VI) to Cr(III) was achieved efficiently by Fe(II). The rapid sand filter of media depth 40 cm removed the total Cr very efficiently. The rapid sand filters were very effectively removed iron and turbidity.

Results of filtration experiments were consistent with batch experiments for the removal of Cr(III). Cr(VI) removal achieved by its reduction to Cr(III) by Fe(II) and consequent filtration with rapid sand filter. Rapid sand filter could be an alternative media for the total chromium removal however, due to availability and low cost quartz sand is affordable also for the developing countries.

Key words: storm water, urban runoff, iron oxide coated sand, quartz sand, stability, adsorptive capacity, chromium removal, chemical reduction of Cr(VI), sand filtration.

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List of Symbols, Acronyms & Abbreviations

AAS	:	Atomic Absorption Spectrometer
Conc.	:	Concentrated
Cr(III)	:	Trivalent Chromium
Cr(VI)	:	Hexavalent Chromium
Demi	:	Demineralised
DPC	:	Diphenylcarbazine
EBCT	:	Empty Bed Contact Time
EC	:	European Community
Eff.	:	Effluent
Filt.	:	Filtered
GF	:	Graphite Furnace
IARC	:	International Agency for Research on Cancer
ICP	:	Inductively Coupled Plasma
Inf.	:	Influent
IOCS	:	Iron Oxide Coated Sand
MCL	:	Maximum Contamination Level
MCLG	:	Maximum Contamination Level Goal
NRDS	:	Natural Resources Defence Council
OSHA	:	Occupational Safety and Health Administration
PAHs	:	Polyaromatic Hydrocarbons
PVC	:	Polyvinylchloride
Unfilt.	:	Unfiltered
USEPA	:	Environmental Protection Agency of the United States of America
WHO	:	World Health Organization

CHAPTER 1 : INTRODUCTION

1.1 Background

Stormwater runoff from urbanized areas originates from a number of source, including residential, commercial and industrial areas; roads, highway and bridges. The pollutants in stormwater from motorways, originate primarily from traffic related sources such as exhaust, tyre and road wearing and dust from brakes. Erosion of building materials influences the stormwater quality (Moller et. al., 2002). Storm water runoff transports significant load of heavy metals, a wide gradation of particulate matter, dissolved solids, organic compounds and inorganic constituents. Roadways and automobiles are considered to be one of the largest sources of heavy metals (<http://www.fairfaxcounty.gov>). On the road surface, most heavy metals become bound to the surfaces of road dust or other particulates. During precipitation, the bound metals will either become soluble (dissolved) or be swept off the roadway with the dust. In either case, the metals enter the soil or are channelled into a storm drain.

The heavy metals which are transported through runoff water, are not degraded in the environment and constitute an important class of contaminants, generated through urban infrastructural activities. Similarly, toxic substance found in stormwater runoff include heavy metals, hydrocarbons, and some chlorinated organics that contribute to adverse water quality of surface and sub-surface water and are also, toxic to aquatic life (Marsalek, 1986; Hall and Anderson, 1988). The urban runoff harms the aquatic life in many ways due to the change in water chemistry and habitat loss (NRDC, 2008). Long term exposures of heavy metals have the serious health effect on the aquatic life of recipient water bodies. In urban runoff, the discharge levels of zinc, copper, cadmium, lead, chromium and nickel significantly exceed the threshold limits (Sansalone et. al., 1999).

Chromium a heavy metal used in a variety of processes is highly toxic to human being. It originates as a contaminant in the environment from the discharges of dye and paint pigments, wood preservative, chrome, plating liquid wastes, and leaching from hazardous waste sites. The two largest source of chromium emission in the atmosphere are chemical manufacturing and combustion of natural gas, oil and coal (Stepek, 2002; Clifford, 1990). Chromium (VI) (Cr(VI)) has been determined by the International Agency for Research on Cancer (IARC) to be carcinogenic to humans(Washington State Department of Health, 1995).

A wide range of technologies have been developed for the removal of chromium from water and wastewater. The chromium removal techniques are based on various physical, chemical and biological processes such as coagulation-precipitation, reduction, ion exchange, membrane filtration and adsorption (Guo et. al., 2002). Advanced treatment methods like membrane technology can effectively remove both forms of chromium i.e. (Cr(III)) and /(Cr (VI)) (Hamann et. al., 1990). Adsorption technology is simple cheap and has a potential to remove heavy metal efficiently however treatment costs are depends on adsorbent cost. Iron oxide coated sand (IOCS) can be used for the removal of some heavy metal from the water and waste water.

A very limited research has been carried out on the removal of chromium by conventional water treatment process such as precipitation followed by rapid sand filtration. Sand filtration could be another reliable option for chromium removal from water and waste water.

1.2 Problem Identification

Heavy metal contaminations in urban runoff contribute to adverse water quality impact on receiving streams (Hall and Anderson, 1988). The soluble forms of heavy metals are more dangerous in the environment because they are easily transported and are more readily available to plants and aquatic animals (Heavy Metal Pollution, 2005). Exposure to heavy metal contamination in runoff water causes the short term (e.g. acute toxicity) and long term (e.g. carcinogenicity and reproducing damages) adverse effects in the aquatic environments therefore, treatment of urban runoff receives more attention these days before its discharge (Genc-Fuhrman et. al., 2006).

Conventional treatment processes currently applied for the removal of chromium from the liquid phase, are generally based on the chemical precipitation and coagulation. It requires pH adjustment, additions of acid, base, coagulants, lime etc. The conventional treatment of chromium has technical limitations such as (i) skilled operator required for dosing chemicals (ii) production of high sludge volume and (iii) need for further sludge treatment. Advanced water treatment methods like membrane technology are effective for the removal of Cr(III) and Cr(VI). Often these technologies are expensive in investment cost, operational cost and complex for removal of chromium from water and wastewater.

In recent years, investigation on different adsorbents for removal of Cr(III) and Cr(VI) had been conducted. Among those media, iron oxide coated sand (IOCS) can be used for the removal of heavy metal from the water and waste water. IOCS has promising adsorption capacity for the removal of Cr(III) (Das, 2004; Tessema, 2004). IOCS is capable of removing several heavy metals present in the urban runoff (Yadav, 2006). Adsorption technology has shown cheaper, easily available and effective removal of iron, manganese, arsenic and some other heavy metals (Petruševski et. al., 2000).

The removal efficiency of the IOCS was decreased with the increase in filtration rate. At higher filtration rate, some of the fine chromium particles escape through the media (Das, 2004). It is necessary to study and investigate for the removal of chromium at high filtration rate through other possible media. In addition to adsorption methods, Cr precipitation followed by rapid sand filter technology can be used for the chromium removal from the water and wastewater which is cost effective and easily available.

1.3 Objectives of the research

The overall objectives of this research were to assess the appropriate technology for the removal of Cr by precipitation, reduction and filtration methods.

The specific objectives of the research were:

- To study the stability of Cr(III) and Cr(VI) in aqueous solution as a function of pH, Ca^{2+} and HCO_3^- concentrations.
- To analyze the particle size of Cr(III) precipitate as a function of pH.
- To study the effect of pH on Cr(III) and Cr(VI) adsorption on IOCS.

- To study and examine Cr(III) removal by precipitation, adsorption and filtration, as a function of pH.
- To study the chemical reduction of Cr(VI) by using Fe(II) and filtration through rapid sand filter.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

This chapter mainly deals with the source of pollutants in urban runoff, chromium occurrence, standards and guidelines, health implications, methods of chromium removal from water and adsorption of chromium onto filter media. In addition, various types of adsorption materials for the chromium removal from the water and waste water are presented.

2.2 Source of Pollutants in Urban Runoff

Rain and snowmelt water contaminated with wide range of pollutants such as particulates, heavy metals and petroleum hydrocarbons, which primarily originate from transportation activities, can accumulate on the highway surface (Brannvall E, 2007; Gan et. al., 2007). Runoff from the construction sites, roofs and roadways are known to contain heavy metals as trace contaminants, and can affect bio ecosystem near these runoff sites. Urban runoff has been recognized as a substantial source of pollutants to receiving water bodies. Therefore, the urban settings are focal point for environmental contamination due to emissions from industrial and municipal activities (Robert et. al., 2003).

Due to the impermeability of pavement, pollutants delivered by highway runoff during wet weather into streams via drainage network in urban area or discharged directly to nearby waters or lands in rural area, causing quality deterioration of receiving waters and roadside soil contamination. The extent of such contamination is dominantly affected by surrounding land use, rainfall, traffic volume and other different random factors because highway runoff is a classic nonpoint pollution source. It is discontinuous in time, unconcentrated at specific location and strongly dependent on changes in climatic conditions (Thomson et. al., 1997).

With rapid urban population growth and industrialisation, pollution of urban water bodies has become an increasingly serious problem, threatening the urban ecological environment. There has been an urgent need for effective pollution control. As the point source pollution is reduced, the contribution of non-point sources within and around the city is becoming an important issue (Buffleben et. al., 2002). The major pollutants and their sources are summarised in the Table 1.

Table 1: Summary of source of urban runoff pollutants (Stormwater management manual, 2005)

	Contaminants	Sources	Impacts
Nutrients	<ul style="list-style-type: none">• Phosphorus• Nitrogen	<ul style="list-style-type: none">• Urban landscape runoff (fertilizers, detergents, plant debris, sediment, dust, gasoline, tires, septic system effluent).• Agricultural runoff (fertilizers, animal waste).	<ul style="list-style-type: none">• Increased algal growth & turbidity.• Decreased dissolved oxygen (DO).• Limited recreational values.• Reduction of animal

			habitat.
Solids	<ul style="list-style-type: none"> • Sediment • Floatables 	<ul style="list-style-type: none"> • Construction sites & other disturbed/non-vegetated lands. • Road & parking lot sanding • Agricultural lands. • Eroding stream banks. • Animal waste. 	<ul style="list-style-type: none"> • Decreased storage capacity • Destruction of benthic habitat. • Interference with animal respiration & digestion. • Reduced aesthetic value.
Pathogens	<ul style="list-style-type: none"> • Bacteria • Viruses 	<ul style="list-style-type: none"> • Septic systems • Illicit sewage connections 	<ul style="list-style-type: none"> • Shellfish bed closures. • Beach closures. • Contamination of drinking water.
Hydrocarbons	<ul style="list-style-type: none"> • Oil & grease • Polycyclic aromatic • Hydrocarbons (PAHs) 	<ul style="list-style-type: none"> • Parking lots & roadways. • Spills, oil leaks & auto emissions. • Illicit sewage connections. • Illegal dumping of waste oil. 	<ul style="list-style-type: none"> • Degraded appearance of water surfaces. • Lowered DO. • Degradation of fisheries.
Toxic Organics	<ul style="list-style-type: none"> • Pesticides • Polychlorinated • biphenyls 	<ul style="list-style-type: none"> • Indoor & outdoor use. • Industrial activities. • Illicit sewage connections. 	<ul style="list-style-type: none"> • Loss of sensitive animal species and fisheries. • Reproductive & behavioral problems from accumulation in food chain.
Acids	<ul style="list-style-type: none"> • Nitrate (NO₃) • Sulfite (SO₂) • Anions HNO₃, HSO₂/H₂SO₄ • That form in the air 	<ul style="list-style-type: none"> • Incomplete combustion process coupled with atmospheric reactions (acid rain). 	<ul style="list-style-type: none"> • Loss of sensitive animal species and fisheries • May affect mobility, availability & toxicity of metals & other toxins.
Humic Substances	<ul style="list-style-type: none"> • Plant materials (grass clippings & leaves) 	<ul style="list-style-type: none"> • Urban & suburban landscapes. 	<ul style="list-style-type: none"> • Degraded fisheries.
Salt	<ul style="list-style-type: none"> • Sodium • chloride 	<ul style="list-style-type: none"> • Road salt storage areas. • Roadway & parking areas. 	<ul style="list-style-type: none"> • Loss of sensitive animal species and fisheries.

			<ul style="list-style-type: none"> • Contaminated surface & ground water.
Metals	<ul style="list-style-type: none"> • Heavy metals (lead, copper, cadmium, zinc, mercury & chromium) 	<ul style="list-style-type: none"> • Industrial activities & waste. • Illicit sewage connections. • Asphalt & atmospheric deposition. • Automobile wear & exhaust & fluid leaks. • Leaching water supply and stormwater delivery systems. 	<ul style="list-style-type: none"> • Accumulation in animal tissue that could be ingested by humans.

2.3 Chromium Occurrence and Chemistry

2.3.1 General

Groundwater contaminates with metals directly by infiltration of leachate from land disposal of solid wastes, sewage or sewage sludge, leachate from mining wastes, seepage from industrial lagoons, and spills and leaks from industrial metal processing or wood preserving facilities.

Chromium is a lustrous, brittle, hard metal with highly polished silver grey in colour. It does not tarnish in air, when heated it burns and forms the green chromic oxide. It is unstable in oxygen and immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal. Chromium is extremely resistant to ordinary corrosive agents, which accounts for its extensive use as an electroplated protective coating (Stepek, 2002).

Chromium is an important industrial metal used in diverse products and processes. It is widely used in many industrial processes such as stainless steel, chrome plating in metal ceramics, leather tanning, textile manufacturing, wood preserving, pigmenting, chromium chemical production, pulp and paper industrial. Chromium plating was once widely used to give steel with a polished silvery mirror coating. It is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and paints and it is used to produce synthetic rubies; as a catalyst in dyeing and in the tanning of leather; to make moulds for the firing of bricks. Cr(IV) oxide (CrO_2) is used to manufacture magnetic tape. These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils (www.lenntech.com).

There are different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the Cr(III) and Cr(VI) form through natural processes and human activities.

In air, chromium compounds are present mostly as fine dust particles. This dust eventually settled over land and water. Rain and snow help to remove chromium from air. Chromium compound will remain in the air usually for less than 10 days (ATSDR 2000). Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater.

In water, chromium will be absorbed on sediment and becomes immobile. Only a small part of the chromium that ends up in water will eventually dissolve.

2.3.2 Chemical and Physical Properties of Chromium

The name, Chromium is derived from Greek word Chroma (Colour) as all compounds of chromium are coloured. Some important properties of chromium are shown in Table 2:

Table 2: Properties of chromium

Atomic Symbol	Cr
Atomic number	24
Atomic mass	51.996 g.mol ⁻¹
Electronegativity	1.6
Density	7.19 g.cm ⁻³ at 20°C
Melting point	1907 °C
Boiling point	2672 °C
Vanderwaals radius	0.127 nm
Ionic radius	0.061 nm (+3) ; 0.044 nm (+6)
Isotopes	6
Electronic shell	[Ar] 3d ⁴ 4s ²
Discovered by	Vaughlin in 1797

2.3.3 Occurrence of Chromium

Chromium is a metallic element widely distributed in the earth's crust and found in natural deposits of ores with other elements mostly as chrome iron ores. Chromium is mined as chromite (FeCr₂O₄) ore. Its ores are mined today in South Africa, Zimbabwe, Finland, India, Kazakhstan and the Philippines. A total of 14 million tonnes of chromite ore is extracted. The reserves are estimated to be about 1 billion tonnes with unexploited deposits in Greenland, Canada and USA (www.lenntech.com).

In many locations, chromium has been released to the environment via leakage, poor storage, or improper disposal practices. Chromium is also widely present in soils and plants. The most common forms are Cr(0), Cr(III) and Cr(VI). Most natural chromium in the environment occurs as Cr(III). Under highly oxidising conditions, pH is greater than 7.0, and with the presence of minerals containing chromium, part of it may occur as Cr(IV) dissolved in ground water. Cr(VI) is readily soluble in water and can migrate in the direction of groundwater gradient. Organic matters, ferrous iron/Fe(II) and sulphide, Cr(VI) can be readily reduced to Cr(III) and immobilised (Stepek, 2002).

The mobility of the chromium in ground water depends also on its solubility and its tendency to be adsorbed by soil or aquifer materials. These factors, in turn depend on the ground water chemistry and the characteristics of soil or aquifer material in contact with the chromium containing ground water (Calder, 1988).

2.3.4 Aqueous Chemistry of Chromium

Chromium is found in nature primarily in the trivalent species, as FeO, Cr₂O₃. Cr(III) is only slightly soluble in ground water and is very strongly adsorbed by soils (Rajesh and Yogesh, 2002). In a water environment chromium is stable in different ionic species i.e. Cr³⁺, CrOH²⁺, Cr(OH)₂⁺, CrO₇²⁺, CrO₄²⁻, HCrO₄⁻.

Redox potential Eh-pH diagrams present equilibrium data and indicate the oxidation states and chemical forms of the chemical substances, which exist within specified Eh and pH ranges. Fig. 2-1 is an Eh-pH diagram for chromium. The data presented in the figures are derived from parameters representing typical aqueous conditions. Although, the diagram implies that the boundary separating one species from another is distinct, the transformation is so clear-cut. Concentration, pressure, temperature, and the absence or presence of other aqueous ions can all affect which chromium species will exist.

Chromium speciation in groundwater is affected by pE (redox potential) and pH conditions. Cr(VI) predominates under oxidising (high redox) conditions; whereas Cr(III) predominates under more reducing (low redox) conditions. Oxidizing conditions generally are found in shallow aquifers within a few meters of the water table, whereas there is a continual replenishment of oxygen from the atmosphere via unsaturated zone. In shallow ground water, oxygen is replaced from the atmosphere and in the deeper ground water that is isolated from the atmosphere, no replenishment of oxygen occurs, and reducing conditions develop.

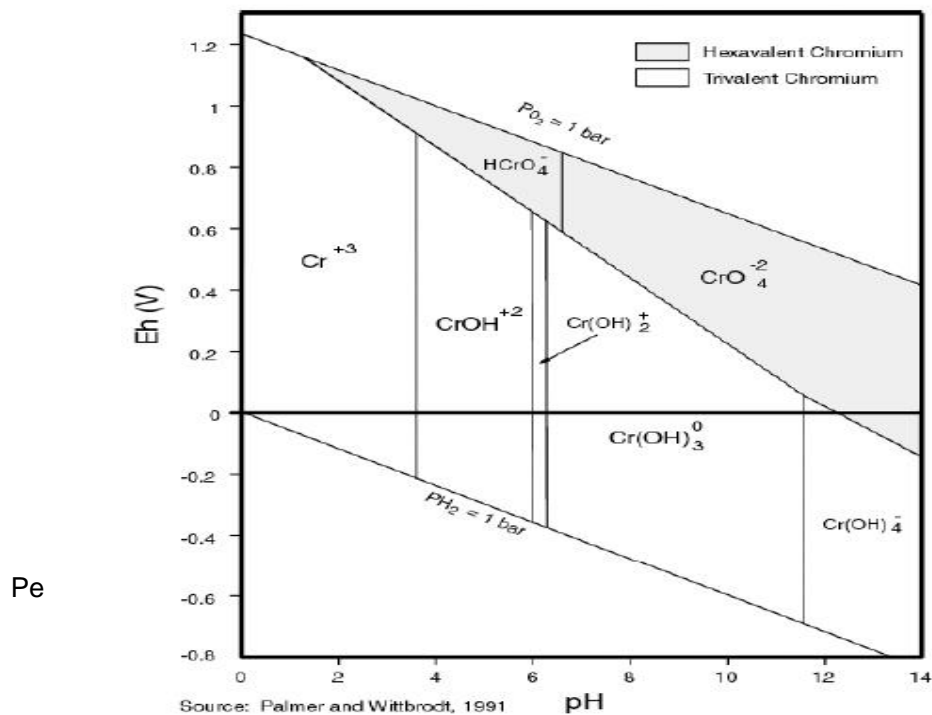


Figure 2-1: Eh-pH diagram for chromium (Source: USEPA, 2000)

Cr(VI) is readily hydrolysed in water. The dominant Cr(VI) species at total chromium concentrations below 500 mg/L are the oxyanions HCrO_4^- and CrO_4^{2-} . The equilibrium equation between the two species is highly dependent on pH,

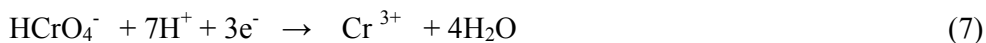
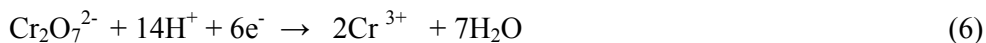


At pH less than 6.5, the concentration of H^+ ions is high, so the reaction tends to the left, and HCrO_4^- is dominant species. At higher pH, the concentration of H^+ ions is lower, the reaction tends to the right and CrO_4^{2-} predominates. In the natural ground water, the pH is typically between 6 and 8 so the CrO_4^{2-} ion is the dominant species.

The dominant Cr(III) species in water also depends on pH, according to the following equilibrium reactions;



$\text{Cr}(\text{OH})_2^+$ species is dominant at pH value between 6 and 8, while $\text{Cr}(\text{OH})^{2+}$ and Cr^{3+} predominate in more acidic conditions below pH 4. $\text{Cr}(\text{OH})_4^-$ and $\text{Cr}(\text{OH})_{3(s)}$ are most likely to be found in alkaline water (Calder, 1988; Selomulya et. al., 1999). Chromium undergoes redox reaction in certain condition;



The reduction reaction requires H^+ ions to drive the reaction.

The dichromate (VI) ion $\text{Cr}_2\text{O}_7^{2-}$ is predominant in acidic environment at pH 2 to 6.5. Cr(VI) does not commonly form complexes with inorganic or organic ligands (Calder, 1988).

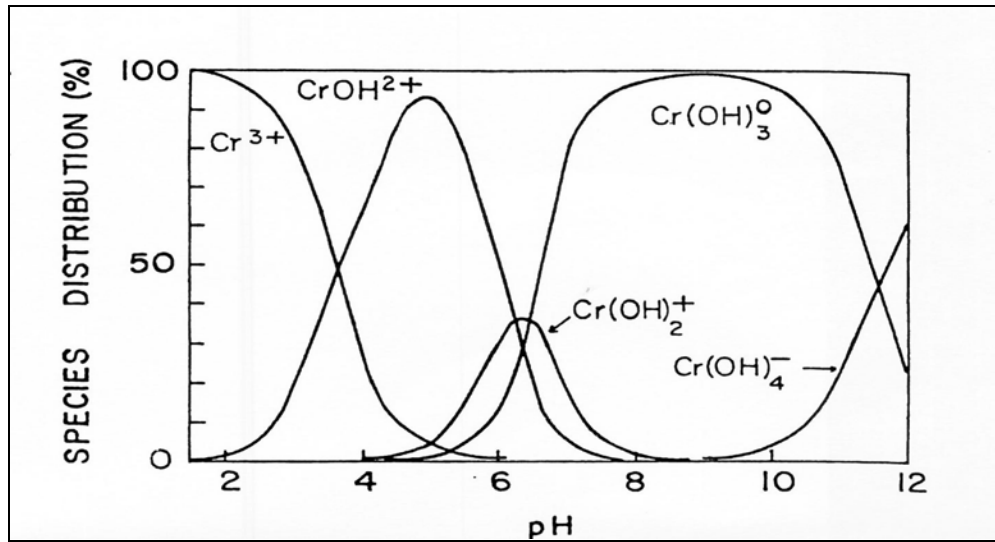


Figure 2-2: Speciation diagram for Cr(III) complexes present in aqueous solution as a function of pH (Source: Richard and Bourg 1991; Leyva-Ramos et al., 1994).

2.3.5 Solubility of Chromium

The solubility is the amount of chromium in moles/L or mg/L that can dissolve in a solution under the given sets of a condition. Chromium solubility depends on its oxidation state. In general Cr(VI) salts are more soluble than Cr(III), making Cr(VI) relatively mobile.

In water, Cr(III) occurs as a cation that forms aqueous complexes and hydroxides precipitates. It is less toxic and readily precipitates as amorphous chromium hydroxide and ferric hydroxide $(\text{Cr,Fe})(\text{OH})_3(\text{s})$ under slightly acidic and basic conditions with strong adsorption onto solids (Rai, et. al., 1987; Calder, 1988; Plmer and Puls, 1994; Leyva-Ramos, et. al., 1994; Sharma, et. al., 2008). However, Cr(III) concentrations in groundwater are generally low and immobile due to low solubility of Cr(III) compounds above pH 4 and the Cr(III) concentration is high in groundwater at very acidic pH less than 4 (Calder, 1988; Sharma et. al., 2008). The low solubility of the Cr(III) is likely the major reason that makes a small percentage of total chromium concentration (i. e. 0.05 mg/L) present in natural or polluted groundwater (Calder, 1988). Cr(III) solution concentrations in equilibrium with Cr_2O_3 are less than 0.005 mg/L above pH 4 whereas Cr(III) solution concentrations in equilibrium with $\text{Cr}(\text{OH})_3$ vary from 0.05 to 0.005 mg/L between pH 5 to 9 (Hem, 1977). The positively charged Cr^{3+} species is generally adsorbed by clay minerals below pH 4.

More toxic Cr(VI) forms are readily reduced in natural water and sediments by ferrous and sulphide compounds. Chromium is transported in water primarily by sediments (Novotny, 2002). The solubility equilibria of Cr(VI) compounds are pH dependent. Dichromate is usually more soluble than corresponding chromates (Calder, 1988). The dichromate (VI) ion $\text{Cr}_2\text{O}_7^{2-}$ concentration is above 500 mg/L in acidic environment at pH 2 to 6.5. The Cr(VI) is transported by groundwater and transform and precipitate as Cr(III) under the redox conditions. Cr(VI) anions are adsorbed onto positively charged surfaces such as oxides and hydroxides of iron, manganese and aluminium. The adsorption of Cr(VI) is usually limited

and decreases with increases in pH and the Cr(VI) is more mobile than Cr(III) (Caldr,1988; Bartlett and Kimble, 1976).

2.3.6 Chemical Reduction of Cr(VI)

The reduction of Cr(VI) to Cr(III) decreases the toxicity and mobility of chromium contaminated in water and soil. Cr(VI) is easily reduced by Fe(II), dissolve sulphides and certain compounds with sulfhydryl groups. In contrast, Cr(III) is oxidised rapidly by excess of manganese oxide (MnO₂) and slowly by oxygen under the conditions similar to natural water (Sharma et. al., 2008).

Batchelor et. al., (1998) reported that the reduction of Cr(VI) to Cr(III) is a viable option to remediate sites contaminant with Cr(VI). Cr(VI) reduction by Fe(II) is interesting because Fe(II) found in various types of soils and is a primarily electron donor in the sub surface environments. Cr(VI) reduction by Fe(II) is very rapid and lead to formation of a mixed iron/chromium solid solution of form Fe_xCr_{1-x}(OH)₃ (Rai et al., 1987; USEPA,2000). During the experiments, the Fe(II) stock solution was used for the chemical reduction of Cr(VI) to Cr(III).

At pH ≥6.5, the redox reaction between Cr(VI) and Fe(II) can be written as:



2.3.7 Health Implications of Chromium

Trivalent chromium occurs naturally in many fresh vegetables, fruits, meats, grains and yeast. It is mineral nutrient essential to the cell membrane receptor sites stimulated by insulin. In the absences of Cr(III), tissues resist insulin's influence. Blood sugar can't enter the cells to be metabolised and signs of type II diabetes may appear. Cr(III) is more stable, less toxic, and listed as an essential element (in trace concentrations) to provide good health (ASTDR, 2000). Most of the chromium that we swallow leaves our body within a few days through the feces and never enters our blood stream, if it is in very small quantity (an intake of 50–200 µg of Cr(III) per day is recommended for adults daily from food) (ATSDR (2004).

In general, human being can be exposed to chromium by breathing air, drinking water, eating food-containing chromium or through skin contact with chromium or chromium compounds. The International Agency for Research on Cancer (IARC) has determined that Cr(VI) is carcinogenic to human beings, based on sufficient evidence in humans for the carcinogenicity of Cr(VI) compounds as found in chromate production, chromate pigment production and chromium planting industries. Lung cancer may occur due to long term exposure to Cr(VI) (Washington State Department of Health, 1995).

Breathing high level of Cr(VI) can cause irritation to the nose, such as runny nose, nosebleeds and ulcers and holes in the nasal septum. Ingesting large amount of Cr(VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage and even death. Skin contact with certain Cr(VI) compounds can cause skin ulcer. Cr(VI) compounds can penetrate the skin more readily than the trivalent compounds. The most commonly affected areas are wrists, fingers and the back and sides of hands (ATSDR, 2000).

Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal.

2.3.8 Standards and Guidelines

The following agencies have set the guidelines and standard values, and the maximum permissible limit of total chromium in drinking water shown in Table 3:

Table 3: Guidelines and standard values of total chromium

Agencies	Maximum level, (mg/L)	Ref.
European Community (EC)	0.05	(Schipper et. al., 2004)
World Health Organisation (WHO)	0.05	(WHO, 2006)
Environment Protection Agency, United State of America (USEPA)	0.10	(USEPA, 1987)

Similarly, the Occupational Safety and Health Administration (OSHA) has set limit of 0.5 mg water soluble Cr(III) compounds per cubic meter of workplace air (0.5 mg/m^3), 1.0 mg/m^3 for metallic chromium (0) and insoluble chromium compounds, and 0.052 mg/m^3 for Cr(VI) compounds for 8 hr work shifts and 40 hr work weeks (ASTDR, 2001).

2.4 Methods of Chromium Removal

Contamination of ground water by chromium at numerous localities primarily results in the uncontrolled or accidental releases of chromium bearing solutions, used in various industrial applications. Chromium in such solutions mostly occurs as oxyacids and oxyanions of Cr(VI). In oxidation state, chromium is highly soluble, mobile and toxic (Mukhopadhyay et. al., 2006). Removal of chromium from contaminated ground water remains an important issue because of the carcinogenic characters of various Cr(VI) compounds (Nriagu and Nieboer, 1988).

A wide range of technologies are available for the removal of chromium from the water and wastewater. Conventional treatment systems, which use chemical coagulation and precipitation, are less effective for removal of Cr(VI) from water. Advanced treatment methods are effective for the removal of Cr(III) and Cr(VI). The following methods are used for removal of the chromium from drinking water.

2.4.1 Coagulation and Filtration

In the conventional water treatment process, coagulation and filtration process can remove insoluble chromium from the water. Chemical coagulation and flocculation consists of adding chemical coagulants combined with flocculation to allow fine suspended and some dissolved solids to clump together. In coagulation, alum and ferric iron (Fe(III)) coagulants

has been used for the Cr(III) removal which is due to precipitation as $\text{Cr}(\text{OH})_3$ (s) and co-precipitation with $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$.

The aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$ is a most effective coagulant for the insoluble chromium removal. The filtration provides the final removal of the chromium by dual media filtering of all flocs and suspended solids (US Department of the Interior, 2001).

The advantages and disadvantages of the coagulation and filtration are as follow:

Advantages:

- Low capital cost.
- Lowest overall operation and maintenance cost.
- Less pre-treatment requirement.
- Effective for Cr(III) removal.

Disadvantages:

- Skilled operator required for chemical dosing.
- Removal of the microflocs formed is often difficult and critical for the process efficiency.
- Production of high sludge volume.

2.4.2 Chemical Precipitation

The oldest and most frequently used method for removal of trivalent chromium from the water and wastewater is the precipitation. Soluble metals can be concentrated in, and separated from water and wastewater by precipitating the insoluble metal hydroxides and carbonates. Various precipitation such as sodium hydroxide, sodium carbonate, sodium hydrogen carbonate, calcium carbonate, calcium hydroxide have shown the residual chromium in tanning baths, can be converted into denser precipitate when less soluble precipitates are used. The process is aimed at the formation of solids (insoluble precipitation) within a solution.

Elmaeili et. al., (2005) studied the removal of chromium from the tanning process by using lime, sodium hydroxide 15%, and magnesium oxide 10%. The optimum pH for precipitating chromium from tannary wastewater is 8-9, and good sludge with high settling rate and lower volume was obtained when using magnesium oxide (MgO) as the precipitating agent. Magnesium oxide is much more desirable for removing and recovering chromium from tannery wastewater.

The solubility is controlled by the pH of the chromium solution. Under the most conditions, Cr(III) is removed from solution as the $\text{Cr}(\text{OH})_3$ (S) precipitated phase, or as a Chromium-Iron hydroxides solid solution $(\text{Cr, Fe}) (\text{OH})_3$ (S), when dissolved iron is present (Rai et. al., 1986).

Reduction of Cr(VI) can be achieved by using the Fe(II) salts and the Fe(II) ions are oxidised to Fe(III) compounds. The removal of chromium by coagulation- precipitation is pH dependent. In general, the reduction of Cr(VI) to Cr(III) is done under acidic conditions and

then, precipitation of hydrated chromium oxide is achieved by raising the pH with the addition of NaOH or lime (Sharma et al., 2008).

Akoi and Munemori (1982) reported the effect of pH on the coprecipitation of Cr(VI) with iron (III) hydroxide. The coprecipitation increased as pH decreased and no coprecipitation occurred above pH 8.5. There was also an increase in the coprecipitation of Cr(VI) with an increase in the amount of iron(III) hydroxide and the 99.9% coprecipitation of Cr(VI) was observed at pH 4.5.

The advantages and disadvantage of the chemical precipitation are as follow:

Advantages:

- Process is effective.
- Percentage of removal of Cr(VI) is high.
- Reduction reaction time is short.
- Recovery of chromium for recycling.

Disadvantages:

- Production of large amount of sludge.
- Skilled operator required for chemical dosing.
- Labour intensive and non economical.
- Higher reagent and energy requirement.
- Precipitation is often ineffective if metals are complexed or if they are present as anions.
- Precipitated metals often form small particles that do not settle readily.
- Generation of toxic sludge and other waste product that require disposal or treatment.

2.4.3 Ion Exchange

Ion exchange is one of the best available technologies as per USEPA recommendation for the removal of chromium. It is proven technology for small systems for removal of low concentration of chromium (USEPA, 2003). Cation exchangers are effective for Cr(III) while anions exchangers are appropriate for Cr(VI) removal. For the removal of Cr(VI) strong basic anion exchangers with an exchangeable counter ions of Cl^- , are commonly used (Sharma et al., 2008). Ion exchangers are insoluble granular substances with their molecular structure acidic or basic radicals that can exchange the ions. The positive or negative ions fixed on these radicals are replaced by ions of the same sign in solutions in the liquid in contact with them.

In solution, salts separate into positively charged cations and negatively charged anions. Deionisation can reduce the amounts of these ions. The process relies on the facts that the water solutions must be electrically neutral therefore, the ions in the resin bed are exchanged with ions of similar charge in water. As a result of exchange process, no reduction in ions is obtained. In case of the Cr(VI) reduction, operation begins with a fully recharged anion resin

bed having enough negative charged ions to carry out the anion exchange (US Department of the Interior, 2001).

As water passes through the resin bed, the negatively charged ions are released into the water, being replaced with chromium anions in water. When passing the strong NaCl or KCl solution over the resin bed exchange, the resin of negative charged ions displaces the chromium ions with chloride ions.

For the removing chromates from water under acidic pH values, weak-base anions exchanger resins are generally used. The resins are regenerated with a stoichiometric ratio of sodium hydroxide. The efficiency of the regeneration can be improved by adding sodium hydroxide to the regeneration solution, which transforms the resin from the HCrO_4^- form to the CrO_4^- form (Sharma et. al., 2008).

The advantages and disadvantages of ion exchange method are as follow:

Advantages:

- Ease of operation, highly reliable.
- Lower initial cost.
- Resin will not wear out with regular regeneration.
- Effective and widely used.
- Suitable for small and large installations.

Disadvantages:

- Pre-treatment lime softening may be required.
- Requires salt storage and regular regeneration.
- Requires concentrate disposal.
- Usually not feasible with high levels of total dissolved solid.
- Process is expensive.

2.4.4 Reverse Osmosis

Membrane technology, especially reverse osmosis is also one of the best available technologies for chromium removal. Reverse osmosis is a physical process in which contaminants are removed by applying pressure in the feed water to direct it through a semi permeable membrane. The membrane rejects ions based on size and electric charge (US Department of the Interior, 2001). Reverse osmosis is effective in removing all forms of chromium.

