

# UNESCO-IHE INSTITUTE FOR WATER EDUCATION



## **Critical Review on the Adsorptive Removal of Heavy Metals by Iron Oxides Based Media**

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Institute for Water Education



# **Critical Review on the Adsorptive Removal of Heavy Metals by Iron Oxides Based Media**

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The findings, interpretations and conclusions expressed in this study do neither necessarily reflect the views of the UNESCO-IHE Institute for Water Education, nor of the individual members of the MSc committee, nor of their respective employers.

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## Abstract

Urban stormwater runoff is defined as the water that is drained from the impervious surfaces in the densely populated areas. Contamination, sedimentation, erosion, and increased flow velocities, which have a negative impact on aquatic ecosystems, are associated with urban runoff. In particular, heavy metals are in the category of first priority pollutants found in the urban runoff. Metals in urban stormwater have potential to cause adverse health effects on aquatic life, as well as to have acute or chronic toxic impact on human health. Therefore, attention should be directed on developing technologies for removal of heavy metals from the stormwater runoff.

There are several treatment methods to remove heavy metals from the stormwater runoff. Conventional removal methods like precipitation and coagulation, adsorption on activated alumina or advance techniques like ion exchange, and reverse osmosis, are not practical because of either their high investment, operation and maintenance costs, or insufficient removal efficiency. The most promising technology for removal of dissolved heavy metal fractions from stormwater is filtration via sorption with effective filtration media.

The goal of this research was to further understand and advance adsorptive removal of selected heavy metals (Cd, Cr(III), Cr(VI), Cu, Pb) by using iron oxides based media. The study focused on the literature review of existing and emerging treatments of urban stormwater runoff with emphasis on heavy metal removal. Further, it focused on competitive removal of selected heavy metals, that are commonly found in urban stormwater runoff, using Iron Oxide Coated Sand (IOCS) as adsorbent.

From literature review two most promising stormwater treatment technologies were determined. The first of treatment technologies consist of a combination of two operational units, a detention pond and adsorption filters. The second treatment proposed consists of constructed bioretention filtration system. Even though the first proposed technology is rather expensive method, it is used in case when open basins or wetlands are not available for biofiltration.

Adsorptive removal efficiency of heavy metals was studied as a function of contact time, heavy metals' concentration, adsorbent dosage and pH value. A series of batch experiments were conducted to remove single metals (Cd, Cu, Cr(III), Cr(VI), and Pb) and combination of different metals with Cr(III) and Cr(VI) by means of adsorption on IOCS. Simultaneously, experiments were conducted without the presence of adsorbent to determine the stability of metals in model water that mirrored the quality of urban stormwater runoff. From the results it was concluded that for all of the metals included in this study, except for Cr(VI), very efficient adsorption on IOCS can be achieved (complete metal removal was achieved within 15 min of contact time. Hexavalent chromium was however removed less effectively. Results of blank experiments conducted without adsorbent showed that only Cr(VI) would not partially precipitate over the time.

From the results it was found, that in the adsorption of Cr(VI) is pH dependent. In the experiments without adsorbent present pH value influenced the co-occurring stability of Cd, Cr(III), Cr(VI), Cu, and Pb. These metal species will form (complexed) compounds which can precipitate depending on the pH. This conclusion is important factor for the future study of competitive adsorption of different heavy metals by IOCS.

**Keywords:** Adsorption, cadmium, chromium, copper, heavy metals, IOCS, lead, precipitation, stormwater, treatment, urban runoff





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## **List of symbols, Acronyms and Abbreviations**

AAS	Atomic Absorption Spectrophotometer
BMPs	Best Management Practices
Cd	Cadmium
Cr(III)	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
Conc.	Concentration
Cu	Copper
Demi	Demineralised
GF	Graphite Furnace
Hrs	Hours
IOCS	Iron Oxide Coated Sand
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
mg/g	Milligram per gram
mg/l	Milligram per litre
µg/l	Microgram per litre
Pb	Lead
SI	Saturation Index
USEPA	U.S. Environmental Protection Agency



# 1. INTRODUCTION

## 1.1 General background

During the rain storm and other precipitation events in urban areas, impervious surfaces (roads, parking lots and sidewalks) along with rooftops carry polluted stormwater to storm drains, instead of allowing the water to percolate through soil. Therefore, groundwater recharge decreases and the amount of water remaining on the surface increases, which in some cases causes flooding. The runoff accumulates debris, chemicals, sediment or other pollutants that could have negative effect on water quality, if the runoff is discharged improperly.

The primary method to control stormwater discharges is the use of best management practices (BMPs). Although most of the BMPs are constructed to control the water flow in order to avoid flooding, in recent years more attention has been directed to construct BMPs that also remove pollutants (Genç-Fuhrman, et al., 2007). The first step is source control, for keeping pollutants from coming into the receiving water body. Namely, it is generally more cost-effective to prevent pollution than to collect and remove pollutants. Source control alone is not sufficient, though, for meeting effluent criteria for direct discharge of stormwater into the receiving water body. The next step should therefore be end-of-pipe treatment (Kellems, et al., 2004). Most of the treatment schemes are based on detention and infiltration principle. However, this system is inadequate for removal of colloidal and dissolved fractions. Consequently, it is necessary to introduce a secondary treatment of stormwater that will remove both, colloidal and dissolved fractions. The biggest concern in secondary treatment is removal of heavy metals from urban runoff.

The primary sources of metals in urban stormwater are industry and automobiles. Atmospheric deposition of metals can make a significant contribution to pollution of runoff, as well. Water supply can be influenced by the metals in urban storm water. Also, metals can be very toxic to aquatic life. In urban runoff typically found metals, in particular heavy metals, are lead (Pb), zinc (Zn), copper (Cu), chromium (Cr), cadmium (Cd), nickel (Ni), arsenic (As), and mercury (Hg).

There are several methods to remove heavy metals from the stormwater runoff. Conventional and advance methods like precipitation and coagulation, ion exchange, activated alumina and reverse osmosis are not practical because of their high investment, operation and maintenance costs. In addition some of conventional techniques can not produce effluent that can fulfil discharge water quality regulations. The most promising technology for removal of dissolved heavy metal fractions from stormwater is adsorptive filtration, with an effective adsorbent. There is a wide range of metal sorbents available as possible filtration media: alumina, bark, fly ash (FA), granulated activated carbon (GAC), granulated ferric hydroxide (GFH), iron oxide-coated sand (IOCS), natural zeolit (NZ), sand etc. (Genç-Fuhrman, et al., 2007). Currently, iron-based bonding materials are widely used as a metal adsorbent. These are usually selected because they are cheap, easily produced and they have low potential for adding a further pollutant to the system

(Deliyanni, et al., 2007). One most commonly used iron oxides based adsorbents is iron oxide-coated sand (IOCS).

## **1.2 Problem statement**

Urban stormwater runoff contains significant concentrations of heavy metals. Treatment of urban runoff is of importance for both, environmental quality and water reuse. Metals in urban stormwater have potential to cause adverse health effects on aquatic life. Also, metals have can have acute or chronic toxic impact on human health. Water quality standards regulate allowed concentrations of metals in the water bodies and in the drinking water. Therefore, attention should be directed on developing technologies for efficient removal of heavy metals from the stormwater runoff.

There are a lot of scientific articles and books written on the problem of heavy metal removal from stormwater runoff, thus there is necessity to assess the existing data. Furthermore, some treatment technologies are still in development. Thus, there should be a tendency to determine the optimal treatment technology for heavy metal removal. In this way, the future studies could be done much easier and with higher quality of results.

Although many studies on heavy metals' removal from stormwater using a variety of sorbents have been carried out in past, the results are difficult to compare directly, because studies usually give information only about removal percentages and do not document all relevant experimental conditions. Furthermore, the majority of previous work on heavy metal removal using filtration/adsorption is conducted as treatment in a single heavy metal system. Only few studies have been carried out with model water mirroring real stormwater composition. (Genç-Fuhrman, et al., 2007).

For the aforementioned reasons, further studies need to be carried out to assess the competitive effects of co-occurrent heavy metals, which are to be removed from stormwater. Additionally, further research needs to be done to assess the effects of selected water quality parameters, that are considered as controlling variable on adsorption efficiency and capacity in case of competitive sorption. In conclusion, to fill the gap of previously carried out research, further understanding of sorption behaviour with realistic stormwater experimental conditions is needed.

## **1.3 Goal and objectives**

The goal of this research is to better understand and advance knowledge on adsorptive removal of selected heavy metals by using iron oxides based adsorbents.

The detailed objectives of the research are:

- To make the state-of-the-art literature review on available treatment technologies for heavy metals removal from urban stormwater runoff.
- To carry out short batch experiments without adsorbent in order to assess the effect of water quality (e.g. pH,  $\text{HCO}_3^-$ ) on co-occurring stability of Cd, Cr(III), Cr(VI), Cu, and Pb in water.

- To screen adsorption efficiency of IOCS for competitive removal of Cd, Cr(III), Cr(VI), Cu, and Pb at different pH values and  $\text{HCO}_3^-$  concentration in short batch adsorption experiments.



## **2. LITERATURE REVIEW**

### **2.1 Characteristic of urban stormwater runoff**

Urban stormwater runoff is defined as the water that is drained from the impervious surfaces like roads, freeways, sidewalks, roofed structures, parking lots, airports, and industrial sites among others, in the densely populated areas. Hydrologic and hydraulic changes of the built urban environment are fundamentally related to the change in the physical and chemical characteristics of urban stormwater. Stormwater quantity and quality are affected by the hydrologic characteristics and the urban hydraulic characteristics. Urbanization effects are typically categorised as (1) change in peak flow characteristics, (2) change in total runoff, (3) change in water quality, and (4) change in hydrologic morphology (Leopold, 1968).

With urban runoff are associated different kind of contaminants, sediments, eroded material, and increased flow velocities which have a negative impact on aquatic ecosystems. Some contaminates most commonly found in urban runoff (like heavy metals, oil and grease) can be very toxic to aquatic life and also detract from the pleasurable use of streams, lakes, and bays. Additionally, many communities use surface water for drinking water supplies, especially the larger communities, and some of the pollutants that are found in water can be very difficult to remove in order to satisfy drinking water standards (Mohr, 1998).

The common sources of contamination include residential and commercial areas, industrial activities, construction, streets and parking lots, as well as atmospheric deposition. The major pollutants found in stormwater runoff and their possible sources are summarized in Table 2.1 (Strassler, et al., 1999).

Dissolved, colloidal, and suspended solids which are transported in stormwater runoff, form a complex heterogeneous mixture that includes heavy metals and (in)organic compounds. Solids which are carried by urban runoff are capable of mediating transport of heavy metals because they have reactive sites and large surface-to-volume ratios (Field and Sullivan, 2003). Figure 2.1 shows major sources of heavy metals in urban runoff.

**Table 2.1:** Sources of contaminants in urban storm water runoff (Strassler, et al., 1999)

Contaminant	Contaminant Sources
Sediment and Floatables	Streets, lawns, driveways, roads, construction activities, atmospheric deposition, drainage channel erosion
Pesticides and Herbicides	Residential lawns and gardens, roadsides, utility right-of-ways, commercial and industrial landscaped areas, soil wash-off
Organic Materials	Residential lawns and gardens, commercial landscaping, animal wastes
Metals	Automobiles, bridges, atmospheric deposition, industrial areas, soil erosion, corroding metal surfaces, combustion processes
Oil and Grease/ Hydrocarbons	Roads, driveways, parking lots, vehicle maintenance areas, gas stations, illicit dumping to storm drains
Bacteria and Viruses	Lawns, roads, leaky sanitary sewer lines, sanitary sewer cross-connections, animal waste, septic systems
Nitrogen and Phosphorus	Lawn fertilizers, atmospheric deposition, automobile exhaust, soil erosion, animal waste, detergents



**Figure 2.1:** Vehicular and pavement sources of constituents generated by traffic activities (Field and Sullivan, 2003)

In particular heavy metals are in the category of first priority pollutants found in urban runoff. In many cases end-of-pipe concentrations exceed EPA environment water quality criteria and drinking water standards. The frequency with which metals were detected as priority pollutants in the NURP study is presented in Table 2.2 (Strassler, et al., 1999).



**Table 2.2:** Most frequently detected priority pollutants in Nationwide Urban Runoff Program Samples (1978-83) (adopted from: Strassler, et al., 1999)

Inorganics	Organics
<b>Detected in 75% or more</b>	
94% Lead 94% Zinc 91% Copper	None
<b>Detected in 50-74%</b>	
58% Chromium 52% Arsenic	None
<b>Detected in 20-49%</b>	
48% Cadmium 43% Nickel 23% Cyanides	22% Bis(2-ethylhexyl)phthalate 20% $\alpha$ -Hexachloro-cyclohexane
<b>Detected in 10-19%</b>	
13% Antimony 12% Beryllium 11% Selenium	19% $\alpha$ -Endosulfan 19% Pentachlorophenol* 17% Chlordane* 15% Lindane* 15% Pyrene** 14% Phenol 12% Phenanthrene** 11% Dichloromethane 10% 4-Nitrophenol 10% Chrysene** 10% Fluoranthene**

\* Chlorinated hydrocarbon

\*\* Polynuclear aromatic hydrocarbon

Many of these metals in very small amounts are necessary to support life. On the other hand, in larger amounts, they become toxic. Heavy metals are non biodegradable and tend to accumulate in living organisms. Consequently, through the food chain heavy metals may end up in human body. In Table 2.3 are given values of pollutants that can exceed the acute toxicity values for cold water fish community.

**Table 2.3:** Probability of event mean concentration of constituents in wisconsin storm water exceeding wisconsin surface water and ground water quality standards: metals  
(adopted from: Strassler, et al., 1999)

Constituent	Probability of exceeding acute toxicity criteria for cold water fish communities (percent)	
	Storm Sewers	Streams
Cadmium, total recoverable	11	0
Copper, total recoverable	87	9
Lead, total recoverable	18	0
Silver, total recoverable	20	-
Zinc, total recoverable	91	7

Heavy metals can be present in water in ionic form. Their dissolution depends on factors such as pH, redox conditions, alkalinity, residence time, complexation agents, and suspended solids. As ionic species, each of these metals exists primarily as cations with a +2 charge (Field and Sullivan, 2003).

### Heavy metal partitioning

Heavy metal partitioning in stormwater is a dynamic process between the dissolved and particulate-bound fractions. It does not matter if it is a pavement runoff, urban stormwater, or any other aqueous system, between heavy metals in solution and solids there is a temporal partitioning. Also, it does not matter if these solids are in suspension or as settleable solids of fixed or mobile bed load. This partitioning includes specific mass transfer mechanisms of sorption, ion exchange, and surface complexation with both organic and inorganic sites on the solid matter. Partitioning is generally described as the nonlinear reversible reactions between the solid phase and soluble phase concentrations. Therefore, the sum of the dissolved and the particulate-bound concentrations is total concentration of a heavy metal (2.1).

$$c_T = c_d + c_p \quad (2.1)$$

where:

$c_T$  ..... total concentration (mg/l)

$c_d$  ..... concentration of dissolved fraction (mg/l)

$c_p$  ..... concentration of particulate-bound fraction (mg/l)

Operationally, the soluble or dissolved fraction is the fraction that passes through 0.45  $\mu\text{m}$  membrane filter and therefore contains the dissolved and part of the colloidal-bound heavy metals. The particle-bound concentration,  $c_p$ , is defined as the product of the heavy metal concentration on the solid phase,  $c_s$ , in terms of mass per mass of solids and the

concentration of the adsorbing solid material in the aqueous system,  $m$ , typically measured as total suspended solids (TSS) in terms of mass per volume of aqueous solution (2.2).

$$c_p = c_s \cdot m \quad (2.2)$$

At equilibrium conditions the rates of sorption and desorption are equal. Under these conditions concentration equilibrium exists between the dissolved and solid phase concentrations of heavy metals (Sansalone et al., 1998). The ratio of these phases at equilibrium is referred to as the partitioning coefficient,  $K_d$ , for a particular heavy metal at a particular pH and redox level (2.3).

$$K_d = \frac{c_p}{c_d} \quad (2.3)$$

From the equations 2.1-2.3 the dissolved fraction ( $f_d$ ) and the particulate-bound fraction ( $f_p$ ) can be defined (2.4, 2.5 respectively).

$$f_d = \frac{D}{D+P} = \frac{c_d}{c_T} = \frac{1}{1+K_d \cdot m} \quad (2.4)$$

$$f_p = \frac{P}{D+P} = \frac{c_p}{c_T} = \frac{K_d \cdot m}{1+K_d \cdot m} \quad (2.5)$$

where:

$D$  .....dissolved mass of a heavy metal (mg)

$P$  ..... particulate-bound mass of a heavy metal (mg).

For  $f_d > 0.5$ , the heavy metal mass is mainly in dissolved form. The product of  $K_d \cdot m$  is dimensionless and  $K_d$  is usually expressed as liters per kilogram (l/kg). The larger the  $K_d$  value, the greater the partitioning to the solid phase. Heavy metals in pavement runoff have  $K_d$  values that range from  $10^2$  to over  $10^6$  (Sansalone and Buchberger, 1997).

During the rainfall runoff event partitioning varies significantly depending on characteristics of hydrologic events and traffic patterns. The partitioning is a function of pH, alkalinity, residence time, and solids' characteristics. When they are in ionic form they can have an immediate toxic impact (Field and Sullivan, 2003).

## 2.2 Management of urban stormwater runoff

As the urban stormwater runoff is dynamic, discontinuous and extensive, its best control and treatment measure cannot be achieved without flexible and creative approach. Especially in stormwater pollution control management, prevention, reduction and treatment approaches are all required within the concerned area. Single method

management usually cannot provide the required water quality of stormwater runoff due to its diffusive and widespread characteristics.

The technologies for stormwater management can be organized by separating the drainage system into three physical areas:

1. Watershed area ( storm runoff generation and/or collection area).
2. Installed modified and/or natural drainage systems (transportation pipelines, channels, storage, etc.).
3. End-of-pipe area(point source).

Generally all the technologies which are used for these areas can be divided into structural and non-structural. While the non-structural approach focuses on the prevention in the upstream collection area, the much more expensive structural approach is mostly used for the drainage system and end-of the-pipe area.

Prevention of potential pollution and protection of the existing water resources are considered more cost-effective than the remediation after the pollution occurs. However, in reality the pollution often already exist, thus the prevention solution is not feasible. For this reason, treatment before discharge might be necessary.

Early review of the existing facilities and improving their utilization and can be of great help in stormwater management since all the implementations must fulfil the financial and (possibly) deadline restrains. In addition, also flood control and pollution reduction should be considered as part of the new solution implementation. The major challenge in stormwater management is to gain the public cooperation and financial support in the implementation of a management plan, due to the fact that public does not generally perceive stormwater to be an environmental pollution problem (Field and Sullivan, 2003).

### **2.1.1 Watershed area**

The goal of upstream stormwater management plan is to provide sufficient stormwater quality in the basin so that further treatments in the downstream are not necessary. As mentioned before, the main practices in the watershed area focus on the non-structural solutions. The technologies and practices are divided into three categories including both, structural and non-structural solutions.

1. **Regulations, Local Ordinances, and Public Education.** This non-structural approach is probably the most cost-effective, and thus the primal, solution. For any regulations to work there needs to be an existing framework within which the regulation are placed (e.g. local ordinances, zoning, planning regulations), together with dedicated resources to enforce them. In addition, for regulations to be effective it is necessary for the institutional systems to set the regulations in place and to enforce them. Also the public education can have significant effect because an aroused and concerned public has the power to alter the behaviour at all levels.
2. **Source Control of Pollutants.** In order to achieve pollutants source control, variety of structural means that divert flow can be used to prevent the contaminated

stormwater to come in contact with uncontaminated stormwater. Pollution prevention options like street sweeping, toxic and hazardous waste management, as well as material and chemical substitution can be highly effective. Many of these source control solutions are referred to as "good house-keeping" practices.

3. **Source Treatment, Flow Attenuation, and Storm Runoff Infiltration.** These are mainly structural practices with aim to remove point source pollutants, control stormwater release to the downstream conveyance system, and to infiltrate stormwater into the ground or reuse stormwater (e.g. vegetative BMPs, detention facilities, infiltration practices).

### 2.1.2 Installed drainage system

The BMPs in the upstream cannot promise a sufficient stormwater quality especially in the urban areas. So further controls are needed in the downstream drainage system and end-of-pipe area.

Control practices that can be applied to the drainage system are relatively limited, especially for existing systems, and involve the items listed below:

- Removal of illicit or inappropriate cross-connections.
- Catch basin cleaning.
- Critical source area treatment devices.
- Infiltration.
- In-line storage.
- Off-line storage.

The effectiveness of each drainage systems depends on lot of different factors (e.g. applied BMPs, urbanization, pollution). However, in order to keep drainage system working efficiently, regular maintenance is necessary.

### 2.1.3 End-of-pipe area

Point sources from the end-of-pipe area can influence the water quality in the receiving water body dramatically. Thus, possible treatment to reduce the impact is necessary. The following are commonly used practices.

- **Biological treatment.** Organic pollutants are largely removed by the micro-organisms either under aerobic or anoxic conditions. Active biomass has the key role in maintaining the effectiveness of the system. It can be achieved by either continuous operation or external biomass acquisition.
- **Physical/Chemical treatment.** These treatments are considered suitable for pollutant shock loads. They can considerably reduce the amount of suspended

solids (SS), and they can be adapted to automatic operation. SS characteristics and the applied level of treatment influence the SS removal rate (Field and Sullivan, 2003).

## **2.3 Treatment of urban stormwater runoff**

### **2.3.1 Nature of stormwater vs. treatment potential**

There is significant difference between domestic wastewater treatment and stormwater treatment. This is because hydrological factors, environmental conditions, as well as physical and chemical characteristics of the stormwater and the domestic wastewater are dramatically different. These major differences in their natures make it harder to achieve an efficient stormwater treatment when compared to the conventional sewerage treatment.

First of all, hydrologic factors require prior considerations in a stormwater treatment design and are the major factors influencing treatment efficiency. The stochastic nature of rainfall gives uncertainty to the temporal occurrence and loading forecasting of stormwater runoff. In addition, unsteady nature of flow process is associated with the stochastic nature of rainfall runoff, as well. In a discontinuous rainfall event, the difference in the runoff flow rate can be of several magnitude orders. Also the unsteady pattern of the flow and the peak flow occurrence are changing with location, season and event conditions. The volume and duration of the runoff are the two basic characteristics to be considered in any stormwater treatment selection. Varying nature of these two characteristics makes them the main constrain in stormwater treatment design.

Another factor affecting stormwater treatment design are environmental factors. These refer to the regional and microclimate characteristics, as well as the spatially and temporally varying demographics in the area. Though there might be similarities between urban areas, the characteristics in each urban site are unique. Thus it is necessary to define appropriate stormwater treatment for the particular urban environment.

The biology of the stormwater is likely dominated by the physicochemical characteristics of the urban stormwater, especially the portion that flows through the pavement area. Physicochemical characteristics are therefore the key in both, treatment and characterization of urban stormwater. The dominating parameters in partitioning mediation, surface complexation, and (in)organic species speciation are redox conditions and pH. Solid particles carried by the stormwater are also not homogenous. The loading, gradation, densities and surface characteristics of the transported solids are all different. Each of these solids characteristics can influence the treatment of stormwater runoff.

Another critical factor in stormwater characterization and treatment design is residence time distribution (RTD). Precipitation type should also be taken into account for treatment selection. For instance, the urban snow and the melting runoff are totally different from the rainfall runoff, thus different approach should be taken in treatment design (Field and Sullivan, 2003).

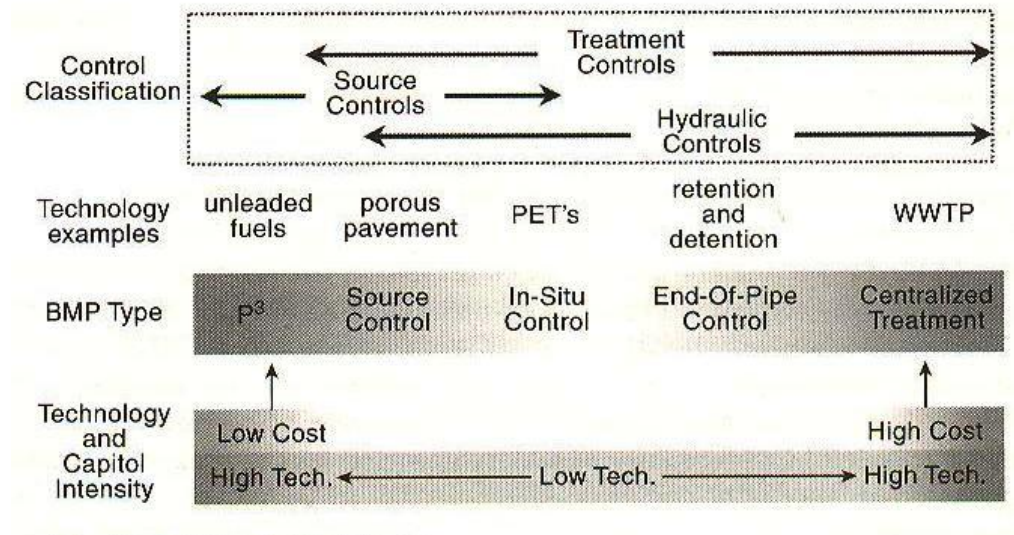
### 2.3.2 Best Management Practices

Best management practices (BMPs) are considered as effective and practical measures that minimize the impact of both the infrastructure and human activities on water quality. BMPs can be structural or non structural practices, or combination of both (U.S. DOT, 1996). Structural BMPs are aimed at intercepting and detaining stormwater runoff for a sufficient period of time, so that target contaminants can settle down from water body or be filtered through the underlying soil. However, the trapped pollutants should be treated properly, as well.

BMPs with non-structural practices aim at pollution prevention or "source control". Minimization of the pollutants' accumulation and initial concentration in the stormwater runoff is the main consideration in the design of the non-structural measures. In order to achieve a better treatment system, the non-structural practices are usually used in combination with the structural ones.

BMPs can be divided into three major categories:

1. **Source controls** are typically non-structural measures that aim at preventing the pollution generation or trapping the pollutants before the rainfall runoff reaches the drainage system.
2. **Treatment-based controls** imply treatment of the stormwater with physical, chemical and/or biological treatment methods.
3. **Hydraulic controls** are structural controls that attenuate the urban hydrograph or divert the flow away from source areas.



**Figure 2.2:** The continuum of BMP controls (Field and Sullivan, 2003)

Figure 2.2 shows layout of the different approaches in stormwater pollution control. The P<sup>3</sup> (pollution prevention plan) is the only true type of source control by definition, because it completely removes the constituents that can potentially become a pollutants. For instance, removal of lead from the gasoline is one example of this practice.

In recent years, regulations forced various structural measures to control the urban runoff. Table 2.4 summarizes the design robustness of different stormwater quality controls from senior stormwater quality management experts. The efficiency of these measures depends largely on the site characteristics, while the pollutants' removal from the urban runoff depends on the environmental and physical factors (Chen and Richard Liew, 2003).

**Table 2.4:** Robustness of best management practice design technology  
(Chen and Richard Liew, 2003)

Type	Hydraulic Design	Removal of Constituents in Stormwater		
		Total Suspended Sediments and Solids	Dissolved	General Performance
Swale	Moderate-high	Low-moderate	None-low	Low
Buffer strip	Low-moderate	Low-moderate	None-low	Low
Infiltration basin	Moderate-high <sup>a</sup>	High	Moderate-high	Moderate
Percolation trench	Low-moderate <sup>a</sup>	High	Moderate-high	Moderate-high
Extended detention	High	Moderate-high	None-low	Moderate-high
Wet retention pond	High	High	Low-moderate	Moderate-high
Wetland	Moderate-high	Moderate-high	Low-moderate	Low-high <sup>b</sup>
Media filter	Low-moderate	Moderate-high	None-low	Low-moderate
Oil separator	Low-moderate	Low	None-low	Low
Catch basin Inserts	Unknown	NA <sup>d</sup>	NA	NA
Monolithic porous pavement <sup>b</sup>	Low-moderate	Moderate-high	Low-high <sup>c</sup>	Low-moderate
Modular porous pavement <sup>b</sup>	Moderate-high	Low-moderate	Low-high <sup>c</sup>	Low-high <sup>c</sup>

<sup>a</sup> Weakest design aspect, hydraulic or constituent removal, governs overall design robustness.

<sup>b</sup> Robustness is site-specific and maintenance dependent.

<sup>c</sup> Low-moderate whenever design with an underdrain and not intended for infiltration and moderate-high when site specific permit infiltration.

<sup>d</sup> Not applicable.

### 2.3.3 Treatment processes for stormwater

The stormwater treatment mechanisms are selected on the basis of water quantity and quality characteristics of urban stormwater stream. Stormwater treatment usually consist of several different unit operations and processes. In part, this may be due to the complicated nature of stormwater. Removal of high risk pollutants, like heavy metals, from urban runoff is essential process in having an acceptable stormwater treatment. For all treatment systems, residual management needs significant consideration.

#### Settling basins

From the historical point of view for almost all forms of water and wastewater treatments, sedimentation has been used as the primary unit operation. From the BMPs point of view usage of settling basins or detention ponds is the most common way of urban stormwater quantity and quality mitigation. Settling basins are capable of reducing downstream flooding and bank erosion when the appropriate regional management is applied. Also,



they intercept and detain the stormwater runoff which provides settling of particulate matter, hence improving stormwater quality.

Purpose of open detention ponds and settling basins is to detain urban stormwater and reduce peak flows. They can be designed as:

1. Extended (dry) detention basins that only temporarily detain stormwater.
2. Wet retention ponds that maintain a permanent body of water.
3. An integrated combination of both of the above.

**Ad 1.** Dry detention basins can have problem with removal of heavy metals from water depending on pH and redox conditions because they are not suitable for removal of pollutants that are mostly in soluble phase. Nevertheless, if most of the basin is managed as shallow wetland, it is possible to achieve removal of the soluble-phase pollutants, because basin utilizes natural biological removal processes. Namely accumulated sediments display a high affinity for metals.

**Ad 2.** Wet retention ponds are capable of achieving high removal rates from stormwater runoff of both, particulate-bound settleable solids, as well as soluble-phase pollutants and nutrients, as long as they are correctly sized and managed. The only difference between wet retention ponds and dry retention basins is, that permanent water body is incorporated in the design of wet retention ponds (Field and Sullivan, 2003).

Comparing removal efficiency of some heavy metals by extended dry basins and wet retention ponds it can be seen that they are practically the same: Pb (70-80%), Zn (40-50%) (WEF, 1998).

## **Filtration systems**

Together with sedimentation, filtration has been traditionally used as a primary treatment of water and wastewater. It has shown to be very effective for stormwater clarification. Primarily filtration systems are operating as a pre-treatment measure and are used as stormwater conveyance for other downstream BMPs. In fact, the main treatment objective of filtration systems is particulate load removal from the runoff, hence preventing clogging or reducing performance efficiency in subsequent downstream BMPs. The two-phase approach of sedimentation and filtration provides higher pollutant removal efficiencies and reduces maintenance requirements, therefore increases the design life of the control facility (Field and Sullivan, 2003). Filtration systems used for urban runoff treatment are:

1. Vegetated swales.
2. Filter strips.
3. Sand filters.
4. Porous pavement.

**Ad 1.** Vegetated grassed swales, or bio-filters, are basically designed as stormwater conveyance systems in form of vegetated channels. Flow depth within them is rarely above the height of the vegetation that grows within them. Physical filtration through grass and infiltration through the soil are the primary pollutant removal mechanisms, despite the fact that runoff is usually not detained for sufficient period of time for fine suspended solids to be effectively removed. In addition, pollutant removal efficiencies of vegetated swales may easily vary during the large storm events and seasons. A well-designed, well maintained swale systems are capable to remove 50 to 90% of trace metals from stormwater runoff (US DOT, 1996).

