

# UNESCO-IHE INSTITUTE FOR WATER EDUCATION



## **Effect of Fulvic Acid on the Adsorptive Removal of Arsenic and Chromium from Groundwater by Iron Oxide Based Adsorbents**

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MSc Thesis (MWI 2010-028)  
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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.



## Abstract

Groundwater as water source has several advantages due to its sustainability, generally good quality, and accessibility. As a natural drinking water source, contamination of groundwater from the natural contaminants and human activities is likely expected. High concentrations of metals such as arsenic and chromium could be present in the groundwater.

Arsenic and chromium are dangerous substances known as human carcinogens. World Health Organization (WHO) recommends 10 µg/l as a guideline value for arsenic and 50 µg/l for chromium in drinking water. Contamination with arsenic and chromium in drinking water source is a worldwide issue. There are several technologies developed for arsenic and chromium removal from water. Adsorption is recognized as an effective method to accomplish the task. Iron oxide based adsorbents such as Iron Oxide Coated Sand (IOCS) and Granular Ferric Hydroxide (GFH) were found to be a potential adsorbent for the absorptive removal of arsenic and chromium.

Under natural conditions, the adsorption of arsenic and chromium at the solid–water interface may be strongly influenced by the adsorption of Natural Organic Matter (NOM), next to pH and concentration of metals. NOM is commonly found in groundwater, it consists of several components and one of them is fulvic acid. Fulvic acid is part of humic substances that are soluble in water at all pH conditions. Fulvic acid was believed to act as a competing ion on the adsorption processes. The role of fulvic acid on the adsorptive removal of arsenic and chromium by IOCS and GFH was not yet studied.

The main goal of this research was to find the effect of fulvic acid on the arsenate -As(V)- and chromate -Cr(VI)- removal by IOCS and GFH at different pH values. The research focused on As(V) and Cr(VI) due to their toxicity and behaviour during adsorption processes such as charge and solubility of the species.

Effect of fulvic acid and pH on the adsorption of arsenic and chromium was investigated in batch adsorption experiments. At adsorption experiments with individual components present -As(V), Cr(VI) and fulvic acid- GFH was found to be better adsorbent compared to IOCS. Cr(VI) was hardly removed by IOCS at all pH values tested and As(V) removal rate was decreased with the increase of pH value. But, both IOCS and GFH seem to be inefficient in the fulvic acid adsorption. In the adsorption experiments with simultaneous metals and FA presence, it was found that role of FA was almost insignificant at all pH values either with IOCS or GFH as adsorbent. Slight influence of FA was detected only in the removal of As(V) by IOCS at pH 6. In the removal of Cr(VI), role of FA as a competitive ion seemed to be undetectable with the poor performance of IOCS and GFH. The adsorptive removal of As(V) and Cr(VI) by preloading GFH was slightly lower than fresh GFH in the presence of FA. Result of FA adsorption isotherm by GFH well fitted Freundlich isotherm. It was found that the adsorption capacity is relatively low.

From the research it was found that IOCS leached significant amount of unknown organic matter during the experiment. The amount of organic matter leached was influenced by the dosage of IOCS and pH. This discovery is important factor for the study of competitive adsorption of metals and organic matter by IOCS.

Key words: Adsorption, arsenic, chromium, fulvic acid, competitive adsorption.





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## List of Symbols, Acronyms and Abbreviations

AAS	: Atomic absorption spectrophotometer
As(III)	: Arsenite
As(V)	: Arsenate
Cr(III)	: Trivalent chromium
Cr(VI)	: Hexavalent chromium
EC	: European community
FA	: Fulvic acid
GF	: Graphite furnace
GFH	: Granular ferric hydroxide
HCO <sub>3</sub> <sup>-</sup>	: Bicarbonate
Hrs	: Hours
IOCS	: Iron oxide coated sand
NOM	: Natural organic matter
MCL	: Maximum Contamination Level
mg/l	: Milligram per liter
mg/g	: Milligram per gram
µg/l	: Microgram per liter
PE	: Polyethylene
Rpm	: Revolution per minute
USEPA	: United States Environmental Protection Agency
WHO	: World health Organization