The pore size of membrane is 0.0001 micron and used for chromium removal from water. According to Hamann et. al., (1990), the effectiveness of reverse osmosis for the treatment of chromium is rated as good (60% to 90% removal) to excellent (90 to 100%) for Cr(VI), and excellent (90% to 100% removal) for Cr(III). Reverse osmosis is one of the best option to remove both species of chromium from the water. It requires a careful review of feed water characteristics and pre-treatment to prevent membranes from fouling, scaling or other membrane degradations that could incur pretreatment investment and operational costs.

The advantages and disadvantages of the reverse osmosis are as follows:

Advantages:

- One of the best options for the removal of both species of chromium.
- Produce highest water quality.
- Effective treatment for wide range of dissolved salts and minerals, turbidity etc.

Disadvantages:

- High investment and operational costs.
- Frequent membrane monitoring and maintenance required.
- Fouling of membranes.
- Brine disposal.

2.4.5 Adsorption

Adsorption involves the interphase accumulation or concentration of substance at surface or interface. The process can occur at an interface between any two phases, such as liquid-liquid, gas- liquid or liquid- solid interphase (Sharma, 2004).

Furthermore, adsorption is the binding of a chemical species at phase boundary, such as the surface of suspended particles. The adsorbent is chosen carefully and the solution chemistry is adjusted appropriately. Adsorption based process is capable of removing metals over a wider pH range and to much lower level than process based on precipitation (Benjamin et. al., 1996). The adsorption technique is one of the preferred methods for the removal of heavy metals because of its high efficiency and low cost (Li et al., 2007). In addition to offering more reliable and more efficient removal of uncomplexed cationic metals, adsorption process can often remove inorganically and organically complexed metals that would not be removed by conventional treatment methodology as well as oxyanionic metal such as SeO_3^- , CrO_4^{2-} and AsO_4^{3-} (Stumm et. al., 1980; Benjamin and Bloom, 1981; Zachara et. al., 1987; Mcneil and Edwards, 1995)

The main causes of adsorption are:

- The primary driving force for adsorption may be a consequence of lypophobic (Solvent-disliking) character of the solute relative to particular solvent.
- The high affinity of the solute for the solid.

The advantages and disadvantages of adsorption process are as follows:

Advantages:

- Effective for the removal of heavy metals over a wider pH range.
- More reliable and efficient removal of uncomplexed cationic metals.
- Remove inorganically and organically complex metals.
- Filter media for adsorption can be regenerated and reused.
- Considerably less sludge production.

- Less expensive.

Disadvantages:

- High adsorption capacity at low pH compared to the high pH.
- After some times adsorption filter media has to be changed.
- More contact time required.
- Disposal of the exhausted media.

2.4.5.1 Factors Affecting Chromium Removal by Adsorption

Molecules of solute are removed from solution and taken up by the adsorbent during the process of adsorption. The following factors affect the chromium removal from the water and wastewater:

- **Characteristics of Adsorbent**

The adsorption capacity of a solid adsorbent is generally proportional to the specific surface area i.e. the adsorption of a certain solute increases with an increase of surface area (Weber, 1972; Faust and Aly, 1998). The surface area per unit volume of non porous adsorbent is increased considerably with a decrease in particle size (Sharma, 2001). As a result the adsorptive capacity per unit weight of adsorbent increases with a reduction in particle diameter.

- **Nature of Adsorbate**

Solubility of the solute is, to a large extent, a controlling factor for adsorption equilibria (Weber, 1972). In general, higher solubility indicates a strong solute–solvent interaction of affinity, and the extent of adsorption is expected to be lower due to the necessity of breaking the solute-solvent bond before adsorption can occur (Faust and Aly, 1998).

The type, polarity, size, molecular mass and degree of ionisation of the solute molecules will all contribute to defining the affinity of the molecules for the adsorbing surface. Utilization of available surface area generally increases with the reduction in solubility and an increase in solute concentration.

- **Temperature and pH of solution**

Adsorption is influenced by pH, concentration of metals and ligands. The pH of the solution, at which adsorption occurs influence the extent of adsorption. Because the hydrogen and hydroxide ions are adsorbed quite strongly and the adsorption of other ions is influenced by the pH of the solution. Furthermore, to the extent to which the ionisation of an acidic or basic compound affects its adsorption, pH affects adsorption in that it governs the degree of ionisation (Weber, 1972).

In general, adsorption of Cr(VI) increases with a reduction in pH and temperature. Partial adsorption occurs if the pH is increased substantially. In general, Cr(III) adsorption increases with the increase in pH.

- **Velocity of Flow**

Adsorption of chromium increases at low filtration rate and decrease at high filtration rate, as slower rate allows more empty bed contact time in the filter (Das, 2004).

- **Organic Matter**

In general, the solubility of any organic compound in water decreases with increasing chain length, because the compound becomes more hydrocarbons like as the number of carbon atoms becomes greater. The greater the solubility, the stronger the solute-solvent bond, and the smaller the extent of adsorption (Weber, 1972). The presence of organic matter in the water considerably affects the adsorption of heavy metals present (chromium). In general, when more than one adsorbable matter is present, the adsorbable of some ions may be limited by the lack of active sites.

- **Ionic Concentration of Water**

In the application of adsorption for purification of water and wastewaters, the material to be adsorbed commonly will be a mixture of many compounds rather than a single one. The compounds may mutually enhance adsorption, may act relatively independently, or may interfere with one another. Mutual inhibition of adsorption capacity can be predicted to occur if, adsorption is confined to a single or a few molecular layers; the adsorption affinities of the solutes do not differ by several order of magnitude; and there is no specific interaction between solutes enhancing the adsorption (Weber, 1972).

Zachara et. al., (1987) reported that major groundwater ions bind to the surface of $\text{FeO}_3 \cdot \text{H}_2\text{O(am)}$, reduce positive charges, and compete directly with CrO_4^{2-} as sites become limited. The surface reaction of these anions reduces CrO_4^{2-} adsorption.

2.5 Adsorption of Chromium on Different Media

Chromium can be removed from water and wastewater by conventional as well as advanced treatment methods. Among those technologies, the adsorption has become popular, interesting and attractive technology for the removal of heavy metals due to its easy availability and cost effective. There are several adsorption filter media are used for the removal of chromium species. The following are some of the adsorption filter media that can be used for the removal of Cr(III) and Cr(VI) which is shown in Table 4.

Table 4: Adsorption filter media for the removal of Cr(III) and Cr(VI) species

S. No.	Adsorption Media	Adsorption capacity	Cr species	Condition	References
1	High performance activated carbon	22.4 mg/g	Cr (VI)	contact time 5 days	Hu et. al., (2003)
		96 mg/g	Cr (VI)	pH = 3	
2	Wood based activated carbon	4.7 mg/g	Total Cr	$C_0 = 5 \text{ mg/L}$ pH = 3	Selomulya et. al., (1999)
		5.2 mg/g	Total Cr	$C_0 = 120 \text{ mg/L}$ pH = 3	

		71.6 mg/g	Cr (VI)	C ₀ = 5 mg/L pH = 2	
		87.6 mg/g	Cr (VI)	C ₀ = 120 mg/L pH = 2	
3	Coconut shell based activated carbon	4.9 mg/g	Total Cr	C ₀ = 5 mg/L pH = 3 & 4	Selomulya et al. (1999)
		5.3 mg/g	Total Cr	C ₀ = 120 mg/L pH = 2	
		77.0 mg/g	Cr (VI)	C ₀ = 5 mg/L	
				pH = 4	
		107.1 mg/g	Cr (VI)	C ₀ = 120 mg/L pH = 2	
4	Dust coal based activated carbon	3.8 mg/g	Total Cr	C ₀ = 5 mg/L pH = 3	Selomulya et al., (1999)
		4.9 mg/g	Total Cr	C ₀ = 120 mg/L pH = 2	
		76.3 mg/g	Cr (VI)	C ₀ = 5 mg/L pH = 4	
		101.9 mg/g	Cr (VI)	C ₀ = 120 mg/L pH = 2	
5	Granular activated carbon	95.98 µg/g	Cr (III)	pH = 7	Tessema (2004)
		45.69 µg/g	Cr (VI)	pH = 7	
6	Activated carbon fibers plated with Cu metal	Maximum	Cr (VI) & Cr(III)	pH = 6	Park and Jung (2001)
7	Modified PVP (4-Vinylpyridine) coated silica gel	100% removal when the initial concentration was 2.5 mg/L to 2.5 gm/L	Cr (VI)	pH = 6	Gang et. al., (1999)
8	Amorphous iron oxide	95% of removal when initial concentration was 8.0 E-4M.	Cr (VI)	pH = 4	Hsia et al. (1992)
9	Iron oxide coated sand	89% and 55% removal when initial concentration of Cr(III) and Cr(VI) were 2.0 mg/L and 2.3 mg /L.	Cr (III)	pH = 4	Bailey et. al., (1992)
			Cr (VI)	pH = 5	
10	Iron oxide coated sand (IHE research)	91% of removal when initial concentration was 2 mg/L and adsorbent dosage = 4 g/L	Cr (III)	pH = 7	Tessema (2004) Das (2004)
		12% of removal when initial concentration was 2 mg/L and adsorbent dosage = 4 g/L	Cr (VI)	pH = 7	

11	Manganese coated sand	Maximum	Cr (VI)	pH = 4	Dokken et. al., (1999)
12	Calcinated hydrotalcite (Mg-Al- CO ₃)	50 mg/g	Cr (VI)	pH = 6	Lazardis and Asouhidou (2003)
13	Bentonite and expanded perlite	20 mmol/g perlite	Cr(III)	pH = 5	Chakir et al. (2001)
		0.48 mmol/g bentonite	Cr(III)	pH = 5	
14	Ash and stem of tobacco	85.67% removal of Cr(VI) from the initial concentration	Cr (VI)	pH = 4	www.psl.ubaya.ac.id
15	Alfalfa bio mass	16.24 mg/g	Cr (III)	pH = 5	Dokken et. al., (1999)
		2.56 mg/g	Cr (VI)	pH = 2	
16	Dead biomass and rice hall	162.23 mg/g chlorella minutissima	Cr (VI)		Bailey et. al., (1999)
		164.31 mg/g rice hall	Cr (VI)		

2.6 Iron Oxide Coated Sand (IOCS)

IOCS adsorbs ammonia complexed metals in synthetic solutions and filter particulate metals out of suspension more efficiently than uncoated filter sand. It is used to remove both the soluble and particulates fractions of the metal from the water and wastewater through the column packed with IOCS. Filtration through IOCS is more effective treatment technology for water and wastewater containing variety of heavy metals over a wide range of concentrations (Benjamin et al. 1996).

The surface characteristics of IOCS are physically and chemically heterogeneous and are expected to change with time. Sharma (2001), analyzed IOCS from twelve different ground water treatment plants and found that IOCS has a very high porosity (110 times) and very large specific surface area (5-200 times) compared to new virgin sand. Iron content of the coating ranged from 27% to 45% as well as the coating development was not uniform and different region of the coating might have different composition and surface characteristics.

IOCS used at laboratory for the removal of cationic and anionic metals like Cr(III), Cr(VI), nickel, cadmium, arsenic etc. The cations are removed at alkaline pH and anions are removed under acidic conditions. Bailey et. al., (1992) studied heavy metal removal from the water and wastewater into the IOCS media. The sand was coated with both ferric nitrate and ferric chloride as the iron source.

According to Bailey et. al., (1992), the adsorption capacity of IOCS deteriorated over a course of eleven runs. The rate of deterioration decreased with increasing number of runs, so after large number of runs, the media reached a stable end point. The adsorption capacity decreased due to highly alkaline regenerant solution. IOCS was not feasible at low pH for the removal of chromium. Bailey et. al., (1992) found that sand coated with ferric chloride had a higher adsorption capacity and was less sensitive to base.

Previous UNESCO-IHE research showed that IOCS could be used as adsorbent in the removal of different heavy metals from water and wastewater (Petruševski et al., 2000). Furthermore, IOCS showed effectiveness for the removing Cr(VI) from the solution.

Adsorption onto sand coated with iron oxide from a ferric chloride solution gave the better result for removal of Cr(VI). The media have longer life when less alkaline solution employed for the regeneration.

Tessema (2004) studied the adsorption capacity of the IOCS for the removal of both species of chromium. Batch experiments were performed at a pH 7 ± 0.2 . The removal of Cr(III) is far greater than Cr(VI). The removal efficiencies of Cr(III) and Cr(VI) was 91% and 12% respectively. IOCS showed promising adsorption capacity for the removal of Cr(III) (Das, 2004; Tessema, 2004; Yadhav, 2006).

2.7 Granular Activated Carbon

Activated carbon has been widely used for the removal of chromium species from water and wastewater. The removal efficiency is influenced by the characteristics of the activated carbon, such as surface properties, area and chemical characteristics. The granular activated carbons can be used for Cr(III) and Cr(VI) removal from water and wastewater.

Tessema (2004) studied the removal of capacity of Cr(VI) by using granular activated carbon. The batch adsorption experiment was conducted at pH 7. The removal efficiency of Cr(VI) was 86% and 95% at contact time 4 and 24 hr respectively.

2.8 Dead biomass and rice hull

Bailey et al. (1999) studied the adsorptive capacity of dead biomass and rice hull for the chromium species removal. Dead biomass adsorbed the chromium species onto the dead biomass and rice hull. The bacterial cell surfaces are anionic due to the presence of ionised groups in the cell wall polymers, causing the cell to attract metal cations.

Bailey et al. (1999) found that Cr(VI) adsorbed by the biomass of green algae, *Chlorella minutissima* and rice hull. Rice hulls, a product from the commercial harvesting of rice, have a structure similar to that of the green algae. Rice hull possessed adsorption capabilities similar that of algae for Cr(VI). The adsorption capacity of the biomass *Chlorella minutissima* and rice hull for the Cr(VI) were 162.23 mg/g and 164.31 mg/g respectively.

CHAPTER 3 : MATERIALS AND METHODOLOGY

3.1 Introduction

This chapter presents the materials used, methods employed and analytical techniques adopted. The purpose of the experiment was to investigate the applicability of using IOCS and quartz sand for the removal of Cr(III) and Cr(VI) in the laboratory prepared model water.

3.2 Chemicals and Materials

Chemicals and Reagents

The following chemicals and reagents were used in the experiments.

- Chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$)
- Sodium bicarbonate (NaHCO_3)
- Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)
- Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)
- Conc. hydrochloric acid 32% (HCl)
- Iron (II) sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)
- Diphenylcarbazide (DPC)
- Nitric acid 65% (HNO_3)
- Sodium hydroxide (NaOH)
- 0.01M EDTA Solution
- Demineralised water
- Delft tap water

Experimental Equipments

The following equipments were used in the experiments.

- Electronic balance
- pH meter
- Polyethylene bottles with cover, tube and stoppers (500 -2000 ml)
- Measuring cylinders (5-500 ml)
- Pipettes
- Beakers 500, 1000 and 2000 ml
- Volumetric flasks
- Membrane filters (0.45 μm , \O 25 mm)
- Syringes with filter heads

- Sampling small polythene bottles.
- Buckets 5, 10 and 20 L capacity.
- Magnetic stirs.
- Rotary Mechanical shaker

- **Model Water**

In order to conduct the laboratory experiments Delft tap water and demineralised water were used to prepare the laboratory based model water. The model water was prepared to conduct stability experiments, precipitate particle's size analysis experiment, batch experiments and filtration experiments. The compositions of the delft tap water and model water are shown in the Table 5.

Table 5: Delft tap water quality parameters and composition of model water. (source: Tekeste 2003)

Parameter	Symbol	Unit	Quantity (Delft Tap Water)	Model Water Quantity
Temp.		°C	20	20
Oxygen	O ₂	mg/L	10.5	10.5
pH		mg/L	8.1	4.0 to 8.0
Calcium	Ca ²⁺	mg/L	53	160
Maganese	Mg ²⁺	mg/L	7.9	7.9
Bicarbonates	HCO ₃ ⁻	mg/L	129	250
Carbonate	CO ₃ ²⁻	mg/L	0	0
Carbondioxide	CO ₂	mg/L	1.5	1.5
Colour	Colour	Mg Pt/L	3	3
Silica Oxide	SiO ₂	mg/L	1.5	1.5
Total Organic Compound	TOC	mg C/L	1.5	1.5
Pottasium Per Maganate	KmnO ₄	mg O ₂ /L	4.9	4.9
Iron	Fe	mg/L	0.03	0.03
Manganese	Mn ²⁺	mg/L	0.005	0.005
Sulphate	SO ₄ ²⁻	mg/L	81	81
Phosphate	PO ₄ ³⁻	mg/L	0.03	0.03
Chloride	Cl ⁻	mg/L	61	61
Sodium	Na ⁺	mg/L	40	40
Chromium	Cr	mg/L	<0.1	0.100 & 4.0

The separate model water has been prepared with Delft tap water/demineralised water to get the required quality of water. The additional quantity of sodium bicarbonate (NaHCO₃) (125

mg/L for increasing the buffering capacity) and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) (105 mg/L for hardness) were added with Delft Tap water to achieve the required amount of alkalinity (250 mg/L) and hardness (160 mg/L) in the model water. Similarly, the required amount of chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$), sodium bicarbonate (NaHCO_3) (250 mg/L for increasing the buffering capacity) and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) (160 mg/L for hardness) were taken and mixed homogeneously together with demineralised water to get the required amount of alkalinity and hardness in the model water. Conc. hydrochloric acid 32% (HCl) and diluted 0.5M HCl were used to get the desired pH.

- **Stock and Standard Solutions**

Stock solutions and standard solutions containing 1000 mg/L of Cr(III) and Cr(VI) were prepared from chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and used in the experiments. Required amount of stock solutions were dosed to prepare the model water having the chromium concentrations as required. Similarly standard solutions were prepared for the measurement in calibration range and the detection limit of Graphite Furnace 95, inductively coupled plasma (ICP) and spectrophotometer respectively.

- **pH Control**

The pH of the model water was adjusted by adding the required amount of hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions. To avoid the high pH due to the exchanges of gases during the experiment the Polyethylene/ PE bottles were covered and kept closed throughout the experiments.

3.3 Experimental Setups

The stability experiments, batch experiments, filtrations experiments were conducted for the both species of chromium. Precipitate particle's sizes analysis and Ca^{2+} concentration analysis experiments were conducted for Cr(III).

3.3.1 Equilibrium Calculations

Equilibrium calculations were done using PHREEQC-2 Interactive software for windows. It is a 32 bit Windows version of the geochemical model. PHREEQC-2 is one of the most powerful tools in geochemical modelling available.

PHREEQC can be used as a speciation program to calculate saturation indices and the distribution of aqueous species. Analytical data for mole balances can be defined for any valence state or combination of valence states for an element. Distribution of redox elements among their valence states can be based on a specified pe or any redox couple for which data are available. PHREEQC allows the concentration of an element to be adjusted to obtain equilibrium (or a specified saturation index or gas partial pressure) with a specified phase. Solution compositions can be specified with a variety of concentration units. In batch-reaction calculations, PHREEQC is oriented toward system equilibrium rather than just aqueous equilibrium. (Parkhurst and Appelo, 1999).

Equilibrium calculations were performed with PHREEQC to predict the final concentration of total chromium that will be in solution at equilibrium. For the chemical equilibria and solubility products, the phreeqc.dat database was used with additions taken from literature.

This combination of the program with the specific database was also used to predict species distribution in the solution, dominant complexed of metals formed and the saturation indices of the compounds formed in the model water.

3.3.2 Stability Experiments

Stability experiments were conducted to determine the stability of Cr(III) and Cr(VI) with demineralised water and Delft tap water. The solution used was model water, as prepared in the laboratory. The model water (500 ml) was kept in polyethylene bottle (PE bottle) and one duplicate PE bottle was prepared in each pH value. The PE bottles were capped properly to prevent escape of gases. PE bottles were put on mechanical shaker and shaken at the speed 100 rpm during contact time. Sampling was done at specified time.

3.3.3 Precipitate Particle's Size Analysis

Precipitate particle's size analysis experiments were conducted to characterize Cr(III) precipitate particle's in model water. The solution used was model water, as prepared in the laboratory. The model water (500 ml) was placed in each PE bottle and one duplicate bottle was prepared in each pH values. The PE bottles were kept in a mechanical shaker and shaken at the speed 100 rpm during contact time. The samples were filtered through 0.45 μm , 1 μm , 10 μm and 20-25 μm pore size filter papers and tried to figure out the extent to which it can be in the form of particulate. Sampling was done at specified time.

3.3.4 Preparation of Adsorbent

The IOCS (supplied by BRUCHT Company) was taken to conduct the batch experiments. The required amount of IOCS was taken and gently crushed in the porcelain basin to make powder. While grinding care was taken so that grinded fraction contains only iron coating but not the sand grains. The pulverized sand was sieved in the mechanical shaker and separate from quartz sands. Finally, the pulverized iron coating was sieved through 63 μm and retained in pan. The pulverized iron coating was placed in plastic bottle to avoid the moisture and other contaminations.

3.3.5 Batch Experiments

The laboratory batch experiments were conducted to determine the adsorption capacity of Cr(III) and Cr(VI) on pulverized IOCS. The model water was prepared as per water quality matrix and maintained the pH by adding hydrochloric acid. The required amount of pulverized IOCS was weight in electronics weighing machine and placed in the polyethylene/(PE) bottles and 500 ml of the model water poured into each PE bottles. The PE bottles were capped properly to prevent escape of gases and placed the innova 2100 mechanical rotor shaker. The agitation speed of the mechanical shaker was 100 rpm throughout the experiments. Figure 3-1 shows the shaker with PE bottles and procedure followed in batch adsorption experiments.



Figure 3-1: Picture of Innova 2100 rotary shaker with PE bottles.

3.3.6 Sampling

The samples were collected at required time by plastic syringe through the small tube installed at polyethylene (PE) bottle. Throughout the sampling, about 10 ml of samples were taken from PE bottles and half of sample was kept unfiltered and the remaining half was filtered through 0.45 μm membrane filter in order to separate solid from the liquid in model water. The samples were kept in the 20 ml capacity sampling polythene bottles and acidified with about 4-5 drops of conc. 32% HCl to preserve the properties of samples till analyzed.

In addition to 0.45 μm membrane filter 1.0 μm , 10.0 μm and 20-25.0 μm pore sizes of filters papers were used to separate the precipitated chromium particles form the model water. These three additional filter papers were specially used for the particle size distribution experiment only.

Specification of filter papers

- 0.45 μm membrane filters (Cellulose acetate), Diameter 25.0 mm, Whatman, Germany.
- 1.0 μm membrane filters (Regenerated Cellulose), Diameter 50.0 mm, Whatman, Germany.
- 10 μm polycarbonate (Hydrophilic), Diameter 47 mm, Whatman, England.
- 20-25.0 μm membrane filters, Diameter 25 mm, Whatman, England.

3.3.7 Grain Size Distribution and Sieve Analysis

Sieve analysis was performed to determine the grain size distribution, the effective size (d_{10}) and uniformity coefficient (UC) of the quartz sand. The quartz sand was taken from IHE store of sizes 0.5 mm to 1.0 mm. Six different opening sizes of sieve were used for sieving of quartz sand i.e. 1.0 mm, 0.9 mm, 0.8 mm, 0.630 mm, 0.560 mm, 0.425 mm and pan. Sieving time of 5 minutes with 5 second shaking interval at 1.0 mm amplitude was employed for sieving of quartz sand. The below Figure 3-2 shows the grain size distribution curve for quartz sand.

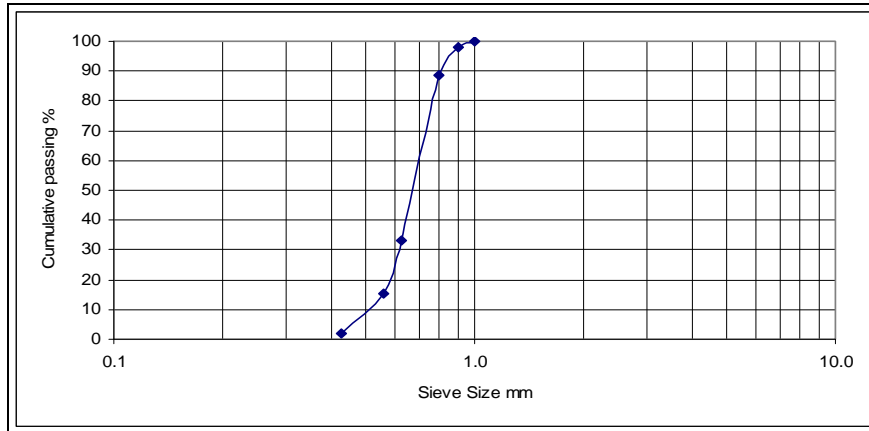


Figure 3-2: rain size distribution curve for quartz sand.

Grain size analysis of quartz sand was done to determine the grain size distribution, effective size (d_{10}), specific diameter (d_s), and uniformity coefficient (UC) (Huisman 1986). Calculation of d_s and UC will be as follows;

$$\frac{W}{d_s} = \sum \frac{W_i}{\sqrt{S_i S_j}} \quad (9)$$

$$UC = \frac{d_{60}}{d_{10}} \quad (10)$$

Where: d_s = specific diameter
 W = total weight of filter media taken
 W_i = weight of media between sieves i and j
 S_i = upper sieve opening
 S_j = lower sieve opening

From the sieve analysis, it was found that 99.88% of quartz sand passed through the 1.0 mm mesh sieve. Details of grain size distribution and sieve analysis experiment is presented in the appendix Table 1. From Fig. 3-2, the d_{10} and d_{60} were found to be 0.50 and 0.70 mm respectively. The calculated specific diameter d_s and uniformity coefficient were 0.69 mm and 1.4 respectively.

3.3.8 Column Filtration Experiments

- For Chromium (III)

The filtration experiment was conducted to evaluate Cr(III) removal efficiency through virgin quartz sand filter media. The filter had a circular cross section of internal diameter 1.8 cm and a total height was 20 cm. The sieved quartz sand of grain size 0.5 mm to 1.0 mm was used as filter media and the depth of filter media was 20 cm, supported by the wool fibres.

Prior to filling the column the quartz sand was washed properly by tap water to remove the clay particles and other dirty particles. Three pumps were used to feed three columns with model water of pH 6, 7, and 8 at 5 m/hr filtration rate. The sampling time was 0, 0.5, 1, 2, 4, 6 and 8 hrs respectively. The filtration experiment was conducted per day 8 hrs for 5 days. The Fig. 3-3 shows filter setup for Cr(III). Figure 3-3 shows small glass column filters for the pH 6, 7, and 8.



Figure 3-3: Picture of small glass column filter.

- For chemical reduction of Cr(VI) and filter through quartz sand media

The filtration experiment was conducted to evaluate chemical reduction of Cr(VI) and removal efficiency through the virgin quartz sand filter media. The filter had a circular cross section of internal diameter 6.0 cm and a total height of 50 cm. The bed depth of the quartz sand media was 20 and 40 cm. The filter column was filled with sieved quartz sand of grain size 0.5 to 1.0 mm. Prior to filling the column the quartz sand was washed properly by tap water to remove the clay particles and other dirty particles. Three pumps were used to feed model water containing Cr(III) and Cr(VI), Fe(II) solution and NaOH solution. Fe(II) was dosed at the rate of 2.3 mg/L to reduce Cr(VI) to Cr(III) and NaOH was dosed to achieve the desired pH of feed water. The experiment was conducted at pH 7, and 8 and the filtration rate was maintained at 5 m/hr. The sampling time was 0, 0.5, 1.0, 2.0, 4.0, 6.0 and 8 hrs respectively. For the bed depth 20 cm, the filtration experiment was conducted per day 8 hrs during 2 days at pH 7. Similarly for the bed depth 40 cm, the filtration experiment was conducted per day 8 hrs during 3 days at pH 7 and 8. The below Fig. 3-4 shows filter setup for chemical reduction of Cr(VI) to Cr(III) and filtration. Figure 3-4 shows the chemical reduction of Cr(VI) and filtration through quartz sand media.



Figure 3-4: Picture of chemical reduction of Cr(VI) to Cr(III) and filter column.

- **Head Loss in Filter Bed**

The Kozeny- Carman equation is a relation used in fluid dynamics to calculate the pressure drop of a fluid flowing through a packed bed of solids. The equation is only valid for laminar flow. Assuming the grain of the filter media used as spherical shape and head loss through the bed of quartz sand used as filter media in the filtration experiments. The following equation is used for the head loss calculation,

$$H_0 = 180 * \frac{v}{g} * \frac{(1 - P_0)^2}{P_0^3} * \frac{V_f}{d_s^2} * L \quad (11)$$

Where,

- H_0 = Head loss through sand bed (m).
- v = Kinematic viscosity (m^2/s)
- g = Specific gravity = 9.81 (m/s^2)
- P_0 = Porosity.
- V_f = Velocity of flow (m/s)
- d_s = Specific diameter of filter media (m)
- L = Depth of the filter media (m)

The kinematic viscosity depends upon the temperature and can be calculated by using the following equation,

$$v = \frac{497 * 10^{-6}}{(T + 42.5)^{1.5}} \quad (12)$$

- T = Water temperature ($^{\circ}C$)

The filtration rate was 5 m/hour. The model water was prepared in laboratory at temperature 20°C. The kinematic viscosity is 1.0×10^{-6} m²/sec at 20°C temperature. The specific diameter of quartz sand is 0.69 mm from above grain size distribution curve. Assuming, the porosity of the quartz sand of size 0.5 – 1.0 mm is 42%. From the above equation the head loss through the bed of quartz sand media is calculated as below,

<u>Bed Depth, m</u>	<u>Head Loss through bed of sand (H₀), m</u>
0.20	0.049
0.40	0.098

3.4 Analytical Methods

The following analytical methods were adopted for the analysis of samples of Cr(III), Cr(VI) and hardness.

- **Atomic Adsorption Spectrometer – Graphite Furnace/AAS-GF**

The lower concentration of total chromium less than 100 µg/L was analyzed with the Atomic Adsorption Spectrometer- Graphite Furnace (AAS-GF). The samples were taken through small tube installed at PE bottle and acidified with concentrated hydrochloric acid. The samples were analyzed in the Atomic Adsorption Spectrometer – Graphite Furnace/AAS-GF. Maximum limit of total chromium 30 µg/L can be analyzed in the AAS-GF and SOLAR software was run to analyze the total chromium. Every run total 60 samples can be analyzed in Graphite Furnace. The equipment was calibrated with blank and three standard solutions of 10, 20 and 30 µg/L respectively. The matrix modifier (MgNO₃) and blank solution were placed at R1 and R2 slots. Similarly 10 µg/L, 20 µg/L and 30 µg/L standard solutions were placed 1, 2 and 3 slots in machine to calibrate. The GF machine automatically gives the calibration line of absorbance versus total chromium. The machine can measured 1 to 30 µg/L of total chromium concentration. The taken samples were placed in slots accordingly to analyze total chromium. After analyzed every 8 to 10 samples, the standard known solution was measured to check the performance of machine GF.

If the taken samples contain high total chromium concentrations, the samples were diluted with demineralised water such way that the total chromium measurement falls within the analyze range.



Figure 3-5: Picture of Atomic Adsorption Spectrometer – Graphite Furnace/AAS-GF

- **Spectrophotometer:**

The Cr(VI) speciation is measured with Perkin Elmer Lambda 20 UV/VIS spectrophotometer at the wave length 540 nm. Spectrophotometer method can be used for routine determination of the Cr(VI) species using reagents in order to form absorbing species that present selectivity in the response. The most common method for determining Cr (VI) in aqueous solution is based on the reaction of diphenylcarbazide (DPC) with Cr (VI) at a pH of 1.0 ± 0.3 . As stated by many researchers, diphenylcarbazide (DPC) is an inexpensive and very sensitive colour reaction with Cr(VI) in acid solution. A red violet colour of unknown composition is produced and it is specific for chromium. The theoretical detection limit of the spectrophotometer was 3% of the highest standard i.e. $7.5 \mu\text{g/L}$ for highest standard of $250 \mu\text{g/L}$. Total chromium concentration was measured with GF Graphite Furnace. Chromium standard solution is prepared at different range blank to $100 \mu\text{g/L}$ (0, 10, 25, 50, $100 \mu\text{g/L}$) to calibrate the spectrophotometer.

- **Inductively Coupled Plasma/ ICP**

The total chromium concentration more than $100 \mu\text{g/L}$ can be analyzed with inductively coupled plasma /ICP, Perkin Elmer 3000. Most commercial plasma source instruments use an argon ICP as in inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). In plasma source instruments, liquid samples are employed to analyze. Samples were acidified prior to introduction to the plasma by a proper nebulization device. The ICP was calibrated with blank and five standard solutions of 1.0, 5.0, 10.0, and 15.0 mg/L respectively and the ICP automatically gives the calibration line of absorbance versus total chromium concentration. The samples were placed in the sampling bottle and passed to the ICP through the small tube. After 30 seconds the ICP machine gives the total chromium concentration of fed sample. After measured every 10 samples know standard solution was measured to check the performance of ICP.

- **Atomic Adsorption Spectrometer – Flame method**

Measurement of iron was done by AAS- flame. The highest concentration that could be measured by flame method is 3 mg/L for iron. The equipment was calibrated with blank and three standard solutions of 0.5, 2.0 and 3.0 mg/L respectively. AAS-flame automatically gives the calibration line of absorbance versus iron concentration. The samples were placed

in the sampling bottle and passed to the AAS-flame through the small tube. AAS-flame gives the concentration of iron. After analyzed every 20 to 25 samples, the standard known solution was measured to check the performance of AAS-flame.



Figure 3-6: Picture of Atomic Absorption Spectrometer (AAS-Flame)

- **Titration**

The term hardness is also directly involved in water and wastewater. The amount of hardness present in water can be determined by the titration methods. The 0.01M EDTA is added in samples to measure the total hardness concentrations contain in the model water. About 18 drops of 1M NaOH and 8-10 drops of murexide added to 25 ml water samples. The colour of water samples changed to red colour. The red samples were titrated with the EDTA solution slowly, with continuous stirring to the proper end point. The colour changed from red to violet. The end point was confirmed by adding 1 to 2 drops of titrate in excess to make certain that no further colour change occurred. From the volume of EDTA solution required to change the colour red to violet gave the total hardness contains in the model water.

CHAPTER 4 : RESULTS AND DISCUSSIONS

4.1 Stability Experiments

Before the start of the batch experiments, the stability experiments were conducted for the Cr(III) and Cr(VI). The stability of Cr(III) experiments were conducted to determine the stability depending on Cr(III) concentrations as function of pH, as well as varying concentrations of HCO_3^- and Ca^{2+} in model water. The solution used was model water, as prepared in laboratory.

Similarly, the stability of Cr(VI) was examine as a function of pH to determine whether the Cr(VI) is stable or reduced to Cr(III).

4.1.1 Stability of Cr(III) as a function of initial Cr concentration

In order to determine the stability of dissolved Cr(III) in model water, the experiment was conducted with varying chromium concentration at pH 6.6. In this experiment only, samples were analyzed in the AAS-Flame methods. The results are presented in Figure 4-1 (0 hr contact time) and Figure 4-2 (21 hrs contact time) and the detailed results are presented in the annex Table 2.

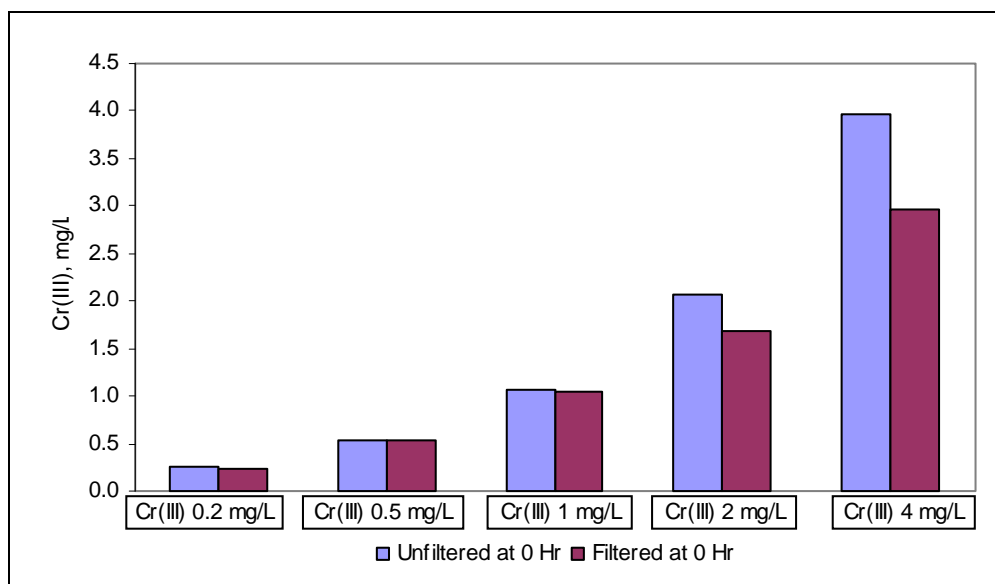


Figure 4-1: Stability of Cr(III) as a function of Cr(III) concentration (model water with $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, initial $\text{pH} = 6.6 \pm 0.1$).