**Ad 2.** Filter strips, or vegetated buffer strips, are vegetated sections of land which are essentially flat, or with low slope. They are designed only to accept stormwater runoff as overland sheet flow. Therefore, the main purpose of filter strips is to intercept flow, lower flow velocities, and spread the runoff as sheet flow. Removal of soluble pollutants is accomplished when pollutants infiltrate into the soil and are subsequently sorbed to the soil or taken up by the plant roots. Measured field data have shown typical removal rate of 40% for zinc (particulate), and 25% for lead. (Field and Sullivan, 2003).

**Ad 3.** The use of sand filters is only as of lately considered as the form of stormwater runoff treatment. The main purpose of sand filters is to remove sediment particulates and the pollutants from the first flush of pavement or impervious area runoff (US DOT, 1996). In the filter media, particulate-bound heavy metals are removed physically.

**Ad 4.** Porous pavements are constructed from either porous concrete or modular porous concrete blocks. They are effective in both, the *in situ* storage, and disposal of stormwater runoff. Also, they are capable of significantly reducing the amount of pollutants that are found in runoff of intensely impervious urban areas. The pollutants are mostly removed in the underlying soil layer. The pollutant removal mechanism is sorption of soluble-phase pollutants onto the surface of soil particles. Soils that are rich with organics have higher pollutant removal efficiencies than the sand soils. Maximum reported heavy metal removal efficiencies for porous pavements are: 99% for Zn, 85% for Cd, 98% for Pb (Field and Sullivan, 2003).

### **Adsorptive-filtration systems**

Adsorptive-filtration systems through a complex combination of infiltration, adsorption, precipitation, and exfiltration, usually offer the highest heavy metal removal efficiency. It is generally no less than 70% and as high as 99%. Also, they have high removal efficiencies for the other target pollutants. On the other hand, they typically have some limitations like ability to operate on a small watershed area and their tendency to premature clogging (Field and Sullivan, 2003).

### **Partial ex-filtration systems**

Infiltration systems are capable of providing qualitative controls on both soluble and particulate pollutants. In infiltration systems runoff is directed into the trench and from there it is either fully ex-filtrated into the soil beneath (complete ex-filtration system), or it enters a perforated pipe under-drain which is routed to outflow facility (partial ex-filtration system, PER). In the PER suspended solids and dissolved metals transported within runoff

are immobilized by filtration and sorption/precipitation. Also, there is a potential for bacterial uptake or conversion in the underlying soil during the ex-filtration process (Field and Sullivan, 2003). Furthermore, the PER has a dual-purpose stormwater BMP, because beside its primary function to improve stormwater quality, it also acts as reservoir to reduce peak runoff rate (Sansalone et al., 1999).

PERs are designed in a unique way. Generally, they consist of an excavated trench, which is lined with a geotextile filter fabric and then backfilled with an aggregate mixture (porosity range 0.3-0.4) to form an underground detention basin. If the media backfill is modified or oxide-coated the sorption characteristics of the PER will be increased (Sansalone, 1997). Consequently, this effectively promotes sorption of dissolved metals and filtration of particulate-bound metals.

Infiltration trenches should not be exposed to runoff with excessive sediment loads or be assigned to trap coarse sediments. Such applications would lead to premature clogging (within 5 years) and, in the long run, system failure. Therefore, PERs are frequently used in combination with vegetated swales to avoid the clogging of the system. In addition, combination of PER and a modular porous pavement capping layer provides a buffering capacity for high runoff volumes that could cause the ponding above the PER (Field and Sullivan, 2003).

At a full-scale PER with an iron-oxide-coated sand backfill along the hard shoulder of a highway, pollutant removal efficiencies remain high after a year of full operation. Dissolved heavy metal mass removal exceeds 90%. The particulate-bound fraction of heavy metal removal rate exceeds 80% (Sansalone and Buchberger, 1997).

### **Below-grade treatment storage systems (sewer systems)**

Sewer conveyance systems can be used as in-line or pipe storage because they usually display significant volumetric redundancy. There is greater opportunity for stormwater quality to improve, if the time of travel to the treatment facility is increased. Runoff detention causes sedimentation of suspended solids and particulate-bound pollutants. Stormwater detention within the conveyance system can be in a variety of forms.

***In-line storage*** is part of conveyance system where extra volume of the oversized conduits provides flow attenuation and temporary detention of the stormwater. Also they are capable of providing treatment facilities for maximum utility of existing dry weather flow, and minimizing their overload to allow for later treatment of the stored excess flow.

***Off-line storage*** diverts the excess flows to a temporary detention facility in the sewer or other facility that is off line to the main sewer. This excess flow is stored until the capacity of treatment facility has been restored and can safely accept the diverted flow.

Detention tunnels are localized expansions in the conduit where stormwater is detained. They are located behind a flow restriction device. Also, detention basins can be used as sedimentation basins, by detaining the runoff for sufficient time for sedimentation to occur. Below-grade tunnels, which function as sedimentation tunnels, are normally kept full of water between storm events with the use of weirs and flow restrictors. The degree of improvement in the water quality depends on few parameters: detention time in the tunnel, the velocity of the runoff within the tunnel, and particle size distribution.

Field data indicates that stormwater is clarified within first 24h of detention, during which separation of pollutants in a detention/settling tunnel occur: 76-82% for Pb, 74-82% for Cd, 48-60% for Cu (Novotny and Olem, 1994).

### **Constructed wetlands**

When there are no issues with price and availability of land, wetlands can be specifically designed in such way to increase their application as a quantitative and qualitative urban stormwater BMP.

Constructed wetlands can significantly diminish the urban storm hydrograph. At the same time they are also highly effective in reducing nearly all contaminants of concern in urban runoff to low levels. A lot of research has been done on constructed wetland applications for the treatment of municipal and industrial wastewaters, but unfortunately this is not the case with applications for stormwater management. The main limiting factors for usage of constructed wetlands as stormwater BMP are the lack of accepted standard design, construction, and operating criteria.

Wetlands can be designed as follows:

1. Free surface (FW) with a lined soil base emergent vegetation and the water surface exposed to the air.
2. Subsurface (SF) or vegetated submerged bed (VSB) with a lined soil base overlain by media, emergent vegetation, and with a water level below the surface.

To summarise, constructed wetlands have higher pollutant removal efficiencies compared to their natural equivalents, because they possess greater process control and use more intensive management practices (Strecker, 1995). Fundamental pollutant removal of this system is through a wide range of physical, chemical and biological processes. A summary of the projected long-term pollutant removal rates for constructed wetlands is: 75-80% for Pb, 50% for Zn (Field and Sullivan, 2003). Reported ranges of constructed wetland design are listed in Table 2.5.

**Table 2.5:** Constructed wetlands pollutant removal mechanisms (Strecher, 1995)

Mechanism	Pollutants Affected	Promoted By
<b>Physical</b>		
Sedimentation	TSS, soluble and particulate BOD and COD, pathogens, P, N, heavy metals, synthetic organics	Low turbulence
Filtration	TSS, soluble and particulate BOD and COD, pathogens, P, N, heavy metals, synthetic organics	Fine, dense herbaceous plants
Soil Incorporation	All	Medium-fine textured soil
<b>Chemical</b>		
Precipitation	Dissolved P, heavy metals	High alkalinity
Adsorption	Dissolved P, heavy metals, synthetic organics	High soil Al, Fe (P), high soil organic concentration, circumneutral pH
Ion exchange	Dissolved metals	High soil exchange capacity
Oxidation	COD, petroleum hydrocarbons, synthetic organics	Aerobic conditions
Photolysis	COD, petroleum hydrocarbons, synthetic organics	High light penetration
Volatilization	Volatile petroleum hydrocarbons, synthetic organics	High temperature and air turbulence
<b>Biological</b>		
Microbial decomposition	BOD, COD, petroleum hydrocarbons, synthetic organics	High plant surface area and soil organics
Plant uptake	P, N, metals	High plant metabolic activity and surface area
Natural die-off	Pathogens	Plant excretions
Nitrification	NH <sub>3</sub> -N	Dissolved O <sub>2</sub> > 2mg/l, low toxics, temp. > 5-7°C, circumneutral pH
Denitrification	NO <sub>3</sub> , NO <sub>2</sub> -N	Anaerobic, low toxics, temp. > 15°C

### 2.3.4 Emerging technologies for treatment of urban stormwater runoff

Because of rising awareness of environmental contaminants that can be found in urban runoff, more research has been done on the removal of pollutants of high concern like heavy metals from stormwater runoff, over the last years. Heavy metals in stormwater runoff originate from the operation of motor vehicles, direct fallout, and the degradation of road materials. These metals are either dissolved in stormwater or bound to particulates (Sansalone and Buchberger, 1997).

Dissolved fraction of metals is more difficult to remove from the stormwater runoff than the particulate-bound fraction ones. Particulate-bound fractions of metals can be easily removed using precipitation process, whereas dissolved fractions need particular consideration as they are highly mobile. Dissolved heavy metals can be removed from stormwater runoff through physical and chemical processes. These can utilize chemical precipitation of hydroxides, carbonates and sulfides, adsorption onto negatively charged anionic sites in clay minerals, adsorption and co-precipitation on iron and manganese hydrous oxides, complexation with organics followed by coagulation and flocculation, and adsorption onto carbonates and phosphates (Harper, 1999).

There is a lot of conventional and advanced methods for removal of heavy metals (e.g. ion-exchange, electrodialysis, precipitation, reverse osmosis) that could be used for stormwater treatment, but unfortunately most of these available physicochemical technologies are either too expensive or too technically complicated (Brown et al., 2000a,b). Simple and cost-effective treatment techniques for removal of heavy metal are necessary. Adsorption is

recognized as an efficient and economical method of water treatment. It has also proved to be a promising method for removing dissolved metal ions from liquid wastes. Adsorption encourages research of commercially available materials to be used as sorbents in purifying water contaminated with metals (Wu and Zhou, 2009). Metal adsorption onto the filter material has been studied using low-cost sorbents like carbonaceous materials, waste by-products, weathered soils, and agricultural/natural products such as activated carbon, iron-oxide coated sand, zeolites, rice bran and hulls, soybean, peanut husk, saw dust, peat and leaves (Naidu et al., 1998; Brown et al., 2000a,b; Ricordel et al., 2001; Färm, 2002; Ho et al., 2002).

Numerous researches have studied different technologies for removal of heavy metals from urban stormwater runoff. Some are listed in continuation.

- **Ion exchange on zeolite.** Numerous researches have studied different technologies for removal of heavy metals from urban stormwater runoff. Some are listed in continuation. Ion exchange on zeolite. As an ion exchange material, zeolite has the ability to replace any toxic heavy metal cations from the runoff with cations such as sodium, calcium or magnesium. Therefore, by using the technology of retention within the ion exchange material, the levels of heavy metals in motorway stormwater can be reduced. Additionally, zeolite can be regenerated for further use. There are two kinds of zeolites: natural and synthetic. Natural zeolites (e.g. mordenite) are found in various mine deposits throughout the world, while the synthetic ones are artificially produced for specific applications. Synthetic zeolites have higher heavy metal removal comparing to natural ones. Research shows that synthetic zeolites can remove 100% of Pb, 98.4% of Cu, 96.8% of Zn, and 100% of Cd (Pitcher et. al., 2004).
- **Sorption on wastes.** Agricultural waste, yard waste, and biomass are possible low cost heavy metal sorbent materials. One of the technologies that has proven to remove heavy metals from stormwater runoff is a compost filter. The compost in the filter is usually from yard waste such as leaves. The leaf compost filter can remove 88% of Zn, 61% of Cr, and 67% of Cu from stormwater (Khan et. al., 2009).
- **Sorption on mulch.** Specially constructed bioretention filter system, which includes filtration and sorption is another possible treatment method for removal of heavy metals from runoff. Mulch, together with a variety of plants and layers of soil, form bioretention system that has the capacity of improving water quality through processes such as infiltration, sorption, precipitation, and binding of organic colloidal material, or through adsorption of metal–ligand complexes (Davis et. al., 2001). Mulch contains extensive organic materials composed mainly of humic substances, polysaccharides and polypeptides (Petrović et al., 1999). Furthermore, due to their chemical nature, humic compounds have a large proportion of functional groups such as carboxyl, hydroxyl, sulfate, phosphate and amino groups, which strongly affect the heavy metal sorption. For instance, Hardwood bark (H) mulch would be effective for removing heavy metals such as Cu, Pb and Zn, with the order of preference: Pb(II) > Cu(II) > Zn(II) (Jang et. al., 2005).
- **Biosorption.** Biosorption has proved to be an efficient technique for the removal of inorganic pollutants. Furthermore, biosorbents have displayed an admirable binding ability towards a variety of heavy metal ions. Marine algae (seaweeds) are biological resources which are available in many parts of the world, but only brown seaweeds proved to be excellent biosorbents. *Sargassum*, brown marine algae, is a well-established biosorbent for a variety of metal ions. The biosorbent can remove 88% of

Pb, 51% of Cu, 15% of Zn, and 10% of Mn from stormwater runoff (Vijayaraghavan et al., 2009).

- **Biofiltration.** Stormwater biofiltration using vegetated filter media has shown to be a promising technology for stormwater treatment (Davis et al., 2001; Melbourne Water, 2005). Biofilters increase the infiltration rate of stormwater, hence restoring predevelopment hydrology condition. Also, they can be used for pre-treatment of stormwater harvesting (Hatt et al., 2007). Commonly, after treatment with biofilters water is collected in a drainage pipe and discharged to a recipient (Melbourne Water, 2005). Moreover, vegetated biofilters have proved to be capable of removing substantial loads of heavy metals from stormwater, such as Pb and Zn in excess of 95%. Research has shown that also Cu can be removed by around 12%, if filter is equipped with a submerged zone. The main metal reduction occurs in the top layer of the filter (Blecken et. al., 2009).
- **Treatment with ZVI.** While trying to develop a suitable stormwater runoff treatment system, zero-valent iron (ZVI) was found to be a feasible option for metal removal. ZVI is in the form of scrap iron, and is capable of removing inorganic contaminants using processes of cementation, adsorption and metal hydroxide precipitation (Rangsivek and Jekel, 2005). It has been observed in lot of studies that  $Fe^0$  is an effective medium for treating heavy metals, including copper and zinc (Shokes and Moller, 1999; Wilkinan d McNeil, 2003).
- **Combined techniques.** Research area that investigates the usage of a mixture of the above mentioned materials for removal of heavy metals from water is relatively new. For instance, one of the studies focus on utilization of commercial porous iron sorbent (Ferosorp Plus, P1) with properties similar to GFH and its mixtures with zeolite and crystal gravel to remove coexistent heavy metals such as As, Cd, Cr, Cu, Ni and Zn from synthetic aqueous samples resembling urban stormwater runoff. Results have shown that sorbents with a Ferosorp base have a high removal rate for Cd, Zn and Ni, whereas for Cu, As and Cr removal is less effective. Moreover, very perceiving thing is that the addition of both, zeolite and crystal gravel, did not significantly change the efficiency of metals' removal (Wu and Zhou, 2009).

In conclusion, emerging treatment technologies for heavy metals' removal from urban stormwater runoff should be cost-effective, highly efficient and environmentally friendly. Research so far has shown that adsorption is the most promising process for heavy metal removal.

## 2.4 Characteristics of selected heavy metals

As it could be seen from Table 2.2 (page no. 3), that among the most common heavy metals detected in urban runoff are: lead (Pb), copper (Cu), chromium (Cr) and cadmium (Cd). Because of high toxicity of these metals, it is necessary to remove them from runoff before they reach the receiving water body, due to their high toxicity.

In order to apply appropriate treatment it is necesery to understand the nature of heavy metals in water and their environmental and health impact. This section gives insight of the chemistry, environment and health impacts of lead, copper, chromium and cadmium.

## **2.4.1 Lead**

### **Chemistry of Lead**

Lead is a main element of group 14 with symbol Pb (Latin: plumbum) and atomic number 82. It is a bluish-white metal of bright luster, very soft, highly malleable, ductile, and poor conductor of electricity. Lead has the highest atomic number of all stable elements (West, et al., 1987).

Lead can be found in nature as:  $\text{PbCO}_{3(s)}$  (cerussite),  $\text{PbS}_{(s)}$  (galena), and  $\text{PbSO}_{4(s)}$  (anglesite). Concentration of lead in natural waters may range from  $<1.0$  to  $890 \mu\text{g/l}^2$  (Faust and Aly, 1998). Physico-chemical speciation of lead indicates there is little or no free ionic lead present in drinking water. Depending on the composition of water a significant portion of lead is bound to colloids, either hydrous iron oxides or organic macromolecules. A substantial fraction is non-ion-exchangeable (Moore and Ramamoorthy, 1984).

It is well known that lead is very resistant to corrosion. It was already used in Roman Empire for making pipelines and it is still used today. Lead is usually used as metal or in its dioxide form (for the storage batteries). As metal it is also used for cable covering, plumbing, ammunition, and in the manufacture of lead tetraethyl, used as an antiknock compound in gasoline. In metal form it is very effective as a sound absorber, it is used as a radiation shield around X-ray equipment and nuclear reactors, and is used for vibration adsorption. For different purposes, lead is also used in building construction (West, et al., 1987).

### **Environmental and health impacts**

The sources of lead in urban stormwater runoff are numerous. Important sources for lead are building sites and atmospheric deposition (Davis, et al., 2001). Close to the sources of lead, ecosystems show a wide range of harmful effects like losses in biodiversity, changes in community composition of plants and animals, and neurological effects in vertebrates (US EPA, 2009). For centuries people are aware of the toxic properties of lead. People are exposed to lead in various quantities that can be found in food, air, and water. Care must be taken in handling lead, as it is a cumulative poison. The largest deposits of lead, once it is absorbed by the body, are in the bones followed by the kidneys and liver. Infants and young children are particularly sensitive to even low levels of lead (Sarkar, 2002). The Maximum Contaminant Level Goal (MCLG) for lead in drinking water is zero (Faust and Aly, 1998).

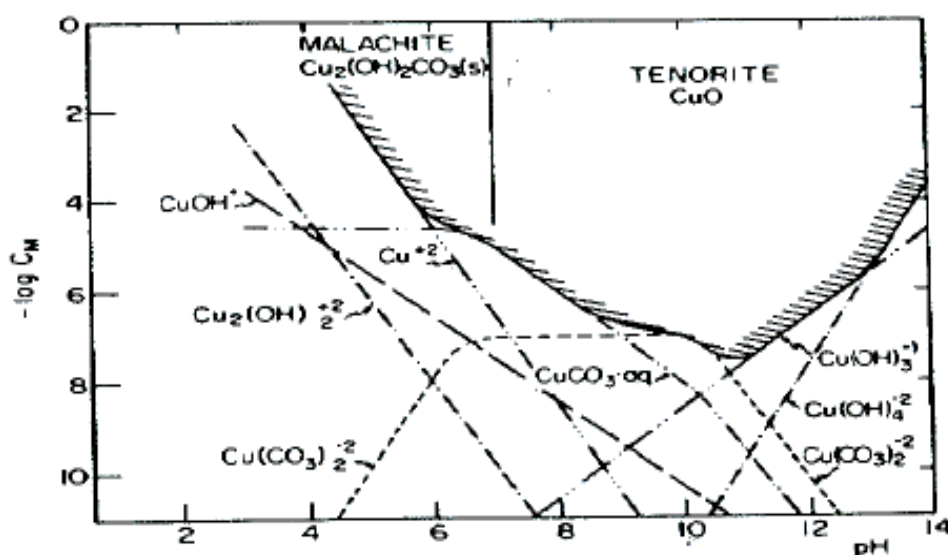


## 2.4.2 Copper

### Chemistry of Copper

Copper is a chemical element with the symbol Cu (Latin: cuprum) and atomic number 29. Copper is reddish coloured, takes on a bright metallic luster, and is malleable, ductile, and a good conductor of heat and electricity (second only to silver) (West, et al., 1987).

In aquatic environments, copper can exist in three broad categories: particulate, colloidal and soluble form. The dissolved phase can contain both, the free ion as well as copper complexes with (in)organic ligands. The physico-chemical and hydro-dynamic characteristics, as well as the biological state of the water determine speciation of copper in natural waters (Moore and Ramamoorthy, 1984). In naturally occurring compounds copper is most often found with a valence of +2 (cupric). It can also be found in its pure metallic state (+0), as well as with +1 valence (cuprous). Less common, it is +3 charge in complexes. In aquatic solutions, Cu(II) ions are more stable than in other oxidation states (Wong, 2004).



**Figure 2.3:** Copper solubility diagram (Stumm and Morgan, 1981)

Figure 2.3 graphically depicts the solubility speciation of copper and its immiscible precipitates. Free copper is predominant species only at  $\text{pH} < 6.0$ - $6.5$  is. In the pH range of most of the natural waters ( $6.5$ - $9.5$ ) the predominant copper species is  $\text{CuCO}_3$  (Grooters, 1998).

The electrical industry is one of the greatest users of copper. Copper has wide use as an agricultural poison and as an algacide in water purification. It is used as a building material, and a constituent of various metal alloys. (West, et al., 1987).

## **Environmental and health impacts**

Important sources of copper identified in urban stormwater runoff are building sites, vehicle brake emission, and atmospheric deposition (Davis, et al., 2001). Despite universal toxicity at high concentrations, the 2+ copper ions at lower concentrations are an essential trace nutrient to all higher plant and animal life. In animals, as well as humans, it is found widely in tissues, with higher concentrations in liver, muscles, and bones.

Copper is an essential nutrient for humans and animals, with an adult recommended daily allowance of 2 to 3mg/day. In ionic form copper is absorbed from the gastrointestinal tract and lungs, and to a lesser degree, through the skin. Following absorption, copper is distributed to all parts of the body, especially the liver. There is no clear relationship between chronic exposure to copper and copper toxicity in adult mammals probably because of homeostatic mechanisms. The purpose of these mechanisms is to maintain a baseline copper level in the body and protect mammals from the adverse effects of different copper levels.

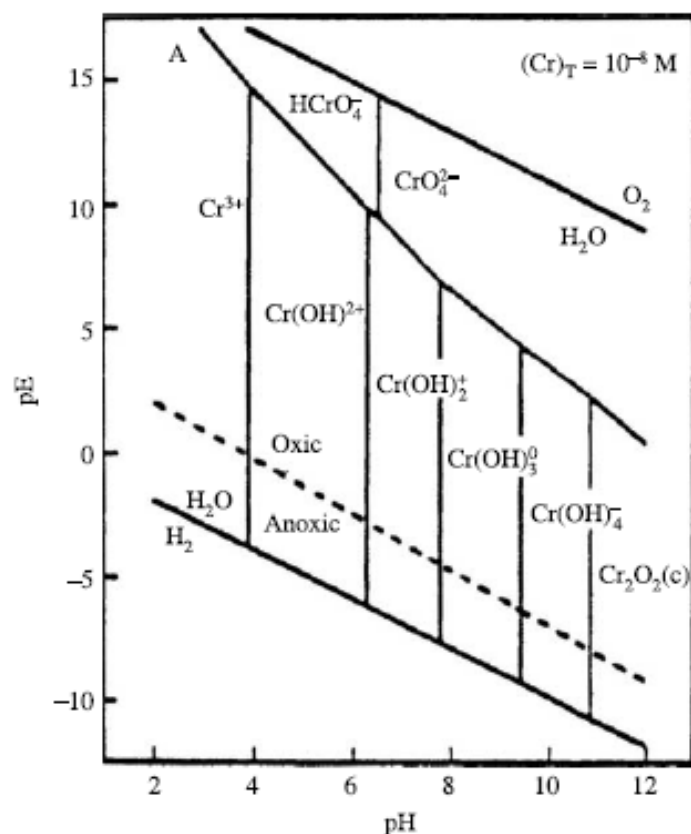
Copper ion exhibits high acute and high chronic toxicity to aquatic organisms, which can result in the death of the organism. The aquatic toxicity of copper ion is depends on water quality factors such as acidity, presence of organic substances, calcium, and carbonate. Toxicity decreases as water hardness (concentration of calcium carbonate), alkalinity or total organic carbon content increases. Copper ion is known to bioconcentrate in certain aquatic species (USEPA, 1996). The MCLG for copper is 1.3 mg/l in drinking water (Faust and Aly, 1998).

### **2.4.3 Chromium**

#### **Chemistry of Chromium**

Chromium is a chemical element which has the symbol Cr and atomic number 24. It is the first element in group 6. It is a steel-gray, lustrous, hard metal that takes high polish (West, et al., 1987).

In general, in water Cr(III) is mostly found as a cation that forms aqueous complexes and hydroxide precipitates. In surface waters, the ratio of Cr(III) to Cr(VI) varies widely, and relatively high concentrations of the latter can be found locally. In general, Cr(VI) salts are more soluble than those of Cr(III), making Cr(VI) relatively mobile (WHO, 2003). Low solubility of Cr(III) limits the amount of chromium detected in natural waters. Natural waters are usually contaminated with chromium from industrial wastewaters discharge (Faust and Aly, 1998). The form in which Cr is present, Cr(III) or Cr(VI), depends on the redox potential, the pH, the kinetics of the redox reactions, the formation of Cr(III) complexes as insoluble Cr(III) salts, and the total chromium concentration (Figure 2.4). The mechanism of toxicity is pH dependent. Chromium (VI) compounds are stable under aerobic conditions, while under anaerobic conditions they are reduced to chromium (III) compounds. Oxidizing environment can reverse the process. (Lenntech, 2009).



**Figure 2.4:** pE–pH diagram of aqueous chromium (Brandhuber, 2005)

Chromium is used to harden steel, to manufacture stainless steel, and to form many useful alloys. It is used in plating to produce a hard, beautiful surface and to prevent corrosion. It is also widely used as a catalyst. Chromium compounds are used in the textile industry as mordants, and by the aircraft and other industries for anodizing aluminium. The refractory industry has found chromium useful for forming bricks and shapes, as it has high melting point, moderate thermal expansion, and stability of crystalline structure. Chromium is typically mined as chromate ore (West, et al., 1987).

### Environmental and health impacts

Chromium can be expected in urban stormwater runoff from moving engine parts (Field and Sullivan, 2003). Health effects of chromium depend on chemical forms of exposure (Calder, 1988). There are a lot of organisms, including humans, for which chromium (III) is a dietary requirement. Cr(III) is a nutritionally essential trace element, non-toxic and poorly absorbed. However, if concentration of chromium exceeds the recommended values than it may be toxic to human health.

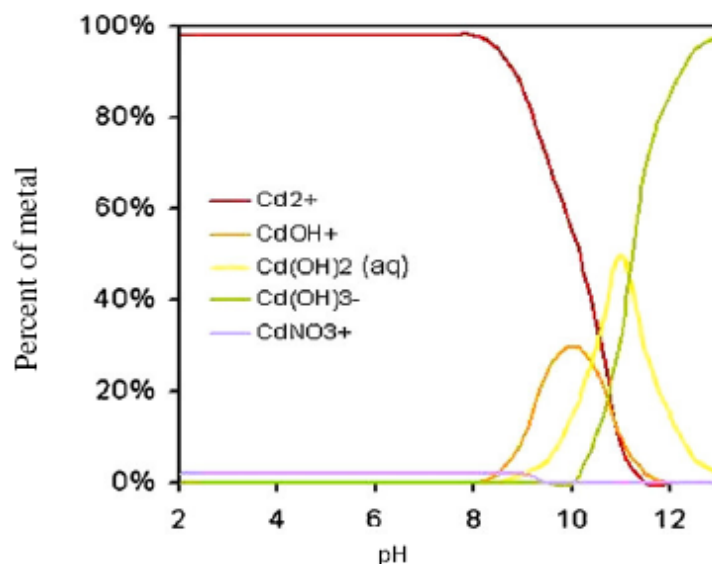
On the other hand, hexavalent chromium is very toxic to all living creatures. Cr(VI) is toxic, producing liver and kidney damage, internal hemorrhage and respiratory disorders. There are also sub-chronic and chronic effects like dermatitis and skin ulceration. Cr(VI) through inhalation exposure can cause cancer, but it is not clear if it's carcinogenic through ingestion exposure (Sharma, et al., 2008). The Maximum Contaminant Level (MCL) for total chromium in drinking water is 0.1 mg/l (Faust and Aly, 1998).

## 2.4.4 Cadmium

### Chemistry of Cadmium

Cadmium is a chemical element with the symbol Cd and atomic number 48. Almost all cadmium is obtained as a by-product in the treatment of zinc, copper, and lead ores. It is a soft, bluish-white metal which is easily cut with a knife. It is similar in many respects to zinc (West, et al., 1987).

Cadmium in water is usually not found due to natural geologic sources, but due to the discharge of wastewaters, especially plating wastes. The aqueous chemistry of cadmium is, for most part, dominated by  $\text{Cd}^{2+}$ ,  $\text{CdCO}_{3(s)}$  (otavite), and  $\text{Cd}(\text{OH})_{2(s)}$  (Faust and Aly, 1998).



**Figure 2.5:** Aqueous speciation of cadmium as a function of pH (Xue, et al., 2009)

From the Figure 2.5 it can be seen pH has a major influence on cadmium species in the solution. Cadmium is predominant as  $\text{Cd}^{2+}$  species over pH 2-9. At pH 10, concentration of  $\text{CdOH}^+$  reaches maximum 30%, whereas the concentration of  $\text{Cd}(\text{OH})_{2(\text{aq})}$  and  $[\text{Cd}(\text{OH})_3]^-$  increases with the decrease of concentration of  $\text{Cd}^{2+}$  and  $\text{CdOH}^+$  at higher pH.

It is used extensively in electroplating, which accounts for about 60% of its use. It is also used in many types of solder, for Ni-Cd batteries, and as a barrier to control atomic fission. Cadmium occurs as a minor component in most zinc ores and therefore is a by-product of zinc production (West, et al., 1987).

## Environmental and health impacts

Important sources of cadmium in urban stormwater runoff are building siding and atmospheric deposition (Davis, et al., 2001). In aquatic ecosystems cadmium can bioaccumulate in mussels, oysters, shrimps, lobsters and fish. This accumulation of cadmium can vary greatly between organisms. For instance, it is known that they are more resistant to cadmium poisoning salt-water organisms than freshwater organisms. If consumed cadmium can sometimes cause high blood-pressures, liver disease and nerve or brain damage. Cadmium in soils is strongly adsorbed to organic matter. This can be extremely dangerous, because the accumulation through food will increase (Lennteh, 2009).

Acute and long-term exposure to cadmium can cause negative health effects. Cadmium tends to accumulate in the body during long periods of time and has an extremely long biological half-life. Because of this most concern is on a long term toxicity. For example, kidney disease may occur because of long-term exposure to Cd in air, food, or water. Other effects due to Cd exposure are lung damage, bone effects, liver dysfunction, and reproductive toxicity (Sarkar, 2002). The MCL for cadmium in drinking water is 0.005 mg/l (Faust and Aly, 1998).

## 2.5 Removal of heavy metals

There are several methods known for the removal of heavy metals from urban stormwater runoff. In continuation, review of literature on some of the methods and techniques recommended for the removal of heavy metals is presented.

### 2.5.1 Chemical precipitation

Heavy metals can be removed from inorganic effluent by using chemical precipitation. The most common method used is precipitation of heavy metals as hydroxides. This process is pH sensitive. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in equation 2.6.



where:

$M^{2+}$  ..... dissolved metal ion

$OH^{-}$  ..... precipitant

$M(OH)_2$  ..... insoluble metal hydroxide

In stormwater runoff, more than one metal is present and usually at high concentration levels, as well. Therefore, the most effective pH for their removal must be determined before treatment. Table 2.5 shows pH ranges for the formation of metal hydroxides (Sultan, 1998). After achieving basic pH conditions (pH = 11), the dissolved metal ions are converted to the insoluble solid phase using a chemical reaction with a precipitant agent such as lime (Kurniawan, 2006).