# 1. INTRODUCTION

## 1.1 General Background

Groundwater as water source has several advantages due to its sustainability, generally good quality, and accessibility. Because of these advantages, groundwater is considered as a major source of drinking water in many countries. As a natural drinking water source, impurities and pollutants of groundwater are predictable. Impurities in groundwater (also referred to as natural contaminants), originate from natural activities (non human) e.g. rain water, rock and soils in the earth crust, seawater intrusion, biological activities in the soil and animal activities. Rock and soil contains many organic and inorganic substances. Nevertheless, pollutants in groundwater can be found as a result of human activities as well e.g. agricultural and industrial contaminants (Petrusevski, 2009). Level of impurities and pollutants in the groundwater directly affect the quality of groundwater. High concentration of metals such as arsenic and chromium are considered as a problem on the impurities of groundwater.

Arsenic is semi-metallic element widely distributed in the earth's crust and introduced into water through the dissolution of minerals and ores. Arsenic can reach the groundwater by oxidation of arsenopyrite ( $\text{FeAsS}$ ) and can form many organic and inorganic compounds. Most common species are: arsenite (III) typically in anaerobic water and arsenate (V) typically in aerobic water. High concentrations of arsenic in groundwater can be found on all five continents, in countries like Argentina, Bangladesh, Pakistan, China, USA, Hungary, Japan, Zimbabwe, etc. (Petrusevski, 2009).

Chromium is a steel-grey metallic element also widely distributed in the earth's crust. Chromium is present in elevated concentrations in many groundwater sources used for drinking water in many countries around the world like USA, Mexico, India, Canada, China, Scotland, Slovenia, Italy, Israel, etc. Naturally occurring chromium concentrations in groundwater are generally very low (less than  $2\text{ }\mu\text{g/l}$ ), although concentrations as high as  $120\text{ }\mu\text{g/l}$  have been reported. In the aquatic environment, Cr is commonly found as hexavalent Cr(VI) and trivalent Cr(III). Cr(VI) compounds are much more soluble than Cr(III) and are much more toxic (mutagenic and carcinogenic) to microorganism, plants, animals and humans. In contrast, Cr(III) has relatively low toxicity and is immobile under moderately alkaline to slightly acidic conditions. Cr(VI) can cause liver and kidney damage, internal hemorrhage and respiratory disorders (Sharma, et al., 2008).

Various organic compounds generated by biological processes in the nature, especially in the water environment, both in the water body (autochthonous material) and in the surrounding watershed (allochthonous material) are found in all surface and many groundwaters. These mixed organic compounds that enter the water as a result of human activities, are referred to as natural organic matter (NOM). They consist of a complex mixture of organic material like humic substances, hydrophobic acids, carbohydrates, amino acids, carboxylic acids, proteins, hydrocarbon, etc (Croue, et al., 2000). In most places, the concentration of naturally occurring organic matters are low and cannot be considered as contaminating natural water (Zaporozec, 2004).

Natural contamination became challenging problem in drinking water production due to arsenic and chromium contamination in the groundwater source all over the world. This problem increases awareness of exposure of humans to those elements through drinking water. The World Health Organization (WHO) set a standard value for maximum contaminant level (MCL)

for arsenic in drinking water to 10 µg/l and 50 µg/l for total chromium. Nevertheless, many countries like Bangladesh, Bolivia, China, Zimbabwe, Canada etc, set a standard value for MCL for arsenic > 10 µg/l (25 µg/l - 50 µg/l) because of lack of proper technology for its removal. Many countries' standard value for MCL for chromium in drinking water refers to WHO value (50 µg/l).

To meet the WHO drinking water guideline values, methods applied for arsenic and chromium removal are relatively similar all around the globe. Treatment methods for the removal of either metal can be classified as conventional or advanced. Coagulation-precipitation-filtration methods are considered conventional. On the other hand, adsorption, ion exchange, and membrane technologies are examples of advanced methods. For every removal technology, efficiency, ease of maintenance, and cost play vital role. From the performance and cost-effectiveness point of view, adsorption is considered as one of more effective methods for arsenic and chromium removal.