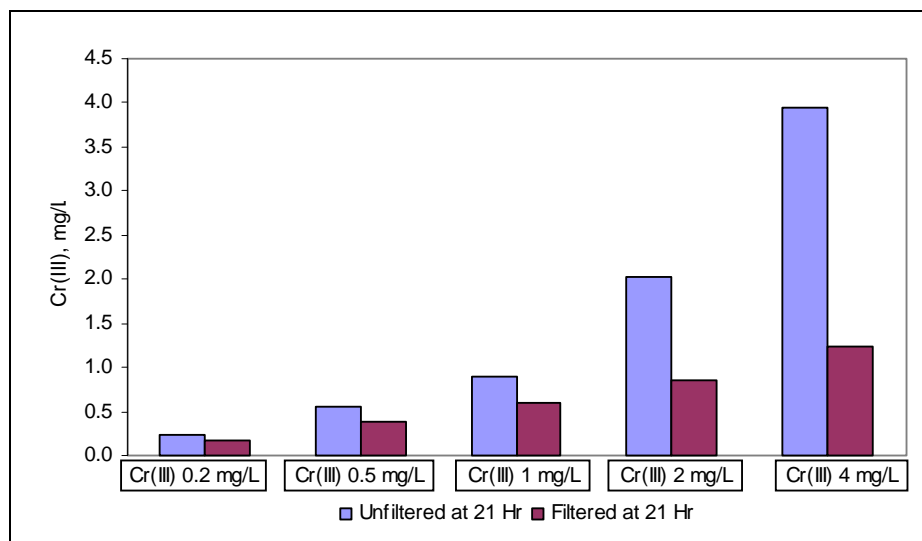


Figure 4-2: Stability of Cr(III) as a function of Cr concentration (model water with $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, initial $\text{pH} = 6.6 \pm 0.10$).

In the filtered samples, the Cr(III) concentrations were found to be lower compared to those in unfiltered samples for both contact time 0 and 21 hrs at all Cr concentrations tested. So, the precipitation took place at both high and low Cr(III) concentrations. At 0 hr the reduction percentage of Cr was 1%, 18%, 25% in 1.0, 2.0 and 4.0 mg/L Cr(III) concentration. Similarly, at 21 hrs the reduction percentage of Cr was 21%, 28%, 44%, 59%, 69% in 0.2, 0.5, 1.0, 2.0 and 4.0 mg/L in Cr(III) concentration respectively. It was found that precipitation took place, precipitation of dissolved Cr(III) was intensive at high initial Cr(III) concentrations. It is concluded that Cr(III) precipitated more at longer contact time for high and low Cr(III) concentrations. Effect of contact time was found on stability of Cr(III) at both high and low concentrations.

From the chromium speciation diagram Figure 2-2, it is found that $\text{Cr}(\text{OH})_2^{2+}$, $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}(\text{OH})_3^0$ species are present at pH 6.6. $\text{Cr}(\text{OH})_2^+$ is the dominant species in the natural ground water with a pH between 6 and 8. Furthermore $\text{Cr}(\text{OH})_3(\text{s})$ is present at pH 5 to 11. Sharma et al. (2008), Calder (1988), McMullen (1994), Palmer and Wittbrodt (1990), Rai et al. (1987) and Hem (1977) reported that under slightly acidic and alkaline conditions Cr(III) precipitates as chromium hydroxide, Palmer and Wittbrodt (1990), added that at pH between 5 to 12 the concentration of Cr(III) is expected to be less than 10^{-6} molar. The Phreeqc interactive program showed that precipitation took place as chromium hydroxide and chromium oxide (Cr_2O_3) at pH 6.6 (for detail see Appendix J). From the Phreeqc calculation (Molality calculation), it was found that at pH 6.6, $\text{Cr}(\text{OH})_2^{2+}$, $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}(\text{OH})_3^0$ species were distributed as 33%, 66% and 1% in chromium solution respectively. The saturation index (SI) of the chromium hydroxide and chromium oxide were greater than zero in this composition of model water and pH. During the stability experiment, Yadav (2007), found that 24% and 38% of Cr(III) precipitates at the sampling time of 19 and 139 hrs, respectively. The experiment was conducted at pH 6 and composition of model water was $\text{Cr}(\text{III}) = 4.93 \text{ mg/L}$, $\text{Ca}^{2+} = 20 \text{ mg/L}$, $\text{HCO}_3^- = 20 \text{ mg/L}$, $\text{Na}^+ = 7.5 \text{ mg/L}$ and $\text{Cl}^- = 35.5 \text{ mg/L}$.

Furthermore, McMullen (1994), reported that at pH value from 6 to 12, the dominant chromium species is reported to be $\text{Cr}(\text{OH})_3^0$. Therefore, throughout the pH range of majority of natural waters, the solubility of Cr(III) is less than the drinking water standard. The mobility of the Cr(III) in the aquatic environment is expected to be low because of the low solubility of $\text{Cr}(\text{OH})_3^0$ (s) and $(\text{Cr}, \text{Fe})(\text{OH})_3^0$ (s) precipitates under slightly acidic to basic conditions. (Rai et. al., 1987; Sharma et. al., 2008)

4.1.2 Stability of Cr(III) as a function of time

The experiment was conducted for two different Cr concentrations to determine the stability of Cr(III) as a function of time. Sampling was done at 0, 24, 48 and 72 hrs and samples were analyzed for Cr(III). The results are presented in Figure 4-3 and Figure 4-4 and the detailed results are presented in the annex Table 3.

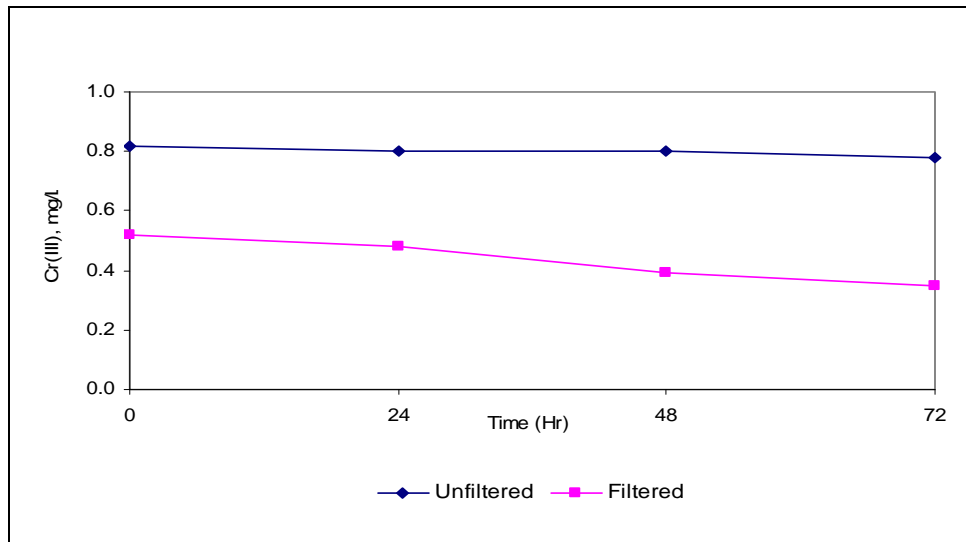


Figure 4-3 : Stability of Cr(III) as a function of time (model water with $c(\text{Cr}(\text{III})) = 0.8$ mg/L, $c(\text{Ca}^{2+}) = 160$ mg/L, $c(\text{HCO}_3^-) = 250$ mg/L, initial pH = 6.6 ± 0.1).

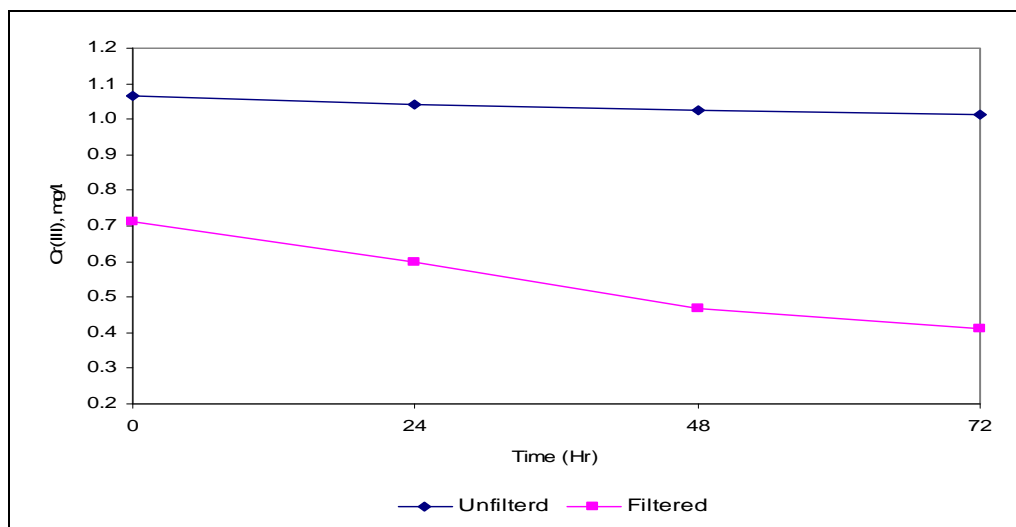


Figure 4-4 : Stability of Cr(III) as a function of time (model water with $c(\text{Cr}(\text{III})) = 1.08$ mg/L, $c(\text{Ca}^{2+}) = 160$ mg/L, $c(\text{HCO}_3^-) = 250$ mg/L, initial pH = 6.6 ± 0.1).

At 0.8 mg/L initial Cr(III) concentration, the reduction percentage of Cr was 37%, 41%, 52% and 57% at 0, 24, 48 and 72 hrs. Similarly, at 1.08 mg/L initial Cr(III) concentration, the reduction percentage of Cr(III) concentration was 35%, 46%, 59% to 65% at 0, 24, 48 and 72 hrs respectively.

It was found that precipitation of chromium was increasing with prolonged contact time.

4.1.3 Stability of Cr(III) as a function of HCO_3^- concentration

In order to determine the stability of Cr(III) as function of HCO_3^- concentration at a fixed Ca^{2+} 160 mg/L concentration, the experiment was conducted with model water at pH 6.6. Sampling was done at 0 hr and 20 hr and samples were analyzed for the Cr(III). The results are presented in Figure 4-5 and the detailed results are presented in the annex Table 4.

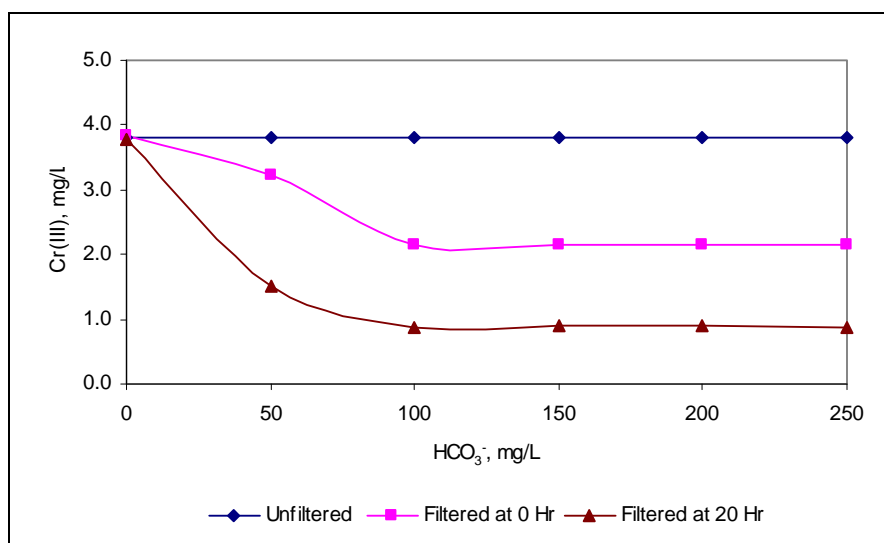


Figure 4-5: Stability of Cr(III) as a function of HCO_3^- concentration (model water with $c(\text{Cr(III)}) = 3.90 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$,).

In all the filtered samples, the Cr(III) concentrations were less compared to those in unfiltered samples at the time 0 hr and 20 hr. So, the precipitation took place at high and low HCO_3^- concentrations in model water.

Model water without HCO_3^- , pH of was only 3.4. At low pH no Cr precipitation was found during the experiment. At 50 mg/L of HCO_3^- concentration, there was less precipitation in comparison to the higher HCO_3^- concentration, possibly because pH of the solution was 6.2. Here, the reduction of Cr(III) was found to be 16 % and 61% during the contact time of 0 and 20 hrs respectively.

HCO_3^- concentrations of 100 to 250 mg/L, the pH of the model water increased due to more concentration of the HCO_3^- and the pH was adjusted by adding HCl. There was reduction of Cr(III) concentration in filtered samples at 0 and 20 hrs. At 0 hrs, the reduction of Cr(III) was found to be 40%, 44%, 44% and 44% in 100, 150, 200 and 250 mg/L of HCO_3^- concentration. Furthermore at 20 hr, the reduction of Cr was found 77%, 76%, 76% and 77% in 100, 150, 200 and 250 mg/L respectively. It was found that the longer the contact time more Cr(III) precipitation observed in the model water.

At pH 3.4, Cr^{3+} and $\text{Cr}(\text{OH})^{2+}$ are the dominant species and the solubility of the Cr(III) species is higher compared to pH 6.2 and 6.6. Phreeqc interactive program showed that at pH 5 and above Cr precipitation took place as chromium hydroxide and chromium oxide with varying concentration of HCO_3^- . So, the saturation index of these chromium species was greater than 0 at pH 6.2 and higher. At pH 3.40, there is no precipitation and the saturation index of Cr(III) species is less than 0.

An additional experiment was conducted to determine the stability of Cr(III) with varying HCO_3^- concentrations and without Ca^{2+} concentration in the model water. The samples were taken after 1 and 24 hrs. The results are presented in Figure 4-6 and the detailed results are presented in the annex Table 6.

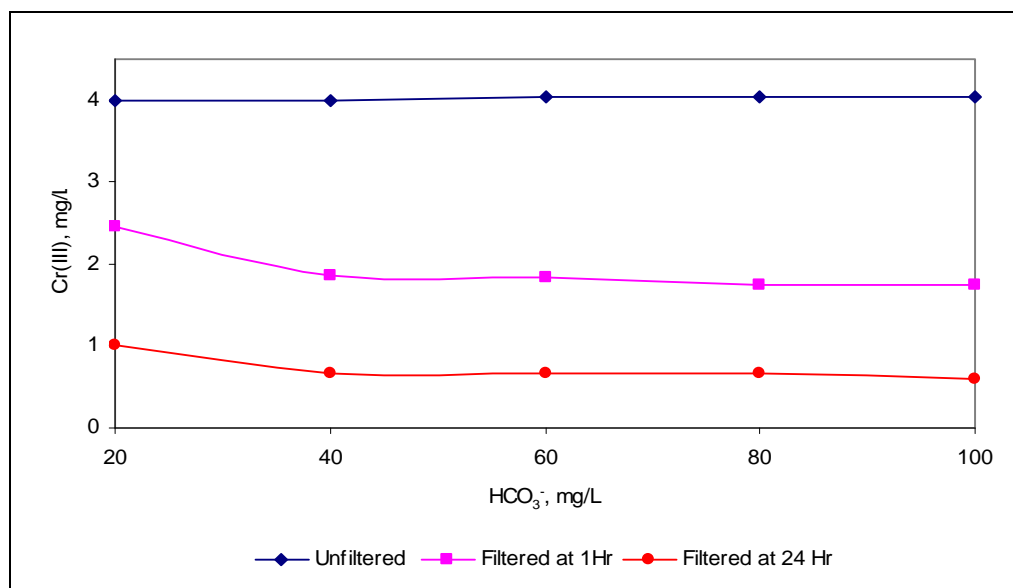


Figure 4-6 : Stability of Cr(III) as a function of HCO_3^- concentration (model water with. $c(\text{Cr}(\text{III})) = 4 \text{ mg/L}$, initial pH = 6.6 ± 0.1 ($\text{HCO}_3^- = 20$, pH = 5.9., $\text{HCO}_3^- = 40 \text{ mg/L}$, pH = 6.40)).

The reduction of dissolved Cr(III) concentration increased with the increase in contact time. From the experiment it was found that the precipitation took place in the model water and the dissolved Cr(III) concentration was reduced after filtration. For the period of 1 hr contact time, the reduction percentage of Cr(III) concentrations were found to be 38%, 38%, 54%, 54% and 57% at 20, 40, 60, 80 and 100 mg/L HCO_3^- concentrations respectively. Similarly, for the period of 24 hr contact time, the reduction percentage of Cr(III) concentrations were found to be 74%, 83%, 83%, 84% and 85% respectively. The effect of contact time and pH was found in the experiment. The reduction of Cr(III) was found to be higher with more contact time and higher pH. Reduction of dissolved Cr(III) was lower at the pH of 5.9 and 6.4 compared to the pH of 6.6. It was found that reduction of Cr(III) more dependent on pH rather than the concentration of HCO_3^- .

The Phreeqc interactive program showed that precipitation took place as chromium hydroxide and chromium oxide with varying concentration of HCO_3^- concentrations at pH of 6.4. So, the saturation indices of these chromium species were greater than 0 in model water at pH 6.4.

4.1.4 Stability of Cr(III) as a function of Ca²⁺ Concentration

Stability of Cr(III) was determined as a function of Ca²⁺ concentration and fixed HCO₃⁻ concentration 250 mg/L at pH 6.6. Sampling was done at 0 hr and 20 hrs and samples were analyzed for total chromium. The results are presented in Figure 4-7 and the detailed results are presented in the annex Table 5.

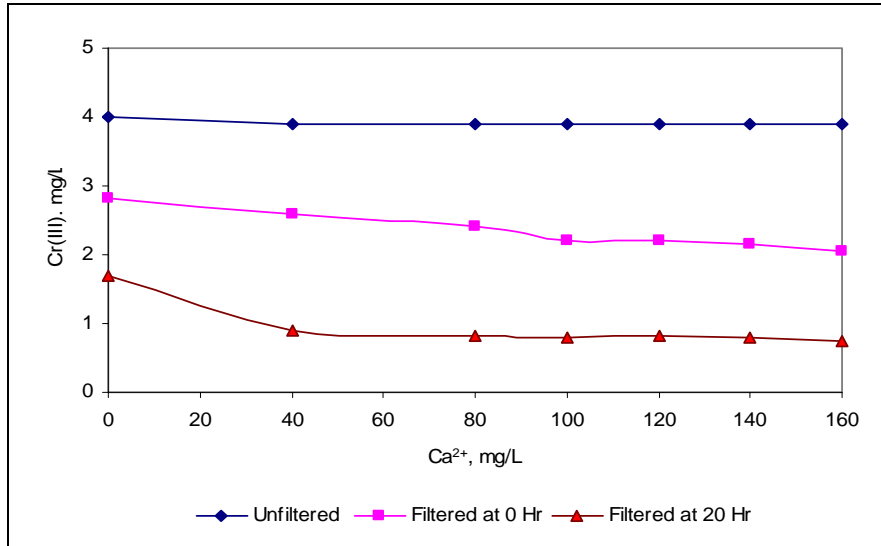


Figure 4-7: Stability of Cr(III) as a function of Ca²⁺ concentration (model water with c(Cr(III)) = 3.90 mg/L, c(HCO₃⁻) = 250 mg/L, initial pH = 6.6±0.1).

In all filtered samples, Cr(III) concentration was less compared to those in unfiltered samples at time 0 hr and 20 hr so, the precipitation took place regardless Ca²⁺ concentration. The reduction of Cr(III) were 31% to 45% and 59% to 80% at 0 and 20 hrs respectively. It was found that reduction of dissolved chromium concentration in the model water was higher at prolonged contact time compared to shorter contact time. The reduction of Cr(III) was increased with increase of Ca²⁺ concentrations in model water. It is concluded that the precipitation took place in the model water so there was reduction in dissolved Cr(III) concentration after filtration.

Additional experiment was conducted to determine the stability of Cr(III) with varying Ca²⁺ concentrations in model water without HCO₃⁻ at pH 6.6. The samples were taken after 1 and 24 hr. The results are presented in Figure 4-8 and the detailed results are presented in the annex Table 7.

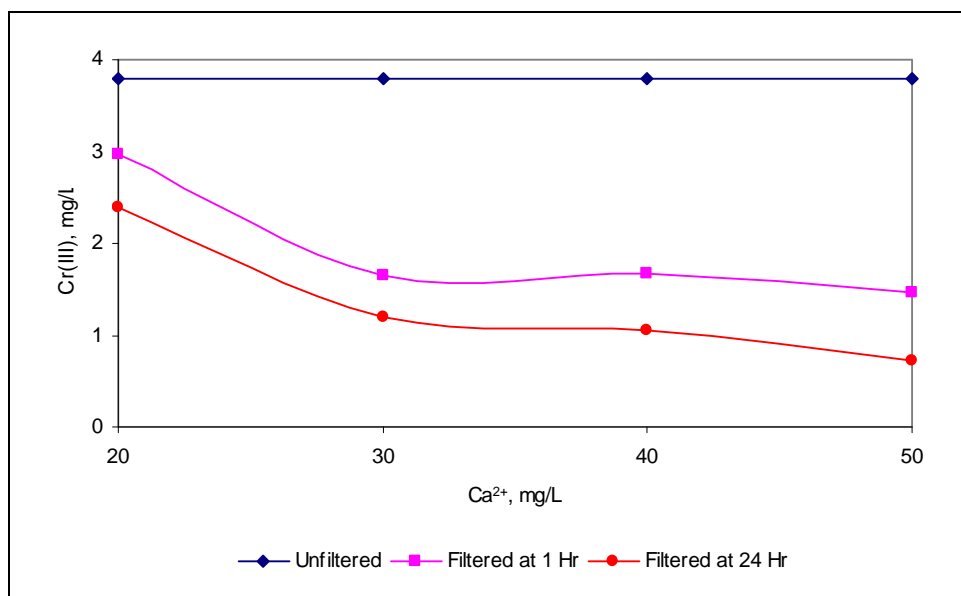


Figure 4-8: Stability of Cr(III) as a function of Ca²⁺ (model water with c(Cr(III)) = 3.8 mg/L, initial pH = 6.6±0.1).

The reduction of Cr(III) concentration in the model water increased with increase in contact time and Ca²⁺ concentration. From the experiment it was found that the precipitation occurred in model water. After 1 hour, reduction of Cr(III) concentration was 22%, 56%, 56%, and 62% at 20, 30, 40, and 80 mg/L Ca²⁺ concentrations, respectively. Similarly after 24 hour, the reduction of the Cr(III) concentration was 37%, 68%, 73% and 81%. Higher the concentration of Ca²⁺ more the precipitation was occurred hence the reduction of dissolved Cr(III) due to the formation of Cr(OH)₃⁰ in the model water. Increase in concentration of Ca²⁺ increased precipitation and reduction of Cr(III).

Another additional experiment was conducted in order to monitor the Ca²⁺ concentration with HCO₃⁻ and Cr(III) concentration after 1 and 24 hrs contact time in the model. The experiment was carried out at pH 6, 7 and 8. The filtered and unfiltered samples were taken after 1 and 24 hrs to measure Ca²⁺ concentration in model water. The detail results are presented in Table 6.

Table 6: Ca²⁺ concentration in model water (c(Cr(III)) = 4 mg/L, HCO₃⁻ = 250 mg/L, Ca²⁺ = 160 mg/L).

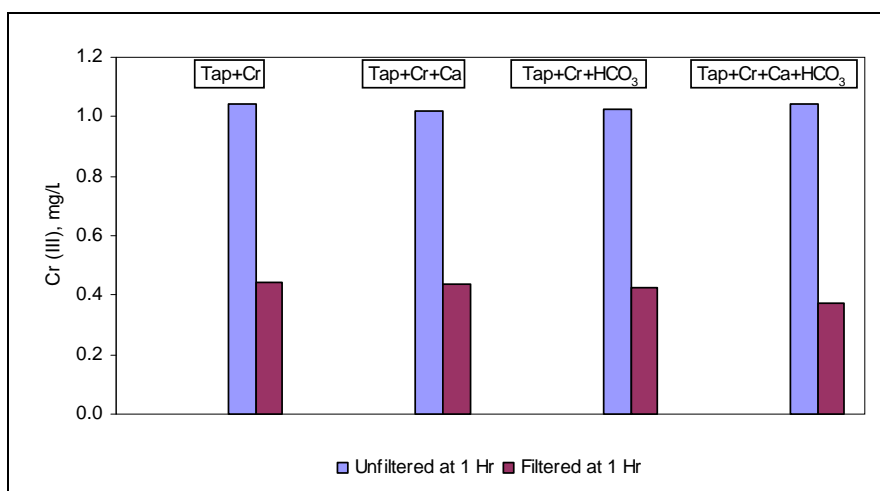
pH	c(Ca ²⁺), mg/L			
	1 Hr		24 Hr	
	Unfiltered	Filtered	Unfiltered	Filtered
6	157	161	160	164
7	160	161	161	163
8	160	161	160	160

From the experiment, there was no significant difference of Ca²⁺ concentration in filtered and unfiltered samples taken after 1 and 24 hrs. During the 24 hour contact time calcium did

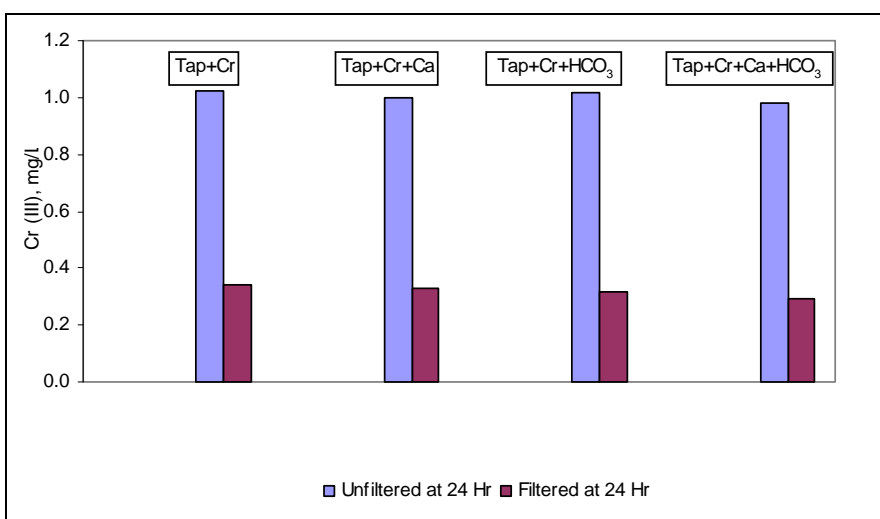
not co-precipitate in the model water and hence it is concluded that there was not interference of Ca^{2+} with Cr(III) in the model water at pH 6, 7 and 8.

4.1.5 Stability of Cr(III) as a function of HCO_3^- and Ca^{2+} presence

The experiments were conducted to determine the stability of Cr(III) as a function of HCO_3^- and Ca^{2+} presence with tap water. The model water was prepared with Delft tap water. The Delft tap water contains Ca^{2+} 55 mg/L and HCO_3^- 125 mg/L. The additional amount of Ca^{2+} 105 mg/l and HCO_3^- 125 mg/L were added to the Delft tap water to achieve final concentration of Ca^{2+} 160 mg/L and HCO_3^- 250 mg/L in the model water. Model water with tap water, Ca^{2+} , HCO_3^- and Cr(III) pH adjusted to 6.6. The samples were taken after 1 and 24 hrs. The results are presented in above Figure 4-9, Figure 4-10, Figure 4-11 and Figure 4-12. The detailed results are presented in the annex Tables 8, 9 10 and 11.

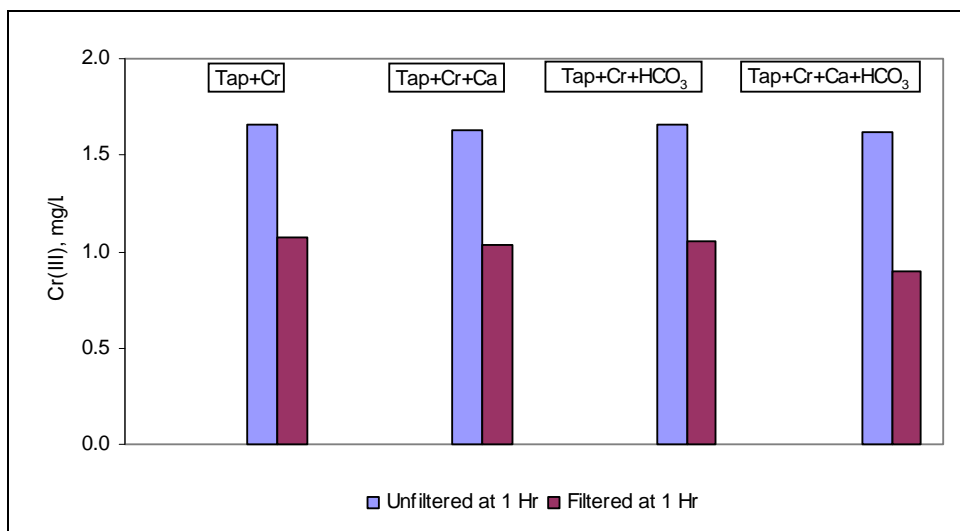


[A]

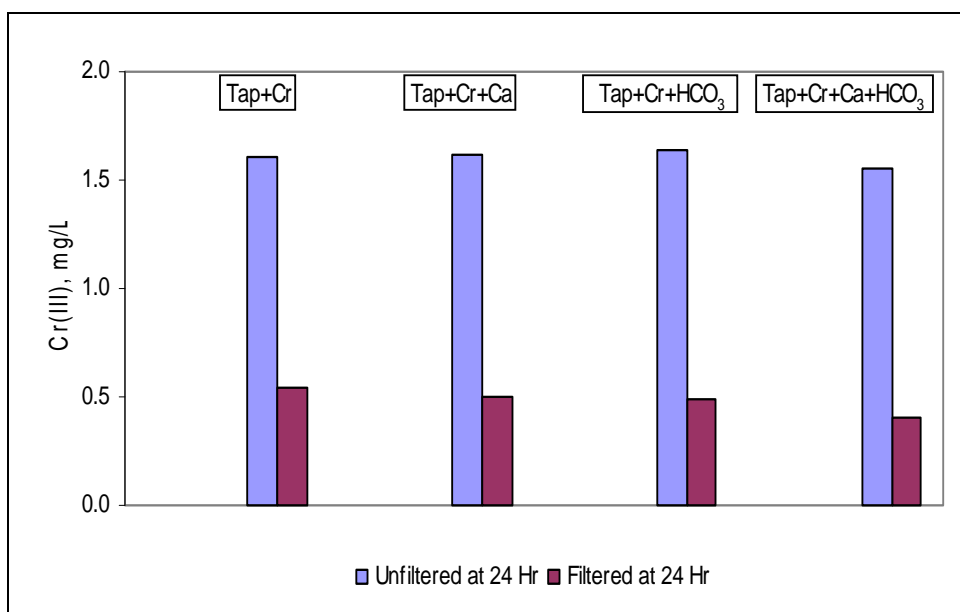


[B]

Figure 4-9: Stability of Cr(III) as a function of HCO_3^- and Ca^{2+} (model water with Cr(III) = 1.1 mg/L, $c(\text{Ca}^{2+}) = 55$ to 160 mg/L), $\text{HCO}_3^- = 125$ to 250 mg/L); [A] 1 Hr, [B] 24 Hr.

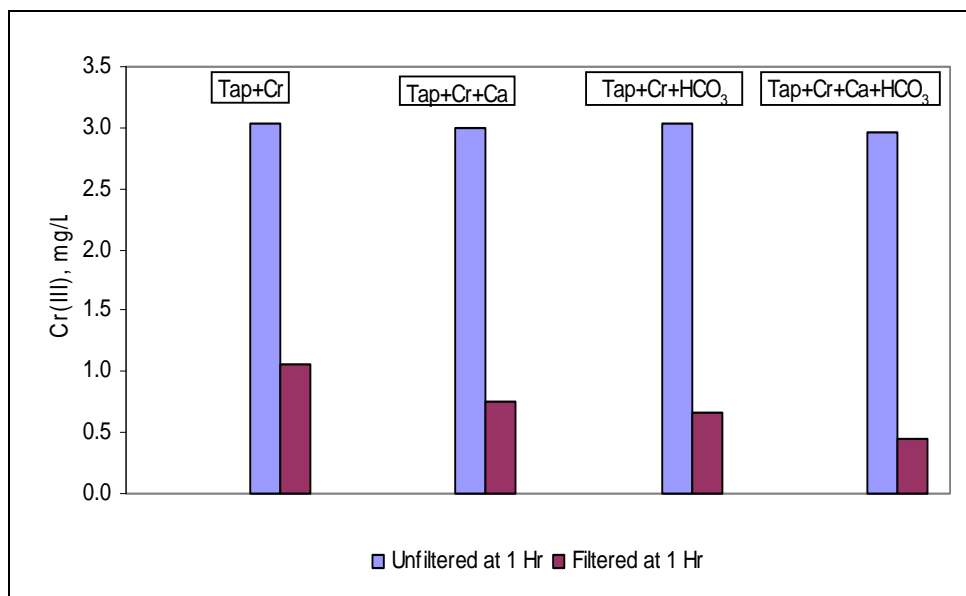


[A]

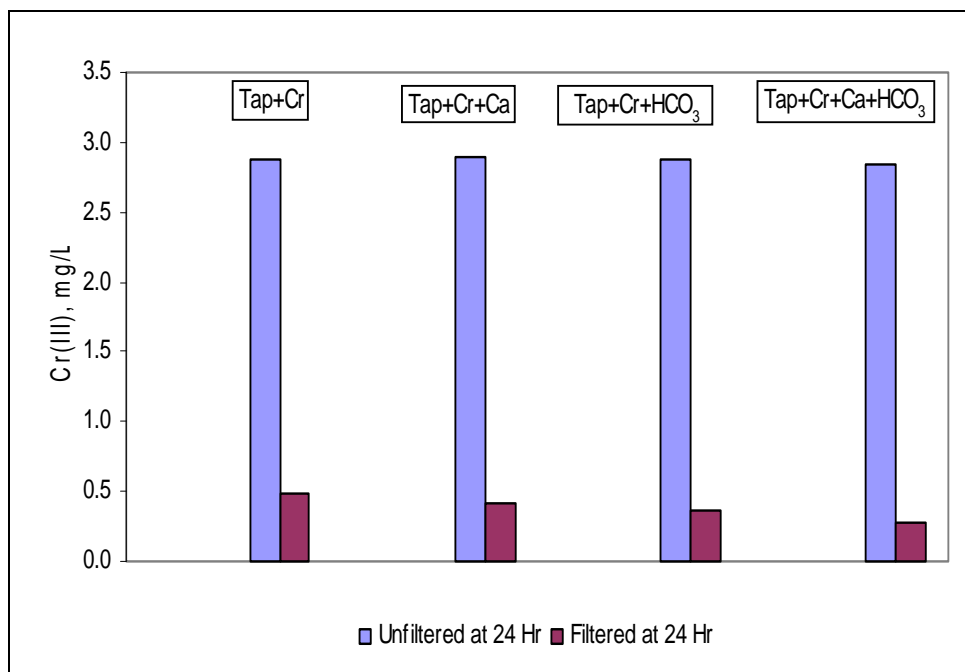


[B]

Figure 4-10: Stability of Cr(III) as a function of HCO₃⁻ and Ca²⁺ (model water with Cr(III) = 1.8 mg/L, c(Ca²⁺) = 55 to 160 mg/L), HCO₃⁻ = 125 to 250 mg/L); [A] 1 Hr, [B] 24 Hr.