**Table 2.6:** Ranges of pH for precipitation of metal hydroxides (Sultan, 1998)

<b>Metal</b>	<b>pH Range</b>
Cadmium	9.0 - 11.0
Chromium (III)	6.5 - 7.0
Copper	7.0 - 7.5
Iron (III)	5.0 - 5.5
Lead	8.5 - 9.0
Nickel	9.0 - 11.0
Silver	9.0 - 12.0
Zinc	8.0 - 8.5

Some of the metals require reduction before they can be precipitated as hydroxide, for example, Cr(VI) must be reduced to Cr (III). Additionally, some of the metals require oxidation, such as As (III). It must be oxidized to As (V) before it can be precipitated as hydroxide (Yadav, 2007).

For chemical precipitation its necessary to use a large amount of chemicals to reduce metals to an acceptable level for discharge, which is one of the main drawback of this method. Other disadvantages are its excessive sludge production that requires further treatment, increased costs due to sludge disposal, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Kurniawan, 2006).

### **2.5.2 Coagulation-flocculation**

One of the techniques that can be used to remove heavy metals from stormwater runoff is coagulation–flocculation. Coagulation is process that destabilizes colloidal particles by adding a coagulant, which results in sedimentation. Flocculation follows the coagulation and it is used to increase the particle size and form bulky flocules. To achieve all this it is necessary to adjust pH and to add ferric/alum salts as coagulant to overcome the repulsive forces between particles.

Coagulation–flocculation process can treat inorganic effluent with a metal concentration below 100 mg/L or above 1000 mg/L. Similar to chemical precipitation, it has been concluded that effective pH for improvement of heavy metal removal using coagulation–flocculation is ranging from 11.0 to 11.5.

Despite all of the advantages, coagulation–flocculation has limitations because of high operational costs caused by consumption of chemicals. Also, during coagulation–flocculation process large amounts of sludge are formed, which limit the usage of this method in practice. (Kurniawan, 2006).

### **2.5.3 Flotation**

Flotation can separate solids or dispersed liquids from a liquid phase using bubble attachment. As the bubbles rise in the liquid, the attached particles are separated from the suspension of heavy metal. Flotation can be classified as:

- (i) dispersed-air flotation,
- (ii) dissolved-air flotation (DAF),
- (iii) vacuum air flotation,
- (iv) electroflotation,
- (v) biological flotation.

Among the various types of flotation, DAF is the most commonly used for the treatment of metal-contaminated wastewater. The metal pollutants are removed by the foaming effect in the adsorptive bubble separation. The floating target substances are kept in the foaming phase away from the liquid phase. Though flotation is only a physical process, the potential for industrial application makes it important in heavy metal removal (Kurniawan, 2006).

### **2.5.4 Membrane filtration**

Membrane filtration process can remove the suspended solids and organic compounds as well as the inorganic contaminants like heavy metals, hence receiving attention for treatment of inorganic effluent. There are various kinds of membrane filtration that can be applied for heavy metal removal. They are categorized by the size of the retained particle as ultrafiltration, nanofiltration and reverse osmosis (Kurniawan, 2006).

In ultrafiltration (UF) the substances like heavy metals, macromolecules and suspended solids bigger than the pore size of 5-20 nm or molecular weight of 1000-100,000 Da, will be separated from the inorganic solution when passed through the membrane (Vigneswaran et. al., 2004).

Nanofiltration (NF) has characteristics between UF and RO membranes. It is unique due to its small pore size and membrane surface charge. As a result, not only the bigger neutral solutes and salts are rejected by the membrane but also the charged solutes smaller than the membrane pores.

Reverse osmosis (RO) employs high pressure to force the pass of water through the membrane removing the heavy metals. Compared to UF and NF RO is considered more effective for heavy metal removal from inorganic solutions (Kurniawan, 2006).

The main disadvantage of membrane filtration is high investment and operational costs. Also, the membranes are prone to fouling.

### 2.5.5 Ion exchange

Another method used regularly in heavy metal removal from water is ion exchange. It utilizes an insoluble substance (resin) to remove the target ions from an electrolytic solution between the solid and liquid phases. This interchange is reversible. While the resin absorbs the target ions it also releases chemically equivalent amount of chemically similar ions so that the structure of the resin remains the same (Vigneswaran et. al, 2004.; Rengaraj et. al., 2001). The resin loaded with target metal is recovered by elution. With suitable reagents, the metal is removed from the resin and stays in a more concentrated form. The ion exchange removes the heavy metal effectively under acidic conditions at pH from 2 to 6. However the efficiency depends a lot on the characteristics of the ion exchanger (Kurniawan, 2006).

One of the limitations of the ion exchange is that not all heavy metals have proper counter ion exchange resins. In addition, pretreatment, such as the removal of suspended solids in the wastewater, is required before starting the ion exchange process. Consequently, capital and operational costs are correspondingly high in ion exchange processes (Ahmed et. al., 1998).

### 2.5.6 Adsorption processes

Adsorption involves an inter-phase accumulation or concentration of substances at a surface or interface. The process can occur at an interface between any two phases, such as liquid-liquid, gas-liquid, gas-solid, or liquid-solid interface. The material being concentrated or adsorbed is adsorbate and the adsorbing phase is termed as adsorbent.

Adsorption from solution onto a solid occurs as the result of one of the two characteristic properties for a given solvent-solute-solid system, or a combination thereof.

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

For the majority of water and wastewater treatment systems, adsorption results from a combined action of the two forces. There are three types of adsorption:

1. **Ion-exchange adsorption** is a process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface.
2. **Physical adsorption** is not site specific and is due to weak forces of attraction between molecules (van der Waals forces). Physical adsorption is generally reversible.
3. **Chemical adsorption** takes place as a result of chemical bond being formed between the molecule of the solute and the adsorbent, comparable with those leading to the formation of chemical compounds.



The adsorption process is influenced by various factors.:

- Nature of the adsorbent (grain size, surface area, pore size and distribution, point of zero charge).
- Nature of the adsorbate (solubility/concentration, surface charge, etc.).
- Nature of solvent (pH, temperature, ionic strength, presence of other adsorbents e.g. natural organic matter, etc.).

In addition, the type of system and filtration rate can also influence the process (Sharma, 2007).

### **Adsorption on IOCS**

In natural systems the mobility and distribution of heavy metals is regulated by sorption/desorption to clay minerals, metal-oxides and materials of organic nature, and (co-)precipitation/dissolution processes. Thus, there is interest to investigate if natural sorbents are suitable for treatment of the dissolved heavy metal fractions. The sorbent should fulfil three preliminary conditions:

1. It should be cheap and easily available
2. It should have high capacity for heavy metals at the actual pH-value of the stormwater.
3. It should enable effective separation of sorbent from water phase after sorption of the heavy metal.

Iron-oxides/hydroxides (hereafter iron-oxides) satisfy the first two conditions. Unfortunately they are very difficult to separate from the water phase or to infiltrate through because of their fine particle size (Moller et. al., 2002). IOCS has proved to be a good solution for overcoming this problem.

IOCS is basically a by-product obtained from iron removal groundwater treatment plants i.e. sand used in filters, is coated by iron oxide during filtration process in the plant and from time to time it has to be replaced by new sand. The development of the iron oxide coating on the filter media in iron removal plants may be affected by the water quality and the treatment schemes used in the plant (Tekeste, 2003).

The presence of such coating as iron (hydro) oxide can remove iron as well as it can adsorb various uncomplexed and complexed heavy metals. UNSECO-IHE has been working on removal of some heavy metals from water, for example, chromium, copper, lead, cadmium, arsenic (Bakhamis, 2009; Yadev, 2007, Kumwenda, 2009, etc). Removal of heavy metals was usually based on principle filtration/adsorption by iron-oxide based media such as IOCS.

IOCS is formed under varying conditions, which might give it different physiochemical characteristics, hence causing different adsorption efficiency. Surface of IOCS is physically and chemically heterogeneous and is expected to change with time. IOCS can contain silica, manganese, magnesium, phosphate etc. Points of zero charge of silica and manganese which likely always present in the IOCS are at 2.0 and in between 2.0-4.5 respectively. This is most possible the reason of low point of zero charge of IOCS which is 3.0-3.5 as shown in table 2.6 (Bakhamis, 2009).

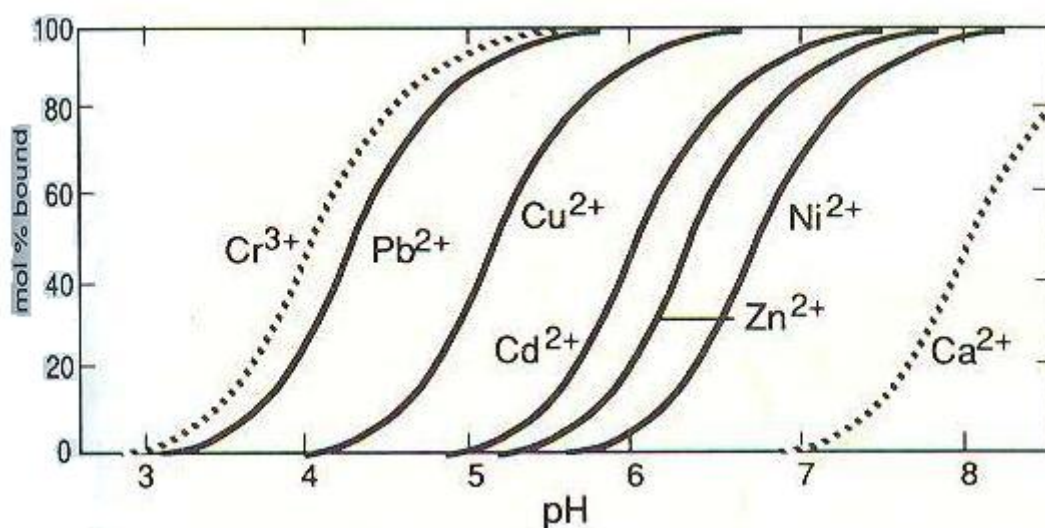
**Table 2.7:** Example of physiochemical characteristics of IOCS

Grain size (mm)	Surface area (m <sup>2</sup> /g)	pH <sub>zpc</sub>	Moisture content (%)	Bulk density (g/cm <sup>3</sup> )
1.8-4.0	201	3.0-3.5	16.1	2.36

The adsorption capacity of the IOCS mainly depends on the amount of iron. As a result, adsorption capacity of the IOCS increases dramatically with the growing of iron oxide coating on the media (Sharma, 2001).

pH is one of the characteristics which affect adsorption capacity of media. The pH affects the speciation and redox potential of adsorbate (Figures 2.3-2.5) and surface charge or better known as the point of zero charge (pH<sub>pzc</sub>) of the adsorbent. The surface of the adsorbent will have a positive charge at pH lower than pH<sub>pzc</sub> and will attract negatively charged ions (anions) present in the solution.

Figure 2.6 illustrates the sorption of various metal ions on hydrous ferric oxide. For each metal ion there is a narrow interval of 1-2 pH units where the extent of sorption rises from zero to almost 100% (Strum and Morgan, 1996).



**Figure 2.6:** pH dependence of the binding of metal ion by solute and surface ligands (Dzombak and Morel, 1990)

Surface area of IOCS usually has a direct effect on the adsorption capacity which has been observed to increase with increasing surface area. The surface area can be external surface

area or internal surface area of a particle. The adsorbent have the ability to adsorb more if the internal structure of the material is porous. Particle size is related to the surface area, so it has effect on the adsorption capacity of the grains. For a particular mass of sample of the same material, smaller sized grains have bigger total surface area than large sized grains, hence smaller sized grains have more area for a possible adsorption of metals (Kumwenda, 2009).

The presence of other (competitive) ions in water should be considered during the removal of heavy metals from water because they may influence the adsorption efficiency. The competitive behaviour of ions depends on their concentration, similarity to intended adsorbate, and order of introducing ions. Higher similarity of competing ion and intended adsorbate will lead to increase of adsorption capacity (Sapurto, 2010).



### 3. MATERIALS AND METHODS

This chapter presents the materials, methodology and analytical techniques used during the research.

#### 3.1 Materials

##### 3.1.1 Model water

For research purposes, the composition of model water was adjusted to meet specific characteristics of urban stormwater runoff. This study considered model water with different concentrations of chromium, cadmium, copper and lead selected to mirror concentrations of these metals in urban-run-off of developed countries (Table 3.1).

**Table 3.1:** Bandwidth of event mean concentrations of parameters and pollutants: rainwater, runoff from roofs, and runoff from trafficked areas (adopted from: Göbel et. al., 2007)

Parameter		Unit	Rainwater		Roofs		Trafficked areas			
							Low density		High density	
			Min	Max	Min	Max	Min	Max	Min	Max
Physico-chemical parameters										
1	EC	µS/cm	28	223	25	269	n.a.	n.a.	108	2436
2	pH	-	3.9	7.5	4.7	6.8	6.4	7.9	6.4	7.9
Sum parameters										
3	TSS	mg/l	0.2	52	13	120	74	74	66	937
4	BOD <sub>5</sub>	mg/l	1.0	2.0	4.0	16.1	n.a.	n.a.	2.0	36.0
5	COD	mg/l	5	55	n.a.	n.a.	n.a.	n.a.	63	146
Nutrients										
6	P <sub>tot</sub>	mg/l	0.01	0.19	0.06	0.50	n.a.	n.a.	0.23	0.34
7	NH <sub>4</sub>	mg/l	0.1	2.0	0.1	6.2	n.a.	n.a.	0.5	2.3
8	NO <sub>3</sub>	mg/l	0.0	7.4	0.1	4.7	n.a.	n.a.	0.0	16.0
Heavy metals										
9	Cd	µm/l	0.1	3.9	0.2	1.0	0.2	0.5	0.3	13.0
10	Zn	µm/l	5	235	24	4880	15	1420	120	2000
11	Cu	µm/l	1	355	6	3.416	21	140	97	140
12	Pb	µm/l	2	76	2	493	98	170	11	525
13	Ni	µm/l	1	14	2	7	n.a.	n.a.	4	70
14	Cr	µm/l	2	8	2	6	n.a.	n.a.	6	50

Parameter		Unit	Rainwater		Roofs		Trafficked areas			
							Low density		High density	
			Min	Max	Min	Max	Min	Max	Min	Max
Main ions										
15	Na	mg/l	0.22	20.00	n.a.	n.a.	n.a.	n.a.	5.0	474.0
16	Mg	mg/l	0.03	0.33	n.a.	n.a.	n.a.	n.a.	1.0	1.4
17	Ca	mg/l	1.10	67.13	1.00	1900			13.7	57.0
18	K	mg/l	0.46	0.65	n.a.	n.a.	n.a.	n.a.	1.7	3.8
19	SO <sub>4</sub>	mg/l	0.56	14.40	n.a.	n.a.	n.a.	n.a.	5.1	139.0
20	Cl	mg/l	0.20	5.20	n.a.	n.a.	n.a.	n.a.	3.9	669.0
Organic parameters										
21	PAH	µm/l	0.04	0.76	0.35	0.60	n.a.	n.a.	0.24	17.10
22	MOH	mg/l	0.29	0.41	0.108	3.14	n.a.	n.a.	0.51	6.50

For the research were considered only maximal concentration of studied metals. Also, it was assumed that of total Cr 50% is Cr(III) and the other 50% is Cr(VI).

Model water was prepared by mixing demineralised (demi) water with selected heavy metals. For one part of experiments model water pH was adjusted to 6, and sodium-bicarbonate (NaHCO<sub>3</sub>) was added in model water to get the concentration of 100 mg/l of HCO<sub>3</sub><sup>-</sup>. For the rest of experiments there was no pH adjustment by adding buffer in model water (starting pH≈7). Composition of model water is given in the table below (Table 3.2).

**Table 3.2:** Composition of model water

Parameters	Model water	Unit
Temperature	21	°C
pH	6 and 7	-
Cd	13	µg/l
Cr(III)	25	µg/l
Cr(VI)	25	µg/l
Cu	140	µg/l
Pb	525	µg/l
Cr(III) + Cr(VI)	25 + 25	µg/l
Cd + Cr(III)	13 + 25	µg/l
Cd + Cr(VI)	13 + 25	µg/l
Cu + Cr(III)	140 + 25	µg/l
Cu + Cr(VI)	140 + 25	µg/l
Pb + Cr(III)	525 + 25	µg/l
Pb + Cr(VI)	525 + 25	µg/l
Na	37.7	mg/l
HCO <sub>3</sub> <sup>-</sup>	0 and 100	mg/l

### 3.1.2 Chemicals

Table 3.3 shows chemicals and reagents used during the research.

**Table 3.3:** Experimental chemicals and reagents and their purpose

Chemical	Concentration	Application
Demineralized water	-	Preparation of model water
Standard Cd solution	100 mg/l	Preparation of model water
Standard Cr(III) solution	100 mg/l	Preparation of model water
Standard Cr(VI) solution	100 mg/l	Preparation of model water
Standard Cu solution	100 mg/l	Preparation of model water
Standard Pb solution	100 mg/l	Preparation of model water
Sodium bicarbonate (NaHCO <sub>3</sub> )	137.7 mg/l	Buffering capacity
Sodium hydroxide (NaOH) solution	0.5 M	Adjustment of pH
Nitric acid (HNO <sub>3</sub> ) solution	1 M	Adjustment of pH
Concentrated nitric acid.	65-70% HNO <sub>3</sub>	Acidification of samples
Ammonium nitrate [NH <sub>4</sub> NO <sub>3</sub> ]	-	Analysis on AAS-GF
Magnesium nitrate [Mg(NO <sub>3</sub> ) <sub>2</sub> ] in 1%HNO <sub>3</sub>	-	Analysis on AAS-GF

### 3.1.3 Adsorbent

For this research, iron oxide coated sand (IOCS) was used as adsorption material. IOCS was obtained from the Brucht groundwater treatment plant- in the Netherlands.

For experimental purposes IOCS was pulverized to the grain size <63 µm. As the first step bulk IOCS was ground, and then sieved to get the required size fraction. In this research, total weight of IOCS was considered instead of total volume. Since complete IOCS grains were grounded adsorbent contained a mixture of all IOCS components, including pulverized quartz sand grains. In addition, sieving and grinding helped to homogenize the adsorbent.

### 3.1.4 Equipment

Equipment and its purpose used for the experiments in this research is listed in Table 3.4.

**Table 3.4:** List of equipments used for the experiments

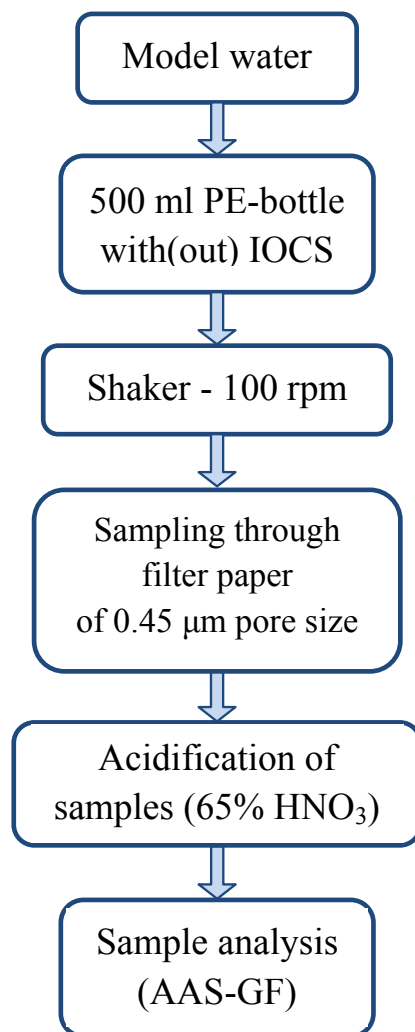
<b>Equipment</b>	<b>Application</b>
Electronic balance	Weighting used chemicals
Erlenmeyer glass	Characterization of IOCS
Magnetic stirrer	Preparing of model water
Measuring cylinder	Preparing of model water
Membranes filters 0.45 $\mu\text{m}$ sizes and holder	Sampling and separation of solid-liquid
pH meter	pH measurement
Polyethylene (PE) bottles of 500 ml capacity	Batch experiments
Rotary mechanical shaker	Batch experiment
Sieve (Frisch analysette 3pro)	Sieve analysis
Various sizes of pipettes	Preparing model water, dilution
Volumetric flask/beakers	Preparing model water, dilution

## 3.2 Experimental methods

### 3.2.1 Short-term batch experiments

This section describes the experimental methods carried out in the study. Two sets of batch adsorption experiment were done using IOCS to assess the effectiveness of Cr(III), Cr(VI), Cu and Pb removal with (i) no pH adjustment (starting  $\text{pH} \approx 7$ ) and (ii) pH of 6. As it can be seen from Table 3.2, removal of metals was first studied individually then with two metals being present in the solution at the same time, the second metal always being either Cr(III) or Cr(VI). Figure 3.1 describes the applied experiment protocol.





**Figure 3.1:** The schematic diagram of batch adsorption experiments protocol

The purpose of the batch adsorption experiments was to investigate competitive removal of e Cd, Cr(III), Cr(VI), Cu, and Pb by IOCS. In these experiments contact time of 24 hour was applied. Model water was kept in 500 ml polyethylene bottles with fixed amount of 0.2 mg/l IOCS. Bottles were then placed on rotary mechanical shakers (Figure 3.2) at shaking speed of 100 rpm, which allow all the surface area of the adsorbent to come in contact with the model water containing heavy metals. Sampling was carried out with syringe and filtered through 0.45 μm membrane filter (unless state otherwise) at time intervals 0 min, 15 min, 30 min, 1, 2, 4, 6, 8 and 24 hr. Samples were immediately acidified to preserve them for further analysis.



**Figure 3.2:** Rotary mechanical shaker

### 3.2.2 Sampling procedure

Samples were collected and filtered through 0.45  $\mu\text{m}$  Whatman membrane filter to separate dissolved from particulate-bound fractions (Figure 3.3). Approximately 1 ml of the sample was passed through the filter and discarded. The remaining sample passed through the filter was collected, acidified with concentrated nitric acid ( $\text{HNO}_3$ ) and stored for further analysis. There was some delay between the preparation of model water and the start of the batch experiments. Therefore, to check stability of metals during this lag phase of approximately 15 minutes, a sample of model water was taken 1 minute after its preparation. Half of the sample was filtered through 0.45  $\mu\text{m}$  membrane filter and other half was preserved as not filtrated. In a similar way another sample was taken at the start of the experiment ( $t=0$ ), approximately 15 minutes after model water preparation. After 24 hours contact time, the experimental bottles were thoroughly mixed before the last sample was taken. This was due to the assumption that there some precipitation occurred during the 24 hours contact time. Also in this case, part of the sample was filtrated and the other part preserved non-filtered.



**Figure 3.3:** Syringe combined with filter holder and 0.45 µm filter paper

### 3.3 Analytical methods

#### 3.3.1 Extraction of IOCS Coating

The purpose of this experiment is to find out the chemical composition of IOCS. Extraction was done by boiling the weighted samples in acidic solution and then after cooling and diluting of samples with demi water the samples were kept for 24 hours so the particles can settle. The extract was measured for several components, using AAS-Flame Perkin-Elmer Aanalist 200 for iron, manganese, magnesium, and calcium measurement (Figure 3.4 [A]), spectrophotometer Perkin-Elmer Lambda 20 for phosphate (Figure 3.4 [B]), inductively compiled plasma (ICP) Perkin-Elmer Optima 3000 for silica (Figure 3.4 [C]), and AAS-GF Solaar MQZ for arsenic measurement (Figure 3.4 [D]).



[A]



[B]



[C]



[D]

**Figure 3.4:** [A] AAS-Flame. [B] Spectrophotometer. [C] Inductively coupled plasma (ICP). [D] AAS-GF.

### 3.3.2 Heavy metals analysis

For metals analysis, AAS-GF Solaar MQZe GF95 with SOLAAR AAS-GF programmer was used (Figure 3.4 [D]). AAS-GF Solaar MQZ was set for appropriate method, then the calibration line was established with prepared standard solution. Based on previous testing done by the laboratory staff the detection limit for Cd analysis with AAS-GF was 1  $\mu\text{g/l}$ . Detection limit for other metals analyzed in this study namely Cr, Cu, and Pb was 2  $\mu\text{g/l}$ .

### 3.3.3 PHREEQC software for equilibrium calculations

Equilibrium calculations were done using PHREEQC (version 2) software. PHREEQC is used for simulating a variety of chemical reactions and transport processes in natural or polluted water or in laboratory experiments. The program is based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces. It also includes the capability to model kinetic reactions with rate equations that are completely user-specified. Programme is utilized in the form of Basic (computer language) statements.

PHREEQC can be used as a speciation program for calculation of 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 (Parkhurst, et al., 1999).

For this research, PHREEQC was used for equilibrium calculation to predict the final concentration of metals that will be in solution at equilibrium conditions. At the same time this program was used to predict species distribution in the solution, dominant complexes of metals formed and the saturation indices of the compounds formed in the model water. The most interesting results were saturation indices, since the basis of occurrence of precipitation occur in model water during the experiment could be predicted and/or explained.



## 4. RESULTS AND DISCUSSION

This chapter presents and discusses the result of experiments that were carried out during the research.

### 4.1 Extraction of IOCS coating

The chemical composition of IOCS from the water treatment plant (WTP) Brucht, that was used in this study, is presented in Table 4.1.

**Table 4.1:** Chemical composition of IOCS from WTP Brucht

Composition	Concentration	Unit	%
Arsenic	0.7	µg/g	0.07
Calcium	12.3	mg/g	1.23
Iron	324.5	mg/g	32.45
Magnesium	0.3	mg/g	0.03
Manganese	1.6	mg/g	0.16
Oxygen	182.5	mg/g	18.25
Phosphorus	19.5	mg/g	1.95
Sand	54.2	mg/g	5.42
Silica	2.2	mg/g	0.22
Unknown compounds	402	mg/g	40.2
<b>Total</b>	<b>1000</b>		<b>100</b>

From Table 4.1 it can be seen that IOCS from the WTP Brucht has very high iron content, namely about 32.5% on weight basis. The second most dominant compound after iron is oxygen accounts for approximately 18% of total IOCS. Concentration of oxygen in the IOCS was calculated assuming that iron is present in the coating as FeOOH (goethite). Quartz sand contribution to the whole IOCS mass is very small, namely around 5.4%.

Due to its complex chemical structure it is not easy to determine the complete chemical composition of IOCS. In this research only 60% of the total composition of IOCS has been experimentally determined. There are around 402.03 mg/g of IOCS of compounds that were still unidentified. This is mainly due to the fact that the coating composition of IOCS is greatly influenced by the quality of groundwater treated at WTP. Generally it can be



concluded that for adsorption purposes this is good IOCS, due to its thick coating and high iron content.

## 4.2 Testing materials for possible interferences on heavy metal removal

To check whether PE bottles could have influence on measured parameters during adsorption experiments, they were tested for possible leaching of metals of interest. Results are shown in the Tables 4.2 and 4.3.

**Table 4.2:** Measured pH value as a function of contact time

Time (h)	pH	
	plastic bottle	glass bottle
0	7.0	6.8
24	6.0	5.9
$\text{pH}_0 - \text{pH}_{24} =$	1.0	0.9

**Table 4.3:** Leached metals of interest after 24 hrs contact time

Compound	Conc. ( $\mu\text{g/l}$ )			
	plastic bottle		glass bottle	
	non-filtered	filtered	non-filtered	filtered
Cd	below DL	below DL	below DL	below DL
Cr	below DL	below DL	below DL	below DL
Cu	below DL	below DL	below DL	below DL
Pb	below DL	below DL	below DL	below DL

DL - detection limit

pH value of demi water was around 5, but unstable, because the pH-meter is not capable to give reliable measurement of totally pure water (that contains no ions). From the results in Table 4.2 it can be seen that pH decreased by 1 unit during the 24 hrs contact time, because there was no buffer in water to maintain the pH value. Probably, some IOCS content species bind with  $\text{OH}^-$  group in water releasing  $\text{H}^+$  and causing the drop of pH. In addition, pH value in PE bottles have slightly higher than that in glass bottles. This is most probably due to the measurement errors. On the other hand, characteristics of the bottle wall may also influence the pH. To determine this it would be necessary to analyse the characteristics of material from which the bottles are made off.

From the Table 4.3 it can be seen that all the measured concentrations of metals were below detection limit of AAS-GF. From this it can be concluded, that there is no leaching of metals from adsorbent into the water.

## 4.3 Short batch experiments

A series of short batch adsorption experiment were conducted to assess potential of IOCS to remove a single metal (Cd, Cu, Cr(III), Cr(VI), or Pb) and combination of each of these

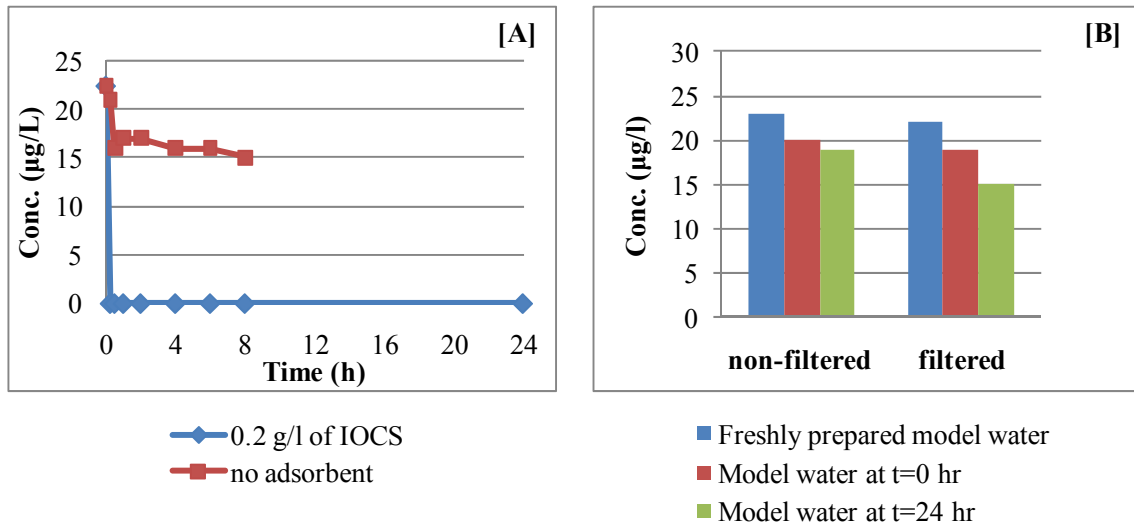


metals with Cr(III) or Cr(VI) from model water. At the same time, blanks were prepared consisting of model water and spiked single, or combination of metals, without adsorbent, to monitor stability of metals.

#### 4.3.1. Adsorption of chromium

##### Adsorption of Cr(III)

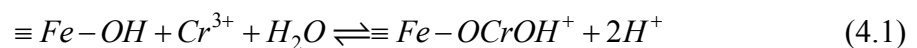
Figure 4.1 shows the change of Cr(III) concentration during 24 hrs contact time with and without adsorbent added.



**Figure 4.1:** Concentration of Cr(III) as a function of contact time. Model water: demi water with initial conc. of Cr(III)=25 µg/l, no pH adjustment (starting pH≈7), IOCS dosage 0.2 g/l. [A] Reduction in concentration with and without adsorbent. [B] Concentration of Cr(III) in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results of blank (without adsorbent) (Figure 4.1 [A]) it can be seen that about 33% of Cr(III) precipitated. Results of blank showed that induction time for Cr(III) precipitation is less than 15 minutes. That means that nuclei in very short time reach critical cluster size dimension after which precipitation occurs.