There are many types of adsorbents available for arsenic and chromium removal such as iron oxide coated sand (IOCS), granular ferric hydroxide (GFH), activated carbon etc. IOCS is a by-product of water treatment plant treating groundwater with high iron concentration, and is consequently cheap. GFH on the other hand is more expensive since it is an industrial product, produced by neutralization and precipitation of ferric chloride.

## **1.2 Problem Identification**

Arsenic and chromium are dangerous compounds for human health. For this reason, WHO guideline values for both substances, have decreased in the last decade. In several developing countries that have arsenic and chromium problem in their water, cheap and effective removal method is required to meet the guidelines.

In the adsorption processes, presence of competing ions in the water can affect the performance of adsorbents. In the natural water there are many substances considered as competing ions like sulphates, phosphates, silica, natural organic matter (NOM), etc. NOM not only influences adsorptive capacity but also complicates adsorption isotherm (Matsui, et al., 2003). Also pH is considered an important factor due to its effect on the adsorbent performance.

One component of NOM that is commonly present in the nature water is fulvic acid. It is believed that fulvic acid influences the performance of adsorbent during adsorption processes. For instance, fulvic acid will enhance the adsorption of Cd(II) on alumina at pH below point zero charge by bridging towards the solid surface and reduce the adsorption above this pH by formation of low-adsorbing fulvic acid complexes in solution (Xu, et al., 1989).

Until now, there were no experiments carried out to find out the effect of fulvic acid on the adsorption of arsenic and chromium on IOCS and GFH. To get relevant results during experiments, it is important to find out and verify the average amount of fulvic acid present in groundwater. This data will be used as a reference to find out the role of fulvic acid on the adsorption of arsenic and chromium in batch experiments.

### **1.3 Goal and Objectives**

The goal of this research was to study the effect of fulvic acid on the adsorptive removal of As(V) and Cr(VI) by IOCS and GFH.

The detailed objectives of the research were:

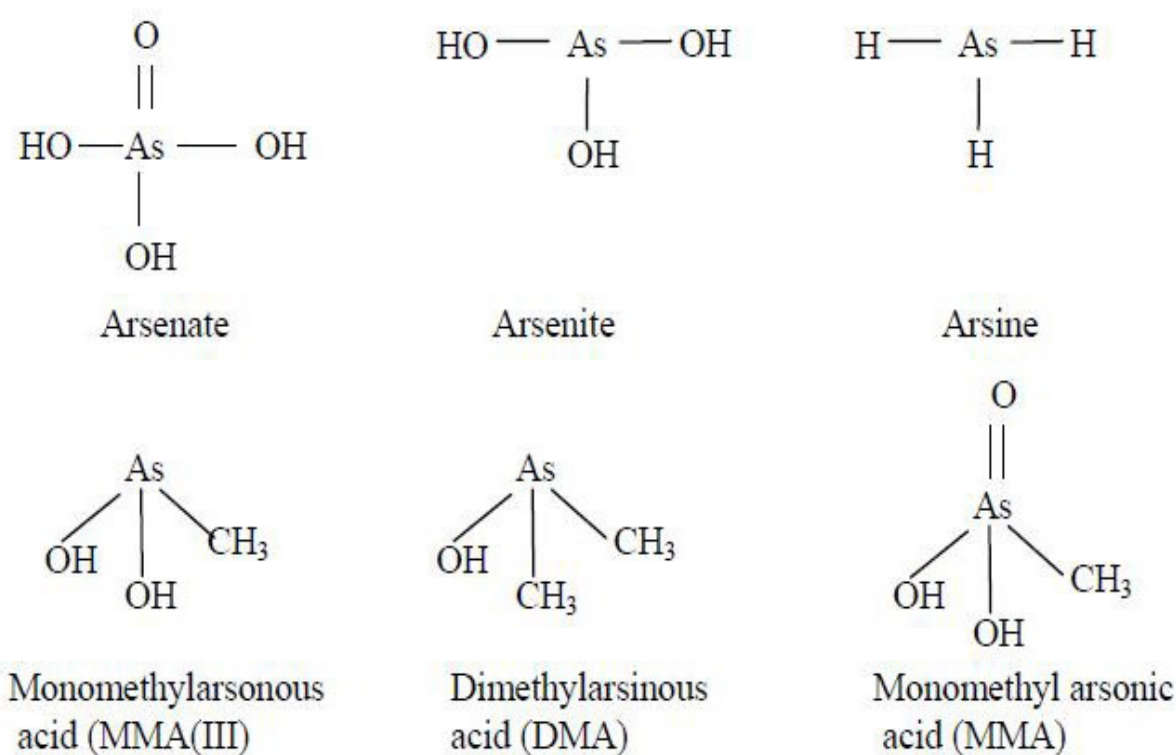
1. To examine the effect of fulvic acid on the As(V) and Cr(VI) adsorption by IOCS and GFH in short-term batch experiment at different pH values.
2. To try to establish the adsorption isotherms for As(V) and Cr(VI) by IOCS and GFH in the presence and absence of fulvic acid.
3. To assess the capability of IOCS and GFH to adsorb fulvic acid.