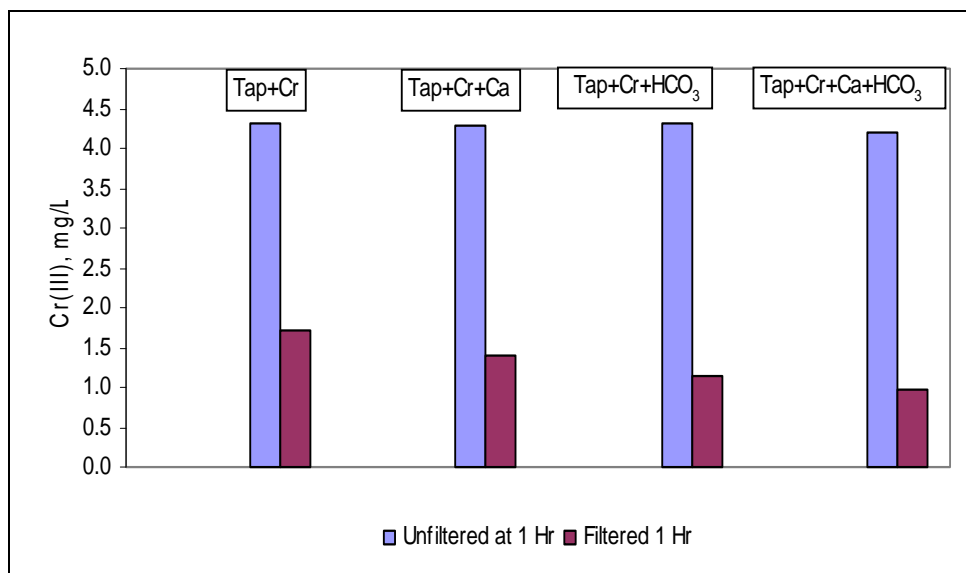


[A]

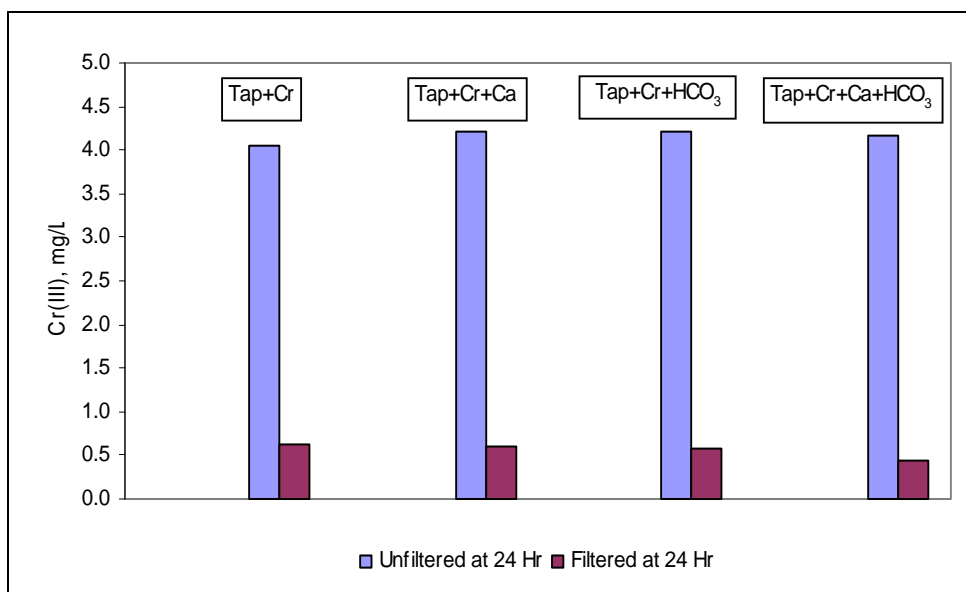


[B]

Figure 4-11: Stability of Cr(III) as a function of HCO_3^- and Ca^{2+} (model water with Cr(III) = 3.0 mg/L, $c(\text{Ca}^{2+}) = 55$ to 160 mg/L), $\text{HCO}_3^- = 125$ to 250 mg/L) ; [A] 1 Hr, [B] 24 Hr.



[A]



[B]

Figure 4-12: Stability of Cr(III) as a function of HCO_3^- and Ca^{2+} (model water with Cr(III) = 4.2 mg/L, $c(\text{Ca}^{2+}) = 55$ to 160 mg/L, $\text{HCO}_3^- = 125$ to 250 mg/L) ; [A] 1 Hr, [B] 24 Hr.

From the experiment, it showed that there was no significant difference in reduction of dissolved Cr(III) at low and high HCO_3^- and Ca^{2+} concentrations presence at pH 6.6. Similarly, longer the contact time more the precipitation occurred. As seen from the above results, at Cr(III) concentrations of 3.0 and 4.2 mg/L, more precipitation occurred as compared to lower Cr(III) concentrations of 1.1 and 1.8 mg/L. It was found that Cr(III) was not stable at high and low Cr(III) concentration with the presence of Ca^{2+} and HCO_3^- .

4.1.6 Stability of Cr(III) as a function of pH

a) Cr(III) concentration 100 µg/L

The experiment was conducted to determine the stability of Cr(III) as a function of pH. The samples were taken at 0 min, 10 min, 20 min, 30 min, 1 hr and 24 hrs. The results are presented in Figure 4-13 and the detailed results are presented in the annex Table 12.

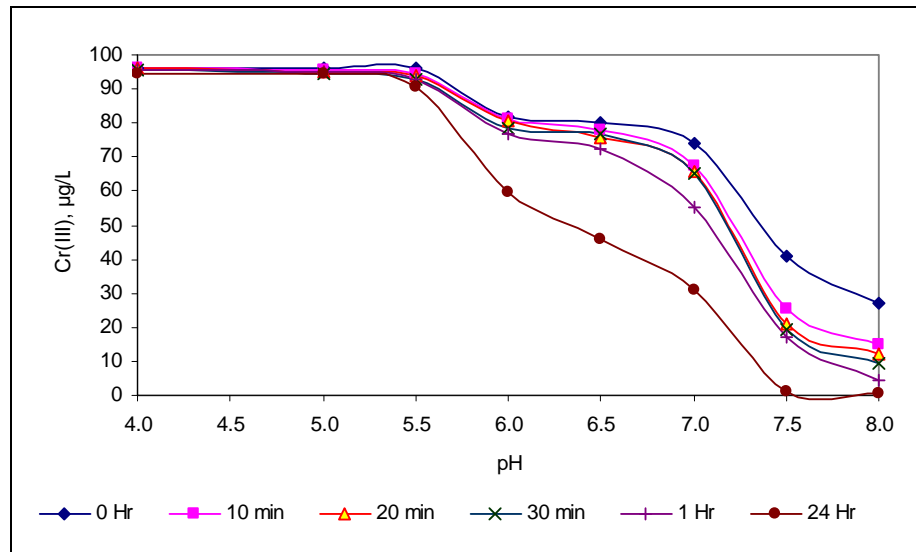


Figure 4-13: Stability of Cr(III) as a function of pH (model water with $c(\text{Cr(III)}) = 100 \pm 5 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$).

At pH 4, 5 and 5.5, there was no significant reduction in dissolved Cr(III) concentration during the contact period of 24 hrs. The reduction of Cr(III) was gradually increased with increased in pH. At pH 6 and 7 the reduction of dissolved Cr(III) was 36% and 50% during 24 hour contact time. Similarly, the reduction of Cr(III) was higher at pH 7, 7.5 to 8 and the reduction was 65%, 97% and 99% during 24 hour contact time. From the experiment, it is confirmed that the precipitation of Cr(III) was greater at higher pH and longer contact time compared to low pH and shorter contact time. At pH 7, 7.5 and 8, the reduction rate of Cr(III) concentration was initially rapid, and the optimum reduction was found for the contact period of 30 minutes.

b) Cr(III) concentration 3.8 mg/L

Another stability test was conducted for Cr(III) concentration 3.8 mg/L as a function pH. The experiment was conducted at pH range from 4 to 11.5. The pH of the model water was brought down to 4 by adding HCl and added the chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) and NaOH solution was added to obtain the desired pH. The results are presented in Figure 4-14 and the detailed results are presented in the annex Table 13.

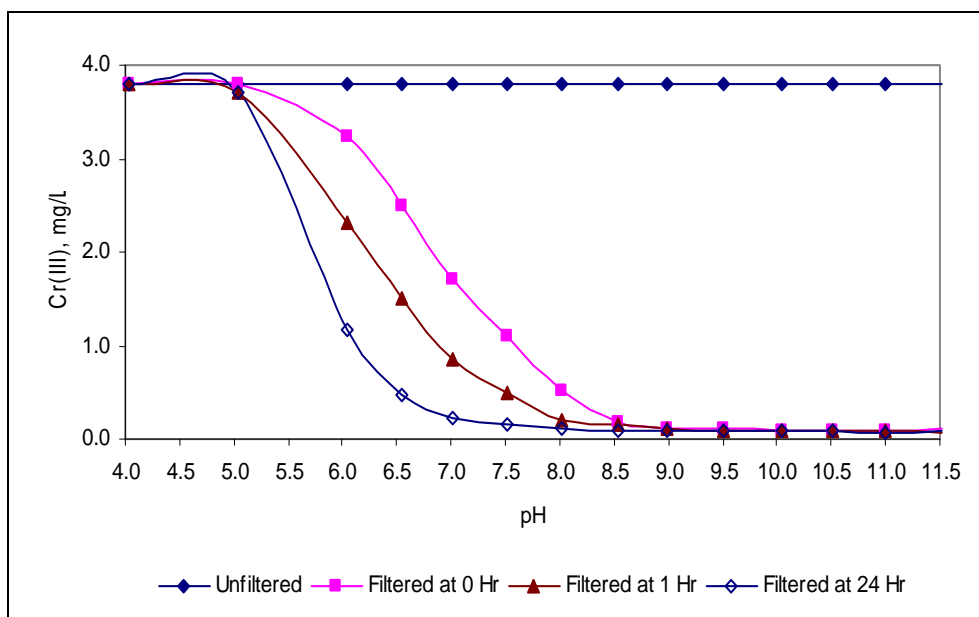


Figure 4-14: Stability of Cr(III) as a function of pH (model water with $c(\text{Cr(III)}) = 3.8$ mg/L, $c(\text{Ca}^{2+}) = 160$ mg/L, $c(\text{HCO}_3^-) = 250$ mg/L).

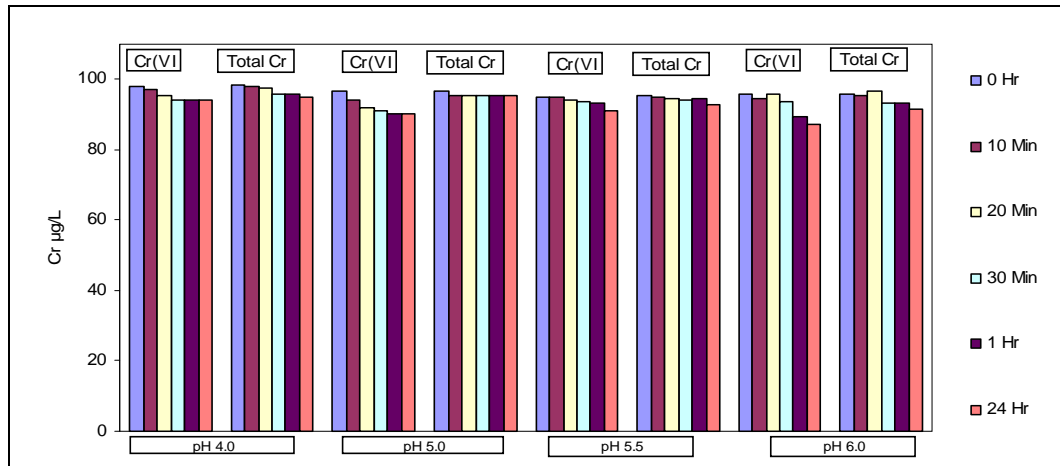
At pH 4 and 5, there was no reduction of dissolved Cr(III) concentration after 24 hrs. At pH 6, 6.5, 7, 7.5 and 8 the Cr(III) concentration reduction was 69%, 88%, 94%, 96% and 97% during 24 hrs contact time. Similarly, at pH 8.5, 9, 9.5, 10, 10.5, 11 and 11.5, the reduction of Cr(III) concentration was 97% at 0 hr. Similarly, after 24 hrs, the reduction was 98%. There was no significant difference in the reduction of Cr(III) above pH 8 during 0, 1 and 24 hour contact time. Hence, all the dissolve Cr(III) precipitated immediately.

Furthermore, increasing the pH implied a proportional increase in the concentration of hydroxide ions $[\text{OH}^-]$ in the model water. So, at high pH of the model water, the more precipitation occurred and the dissolved Cr(III) concentration was less compared to low pH.

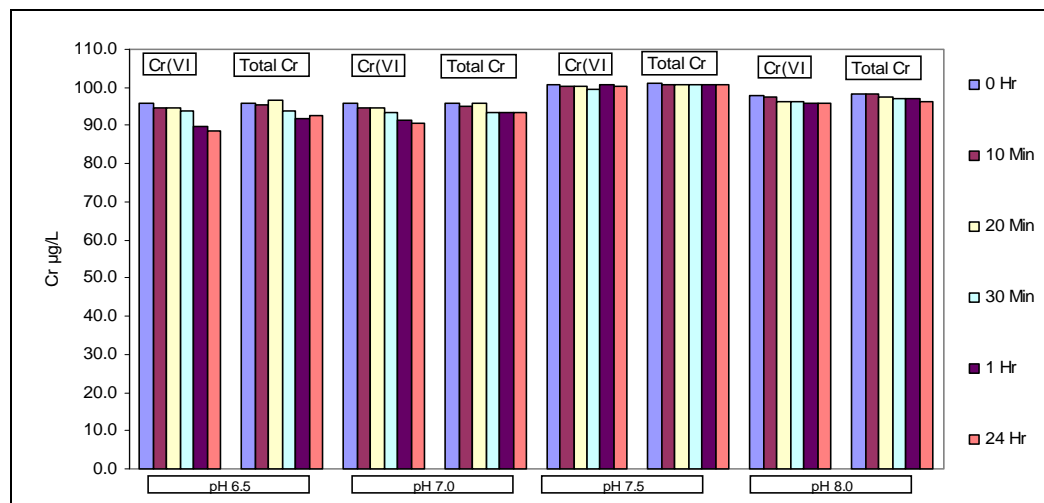
The distribution of Cr species clearly indicate that at pH values 4 to 5.5, the complexes Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$ are present and there was no precipitation and the dissolved Cr(III) concentration almost remained the same for the contact period of 24 hrs. At pH 5.5, about 5% of $\text{Cr}(\text{OH})_3^0$ species is present which means some precipitation took place. From pH 5.5 and above $\text{Cr}(\text{OH})_3^0$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3^0$ species are dominant. The distribution of $\text{Cr}(\text{OH})_3^0$ species is increased rapidly with increase in pH. So, the precipitation also increased rapidly above pH 5.5. At pH above 8 distribution of $\text{Cr}(\text{OH})_3^0$ species is about 98% based on the Figure 2-2. At pH 7 to 8, almost all Cr is present in the form of $\text{Cr}(\text{OH})_3^0$ species, so the most precipitation took place. From the Phreeqc calculation, it was found that from pH 5 and above Cr(III) precipitated as chromium hydroxide and chromium oxide. The saturation indices (SI) of the chromium hydroxide and chromium oxide were greater than zero. From the experiment it was found that the stability of Cr(III) pH dependent.

4.1.7 Stability of Cr(VI) as function of pH

The experiment was carried out to determine the stability of Cr(VI) as a function of pH. Objective of the experiment was to check whether Cr(VI) is stable or will reduce to Cr(III). The samples were taken at specified time and samples were analyzed for total Cr and Cr(VI). The experiment was run for 24 hrs. The experiment was conducted at pH 4, 5, 5.5, 6, 6.5, 7, 7.5 and 8. The results are presented in Figure 4-15 [A and B] and the detailed results are presented at the annex Table 14.



[A]



[B]

Figure 4-15: Stability of total Cr and Cr(VI) as a function of pH (model water with $c(\text{Cr(VI)}) = 100 \pm 5 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$); [A] pH = 4-6, [B] pH = 6.5-8.

The results obtained from the experiment confirmed that there was no significant reduction of Cr(VI) to Cr(III) as a function of pH and contact time. Therefore, it is concluded that Cr(VI) was stable as a function of pH and time.

4.2 Precipitate Particle Size Analysis

The experiment was carried out at pH 6, 7 and 8 to characterize precipitate particle size of Cr(III) in model water. The samples were filtered through 0.45 μm , 1 μm , 10 μm and 20-25 μm pore size filters (membrane and paper ones). The amount of Cr(III) retained in the filter was an indication of the size of the precipitated chromium.

4.2.1 pH 6

a) Cr(III) 100 concentration $\mu\text{g/L}$

Figure 4-16 shows size distribution of precipitated particles in model water with 100 $\mu\text{g/L}$ of Cr as a function of time. Initially ($t=0$ hr), there was no reduction of Cr(III) concentration in samples filtered through any pore size of filters. Gradually precipitation occurred and reduction of dissolved Cr(III) concentration took place. Detailed results are presented in the annex Table 15.

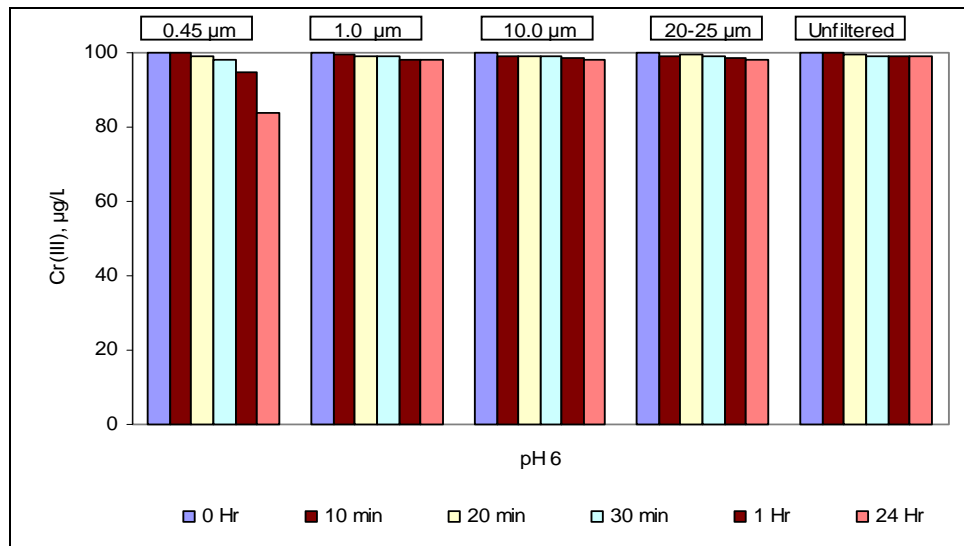


Figure 4-16: Size distribution of Cr(III) precipitated at pH 6 (model water with $c(\text{Cr(III)}) = 100 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$).

The retention of precipitate Cr(III) in filter paper corresponds to the size of the precipitate Cr(III) particles bigger than the pore size of filter paper. The retention of precipitate particles out of total dissolved Cr(III) concentration was 0% and 16% at 0 and 24 hrs contact time, respectively when filtered through 0.45 μm filter paper. Similarly, there was 2% retention when filtered through 1, 10 and 20-25 μm after 24 hrs contact time. So, it was found that there was less precipitation in the model water. About 16% precipitate particulates were bigger than 0.45 μm size during 24 hrs contact time.

b) Cr(III) Concentration 3.8 mg/L

Figure 4-17 shows size distribution of precipitated particles in model water with 3.8 mg/L of Cr(III) as a function of time. Detailed results are presented in the annex table 16.

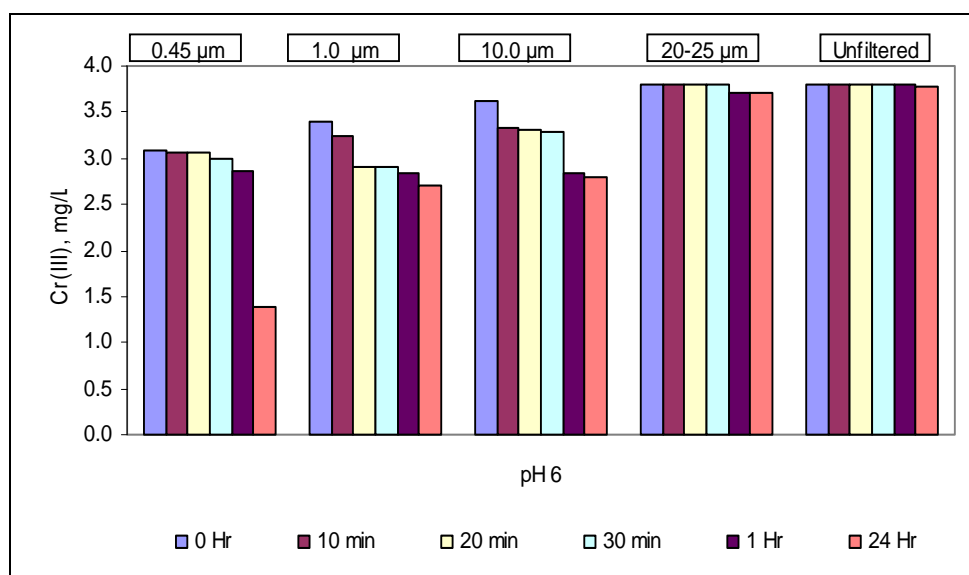


Figure 4-17: Size distribution of Cr(III) precipitated at pH 6 (model water with $c(\text{Cr(III)}) = 3.8 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$).

The samples were filtered through the $0.45 \mu\text{m}$ membrane filter paper, there was 19% and 63% retention out of total dissolved Cr(III) concentration at 0 and 24 hrs contact time respectively. Similarly, the samples were filtered through the 1, 10 and $20\text{-}25 \mu\text{m}$, there were retentions of 11%, 5% and 1% at 0 hr contact time and it was 29%, 26% and 8% after 24 hrs contact time, respectively.

At 3.80 mg/L Cr(III) concentration, 63% of the precipitated chromium particles were found to be bigger than $0.45 \mu\text{m}$ after 24 hour contact time. Similarly, at $100 \mu\text{g/L}$ Cr(III) concentration, there was less precipitation and all most all the Cr concentration found after filtered through any pore size of filters. It was found that higher the Cr(III) concentration higher the precipitation rate and greater the precipitate particles size.

4.2.2 pH 7

a) Cr(III) 100 concentration $\mu\text{g/L}$

Figure 4-18 shows size distribution of precipitated particles in model water with $100 \mu\text{g/L}$ of Cr(III) as a function of time. Initially ($t=0 \text{ hr}$), there was reduction of Cr(III) concentration in samples filtered through $0.45 \mu\text{m}$ and $1.0 \mu\text{m}$ pore size of filters. Gradually precipitation increase and reduction of dissolved Cr(III) concentration took place. Detailed results are presented in the annex Table 15.

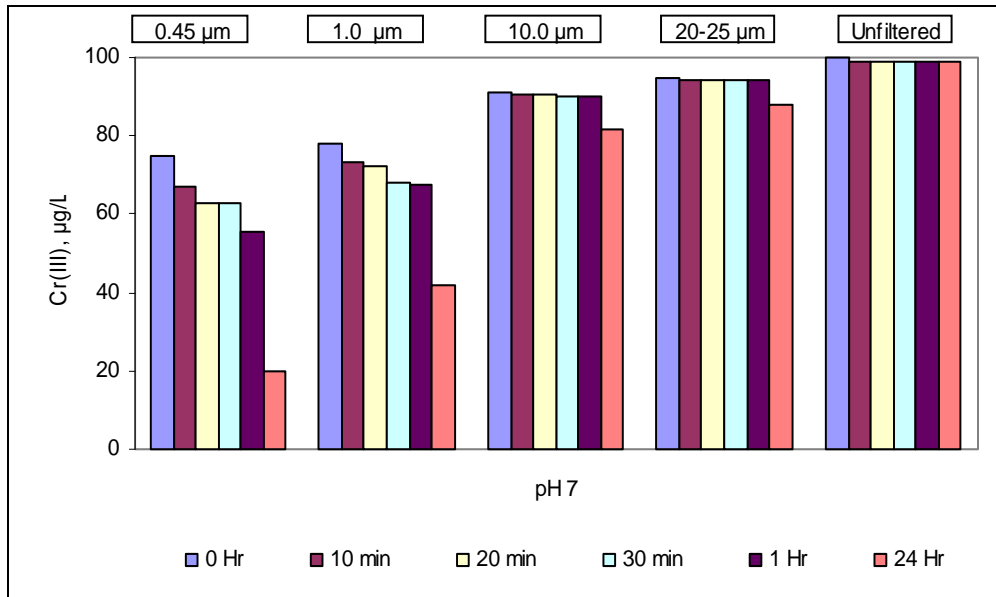


Figure 4-18: Size distribution of Cr (III) precipitated at pH 7 (model water with $c(\text{Cr(III)}) = 100 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$).

With the $0.45 \mu\text{m}$ filter paper, there was 25% and 80% retention of precipitate particles out of total dissolved Cr(III) at 0 and 24 hrs contact time. Hence the precipitated particles were bigger than $0.45 \mu\text{m}$. Similarly, the sample was filtered through 1, 10 and 20-25 μm filter papers, there were 22%, 9% and 5% retention of precipitate particles at 0 hr and for the same size of filter papers, the retention was 58%, 19% and 12% after 24 hrs contact time.

b) Cr(III) Concentration 3.8 mg/L

Figure 4-19 shows size distribution of precipitated particles in model water with 3.8 mg/L of Cr as a function of time. Detailed results are presented in the annex Table 16.

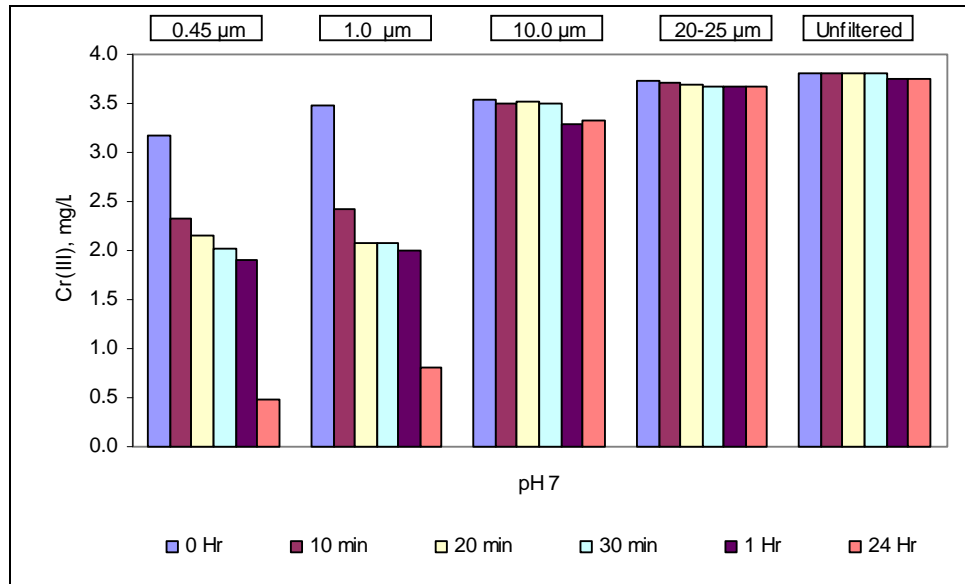


Figure 4-19: Size distribution of Cr (III) precipitated at pH 7 (model water with $c(\text{Cr(III)}) = 3.8 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$)

During the contact time 0 and 24 hrs, there was 17% and 87% retention of precipitate out of total dissolved Cr(III) filtered through 0.45 µm filter paper. Similarly, the samples were filtered through the 1.0 µm, 10 µm and 20-25 µm filter papers, there was 8%, 7% and 0% retention at 0 hr and for the same size of filter papers, and the retention was 79%, 13% and 3% after 24 hrs contact time respectively.

Hence, for both the Cr(III) concentration, longer the contact time greater the precipitate particle size was observed and most of the precipitate particle size was bigger than 1 µm so about 79% of the precipitate particle was retained in filter paper of 1 µm size during 24 hr contact time.

4.2.3 pH 8

a) Cr(III) 100 concentration µg/L

Figure 4-20 shows size distribution of precipitated particles in model water with 100 µg/L of Cr as a function of time. Initially ($t=0 \text{ hr}$), there was reduction of Cr(III) concentration in samples filtered through 0.45µm and 1.0 µm pore size of filters. Detailed results are presented in the annex Table 15.

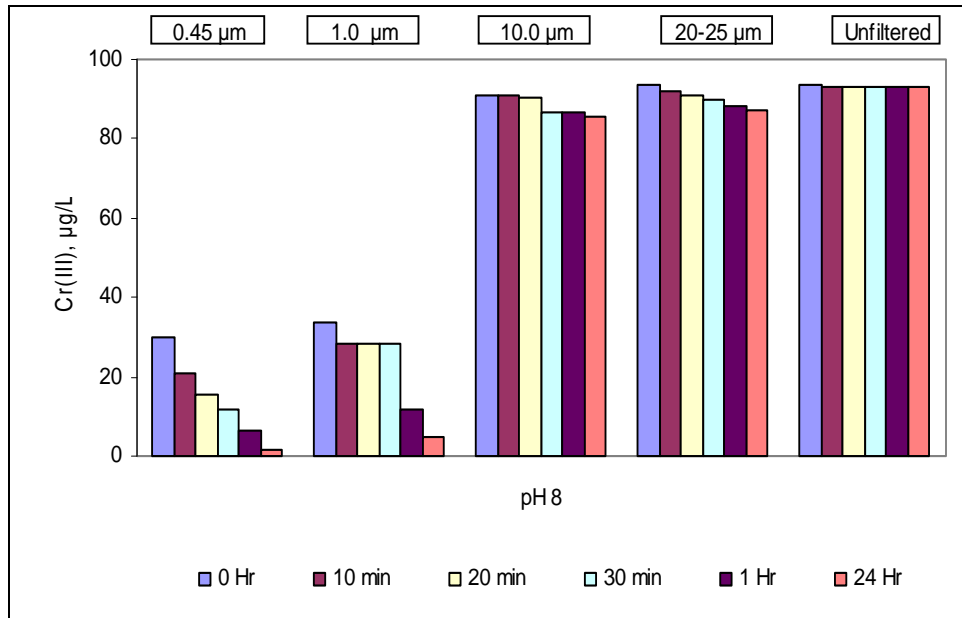


Figure 4-20: Size distribution of Cr (III) precipitated at pH 8 (model water with $c(\text{Cr(III)}) = 100 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$).

There was 68% and 98% of retention when filtered through 0.45 μm size filter paper at 0 and 24 hrs contact time respectively. Furthermore, the samples were filtered through 1.0 μm , 10 μm and 20-25 μm size filter papers, there were 66%, 9% and 6.5% retention at 0 hr contact time, respectively. Similarly, there were 95%, 14.5% and 13% retention after 24 hrs contact time.

b) Cr(III) Concentration 3.8 mg/L

Figure 4-21 shows size distribution of precipitated particles in model water with 3.8 mg/L of Cr as a function of time. Detailed results are presented in the annex Table 16.

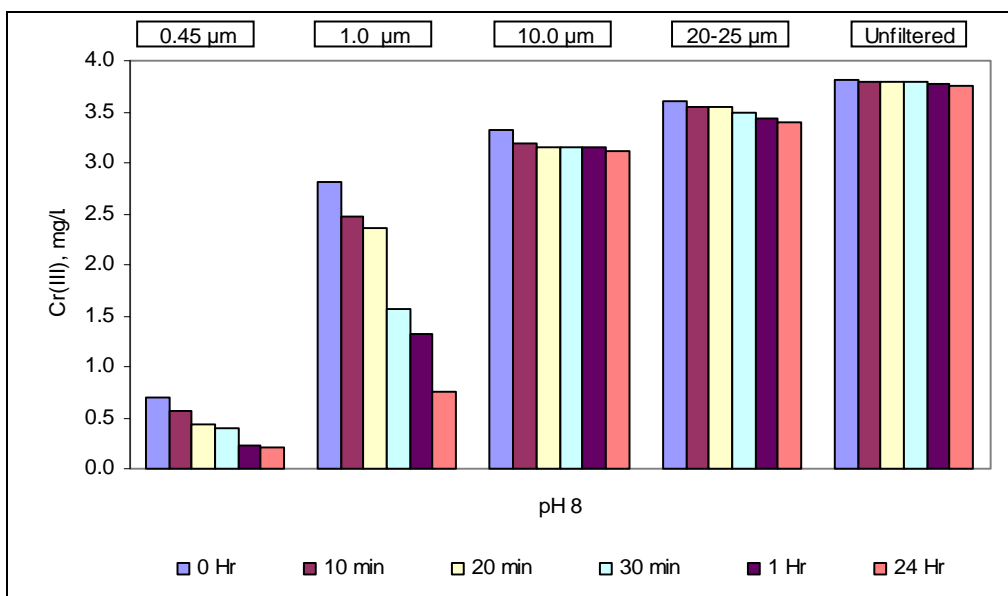


Figure 4-21: Size distribution of Cr(III) precipitated at pH 8 (model water with $c(\text{Cr(III)}) = 3.8 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$)

The samples were filtered through the $0.45 \mu\text{m}$ size filter paper. There was 81% and 95% retention at 0 and 24 hrs contact time. Furthermore, the samples were filtered through the $1.0 \mu\text{m}$, $10 \mu\text{m}$ and $20\text{-}25 \mu\text{m}$ size filter papers, there were 27%, 12% and 5% at 0 hr contact time. Similarly 80%, 18% and 11% retention after 24 hrs contact time, respectively. Initially precipitate particles was retained in $0.45 \mu\text{m}$ filter paper and gradually with the increase in contact time the precipitate particles size also increased and retained in $1 \mu\text{m}$ filter size after 24 hrs contact time. Hence, about 80% of precipitate particles were bigger than $1 \mu\text{m}$ size.

The reduction of dissolved Cr(III) indicated the formation of precipitate particulate in the model water and the precipitate particles were retained in any size of filter papers. The difference in retention of Cr(III) at pH 6, 7 and 8 in the filter paper was due to the model water pH influenced the distribution of precipitate particle size of Cr(III). Increasing pH implied a proportional increase in the concentration of hydroxide ions $[\text{OH}^-]$ in the solution. So, precipitation particle was greater at pH 7 and 8 as compared to pH 6. It was concluded that higher the pH and longer the contact time greater the precipitated particles size in the model water.

4.3 Adsorption Experiments

Adsorption experiments were conducted to determine the removal capacity of IOCS for both species of chromium. The experiments were carried out with the varying dosages of IOCS and as a function of pH. Furthermore, the adsorption experiment was done also with virgin quartz sand for the removal of Cr(III) to evaluate the adsorption capacity.

4.3.1 Adsorption of Cr(III) as a function of IOCS concentration

The effect of the adsorbent dosages on adsorption of Cr(III) was studied by varying IOCS dosages of 0.4, 0.6, 0.8, 1 and 1.2 mg/L in model water. Sample was taken at 0.5, 2, 6 and 24

hrs. The results are presented in Figure 4-22 and the detailed results are presented in the annex Table 17.