From the Figure 4.1 [A] it can be seen that using 0.2 g/l of IOCS Cr(III) is totally removed from the water (within 15 minutes of contact time). When adsorbent was present, all was removed, but some probably due to precipitation, as it can be seen from the results of blank above. In the presence of adsorbent pH dropped from 6.8 to 6.4 during the 24 hrs of contact time. It is known that pH depends on surface complex formation. The adsorbent,  $\equiv\text{Fe}-\text{OH}$ , in contact with metal cation,  $\text{M}^{2+}$ , binds the cation and releases the  $\text{H}^+$  into the water (4.1). With increase of  $\text{H}^+$  in water pH value will drop.



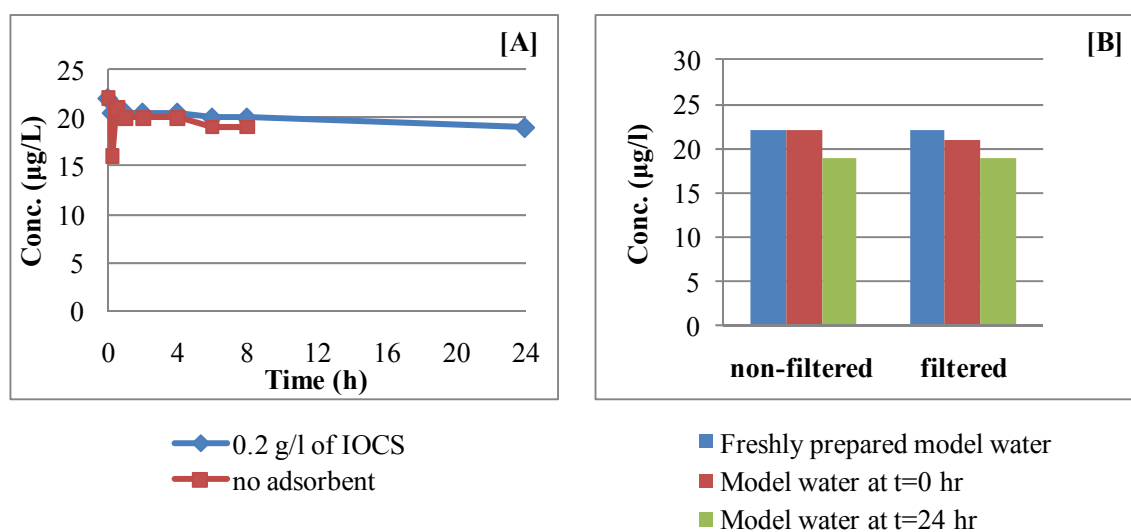
Also, there is possibility that interaction of IOCS and model water could cause change of pH value.

Experimental results are in line with PHREEQC results, which showed that precipitation will occur. Results showed that precipitated fractions are in the form of  $\text{Cr}(\text{OH})_3$  and  $\text{Cr}_2\text{O}_3$  species.

Figure 4.1 [B] shows that Cr(III) concentrations in blank are slightly lower after filtration of samples. Results also showed that around 5% of Cr(III) was remained on the filter during filtration of samples taken at  $t=0$  hr. Higher removal of Cr(III) (about 20% of concentration) by filters at 24 hr is probably due to kinetics of Cr(III) precipitation. These results indicate, that some colloidal particles of metals in model water are greater than 0.45  $\mu\text{m}$  pore size, therefore only the smaller colloidal particles and dissolved fractions passed through the filter. The precipitation of Cr(III) was also analyzed in previous studies (Thapa, 2009). The amount of Cr(III) retained in the filter was an indication of the size of the precipitated chromium.

### Adsorption of Cr(VI)

Figure 4.2 shows the change of Cr(VI) concentration during 24 hrs contact time with and without adsorbent added.

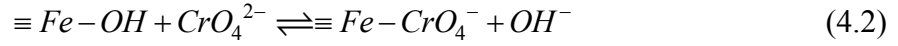


**Figure 4.2:** Concentration of Cr(VI) as a function of contact time. Model water: demi water with initial conc. of Cr(VI)=25  $\mu\text{g/l}$ , no pH adjustment (starting  $\text{pH}\approx 7$ ), IOCS dosage 0.2 g/l. [A] Reduction in concentration with and without adsorbent. [B] Concentration of Cr(VI) in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the blank (model water without adsorbent) (Figure 4.2 [A]) it can be seen that about 14% of Cr(VI) precipitated. Also in this case, the induction time is less than 15 minutes. It was expedited that Cr(VI) would be stable under experimental conditions, so there is possibility that there was not precipitation and that is was a measurement error.

From the Figure 4.2 [A] it can be seen that using 0.2 g/l of IOCS was insufficient to remove effectively Cr(VI) from model water (around 14% of removal during contact time).

Removal rate of Cr(VI) with adsorbent was the same (=14%) as removal by precipitation, which indicates, the only removal mechanism here was precipitation. During the contact time slight increase of pH from 6.8 to 6.9 was observed. As mentioned before, pH is depends on surface complex formation. The adsorbent,  $\equiv\text{Fe}-\text{OH}$ , in contact with anions such as  $\text{CrO}_4^{2-}$ , will bind and release the  $\text{OH}^-$  into the water (4.2).



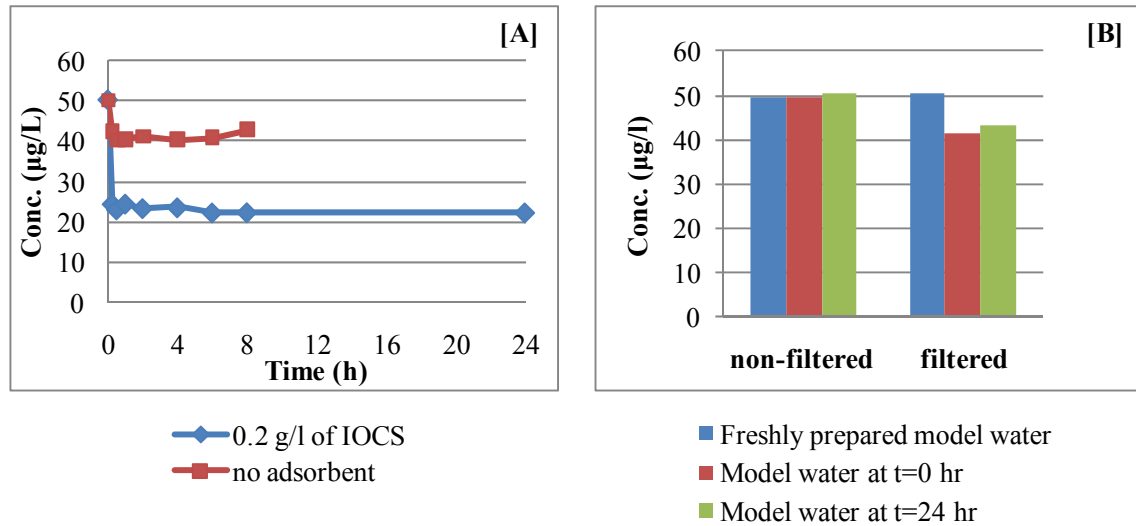
With increase of  $\text{OH}^-$  in water pH value will rise. There is slight increase in pH indicates very small amount of Cr(VI) was adsorbed.

Experimental results PHREEQC shows that precipitation does not occur. Precipitation was probably detected due to a very small concentration of Cr(VI) and possible measurement errors. Adsorption is not supported by electrostatic attraction because at  $\text{pH} \approx 7$  the adsorbent is negatively charged and Cr(VI) at this pH is present as  $\text{CrO}_4^{2-}$  which is also negative.

Figure 4.2 [B] shows that Cr(VI) concentrations are very similar for the non-filtered and filtered samples. At the 0 hr around 5% of Cr(VI) remained on the filter probably because colloidal particles were formed during the preparation of model water.

#### Adsorption of total Cr

Figure 4.3 shows the change of total Cr (a mixture of Cr(III) + Cr(VI)) concentration during 24 hrs contact time with and without IOCS addition.



**Figure 4.3:** Concentration of total Cr as a function of contact time. Model water: demi water with initial conc. of Cr(III)=25 µg/l and Cr(VI)=25 µg/l, no pH adjustment (starting  $\text{pH} \approx 7$ ), IOCS dosage 0.2 g/l. [A] Reduction in concentration with and without adsorbent. [B] Concentration of total Cr in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results of blank (Figure 4.3 [A]) it can be seen that approximately 19% of total Cr precipitated. Results of this experiment are in correlation with the results of Cr(III) and Cr(VI).

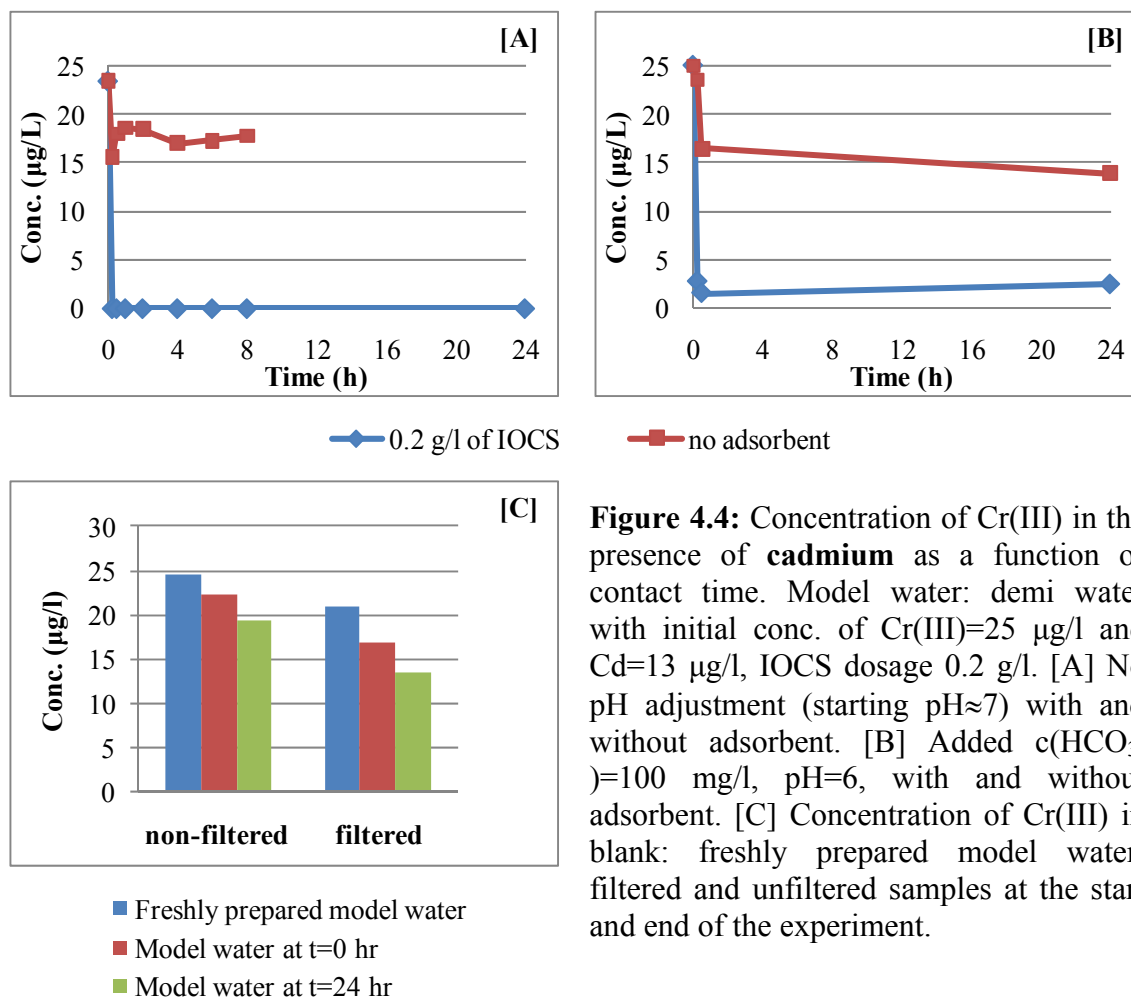
From the Figure 4.3 [A] it can be seen that using 0.2 g/l of IOCS approximately 55% of total Cr can be removed during 24 hrs contact time. Figure 4.3 [B] shows results that are also in correlation with the results presented in Figs 4.1 [B] and 4.2 [B].

Experimental results are in line with PHREEQC results. PHREEQC also predicts that there will be precipitation of  $\text{Cr}(\text{OH})_3$  and  $\text{Cr}_2\text{O}_3$ .

Around 17% of total Cr concentration remained on the 0.45  $\mu\text{m}$  filter during filtration of the sample. Conclusions are the same as above.

#### Effect of Cd on Cr(III) adsorption

Figure 4.4 shows the change of Cr(III) concentration in model water in the presence of **cadmium** during 24 hrs contact time with and without adsorbent added.



**Figure 4.4:** Concentration of Cr(III) in the presence of **cadmium** as a function of contact time. Model water: demi water with initial conc. of Cr(III)=25  $\mu\text{g/l}$  and Cd=13  $\mu\text{g/l}$ , IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added  $\text{c}(\text{HCO}_3^-) = 100 \text{ mg/l}$ , pH=6, with and without adsorbent. [C] Concentration of Cr(III) in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the Figure 4.4 [A] it can be seen that approximately 26% of Cr(III) precipitated in blank. Results show that induction time is less than 15 minutes. There is less precipitation,

when the results are compared with results when Cd is not present in water. Presence of Cd in water probably has influenced the precipitation of Cr(III). Figure 4.4 [B] shows that approximately 44% of Cr(III) precipitated in blank. Thus, it can be said that under conditions applied there was influence of  $\text{HCO}_3^-$  and adjusted pH on Cr(III) precipitation.

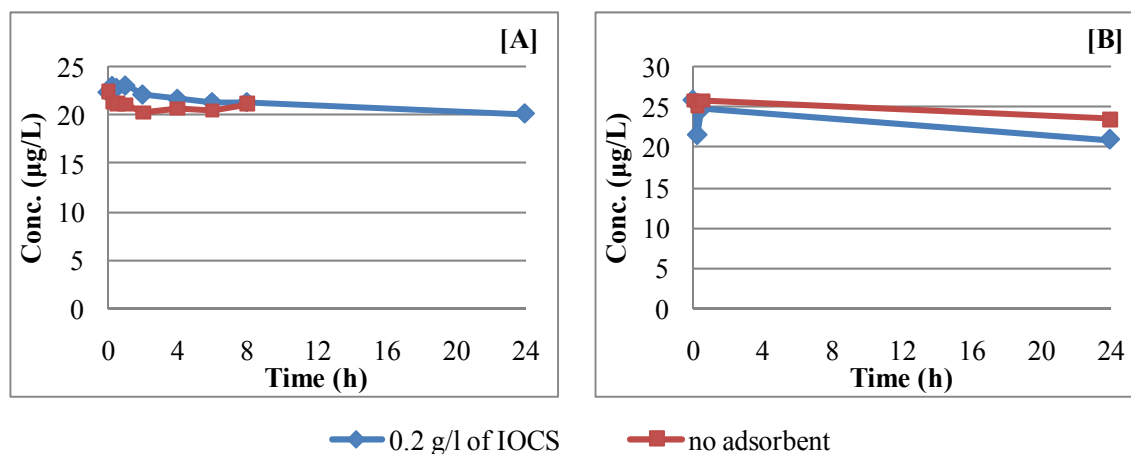
From the Figure 4.4 [A] it can be seen that complete removal of Cr(III) was achieved within 15 min. Results show that induction time is less than 15 minutes. From the results above it can be seen that Cr(III) is removed from water not only by adsorption but also by precipitation. Figure 4.4 [B] shows that not all Cr(III) is removed from water. Results are close to the value of detection limit. Differences in results can be considered as a measurement mistake.

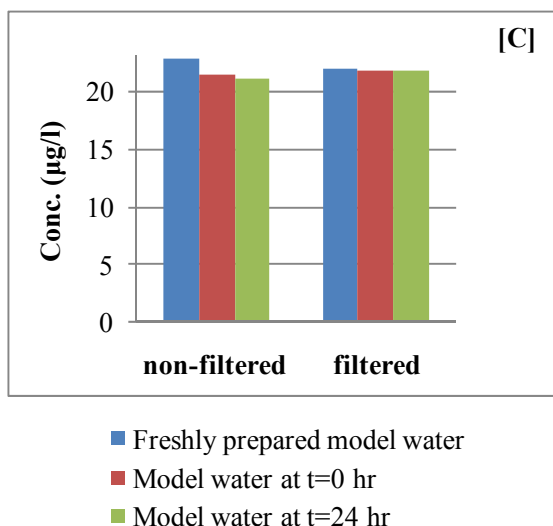
Experimental results with and without pH adjustment are in line with PHREEQC results, which showed that precipitated fractions are in the form of  $\text{Cr}(\text{OH})_3$  and  $\text{Cr}_2\text{O}_3$  species. From values of saturation indices (SI) it can be seen that Cr(III) would precipitate less when pH is adjusted to 6 than when initial  $\text{pH} \approx 7$  and there is no pH buffering.

Figure 4.4 [C] shows that Cr(III) concentrations at 0 hr are different for non-filtered and filtered samples, as well as for Cr(III) concentrations after 24 hrs. From the Figure 4.4 [C] it can be seen a trend in dropping of concentrations for non-filtered and filtered samples. Probably with presence of Cd in water the bigger colloids and more stable colloids are formed.

#### Effect of Cd on Cr(VI) adsorption

Figure 4.5 shows the change of Cr(VI) concentration in model water in the presence of **cadmium** during 24 hrs contact time with and without adsorbent added.





**Figure 4.5:** Concentration of Cr(VI) in the presence of **cadmium** as a function of contact time. Model water: demi water with initial conc. of Cr(VI)=25 µg/l and Cd=13 µg/l, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added  $c(\text{HCO}_3^-)$ =100 mg/l, pH=6, with and without adsorbent. [C] Concentration of Cr(VI) in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results without adsorbent (Figure 4.5 [A]) it can be seen that approximately 8.5% of Cr(VI) precipitated. Precipitation was probably detected due to a very small concentration of Cr(VI) and possible measurement errors. Results are similar to the results when Cd is not present in water. Also, in the case of Figure 4.2 [B] precipitation was detected probably due to measurement errors. Thus, probably there was no influence of Cd on Cr(VI) removal from model water.

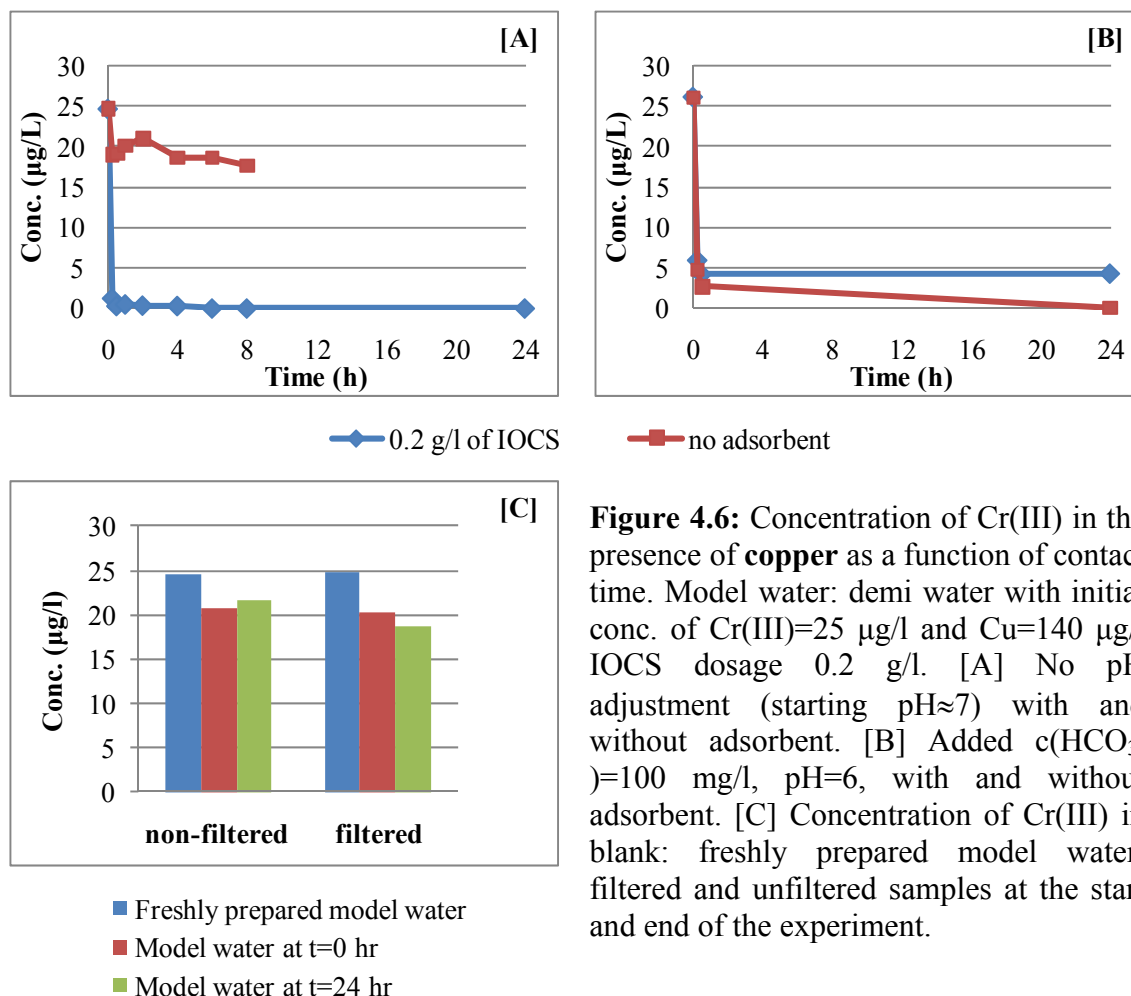
From the Figure 4.5 [A] it can be seen that 0.2 g/l of IOCS could not achieve effective Cr(VI) removal from model water (only approximately 10% removal achieved within 24h contact time). As stated above, precipitation was probably detected due to small concentration of Cr(VI) and possible measurement errors. Figure 4.4 [B] shows somewhat higher Cr(VI) removal in model water with 100 mg/l of  $\text{HCO}_3^-$  (around 19% removal during contact time of 24h) than in model water without  $\text{HCO}_3^-$ , Figure 4.4 [A], approximately 10% removal during contact time of 24h). This is probably due to a surface charge of IOCS in water that may be strongly affected by pH. Performance of the adsorbent is influenced by its point of zero charge ( $\text{pH}_{\text{pzc}}$ ).  $\text{pH}_{\text{pzc}}$  of IOCS coating (iron oxide) is around 7, but  $\text{pH}_{\text{pzc}}$  of silica sand is about 2-4.5. Therefore, it is possible that the  $\text{pH}_{\text{pzc}}$  of IOCS is below working pH of these experiments which would lead to the negatively charge. When pH is adjusted to 6 its means that predominant species of Cr(VI) is  $\text{HCrO}_4^-$  which is less negative than predominant Cr(VI) species at pH≈7 ( $\text{CrO}_4^{2-}$ ), hence they are more adsorbed by IOCS.

Comparing to experimental results PHREEQC results shown that precipitation would not appear in water. This is confirmed by looking at a SI of Cr(VI) species. Therefore, experimental results are in correlation with PHREEQC.

Figure 4.5 [C] shows that Cr(VI) concentrations at 0 hr and after 24 hrs are very similar. There is no drop of Cr(VI) concentration during the time. This probably means that Cr(VI) species stay dissolved in water during the experiment period.

#### Effect of Cu on Cr(III) adsorption

Figure 4.6 shows the change of Cr(III) concentration in model water in the presence of **copper** during 24 hrs contact time with and without adsorbent added.



**Figure 4.6:** Concentration of Cr(III) in the presence of **copper** as a function of contact time. Model water: demi water with initial conc. of Cr(III)=25 µg/l and Cu=140 µg/, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added  $c(\text{HCO}_3^-)$ =100 mg/l, pH=6, with and without adsorbent. [C] Concentration of Cr(III) in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results of blank it can be seen that approximately 29% of Cr(III) precipitated. Results are similar to the case above when there is no Cu in water. The interesting part of experiment in Figure 4.6 [B] is without adsorbent were after 24 hrs all of Cr(III) is removed. This result is not logical because the part of experiment without adsorbent has higher removal comparing to the part of experiment with 0.2 g/l IOCS. Probably because of measurement error the results are like this.

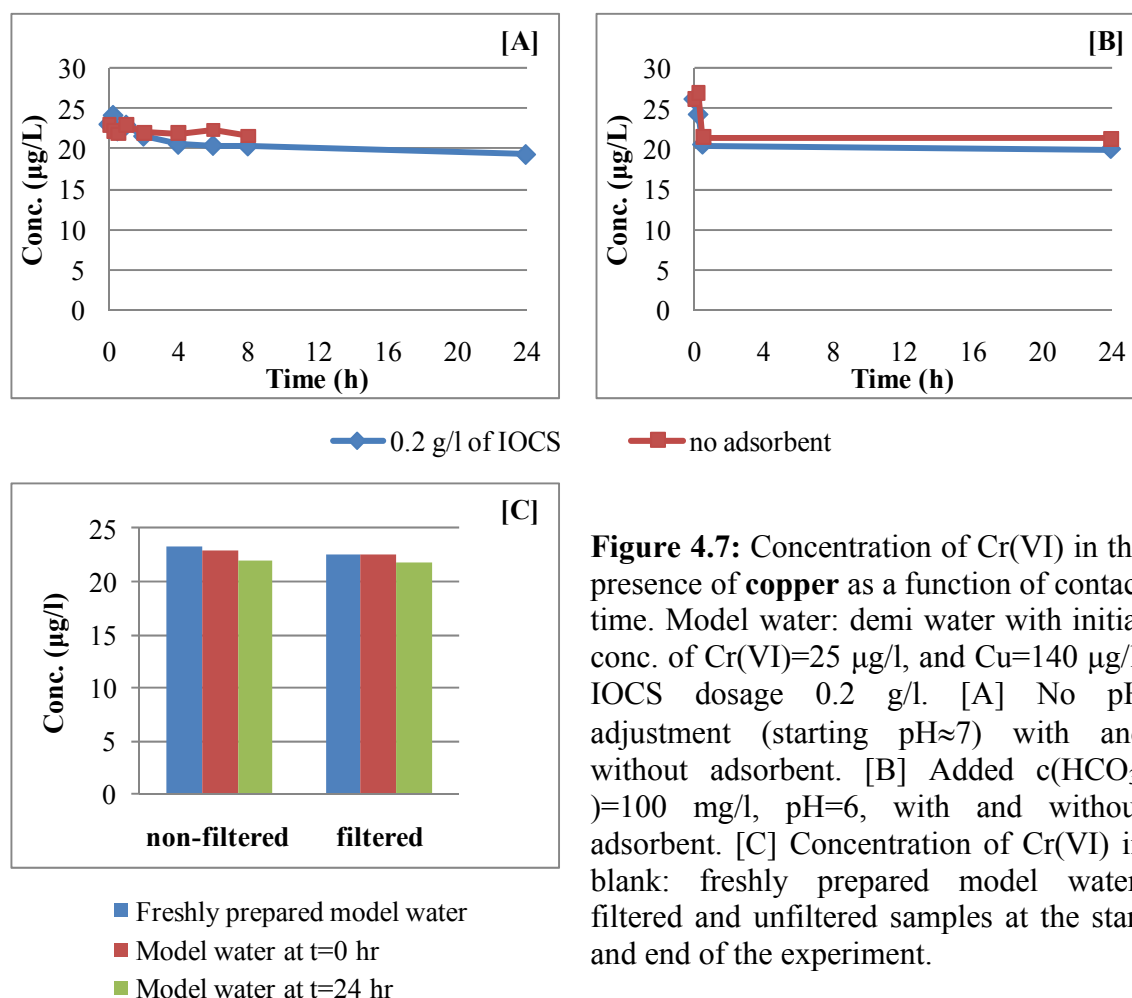
Figure 4.6 shows Cr(III) removal with IOCS from Cu containing model water without  $\text{HOC}_3^-$  (Figure 4.6 [A]) and with  $\text{HCO}_3^-$  (Figure 4.6 [B]). Complete removal of Cr(III) was achieved within 15 minutes of contact time (Figure 4.6 [A]). From the Figure 4.6 [B] it can be seen that about 84% of C(III) is removed during the contact time. Thus, it can be said that under conditions applied there was influence of  $\text{HCO}_3^-$  and adjusted pH on Cr(III) precipitation.

Experimental results are in line with PHREEQC results, which showed that precipitated fractions are in the form of  $\text{Cr}(\text{OH})_3$  and  $\text{Cr}_2\text{O}_3$  species. There would be less precipitation when pH is adjusted to 6. This can be seen from at a SI of Cr(III) species.

Figure 4.6 [C] shows that Cr(III) concentrations of blank for non-filtered and filtered sample are very similar. Also, Cr(III) concentrations at 0 hr and 24 h are very similar. Change of Cr(III) concentrations occur during preparation process and is about 18% for non-filtered and for filtered samples. This is probably because nucleation occur during preparation process and possibly some of the Cr(III) has precipitated in very short time.

### Effect of Cu on Cr(VI) adsorption

Figure 4.7 shows the change of Cr(VI) concentration in model water in the presence of **copper** during 24 hrs contact time with and without adsorbent added.



**Figure 4.7:** Concentration of Cr(VI) in the presence of **copper** as a function of contact time. Model water: demi water with initial conc. of Cr(VI)=25 µg/l, and Cu=140 µg/l, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added  $c(\text{HCO}_3^-) = 100 \text{ mg/l}$ , pH=6, with and without adsorbent. [C] Concentration of Cr(VI) in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results of blank it can be seen that approximately 6% of Cr(VI) precipitated (Figure 4.7 [A]). Results are similar to the results when Cu is not present in water. From the results of blank (Figure 4.7 [B]) it can be seen that around 19% of Cr(VI) precipitates. It can be said that under conditions applied there was influence of  $\text{HCO}_3^-$  and adjusted pH on Cr(VI) precipitation.

From the Figure 4.7 [A] it can be seen that removal of relatively low concentration of Cr(VI) of 25 µg/l, through adsorption on IOCS (dosage: 0.2 g/l) is ineffective only approximately 16% removal during contact time of 24 hrs. Figure 4.7 [B] shows that approximately 24% of Cr(III) is removed during the contact time. If compared with results from Figure 4.7 [A] it can be seen that removal is slightly higher. It is the same case as for Cr(VI) in the presence of Cu mentioned above.