## 2. LITERATURE REVIEW

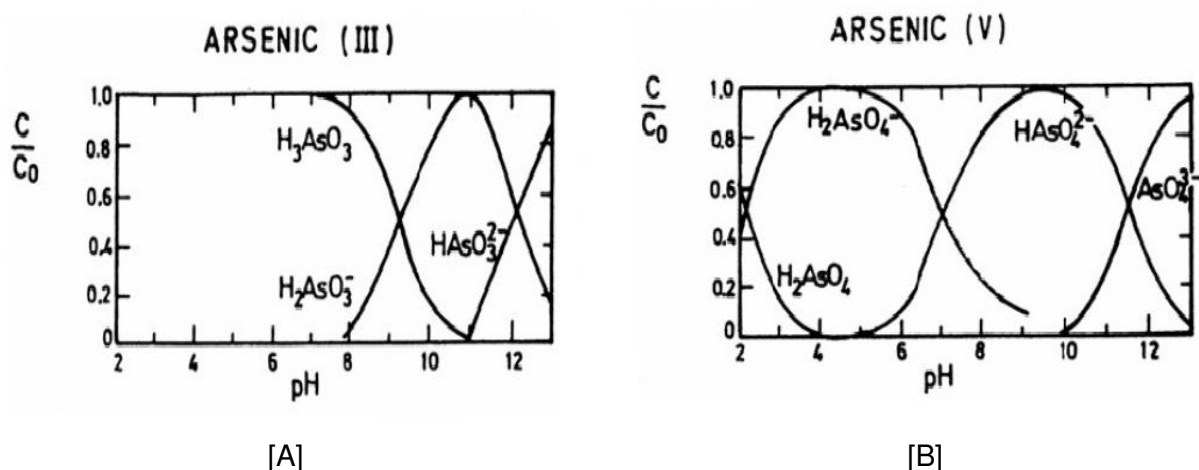
### 2.1 Chemistry and Toxicity of Arsenic

Arsenic is a chemical element that has the symbol **As** and atomic number 33. Its atomic mass is 74.92. It is known as disreputably poisonous metalloid (semi metal) substance with many chemical forms. Arsenic might be found in the water that flows through As-rich rocks. Metalloidal forms of arsenic, each with a different crystal structure, are found free in nature. Arsenic can reach the groundwater by oxidation of arsenopyrite (FeAsS). Arsenopyrite is the most common arsenic-bearing mineral and also can form many organic and inorganic compounds. Organic compounds are commonly found as monomethylarsonate (MMA) and dimethylarsinate (DMA), and inorganic compound found as arsenite [As(III)] and arsenate [As(V)] (Thirunavukkarasu, et al., 2002). Most representative structures of arsenic are shown in figure 2.1.