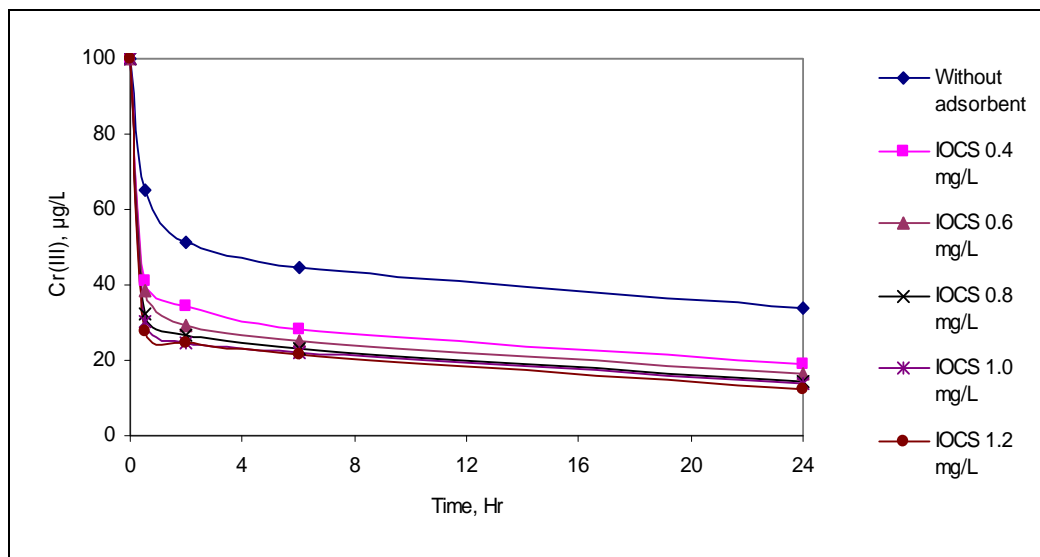


Figure 4-22: Removal kinetics of Cr (III) as a function of IOCS concentration (model water with $c(\text{Cr(III)}) = 100 \pm 5 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, $\text{pH} = 7$).

After 0.5, the reduction of Cr(III) was 59%, 62%, 68%, 70 and 72% in IOCS dosage 0.4, 0.6, 0.8, 1 and 1.2 mg/L respectively. Similarly the reduction was 81%, 83%, 85%, 86% to 88% after 24 hrs. In the blank bottles, 35% and 66% reduction of dissolved Cr(III) concentration was observed after 0.5 and 24 hrs contact time respectively. The reduction of dissolved Cr(III) concentration in the blank polyethylene (PE) bottle indicates that the precipitation took place in model water. The difference of Cr(III) concentration in blank and IOCS containing PE bottles gave the actual adsorption of Cr(III) as a function of IOCS dosages. For the initial concentration of $100 \mu\text{g/L}$, the net uptake of Cr(III) varied from 15, 18, 19, 20 and 22 μg for adsorbents doses of 0.4, 0.6, 0.8, 1 and 1.2 mg/L during 24 contact time. The adsorption is higher in higher dosage of IOCS. The increase in adsorption with increased IOCS dose can be attributed to the increase in surface area and availability of more binding sites for adsorption. It is concluded that the rate of Cr(III) binding with adsorbent was greater at the initial 30 min contact time, then gradually decreased for 24 hrs contact time. There was no significant change in Cr(III) concentration after 6 hr.

At pH 7, Cr(OH)^{2+} , Cr(OH)_2^+ and Cr(OH)_3^0 species were presented among these Cr(III) species Cr(OH)^{2+} and Cr(OH)_2^+ species were likely adsorbed by IOCS.

4.3.2 Adsorption of Cr(III) on IOCS as a function of pH

Additional batch experiment was carried out as a function of pH. The effect of pH for the adsorption of Cr(III) was studied with IOCS adsorbent in model water. The results are presented in Figure 4-23 and the detailed results are presented in the annex Table 18.

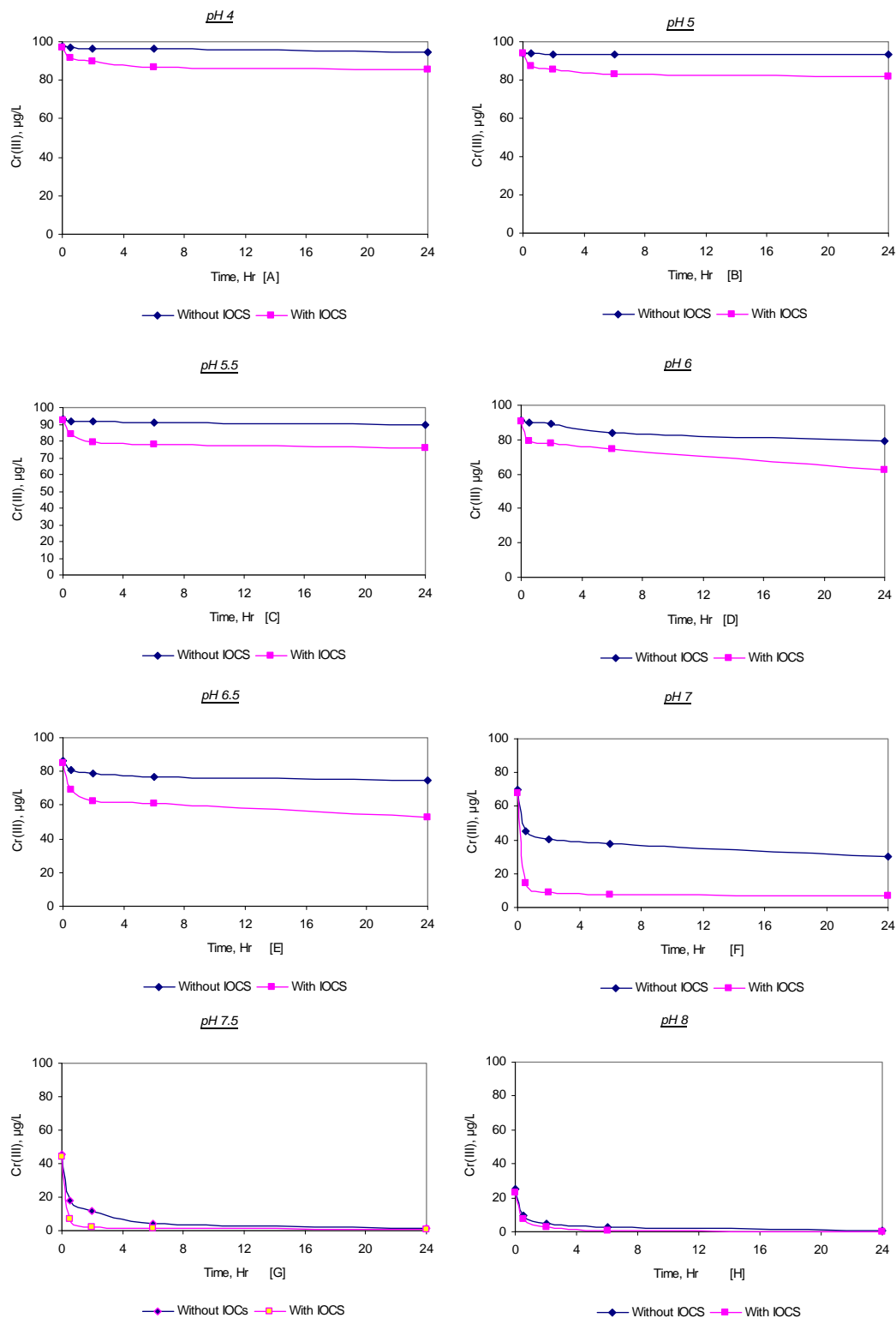


Figure 4-23: Removal kinetics of Cr(III) on IOCS as function of pH (model water with $c(\text{Cr(III)}) = 100 \pm 5 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, $c(\text{IOCS}) = 1 \text{ mg/L}$); [A] pH = 4, [B] pH = 5, [C] pH = 5.5, [D] pH = 6, [E] pH = 6.5, [F] pH = 7, [G] pH = 7.5, [H] pH = 8.

The reduction of the Cr(III) concentration at 0.5, 2, 4, 6 and 24 hrs was observed. For the initial concentration of 100 µg/L, the net uptake of Cr(III) was 13, 14, 15, 16, 17, 18, 0 and 0 µg at pH 4, 5, 5.5, 6, 6.5, 7, 7.5 and 8 for an adsorbent IOCS dose 1 mg/L during 24 hrs contact time. The removal of Cr(III) by adsorb is dependent on pH of the model water. The higher pH adsorption and precipitation was obtained. Higher the pH values higher the precipitation. The most intensive adsorption took place within first hrs at all pH. There was no significant change in Cr(III) concentration after 6 to 24 hrs. As it is shown, adsorption rate initially increased rapidly, and the optimum removal efficiency was observed within 30 minutes. From this result it is concluded that the adsorption and precipitation of Cr(III) took place in the model water. So, the total Cr(III) concentration was reduced during 24 hrs contact time.

At pH 4 to 6.0, the complexes Cr^{+3} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$ were present and these species were likely adsorbed by IOCS. At pH 6 to 8, the species $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}(\text{OH})_3^0$ species were present and among these species $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})_2^+$ species likely adsorbed by IOCS. At slightly acidic and basic pH, the $\text{Cr}(\text{OH})_3^0$ species is dominant. Formation of $\text{Cr}(\text{OH})_3^0$ insoluble precipitate particulates enhanced the reduction of dissolved chromium concentration in model water. At low pH, the adsorption took place and the slightly acidic to basic pH both adsorption and precipitation took place. Longer the contact time more the adsorption and precipitation took place. The removal of Cr(III) was effective at high pH as compared to lower pH.

Ghaffar A. (2005) stated that the removal of Cr(III) by adsorbents is highly dependent on the pH of the solution which affects the surface charge of the adsorbents, degree of ionization and speciation of adsorbent. The difference in removal efficiency due to the solution pH could be, however attributed to precipitation of chromium hydroxide $\text{Cr}(\text{OH})_3^0$ at the higher pH. Increasing the pH implied a promotional increasing in OH^- ions concentration in solution.

4.3.3 Adsorption of Cr(III) on Quartz Sand

Another additional batch experiment was carried out to evaluate the adsorptive capacity of quartz sand. The model water was prepared with demineralised and tap water in the laboratory. Cr(III) 100 µg/L was properly mixed with demineralised water at pH 5.5. Similarly, tap water pH adjusted to 6 with HCl and added Cr(III) 100 µg/L. In the model water pH was adjusted to prevent chromium precipitation. The adsorbent dosage on adsorption of Cr(III) was studied by dosing virgin quartz sand 10 g/L in model water. After 48 hrs contact time, the results indicated that a 16% of the dissolved Cr(III) in the blank precipitated (98 µg/L to 82 µg/L) measured as total chromium at pH 5.5 and 6. The results are presented in Figure 4-24 and Figure 4-25 and the detailed results are presented in the annex Table 19.

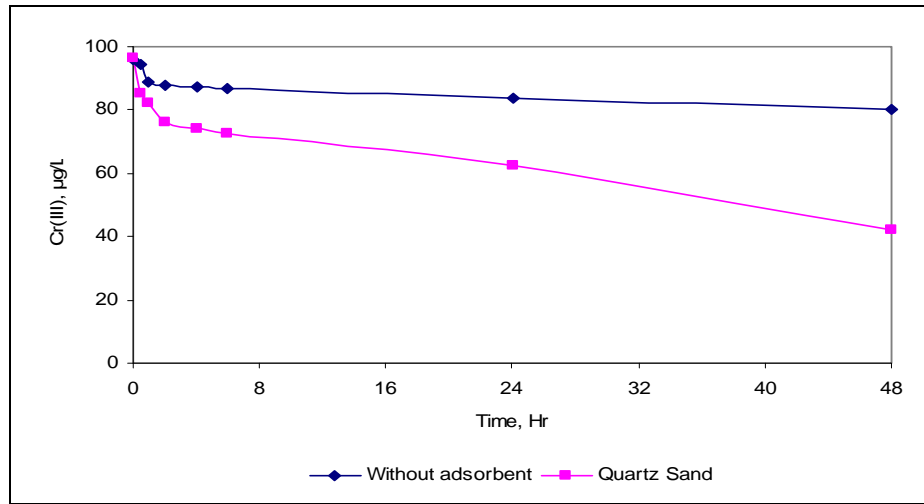


Figure 4-24: Removal kinetics of Cr(III) with quartz sand (model water with $c(\text{Cr(III)}) = 100 \pm 5 \mu\text{g/L}$, initial pH = 5.5, quartz sand dose = 10 mg/L).

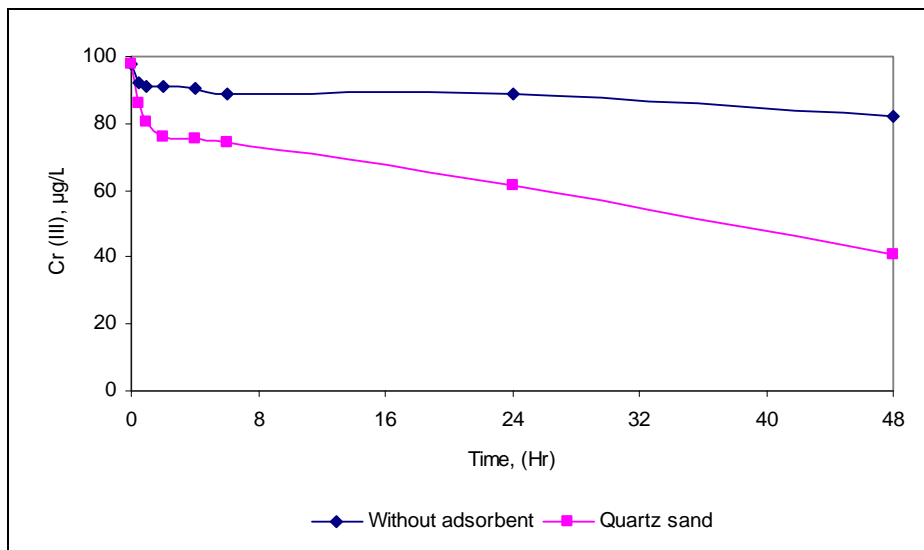


Figure 4-25: Removal kinetics of Cr(III) with quartz sand (model water with $c(\text{Cr(III)}) = 100 \pm 5 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 55 \text{ mg/L}$, $c(\text{HCO}_3^-) = 125 \text{ mg/L}$, initial pH = 6, quartz sand dose = 10 mg/L).

The reduction of Cr(III) concentration was observed during 48 hrs contact time. After 0.5 hr contact time, Cr(III) decreased 97 $\mu\text{g/L}$ to 85.5 mg/L which is 11% removal at pH 5.5. After 48 hrs, Cr decreased 42 $\mu\text{g/L}$, which is 57% removal. At pH 6.0, Cr(III) decreased 98 $\mu\text{g/L}$ to 86 $\mu\text{g/L}$ which is 12% removal. Similarly after 48 hrs, Cr decreased 41 $\mu\text{g/L}$, which is 58% removal.

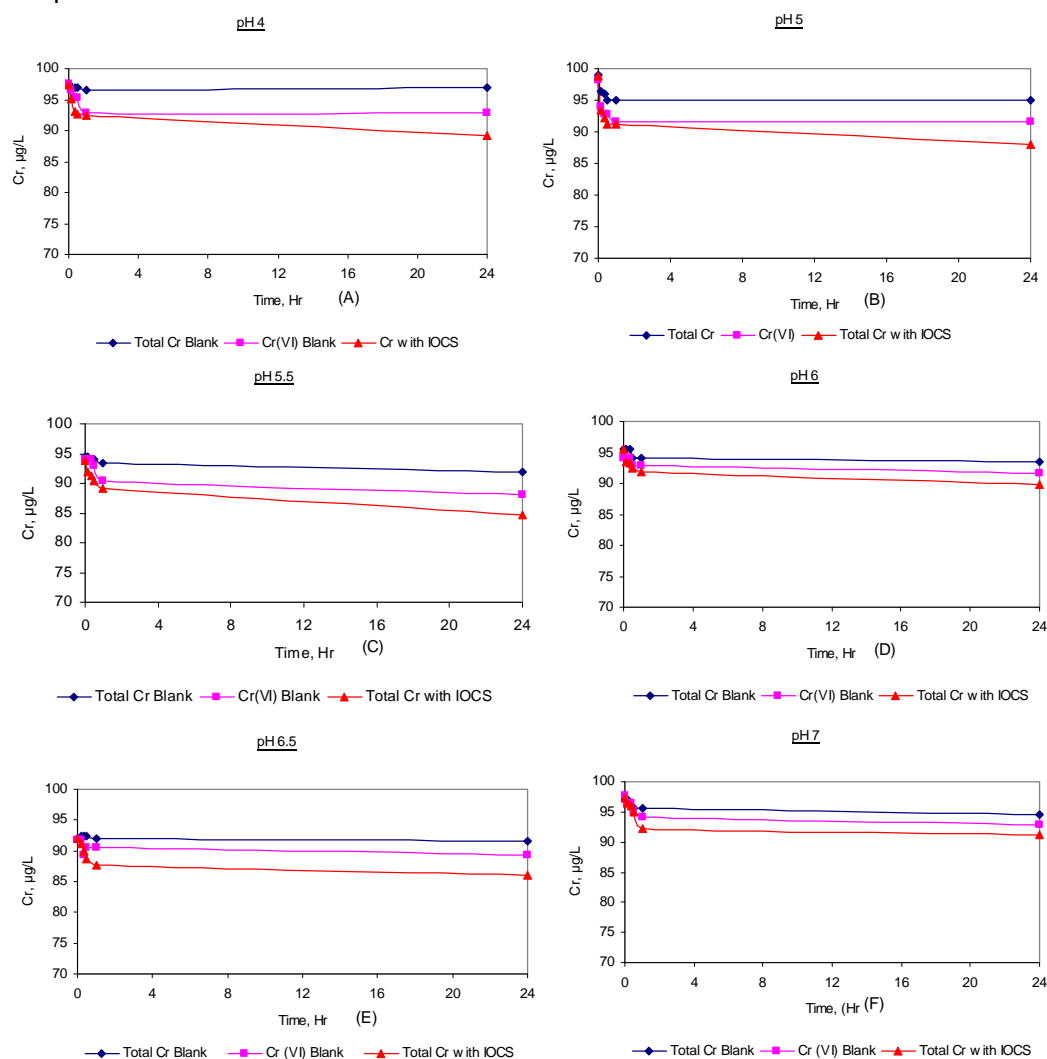
The effect of contact time on Cr(III) adsorption efficiency was observed from the experiment. Adsorption gradually increased, and the optimum removal efficiency achieved during 48 hrs contact time. It is concluded that the adsorption of Cr(III) took place on quartz

sand and the total Cr(III) concentration has been considerably reduced during 48 hrs contact time.

At pH 5.5 and 6, Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, and $\text{Cr}(\text{OH})_3^0$ species are present and among these Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})_2^+$ species are likely adsorbed by quartz sand. The adsorption of Cr(III) can be explained on the basis of negatively charge of quartz sand and Cr(III) positively charged species. The electrostatic attraction consequently enhances the removal of Cr(III) species. So, the quartz sand adsorbs the positively charged Cr(III) species and there is a reduction of Cr(III) concentrations in model water.

4.3.4 Adsorption of Cr(VI) on IOCS

Batch experiment was carried out in the laboratory as a function of pH (i.e. pH 4, 5, 5.5, 6, 6.5, 7, 7.5 and 8) to evaluate the removal efficiency of Cr(VI) by IOCS. To monitor the stability of Cr(VI) in the model water, one blank PE bottle was kept without adsorbent IOCS in each pH values. The results are presented in Figure 4-26 and the detailed results are presented in the annex table 20.



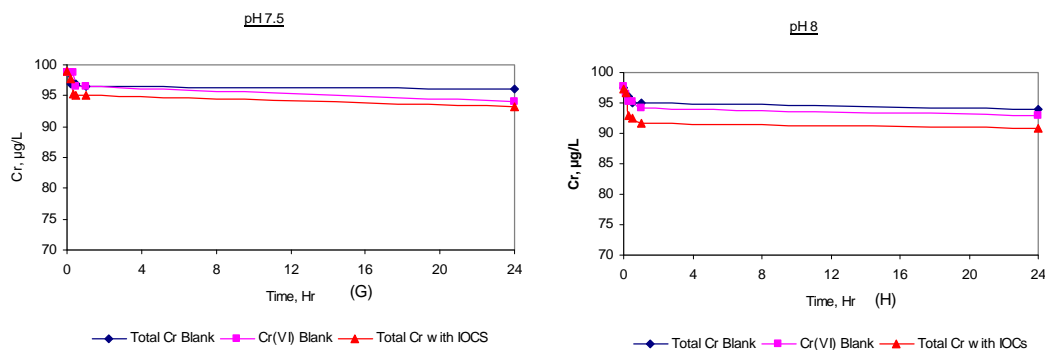


Figure 4-26: Removal kinetics of Cr(VI) as function of pH (model water with $c(\text{Cr(VI)}) = 100 \pm 5 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, $c(\text{IOCS}) = 1 \text{ mg/L}$); [A] pH = 4, [B] pH = 5, [C] pH = 5.5, [D] pH = 6, [E] pH = 6.5, [F] pH = 7, [G] pH = 7.5, [H] pH = 8.

Influence of pH in model water

There was 10%, 11%, 10%, 7%, 6%, 6% 6% and 6% reduction of Cr(VI) concentration at pH 4, 5, 5.5, 6, 6.5, 7, 7.5 and 8 respectively during 24 hrs contact time. From this experiment, it was found that there was decreased in adsorption rate of Cr(VI) with an increase in pH of the model water.

Mor et al., (2002), reported that the pH dependence of metal adsorption can largely be related to type and ionic state of the functional group present in the adsorbent. Higher adsorption of Cr(VI) on IOCS at low pH be explained by present species of Cr and charge of adsorbent surface. At acidic pH, the predominant species of Cr are $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, and $\text{Cr}_4\text{O}_{13}^{2-}$. Decreasing pH results in the formation of more Cr oxide species. On the other hand, under acidic conditions, the surface of the adsorbent become highly protonated and favours the uptake of Cr(VI) in the anionic form. With an increase in pH, the degree of protonation of the surfaces reduced gradually and hence, adsorption is decreased. Furthermore, as pH increases, there is competition between OH^- and chromate ions (CrO_4^{2-}), the former being the dominant species at higher pH values.

The high pH value causes a reduction in the electrostatic attraction between the negatively charged chromium ions and positively charged adsorbents surfaces, therefore, less efficient removal was found at high pH.

4.4 Column Filtration Experiments

After conducting several experiments on chromium stability, precipitate particle's size analysis and adsorption, it was concluded the necessity of performing the filtration experiments in order to verify the results obtained in batch experiments. During batch experiments design to examine stability of Cr(III) in solution, Cr(III) was precipitate above pH 6 found in the model water. In order to verify removal of Cr(III) by precipitation and adsorption processes, the filtration experiments were conducted by using small scale laboratory filter column with quartz sand media. The filtration experiments were conducted for Cr(III) at pH 6, 7 and 8. For Cr(VI), chemical reduction of Cr(VI) to Cr(III) was carried out by dosing the Fe(II) solution, and the pH of the feed water was raised by adding the NaOH solution. The experiments with Cr(VI) were conducted at pH 7 and 8.

4.4.1 Filtration of Cr(III)

Filtration experiments were carried out in the laboratory at pH 6, 7 and 8. The filter was run 8 hr per day during three days and back washed by the Delft tap water and again filter was continuous for 2 days. After 8 hr run, every day the filter was stopped and again another day filter was re-started. Fresh model water was prepared every 1.5 hr. The purpose of making fresh model water was to prevent the formation of Cr(III) precipitated particles in the model water. The empty bed contact time was 2.4 min. The results are presented in Figure 4-27 and the detailed results are presented at the annex Table 21.

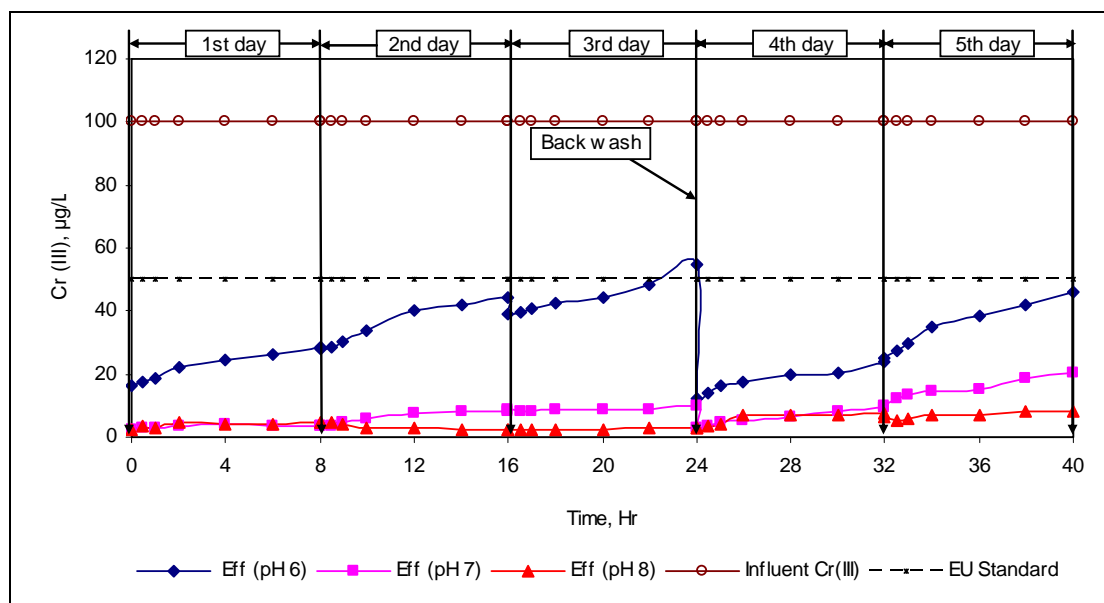


Figure 4-27: Removal of Cr(III) with quartz sand as a function of pH (model water with $c(\text{Cr (III)}) = 100 \pm 5 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, filtration rate (V_f) = 5 m/hr, Media depth = 20 cm).

Effect of pH on Filter Media

At pH 6, initially the removal efficiency of Cr(III) was 83% and 45% after three days (24 hrs) of filter operation. After 22 hrs of continuous filter run, the break through was observed and the Cr(III) particles escaped through media. After three days run of filter, media was back washed by the tap water and again, run for two days. After back washing, initially the removal efficiency of Cr(III) showed 88% and 54% during 16 hrs filter operation.

At pH 7, initially the removal efficiency of Cr(III) was 98 and 90% after three days (24 hrs) filter operation. Gradually head loss increased and filter media was back washed after 24 hrs filter operation. After back washing the filtered media showed the removal efficiencies of 97% at the beginning and 80% during 16 hr filter operation. Due to continuous filter operation, the flocs blocked the pore of the filter media and gradually head loss was increased. Due head loss increase, the Cr(III) particles started to escape through the media so the efficiency reduced gradually.

At pH 8, initially Cr(III) removal efficiencies was 98% and 92% after three days filter operation. After 16 hrs run, the head loss increased and back washing was done after 24 hrs

filter operation. After back washing, initially the removal efficiency was 98% and 90% at 16 hrs filter operation.

From the experiment, it was found that the removal efficiencies of Cr(III) was higher at pH 7 and 8 as compared to pH 6. The pH played an important role for Cr(III) removal through filtration those small laboratory filters equipped with quartz sand media. At pH 7 and 8, the formation of chromium hydroxide $[\text{Cr}(\text{OH})_3^0]$ precipitate more pronounced so the removal efficiencies were found to be higher. From the Chromium speciation diagram, it is found that $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$ and $\text{Cr}(\text{OH})_3^0$ are present at pH 6, 7 and 8. Increasing the pH implies a proportional increase in concentration of hydroxide ions $[\text{OH}^-]$ in model water and precipitating rate is high in higher pH. It is concluded that the quartz sand filter media of size 0.5 to 1.0 mm is very effective and efficient for the removal of Cr(III) from the water and wastewater at pH 7 and 8 at flow rate 5 m/hr. Baig et al. (2003) reported that sand filters are very effective in removing chromium from waste water even with very high concentration e. g. 250 mg/L.

The batch adsorption experiment also showed the quartz sand media had ability to adsorb Cr(III) species from the model water. So, the filtration experiment showed the quartz sand media has ability to remove the Cr(III) through both filtration and adsorption from the model water.

Mass Balance of Cr(III) in Filter Run with Quartz Sand Media

Removal of Cr(III) can be partly due to the adsorption and Cr precipitates flocs formed trapped in the filter column. At the end of 3 days filter run, the filtration column was back washed with Delft tap water. The back washing was done at higher flow velocity to ensure the removal of all flocs which trapped into the quartz sand column. The back washed water was collected in the clean vessels and mixed properly to obtain homogeneous solution. About 16 ml of sample was taken from the homogeneously mixed vessel and acidified with concentrated hydrochloric acid. The Cr precipitates were consequently dissolved and then the samples were analyzed for the total chromium content in the back washed water. The summary of the calculation of Cr content are shown in Table 7:

Table 7: Summary of the calculation of Cr content at pH 6, 7 and 8

Description	Unit	Mass (pH 6)	Mass (pH 7)	Mass (pH 8)
Total inflow of chromium	µg	3052.7	3052.8	3052.8
Total outflow via filtrate	µg	1090.4 (35.7%)	399.9 (13.1%)	98.8 (3.2%)
Total chromium removed in the system	µg	1962.4 (64.3%)	2652.9 (86.9%)	2954.0 (96.8%)
Chromium recovered from back wash	µg	763.1 (22%)	1789.9 (58.6%)	2278.4 (74.6%)
Removal of chromium through adsorption	µg	1090.8 (35.7%)	863.0 (28.3%)	675.6 (22.1%)

Mass balance of pH 6, 7 and 8 results showed the removal of total Cr(III) precipitation and adsorption. The results showed the very good removal capacity of Cr(III) by the rapid sand

filtration. The recovery of Cr(III) from the back wash was lower at lower pH and the adsorption rate was decreased with increase in pH. It was found that the Cr(III) removed by adsorption and precipitation of $\text{Cr}(\text{OH})_3^0$.

4.4.2 Chemical Reduction of Cr(VI) by using Fe(II) and Filtration Through Quartz Sand Media

From the batch adsorption experiments, it is found that the removal capacity of IOCS for Cr(VI) was not satisfactory as compared to that for Cr(III). Consequently, the reduction of Cr(VI) into its trivalent form, Cr(III) could possibly improve Cr(VI) removal. Filtration experiment was carried out in laboratory to evaluate Cr(VI) removal efficiency through reduction with Fe(II) and filtration through laboratory filter with virgin quartz sand media.

4.4.2.1 Filter Media of Depth 20 cm at pH 7

Filter was run 8 hrs per day during two days. After 8 hrs operation of filter, the filter was stopped and again next day filter was re-started. Feed water containing Cr(VI) and Cr(III) solutions were prepared every day to feed the filter media. Similarly, every day the fresh Fe(II) solution was prepared. The concentration of Fe(II) stock solution was 200 mg/L and dosage was 2.3 mg/L. The pH of the Fe(II) solution was maintained about 1.44 to achieve the feed water pH 7. The empty bed contact time was 2.4 minute. The effluent samples (filtered through quartz sand) were collected at a specified time. Half of the samples were filtered through 0.45 μm membrane filter to separate precipitate particles and the remaining half of the samples were kept without filtration. The results are presented in Figure 4-28 and Figure 4-29 and the detailed results are presented at the annex Table 22.

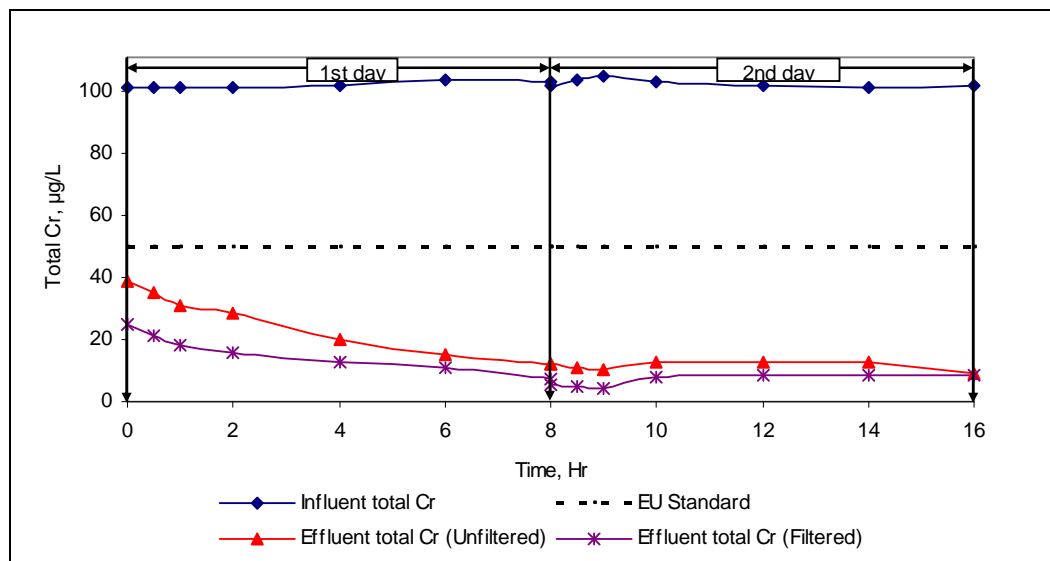


Figure 4-28: Removal of Cr(III) and Cr(VI) through quartz sand filter media (model water with total $c(\text{Cr}) = 100 \pm 5 \mu\text{g/L}$ ($\text{Cr}(\text{III}) = 50 \mu\text{g/L}$ & $\text{Cr}(\text{VI}) = 50 \mu\text{g/L}$), $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, $\text{Fe}(\text{II}) = 2.3 \text{ mg/L}$, media depth = 20 cm, EBCT = 2.4 min, $\text{pH} = 7 \pm 0.1$).

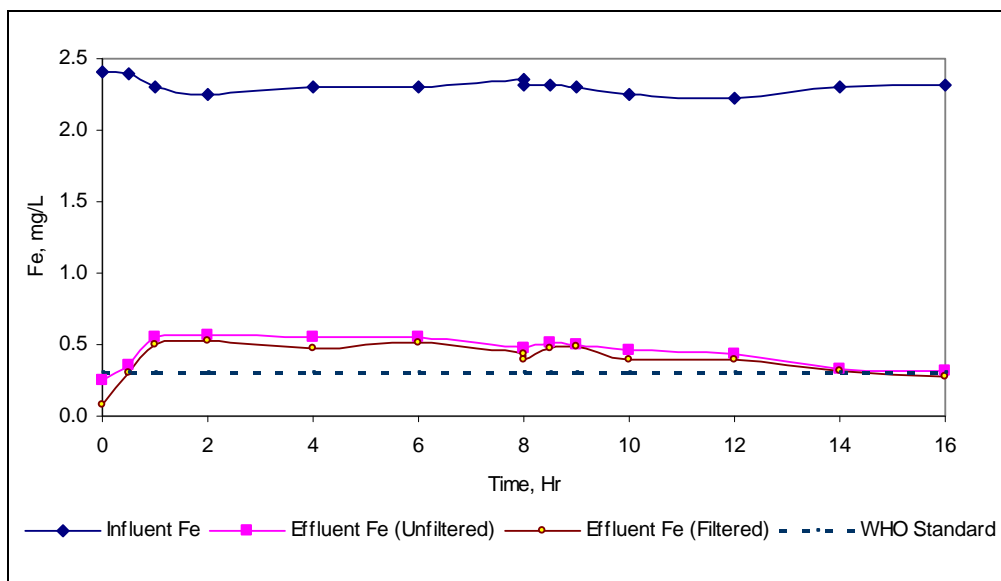


Figure 4-29: Removal of Fe through quartz sand filter media (model water with total $c(\text{Cr}) = 100 \pm 5 \mu\text{g/L}$ ($\text{Cr}(\text{III}) = 50 \mu\text{g/L}$ & $\text{Cr}(\text{VI}) = 50 \mu\text{g/L}$), $\text{Fe}(\text{II}) = 2.3 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, media depth = 20 cm, EBCT = 2.4 min, $\text{pH} = 7 \pm 0.1$).

Removal efficiencies of total chromium were found to be 61% to 91% during 16 hrs filter operation. At the beginning of filter run, the removal efficiency of total chromium was low and it increased with filter run time. The effect of filter operation time on Cr removal was also observed. At the beginning of filter run chromium particles partially escaped through the media and after 6 hrs operation of filter, the removal efficiency was reached to 85%. The precipitate Cr particles blocked the pores of the filter media and the efficiency increased gradually.