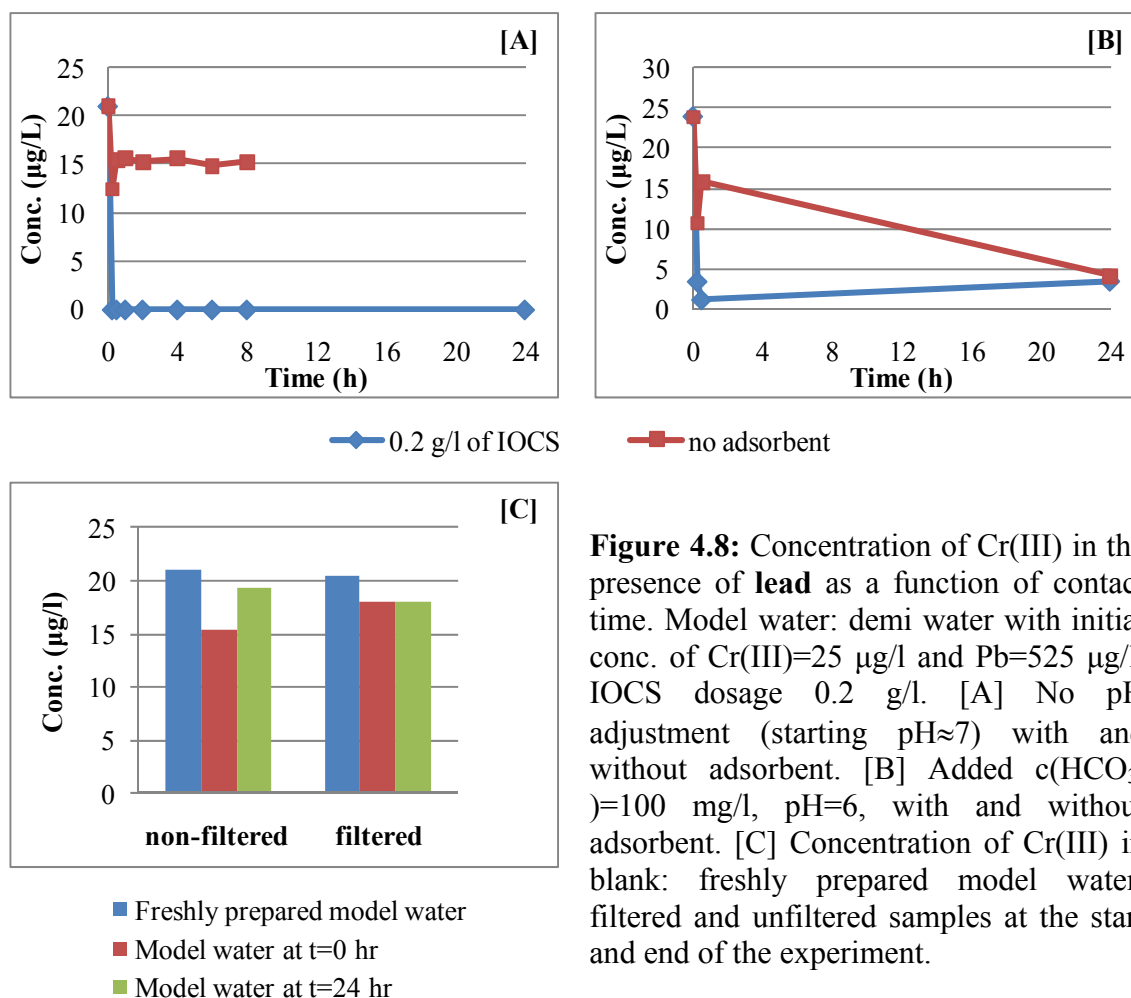
Comparing to experimental results PHREEQC results shown that precipitation would not appear in water. This is confirmed by looking at a SI of Cr(VI) species.



Figure 4.7 [C] shows that Cr(III) concentrations at 0 hr and after 24 hrs are very similar. Difference in concentrations between 0 hr and 24 hrs is around 4% which is very small. This probably means that Cr(VI) species stay dissolved in water during the experiment period.

#### Effect of Pb on Cr(III) adsorption

Figure 4.8 shows the change of Cr(III) concentration in model water in the presence of **lead** during 24 hrs contact time with and without adsorbent added.



**Figure 4.8:** Concentration of Cr(III) in the presence of **lead** as a function of contact time. Model water: demi water with initial conc. of Cr(III)=25 µg/l and Pb=525 µg/l, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added  $c(\text{HCO}_3^-)=100$  mg/l, pH=6, with and without adsorbent. [C] Concentration of Cr(III) in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results without adsorbent (Figure 4.8 [A]) it can be seen that approximately 29% of Cr(III) precipitated. Results are similar to the results when Pb is not present in water. Also, in Figure 4.8 [B] it is noticed the drop of Cr(III) concentration approximately 83% during 24 hrs when there is no adsorbent present in water. This results imply that when pH is adjusted to 6, Pb would probably form some compound with Cr(III) which will precipitates.

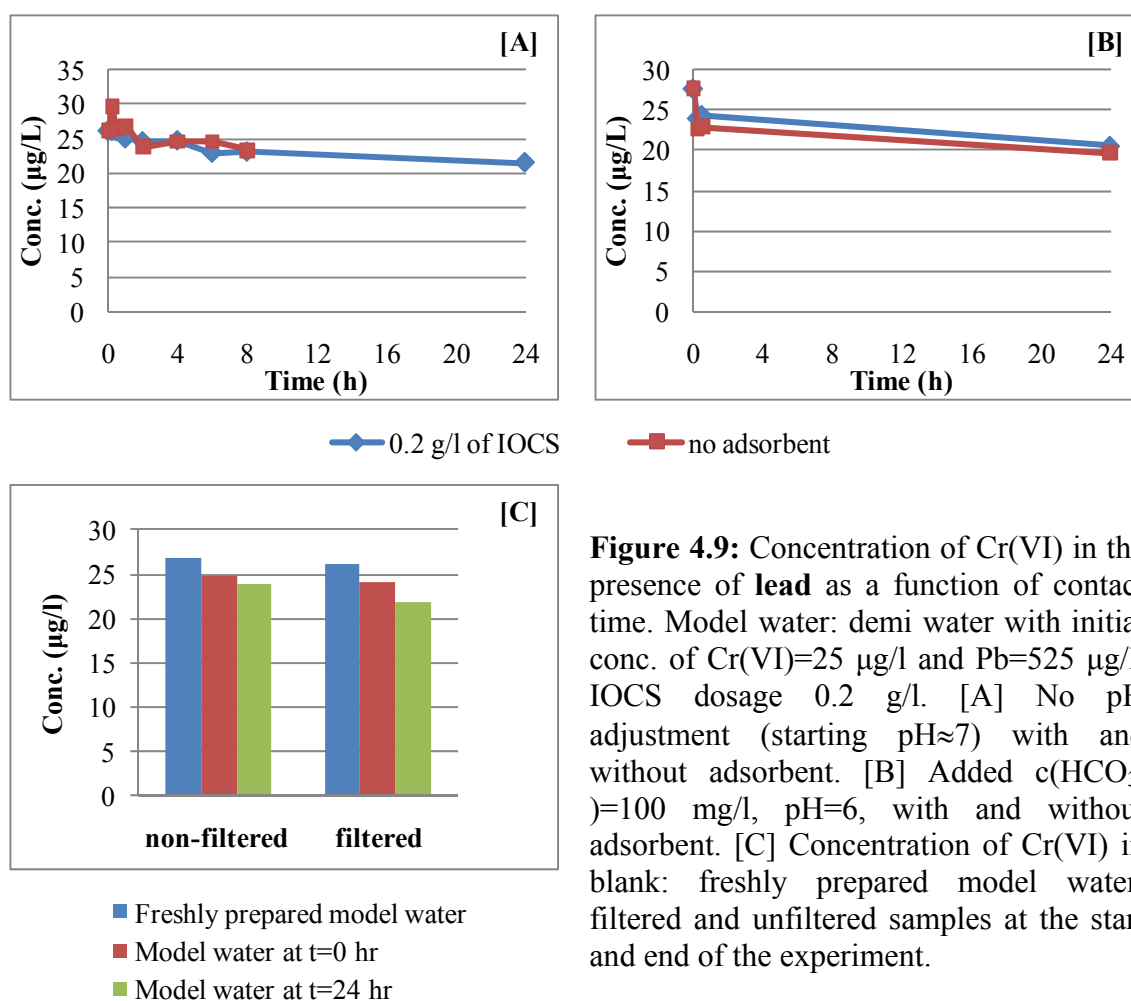
From the Figure 4.8 [A] it can be seen that probably adsorbent was overdosed, since all was removed within 15 min. From the Figure 4.8 [B] it can be seen that approximately 86% of C(III) is removed during the contact time. Thus, it can be said that under conditions applied there was influence of  $\text{HCO}_3^-$  and adjusted pH on Cr(VI) precipitation.

Experimental results are in line with PHREEQC results, which showed that precipitated fractions are in the form of  $\text{Cr}(\text{OH})_3$  and  $\text{Cr}_2\text{O}_3$  species. There would be less precipitation when pH is adjusted to 6. This can be seen from at a SI of Cr(III) species.

Figure 4.5 [C] shows that Cr(III) concentrations would not be affected by filtration of samples. The difference of non-filtered and filtered sample at  $t=0$  h is probably a measurement mistake. Also, its noticed the drop of about 10% of Cr(III) concentration during preparation of model water. This is probably because nuclei are formed in very short time with possible precipitation. Measurement after 24 hrs shows concentration similar to initial concentration of Cr(VI). This is because, shacking of batch before taking of sample causes for bigger colloids to break into the smaller fractions that are capable to pass through the filter paper of  $0.45\ \mu\text{m}$  pore size. Also, shaking makes solution more homogenous.

#### Effect of Pb on Cr(VI) adsorption

Figure 4.9 shows the change of Cr(VI) concentration in model water in the presence of **lead** during 24 hrs contact time with and without adsorbent added.



**Figure 4.9:** Concentration of Cr(VI) in the presence of **lead** as a function of contact time. Model water: demi water with initial conc. of Cr(VI)=25 µg/l and Pb=525 µg/l, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH ≈ 7) with and without adsorbent. [B] Added  $\text{c}(\text{HCO}_3^-) = 100\ \text{mg/l}$ , pH=6, with and without adsorbent. [C] Concentration of Cr(VI) in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results without adsorbent (Figure 4.9 [A]) it can be seen that approximately 10.5% of Cr(VI) precipitated. Precipitation was probably detected due to a very small concentration of Cr(VI) and possible measurement errors. Results are similar to the results when Pb is not present in water. From the results of blank (Figure 4.9 [B]) it can be seen that around 29% of Cr(VI) precipitates. This results are not logical because there is higher removal when there no adsorbent present in water. This is probably due to measurement error.

From the Figure 4.9 [A] it can be seen that using 0.2 g/l of IOCS Cr(VI) is very hard to remove from water (around 17.5% of removal during contact time). From the Figure 4.7 [B] it can be seen that about 26% of Cr(VI) is removed during the contact time. As stated above, pH has a big role in removal of Cr(VI) from water.

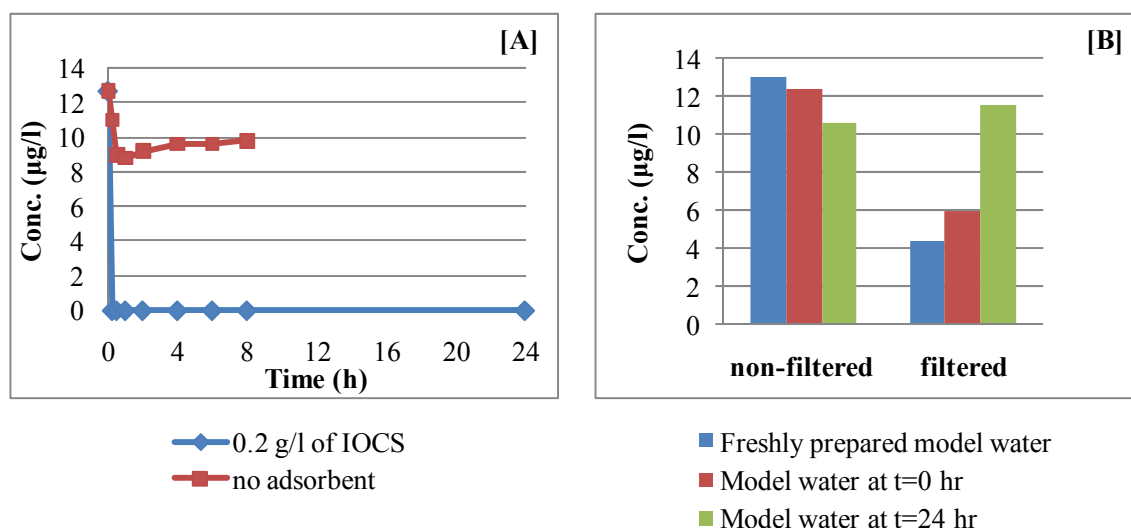
Comparing to experimental results PHREEQC results shown that precipitation would not appear in water. This is confirmed by looking at a SI of Cr(VI) species. This means that Cr(VI) is removed from water only by adsorption.

Figure 4.5 [C] shows that results for non-filtered and filtered samples very similar. During the preparation of model water there is a drop of 7.5% Cr(VI) concentration. Also, there is a similar drop in concentrations after 24 hrs. This happens probably due to nucleation which is probably faster with presence of Pb in water.

#### 4.3.2. Adsorption of cadmium

##### Adsorption of Cd

Figure 4.10 shows the change of Cd concentration during 24 hrs contact time with and without adsorbent added.



**Figure 4.10:** Concentration of Cd as a function of contact time. Model water: demi water with initial conc. of Cd=13 µg/l, no pH adjustment (starting pH≈7), IOCS dosage 0.2 g/l. [A] Reduction in concentration with and without adsorbent. [B] Concentration of Cd in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results without adsorbent (figure 4.10 [A]) it can be seen that approximately 24.5% of Cd precipitated. Presence of Cr(III) in water probably did not influence the precipitation of Cd.

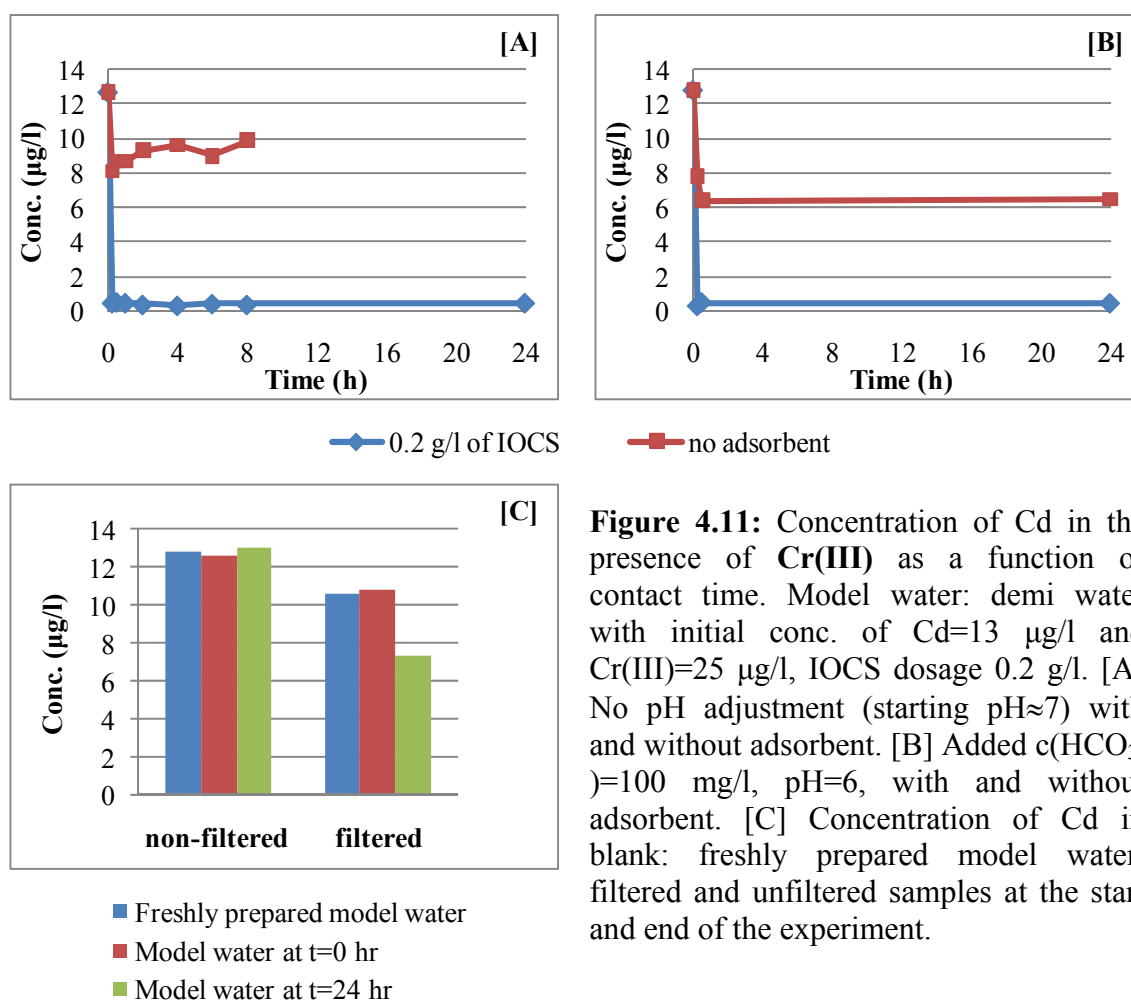
From the Figure 4.10 [A] it can be seen that using 0.2 g/l of IOCS Cd is totally removed from the water (within 15 minutes of contact time). In case when adsorbent is used, all Cd is removed, but one part due to precipitation.

In contrast, to experimental results PHRQC shows that precipitation does not occur. This can be seen by looking at a SI of Cd species. Probably due to a very small concentration of Cd precipitation is detected.

Figure 4.10 [B] shows that Cd concentrations of sample at 0 hr when they are filtered was lower more than 50%. That means that part of Cd would remain on the filter during filtration of samples. This is probably because bigger colloidal particles of metals in model water remain on the filter paper while the smaller colloidal particles and dissolved fractions pass through the filter.

### Effect of Cr(III) on Cd adsorption

Figure 4.11 shows the change of Cd concentration in model water in the presence of **Cr(III)** during 24 hrs contact time with and without adsorbent added.



**Figure 4.11:** Concentration of Cd in the presence of **Cr(III)** as a function of contact time. Model water: demi water with initial conc. of Cd=13 µg/l and Cr(III)=25 µg/l, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added  $c(\text{HCO}_3^-) = 100 \text{ mg/l}$ , pH=6, with and without adsorbent. [C] Concentration of Cd in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results of blank it can be seen that approximately 29% of Cd precipitated (Figure 4.11 [A]). When compared with results above, when only Cd is present in water, it can be said that there was no influence of Cr(III) on Cd removal. From the results without adsorbent (Figure 4.11 [B]) it can be seen that around 50% of Cd precipitates. Thus, there is an influence of  $\text{HCO}_3^-$  and adjusted pH on Cd precipitation.

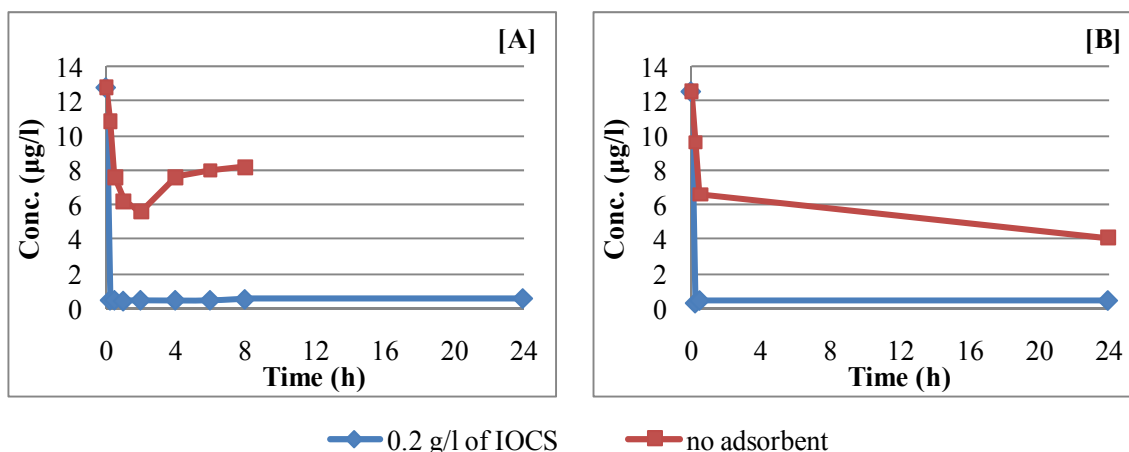
From the Figure 4.11 [A] it can be seen that in case when adsorbent is used, all is removed, but one part due to precipitation. From the Figure 4.11 [B] it can be seen that approximately 97% of Cd is removed during the contact time.

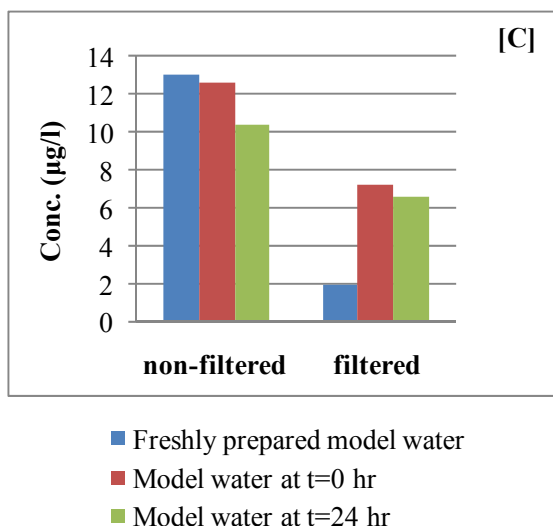
In contrast, to experimental results PHRQC shows that precipitation does not occur. At the working pH of experiments the Cd exists only as  $\text{Cd}^{2+}$  specie. Adsorbent has a negative surface charge under working pH so most possible is that Cd is totally adsorbed because of its positive charge.

Figure 4.11 [C] shows that Cd concentrations for non-filtered and filtered samples are very similar, except in case of filtered sample at  $t=24$  hr. After filtration on the filters remain about 15% of Cd concentration. This is probably because the bigger colloids that are formed stay on the filter paper during filtration process.

#### Effect of Cr(VI) on Cd adsorption

Figure 4.12 shows the change of Cd concentration in model water in the presence of **Cr(VI)** during 24 hrs contact time with and without adsorbent added.





**Figure 4.12:** Concentration of Cd in the presence of **Cr(VI)** as a function of contact time. Model water: demi water with initial conc. of Cd=13 µg/l and Cr(VI)=25 µg/l, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, pH=6, with and without adsorbent. [C] Concentration of Cd in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results of blank (Figure 4.12 [A]) it can be seen that approximately 40% of Cd precipitated. Looking at results above in this case there is probably small influence of Cr(VI) on Cd removal. From the results of blank (figure 4.12 [B]) it can be seen that around 67.5% of Cd precipitates. Therefore, there is an influence of HCO<sub>3</sub><sup>-</sup> and adjusted pH on Cd precipitation.

From the Figure 4.12 [A] it can be seen that using 0.2 g/l of IOCS Cd is totally removed from the water (within 15 minutes of contact time). From the Figure 4.12 [B] it can be seen that about 96% of Cd is removed during the contact time.

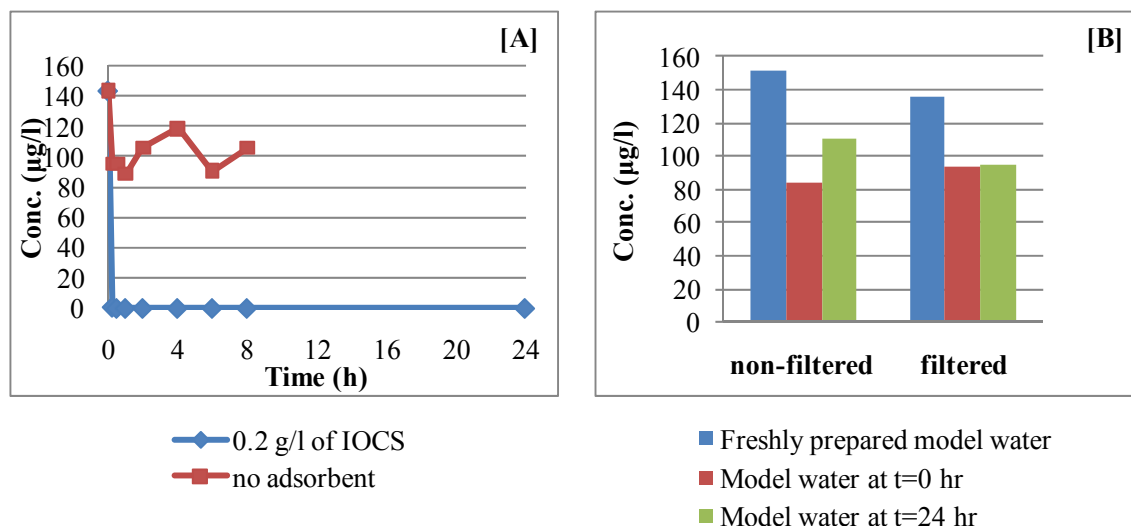
In contrast, to experimental results PHRQC shows that precipitation does not occur. At the working pH of experiments as mentioned before the Cd exists only as Cd<sup>2+</sup> specie. Therefore, probably only removal is by adsorption.

From the Figure 4.12 [C] it can be seen that filtered sample of freshly prepared model water is measured incorrectly. From the results at t=0 hr and t=24 hr it can be seen that about 40% Cd remained on the filter paper. Therefore, probably in presence of Cr(VI) in water bigger colloids are formed, which cannot pass through filter. Also, there is possibility that mistakes were made during diltion of samples. In summary, there is probably no influence of Cr(VI) on Cd removal.

#### 4.3.1. Adsorption of copper

##### Adsorption of Cu

Figure 4.13 shows the change of Cu concentration during 24 hrs contact time with and without adsorbent added.



**Figure 4.13:** Concentration of Cu as a function of contact time. Model water: demi water with initial conc. of Cu=140 µg/l, no pH adjustment (starting pH≈7), IOCS dosage 0.2 g/l. [A] Reduction in concentration with and without adsorbent. [B] Concentration of Cu in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results without adsorbent it can be seen that approximately 26% of Cu precipitated Figure 4.13 [A]). In addition, from the results without adsorbent it can be seen that induction time is less than 15 minutes.

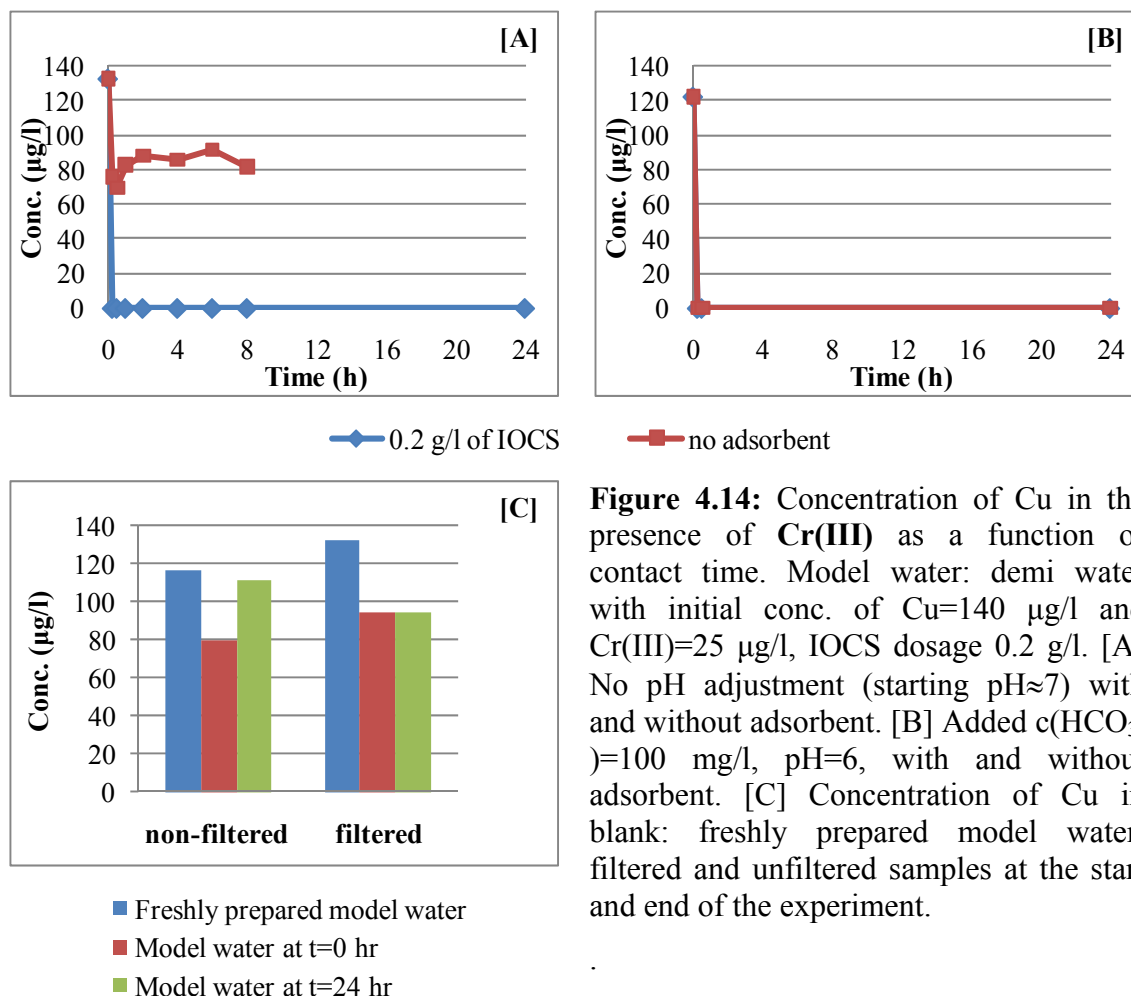
From the Figure 4.13 [A] it can be seen that using 0.2 g/l of IOCS Cu is totally removed from the water (within 15 minutes of contact time).

Experimental results are in line with PHREEQC results, which showed that precipitated fractions are in the form of tenorite (CuO) specie.

Figure 4.13 [B] shows that Cu concentrations of samples when they are filtered are around 30% less. That means that part of Cu will remain on the filter during filtration of samples. This is probably because bigger colloidal particles of metals in model water remain on the filter paper while the smaller colloidal particles and dissolved fractions pass through the filter. Also, probably results are affected by the quality of dilution of sample.

#### Effect of Cr(III) on Cu adsorption

Figure 4.14 shows the change of Cu concentration in model water in the presence of **Cr(III)** during 24 hrs contact time with and without adsorbent added.



**Figure 4.14:** Concentration of Cu in the presence of **Cr(III)** as a function of contact time. Model water: demi water with initial conc. of Cu=140 µg/l and Cr(III)=25 µg/l, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, pH=6, with and without adsorbent. [C] Concentration of Cu in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results without adsorbent it can be seen that about 38.5% of Cu is precipitated. Probably there is influence of Cr(III) on the Cu precipitation.

From the Figure 4.14 [A] it can be seen that all of Cu was removed within 15 minutes of contact time. Figure 4.14 [B] shows that Cu is totally removed in both cases when there is adsorbent in water. Everything is removed in less than 15 minutes. This probably means that instantaneous precipitation of Cu occurs. Previous results of Cr(III) concentration in presence of Cu are very similar to results given in Figure 4.14 [B]. Therefore, probably some compound is formed between the Cu and Cr(III) under pH=6 conditions which causes for them to precipitate in very short time.

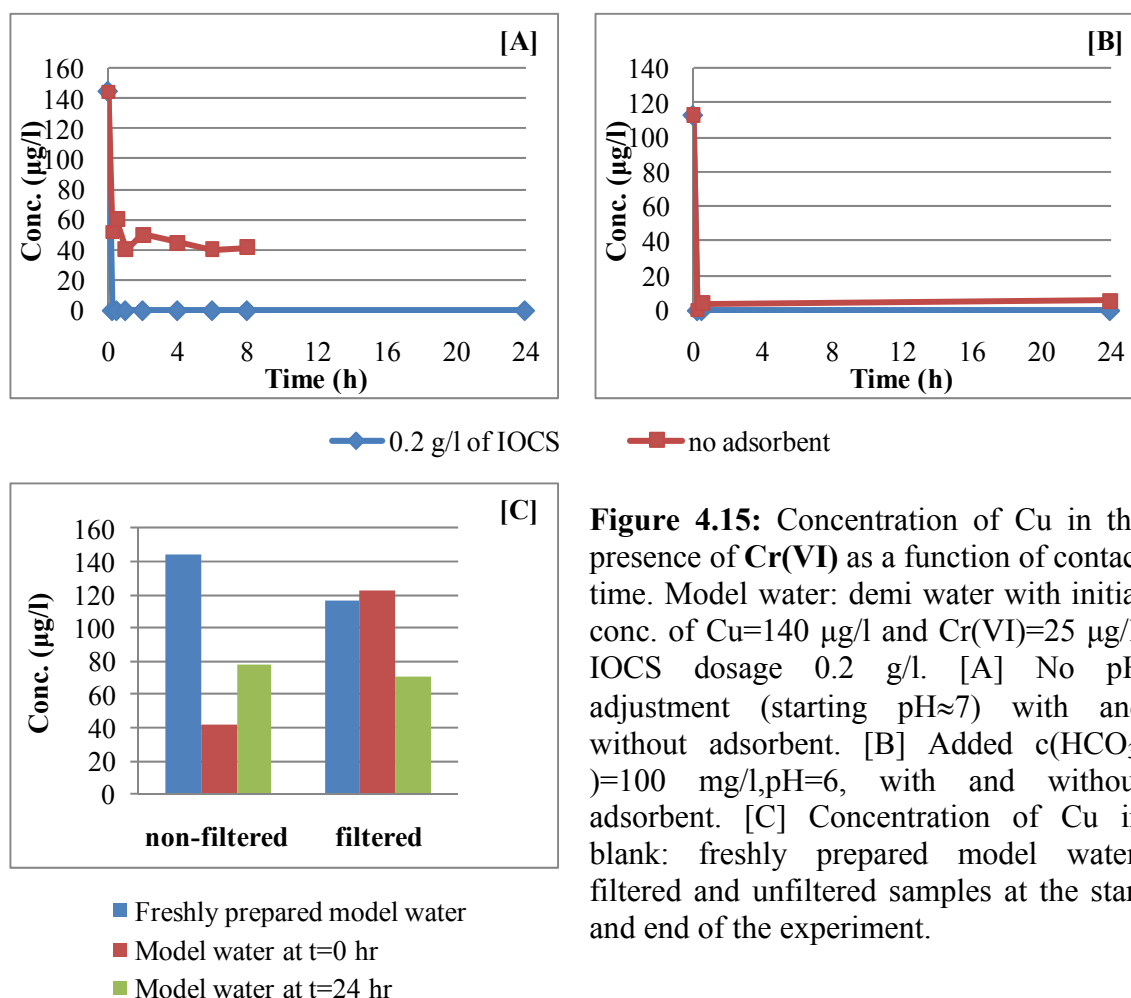
Experimental results are in line with PHREEQC results, which showed that precipitated fractions are in the form of tenorite (CuO) specie.

Figure 4.14 [C] shows that Cu concentrations of filtered samples are higher comparing to non-filtered samples. This probably occur because of dilution mistake. Anyway, from the result it can be noticed that about 30% of Cu remains on the filter. This is probably due to formation of nuclei and colloidal particles.



### Effect of Cr(VI) on Cu adsorption

Figure 4.15 shows the change of Cu concentration in model water in the presence of Cr(VI) during 24 hrs contact time with and without adsorbent added.



**Figure 4.15:** Concentration of Cu in the presence of Cr(VI) as a function of contact time. Model water: demi water with initial conc. of Cu=140 µg/l and Cr(VI)=25 µg/l, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added  $c(\text{HCO}_3^-)=100 \text{ mg/l}$ , pH=6, with and without adsorbent. [C] Concentration of Cu in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results of blank (Figure 4.15 [A]) it can be seen that approximately 72% of Cu precipitated. There is more precipitation than in case when only Cu is present in water. This means that presence of Cr(VI) influence the removal of Cu in water. Figure 4.15 [B] shows that Cu is totally removed in both cases when there is adsorbent and when there is no adsorbent in water. Everything is removed in less than 15 minutes. This means that with pH of 6 instantaneous precipitation of Cu occurs.

From the Figure 4.15 [A] it can be seen that all of Cu was removed within 15 minutes of contact time. Therefore, in case when adsorbent is used, all of Cu is removed, but probably most due to precipitation.

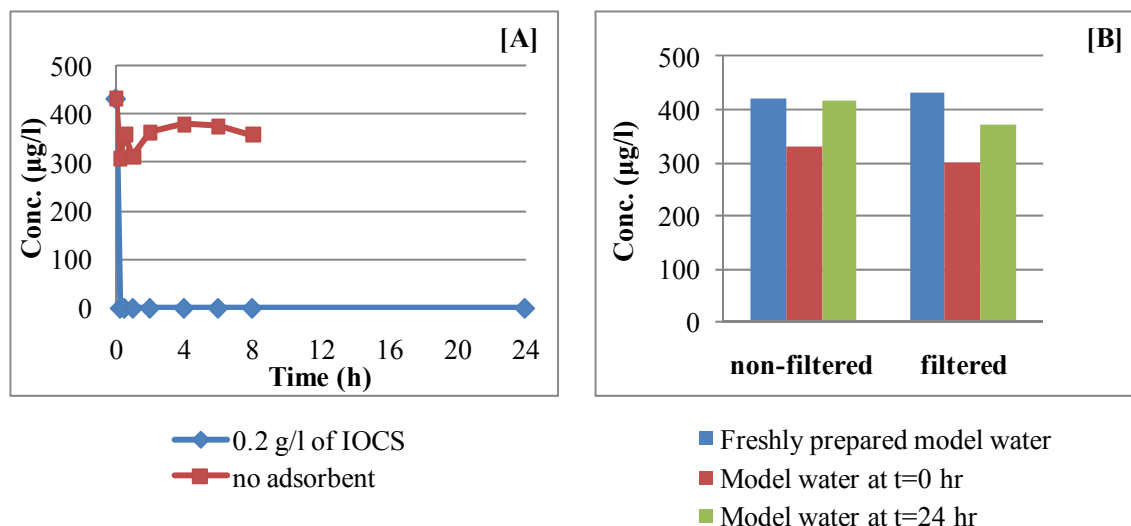
Experimental results are in line with PHREEQC results, which showed that precipitated fractions are in the form of tenorite (CuO) specie.

Figure 4.15 [C] shows that Cu concentrations drop when the samples are filtered. From the result it can be noticed that about 10-20% of Cu remains on the filter. This is probably due to formation of nuclei and colloidal particles.

### 4.3.3. Adsorption of lead

#### Adsorption of Pb

Figure 4.16 shows the change of Pb concentration during 24 hrs contact time with and without adsorbent added.



**Figure 4.16:** Concentration of Pb as a function of contact time. Model water: demi water with initial conc. of Pb=525 µg/l, no pH adjustment (starting pH≈7), IOCS dosage 0.2 g/l. [A] Reduction in concentration with and without adsorbent. [B] Concentration of Pb in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results without adsorbent (Figure 4.16 [A]) it can be seen that approximately 17% of Pb precipitated.

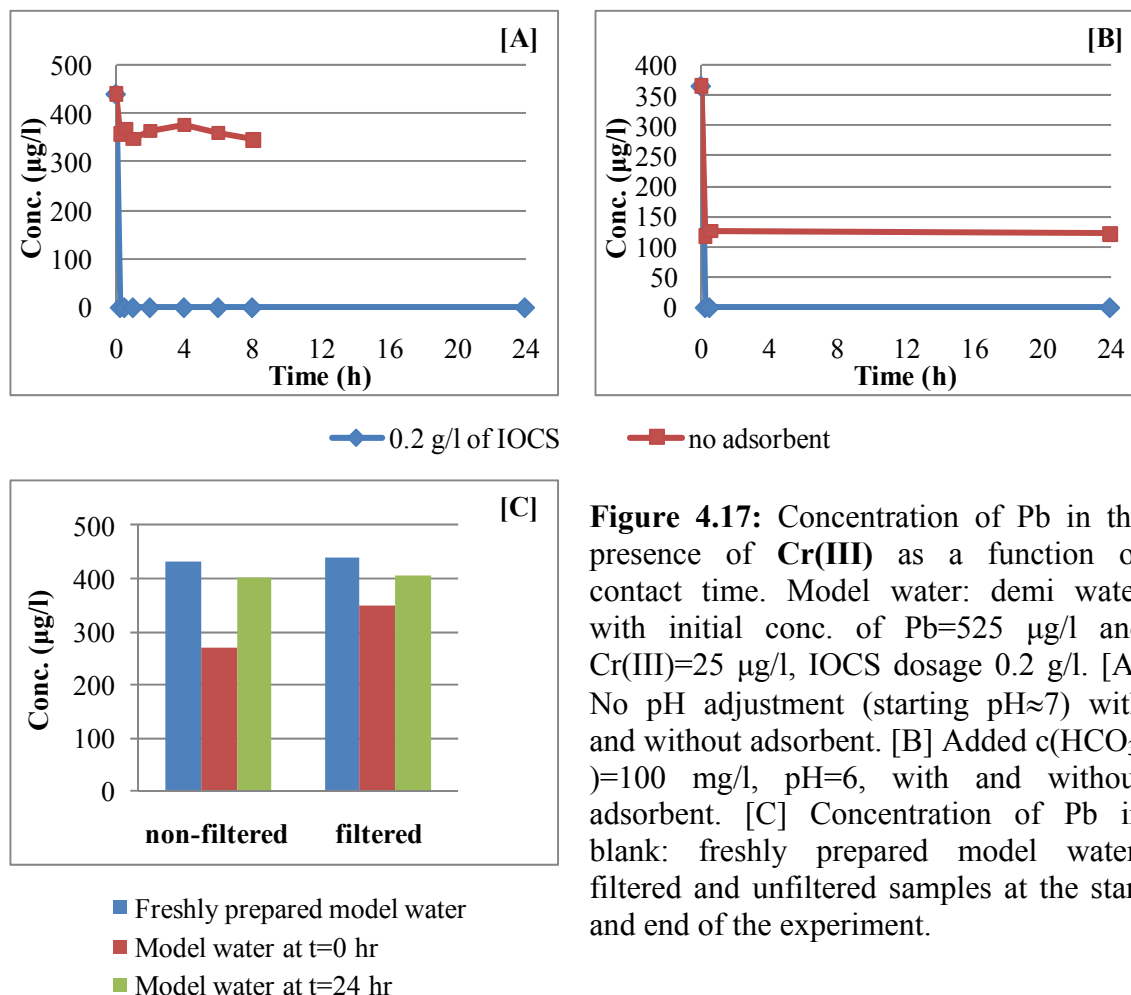
From the Figure 4.16 [A] it can be seen that using 0.2 g/l of IOCS Pb is totally removed from the water (within 15 minutes of contact time). Probably adsorbent was overdosed, since all was removed within 15 minutes.

Experimental results are in line with PHREEQC results, which showed that precipitated fractions are in the form of  $\text{Pb}(\text{OH})_2$  specie. SI is practically zero so it can be said that small amount of Pb would precipitate.

Figure 4.13 [B] shows that Pb concentrations of non-filtered and filtered samples are very similar. During preparation of model water around 20-30% of Pb precipitates. This is probably because molecular mass of Pb is relatively big so Pb tends in sort time to stratify but that does not mean precipitate. When the batches are shaken after 24 hrs the Pb is again homogeneously dispersed in water. Very small amount of Pb remains on filter during filtration. This is probably because bigger colloidal particles of metals in model water remain on the filter paper while the smaller colloidal particles and dissolved fractions pass through the filter.

### Effect of Cr(III) on Pb adsorption

Figure 4.17 shows the change of Pb concentration in model water in the presence of **Cr(III)** during 24 hrs contact time with and without adsorbent added.



**Figure 4.17:** Concentration of Pb in the presence of **Cr(III)** as a function of contact time. Model water: demi water with initial conc. of Pb=525 µg/l and Cr(III)=25 µg/l, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added  $c(\text{HCO}_3^-) = 100 \text{ mg/l}$ , pH=6, with and without adsorbent. [C] Concentration of Pb in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results of blank (Figure 4.17 [A]) it can be seen that approximately 21% of Pb precipitated. Looking at results above in this case there is probably no influence of Cr(VI) on Pb precipitation. From the results without adsorbent (Figure 4.17 [B]) it can be seen that approximately 66% of Pb precipitates. There is an influence of  $\text{HCO}_3^-$  and adjusted pH on Pb precipitation.

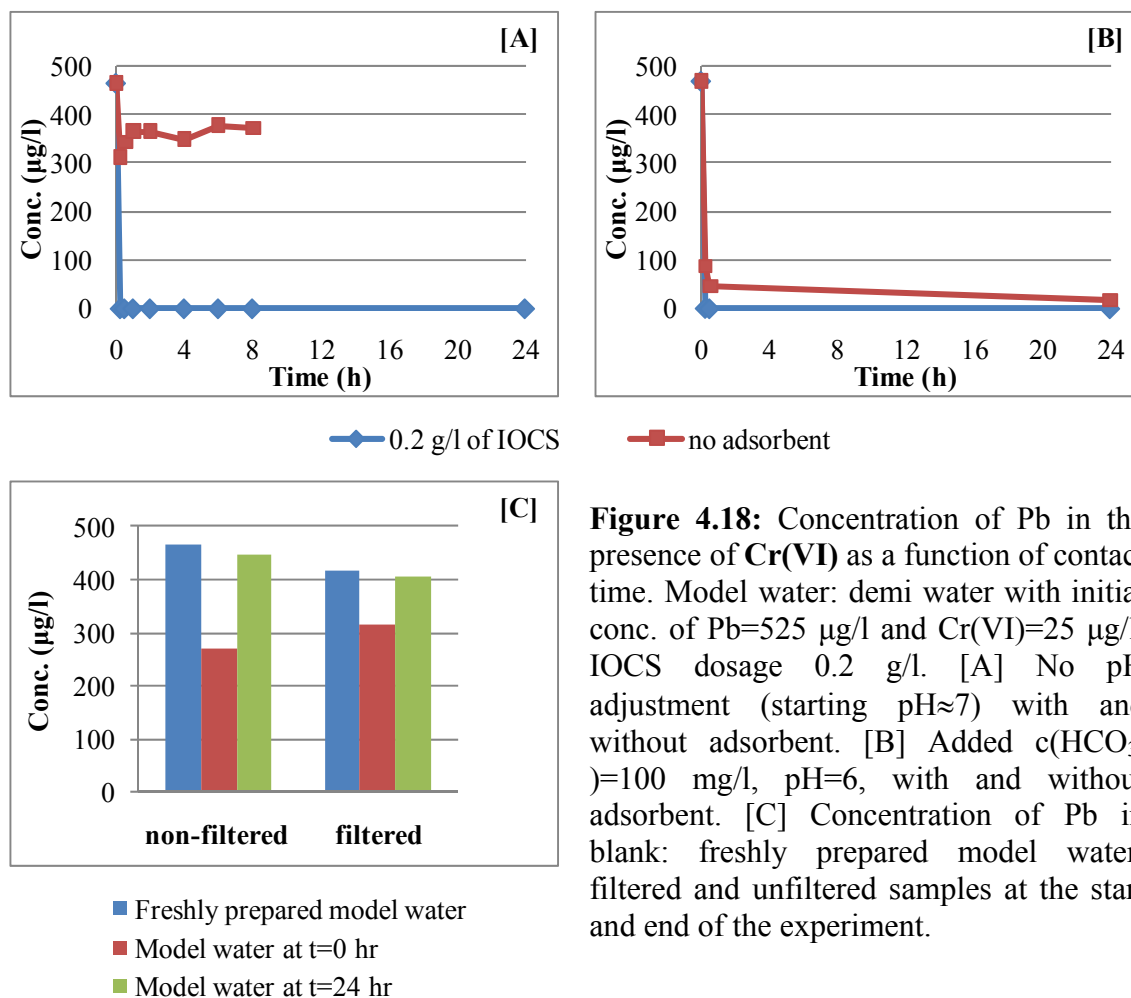
From the Figure 4.17 [A] it can be seen that using 0.2 g/l of IOCS Pb is totally removed from the water (within 15 minutes of contact time). From the Figure 4.17 [B] it can be seen that all the lead is removed during the first 15 minutes of contact time. Results in the case of Cr(III) concentration in presence of Pb are probably in correlation to results given in Figure 4.17 [B]. Therefore, probably some compound is formed between the Pb and Cr(III) under pH=6 conditions which causes for them to precipitate in very short time.

Experimental results are in line with PHREEQC results, which showed that precipitated fractions are in the form of  $\text{Pb}(\text{OH})_2$  specie. SI is practically zero so it can be said that small amount of Pb would precipitate.

Figure 4.17 [C] shows that Pb concentrations of non-filtered and filtered samples are very similar. That means that very small amount of Pb remains on filter during filtration. There is a 20-30% drop in Pb concentrations during the preparation period for start of experiment. This is probably like in case above when only Pb is present in water.

#### Effect of Cr(VI) on Pb adsorption

Figure 4.18 shows the change of Pb concentration in model water in the presence of **Cr(VI)** during 24 hrs contact time with and without adsorbent added.



**Figure 4.18:** Concentration of Pb in the presence of **Cr(VI)** as a function of contact time. Model water: demi water with initial conc. of Pb=525 µg/l and Cr(VI)=25 µg/l, IOCS dosage 0.2 g/l. [A] No pH adjustment (starting pH ≈ 7) with and without adsorbent. [B] Added  $c(\text{HCO}_3^-) = 100 \text{ mg/l}$ , pH=6, with and without adsorbent. [C] Concentration of Pb in blank: freshly prepared model water, filtered and unfiltered samples at the start and end of the experiment.

From the results of blank (Figure 4.18 [A]) it can be seen that approximately 21% of Pb precipitated. From the results shown in Figure 4.18 [B] it can be seen that around 96% of Pb precipitates. That means that probably instantaneous precipitation of Pb occur under existing working conditions.

From the Figure 4.18 [A] it can be seen that probably adsorbent was overdosed, since all was removed within 15 min. Also, from the Figure 4.11 [B] it can be seen that all the lead is removed during the first 15 minutes of contact time.

Experimental results are in line with PHREEQC results, which showed that precipitated fractions are in the form of  $\text{Pb}(\text{OH})_2$  and  $\text{PbCrO}_4$  specie.

Figure 4.18 [C] shows that about 10-20% of Cu remains on the filter. From the result it can be noticed that about 10% of Pb concentration remains on the filter after filtration. This is probably due to formation of nuclei and colloidal particles. Also, there is a 25-40% drop in Pb concentrations during the preparation period for start of experiment. This is probably for similar reasons like in Figure 4.16 [B]. This means that presence of Cr(VI) influence the removal of Pb in water.



## 5. CONCLUSIONS AND RECOMMENDATIONS

### 5.1 Conclusions

This study was carried out to further understand and advance adsorptive removal of selected heavy metals by using iron oxides based medium. The following conclusions were drawn on the basis of literature review and the results obtained from the experiments.

#### Literature review:

From abounded amount of scientific articles and books written on the problem of heavy metal removal from urban stormwater runoff, two stormwater treatment technologies were determined as being able to achieve the best possible urban stormwater quantity and quality mitigation:

- Constructed bioretention filter system. Based on published removal efficiencies, stormwater biofiltration using vegetated filter media has shown to be a promising technology for stormwater treatment. System should be built together with watertight membrane to prevent uncontrolled infiltration. This method is generally cost-effective.
- Combination of two operational units, i.e. a detention pond and adsorption filters. Filters with layers of different adsorbents will have higher removal efficiency then the above mentioned technology. However, this technology is rather expensive method and is used unless open basins or wetlands are available for biofiltration.

#### Short-term batch experiments:

- In the experiments without adsorbent it was found that pH value influences the co-occurring stability of Cd, Cr(III), Cr(VI), Cu, and Pb in water. Since pH was adjusted by adding  $\text{HCO}_3^-$  it is likely this anion that has influence on the stability of studied heavy metals.
- Under different pH values different metal species exist. The existence of these species depends on pH and can precipitate, also depending on the pH. Most likely, compounds are formed between Cu and Cr(III), Pb and Cr(III), Pb and Cr(VI).
- Co-occurrence of metals under conditions applied could enhance the precipitation of some metals or could play no role in removal of studied metal.
- In the adsorption experiments for majority of the metals the adsorbent was overdosed (everything was removed within 15 min). The only exception was Cr(VI).
- In the adsorption experiments with Cr(VI) it was found that pH value influences the removal. When pH is adjusted to 6 the existing species of Cr(VI) were more adsorbed by IOCS, probably because the surface charge of particles in water was affected by pH.

- From the experiments it was found, that induction time is less than 15 minutes. This means that nuclei are formed very fast and reach critical cluster size and precipitate in short period of time.

## **5.2 Recommendations**

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

- To perform similar experiments as carried out in this research, but with different metal's concentrations and adsorbent dosage.
- To perform experiments with GFH or other kind of iron oxides based media (preferably low-cost adsorbent).
- To carry out the experiments to determine competitive adsorption isotherms of selected heavy metals.
- To assess the effect of water quality (e.g.  $\text{Ca}^{2+}$  concentration) on co-occurring stability of studied heavy metals in water.
- To study competitive removal of 3-5 different metals, so to get a better picture on the removal of metals as they would occur in real stormwater runoff conditions.



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## **7. APPENDIX**

<b>Appendix A:</b> Short batch experiment .....	III
<b>Appendix B:</b> Equilibrium Calculation for the experiments with PHREEQC interactive ..	XII



## Appendix A: Short batch experiment

[A]	Conc. Cr(III) (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	23	23
0.25	<2	21
0.5	<2	16
1	<2	17
2	<2	17
4	<2	16
6	<2	16
8	<2	15
24	<2	-

**Table 1:** Concentration of Cr(III) as a function of time. Model water: demi water with initial conc. of Cr(III)=25 µg/l, no pH adjustment (starting pH≈7). [A] Reduction in concentration with and without adsorbent present. [B] Concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[B]	Conc. Cr(III) (µg/L)	
	non-filtered	filtered
Freshly prepared model water	23	20
Model water at time 0h	22	19
Model water at time 24h	19	15

[A]	Conc. Cr(VI) (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	22	22
0.25	21	16
0.5	21	21
1	21	20
2	21	20
4	21	20
6	20	19
8	20	19
24	19	-

**Table 2:** Concentration of Cr(VI) as a function of time. Model water: demi water with initial conc. of Cr(VI)=25 µg/l, no pH adjustment (starting pH≈7). [A] Reduction in concentration with and without adsorbent present. [B] Concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[B]	Conc. Cr(VI) (µg/L)	
	non-filtered	filtered
Freshly prepared model water	22	22
Model water at time 0h	22	21
Model water at time 24h	21	19

[A] Contact Time (hr)	Conc. Cr(VI) (mg/l)	
	with IOCS	without IOCS
0	50	50
0.25	25	42
0.5	23	40
1	25	41
2	23	41
4	24	40
6	22	41
8	22	43
24	22	-

**Table 3:** Concentration of total Cr as a function of time. Model water: demi water with initial conc. of Cr(III)=25 µg/l and Cr(VI)=25 µg/l, no pH adjustment (starting pH≈7). [A] Reduction in concentration with and without adsorbent present. [B] Concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[B]	Conc. Cr(VI) (µg/L)	
	non-filtered	filtered
Freshly prepared model water	50	51
Model water at time 0h	50	41
Model water at time 24h	51	43

[A] Contact Time (hr)	Conc. Cr(III)+Cd (mg/l)	
	with IOCS	without IOCS
0	23	23
0.25	<2	16
0.5	<2	18
1	<2	19
2	<2	19
4	<2	17
6	<2	17
8	<2	18
24	<2	-

[B] Contact Time (hr)	Conc. Cr(III)+Cd (mg/l)	
	with IOCS	without IOCS
0	25	25
0.25	3	24
0.5	<2	17
24	2	14

[C]	Conc. Cr(III)+Cd (µg/L)	
	non-filtered	filtered
Freshly prepared model water	25	21
Model water at time 0h	22	17
Model water at time 24h	19	14

**Table 4:** Concentration of Cr(III) in the presence of **cadmium** as a function of time. Model water: demi water with initial conc. of Cr(III)=25 µg/l, and Cd=13 µg/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, adjusted pH=6, with and without adsorbent. [C] Cr(III) concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.



[A]	Conc. Cr(VI)+Cd (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	22	22
0.25	23	21
0.5	23	21
1	23	21
2	22	20
4	22	21
6	21	21
8	21	21
24	20	-

[B]	Conc. Cr(VI)+Cd (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	26	26
0.25	22	25
0.5	25	26
24	21	24

[C]	Conc. Cr(VI)+Cd ( $\mu\text{g/L}$ )	
	non-filtered	filtered
Freshly prepared model water	23	22
Model water at time 0h	22	22
Model water at time 24h	21	22

**Table 5:** Concentration of Cr(VI) in the presence of **cadmium** as a function of time. Model water: demi water with initial conc. of Cr(VI)=25  $\mu\text{g/l}$ , and Cd=13  $\mu\text{g/l}$ . [A] No pH adjustment (starting pH $\approx$ 7) with and without adsorbent. [B] Added  $\text{c}(\text{HCO}_3^-)$ =100 mg/l, adjusted pH=6, with and without adsorbent. [C] Cr(VI) concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[A]	Conc. Cr(III)+Cu (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	25	25
0.25	<2	19
0.5	<2	19
1	<2	20
2	<2	21
4	<2	19
6	<2	19
8	<2	18
24	<2	-

[B]	Conc. Cr(III)+Cu (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	26	26
0.25	6	5
0.5	4	3
24	4	<2

[C]	Conc. Cr(III)+Cu ( $\mu\text{g/L}$ )	
	non-filtered	filtered
Freshly prepared model water	25	25
Model water at time 0h	21	20
Model water at time 24h	22	19

**Table 6:** Concentration of Cr(III) in the presence of **copper** as a function of time. Model water: demi water with initial conc. of Cr(III)=25  $\mu\text{g/l}$ , and Cu=140  $\mu\text{g/l}$ . [A] No pH adjustment (starting pH $\approx$ 7) with and without adsorbent. [B] Added  $\text{c}(\text{HCO}_3^-)$ =100 mg/l, adjusted pH=6, with and without adsorbent. [C] Cr(III) concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[A]	Conc.Cr(VI)+Cu (mg/l)	
	with IOCS	without IOCS
Contact Time (hr)		
0	23	23
0.25	24	22
0.5	22	22
1	23	23
2	22	22
4	21	22
6	20	22
8	20	22
24	19	-

[B]	Conc.Cr(VI)+Cu (mg/l)	
	with IOCS	without IOCS
Contact Time (hr)		
0	26	26
0.25	24	27
0.5	20	21
24	20	21

[C]	Conc. Cr(VI)+Cu (µg/L)	
	non-filtered	filtered
Freshly prepared model water	23	23
Model water at time 0h	23	23
Model water at time 24h	22	22

**Table 7:** Concentration of Cr(VI) in the presence of **copper** as a function of time. Model water: demi water with initial conc. of Cr(VI)=25 µg/l, and Cu=140 µg/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, adjusted pH=6, with and without adsorbent. [C] Cr(VI) concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[A]	Conc.Cr(III)+Pb (mg/l)	
	with IOCS	without IOCS
Contact Time (hr)		
0	21	21
0.25	<2	12
0.5	<2	15
1	<2	16
2	<2	15
4	<2	16
6	<2	15
8	<2	15
24	<2	-

[B]	Conc.Cr(III)+Pb (mg/l)	
	with IOCS	without IOCS
Contact Time (hr)		
0	24	24
0.25	3	11
0.5	1	16
24	3	4

[C]	Conc. Cr(III)+Pb (µg/L)	
	non-filtered	filtered
Freshly prepared model water	21	21
Model water at time 0h	15	18
Model water at time 24h	19	18

**Table 8:** Concentration of Cr(III) in the presence of **lead** as a function of time. Model water: demi water with initial conc. of Cr(III)=25 µg/l, and Pb=525 µg/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, adjusted pH=6, with and without adsorbent. [C] Cr(III) concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[A]	Conc. Cr(VI)+Pb (mg/l)	
	with IOCS	without IOCS
0	26	26
0.25	26	30
0.5	26	26
1	25	27
2	25	24
4	25	25
6	23	25
8	23	23
24	22	-

[B]	Conc. Cr(VI)+Pb (mg/l)	
	with IOCS	without IOCS
0	28	28
0.25	24	23
0.5	24	23
24	21	20

[C]	Conc. Cr(VI)+Pb (µg/L)	
	non-filtered	filtered
Freshly prepared model water	27	25
Model water at time 0h	26	27
Model water at time 24h	24	22

**Table 9:** Concentration of Cr(VI) in the presence of **lead** as a function of time. Model water: demi water with initial conc. of Cr(VI)=25 µg/l, and Pb=525 µg/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, adjusted pH=6, with and without adsorbent. [C] Cr(VI) concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[A]	Conc. Cd (mg/l)	
	with IOCS	without IOCS
0	13	13
0.25	<1	11
0.5	<1	9
1	<1	9
2	<1	9
4	<1	10
6	<1	10
8	<1	10
24	<1	-

**Table 10:** Concentration of Cd as a function of time. Model water: demi water with initial conc. of Cd=13 µg/l, no pH adjustment (starting pH≈7). [A] Reduction in concentration with and without adsorbent present. [B] Concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[B]	Conc. Cd (µg/L)	
	non-filtered	filtered
Freshly prepared model water	13	4
Model water at time 0h	12	6
Model water at time 24h	11	12

[A]	Conc. Cr(III)+Cd (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	13	13
0.25	<1	8
0.5	<1	9
1	<1	9
2	<1	9
4	<1	10
6	<1	9
8	<1	10
24	<1	-

[B]	Conc. Cr(III)+Cd (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	13	13
0.25	<1	8
0.5	<1	6
24	<1	7

[C]	Conc. Cr(III)+Cd (μg/L)	
	non-filtered	filtered
Freshly prepared model water	13	11
Model water at time 0h	13	11
Model water at time 24h	13	7

**Table 11:** Concentration of Cd in the presence of Cr(III) as a function of time. Model water: demi water with initial conc. of Cd=13 μg/l, and Cr(III)=25 μg/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, adjusted pH=6, with and without adsorbent. [C] Cd concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[A]	Conc. Cr(VI)+Cd (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	13	13
0.25	<1	11
0.5	<1	8
1	<1	6
2	<1	6
4	<1	8
6	<1	8
8	<1	8
24	<1	-

[B]	Conc. Cr(VI)+Cd (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	13	13
0.25	<1	10
0.5	<1	7
24	<1	4

[C]	Conc. Cr(VI)+Cd (μg/L)	
	non-filtered	filtered
Freshly prepared model water	13	2
Model water at time 0h	13	7
Model water at time 24h	10	7

**Table 12:** Concentration of Cd in the presence of Cr(VI) as a function of time. Model water: demi water with initial conc. of Cd=13 μg/l, and Cr(VI)=25 μg/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, adjusted pH=6, with and without adsorbent. [C] Cd concentration in filtered and unfiltered sample at the start

and end of the experiment, without adsorbent present.