It was found that the $\text{Fe}(\text{II})$ efficiently reduced the $\text{Cr}(\text{VI})$ to $\text{Cr}(\text{III})$. The influent and effluent samples, there was no measurable $\text{Cr}(\text{VI})$. The increase in filter operation time increased the efficiency of the media for the removal of both Fe and total chromium. The quartz sand media showed the capacity to remove the total chromium.

Mass Balance of Total Chromium and Iron in Filter Run with Quartz Sand Media

At the end of 2 days filter run, the filtration column was back washed with tap water. The back washing was done at higher flow velocity to ensure the removal of all flocs which trapped into the quartz sand column. The samples were analyzed for the total chromium and iron content in the back washed water. The summary of the calculation of $\text{Cr}(\text{III})$ and Fe content are shown in Tables 8 and 9.

Table 8: Summary of the calculation of Cr content at pH 7

Description	Unit	Mass
Total inflow of chromium	µg	23112.7
Total outflow via filtrate	µg	3812 (16.80%)
Total chromium removed in the system	µg	19300 (83.5%)
Chromium recovered from back wash	µg	11250 (48.7%)
Removal of chromium through adsorption	µg	8050 (34.8%)

Table 9: Summary of the calculation of Fe content at pH 7

Description	Unit	Mass
Total inflow of Fe	mg	517
Total outflow via Fe	mg	46 (9.0%)
Total iron removed in the system	mg	471 (91.0%)
Iron recovered from back wash	mg	53 (10.2%)
Removal of iron through adsorption	mg	359 (69.4%)

4.4.2.2 Filter Media of Bed Depth 40 cm at pH 7

Experiment was done with filter media depth 40 cm instead of 20 cm applied in the previous experiment. The filter was operated 8 hrs per day during 3 days. For the measurement of total Cr, Fe and turbidity, influent and effluent samples were collected at specified time. The results are presented in Figure 4-30, Figure 4-31 and Figure 4-32 and the detailed results are presented at the annex Tables 23 and 24.

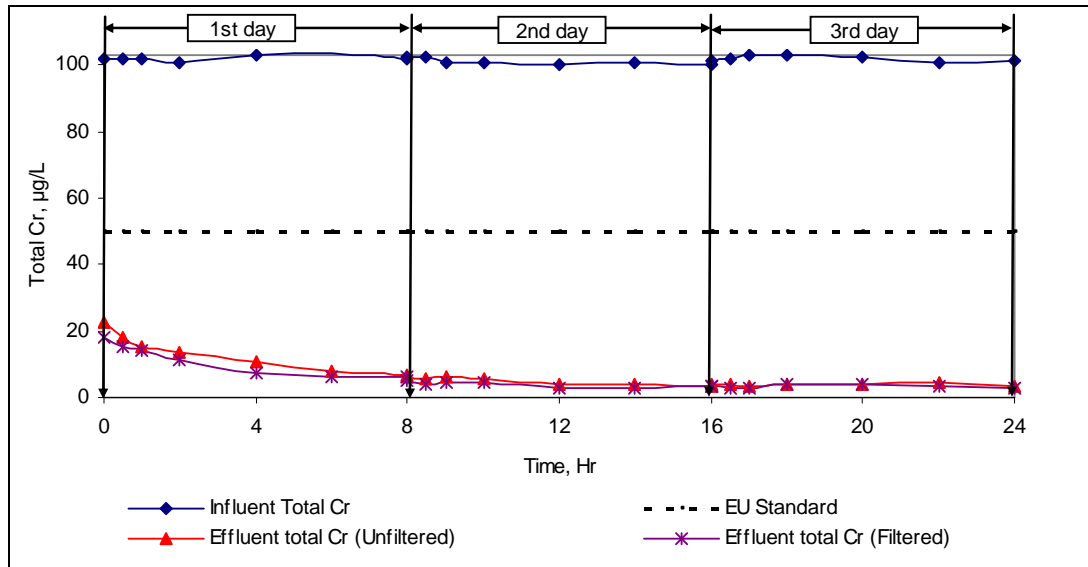


Figure 4-30: Removal of total Cr through quartz sand filter media (model water with total $c(\text{Cr}) = 100 \pm 5 \mu\text{g/L}$, $(\text{Cr}(\text{III}) = 50 \mu\text{g/L}$ and $\text{Cr}(\text{VI}) = 50 \mu\text{g/L}$), $\text{Fe}(\text{II}) = 2.3 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, media depth = 40 cm, EBCT = 4.8 min, $\text{pH} = 7 \pm 0.1$).

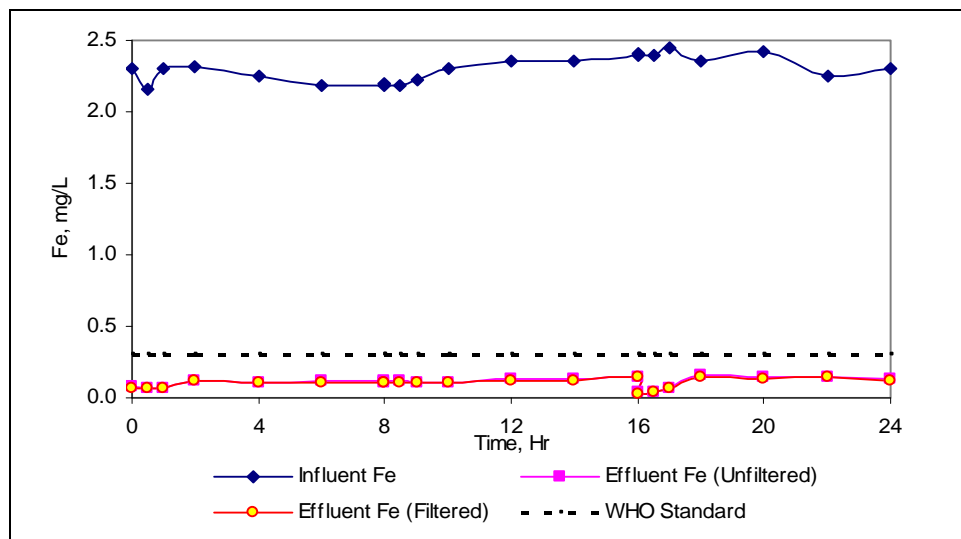


Figure 4-31: Removal of Fe through quartz sand filter media (model water with total $c(\text{Cr}) = 100 \pm 5 \mu\text{g/L}$ ($\text{Cr}(\text{III}) = 50 \mu\text{g/L}$ & $\text{Cr}(\text{VI}) = 50 \mu\text{g/L}$), $\text{Fe}(\text{II}) = 2.3 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, media depth = 40 cm, EBCT = 4.8 min, $\text{pH} = 7 \pm 0.1$).

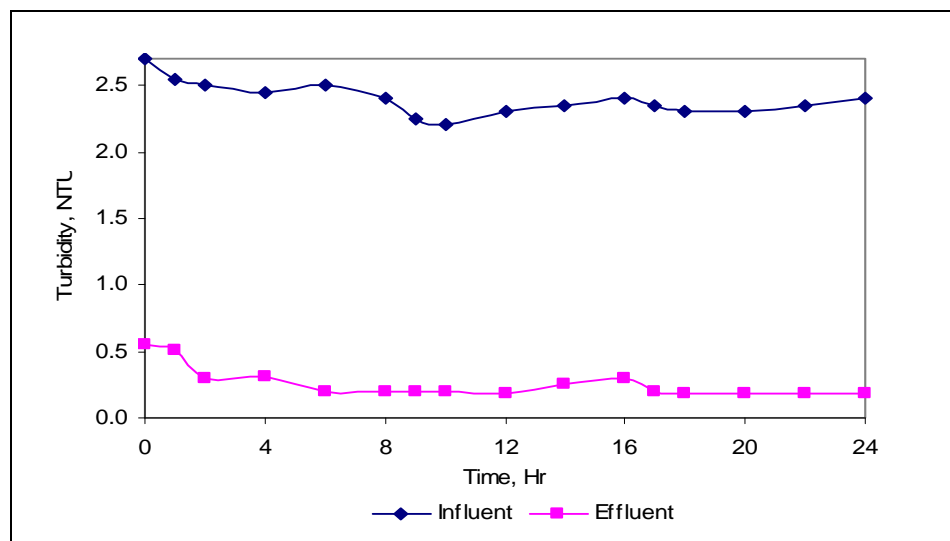


Figure 4-32: Reduction of turbidity through quartz filter sand media (model water with total $c(\text{Cr}) = 100 \pm 5 \mu\text{g/L}$ ($\text{Cr(III)} = 50 \mu\text{g/L}$ & $\text{Cr(VI)} = 50 \mu\text{g/L}$), $\text{Fe(II)} = 2.3 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, media depth = 40 cm, EBCT = 4.8 min, $\text{pH} = 7 \pm 0.1$).

The removal efficiencies of total Cr was 80% to 95.5% during three days (24 hrs) of filter operation. At the beginning of filter run, the removal efficiency of total Cr was less and with the increase in filter operation time the filter efficiency increased gradually. At the beginning of filter operation, the chromium fine particles partially escaped through the media and after 4 hrs of filter operation, the removal efficiency was to 92.5%. So, the precipitated particles blocked the pores of the filter media and the efficiency increased gradually with increase in filter operation time. The removal efficiency of Cr(III) was greater as compared to 20 cm media depth. Higher depth of media allowed more contact time hence the removal of the Cr(III) and Fe was greater.

It is found that the Fe(II) efficiently reduced the Cr(VI) to Cr(III). The influent and effluent samples, there was no measurable Cr(VI). The increase in filter operation time the efficiency was increased for the removal of Fe and total chromium. The quartz sand media showed the capacity to remove efficiently total chromium, Fe and turbidity.

Mass Balance of Cr in Filter Run with Quartz Sand Media

At the end of 3 days filter run, the filtration column was back washed with Delft tap water. The back washing was done at higher flow velocity to ensure the removal of all flocs which trapped into the quartz sand column. The samples were analyzed for the total Cr and Fe content in the back washed water. Summary of the calculation of Cr and Fe content are shown in Table 10 and 11.

Table 10: Summary of the calculation of Cr content at pH 7

Description	Unit	Mass
Total inflow of chromium	μg	40263.2
Total outflow via filtrate	μg	2538.8 (6.3%)
Total chromium removed in the system	μg	37724.2 (93.7%)
Chromium recovered from back wash	μg	18275.0 (45.3%)
Removal of chromium through adsorption	μg	19449.2 (48.3%)

Table 11: Summary of the calculation of Fe content at pH 7

Description	Unit	Mass
Total inflow of Fe	mg	780.2
Total outflow via Fe	mg	41.1 (5.3%)
Total iron removed in the system	mg	739.1 (94.7%)
Iron recovered from back wash	mg	118.3 (15.2%)
Removal of iron through adsorption	mg	620.9 (80.6%)

4.4.2.3 Filter Media of Bed Depth 40 cm at pH 8

For the measurement of total Cr, Fe and turbidity, influent and effluent samples were collected at the specified time. The filter was operated for 8 hrs during three days. The results are presented in Figure 4-33, Figure 4-34 and Figure 4-35, and the detailed results are presented in the annex Tables 25 and 26.

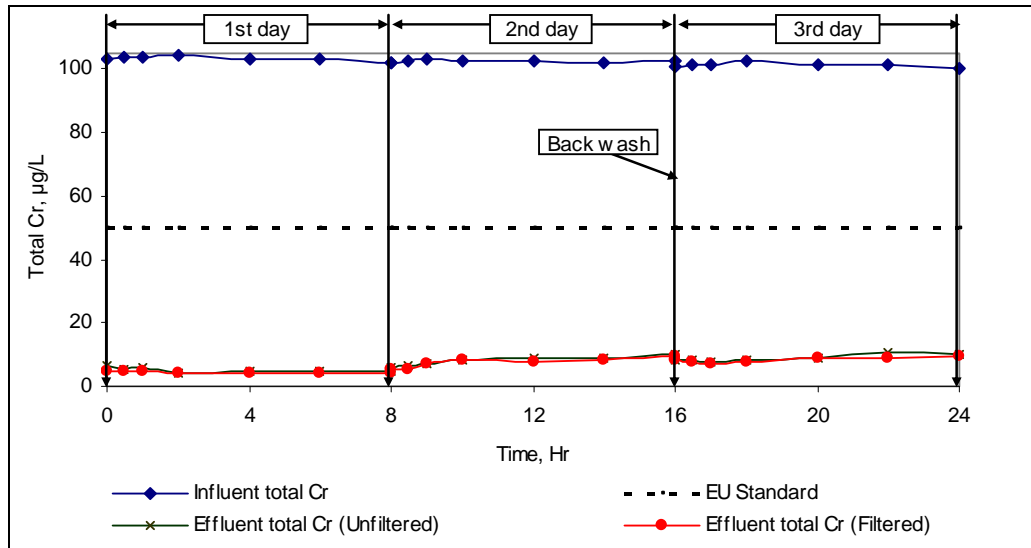


Figure 4-33: Removal of total Cr through quartz sand filter media (model water with total $c(\text{Cr}) = 100 \pm 5 \mu\text{g/L}$, $(\text{Cr (III)}) = 50 \mu\text{g/L}$ and $\text{Cr(VI)} = 50 \mu\text{g/L}$, $\text{Fe(II)} = 2.3 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, media depth = 40 cm, EBCT = 4.8 min, $\text{pH} = 8 \pm 0.1$).

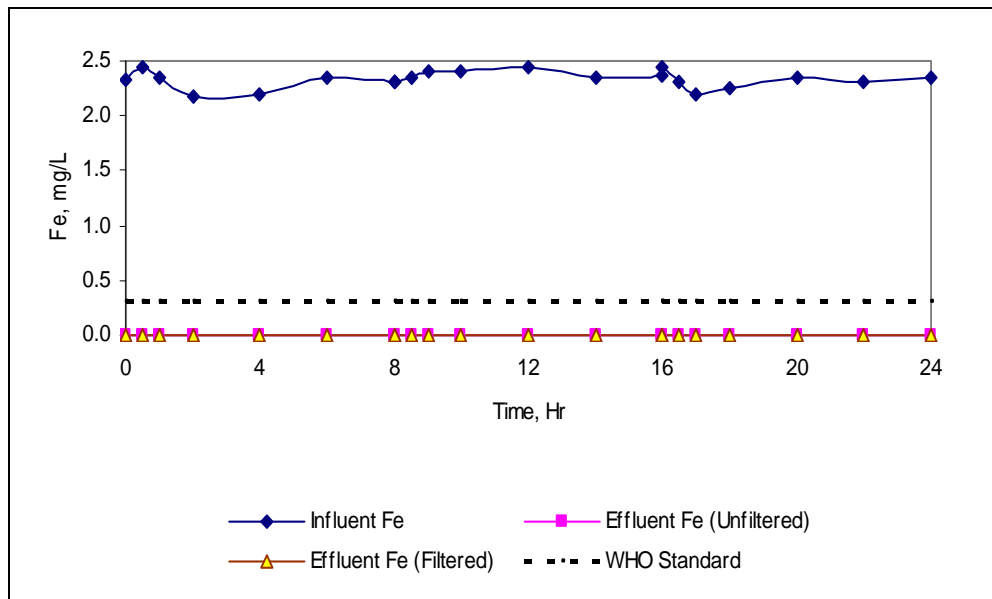


Figure 4-34: Removal of Fe through quartz sand filter media (model water with total $c(\text{Cr}) = 100 \pm 5 \mu\text{g/L}$ ($\text{Cr (III)} = 50 \mu\text{g/L}$ & $\text{Cr(VI)} = 50 \mu\text{g/L}$), $\text{Fe(II)} = 2.3 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, media depth = 40 cm, EBCT = 4.8 min, $\text{pH} = 8 \pm 0.1$).

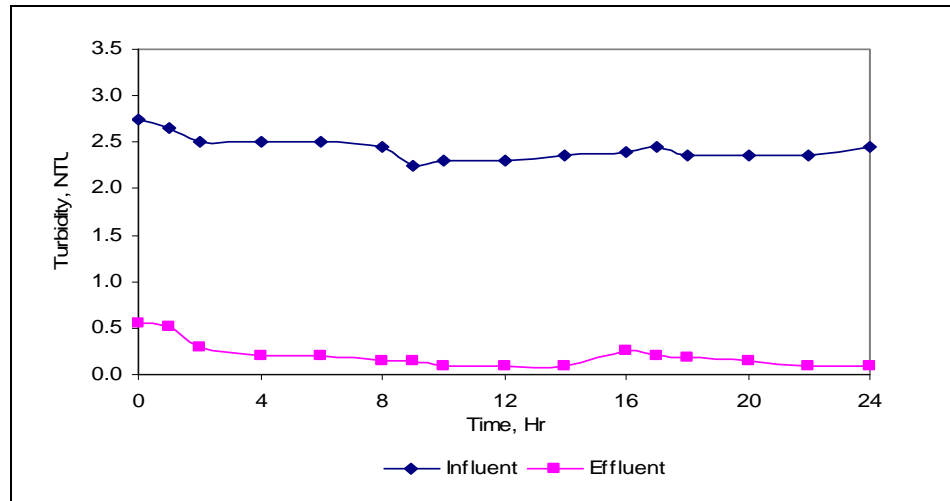


Figure 4-35: Reduction of turbidity through quartz sand filter media (model water with total $c(\text{Cr}) = 100 \pm 5 \mu\text{g/L}$ ($\text{Cr(III)} = 50 \mu\text{g/L}$ & $\text{Cr(VI)} = 50 \mu\text{g/L}$), $\text{Fe(II)} = 2.3 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, media depth = 40 cm, EBCT = 4.8 min, $\text{pH} = 8 \pm 0.1$).

The removal efficiencies of total chromium was 90% to 96% during 24 hrs of (three days) filter operation and the iron removal was 100%. From the beginning of filter operation, the removal efficiency of total chromium was excellent (i.e., about 94%). gradually the head loss increased with filter run time and after 16 hrs it reached about 2.5 m. After 16 hrs of filter operation, the media was back washed by the Delft tap water and the filter operated again for 8 hrs.

It was found that the Fe(II) efficiently reduced the Cr(VI) to Cr(III) . The influent and effluent samples, there was no measurable Cr(VI) . The media efficiently removed the turbidity, iron and total chromium. The quartz sand media showed the capacity to remove the turbidity, Fe and total chromium.

From the Chromium speciation, it is found that Cr(OH)^{2+} , Cr(OH)_2^+ and Cr(OH)_3^0 are present at pH 7 and 8. The increase in pH implies a proportional increase in the concentration of hydroxide ions $[\text{OH}^-]$ in model water. The Cr(OH)_3^0 is the dominant species at pH 7 and 8, and the precipitation occurred in the feed water. So, the quartz sand filter media efficiently filtered the co-precipitation of Fe, Cr(OH)_3^0 flocs.

Mass Balance of Cr and Fe in Filter Run with Quartz Sand Media

At the end of 2 days filter run, the filtration column was back washed with Delft tap water. The back washing was done at higher flow velocity to ensure the removal of all flocs which trapped into the quartz sand column. The samples were analyzed for the total chromium and iron content in the back washed water. Summary of the calculation of Cr and Fe content are shown in the Table 12 and 13.

Table 12: Summary of the calculation of Cr content at pH 8.

Description	Unit	Mass
Total inflow of chromium	μg	23266.2
Total outflow via filtrate	μg	964.4 (4.2%)
Total chromium removed in the system	μg	22301.8 (95.9%)
Chromium recovered from back wash	μg	15745.0 (67.7%)
Removal of chromium through adsorption	μg	6008.5 (25.8%)

Table 13: Summary of the calculation of Fe content at pH 8.

Description	Unit	Mass
Total inflow of Fe	mg	527.3
Total outflow via Fe	mg	0 (0%)
Total iron removed in the system	mg	527.3 (100%)
Iron recovered from back wash	mg	136.3 (25.9%)
Removal of iron through adsorption	mg	391.0 (74.1%)

Mass balance of pH 7 and 8 results showed the removal of total Cr by co-precipitation and adsorption. The results showed the very good removal capacity of Cr(VI) when subjected to continuous dosing of Fe(II) solution. Here, the Fe(II) reduced Cr(VI) to Cr(III) as it was oxidised to Fe(III) which rapidly formed ferric hydroxide $[\text{Fe}(\text{OH})_3]$ and it is good coagulant. Thus, the Cr(III) removed by sorption and co-precipitation of $\text{Fe}(\text{OH})_3$. Above calculations showed that the removal through the adsorption was quite higher. During back washing the trapped flocs were not washed properly and hence the adsorption percentage showed the higher value.

4.5 Conceptual model for the chromium removal from water by IOCS and quartz sand

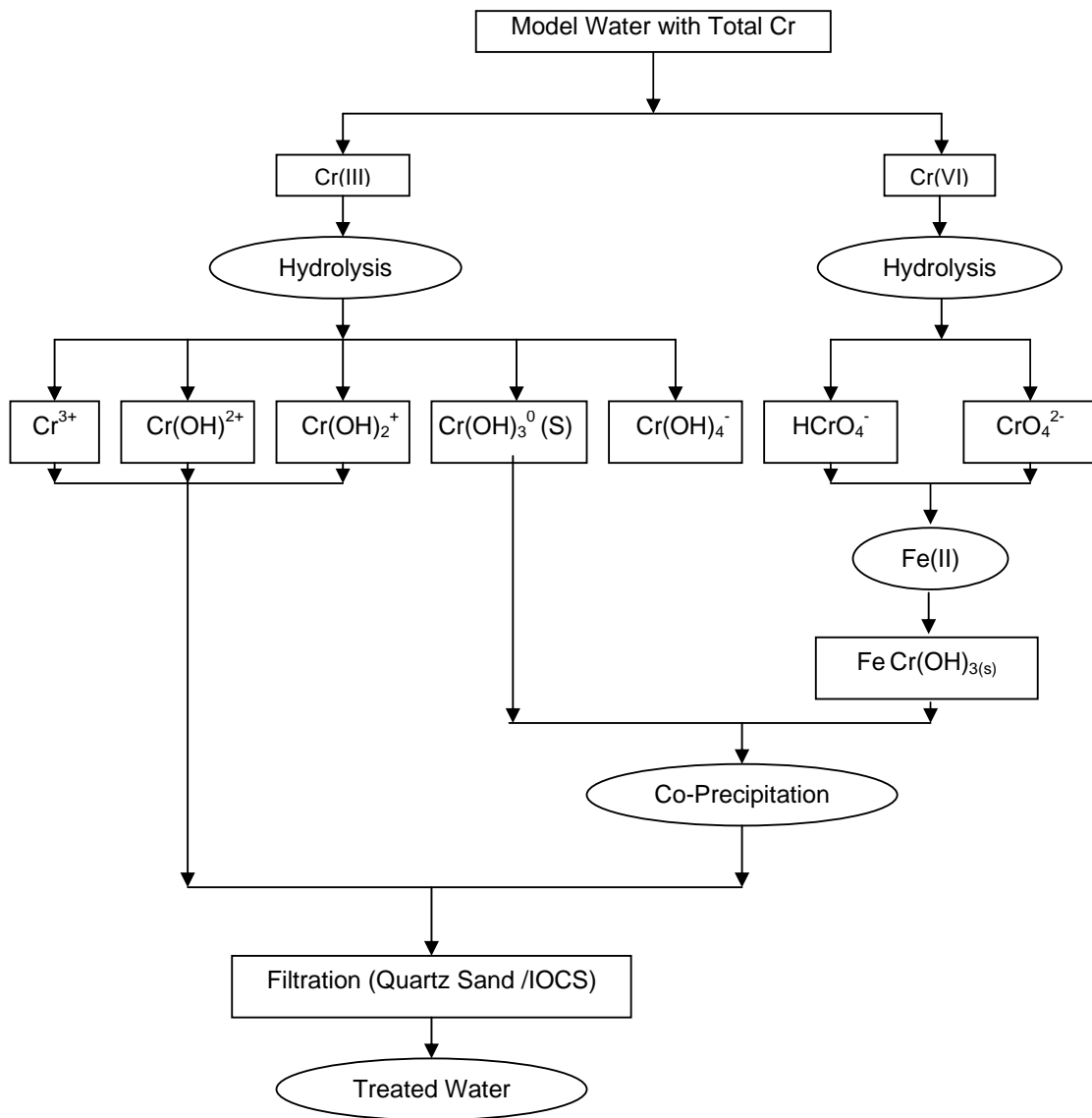


Figure 4-36: Conceptual model for the chromium removal from water by IOCS and quartz sand.

Figure 4-36 describes the conceptual model for the removal of Cr mechanism the water. The removal of Cr is due to the precipitation, reduction and filtration. At pH 6-8, Cr(OH)_2^+ , Cr(OH)_2^{2+} and Cr(OH)_3 species are present. Among these species of Cr (III), Cr(OH)_2^+ and Cr(OH)_2^{2+} are highly soluble thus likely adsorbed on to the virgin IOCS or virgin quartz sand. Insoluble solids Cr(OH)_3 does not come under adsorptive removal of Cr(III). Increasing the pH implies a proportional increase in concentration of hydroxide ions $[\text{OH}^-]$ in model water and precipitating rate is high in higher pH. During the filtration, Cr(OH)_3 species retained in rapid sand filter.

Cr (VI) being highly soluble and stable at pH 4 to 8. All of its species are likely to be adsorbed onto the IOCS. However, adsorption of Cr (VI) to IOCS is favoured at lower pH. Adsorption of Cr (VI) is low at pH 6-8 due to relatively less positive charge of the oxide surfaces. The reduction of Cr(VI) to Cr(III) is achieved by dosing Fe(II). The reduction of Cr(VI) to Cr(III) decreases the toxicity and mobility of chromium contaminated in water. Cr(VI) reduction by Fe(II) is very rapid and lead to formation of a mixed iron/chromium insoluble solid solution of form Fe,Cr(OH)_3 . Insoluble solid is removed through the filtration.

CHAPTER 5 : CONCLUSIONS AND RECOMMENDATIONS

The followings are the concluding results based on this experimental study:

5.1 Conclusions

- 1.0 At pH 6 and above, the Cr(III) was found to be unstable. The increase in pH implied a proportional increase in the concentration of hydroxide ions [OH⁻] and the reduction of dissolved Cr(III) was found to be higher. The longer the contact time, the higher was Cr(III) precipitation. The Phreeqc interactive program showed that the precipitation took place as chromium hydroxide, and chromium oxide. Cr(VI) was found to be stable as a function pH.
- 2.0 Precipitate particle size was influenced by the initial concentration of Cr(III), contact time and pH of model water. Under the condition tested, the precipitate particle sizes were greater at higher pH, higher initial Cr(III) concentration and longer contact time.
- 3.0 Chromium adsorption on IOCS was influenced by the pH of the model water. Adsorption efficiency of the IOCS for Cr(III) increased with increase in pH and Cr(III) removal was high at higher pH due to both adsorption and precipitation. However the, adsorption capacity of IOCS for Cr(VI) decreased with the increase pH.
- 4.0 Virgin quartz sand was capacity for the adsorption of Cr(III). Under the conditions tested, Cr(III) removal was 57% (97 µg to 42 µg) and 58% (98 µg to 41µg) at pH 5.5 and 6.
- 5.0 Under the conditions tested (filtration rate = 5 m/hr, initial Cr(III) = 100 µg/L, Ca²⁺ = 160 mg/L, HCO₃⁻ = 250 mg/L, quartz sand size = 1.0 – 0.5 mm, media depth = 20 cm) rapid sand filter showed the removal of Cr(III) at pH 6, 7 and 8. The removal efficiency of Cr(III) was greater at pH 7 and 8 due to the precipitate particles formation as compared to pH 6.
- 6.0 The chemical reduction of Cr(VI) to Cr(III) was achieved efficiently by dosing Fe(II). Under the conditions tested, rapid sand filter showed that the total Cr removed efficiently at pH 7 and 8. Similarly, rapid sand filter effectively removed iron and turbidity.

5.2 Recommendations

Based on the results and conclusions obtained from the study, the following recommendations are made:

- 1.0 Quartz sand showed the potential to remove total chromium with filtration. More research should be carried out with the column experiments to study the removal of varying concentrations of total chromium as a function of pH.
- 2.0 Reduction of Cr(VI) to Cr(III) by dosing ferrous sulphate was efficient and its consequent removal by sand filters could be an effective method for the developing countries. The chemical reduction of Cr(VI) by using Fe(II) could be tested with dosages less than 2.3 mg/L.
- 3.0 Further research on filtration experiments could be conducted at different filtration rates and different size of quartz sand media to optimize the removal efficiency of the total Cr from the water and wastewater.
- 4.0 Further research on filtration experiments should be carried out with the real groundwater for the removal of both species of Cr.
- 5.0 The further research could be conducted for the removal of other heavy metals with varying concentrations, and as a function of pH.

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APPENDIX

- Appendix A : Sieve analysis and grain size distribution**
- Appendix B : Stability of Cr(III)**
- Appendix C : Stability of Cr(VI)**
- Appendix D : Precipitate particle's size analysis**
- Appendix E : Removal of Cr(III) in batch adsorption experiment with IOCS**
- Appendix F : Removal of Cr(III) in batch adsorption experiment with quartz sand**
- Appendix G : Removal of Cr(VI) in batch adsorption experiment with IOCS**
- Appendix H : Filtration experiment with quartz sand**
- Appendix I : Chemical reduction of Cr(VI) and Filter with quartz sand**
- Appendix J : Equilibrium Calculation with Phreeqc interactive for Cr(III)**
- Appendix K : Calibration data (Spectrophotometer)**

Appendix A : Sieve analysis and grain size distribution

Table 1: Test results of sieve analysis and grain size distribution of quartz sand.

Sieve Size, mm	Retained, gm	Cumulative Retained, gm	Retained %	Passing, gm	Cumulative Passing, %
				500.00	100.00
1.000	0.60	0.60	0.12	499.40	99.88
0.900	10.00	10.60	2.12	489.40	97.88
0.800	46.50	57.10	11.42	442.90	88.58
0.630	277.80	334.90	66.98	165.10	33.02
0.560	88.60	423.50	84.70	76.50	15.30
0.425	66.20	489.70	97.94	10.30	2.06
0.000	5.60	495.30	99.06	4.70	0.94
Total	495.30				

Appendix B : Stability of Cr(III)

Table 2: Stability of Cr(III) as function of Cr concentration (model water with $c(\text{Ca}^{2+}) = 160$ mg/L, $c(\text{HCO}_3^-) = 250$ mg/L).

S. No.	Cr(III), mg/L						
	T_0 , (0 Hr)				T_1 , (21 Hr)		
	Initial pH	unfil	fil	% of Pre.	unfil	fil	% of Pre.
1	6.8	0.3	0.2	4.00	0.2	0.2	28.00
2	6.7	0.5	0.5	0.00	0.6	0.4	27.78
3	6.7	1.1	1.1	0.94	0.9	0.6	44.34
4	6.6	2.1	1.7	17.96	2.0	0.9	58.74
5	6.5	4.0	3.0	25.44	4.0	1.2	68.77

Table 3: Stability of Cr(III) as function of time (model water with $c(\text{Ca}^{2+}) = 160$ mg/L, $c(\text{HCO}_3^-) = 250$ mg/L)

pH at T_0 (Hr)	Cr(III), mg/L											
	T_0 (0 Hr)			T_1 (24 Hr)			T_2 (48 Hr)			T_3 (72 Hr)		
	Unfil	Fil	% of Pre.	Unfil	Fil	% of Pre.	Unfil	Fil	% of Pre.	Unfil	Fil	% of Pre.
6.6	0.8	0.5	36.59	0.8	0.5	41.46	0.8	0.4	52.4	0.8	0.4	57.32
6.6	1.0	0.7	35.29	1.0	0.6	46.08	1.0	0.4	58.8	1.0	0.4	64.71

Table 4: Stability of Cr(III) as a function of HCO_3^- concentration (model water with $c(\text{Ca}^{2+}) = 160$ mg/L, $c(\text{HCO}_3^-) = 0-250$ mg/L).

S. No.	HCO_3^- , mg/L	Cr(III), mg/L									
		Time, 0 Hr				Time, 20 Hr					
		Initial pH	Unfil	Fil	% of Pre.	pH	Unfil	Fil	% of Pre.		
1	0	3.4	3.8	3.8	-0.79	3.5	3.7	3.8	0.53		
2	50	6.2	3.8	3.2	15.26	6.4	3.6	1.5	60.53		
3	100	6.6	3.8	2.2	43.42	6.8	3.6	0.9	77.11		
4	150	6.6	3.8	2.1	43.68	6.8	3.7	0.9	76.32		
5	200	6.6	3.8	2.1	43.68	6.7	3.4	0.9	76.32		
6	250	6.6	3.8	2.1	43.68	6.8	3.7	0.9	77.11		

Table 5: Stability of Cr(III) as function of Ca²⁺ concentration (model water with c(Ca²⁺) = 0-160 mg/L, c(HCO₃⁻) = 250 mg/L).

S. No.	Ca ²⁺ , mg/L	Cr(III), mg/L							
		Time, 0 Hr				Time, 20 Hr			
		pH	Unfil	Fil	% of Pre.	pH	Unfil	Fil	% of Pre.
1	0	6.6	4.0	2.8	29.25	6.8	4.0	1.7	57.50
2	40	6.6	3.9	2.6	33.33	7.0	3.8	0.9	76.92
3	80	6.6	3.9	2.4	38.46	6.9	3.8	0.8	78.72
4	100	6.6	3.9	2.2	43.59	6.9	3.8	0.8	79.49
5	120	6.6	3.9	2.2	43.59	6.9	3.8	0.8	78.97
6	140	6.6	3.9	2.2	44.62	6.9	3.8	0.8	79.74
7	160	6.6	3.9	2.1	47.18	6.8	3.8	0.8	80.77

Pre. – Precipitation.

Table 6: Stability of Cr(III) as function of HCO₃⁻ concentration (model water with c(HCO₃⁻) = 20-100 mg/L).

Test	HCO ₃ ⁻ , mg/L	pH	Cr(III) (mg/L) at 1 hour					Cr(III) (mg/L) at 24 hour				
			Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.	Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.
Test 1	20.0	5.9	4.0	2.6			35.19	4.0	1.1			72.91
			4.0	2.3	4.0	2.5	40.76	3.8	1.0	3.9	1.0	75.95
Test 2	40.0	6.4	4.0	1.9			53.71	3.9	0.7			83.17
			4.0	1.9	4.0	1.9	53.85	3.8	0.7	3.8	0.7	83.62
Test 3	60.0	6.6	4.0	1.8			54.46	3.9	0.7			83.42
			4.0	1.8	4.0	1.8	54.46	3.9	0.7	3.9	0.7	83.17
Test 4	80.0	6.6	4.0	1.8			56.58	4.0	0.7			83.13
			4.0	1.7	4.0	1.7	57.18	3.9	0.6	3.9	0.7	84.41
Test 5	100.0	6.6	4.0	1.7			56.93	3.8	0.6			84.90
			4.0	1.7	4.0	1.7	57.18	3.9	0.6	3.9	0.6	85.15

Table 7: Stability of Cr(III) as a function of Ca²⁺ concentration (model water with c(Ca²⁺) = 20-50 mg/L).

Test	Ca, mg/L	pH	Cr(III) (mg/L) at 1 hour					Cr(III) (mg/L) at 24 hour				
			Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.	Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.
Test 1	20.0	6.6	3.8	3.0			21.05	3.5	2.4			37.89
			3.8	3.0	3.8	3.0	22.37	3.6	2.4	3.6	2.4	35.79
Test 2	30.0	6.6	3.8	1.7			55.26	3.6	1.2			68.68
			3.8	1.6	3.8	1.7	57.63	3.5	1.2	3.5	1.2	68.16
Test 3	40.0	6.6	3.8	1.8			53.42	3.5	1.2			69.47
			3.8	1.6	3.8	1.7	58.95	3.4	0.9	3.5	1.0	75.53
Test 4	50.0	6.6	3.8	1.4			62.89	3.5	0.8			78.42
			3.8	1.5	3.8	1.5	60.53	3.5	0.6	3.5	0.7	83.42

Table 8: Stability of Cr(III) as a function of HCO_3^- and Ca^{2+} (model tap water with $c(\text{Cr}) = 1.1 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 0$ to 160 mg/L , $c(\text{HCO}_3^-) = 0$ to 250 mg/L).