[A]	Conc. Cu (mg/l)	
	with IOCS	without IOCS
0	144	144
0.25	<2	96
0.5	<2	96
1	<2	89
2	<2	106
4	<2	119
6	<2	91
8	<2	106
24	<2	-

**Table 13:** Concentration of Cu as a function of time. Model water: demi water with initial conc. of Cu=140 µg/l, no pH adjustment (starting pH≈7). [A] Reduction in concentration with and without adsorbent present. [B] Concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[B]	Conc. Cu (µg/L)	
	non-filtered	filtered
Freshly prepared model water	151	136
Model water at time 0h	84	94
Model water at time 24h	110	95

[A]	Conc. Cr(III)+Cu (mg/l)	
	with IOCS	without IOCS
0	133	133
0.25	<2	76
0.5	<2	70
1	<2	83
2	<2	88
4	<2	86
6	<2	92
8	<2	82
24	<2	-

[B]	Conc. Cr(III)+Cu (mg/l)	
	with IOCS	without IOCS
0	123	123
0.25	<2	<2
0.5	<2	<2
24	<2	<2

[C]	Conc. Cr(III)+Cu (µg/L)	
	non-filtered	filtered
Freshly prepared model water	117	133
Model water at time 0h	80	95
Model water at time 24h	112	95

**Table 14:** Concentration of Cu in the presence of Cr(III) as a function of time. Model water: demi water with initial conc. of Cu=140 µg/l, and Cr(III)=25 µg/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, adjusted pH=6, with and without adsorbent. [C] Cu concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[A]	Conc. Cr(VI)+Cu (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	145	145
0.25	<2	52
0.5	<2	60
1	<2	40
2	<2	50
4	<2	45
6	<2	40
8	<2	42
24	<2	-

[B]	Conc. Cr(VI)+Cu (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	113	113
0.25	<2	<2
0.5	<2	4
24	<2	5

[C]	Conc. Cr(VI)+Cu (µg/L)	
	non-filtered	filtered
Freshly prepared model water	145	116
Model water at time 0h	42	122
Model water at time 24h	78	71

**Table 15:** Concentration of Cu in the presence of Cr(VI) as a function of time. Model water: demi water with initial conc. of Cu=140 µg/l, and Cr(VI)=25 µg/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, adjusted pH=6, with and without adsorbent. [C] Cu concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[A]	Conc. Pb (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	432	432
0.25	<2	309
0.5	<2	359
1	<2	314
2	<2	363
4	<2	380
6	<2	375
8	<2	357
24	<2	-

**Table 16:** Concentration of Pb as a function of time. Model water: demi water with initial conc. of Pb=525 µg/l, no pH adjustment (starting pH≈7). [A] Reduction in concentration with and without adsorbent present. [B] Concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[B]	Conc. Pb (µg/L)	
	non-filtered	filtered
Freshly prepared model water	422	432
Model water at time 0h	332	300
Model water at time 24h	416	372

[A]	Conc. Cr(III)+Pb (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	440	440
0.25	<2	357
0.5	<2	368
1	<2	348
2	<2	365
4	<2	377
6	<2	360
8	<2	347
24	<2	-

[B]	Conc. Cr(III)+Pb (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	366	366
0.25	<2	117
0.5	<2	126
24	<2	122

[C]	Conc. Cr(III)+Pb (µg/L)	
	non-filtered	filtered
Freshly prepared model water	432	440
Model water at time 0h	272	351
Model water at time 24h	401	407

**Table 17:** Concentration of Pb in the presence of Cr(III) as a function of time. Model water: demi water with initial conc. of Pb=525 µg/l, and Cr(III)=25 µg/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, adjusted pH=6, with and without adsorbent. [C] Pb concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

[A]	Conc. Cr(VI)+Pb (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	465	465
0.25	<2	314
0.5	<2	344
1	<2	366
2	<2	366
4	<2	350
6	<2	378
8	<2	372
24	<2	-

[B]	Conc. Cr(VI)+Pb (mg/l)	
Contact Time (hr)	with IOCS	without IOCS
0	470	470
0.25	<2	87
0.5	<2	45
24	<2	17

[C]	Conc. Cr(VI)+Pb (µg/L)	
	non-filtered	filtered
Freshly prepared model water	465	416
Model water at time 0h	272	317
Model water at time 24h	446	407

**Table 18:** Concentration of Pb in the presence of Cr(VI) as a function of time. Model water: demi water with initial conc. of Pb=525 µg/l, and Cr(VI)=25 µg/l. [A] No pH adjustment (starting pH≈7) with and without adsorbent. [B] Added c(HCO<sub>3</sub><sup>-</sup>)=100 mg/l, adjusted pH=6, with and without adsorbent. [C] Pb concentration in filtered and unfiltered sample at the start and end of the experiment, without adsorbent present.

## Appendix B: Equilibrium Calculation for the experiments with PHREEQC interactive

### Conc. of Cr(III)=25 µg/l, no pH adjustment

-----  
 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
  temp      21
  pH         7
  pe         4
  redox      pe
  units      ug/l
  density    1
  Cr(3)      25
  water      0.5 # kg
```

-----  
 Beginning of initial solution calculations.  
 -----

Initial solution 1.

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

Elements	Molality	Moles
Cr(3)	4.808e-007	2.404e-007

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	3.976e-007
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	-6.187e-008
Total carbon (mol/kg)	=	0.000e+000
Total CO2 (mol/kg)	=	0.000e+000
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	2.713e-007
Percent error, 100*(Cat- An )/(Cat+ An )	=	78.50
Iterations	=	3
Total H	=	5.550683e+001
Total O	=	2.775342e+001



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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.001e-007	1.000e-007	-7.000	-7.000	-0.000
OH-	7.419e-008	7.414e-008	-7.130	-7.130	-0.000
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cr(3)	4.808e-007				
Cr(OH)2+	4.132e-007	4.129e-007	-6.384	-6.384	-0.000
Cr(OH)+2	5.182e-008	5.167e-008	-7.285	-7.287	-0.001
Cr(OH)3	1.562e-008	1.562e-008	-7.806	-7.806	0.000
CrO2-	7.423e-011	7.417e-011	-10.129	-10.130	-0.000
Cr(OH)4-	6.266e-011	6.261e-011	-10.203	-10.203	-0.000
Cr+3	3.135e-011	3.115e-011	-10.504	-10.507	-0.003
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000

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

Phase	SI	log IAP	log KT	
Cr(OH)3	-0.79	0.62	1.41	Cr(OH)3
Cr(OH)3(am)	1.37	0.62	-0.75	Cr(OH)3
Cr2O3	3.47	1.23	-2.24	Cr2O3
O2(g)	-40.45	44.00	84.45	O2

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(VI)=25 µg/l, no pH adjustment

-----  
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  
temp 21  
pH 7  
pe 4  
redox pe  
units ug/l  
density 1  
Cr(6) 25  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
Cr(6)	4.808e-007	2.404e-007

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	8.743e-007
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	3.386e-007
Total carbon (mol/kg)	=	0.000e+000
Total CO2 (mol/kg)	=	0.000e+000
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	-4.097e-007
Percent error, 100*(Cat- An )/(Cat+ An )	=	-80.36
Iterations	=	4
Total H	=	5.550683e+001
Total O	=	2.775342e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.001e-007	1.000e-007	-7.000	-7.000	-0.000
OH-	7.422e-008	7.414e-008	-7.129	-7.130	-0.000
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cr(6)	4.808e-007				
CrO4-2	3.645e-007	3.629e-007	-6.438	-6.440	-0.002
HCrO4-	1.163e-007	1.162e-007	-6.934	-6.935	-0.000
Cr2O7-2	5.215e-013	5.193e-013	-12.283	-12.285	-0.002
H2CrO4	7.686e-015	7.686e-015	-14.114	-14.114	0.000
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000

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

Phase	SI	log IAP	log KT
CrO3	-17.24	-20.44	-3.20
O2(g)	-40.45	44.00	84.45

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(III)= 25 µg/l, and Cr(VI)=25 µg/l, no pH adjustment

-----  
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  
temp 21  
pH 7  
pe 4  
redox pe  
units ug/l  
density 1  
Cr(3) 25  
Cr(6) 25  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
Cr(3)	4.808e-007	2.404e-007
Cr(6)	4.808e-007	2.404e-007

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	1.185e-006
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	3.026e-007
Total carbon (mol/kg)	=	0.000e+000
Total CO2 (mol/kg)	=	0.000e+000
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	-1.513e-007
Percent error, 100*(Cat- An )/(Cat+ An )	=	-19.69
Iterations	=	4
Total H	=	5.550683e+001
Total O	=	2.775342e+001

-----Redox couples-----

Redox couple	pe	Eh (volts)
Cr(3)/Cr(6)	8.5218	0.4974

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.001e-007	1.000e-007	-6.999	-7.000	-0.001
OH-	7.423e-008	7.414e-008	-7.129	-7.130	-0.001
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cr(3)	4.808e-007				
Cr(OH)2+	4.131e-007	4.126e-007	-6.384	-6.384	-0.001
Cr(OH)+2	5.190e-008	5.163e-008	-7.285	-7.287	-0.002
Cr(OH)3	1.561e-008	1.561e-008	-7.807	-7.807	0.000
CrO2-	7.421e-011	7.412e-011	-10.130	-10.130	-0.001
Cr(OH)4-	6.265e-011	6.257e-011	-10.203	-10.204	-0.001
Cr+3	3.148e-011	3.113e-011	-10.502	-10.507	-0.005
Cr(6)	4.808e-007				
CrO4-2	3.646e-007	3.627e-007	-6.438	-6.440	-0.002
HCrO4-	1.162e-007	1.161e-007	-6.935	-6.935	-0.001
Cr2O7-2	5.213e-013	5.187e-013	-12.283	-12.285	-0.002
H2CrO4	7.682e-015	7.682e-015	-14.115	-14.115	0.000
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000

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

Phase	SI	log IAP	log KT	
Cr(OH)3	-0.79	0.62	1.41	Cr(OH)3
Cr(OH)3(am)	1.37	0.62	-0.75	Cr(OH)3
Cr2O3	3.47	1.23	-2.24	Cr2O3
CrO3	-17.24	-20.44	-3.20	CrO3
O2(g)	-40.45	44.00	84.45	O2

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cd= 13 µg/l, no pH adjustment

-----  
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  
temp 21  
pH 7

```

pe      4
redox   pe
units   ug/l
density 1
Cd       13
water   0.5 # kg

```

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
Cd	1.156e-007	5.782e-008

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

```

pH      = 7.000
pe      = 4.000
Activity of water = 1.000
Ionic strength = 3.183e-007
Mass of water (kg) = 5.000e-001
Total alkalinity (eq/kg) = -2.581e-008
Total carbon (mol/kg) = 0.000e+000
Total CO2 (mol/kg) = 0.000e+000
Temperature (deg C) = 21.000
Electrical balance (eq) = 1.286e-007
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 63.41
Iterations = 3
Total H = 5.550683e+001
Total O = 2.775342e+001

```

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.001e-007	1.000e-007	-7.000	-7.000	-0.000
OH-	7.419e-008	7.414e-008	-7.130	-7.130	-0.000
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cd	1.156e-007				
Cd+2	1.156e-007	1.153e-007	-6.937	-6.938	-0.001
CdOH+	6.831e-011	6.826e-011	-10.166	-10.166	-0.000
Cd(OH)2	5.858e-014	5.858e-014	-13.232	-13.232	0.000
Cd2OH+3	4.168e-017	4.143e-017	-16.380	-16.383	-0.003
Cd(OH)3-	3.606e-019	3.604e-019	-18.443	-18.443	-0.000
Cd(OH)4-2	5.955e-027	5.939e-027	-26.225	-26.226	-0.001
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000

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

Phase	SI	log IAP	log KT	
Cd(OH)2	-6.81	7.06	13.87	Cd(OH)2
Cd(OH)2(am)	-6.88	7.06	13.94	Cd(OH)2
Cdmetal(alpha)	-28.63	-14.94	13.69	Cd
Cdmetal(gamma)	-28.74	-14.94	13.80	Cd
Monteponite	-8.29	7.06	15.35	CdO
O2(g)	-40.45	44.00	84.45	O2

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cu= 140 µg/l, no pH adjustment

-----  
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  
temp 21  
pH 7  
pe 4  
redox pe  
units ug/l  
density 1  
Cu(2) 140  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
Cu(2)	2.203e-006	1.102e-006

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	3.786e-006
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	4.561e-007
Total carbon (mol/kg)	=	0.000e+000
Total CO2 (mol/kg)	=	0.000e+000
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	1.975e-006
Percent error, 100*(Cat- An )/(Cat+ An )	=	96.37
Iterations	=	4
Total H	=	5.550683e+001
Total O	=	2.775342e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.002e-007	1.000e-007	-6.999	-7.000	-0.001
OH-	7.431e-008	7.414e-008	-7.129	-7.130	-0.001
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cu(2)	2.203e-006				
Cu+2	1.732e-006	1.716e-006	-5.761	-5.765	-0.004
CuOH+	4.501e-007	4.491e-007	-6.347	-6.348	-0.001
Cu(OH)2	1.098e-008	1.098e-008	-7.959	-7.959	0.000
Cu2(OH)2+2	4.974e-009	4.929e-009	-8.303	-8.307	-0.004
Cu(OH)3-	2.273e-012	2.268e-012	-11.643	-11.644	-0.001
Cu(OH)4-2	1.814e-018	1.797e-018	-17.741	-17.745	-0.004
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000

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

Phase	SI	log IAP	log KT	
Cu(OH)2	-0.57	8.23	8.81	Cu(OH)2
O2(g)	-40.45	44.00	84.45	O2
Tenorite	0.44	8.23	7.80	CuO

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Pb= 525 µg/l, no pH adjustment

-----  
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  
temp 21  
pH 7  
pe 4  
redox pe  
units ug/l  
density 1  
Pb 525  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
Pb	2.534e-006	1.267e-006

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	4.389e-006
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	4.855e-007
Total carbon (mol/kg)	=	0.000e+000
Total CO2 (mol/kg)	=	0.000e+000
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	2.291e-006
Percent error, 100*(Cat- An )/(Cat+ An )	=	96.86
Iterations	=	4
Total H	=	5.550683e+001
Total O	=	2.775342e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.002e-007	1.000e-007	-6.999	-7.000	-0.001
OH-	7.432e-008	7.414e-008	-7.129	-7.130	-0.001
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000
Pb	2.534e-006				
Pb+2	2.024e-006	2.004e-006	-5.694	-5.698	-0.004
PbOH+	5.082e-007	5.070e-007	-6.294	-6.295	-0.001
Pb(OH)2	1.614e-009	1.614e-009	-8.792	-8.792	0.000
Pb2OH+3	1.646e-011	1.610e-011	-10.784	-10.793	-0.010
Pb(OH)3-	1.629e-013	1.625e-013	-12.788	-12.789	-0.001
Pb3(OH)4+2	5.593e-014	5.538e-014	-13.252	-13.257	-0.004
Pb4(OH)4+4	1.063e-015	1.023e-015	-14.973	-14.990	-0.017
Pb(OH)4-2	4.048e-018	4.008e-018	-17.393	-17.397	-0.004

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

Phase	SI	log IAP	log KT	
Litharge	-4.55	8.30	12.85	PbO
Massicot	-4.75	8.30	13.05	PbO
Minium	-27.62	46.91	74.53	Pb3O4
O2(g)	-40.45	44.00	84.45	O2
Pb(OH)2	0.01	8.30	8.29	Pb(OH)2
Pb2O(OH)2	-9.58	16.60	26.19	Pb2O(OH)2
Pb2O3	-22.44	38.60	61.04	Pb2O3
Pbmetal	-17.94	-13.70	4.24	Pb
PbO:0.3H2O	-4.68	8.30	12.98	PbO:0.33H2O
Plattnerite	-20.00	30.30	50.31	PbO2

-----  
End of simulation.  
-----



-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(III)= 25 µg/l, and Cd=13 µg/l, pH=6

-----  
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  
temp 21  
pH 6  
pe 4  
redox pe  
units ug/l  
density 1  
C(4) 98.4 mg/l  
Na 37.7 mg/l  
Cr(3) 25  
Cd 13  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
C(4)	1.640e-003	8.200e-004
Cd	1.157e-007	5.783e-008
Cr(3)	4.809e-007	2.404e-007
Na	1.640e-003	8.200e-004

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

pH	=	6.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	1.071e-003
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	4.988e-004
Total CO2 (mol/kg)	=	1.640e-003
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	5.710e-004
Percent error, 100*(Cat- An )/(Cat+ An )	=	53.33
Iterations	=	8
Total H	=	5.550822e+001

Total O = 2.775588e+001

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

Species		Molality	Activity	Log Molality	Log Activity	Log Gamma
H+		1.037e-006	1.000e-006	-5.984	-6.000	-0.016
OH-		7.691e-009	7.413e-009	-8.114	-8.130	-0.016
H2O		5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	1.640e-003					
H2CO3		1.140e-003	1.140e-003	-2.943	-2.943	0.000
HCO3-		4.996e-004	4.820e-004	-3.301	-3.317	-0.016
NaHCO3		4.619e-007	4.619e-007	-6.335	-6.335	0.000
CO3-2		2.414e-008	2.086e-008	-7.617	-7.681	-0.063
NaCO3-		7.116e-010	6.864e-010	-9.148	-9.163	-0.016
CdHCO3+		1.050e-010	1.011e-010	-9.979	-9.995	-0.017
CdCO3		4.744e-011	4.744e-011	-10.324	-10.324	0.000
Cd(CO3)2-2		8.543e-016	7.334e-016	-15.068	-15.135	-0.066
Cd	1.157e-007					
Cd+2		1.155e-007	9.980e-008	-6.937	-7.001	-0.063
CdHCO3+		1.050e-010	1.011e-010	-9.979	-9.995	-0.017
CdCO3		4.744e-011	4.744e-011	-10.324	-10.324	0.000
CdOH+		6.139e-012	5.909e-012	-11.212	-11.228	-0.017
Cd(CO3)2-2		8.543e-016	7.334e-016	-15.068	-15.135	-0.066
Cd(OH)2		5.071e-016	5.071e-016	-15.295	-15.295	0.000
Cd2OH+3		4.376e-018	3.105e-018	-17.359	-17.508	-0.149
Cd(OH)3-		3.240e-022	3.119e-022	-21.489	-21.506	-0.017
Cd(OH)4-2		5.988e-031	5.141e-031	-30.223	-30.289	-0.066
Cr(3)	4.809e-007					
Cr(OH)+2		2.792e-007	2.397e-007	-6.554	-6.620	-0.066
Cr(OH)2+		1.990e-007	1.915e-007	-6.701	-6.718	-0.017
Cr+3		2.036e-009	1.445e-009	-8.691	-8.840	-0.149
Cr(OH)3		7.244e-010	7.244e-010	-9.140	-9.140	0.000
CrO2-		3.574e-013	3.440e-013	-12.447	-12.463	-0.017
Cr(OH)4-		3.016e-013	2.904e-013	-12.520	-12.537	-0.017
H(0)	1.474e-023					
H2		7.369e-024	7.371e-024	-23.133	-23.132	0.000
Na	1.640e-003					
Na+		1.640e-003	1.581e-003	-2.785	-2.801	-0.016
NaHCO3		4.619e-007	4.619e-007	-6.335	-6.335	0.000
NaCO3-		7.116e-010	6.864e-010	-9.148	-9.163	-0.016
O(0)	0.000e+000					
O2		0.000e+000	0.000e+000	-47.142	-47.142	0.000

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

Phase	SI	log IAP	log KT	
Cd(OH)2	-8.87	5.00	13.87	Cd(OH)2
Cd(OH)2(am)	-8.94	5.00	13.94	Cd(OH)2
Cdmetal(alpha)	-28.70	-15.00	13.69	Cd
Cdmetal(gamma)	-28.80	-15.00	13.80	Cd
CH4(g)	-58.02	-99.68	-41.66	CH4
CO2(g)	-1.52	-19.68	-18.16	CO2
Cr(OH)3	-2.12	-0.72	1.41	Cr(OH)3
Cr(OH)3(am)	0.03	-0.72	-0.75	Cr(OH)3
Cr2O3	0.80	-1.44	-2.24	Cr2O3
Monteponite	-10.35	5.00	15.35	CdO
Natron	-11.82	-13.28	-1.47	Na2CO3:10H2O
O2(g)	-44.45	40.00	84.45	O2
Otavite	-2.68	-14.68	-12.00	CdCO3
Thermonatrite	-13.95	-13.28	0.66	Na2CO3:H2O

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(III)= 25 µg/l, and Cd=13 µg/l, no pH adjustment

-----  
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  
temp 21  
pH 7  
pe 4  
redox pe  
units ug/l  
density 1  
Cd 13  
Cr(3) 25  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
Cd	1.156e-007	5.782e-008
Cr(3)	4.808e-007	2.404e-007

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	6.288e-007
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	-6.184e-008
Total carbon (mol/kg)	=	0.000e+000
Total CO2 (mol/kg)	=	0.000e+000
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	3.870e-007
Percent error, 100*(Cat- An )/(Cat+ An )	=	83.88
Iterations	=	3
Total H	=	5.550683e+001
Total O	=	2.775342e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.001e-007	1.000e-007	-7.000	-7.000	-0.000
OH-	7.421e-008	7.414e-008	-7.130	-7.130	-0.000
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cd	1.156e-007				
Cd+2	1.156e-007	1.152e-007	-6.937	-6.939	-0.002
CdOH+	6.825e-011	6.819e-011	-10.166	-10.166	-0.000
Cd(OH)2	5.852e-014	5.852e-014	-13.233	-13.233	0.000
Cd2OH+3	4.169e-017	4.135e-017	-16.380	-16.384	-0.004
Cd(OH)3-	3.603e-019	3.600e-019	-18.443	-18.444	-0.000
Cd(OH)4-2	5.955e-027	5.933e-027	-26.225	-26.227	-0.002
Cr(3)	4.808e-007				
Cr(OH)2+	4.132e-007	4.128e-007	-6.384	-6.384	-0.000
Cr(OH)+2	5.185e-008	5.166e-008	-7.285	-7.287	-0.002
Cr(OH)3	1.561e-008	1.561e-008	-7.806	-7.806	0.000
CrO2-	7.422e-011	7.415e-011	-10.129	-10.130	-0.000
Cr(OH)4-	6.265e-011	6.259e-011	-10.203	-10.203	-0.000
Cr+3	3.140e-011	3.114e-011	-10.503	-10.507	-0.004
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000

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

Phase	SI	log IAP	log KT	
Cd(OH)2	-6.81	7.06	13.87	Cd(OH)2
Cd(OH)2(am)	-6.88	7.06	13.94	Cd(OH)2
Cdmetal(alpha)	-28.63	-14.94	13.69	Cd
Cdmetal(gamma)	-28.74	-14.94	13.80	Cd
Cr(OH)3	-0.79	0.62	1.41	Cr(OH)3
Cr(OH)3(am)	1.37	0.62	-0.75	Cr(OH)3
Cr2O3	3.47	1.23	-2.24	Cr2O3
Monteponite	-8.29	7.06	15.35	CdO
O2(g)	-40.45	44.00	84.45	O2

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(VI)= 25 µg/l, and Cd=13 µg/l, pH=6

-----  
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

temp 21  
 pH 6  
 pe 4  
 redox pe  
 units ug/l  
 density 1  
 C(4) 98.4 mg/l  
 Na 37.7 mg/l  
 Cd 13  
 Cr(6) 25  
 water 0.5 # kg

-----  
 Beginning of initial solution calculations.  
 -----

Initial solution 1.

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

Elements	Molality	Moles
C(4)	1.640e-003	8.200e-004
Cd	1.157e-007	5.783e-008
Cr(6)	4.809e-007	2.404e-007
Na	1.640e-003	8.200e-004

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

pH	=	6.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	1.071e-003
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	4.992e-004
Total CO2 (mol/kg)	=	1.640e-003
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	5.703e-004
Percent error, 100*(Cat- An )/(Cat+ An )	=	53.27
Iterations	=	8
Total H	=	5.550822e+001
Total O	=	2.775588e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.037e-006	1.000e-006	-5.984	-6.000	-0.016
OH-	7.691e-009	7.413e-009	-8.114	-8.130	-0.016
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	1.640e-003				
H2CO3	1.140e-003	1.140e-003	-2.943	-2.943	0.000
HCO3-	4.996e-004	4.820e-004	-3.301	-3.317	-0.016
NaHCO3	4.619e-007	4.619e-007	-6.335	-6.335	0.000
CO3-2	2.414e-008	2.086e-008	-7.617	-7.681	-0.063
NaCO3-	7.116e-010	6.864e-010	-9.148	-9.163	-0.016
CdHCO3+	1.050e-010	1.011e-010	-9.979	-9.995	-0.017
CdCO3	4.744e-011	4.744e-011	-10.324	-10.324	0.000
Cd(CO3)2-2	8.543e-016	7.335e-016	-15.068	-15.135	-0.066
Cd	1.157e-007				
Cd+2	1.155e-007	9.980e-008	-6.937	-7.001	-0.063
CdHCO3+	1.050e-010	1.011e-010	-9.979	-9.995	-0.017
CdCO3	4.744e-011	4.744e-011	-10.324	-10.324	0.000

CdOH+	6.139e-012	5.909e-012	-11.212	-11.228	-0.017
Cd(CO3)2-2	8.543e-016	7.335e-016	-15.068	-15.135	-0.066
Cd(OH)2	5.071e-016	5.071e-016	-15.295	-15.295	0.000
Cd2OH+3	4.376e-018	3.105e-018	-17.359	-17.508	-0.149
Cd(OH)3-	3.240e-022	3.119e-022	-21.489	-21.506	-0.017
Cd(OH)4-2	5.988e-031	5.141e-031	-30.223	-30.289	-0.066
Cr(6)	4.809e-007				
HCrO4-	3.561e-007	3.427e-007	-6.448	-6.465	-0.017
CrO4-2	1.239e-007	1.071e-007	-6.907	-6.970	-0.063
NaCrO4-	8.739e-010	8.412e-010	-9.059	-9.075	-0.017
Cr2O7-2	5.265e-012	4.521e-012	-11.279	-11.345	-0.066
H2CrO4	2.268e-013	2.268e-013	-12.644	-12.644	0.000
H(0)	1.474e-023				
H2	7.369e-024	7.371e-024	-23.133	-23.132	0.000
Na	1.640e-003				
Na+	1.640e-003	1.581e-003	-2.785	-2.801	-0.016
NaHCO3	4.619e-007	4.619e-007	-6.335	-6.335	0.000
NaCrO4-	8.739e-010	8.412e-010	-9.059	-9.075	-0.017
NaCO3-	7.116e-010	6.864e-010	-9.148	-9.163	-0.016
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-47.142	-47.142	0.000

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

Phase	SI	log IAP	log KT	
Cd(OH)2	-8.87	5.00	13.87	Cd(OH)2
Cd(OH)2(am)	-8.94	5.00	13.94	Cd(OH)2
Cdmetal(alpha)	-28.70	-15.00	13.69	Cd
Cdmetal(gamma)	-28.80	-15.00	13.80	Cd
CH4(g)	-58.02	-99.68	-41.66	CH4
CO2(g)	-1.52	-19.68	-18.16	CO2
CrO3	-15.77	-18.97	-3.20	CrO3
Monteponite	-10.35	5.00	15.35	CdO
Na2Cr2O7	-21.59	-31.54	-9.95	Na2Cr2O7
Na2CrO4	-15.55	-12.57	2.98	Na2CrO4
Natron	-11.82	-13.28	-1.47	Na2CO3:10H2O
O2(g)	-44.45	40.00	84.45	O2
Otavite	-2.68	-14.68	-12.00	CdCO3
Thermonatrite	-13.95	-13.28	0.66	Na2CO3:H2O

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(VI)= 25 µg/l, and Cd=13 µg/l, no pH adjusment

-----  
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  
     temp        21  
     pH          7  
     pe          4  
     redox       pe  
     units       ug/l  
     density     1  
     Cd          13  
     Cr(6)       25  
     water       0.5 # kg

-----  
 Beginning of initial solution calculations.  
 -----

Initial solution 1.

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

Elements	Molality	Moles
Cd	1.156e-007	5.782e-008
Cr(6)	4.808e-007	2.404e-007

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	1.106e-006
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	3.387e-007
Total carbon (mol/kg)	=	0.000e+000
Total CO2 (mol/kg)	=	0.000e+000
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	-2.941e-007
Percent error, 100*(Cat- An )/(Cat+ An )	=	-47.02
Iterations	=	4
Total H	=	5.550683e+001
Total O	=	2.775342e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.001e-007	1.000e-007	-6.999	-7.000	-0.001
OH-	7.423e-008	7.414e-008	-7.129	-7.130	-0.001
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cd	1.156e-007				
Cd+2	1.156e-007	1.150e-007	-6.937	-6.939	-0.002
CdOH+	6.819e-011	6.811e-011	-10.166	-10.167	-0.001
Cd(OH)2	5.845e-014	5.845e-014	-13.233	-13.233	0.000
Cd2OH+3	4.170e-017	4.125e-017	-16.380	-16.385	-0.005
Cd(OH)3-	3.600e-019	3.595e-019	-18.444	-18.444	-0.001
Cd(OH)4-2	5.955e-027	5.926e-027	-26.225	-26.227	-0.002
Cr(6)	4.808e-007				
CrO4-2	3.646e-007	3.628e-007	-6.438	-6.440	-0.002
HCrO4-	1.163e-007	1.161e-007	-6.935	-6.935	-0.001
Cr2O7-2	5.214e-013	5.188e-013	-12.283	-12.285	-0.002
H2CrO4	7.683e-015	7.683e-015	-14.114	-14.114	0.000
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				

O2 0.000e+000 0.000e+000 -43.142 -43.142 0.000

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

Phase	SI	log IAP	log KT	
Cd(OH)2	-6.81	7.06	13.87	Cd(OH)2
Cd(OH)2(am)	-6.88	7.06	13.94	Cd(OH)2
Cdmetal(alpha)	-28.63	-14.94	13.69	Cd
Cdmetal(gamma)	-28.74	-14.94	13.80	Cd
CrO3	-17.24	-20.44	-3.20	CrO3
Monteponite	-8.29	7.06	15.35	CdO
O2(g)	-40.45	44.00	84.45	O2

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(III)= 25 µg/l, and Cu=140 µg/l, pH=6

-----  
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  
temp 21  
pH 6  
pe 4  
redox pe  
units ug/l  
density 1  
C(4) 98.4 mg/l  
Na 37.7 mg/l  
Cr(3) 25  
Cu(2) 140  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
C(4)	1.640e-003	8.200e-004
Cr(3)	4.809e-007	2.404e-007



Cu(2) 2.203e-006 1.102e-006  
Na 1.640e-003 8.200e-004

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

pH = 6.000  
pe = 4.000  
Activity of water = 1.000  
Ionic strength = 1.075e-003  
Mass of water (kg) = 5.000e-001  
Total alkalinity (eq/kg) = 4.993e-004  
Total CO2 (mol/kg) = 1.640e-003  
Temperature (deg C) = 21.000  
Electrical balance (eq) = 5.728e-004  
Percent error, 100\*(Cat-|An|)/(Cat+|An|) = 53.41  
Iterations = 9  
Total H = 5.550822e+001  
Total O = 2.775588e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.037e-006	1.000e-006	-5.984	-6.000	-0.016
OH-	7.691e-009	7.413e-009	-8.114	-8.130	-0.016
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	1.640e-003				
H2CO3	1.140e-003	1.140e-003	-2.943	-2.943	0.000
HCO3-	4.996e-004	4.819e-004	-3.301	-3.317	-0.016
NaHCO3	4.618e-007	4.618e-007	-6.336	-6.336	0.000
CuCO3	2.024e-007	2.024e-007	-6.694	-6.694	0.000
CuHCO3+	4.806e-008	4.625e-008	-7.318	-7.335	-0.017
CO3-2	2.414e-008	2.085e-008	-7.617	-7.681	-0.064
NaCO3-	7.115e-010	6.862e-010	-9.148	-9.164	-0.016
Cu(CO3)2-2	1.323e-011	1.136e-011	-10.878	-10.945	-0.066
Cr(3)	4.809e-007				
Cr(OH)+2	2.792e-007	2.396e-007	-6.554	-6.620	-0.066
Cr(OH)2+	1.989e-007	1.915e-007	-6.701	-6.718	-0.017
Cr+3	2.037e-009	1.445e-009	-8.691	-8.840	-0.149
Cr(OH)3	7.243e-010	7.243e-010	-9.140	-9.140	0.000
CrO2-	3.574e-013	3.440e-013	-12.447	-12.463	-0.017
Cr(OH)4-	3.016e-013	2.903e-013	-12.521	-12.537	-0.017
Cu(2)	2.203e-006				
Cu+2	1.908e-006	1.648e-006	-5.719	-5.783	-0.064
CuCO3	2.024e-007	2.024e-007	-6.694	-6.694	0.000
CuHCO3+	4.806e-008	4.625e-008	-7.318	-7.335	-0.017
CuOH+	4.473e-008	4.312e-008	-7.349	-7.365	-0.016
Cu(OH)2	1.054e-010	1.054e-010	-9.977	-9.977	0.000
Cu2(OH)2+2	5.294e-011	4.544e-011	-10.276	-10.343	-0.066
Cu(CO3)2-2	1.323e-011	1.136e-011	-10.878	-10.945	-0.066
Cu(OH)3-	2.262e-015	2.177e-015	-14.645	-14.662	-0.017
Cu(OH)4-2	2.010e-022	1.725e-022	-21.697	-21.763	-0.066
H(0)	1.474e-023				
H2	7.369e-024	7.371e-024	-23.133	-23.132	0.000
Na	1.640e-003				
Na+	1.640e-003	1.581e-003	-2.785	-2.801	-0.016
NaHCO3	4.618e-007	4.618e-007	-6.336	-6.336	0.000
NaCO3-	7.115e-010	6.862e-010	-9.148	-9.164	-0.016
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-47.142	-47.142	0.000

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

Phase	SI	log IAP	log KT	
Azurite	-4.03	-20.71	-16.68	Cu3(OH)2(CO3)2
CH4(g)	-58.02	-99.68	-41.66	CH4
CO2(g)	-1.52	-19.68	-18.16	CO2

Cr(OH)3	-2.12	-0.72	1.41	Cr(OH)3
Cr(OH)3(am)	0.03	-0.72	-0.75	Cr(OH)3
Cr2O3	0.80	-1.44	-2.24	Cr2O3
Cu(OH)2	-2.59	6.22	8.81	Cu(OH)2
CuCO3	-1.96	-13.46	-11.50	CuCO3
Malachite	-1.76	-7.25	-5.49	Cu2(OH)2CO3
Natron	-11.82	-13.28	-1.47	Na2CO3:10H2O
O2(g)	-44.45	40.00	84.45	O2
Tenorite	-1.58	6.22	7.80	CuO
Thermonatrite	-13.95	-13.28	0.66	Na2CO3:H2O

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(III)= 25 µg/l, and Cu=140 µg/l, no pH adjustment

-----  
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  
temp 21  
pH 7  
pe 4  
redox pe  
units ug/l  
density 1  
Cr(3) 25  
Cu(2) 140  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
Cr(3)	4.808e-007	2.404e-007
Cu(2)	2.203e-006	1.102e-006

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

pH = 7.000  
pe = 4.000

XXX

```

Activity of water = 1.000
Ionic strength = 4.097e-006
Mass of water (kg) = 5.000e-001
Total alkalinity (eq/kg) = 4.197e-007
Total carbon (mol/kg) = 0.000e+000
Total CO2 (mol/kg) = 0.000e+000
Temperature (deg C) = 21.000
Electrical balance (eq) = 2.234e-006
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 96.77
Iterations = 4
Total H = 5.550683e+001
Total O = 2.775342e+001

```

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.002e-007	1.000e-007	-6.999	-7.000	-0.001
OH-	7.431e-008	7.414e-008	-7.129	-7.130	-0.001
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cr(3)	4.808e-007				
Cr(OH)2+	4.130e-007	4.120e-007	-6.384	-6.385	-0.001
Cr(OH)+2	5.205e-008	5.156e-008	-7.284	-7.288	-0.004
Cr(OH)3	1.559e-008	1.559e-008	-7.807	-7.807	0.000
CrO2-	7.419e-011	7.402e-011	-10.130	-10.131	-0.001
Cr(OH)4-	6.263e-011	6.248e-011	-10.203	-10.204	-0.001
Cr+3	3.175e-011	3.108e-011	-10.498	-10.507	-0.009
Cu(2)	2.203e-006				
Cu+2	1.732e-006	1.716e-006	-5.761	-5.765	-0.004
CuOH+	4.500e-007	4.490e-007	-6.347	-6.348	-0.001
Cu(OH)2	1.098e-008	1.098e-008	-7.959	-7.959	0.000
Cu2(OH)2+2	4.973e-009	4.926e-009	-8.303	-8.308	-0.004
Cu(OH)3-	2.273e-012	2.267e-012	-11.643	-11.644	-0.001
Cu(OH)4-2	1.814e-018	1.797e-018	-17.741	-17.745	-0.004
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000

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

Phase	SI	log IAP	log KT	
Cr(OH)3	-0.79	0.61	1.41	Cr(OH)3
Cr(OH)3(am)	1.36	0.61	-0.75	Cr(OH)3
Cr2O3	3.47	1.23	-2.24	Cr2O3
Cu(OH)2	-0.57	8.23	8.81	Cu(OH)2
O2(g)	-40.45	44.00	84.45	O2
Tenorite	0.44	8.23	7.80	CuO

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(VI)= 25 µg/l, and Cu=140 µg/l, pH=6

-----  
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  
     temp        21  
     pH          6  
     pe          4  
     redox       pe  
     units       ug/l  
     density     1  
     C(4)        98.4 mg/l  
     Na          37.7 mg/l  
     Cu(2)       140  
     Cr(6)       25  
     water       0.5 # kg

-----  
 Beginning of initial solution calculations.  
 -----

Initial solution 1.

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

Elements	Molality	Moles
C(4)	1.640e-003	8.200e-004
Cr(6)	4.809e-007	2.404e-007
Cu(2)	2.203e-006	1.102e-006
Na	1.640e-003	8.200e-004

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

pH	=	6.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	1.074e-003
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	4.997e-004
Total CO2 (mol/kg)	=	1.640e-003
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	5.722e-004
Percent error, 100*(Cat- An )/(Cat+ An )	=	53.35
Iterations	=	9
Total H	=	5.550822e+001
Total O	=	2.775588e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.037e-006	1.000e-006	-5.984	-6.000	-0.016
OH-	7.691e-009	7.413e-009	-8.114	-8.130	-0.016
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	1.640e-003				
H2CO3	1.140e-003	1.140e-003	-2.943	-2.943	0.000
HCO3-	4.996e-004	4.819e-004	-3.301	-3.317	-0.016
NaHCO3	4.618e-007	4.618e-007	-6.336	-6.336	0.000
CuCO3	2.024e-007	2.024e-007	-6.694	-6.694	0.000

CuHCO3+	4.806e-008	4.626e-008	-7.318	-7.335	-0.017
CO3-2	2.414e-008	2.085e-008	-7.617	-7.681	-0.064
NaCO3-	7.115e-010	6.862e-010	-9.148	-9.164	-0.016
Cu(CO3)2-2	1.323e-011	1.136e-011	-10.878	-10.945	-0.066
Cr(6)	4.809e-007				
HCrO4-	3.560e-007	3.427e-007	-6.449	-6.465	-0.017
CrO4-2	1.240e-007	1.071e-007	-6.907	-6.970	-0.064
NaCrO4-	8.738e-010	8.411e-010	-9.059	-9.075	-0.017
Cr2O7-2	5.266e-012	4.520e-012	-11.279	-11.345	-0.066
H2CrO4	2.268e-013	2.268e-013	-12.644	-12.644	0.000
Cu(2)	2.203e-006				
Cu+2	1.908e-006	1.648e-006	-5.719	-5.783	-0.064
CuCO3	2.024e-007	2.024e-007	-6.694	-6.694	0.000
CuHCO3+	4.806e-008	4.626e-008	-7.318	-7.335	-0.017
CuOH+	4.473e-008	4.312e-008	-7.349	-7.365	-0.016
Cu(OH)2	1.054e-010	1.054e-010	-9.977	-9.977	0.000
Cu2(OH)2+2	5.294e-011	4.544e-011	-10.276	-10.343	-0.066
Cu(CO3)2-2	1.323e-011	1.136e-011	-10.878	-10.945	-0.066
Cu(OH)3-	2.262e-015	2.177e-015	-14.645	-14.662	-0.017
Cu(OH)4-2	2.010e-022	1.725e-022	-21.697	-21.763	-0.066
H(0)	1.474e-023				
H2	7.369e-024	7.371e-024	-23.133	-23.132	0.000
Na	1.640e-003				
Na+	1.640e-003	1.581e-003	-2.785	-2.801	-0.016
NaHCO3	4.618e-007	4.618e-007	-6.336	-6.336	0.000
NaCrO4-	8.738e-010	8.411e-010	-9.059	-9.075	-0.017
NaCO3-	7.115e-010	6.862e-010	-9.148	-9.164	-0.016
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-47.142	-47.142	0.000

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

Phase	SI	log IAP	log KT	
Azurite	-4.03	-20.71	-16.68	Cu3(OH)2(CO3)2
CH4(g)	-58.02	-99.68	-41.66	CH4
CO2(g)	-1.52	-19.68	-18.16	CO2
CrO3	-15.77	-18.97	-3.20	CrO3
Cu(OH)2	-2.59	6.22	8.81	Cu(OH)2
CuCO3	-1.96	-13.46	-11.50	CuCO3
CuCrO4	-7.31	-12.75	-5.44	CuCrO4
Malachite	-1.76	-7.25	-5.49	Cu2(OH)2CO3
Na2Cr2O7	-21.59	-31.54	-9.95	Na2Cr2O7
Na2CrO4	-15.55	-12.57	2.98	Na2CrO4
Natron	-11.82	-13.28	-1.47	Na2CO3:10H2O
O2(g)	-44.45	40.00	84.45	O2
Tenorite	-1.58	6.22	7.80	CuO
Thermonatrite	-13.95	-13.28	0.66	Na2CO3:H2O

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(VI)= 25 µg/l, and Cu=140 µg/l, no pH adjustment

-----  
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  
     temp        21  
     pH          7  
     pe          4  
     redox       pe  
     units       ug/l  
     density     1  
     Cr(6)       25  
     Cu(2)       140  
     water       0.5 # kg

-----  
 Beginning of initial solution calculations.  
 -----

Initial solution 1.

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

Elements	Molality	Moles
Cr(6)	4.808e-007	2.404e-007
Cu(2)	2.203e-006	1.102e-006

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	4.575e-006
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	8.207e-007
Total carbon (mol/kg)	=	0.000e+000
Total CO2 (mol/kg)	=	0.000e+000
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	1.552e-006
Percent error, 100*(Cat- An )/(Cat+ An )	=	62.79
Iterations	=	4
Total H	=	5.550683e+001
Total O	=	2.775342e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.002e-007	1.000e-007	-6.999	-7.000	-0.001
OH-	7.432e-008	7.414e-008	-7.129	-7.130	-0.001
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cr(6)	4.808e-007				
CrO4-2	3.649e-007	3.613e-007	-6.438	-6.442	-0.004
HCrO4-	1.159e-007	1.156e-007	-6.936	-6.937	-0.001
Cr2O7-2	5.197e-013	5.145e-013	-12.284	-12.289	-0.004
H2CrO4	7.651e-015	7.651e-015	-14.116	-14.116	0.000
Cu(2)	2.203e-006				
Cu+2	1.732e-006	1.715e-006	-5.761	-5.766	-0.004
CuOH+	4.499e-007	4.488e-007	-6.347	-6.348	-0.001
Cu(OH)2	1.097e-008	1.097e-008	-7.960	-7.960	0.000
Cu2(OH)2+2	4.971e-009	4.922e-009	-8.304	-8.308	-0.004

Cu(OH)3-	2.272e-012	2.266e-012	-11.644	-11.645	-0.001
Cu(OH)4-2	1.814e-018	1.796e-018	-17.741	-17.746	-0.004
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000

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

Phase	SI	log IAP	log KT	
CrO3	-17.24	-20.44	-3.20	CrO3
Cu(OH)2	-0.57	8.23	8.81	Cu(OH)2
CuCrO4	-6.77	-12.21	-5.44	CuCrO4
O2(g)	-40.45	44.00	84.45	O2
Tenorite	0.44	8.23	7.80	CuO

-----  
End of simulation.  
-----

-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(III)= 25 µg/l, and Pb=525 µg/l, pH=6

-----  
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
  temp      21
  pH        6
  pe        4
  redox     pe
  units     ug/l
  density   1
  C(4)     98.4 mg/l
  Na       37.7 mg/l
  Cr(3)    25
  Pb      525
  water    0.5 # kg

```

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

-----Solution composition-----					
Elements	Molality		Moles		
C(4)	1.640e-003	8.200e-004			
Cr(3)	4.809e-007	2.404e-007			
Na	1.640e-003	8.200e-004			
Pb	2.534e-006	1.267e-006			
-----Description of solution-----					
	pH	=	6.000		
	pe	=	4.000		
	Activity of water	=	1.000		
	Ionic strength	=	1.075e-003		
	Mass of water (kg)	=	5.000e-001		
	Total alkalinity (eq/kg)	=	4.995e-004		
	Total CO2 (mol/kg)	=	1.640e-003		
	Temperature (deg C)	=	21.000		
	Electrical balance (eq)	=	5.731e-004		
Percent error, 100*(Cat- An )/(Cat+ An )		=	53.43		
	Iterations	=	9		
	Total H	=	5.550822e+001		
	Total O	=	2.775588e+001		
-----Distribution of species-----					
Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.037e-006	1.000e-006	-5.984	-6.000	-0.016
OH-	7.691e-009	7.413e-009	-8.114	-8.130	-0.016
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	1.640e-003				
H2CO3	1.139e-003	1.139e-003	-2.943	-2.943	0.000
HCO3-	4.995e-004	4.818e-004	-3.301	-3.317	-0.016
PbHCO3+	5.471e-007	5.266e-007	-6.262	-6.278	-0.017
NaHCO3	4.617e-007	4.617e-007	-6.336	-6.336	0.000
PbCO3	9.989e-008	9.989e-008	-7.000	-7.000	0.000
CO3-2	2.413e-008	2.085e-008	-7.617	-7.681	-0.064
NaCO3-	7.113e-010	6.861e-010	-9.148	-9.164	-0.016
Pb(CO3)2-2	6.997e-012	6.006e-012	-11.155	-11.221	-0.066
Cr(3)	4.809e-007				
Cr(OH)+2	2.792e-007	2.396e-007	-6.554	-6.620	-0.066
Cr(OH)2+	1.989e-007	1.915e-007	-6.701	-6.718	-0.017
Cr+3	2.037e-009	1.445e-009	-8.691	-8.840	-0.149
Cr(OH)3	7.243e-010	7.243e-010	-9.140	-9.140	0.000
CrO2-	3.574e-013	3.440e-013	-12.447	-12.463	-0.017
Cr(OH)4-	3.016e-013	2.903e-013	-12.521	-12.537	-0.017
H(0)	1.474e-023				
H2	7.369e-024	7.371e-024	-23.133	-23.132	0.000
Na	1.640e-003				
Na+	1.640e-003	1.581e-003	-2.785	-2.801	-0.016
NaHCO3	4.617e-007	4.617e-007	-6.336	-6.336	0.000
NaCO3-	7.113e-010	6.861e-010	-9.148	-9.164	-0.016
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-47.142	-47.142	0.000
Pb	2.534e-006				
Pb+2	1.845e-006	1.594e-006	-5.734	-5.798	-0.064
PbHCO3+	5.471e-007	5.266e-007	-6.262	-6.278	-0.017
PbCO3	9.989e-008	9.989e-008	-7.000	-7.000	0.000
PbOH+	4.188e-008	4.031e-008	-7.378	-7.395	-0.017
Pb(OH)2	1.284e-011	1.284e-011	-10.892	-10.892	0.000
Pb(CO3)2-2	6.997e-012	6.006e-012	-11.155	-11.221	-0.066
Pb2OH+3	1.436e-012	1.018e-012	-11.843	-11.992	-0.149
Pb(OH)3-	1.343e-016	1.292e-016	-15.872	-15.889	-0.017
Pb3(OH)4+2	3.244e-018	2.785e-018	-17.489	-17.555	-0.066
Pb4(OH)4+4	7.532e-020	4.088e-020	-19.123	-19.388	-0.265
Pb(OH)4-2	3.713e-022	3.187e-022	-21.430	-21.497	-0.066



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

Phase	SI	log IAP	log KT	
Cerrusite	-0.29	-13.48	-13.19	PbCO <sub>3</sub>
CH <sub>4</sub> (g)	-58.02	-99.68	-41.66	CH <sub>4</sub>
CO <sub>2</sub> (g)	-1.52	-19.68	-18.16	CO <sub>2</sub>
Cr(OH) <sub>3</sub>	-2.12	-0.72	1.41	Cr(OH) <sub>3</sub>
Cr(OH) <sub>3</sub> (am)	0.03	-0.72	-0.75	Cr(OH) <sub>3</sub>
Cr <sub>2</sub> O <sub>3</sub>	0.80	-1.44	-2.24	Cr <sub>2</sub> O <sub>3</sub>
Hydrocerrusite	-1.98	-20.75	-18.77	Pb <sub>3</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub>
Litharge	-6.65	6.20	12.85	PbO
Massicot	-6.85	6.20	13.05	PbO
Minium	-35.92	38.61	74.53	Pb <sub>3</sub> O <sub>4</sub>
Natron	-11.82	-13.28	-1.47	Na <sub>2</sub> CO <sub>3</sub> :10H <sub>2</sub> O
O <sub>2</sub> (g)	-44.45	40.00	84.45	O <sub>2</sub>
Pb(OH) <sub>2</sub>	-2.09	6.20	8.29	Pb(OH) <sub>2</sub>
Pb <sub>10</sub> (OH) <sub>6</sub> O(CO <sub>3</sub> ) <sub>6</sub>	-47.30	-56.06	-8.76	Pb <sub>10</sub> (OH) <sub>6</sub> O(CO <sub>3</sub> ) <sub>6</sub>
Pb <sub>2</sub> O(OH) <sub>2</sub>	-13.78	12.40	26.19	Pb <sub>2</sub> O(OH) <sub>2</sub>
Pb <sub>2</sub> O <sub>3</sub>	-28.64	32.40	61.04	Pb <sub>2</sub> O <sub>3</sub>
Pb <sub>2</sub> OCO <sub>3</sub>	-6.82	-7.28	-0.46	Pb <sub>2</sub> OCO <sub>3</sub>
Pb <sub>3</sub> O <sub>2</sub> CO <sub>3</sub>	-12.36	-1.07	11.28	Pb <sub>3</sub> O <sub>2</sub> CO <sub>3</sub>
Pbmetal	-18.04	-13.80	4.24	Pb
PbO:0.3H <sub>2</sub> O	-6.78	6.20	12.98	PbO:0.33H <sub>2</sub> O
Plattnerite	-24.10	26.20	50.31	PbO <sub>2</sub>
Thermonatrite	-13.95	-13.28	0.66	Na <sub>2</sub> CO <sub>3</sub> :H <sub>2</sub> O

-----  
End of simulation.  
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-----  
Reading input data for simulation 2.  
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-----  
End of run.  
-----

Conc. of Cr(III)= 25 µg/l, and Pb=525 µg/l, no pH adjustment

-----  
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  
temp 21  
pH 7  
pe 4  
redox pe  
units ug/l  
density 1  
Cr(3) 25  
Pb 525  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
Cr(3)	4.808e-007	2.404e-007
Pb	2.534e-006	1.267e-006

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	4.700e-006
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	4.491e-007
Total carbon (mol/kg)	=	0.000e+000
Total CO2 (mol/kg)	=	0.000e+000
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	2.550e-006
Percent error, 100*(Cat- An )/(Cat+ An )	=	97.16
Iterations	=	4
Total H	=	5.550683e+001
Total O	=	2.775342e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.003e-007	1.000e-007	-6.999	-7.000	-0.001
OH-	7.433e-008	7.414e-008	-7.129	-7.130	-0.001
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cr(3)	4.808e-007				
Cr(OH)2+	4.130e-007	4.119e-007	-6.384	-6.385	-0.001
Cr(OH)+2	5.207e-008	5.155e-008	-7.283	-7.288	-0.004
Cr(OH)3	1.558e-008	1.558e-008	-7.807	-7.807	0.000
CrO2-	7.419e-011	7.400e-011	-10.130	-10.131	-0.001
Cr(OH)4-	6.262e-011	6.246e-011	-10.203	-10.204	-0.001
Cr+3	3.179e-011	3.108e-011	-10.498	-10.508	-0.010
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000
Pb	2.534e-006				
Pb+2	2.024e-006	2.004e-006	-5.694	-5.698	-0.004
PbOH+	5.081e-007	5.068e-007	-6.294	-6.295	-0.001
Pb(OH)2	1.614e-009	1.614e-009	-8.792	-8.792	0.000
Pb2OH+3	1.647e-011	1.609e-011	-10.783	-10.793	-0.010
Pb(OH)3-	1.629e-013	1.625e-013	-12.788	-12.789	-0.001
Pb3(OH)4+2	5.590e-014	5.534e-014	-13.253	-13.257	-0.004
Pb4(OH)4+4	1.063e-015	1.021e-015	-14.973	-14.991	-0.018
Pb(OH)4-2	4.048e-018	4.007e-018	-17.393	-17.397	-0.004

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

Phase	SI	log IAP	log KT	
Cr(OH)3	-0.79	0.61	1.41	Cr(OH)3
Cr(OH)3(am)	1.36	0.61	-0.75	Cr(OH)3
Cr2O3	3.47	1.23	-2.24	Cr2O3
Litharge	-4.55	8.30	12.85	PbO
Massicot	-4.75	8.30	13.05	PbO
Minium	-27.62	46.91	74.53	Pb3O4

O2(g)	-40.45	44.00	84.45	O2
Pb(OH)2	0.01	8.30	8.29	Pb(OH)2
Pb2O(OH)2	-9.58	16.60	26.19	Pb2O(OH)2
Pb2O3	-22.44	38.60	61.04	Pb2O3
Pbmetal	-17.94	-13.70	4.24	Pb
PbO:0.3H2O	-4.68	8.30	12.98	PbO:0.33H2O
Plattnerite	-20.00	30.30	50.31	PbO2

-----  
End of simulation.  
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-----  
Reading input data for simulation 2.  
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-----  
End of run.  
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Conc. of Cr(VI)= 25 µg/l, and Pb=525 µg/l, pH=6

-----  
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  
temp 21  
pH 6  
pe 4  
redox pe  
units ug/l  
density 1  
C(4) 98.4 mg/l  
Na 37.7 mg/l  
Pb 525  
Cr(6) 25  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
C(4)	1.640e-003	8.200e-004
Cr(6)	4.809e-007	2.404e-007
Na	1.640e-003	8.200e-004
Pb	2.534e-006	1.267e-006

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

pH = 6.000  
 pe = 4.000  
 Activity of water = 1.000  
 Ionic strength = 1.075e-003  
 Mass of water (kg) = 5.000e-001  
 Total alkalinity (eq/kg) = 4.999e-004  
 Total CO2 (mol/kg) = 1.640e-003  
 Temperature (deg C) = 21.000  
 Electrical balance (eq) = 5.724e-004  
 Percent error, 100\*(Cat-|An|)/(Cat+|An|) = 53.37  
 Iterations = 9  
 Total H = 5.550822e+001  
 Total O = 2.775588e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.037e-006	1.000e-006	-5.984	-6.000	-0.016
OH-	7.691e-009	7.413e-009	-8.114	-8.130	-0.016
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	1.640e-003				
H2CO3	1.139e-003	1.139e-003	-2.943	-2.943	0.000
HCO3-	4.995e-004	4.818e-004	-3.301	-3.317	-0.016
PbHCO3+	5.471e-007	5.266e-007	-6.262	-6.278	-0.017
NaHCO3	4.617e-007	4.617e-007	-6.336	-6.336	0.000
PbCO3	9.989e-008	9.989e-008	-7.000	-7.000	0.000
CO3-2	2.413e-008	2.085e-008	-7.617	-7.681	-0.064
NaCO3-	7.113e-010	6.861e-010	-9.148	-9.164	-0.016
Pb(CO3)2-2	6.997e-012	6.006e-012	-11.155	-11.221	-0.066
Cr(6)	4.809e-007				
HCrO4-	3.560e-007	3.427e-007	-6.449	-6.465	-0.017
CrO4-2	1.240e-007	1.071e-007	-6.907	-6.970	-0.064
NaCrO4-	8.738e-010	8.411e-010	-9.059	-9.075	-0.017
Cr2O7-2	5.266e-012	4.520e-012	-11.279	-11.345	-0.066
H2CrO4	2.268e-013	2.268e-013	-12.644	-12.644	0.000
H(0)	1.474e-023				
H2	7.369e-024	7.371e-024	-23.133	-23.132	0.000
Na	1.640e-003				
Na+	1.640e-003	1.581e-003	-2.785	-2.801	-0.016
NaHCO3	4.617e-007	4.617e-007	-6.336	-6.336	0.000
NaCrO4-	8.738e-010	8.411e-010	-9.059	-9.075	-0.017
NaCO3-	7.113e-010	6.861e-010	-9.148	-9.164	-0.016
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-47.142	-47.142	0.000
Pb	2.534e-006				
Pb+2	1.845e-006	1.594e-006	-5.734	-5.798	-0.064
PbHCO3+	5.471e-007	5.266e-007	-6.262	-6.278	-0.017
PbCO3	9.989e-008	9.989e-008	-7.000	-7.000	0.000
PbOH+	4.188e-008	4.031e-008	-7.378	-7.395	-0.017
Pb(OH)2	1.284e-011	1.284e-011	-10.892	-10.892	0.000
Pb(CO3)2-2	6.997e-012	6.006e-012	-11.155	-11.221	-0.066
Pb2OH+3	1.436e-012	1.018e-012	-11.843	-11.992	-0.149
Pb(OH)3-	1.343e-016	1.292e-016	-15.872	-15.889	-0.017
Pb3(OH)4+2	3.244e-018	2.785e-018	-17.489	-17.555	-0.066
Pb4(OH)4+4	7.532e-020	4.088e-020	-19.123	-19.388	-0.265
Pb(OH)4-2	3.713e-022	3.187e-022	-21.430	-21.497	-0.066

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

Phase	SI	log IAP	log KT	
Cerrusite	-0.29	-13.48	-13.19	PbCO3
CH4(g)	-58.02	-99.68	-41.66	CH4
CO2(g)	-1.52	-19.68	-18.16	CO2
CrO3	-15.77	-18.97	-3.20	CrO3

Hydrocerrusite	-1.98	-20.75	-18.77	Pb <sub>3</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub>
Litharge	-6.65	6.20	12.85	PbO
Massicot	-6.85	6.20	13.05	PbO
Minium	-35.92	38.61	74.53	Pb <sub>3</sub> O <sub>4</sub>
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	-21.59	-31.54	-9.95	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>
Na <sub>2</sub> CrO <sub>4</sub>	-15.55	-12.57	2.98	Na <sub>2</sub> CrO <sub>4</sub>
Natron	-11.82	-13.28	-1.47	Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O
O <sub>2</sub> (g)	-44.45	40.00	84.45	O <sub>2</sub>
Pb(OH) <sub>2</sub>	-2.09	6.20	8.29	Pb(OH) <sub>2</sub>
Pb <sub>10</sub> (OH) <sub>6</sub> O(CO <sub>3</sub> ) <sub>6</sub>	-47.30	-56.06	-8.76	Pb <sub>10</sub> (OH) <sub>6</sub> O(CO <sub>3</sub> ) <sub>6</sub>
Pb <sub>2</sub> O(OH) <sub>2</sub>	-13.78	12.40	26.19	Pb <sub>2</sub> O(OH) <sub>2</sub>
Pb <sub>2</sub> O <sub>3</sub>	-28.64	32.40	61.04	Pb <sub>2</sub> O <sub>3</sub>
Pb <sub>2</sub> OCO <sub>3</sub>	-6.82	-7.28	-0.46	Pb <sub>2</sub> OCO <sub>3</sub>
Pb <sub>3</sub> O <sub>2</sub> CO <sub>3</sub>	-12.36	-1.07	11.28	Pb <sub>3</sub> O <sub>2</sub> CO <sub>3</sub>
PbCrO <sub>4</sub>	-0.06	-12.77	-12.71	PbCrO <sub>4</sub>
Pbmetal	-18.04	-13.80	4.24	Pb
PbO·0.3H <sub>2</sub> O	-6.78	6.20	12.98	PbO·0.33H <sub>2</sub> O
Plattnerite	-24.10	26.20	50.31	PbO <sub>2</sub>
Thermonatrite	-13.95	-13.28	0.66	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O

-----  
End of simulation.  
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-----  
Reading input data for simulation 2.  
-----

-----  
End of run.  
-----

Conc. of Cr(VI)= 25 µg/l, and Pb=525 µg/l, no pH adjustment

-----  
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  
temp 21  
pH 7  
pe 4  
redox pe  
units ug/l  
density 1  
Cr(6) 25  
Pb 525  
water 0.5 # kg

-----  
Beginning of initial solution calculations.  
-----

Initial solution 1.

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

Elements	Molality	Moles
Cr(6)	4.808e-007	2.404e-007
Pb	2.534e-006	1.267e-006

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	5.178e-006
Mass of water (kg)	=	5.000e-001
Total alkalinity (eq/kg)	=	8.502e-007
Total carbon (mol/kg)	=	0.000e+000
Total CO2 (mol/kg)	=	0.000e+000
Temperature (deg C)	=	21.000
Electrical balance (eq)	=	1.868e-006
Percent error, 100*(Cat- An )/(Cat+ An )	=	67.00
Iterations	=	4
Total H	=	5.550683e+001
Total O	=	2.775342e+001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.003e-007	1.000e-007	-6.999	-7.000	-0.001
OH-	7.433e-008	7.414e-008	-7.129	-7.130	-0.001
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
Cr(6)	4.808e-007				
CrO4-2	3.649e-007	3.611e-007	-6.438	-6.442	-0.005
HCrO4-	1.159e-007	1.156e-007	-6.936	-6.937	-0.001
Cr2O7-2	5.195e-013	5.140e-013	-12.284	-12.289	-0.005
H2CrO4	7.647e-015	7.647e-015	-14.116	-14.116	0.000
H(0)	1.474e-025				
H2	7.371e-026	7.371e-026	-25.132	-25.132	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-43.142	-43.142	0.000
Pb	2.534e-006				
Pb+2	2.024e-006	2.003e-006	-5.694	-5.698	-0.005
PbOH+	5.079e-007	5.066e-007	-6.294	-6.295	-0.001
Pb(OH)2	1.613e-009	1.613e-009	-8.792	-8.792	0.000
Pb2OH+3	1.647e-011	1.608e-011	-10.783	-10.794	-0.010
Pb(OH)3-	1.629e-013	1.624e-013	-12.788	-12.789	-0.001
Pb3(OH)4+2	5.585e-014	5.527e-014	-13.253	-13.258	-0.005
Pb4(OH)4+4	1.064e-015	1.020e-015	-14.973	-14.992	-0.018
Pb(OH)4-2	4.048e-018	4.006e-018	-17.393	-17.397	-0.005

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

Phase	SI	log IAP	log KT	
CrO3	-17.24	-20.44	-3.20	CrO3
Litharge	-4.55	8.30	12.85	PbO
Massicot	-4.75	8.30	13.05	PbO
Minium	-27.62	46.90	74.53	Pb3O4
O2(g)	-40.45	44.00	84.45	O2
Pb(OH)2	0.01	8.30	8.29	Pb(OH)2
Pb2O(OH)2	-9.58	16.60	26.19	Pb2O(OH)2
Pb2O3	-22.44	38.60	61.04	Pb2O3
PbCrO4	0.56	-12.14	-12.71	PbCrO4
Pbmetal	-17.94	-13.70	4.24	Pb
PbO:0.3H2O	-4.68	8.30	12.98	PbO:0.33H2O
Plattnerite	-20.00	30.30	50.31	PbO2

-----  
End of simulation.  
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-----  
Reading input data for simulation 2.  
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-----  
End of run.  
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