Test	Description	pH	Cr(III), mg/L at T ₁ , 1 hour					Cr(III), mg/L at T ₂ , 24 hour					
			Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.	Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.	
Test 1	a) bottle 1	Demi+Cr(III)	4.2	1.18	1.18				1.21	1.10			
	b) bottle 2	Demi+Cr(III)	4.2	1.20	1.15	1.19	1.17	2.10	1.14	1.16	1.18	1.13	5.83
Test 2	a) bottle 1	Tap water+ Cr(III)	6.6	1.05	0.46				1.02	0.34			
	b) bottle 2	Tap water+ Cr(III)	6.6	1.03	0.43	1.04	0.45	57.21	1.03	0.34	1.03	0.34	66.99
Test 3	a) bottle 1	Tap water+ Cr(III) + Ca	+6.6	1.02	0.43				0.99	0.31			
	b) bottle 2	Tap water+ Cr(III) + Ca	+6.6	1.02	0.44	1.02	0.44	57.35	1.01	0.35	1.00	0.33	67.65
Test 4	a) bottle 1	Tap water+ Cr(III) + HCO ₃	+6.6	1.06	0.43				1.02	0.31			
	b) bottle 2	Tap water+ Cr(III) + HCO ₃	+6.6	0.99	0.42	1.03	0.43	58.54	1.01	0.32	1.02	0.32	68.18
Test 5	a) bottle 1	Tap water+ Cr(III) + Ca+ HCO ₃	+6.6	1.09	0.37				0.99	0.30			
	b) bottle 2	Tap water+ Cr(III) + Ca+ HCO ₃	+6.6	1.00	0.38	1.05	0.38	64.11	0.97	0.29	0.98	0.30	70.50

Table 9: Stability of Cr(III) as a function of HCO_3^- and Ca^{2+} (model water with $c(\text{Cr}) = 1.8 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 0$ to 160 mg/L , $c(\text{HCO}_3^-) = 0$ to 250 mg/L).

Test	Description	pH	Cr(III), mg/L at T ₁ , at 1 hour					Cr(III), mg/L at T ₂ , 24 hour					
			Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.	Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.	
Test 1	a) bottle 1	Demi+Cr(III)	4.1	1.78	1.64				1.69	1.60			
	b) bottle 2	Demi+Cr(III)	4.1	1.81	1.66	1.80	1.65	8.08	1.69	1.68	1.69	1.64	8.64
Test 2	a) bottle 1	Tap water+ Cr(III)	6.6	1.68	1.11				1.60	0.54			
	b) bottle 2	Tap water+ Cr(III)	6.6	1.63	1.03	1.66	1.07	35.35	1.62	0.54	1.61	0.54	67.37
Test 3	a) bottle 1	Tap water+ Cr(III) + Ca	+6.6	1.64	1.04				1.61	0.54			
	b) bottle 2	Tap water+ Cr(III) + Ca	+6.6	1.62	1.03	1.63	1.04	36.50	1.62	0.45	1.62	0.50	69.63
Test 4	a) bottle 1	Tap water+ Cr(III) + HCO ₃	+6.6	1.68	1.08				1.68	0.50			
	b) bottle 2	Tap water+ Cr(III) + HCO ₃	+6.6	1.64	1.02	1.66	1.05	36.75	1.60	0.48	1.64	0.49	70.48
Test 5	a) bottle 1	Tap water+ Cr(III) + Ca+ HCO ₃	+6.6	1.61	0.88				1.55	0.39			
	b) bottle 2	Tap water+ Cr(III) + Ca+ HCO ₃	+6.6	1.63	0.92	1.62	0.90	44.44	1.56	0.42	1.56	0.41	75.00

Table 10: Stability of Cr(III) as a function of HCO_3^- and Ca^{2+} (model water with $c(\text{Cr}) = 3$ mg/L, $c(\text{Ca}^{2+}) = 0$ to 160 mg/L, $c(\text{HCO}_3^-) = 0$ to 250 mg/L).

Test	Description	pH	Cr(III), mg/L at T ₁ , After 1 hour					Cr(III), mg/L at T ₂ , After 24 hour					
			Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.	Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.	
Test 1	a) bottle 1	Demi+Cr(III)	4.1	3.11	3.06				3.00	2.83			
	b) bottle 2	Demi+Cr(III)	4.1	3.15	3.06	3.13	3.06	2.24	3.03	2.93	3.03	2.93	6.39
Test 2	a) bottle 1	Tap water+ Cr(III)	6.6	3.04	1.05				2.91	0.55			
	b) bottle 2	Tap water+ Cr(III)	6.6	3.03	1.07	3.04	1.06	65.07	2.88	0.48	2.88	0.48	84.18
Test 3	a) bottle 1	Tap water+ Cr(III) + Ca	6.6	2.98	0.82				2.85	0.42			
	b) bottle 2	Tap water+ Cr(III) + Ca	6.7	3.02	0.70	3.00	0.76	74.67	2.90	0.42	2.90	0.42	86.00
Test 4	a) bottle 1	Tap water+ Cr(III) + HCO_3^-	6.6	3.02	0.77				2.84	0.49			
	b) bottle 2	Tap water+ Cr(III) + HCO_3^-	6.7	3.05	0.57	3.04	0.67	77.92	2.88	0.37	2.88	0.37	87.81
Test 5	a) bottle 1	Tap water+ Cr(III) + Ca+ HCO_3^-	6.6	2.96	0.48				2.87	0.33			
	b) bottle 2	Tap water+ Cr(III) + Ca+ HCO_3^-	6.6	2.98	0.42	2.97	0.45	84.85	2.85	0.28	2.85	0.28	90.57

Table 11: Stability of Cr(III) as a function of HCO_3^- and Ca^{2+} (model water with $c(\text{Cr}) = 4.2$ mg/L, $c(\text{Ca}^{2+}) = 0$ to 160 mg/L, $c(\text{HCO}_3^-) = 0$ to 250 mg/L).

Test	Description	pH	Cr(III), mg/L at T ₁ , 1 hour					Cr(III), mg/L at T ₂ , 24 hour					
			Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.	Unfil	Fil	Avg, Unfil	Avg, Fil	% of pre.	
Test 1	a) bottle 1	Demi+Cr(III)	4.0	4.20	4.20				4.11	4.10			
	b) bottle 2	Demi+Cr(III)	4.0	4.30	4.30	4.25	4.25	0.00	4.16	4.15	4.14	4.13	2.94
Test 2	a) bottle 1	Tap water+ Cr(III)	6.6	4.30	1.82				4.00	0.67			
	b) bottle 2	Tap water+ Cr(III)	6.6	4.31	1.62	4.31	1.72	60.05	4.10	0.58	4.05	0.63	85.48
Test 3	a) bottle 1	Tap water+ Cr(III) + Ca	6.6	4.26	1.45				4.15	0.68			
	b) bottle 2	Tap water+ Cr(III) + Ca	6.6	4.30	1.35	4.28	1.40	67.29	4.29	0.51	4.22	0.60	86.10
Test 4	a) bottle 1	Tap water+ Cr(III) + HCO_3^-	6.6	4.33	1.20				4.19	0.59			
	b) bottle 2	Tap water+ Cr(III) + HCO_3^-	6.6	4.32	1.09	4.33	1.15	73.53	4.22	0.58	4.21	0.59	86.47
Test 5	a) bottle 1	Tap water+ Cr(III) + Ca+ HCO_3^-	6.6	4.25	1.03				4.20	0.43			
	b) bottle 2	Tap water+ Cr(III) + Ca+ HCO_3^-	6.6	4.16	0.90	4.21	0.97	77.05	4.14	0.47	4.17	0.45	89.30

Table 12: Stability of Cr(III) as a function of pH. (model water with $c(\text{Cr(III)}) = 100 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{mg/L}$, $c(\text{HCO}_3^-) = 250 \text{mg/L}$).

S.No.	PE Bottle	pH	0 Hr		0.17 Hr (10 min)		20 min (0.34 Hr)		30 min (0.5 Hr)		1 Hr		24 Hr	
			Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)
1	8A	4.0	97.5		97.5		97.5		97.0		96.5		94.5	
	8B		94.5	96.0	94.5	96.0	94.5	96.0	94.0	95.5	94.5	95.5	94.5	94.5
2	7A	5.0	95.0		93.5		92.0		91.5		85.5		91.0	
	7B		97.0	96.0	97.5	95.5	98.0	95.0	98.0	94.8	104.5	95.0	98.5	94.8
3	6A	5.5	95.5		94.5		92.0		92.0		93.5		91.0	
	6B		97.0	96.3	94.5	94.5	95.5	93.8	94.0	93.0	92.5	93.0	90.0	90.5
4	5A	6.0	82.5		75.5		75.5		74.0		73.5		63.5	
	5B		81.0	81.8	86.5	81.0	85.5	80.5	82.5	78.3	80.5	77.0	56.0	59.8
5	4A	6.5	80.5		76.0		80.5		81.5		73.0		44.0	
	4B		79.5	80.0	79.5	77.8	70.5	75.5	72.5	77.0	71.5	72.3	47.5	45.8
6	8A	6.6	78.0		76.5		77.0		73.5		81.7		36.5	
	8B		80.0	79.0	78.0	77.3	70.5	73.8	67.5	70.5	59.0	70.4	42.0	39.3
7	7A	6.7	76.0		77.5		71.0		59.5		64.0		37.0	
	7B		84.5	80.3	77.0	77.3	76.5	73.8	74.5	67.0	69.5	66.8	41.0	39.0
8	6A	6.8	76.0		75.0		72.5		72.0		69.5		40.5	
	6B		80.0	78.0	79.0	77.0	65.5	69.0	62.0	67.0	58.5	64.0	36.5	38.5
9	5A	6.9	76.5		75.5		72.5		67.5		62.0		39.0	
	5B		77.5	77.0	76.0	75.8	74.0	73.3	66.0	66.8	60.0	61.0	35.5	37.3
10	3A	7.0	74.5		68.0		65.0		65.0		60.5		33.0	
	3B		73.5	74.0	67.0	67.5	66.0	65.5	65.0	65.0	49.5	55.0	28.5	30.8
11	2A	7.5	52.8		31.8		26.7		25.2		15.6		1.8	
	2B		29.1	41.0	19.2	25.5	15.7	21.2	13.2	19.2	18.8	17.2	0.0	0.9
12	1A	8.0	33.9		16.9		15.8		11.3		5.8		1.0	
	1B		20.1	27.0	12.6	14.8	8.6	12.2	7.3	9.3	3.2	4.5	0.0	0.5

Table 13: Stability of Cr(III) as a function of pH. (model water with $c(\text{Cr(III)}) = 3.8 \text{mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{mg/L}$, $c(\text{HCO}_3^-) = 250 \text{mg/L}$).

Sample Bottle	pH	Cr(III), mg/L								
		0 Hr			1 Hr			24 Hr		
		Unfiltered	Filtered	% Reduction	Unfiltered	Filtered	% Reduction	Unfiltered	Filtered	% Reduction
1A	4.0	3.8	3.7	1.6	3.8	3.7	2.4	3.8	3.7	2.90
1B	5.0	3.8	3.7	2.6	3.8	3.7	2.6	3.7	3.7	3.68
2A	6.0	3.7	3.2	13.2	3.7	2.3	37.9	3.5	1.2	68.55
2B	6.6	3.8	2.5	33.9	3.8	1.5	60.3	3.6	0.5	87.57
3A	7.0	3.7	1.7	53.7	3.6	0.9	76.8	3.6	0.2	93.73
3B	7.5	3.7	1.1	70.0	3.7	0.5	86.6	3.7	0.2	95.64
4A	8.0	3.8	0.5	86.6	3.7	0.2	94.7	3.7	0.1	97.11
4B	8.5	3.8	0.2	95.5	3.8	0.2	95.8	3.5	0.1	97.63
5A	9.0	3.8	0.1	96.9	3.7	0.1	97.1	3.8	0.1	97.64
5B	9.5	3.8	0.1	97.1	3.7	0.1	97.6	3.7	0.1	97.34
6A	10.1	3.7	0.1	97.6	3.4	0.1	97.8	3.6	0.1	97.83
6B	10.5	3.7	0.1	97.3	3.6	0.1	97.8	3.6	0.1	97.85
7A	11.0	3.7	0.1	97.3	3.6	0.1	97.8	3.6	0.1	98.11
7B	11.5	3.7	0.1	97.3	3.6	0.1	98.1	3.6	0.1	98.38

Appendix C : Stability of Cr(VI)

Table 14: Stability of Cr(VI) as a function of pH (model water with $c(\text{Cr(VI)})=100 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-)= 250 \text{ mg/L}$).

Time, (Hr)	pH 4.0		pH 5		pH 5.5		pH 6.0		pH 6.5		pH 7.0		pH 7.5		pH 8.0	
	Cr (VI) ($\mu\text{g/L}$)	Total Cr ($\mu\text{g/L}$)	Cr (VI) ($\mu\text{g/L}$)	Total Cr ($\mu\text{g/L}$)	Cr (VI) ($\mu\text{g/L}$)	Total Cr ($\mu\text{g/L}$)	Cr (VI) ($\mu\text{g/L}$)	Total Cr ($\mu\text{g/L}$)	Cr (VI) ($\mu\text{g/L}$)	Total Cr ($\mu\text{g/L}$)	Cr (VI) ($\mu\text{g/L}$)	Total Cr ($\mu\text{g/L}$)	Cr (VI) ($\mu\text{g/L}$)	Total Cr ($\mu\text{g/L}$)	Cr (VI) ($\mu\text{g/L}$)	Total Cr ($\mu\text{g/L}$)
0.00	98.0	98.3	96.5	96.8	94.9	95.3	95.9	96.0	95.8	96.0	95.8	96.0	100.7	101.0	97.7	98.3
0.17	96.9	98.0	94.2	95.3	94.8	95.0	94.4	95.3	94.7	95.3	94.7	95.0	100.1	100.8	97.3	98.1
0.33	95.3	97.5	92.1	95.5	94.2	94.5	95.8	96.5	94.7	96.5	94.7	95.8	100.2	100.5	96.1	97.5
0.50	94.2	96.0	91.1	95.5	93.7	94.0	93.7	93.3	94.0	94.0	93.3	93.5	99.6	100.5	96.4	97.2
1.00	94.1	96.0	90.1	95.5	93.1	94.5	89.5	93.1	89.8	91.8	91.2	93.3	100.6	100.5	96.0	97.0
24.00	94.1	95.0	90.1	95.5	91.0	93.0	87.4	91.5	88.4	92.5	90.5	93.3	100.1	100.5	95.7	96.2

Appendix D : Precipitate particle's size analysis

Table 15: Precipitate particle's size analysis as a function of pH (model water with $c(\text{Cr}) = 100 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-)= 250 \text{ mg/L}$).

Time	Cr(III) ($\mu\text{g/L}$) at pH6					Cr(III) ($\mu\text{g/L}$) at pH7					Cr(III) ($\mu\text{g/L}$) at pH8				
	0.45 μm	1.0 μm	10.0 μm	20-25 μm	Unfiltered	0.45 μm	1.0 μm	10.0 μm	20-25 μm	Unfiltered	0.45 μm	1.0 μm	10.0 μm	20-25 μm	Unfiltered
0 min	100.0	100.0	100.0	100.0	100.0	75.0	78.0	91.0	95.0	100.0	30.0	33.6	91.0	93.5	98.5
10 min	100.0	99.5	99.0	99.0	100.0	66.9	73.5	90.5	94.5	99.0	21.0	28.2	91.0	92.0	98.0
20 min	99.0	99.0	99.0	99.5	99.5	63.0	72.0	90.5	94.5	99.0	15.3	28.2	90.5	91.0	93.0
30 min	98.0	99.0	99.0	99.0	99.0	63.0	68.1	90.0	94.5	99.0	12.0	28.2	86.5	90.0	93.0
1 Hr	95.0	98.0	98.5	98.5	99.0	55.5	69.6	90.0	94.0	99.0	6.6	12.0	86.5	88.0	93.0
24 Hr	84.0	98.0	98.0	98.0	99.0	20.1	41.7	81.5	88.0	99.0	1.5	4.8	85.5	87.0	93.0

Table 16: Precipitate particle's size analysis as a function of pH (model water with $c(\text{Cr}) = 3.8 \text{ mg/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-)= 250 \text{ mg/L}$).

Time	Cr(III) (mg/L) at pH6					Cr(III) (mg/L) at pH7					Cr(III) (mg/L) at pH8				
	0.45 μm	1.0 μm	10.0 μm	20-25 μm	Unfiltered	0.45 μm	1.0 μm	10.0 μm	20-25 μm	Unfiltered	0.45 μm	1.0 μm	10.0 μm	20-25 μm	Unfiltered
0 min	3.08	3.40	3.61	3.78	3.79	3.17	3.48	3.54	3.68	3.79	0.71	2.80	3.33	3.60	3.81
10 min	3.07	3.24	3.33	3.78	3.78	2.33	2.42	3.51	3.72	3.78	0.56	2.46	3.19	3.55	3.73
20 min	3.07	2.90	3.30	3.80	3.78	2.16	2.08	3.51	3.69	3.81	0.43	2.36	3.15	3.55	3.70
30 min	3.00	2.90	3.29	3.80	3.80	2.03	2.09	3.61	3.80	3.80	0.40	1.57	3.15	3.50	3.70
1 Hr	2.86	2.84	2.84	3.70	3.79	1.90	2.00	3.28	3.68	3.70	0.23	1.32	3.15	3.43	3.70
24 Hr	1.39	2.70	2.80	3.50	3.76	0.48	0.80	3.32	3.68	3.72	0.20	0.75	3.12	3.40	3.65

Appendix E : Removal of Cr(III) in batch adsorption experiment with IOCS

Table 17: Removal kinetics of Cr(III) as a function of IOCS concentration (model water with $c(\text{Cr}) = 100 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, initial $\text{pH} = 7$).

S.N o.	PE Bottle	IOCS dosage, (mg/.5 L)	Time 0.5 Hr		Time 2 Hr		Time 6 Hr		Time 24 Hr	
			Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)
1	1A	0.22	42.0		32.8		27.8		17.1	
	1B	0.23	40.0	41.0	35.6	34.2	28.6	28.2	21.0	19.1
2	2A	0.34	38.5		29.9		25.1		16.7	
	2B	0.31	38.0	38.3	28.3	29.1	24.7	24.9	15.7	16.2
3	3A	0.40	31.8		24.9		22.2		16.8	
	3B	0.39	32.4	32.1	28.8	26.9	23.7	23.0	12.3	14.6
4	4A	0.53	30.6		26.7		18.9		13.8	
	4B	0.52	30.3	30.5	22.2	24.5	25.2	22.1	13.5	13.7
5	5A	0.60	27.3		22.2		21.6		12.3	
	5B	0.62	27.9	27.6	27.0	24.6	21.6	21.6	12.6	12.5
6	Blank	0.00	65.0	65.0	51.5	51.5	44.5	44.5	34.0	34.0

Table 18: Removal of Cr(III) removal as a function of pH (model water with $c(\text{Cr(III)}) = 100 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, $c(\text{IOCS}) = 1 \text{ mg/L}$).

S.N o.	PE Bottle	pH	IOCS dosage, (mg/.5 L)	0 Hr		0.5 Hr		2 Hr		6 Hr		24 Hr	
				Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)	Cr(III) ($\mu\text{g/L}$)	Avg. Cr(III) ($\mu\text{g/L}$)
1	8A	4.0	0.54	97.0		94.0		91.5		86.0		85.0	
	8B		0.55	97.0	97.0	89.0	91.5	88.0	89.8	87.5	86.8	86.5	85.8
	8Blank		Blank	97.5	97.5	97.0	97.0	96.5	96.5	96.5	96.5	94.5	94.5
2	7A	5.0	0.48	94.0		89.0		85.0		82.5		82.5	
	7B		0.53	93.5	93.8	86.0	87.5	86.0	85.5	83.0	82.8	81.5	82.0
	7Blank		Blank	94.0	94.0	94.0	94.0	93.5	93.5	93.5	93.5	93.5	93.5
3	6A	5.5	0.55	92.5		84.0		79.0		78.5		78.0	
	6B		0.50	93.0	92.8	84.0	84.0	79.5	79.3	77.0	77.8	74.0	76.0
	6Blank		Blank	93.0	93.0	91.5	91.5	91.5	91.5	91.0	91.0	90.0	90.0
4	5A	6.0	0.54	90.0		77.0		79.0		75.5		62.5	
	5B		0.49	91.6	90.8	82.0	79.5	77.0	78.0	73.5	74.5	62.5	62.5
	5Blank		Blank	91.5	91.5	90.0	90.0	89.0	89.0	84.0	84.0	79.0	79.0
5	4A	6.5	0.53	84.0		72.5		60.5		59.0		51.5	
	4B		0.51	85.5	84.8	65.5	69.0	64.0	62.3	62.5	60.8	54.5	53.0
	4Blank		Blank	86.5	86.5	80.5	80.5	79.0	79.0	77.0	77.0	74.5	74.5
6	3A	7.0	0.48	69.0		8.6		4.2		3.1		2.9	
	3B		0.53	67.0	68.0	19.7	14.2	14.0	9.1	11.8	7.5	10.9	6.9
	3Blank		Blank	70.0	70.0	45.0	45.0	40.5	40.5	37.5	37.5	30.3	30.3
7	2A	7.5	0.57	42.6		5.0		0.4		0.7		0.0	
	2B		0.51	45.9	44.3	8.6	6.8	3.7	2.1	2.4	1.6	2.0	1.0
	2Blank		Blank	45.3	45.3	18.2	18.2	12.0	12.0	4.0	4.0	1.5	1.5
8	1A	8.0	0.48	21.6		8.0		5.3		1.1		0.0	
	1B		0.51	25.2	23.4	7.0	7.5	0.0	2.7	0.0	0.6	0.0	0.0
	1Blank		Blank	25.5	25.5	9.3	9.3	4.5	4.5	3	3	0.5	0.5

Appendix F : Removal of Cr(III) in batch adsorption experiment with quartz sand

Table 19: Removal of Cr(III) with quartz sand (model water with c(Cr(III)) = 100 µg/L, quartz sand dose of = 10 gm/L).

S.No.	Sam	pH	Quartz Sand Dosage, gm	0Hr		0.5Hr		1Hr		2Hr		4Hr		6Hr		24Hr		48Hr	
				Cr(III) µg/L	Avg. Cr(III) µg/L	Cr(III) µg/L	Avg. Cr(III) µg/L	Cr(III) µg/L	Avg. Cr(III) µg/L	Cr(III) µg/L	Avg. Cr(III) µg/L	Cr(III) µg/L	Avg. Cr(III) µg/L	Cr(III) µg/L	Avg. Cr(III) µg/L	Cr(III) µg/L	Avg. Cr(III) µg/L	Cr(III) µg/L	Avg. Cr(III) µg/L
1	2A	5.5	5.006	96.5		85.5		80.5		77.0		74.0		72.5		64.5		42.0	
	2B	5.5	5.001	96.5	96.5	85.5	85.5	83.5	82.0	75.5	76.3	74.0	74.0	73.0	72.8	60.0	62.3	42.5	42.3
	2Blank	5.5		96	96.0	94.5	94.5	89.0	89.0	88.0	88.0	87.5	87.5	87.0	87.0	84.0	84.0	80.0	80.0
	23A	6.0	5.003	97.5		86.0		80.5		76.0		76.5		75.5		60.0		40.5	
	3B	6.0	5.003	97.5	97.5	86.5	86.3	80.0	80.3	76.0	76.0	74.0	75.3	73.0	74.3	62.5	61.3	41.0	40.8
	3Blank	6.0		98	98.0	92.0	92.0	91.0	91.0	91.0	91.0	90.5	90.5	89.0	89.0	89.0	89.0	82.0	82.0

Appendix G : Removal of Cr(VI) in batch adsorption experiment with IOCS

Table 20: Removal of Cr(VI) as a function of pH (model water with c(Cr(VI)) = 100 µg/L, c(Ca²⁺) = 160 mg/L, c(HCO₃⁻) = 250 mg/L, c(IOCS) = 1 mg/L).

S. No.	pH	IOCS, (mg/.5 L)	0 Hr		0.17 Hr (10 min)		20 min (0.34 Hr)		30 min (0.5 Hr)		1 Hr		24 Hr	
			Total Cr (µg/L)	Avg. Total Cr (µg/L)	Total Cr (µg/L)	Avg. Total Cr (µg/L)	Total Cr (µg/L)	Avg. Total Cr (µg/L)	Total Cr (µg/L)	Avg. Total Cr (µg/L)	Total Cr (µg/L)	Avg. Total Cr (µg/L)	Total Cr (µg/L)	Avg. Total Cr (µg/L)
1	4.0	0.55	96.5		94.5		93.5		93.0		92.5		89.5	
		0.55	98.0	97.3	95.5	95.0	92.5	93.0	92.5	92.8	92.5	92.5	89.0	89.3
		Blank	97.5	97.5	97.0	97.0	97.0	97.0	97.0	97.0	96.5	96.5	97.0	97.0
2	5.0	0.47	98.5		93.0		92.0		91.0		89.0		85.5	
		0.54	99.0	98.8	94.0	93.5	92.5	92.3	91.5	91.3	93.5	91.3	90.5	88.0
		Blank	99.0	99.0	96.5	96.5	96.0	96.0	95.0	95.0	95.0	95.0	95.0	95.0
3	5.5	0.52	90.0		86.5		87.0		87.0		85.0		80.5	
		0.48	97.5	93.8	97.5	92.0	95.5	91.3	94.0	90.5	93.5	89.3	89.0	84.8
		Blank	94.5	94.5	94.5	94.5	94.0	94.0	94.0	94.0	93.5	93.5	92.0	92.0
4	6.0	0.48	92.0		91.5		91.5		90.0		90.0		87.0	
		0.53	99.0	95.5	95.5	93.5	95.0	93.3	95.0	92.5	93.5	91.8	92.5	89.8
		Blank	95.5	95.5	95.5	95.5	95.5	95.5	94.0	94.0	94.0	94.0	93.5	93.5
5	6.5	0.50	91.5		90.0		88.0		88.0		87.0		85.5	
		0.53	92.5	92.0	92.5	91.3	92.0	90.0	89.5	88.8	88.5	87.8	86.5	86.0
		Blank	92.0	92.0	92.5	92.5	92.5	92.5	92.5	92.5	92.0	92.0	91.5	91.5
6	7.0	0.53	96.5		98.5		96.5		94.5		94.0		92.5	
		0.53	98.0	97.3	94.5	96.5	95.5	96.0	95.5	95.0	90.5	92.3	90.0	91.3
		Blank	97.0	97.0	97.0	97.0	96.0	96.0	95.5	95.5	95.5	95.5	94.5	94.5
7	7.5	0.55	99.5		98.0		94.5		95.0		95.0		93.5	
		0.49	98.5	99.0	97.5	97.8	96.0	95.3	95.0	95.0	95.0	95.0	93.0	93.3
		Blank	99.0	99.0	97.0	97.0	97.0	97.0	97.0	97.0	96.5	96.5	96.0	96.0
8	8.0	0.54	99.0		99.0		96.0		94.0		93.0		91.5	
		0.50	95.5	97.3	94.5	96.8	90.0	93.0	91.0	92.5	90.5	91.8	90.0	90.8
		Blank	97.5	97.5	96.5	96.5	96.0	96.0	95.0	95.0	95.0	95.0	94.0	94.0

Appendix H : Filtration experiment with quartz sand

Table 21: Filtration of Cr(III) with quartz sand media in glass column (model water with $c(\text{Cr (III)}) = 100 \mu\text{g/L}$, $c(\text{Ca}^{2+}) = 160 \text{ mg/L}$, $c(\text{HCO}_3^-) = 250 \text{ mg/L}$, diameter of column = 1.8 cm, media depth = 20 cm, quartz sand sizes = 0.5 to 1.0 mm, EBCT = 2.4 min).

Time, (Hr)	Cr (III) ($\mu\text{g/L}$)								
	pH 6			pH 7			pH 8		
	Influent	Effluent	Removal	Influent	Effluent	Removal	Influent	Effluent	Removal
0.0	100	16.5	83.5	100	2.3	97.7	100	2.3	97.7
0.5	100	17.5	82.5	100	2.9	97.1	100	3.3	96.7
1.0	100	18.5	81.5	100	2.8	97.2	100	3.1	96.9
2.0	100	22.0	78.0	100	3.6	96.4	100	4.5	95.5
4.0	100	24.5	75.5	100	3.8	96.2	100	4.3	95.7
6.0	100	26.0	74.0	100	3.5	96.5	100	4.3	95.7
8.0	100	28.5	71.5	100	3.4	96.6	100	4.4	95.6
8.0	100	27.9	72.1	100	3.5	96.5	100	4.5	95.5
8.5	100	28.8	71.2	100	3.5	96.5	100	4.5	95.5
9.0	100	30.3	69.7	100	4.5	95.5	100	3.8	96.2
10.0	100	33.5	66.5	100	5.8	94.2	100	2.9	97.1
12.0	100	40.3	59.7	100	7.6	92.4	100	2.7	97.3
14.0	100	42.1	57.9	100	7.9	92.1	100	2.6	97.4
16.0	100	44.2	55.8	100	8.2	91.8	100	2.6	97.4
16.0	100	39.0	61.0	100	8.6	91.4	100	2.3	97.7
16.5	100	39.5	60.5	100	8.4	91.6	100	2.3	97.7
17.0	100	40.5	59.5	100	8.2	91.8	100	2.5	97.5
18.0	100	42.5	57.5	100	8.5	91.5	100	2.6	97.4
20.0	100	44.5	55.5	100	8.6	91.4	100	2.6	97.4
22.0	100	48.5	51.5	100	9.0	91.0	100	2.7	97.3
24.0	100	55.0	45.0	100	9.7	90.3	100	2.9	97.1
24.0	100	12.1	87.9	100	2.9	97.1	100	3.1	96.9
24.5	100	13.9	86.1	100	3.3	96.7	100	3.3	96.7
25.0	100	16.3	83.7	100	4.6	95.4	100	3.9	96.1
26.0	100	17.2	82.8	100	5.4	94.6	100	6.8	93.2
28.0	100	19.7	80.3	100	6.3	93.7	100	7.0	93.0
30.0	100	20.2	79.8	100	8.3	91.7	100	7.2	92.8
32.0	100	23.7	76.3	100	9.2	90.8	100	7.6	92.4
32.0	100	25.0	75.0	100	10.0	90.0	100	6.2	93.8
32.5	100	27.4	72.6	100	12.2	87.8	100	5.4	94.6
33.0	100	30.0	70.0	100	13.3	86.7	100	5.8	94.2
34.0	100	35.0	65.0	100	14.3	85.7	100	6.7	93.3
36.0	100	38.6	61.4	100	15.3	84.7	100	7.2	92.8
38.0	100	42.0	58.0	100	18.5	81.5	100	8.3	91.7
40.0	100	46.0	54.0	100	20.5	79.5	100	8.4	91.6

Appendix I : Chemical reduction of Cr(VI) and Filter with quartz sand

Table 22: Removal of total Cr with quartz sand filter media (model water with total c(Cr) = 100 µg/L, (Cr (III) = 50 µg/L and Cr(VI) = 50 µg/L), Fe(II) = 2.3 mg/L, c(Ca²⁺) = 160 mg/L, c(HCO₃⁻) = 250 mg/L, media bed depth = 20 cm, quartz sand sizes = 0.5 to 1.0 mm, EBCT = 2.4 min, pH = 7±0.1).

Time, Hr	Total Cr, µg/L					Fe, mg/L				
	Influent	Effluent		Removal Cr		Influent Fe(II)	Effluent Fe(III)		Removal Fe(III)	Removal %
		Unfil	Fil	Removal Cr	Removal %		Unfil	Fil		
0.0	101.0	39.0	25.0	62.0	61.4	2.41	0.25	0.08	2.16	89.6
0.5	101.0	35.0	21.0	66.0	65.3	2.40	0.35	0.30	2.05	85.4
1.0	101.5	31.0	18.0	70.5	69.5	2.30	0.55	0.50	1.75	76.1
2.0	101.0	28.5	16.0	72.5	71.8	2.25	0.56	0.53	1.69	75.1
4.0	102.0	20.0	13.0	82.0	80.4	2.30	0.55	0.47	1.75	76.1
6.0	103.5	15.0	11.0	88.5	85.5	2.30	0.55	0.51	1.75	76.1
8.0	103.0	12.0	7.5	91.0	88.3	2.35	0.48	0.43	1.87	79.6
8.0	102.0	12.3	5.7	89.7	87.9	2.32	0.47	0.39	1.85	79.7
8.5	103.5	10.8	4.8	92.7	89.6	2.32	0.51	0.48	1.81	78.0
9.0	105.0	10.5	4.5	94.5	90.0	2.30	0.50	0.49	1.80	78.3
10.0	103.0	12.6	7.8	90.4	87.8	2.25	0.46	0.40	1.79	79.6
12.0	102.0	12.5	8.5	89.5	87.7	2.22	0.44	0.39	1.78	80.2
14.0	101.5	12.6	8.2	88.9	87.6	2.30	0.33	0.31	1.97	85.7
16.0	102.0	9.3	8.4	92.7	90.9	2.31	0.31	0.28	2.00	86.6

Table 23: Removal of total Cr with quartz sand filter media (model water with total c(Cr) = 100 µg/L, (Cr (III) = 50 µg/L and Cr(VI) = 50 µg/L), Fe(II) = 2.3 mg/L, c(Ca²⁺) = 160 mg/L, c(HCO₃⁻) = 250 mg/L, media bed depth = 40 cm, quartz sand sizes = 0.5 to 1.0 mm, EBCT = 4.8 min, pH = 7±0.1).

Time, Hr	Total Cr				Removal %	Fe, mg/L				
	Influent, µg/L	Effluent Cr µg/L		Removal Cr µg/L		Influent Fe(II)	Effluent Fe(III)		Removal Fe(III)	Removal %
		Unfil	Fil				Unfil	Fil		
0.0	102.0	22.5	18.0	79.5	77.9	2.30	0.08	0.06	2.22	96.52
0.5	102.0	18.3	15.0	83.7	82.1	2.16	0.07	0.06	2.09	96.76
1.0	102.0	15.0	13.9	87.0	85.3	2.30	0.06	0.06	2.24	97.39
2.0	101.0	13.5	11.4	87.5	86.6	2.32	0.12	0.12	2.20	94.83
4.0	103.0	10.5	7.4	92.5	89.8	2.25	0.11	0.11	2.14	95.11
6.0	103.5	10.1	8.9	93.4	90.2	2.18	0.12	0.11	2.06	94.50
8.0	102.0	8.7	8.1	93.3	91.5	2.18	0.12	0.11	2.06	94.50
8.0	102.5	8.8	8.2	93.7	91.4	2.20	0.11	0.10	2.09	95.00
8.5	102.5	5.7	4.1	96.8	94.4	2.18	0.12	0.10	2.06	94.50
9.0	100.5	6.3	4.5	94.2	93.7	2.22	0.11	0.10	2.11	95.05
10.0	100.5	5.7	4.5	94.8	94.3	2.30	0.11	0.10	2.19	95.22
12.0	100.0	4.2	2.7	95.8	95.8	2.35	0.13	0.12	2.22	94.47
14.0	101.0	3.8	2.8	97.2	96.2	2.35	0.13	0.12	2.22	94.47
16.0	100.0	3.5	3.3	96.5	96.5	2.40	0.15	0.14	2.25	93.75
16.0	101.5	3.8	3.3	97.7	96.3	2.41	0.04	0.03	2.37	98.34
16.5	102.0	3.7	3.1	98.3	96.4	2.39	0.04	0.04	2.35	98.33
17.0	103.0	3.3	3.0	99.7	96.8	2.45	0.07	0.06	2.38	97.14
18.0	103.0	3.9	3.7	99.1	96.2	2.35	0.16	0.15	2.19	93.19
20.0	102.5	4.0	4.0	98.5	96.1	2.42	0.15	0.13	2.27	93.80
22.0	101.0	4.3	3.5	96.7	95.7	2.25	0.15	0.15	2.10	93.33
24.0	101.5	3.6	3.1	97.9	96.5	2.30	0.13	0.12	2.17	94.35

Table 24: Reduction of turbidity at pH 7.

Turbidity (NTU) at pH 7				
Time, Hr	Influent	Effluent	Removal	Removal %
0	2.70	0.55	2.15	79.63
1	2.55	0.51	2.04	80.00
2	2.50	0.30	2.20	88.00
4	2.45	0.31	2.14	87.35
6	2.50	0.20	2.30	92.00
8	2.40	0.20	2.20	91.67
9	2.25	0.20	2.05	91.11
10	2.20	0.20	2.00	90.91
12	2.30	0.19	2.11	91.74
14	2.35	0.25	2.10	89.36
16	2.40	0.30	2.10	87.50
17	2.35	0.20	2.15	91.49
18	2.30	0.18	2.12	92.17
20	2.30	0.19	2.11	91.74
22	2.35	0.19	2.16	91.91
24	2.40	0.18	2.22	92.50

Table 25: Removal of total Cr with quartz sand filter media (model water with total c(Cr) = 100 µg/L, (Cr (III) = 50 µg/L and Cr(VI) = 50 µg/L), Fe(II) = 2.3 mg/L, c(Ca2+) = 160 mg/L, c(HCO3-) = 250 mg/L, media bed depth = 40 cm, quartz sand size = 0.5 to 1.0 mm, EBCT = 4.8 min, pH = 8±0.1).

Time, Hr	Total Cr, µg/L					Fe, mg/L				
	Influent, µg/L	Effluent Cr µg/L		Removal Cr µg/L	Removal %	Influent Fe(II)	Effluent Fe(III),		Removal Fe(III)	Removal %
		Unfil	Fil				Unfil	Fil		
0.0	103.0	6.8	4.7	96.2	93.4	2.33	0.0	0.0	2.33	100
0.5	104.0	5.3	4.8	98.8	95.0	2.45	0.0	0.0	2.45	100
1.0	104.0	5.7	5.0	98.3	94.5	2.35	0.0	0.0	2.35	100
2.0	104.5	4.2	4.2	100.3	96.0	2.18	0.0	0.0	2.18	100
4.0	103.5	4.9	4.2	98.6	95.3	2.19	0.0	0.0	2.19	100
6.0	103.5	4.8	4.2	98.7	95.3	2.35	0.0	0.0	2.35	100
8.0	102.0	4.5	4.3	97.5	95.6	2.30	0.0	0.0	2.30	100
8.0	102.0	5.8	5.6	96.2	94.3	2.30	0.0	0.0	2.30	100
8.5	102.5	6.6	5.5	95.9	93.6	2.35	0.0	0.0	2.35	100
9.0	103.5	7.4	6.9	96.1	92.9	2.40	0.0	0.0	2.40	100
10.0	102.5	8.2	8.1	94.3	92.0	2.41	0.0	0.0	2.41	100
12.0	102.5	8.9	7.9	93.6	91.3	2.45	0.0	0.0	2.45	100
14.0	102.0	9.0	8.1	93.0	91.2	2.35	0.0	0.0	2.35	100
16.0	102.5	9.9	9.2	92.6	90.3	2.36	0.0	0.0	2.36	100
16.0	101.0	8.4	8.1	92.6	91.7	2.45	0.0	0.0	2.45	100
16.5	101.5	8.2	7.7	93.3	91.9	2.30	0.0	0.0	2.30	100
17.0	101.5	7.5	7.3	94.0	92.6	2.20	0.0	0.0	2.20	100
18.0	102.5	8.1	7.9	94.4	92.1	2.25	0.0	0.0	2.25	100
20.0	101.5	9.1	8.9	92.4	91.0	2.35	0.0	0.0	2.35	100
22.0	101.5	10.4	9.0	91.1	89.8	2.31	0.0	0.0	2.31	100
24.0	100.5	10.2	9.7	90.3	89.9	2.35	0.0	0.0	2.35	100

Table 26: Removal of turbidity at pH 8.

Turbidity (NTU) for pH 8				
Time, Hr	Influent	Effluent	Removal	Removal %
0	2.75	0.55	2.20	80.00
1	2.65	0.51	2.14	80.75
2	2.50	0.30	2.20	88.00
4	2.50	0.20	2.30	92.00
6	2.50	0.20	2.30	92.00
8	2.45	0.15	2.30	93.88
9	2.25	0.15	2.10	93.33
10	2.30	0.10	2.20	95.65
12	2.30	0.10	2.20	95.65
14	2.35	0.10	2.25	95.74
16	2.40	0.25	2.15	89.58
17	2.45	0.20	2.25	91.84
18	2.35	0.18	2.17	92.34
20	2.35	0.15	2.20	93.62
22	2.35	0.10	2.25	95.74
24	2.45	0.10	2.35	95.92

Appendix J : Equilibrium Calculation with Phreeqc interactive for Cr(III)

Cr(III) Concentration 100 µg/L

Reading data base.

```
SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES
SOLUTION_SPECIES
PHASES
PHASES
SURFACE_MASTER_SPECIES
SURFACE_SPECIES
END
```

Reading input data for simulation 1.

```
DATABASE C:\Program Files\USGS\Phreeqc Interactive 2.15.0\minteq.v4.dat
SOLUTION 1-1
  temp      20
  pH        6
  pe        4
  redox     pe
  units     mg/kgw
  density   1
  C(4)     250
  Ca       160
  Cr       0.1
  water    1 # kg
```

Beginning of initial solution calculations.

Initial solution 1.

-----Solution composition-----

Elements	Molality	Moles
C(4)	4.166e-003	4.166e-003
Ca	3.992e-003	3.992e-003
Cr	1.923e-006	1.923e-006

-----Description of solution-----

```

pH = 6.000
pe = 4.000
Activity of water = 1.000
Ionic strength = 8.549e-003
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 1.345e-003
Total CO2 (mol/kg) = 4.166e-003
Temperature (deg C) = 20.000
Electrical balance (eq) = 6.641e-003
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 72.01
Iterations = 8
Total H = 1.110207e+002
Total O = 5.551933e+001
```

-----Distribution of species-----

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.100e-006	1.000e-006	-5.959	-6.000	-0.041
OH-	7.558e-009	6.858e-009	-8.122	-8.164	-0.042
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	4.166e-003				
H2CO3	2.819e-003	2.819e-003	-2.550	-2.550	0.000
HCO3-	1.291e-003	1.177e-003	-2.889	-2.929	-0.040
CaHCO3+	5.619e-005	5.130e-005	-4.250	-4.290	-0.040
CaCO3	1.903e-007	1.903e-007	-6.721	-6.721	0.000
CO3-2	7.309e-008	4.990e-008	-7.136	-7.302	-0.166
Ca	3.992e-003				
Ca+2	3.936e-003	2.687e-003	-2.405	-2.571	-0.166
CaHCO3+	5.619e-005	5.130e-005	-4.250	-4.290	-0.040
CaCO3	1.903e-007	1.903e-007	-6.721	-6.721	0.000
CaOH+	3.803e-010	3.472e-010	-9.420	-9.459	-0.040
Cr(2)	7.625e-020				
Cr+2	7.625e-020	4.960e-020	-19.118	-19.305	-0.187
Cr(3)	1.923e-006				
Cr(OH)+2	1.255e-006	8.165e-007	-5.901	-6.088	-0.187
Cr(OH)2+	6.517e-007	5.852e-007	-6.186	-6.233	-0.047
Cr+3	1.393e-008	5.291e-009	-7.856	-8.276	-0.420
Cr(OH)3	2.213e-009	2.213e-009	-8.655	-8.655	0.000
CrO2-	1.171e-012	1.051e-012	-11.932	-11.978	-0.047
Cr(OH)4-	9.879e-013	8.872e-013	-12.005	-12.052	-0.047
Cr(6)	6.082e-026				
HCrO4-	4.307e-026	3.868e-026	-25.366	-25.413	-0.047
CrO4-2	1.775e-026	1.212e-026	-25.751	-25.917	-0.166
H2CrO4	2.431e-032	2.431e-032	-31.614	-31.614	0.000
Cr2O7-2	0.000e+000	0.000e+000	-49.041	-49.228	-0.187
H(0)	1.487e-023				
H2	7.433e-024	7.447e-024	-23.129	-23.128	0.001
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-47.434	-47.433	0.001

-----Saturation indices-----

Phase	SI	log IAP	log KT	
Aragonite	-1.61	-9.87	-8.26	CaCO3
CaCrO4	-26.30	-28.49	-2.19	CaCrO4
Calcite	-1.42	-9.87	-8.46	CaCO3
CH4(g)	-57.49	-99.30	-41.81	CH4
CO2(g)	-1.14	-19.30	-18.16	CO2
Cr(OH)2	-18.23	-7.30	10.93	Cr(OH)2
Cr(OH)3	-1.66	-0.23	1.42	Cr(OH)3
Cr(OH)3(am)	0.52	-0.23	-0.75	Cr(OH)3
Cr2O3	1.74	-0.47	-2.21	Cr2O3
Crmetal	-58.30	-27.30	31.00	Cr
CrO3	-34.72	-37.92	-3.19	CrO3
Lime	-23.85	9.43	33.28	CaO
O2(g)	-44.80	40.00	84.80	O2
Portlandite	-13.76	9.43	23.19	Ca(OH)2

End of simulation.

Reading input data for simulation 2.

End of run.

Reading data base.

SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES
SOLUTION_SPECIES
PHASES
PHASES
SURFACE_MASTER_SPECIES
SURFACE_SPECIES
END

Reading input data for simulation 1.

DATABASE C:\Program Files\USGS\Phreeqc Interactive 2.15.0\minteq.v4.dat
SOLUTION 1-1
temp 20
pH 7
pe 4
redox pe
units mg/kgw
density 1
C(4) 250
Ca 160
Cr .1
water 1 # kg

Beginning of initial solution calculations.

Initial solution 1.

-----Solution composition-----

Elements	Molality	Moles
C(4)	4.166e-003	4.166e-003
Ca	3.992e-003	3.992e-003
Cr	1.923e-006	1.923e-006

-----Description of solution-----

pH = 7.000
pe = 4.000
Activity of water = 1.000
Ionic strength = 9.424e-003
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 3.454e-003
Total CO2 (mol/kg) = 4.166e-003
Temperature (deg C) = 20.000
Electrical balance (eq) = 4.533e-003
Percent error, $100 * (Cat - |An|) / (Cat + |An|)$ = 40.67
Iterations = 6
Total H = 1.110185e+002
Total O = 5.551933e+001

-----Distribution of species-----

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.105e-007	1.000e-007	-6.957	-7.000	-0.043
OH-	7.591e-008	6.858e-008	-7.120	-7.164	-0.044
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	4.166e-003				
HCO3-	3.303e-003	2.999e-003	-2.481	-2.523	-0.042
H2CO3	7.184e-004	7.184e-004	-3.144	-3.144	0.000
CaHCO3+	1.383e-004	1.258e-004	-3.859	-3.900	-0.041
CaCO3	4.665e-006	4.665e-006	-5.331	-5.331	0.000
CO3-2	1.894e-006	1.272e-006	-5.723	-5.896	-0.173
Ca	3.992e-003				
Ca+2	3.849e-003	2.584e-003	-2.415	-2.588	-0.173
CaHCO3+	1.383e-004	1.258e-004	-3.859	-3.900	-0.041
CaCO3	4.665e-006	4.665e-006	-5.331	-5.331	0.000
CaOH+	3.672e-009	3.340e-009	-8.435	-8.476	-0.041
Cr(2)	1.859e-021				
Cr+2	1.859e-021	1.183e-021	-20.731	-20.927	-0.196
Cr(3)	1.923e-006				
Cr(OH)2+	1.563e-006	1.397e-006	-5.806	-5.855	-0.049
Cr(OH)+2	3.061e-007	1.949e-007	-6.514	-6.710	-0.196
Cr(OH)3	5.282e-008	5.282e-008	-7.277	-7.277	0.000
Cr+3	3.488e-010	1.263e-010	-9.457	-9.899	-0.441
CrO2-	2.809e-010	2.509e-010	-9.552	-9.601	-0.049
Cr(OH)4-	2.370e-010	2.117e-010	-9.625	-9.674	-0.049
Cr(6)	5.341e-020				
CrO4-2	4.308e-020	2.892e-020	-19.366	-19.539	-0.173
HCrO4-	1.033e-020	9.230e-021	-19.986	-20.035	-0.049
H2CrO4	5.800e-028	5.800e-028	-27.237	-27.237	0.000
Cr2O7-2	5.289e-039	3.367e-039	-38.277	-38.473	-0.196
H(0)	1.486e-025				
H2	7.431e-026	7.447e-026	-25.129	-25.128	0.001
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.434	-43.433	0.001

-----Saturation indices-----

Phase	SI	log IAP	log KT	
Aragonite	-0.22	-8.48	-8.26	CaCO3
CaCrO4	-19.94	-22.13	-2.19	CaCrO4
Calcite	-0.03	-8.48	-8.46	CaCO3
CH4(g)	-66.08	-107.90	-41.81	CH4
CO2(g)	-1.74	-19.90	-18.16	CO2
Cr(OH)2	-17.85	-6.93	10.93	Cr(OH)2
Cr(OH)3	-0.28	1.14	1.42	Cr(OH)3
Cr(OH)3(am)	1.89	1.14	-0.75	Cr(OH)3
Cr2O3	4.50	2.29	-2.21	Cr2O3
Crmetal	-59.92	-28.93	31.00	Cr
CrO3	-30.34	-33.54	-3.19	CrO3
Lime	-21.87	11.41	33.28	CaO
O2(g)	-40.80	44.00	84.80	O2
Portlandite	-11.78	11.41	23.19	Ca(OH)2

End of simulation.

Reading input data for simulation 2.

End of run.

Reading data base.

SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES
SOLUTION_SPECIES
PHASES
PHASES
SURFACE_MASTER_SPECIES
SURFACE_SPECIES
END

Reading input data for simulation 1.

DATABASE C:\Program Files\USGS\Phreeqc Interactive 2.15.0\minteq.v4.dat
SOLUTION 1-1
temp 20
pH 8
pe 4
redox pe
units mg/kgw
density 1
C(4) 250
Ca 160
Cr 0.1
water 1 # kg

Beginning of initial solution calculations.

Initial solution 1.

-----Solution composition-----

Elements	Molality	Moles
C(4)	4.166e-003	4.166e-003
Ca	3.992e-003	3.992e-003
Cr	1.923e-006	1.923e-006

-----Description of solution-----

pH = 8.000
pe = 4.000
Activity of water = 1.000
Ionic strength = 9.611e-003
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 4.159e-003
Total CO2 (mol/kg) = 4.166e-003
Temperature (deg C) = 20.000
Electrical balance (eq) = 3.827e-003
Percent error, $100 * (Cat - |An|) / (Cat + |An|)$ = 32.95
Iterations = 7
Total H = 1.110178e+002
Total O = 5.551934e+001

-----Distribution of species-----

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	7.598e-007	6.858e-007	-6.119	-6.164	-0.045
H+	1.106e-008	1.000e-008	-7.956	-8.000	-0.044
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	4.166e-003				
HCO3-	3.849e-003	3.493e-003	-2.415	-2.457	-0.042
CaHCO3+	1.578e-004	1.434e-004	-3.802	-3.844	-0.042
H2CO3	8.366e-005	8.366e-005	-4.077	-4.077	0.000
CaCO3	5.319e-005	5.319e-005	-4.274	-4.274	0.000
CO3-2	2.214e-005	1.481e-005	-4.655	-4.829	-0.175
Ca	3.992e-003				
Ca+2	3.781e-003	2.530e-003	-2.422	-2.597	-0.175
CaHCO3+	1.578e-004	1.434e-004	-3.802	-3.844	-0.042
CaCO3	5.319e-005	5.319e-005	-4.274	-4.274	0.000
CaOH+	3.597e-008	3.269e-008	-7.444	-7.486	-0.042
Cr(2)	1.650e-023				
Cr+2	1.650e-023	1.046e-023	-22.782	-22.980	-0.198
Cr(3)	1.923e-006				
Cr(OH)2+	1.383e-006	1.234e-006	-5.859	-5.909	-0.050
Cr(OH)3	4.668e-007	4.668e-007	-6.331	-6.331	0.000
Cr(OH)+2	2.717e-008	1.722e-008	-7.566	-7.764	-0.198
CrO2-	2.485e-008	2.217e-008	-7.605	-7.654	-0.050
Cr(OH)4-	2.097e-008	1.871e-008	-7.678	-7.728	-0.050
Cr+3	3.114e-012	1.116e-012	-11.507	-11.952	-0.446
Cr(6)	3.912e-014				
CrO4-2	3.820e-014	2.556e-014	-13.418	-13.592	-0.175
HCrO4-	9.143e-016	8.158e-016	-15.039	-15.088	-0.050
H2CrO4	5.126e-024	5.126e-024	-23.290	-23.290	0.000
Cr2O7-2	4.150e-029	2.630e-029	-28.382	-28.580	-0.198
H(0)	1.486e-027				
H2	7.431e-028	7.447e-028	-27.129	-27.128	0.001
O(0)	7.358e-040				
O2	3.679e-040	3.687e-040	-39.434	-39.433	0.001

-----Saturation indices-----

Phase	SI	log IAP	log KT	
Aragonite	0.84	-7.43	-8.26	CaCO3
CaCrO4	-14.00	-16.19	-2.19	CaCrO4
Calcite	1.03	-7.43	-8.46	CaCO3
CH4(g)	-75.02	-116.83	-41.81	CH4
CO2(g)	-2.67	-20.83	-18.16	CO2
Cr(OH)2	-17.91	-6.98	10.93	Cr(OH)2
Cr(OH)3	0.67	2.09	1.42	Cr(OH)3
Cr(OH)3(am)	2.84	2.09	-0.75	Cr(OH)3
Cr2O3	6.39	4.18	-2.21	Cr2O3
Crmetal	-61.98	-30.98	31.00	Cr
CrO3	-26.40	-29.59	-3.19	CrO3
Lime	-19.88	13.40	33.28	CaO
O2(g)	-36.80	48.00	84.80	O2
Portlandite	-9.79	13.40	23.19	Ca(OH)2

End of simulation.

Reading input data for simulation 2.

End of run.

For Cr(III) Concentration 4.0 mg/L

Reading data base.

SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES
SOLUTION_SPECIES
PHASES
PHASES
SURFACE_MASTER_SPECIES
SURFACE_SPECIES
END

Reading input data for simulation 1.

DATABASE F:\PHREEQC\Phreeqc\Databases\minteq.v4.dat
SOLUTION 1-1
temp 20
pH 6
pe 4
redox pe
units mg/kgw
density 1
C(4) 250
Ca 160
Cr 4
water 1 # kg

Beginning of initial solution calculations.

Initial solution 1.

-----Solution composition-----

Elements	Molality	Moles
C(4)	4.166e-003	4.166e-003
Ca	3.992e-003	3.992e-003
Cr	7.693e-005	7.693e-005

-----Description of solution-----

pH = 6.000
pe = 4.000
Activity of water = 1.000
Ionic strength = 8.662e-003
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 1.295e-003
Total CO2 (mol/kg) = 4.166e-003
Temperature (deg C) = 20.000
Electrical balance (eq) = 6.766e-003
Percent error, $100 * (Cat - |An|) / (Cat + |An|)$ = 72.37
Iterations = 8
Total H = 1.110208e+002
Total O = 5.551943e+001

-----Distribution of species-----

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.101e-006	1.000e-006	-5.958	-6.000	-0.042
OH-	7.562e-009	6.858e-009	-8.121	-8.164	-0.042
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	4.166e-003				
H2CO3	2.818e-003	2.818e-003	-2.550	-2.550	0.000
HCO3-	1.291e-003	1.177e-003	-2.889	-2.929	-0.040
CaHCO3+	5.609e-005	5.118e-005	-4.251	-4.291	-0.040
CaCO3	1.899e-007	1.899e-007	-6.722	-6.722	0.000
CO3-2	7.325e-008	4.989e-008	-7.135	-7.302	-0.167
Ca	3.992e-003				
Ca+2	3.936e-003	2.681e-003	-2.405	-2.572	-0.167
CaHCO3+	5.609e-005	5.118e-005	-4.251	-4.291	-0.040
CaCO3	1.899e-007	1.899e-007	-6.722	-6.722	0.000
CaOH+	3.797e-010	3.465e-010	-9.421	-9.460	-0.040
Cr(2)	2.655e-018				
Cr+2	2.655e-018	1.722e-018	-17.576	-17.764	-0.188
Cr(3)	7.693e-005				
Cr(OH)+2	5.025e-005	3.259e-005	-4.299	-4.487	-0.188
Cr(OH)2+	2.603e-005	2.336e-005	-4.585	-4.632	-0.047
Cr+3	5.595e-007	2.112e-007	-6.252	-6.675	-0.423
Cr(OH)3	8.835e-008	8.835e-008	-7.054	-7.054	0.000
CrO2-	4.676e-011	4.196e-011	-10.330	-10.377	-0.047
Cr(OH)4-	3.946e-011	3.541e-011	-10.404	-10.451	-0.047
Cr(6)	2.545e-025				
HCrO4-	1.802e-025	1.617e-025	-24.744	-24.791	-0.047
CrO4-2	7.437e-026	5.066e-026	-25.129	-25.295	-0.167
H2CrO4	1.016e-031	1.016e-031	-30.993	-30.993	0.000
Cr2O7-2	0.000e+000	0.000e+000	-47.798	-47.986	-0.188
H(0)	1.486e-023				
H2	7.432e-024	7.447e-024	-23.129	-23.128	0.001
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-47.434	-47.433	0.001

-----Saturation indices-----

Phase	SI	log IAP	log KT	
Aragonite	-1.61	-9.87	-8.26	CaCO3
CaCrO4	-25.68	-27.87	-2.19	CaCrO4
Calcite	-1.42	-9.87	-8.46	CaCO3
CH4(g)	-57.49	-99.30	-41.81	CH4
CO2(g)	-1.14	-19.30	-18.16	CO2
Cr(OH)2	-16.69	-5.76	10.93	Cr(OH)2
Cr(OH)3	-0.06	1.37	1.42	Cr(OH)3
Cr(OH)3(am)	2.12	1.37	-0.75	Cr(OH)3
Cr2O3	4.94	2.74	-2.21	Cr2O3
Crmetal	-56.76	-25.76	31.00	Cr
CrO3	-34.10	-37.30	-3.19	CrO3
Lime	-23.85	9.43	33.28	CaO
O2(g)	-44.80	40.00	84.80	O2
Portlandite	-13.76	9.43	23.19	Ca(OH)2

End of simulation.

End of run.

Reading data base.

```
-----  
SOLUTION_MASTER_SPECIES  
SOLUTION_SPECIES  
SOLUTION_SPECIES  
PHASES  
PHASES  
SURFACE_MASTER_SPECIES  
SURFACE_SPECIES  
END  
-----
```

Reading input data for simulation 1.

```
-----  
DATABASE C:\Program Files\USGS\Phreeqc Interactive 2.15.0\minteq.v4.dat  
SOLUTION 1-1  
temp      20  
pH        6.6  
pe        4  
redox     pe  
units     mg/kgw  
density   1  
C(4)      250  
Ca        160  
Cr        4  
water    1 # kg  
-----
```

Beginning of initial solution calculations.

Initial solution 1.

-----Solution composition-----

Elements	Molality	Moles
C(4)	4.166e-003	4.166e-003
Ca	3.992e-003	3.992e-003
Cr	7.693e-005	7.693e-005

-----Description of solution-----

```
pH = 6.600  
pe = 4.000  
Activity of water = 1.000  
Ionic strength = 9.202e-003  
Mass of water (kg) = 1.000e+000  
Total alkalinity (eq/kg) = 2.710e-003  
Total CO2 (mol/kg) = 4.166e-003  
Temperature (deg C) = 20.000  
Electrical balance (eq) = 5.351e-003  
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 50.51  
Iterations = 7  
Total H = 1.110194e+002  
Total O = 5.551946e+001
```

-----Distribution of species-----

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	2.772e-007	2.512e-007	-6.557	-6.600	-0.043
OH-	3.019e-008	2.730e-008	-7.520	-7.564	-0.044
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	4.166e-003				
HCO3-	2.620e-003	2.382e-003	-2.582	-2.623	-0.041
H2CO3	1.433e-003	1.433e-003	-2.844	-2.844	0.000
CaHCO3+	1.110e-004	1.011e-004	-3.955	-3.995	-0.041
CaCO3	1.493e-006	1.493e-006	-5.826	-5.826	0.000
CO3-2	5.963e-007	4.020e-007	-6.224	-6.396	-0.171
Ca	3.992e-003				
Ca+2	3.880e-003	2.615e-003	-2.411	-2.582	-0.171
CaHCO3+	1.110e-004	1.011e-004	-3.955	-3.995	-0.041
CaCO3	1.493e-006	1.493e-006	-5.826	-5.826	0.000
CaOH+	1.478e-009	1.346e-009	-8.830	-8.871	-0.041
Cr(2)	3.820e-019				
Cr+2	3.820e-019	2.445e-019	-18.418	-18.612	-0.194
Cr(3)	7.693e-005				
Cr(OH)2+	5.113e-005	4.573e-005	-4.291	-4.340	-0.048
Cr(OH)+2	2.504e-005	1.603e-005	-4.601	-4.795	-0.194
Cr(OH)3	6.885e-007	6.885e-007	-6.162	-6.162	0.000
Cr+3	7.120e-008	2.609e-008	-7.148	-7.584	-0.436
CrO2-	1.456e-009	1.302e-009	-8.837	-8.885	-0.048
Cr(OH)4-	1.228e-009	1.099e-009	-8.911	-8.959	-0.048
Cr(6)	8.971e-021				
CrO4-2	5.592e-021	3.770e-021	-20.252	-20.424	-0.171
HCrO4-	3.379e-021	3.022e-021	-20.471	-20.520	-0.048
H2CrO4	4.771e-028	4.771e-028	-27.321	-27.321	0.000
Cr2O7-2	5.640e-040	3.610e-040	-39.249	-39.443	-0.194
H(0)	9.378e-025				
H2	4.689e-025	4.699e-025	-24.329	-24.328	0.001
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-45.034	-45.033	0.001

-----Saturation indices-----

Phase	SI	log IAP	log KT	
Aragonite	-0.71	-8.98	-8.26	CaCO3
CaCrO4	-20.82	-23.01	-2.19	CaCrO4
Calcite	-0.52	-8.98	-8.46	CaCO3
CH4(g)	-62.58	-104.40	-41.81	CH4
CO2(g)	-1.44	-19.60	-18.16	CO2
Cr(OH)2	-16.34	-5.41	10.93	Cr(OH)2
Cr(OH)3	0.84	2.26	1.42	Cr(OH)3
Cr(OH)3(am)	3.01	2.26	-0.75	Cr(OH)3
Cr2O3	6.73	4.52	-2.21	Cr2O3
Crmetal	-57.61	-26.61	31.00	Cr
CrO3	-30.43	-33.62	-3.19	CrO3
Lime	-22.66	10.62	33.28	CaO
O2(g)	-42.40	42.40	84.80	O2
Portlandite	-12.57	10.62	23.19	Ca(OH)2

End of simulation.

End of run.

Reading data base.

```
-----  
SOLUTION_MASTER_SPECIES  
SOLUTION_SPECIES  
SOLUTION_SPECIES  
PHASES  
PHASES  
SURFACE_MASTER_SPECIES  
SURFACE_SPECIES  
END  
-----
```

Reading input data for simulation 1.

```
-----  
DATABASE F:\PHREEQC\Phreeqc\Databases\minteq.v4.dat  
SOLUTION 1-1  
temp 20  
pH 7  
pe 4  
redox pe  
units mg/kgw  
density 1  
C(4) 250  
Ca 160  
Cr 4  
water 1 # kg  
-----
```

Beginning of initial solution calculations.

Initial solution 1.

-----Solution composition-----

Elements	Molality	Moles
C(4)	4.166e-003	4.166e-003
Ca	3.992e-003	3.992e-003
Cr	7.693e-005	7.693e-005

-----Description of solution-----

```
pH = 7.000  
pe = 4.000  
Activity of water = 1.000  
Ionic strength = 9.479e-003  
Mass of water (kg) = 1.000e+000  
Total alkalinity (eq/kg) = 3.444e-003  
Total CO2 (mol/kg) = 4.166e-003  
Temperature (deg C) = 20.000  
Electrical balance (eq) = 4.617e-003  
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 41.11  
Iterations = 6  
Total H = 1.110187e+002  
Total O = 5.551947e+001
```

-----Distribution of species-----

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.105e-007	1.000e-007	-6.957	-7.000	-0.043
OH-	7.593e-008	6.858e-008	-7.120	-7.164	-0.044
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	4.166e-003				
HCO3-	3.303e-003	2.999e-003	-2.481	-2.523	-0.042
H2CO3	7.183e-004	7.183e-004	-3.144	-3.144	0.000
CaHCO3+	1.381e-004	1.256e-004	-3.860	-3.901	-0.041
CaCO3	4.660e-006	4.660e-006	-5.332	-5.332	0.000
CO3-2	1.896e-006	1.271e-006	-5.722	-5.896	-0.174
Ca	3.992e-003				
Ca+2	3.849e-003	2.582e-003	-2.415	-2.588	-0.174
CaHCO3+	1.381e-004	1.256e-004	-3.860	-3.901	-0.041
CaCO3	4.660e-006	4.660e-006	-5.332	-5.332	0.000
CaOH+	3.669e-009	3.336e-009	-8.435	-8.477	-0.041
Cr(2)	6.475e-020				
Cr+2	6.475e-020	4.116e-020	-19.189	-19.385	-0.197
Cr(3)	7.693e-005				
Cr(OH)2+	6.253e-005	5.583e-005	-4.204	-4.253	-0.049
Cr(OH)+2	1.225e-005	7.790e-006	-4.912	-5.108	-0.197
Cr(OH)3	2.112e-006	2.112e-006	-5.675	-5.675	0.000
Cr+3	1.399e-008	5.048e-009	-7.854	-8.297	-0.443
CrO2-	1.123e-008	1.003e-008	-7.950	-7.999	-0.049
Cr(OH)4-	9.479e-009	8.464e-009	-8.023	-8.072	-0.049
Cr(6)	2.238e-019				
CrO4-2	1.806e-019	1.211e-019	-18.743	-18.917	-0.174
HCrO4-	4.328e-020	3.865e-020	-19.364	-19.413	-0.049
H2CrO4	2.429e-027	2.429e-027	-26.615	-26.615	0.000
Cr2O7-2	9.285e-038	5.903e-038	-37.032	-37.229	-0.197
H(0)	1.486e-025				
H2	7.431e-026	7.447e-026	-25.129	-25.128	0.001
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.434	-43.433	0.001

-----Saturation indices-----

Phase	SI	log IAP	log KT	
Aragonite	-0.22	-8.48	-8.26	CaCO3
CaCrO4	-19.32	-21.51	-2.19	CaCrO4
Calcite	-0.03	-8.48	-8.46	CaCO3
CH4(g)	-66.08	-107.90	-41.81	CH4
CO2(g)	-1.74	-19.90	-18.16	CO2
Cr(OH)2	-16.31	-5.39	10.93	Cr(OH)2
Cr(OH)3	1.32	2.75	1.42	Cr(OH)3
Cr(OH)3(am)	3.50	2.75	-0.75	Cr(OH)3
Cr2O3	7.70	5.49	-2.21	Cr2O3
Crmetal	-58.38	-27.39	31.00	Cr
CrO3	-29.72	-32.92	-3.19	CrO3
Lime	-21.87	11.41	33.28	CaO
O2(g)	-40.80	44.00	84.80	O2
Portlandite	-11.78	11.41	23.19	Ca(OH)2

End of simulation.

Reading input data for simulation 2.

End of run.

Reading data base.

SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES
SOLUTION_SPECIES
PHASES
PHASES
SURFACE_MASTER_SPECIES
SURFACE_SPECIES
END

Reading input data for simulation 1.

DATABASE F:\PHREEQC\Phreeqc\Databases\minteq.v4.dat
SOLUTION 1-1
temp 20
pH 8
pe 4
redox pe
units mg/kgw
density 1
C(4) 250
Ca 160
Cr 4
water 1 # kg

Beginning of initial solution calculations.

Initial solution 1.

-----Solution composition-----

Elements	Molality	Moles
C(4)	4.166e-003	4.166e-003
Ca	3.992e-003	3.992e-003
Cr	7.693e-005	7.693e-005

-----Description of solution-----

pH = 8.000
pe = 4.000
Activity of water = 1.000
Ionic strength = 9.642e-003
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 4.180e-003
Total CO2 (mol/kg) = 4.166e-003
Temperature (deg C) = 20.000
Electrical balance (eq) = 3.882e-003
Percent error, $100 * (Cat - |An|) / (Cat + |An|)$ = 33.25
Iterations = 7
Total H = 1.110180e+002
Total O = 5.551950e+001

-----Distribution of species-----

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	7.599e-007	6.858e-007	-6.119	-6.164	-0.045
H+	1.106e-008	1.000e-008	-7.956	-8.000	-0.044
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	4.166e-003				
HCO3-	3.849e-003	3.492e-003	-2.415	-2.457	-0.042
CaHCO3+	1.577e-004	1.433e-004	-3.802	-3.844	-0.042
H2CO3	8.365e-005	8.365e-005	-4.078	-4.078	0.000
CaCO3	5.315e-005	5.315e-005	-4.274	-4.274	0.000
CO3-2	2.215e-005	1.481e-005	-4.655	-4.830	-0.175
Ca	3.992e-003				
Ca+2	3.781e-003	2.528e-003	-2.422	-2.597	-0.175
CaHCO3+	1.577e-004	1.433e-004	-3.802	-3.844	-0.042
CaCO3	5.315e-005	5.315e-005	-4.274	-4.274	0.000
CaOH+	3.596e-008	3.268e-008	-7.444	-7.486	-0.042
Cr(2)	5.747e-022				
Cr+2	5.747e-022	3.639e-022	-21.241	-21.439	-0.198
Cr(3)	7.693e-005				
Cr(OH)2+	5.534e-005	4.937e-005	-4.257	-4.307	-0.050
Cr(OH)3	1.867e-005	1.867e-005	-4.729	-4.729	0.000
Cr(OH)+2	1.088e-006	6.888e-007	-5.964	-6.162	-0.198
CrO2-	9.941e-007	8.868e-007	-6.003	-6.052	-0.050
Cr(OH)4-	8.389e-007	7.483e-007	-6.076	-6.126	-0.050
Cr+3	1.247e-010	4.463e-011	-9.904	-10.350	-0.446
Cr(6)	1.639e-013				
CrO4-2	1.601e-013	1.071e-013	-12.796	-12.970	-0.175
HCrO4-	3.830e-015	3.417e-015	-14.417	-14.466	-0.050
H2CrO4	2.147e-023	2.147e-023	-22.668	-22.668	0.000
Cr2O7-2	7.286e-028	4.614e-028	-27.138	-27.336	-0.198
H(0)	1.486e-027				
H2	7.431e-028	7.447e-028	-27.129	-27.128	0.001
O(0)	7.358e-040				
O2	3.679e-040	3.687e-040	-39.434	-39.433	0.001

-----Saturation indices-----

Phase	SI	log IAP	log KT	
Aragonite	0.84	-7.43	-8.26	CaCO3
CaCrO4	-13.38	-15.57	-2.19	CaCrO4
Calcite	1.03	-7.43	-8.46	CaCO3
CH4(g)	-75.02	-116.83	-41.81	CH4
CO2(g)	-2.67	-20.83	-18.16	CO2
Cr(OH)2	-16.36	-5.44	10.93	Cr(OH)2
Cr(OH)3	2.27	3.69	1.42	Cr(OH)3
Cr(OH)3(am)	4.44	3.69	-0.75	Cr(OH)3
Cr2O3	9.59	7.39	-2.21	Cr2O3
Crmetal	-60.44	-29.44	31.00	Cr
CrO3	-25.78	-28.97	-3.19	CrO3
Lime	-19.88	13.40	33.28	CaO
O2(g)	-36.80	48.00	84.80	O2
Portlandite	-9.79	13.40	23.19	Ca(OH)2

End of simulation.

Reading input data for simulation 2.

End of run.

Appendix K : Calibration data (Spectrophotometer)

Figure 1. Calibration curve for determination of Cr(VI).