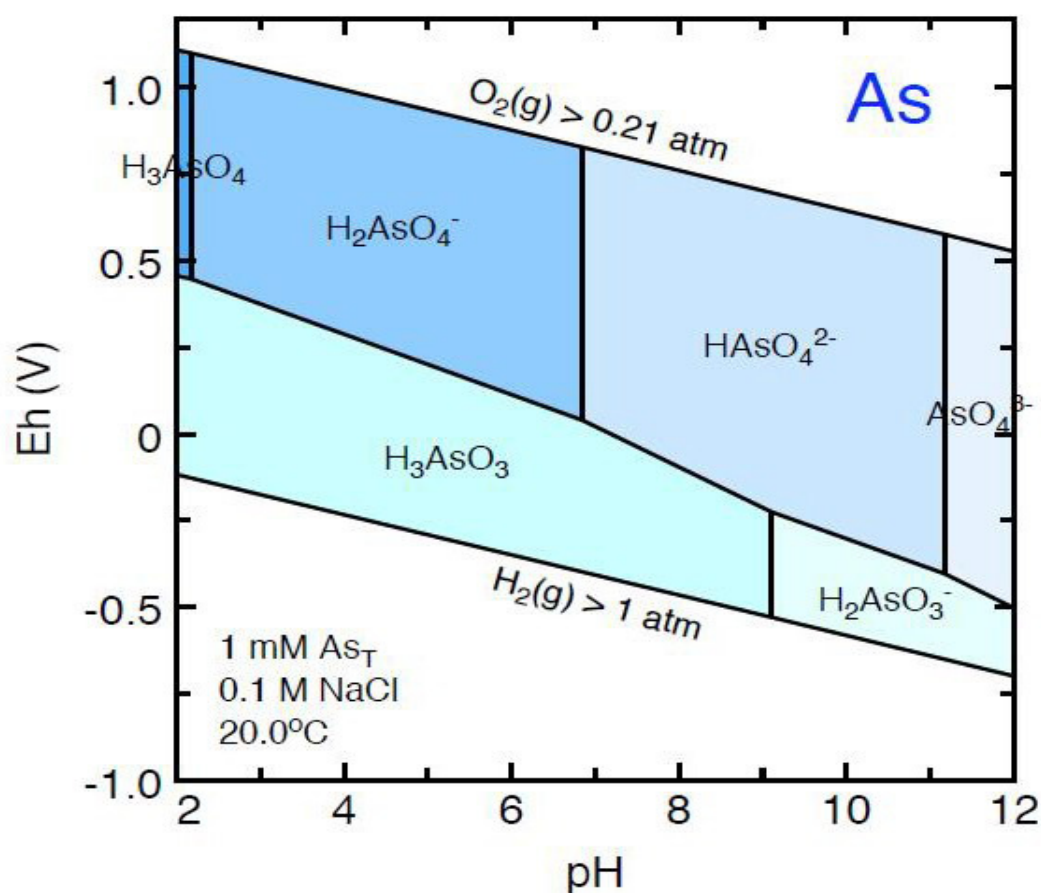
**Figure 2.1:** Different form of arsenic as an organic and inorganic compound.

As illustrated in figure 2.2, arsenic occurs in several different species depending on the pH and oxidation potential of the water. In oxygen-rich environments where aerobic condition persist, As(V) is common and exist as monovalent ( $\text{H}_2\text{AsO}_4^-$ ) or divalent ( $\text{HAsO}_4^{2-}$ ) anion. Whereas, As(III) exists in an uncharged molecule ( $\text{H}_3\text{AsO}_3^0$ ) and anionic ( $\text{H}_3\text{AsO}_3^-$ ) species in the environment where anoxic conditions persist (Ferguson, et al., 1972). The uncharged arsenite species  $\text{H}_3\text{AsO}_3^0$  also predominates over a wide range of pH value. However, under oxic conditions at thermodynamic equilibrium, As in water is dominated by arsenate oxyanions ( $[\text{H}_2\text{As(V)}\text{O}_4^-]$  or  $[\text{HAs(V)}\text{O}_4^{2-}]$  depending on pH conditions).



**Figure 2.2:** [A] The stability and dominant As(III) species at different pH levels; [B] The stability and dominant As(V) species at different pH levels.

The predominate As(V) species in groundwater are  $H_2AsO_4^-$  between pH 2.2 and 6.9, and  $HAsO_4^{2-}$  between pH 6.9 and 11.5. As(III) species  $H_3AsO_3$  predominates up to pH 9.2, while  $H_2AsO_3^-$  is predominant from pH 9.2 to 12. Figure 2.3 below is a diagram of Eh-pH to explain the forms of As under different pH value.



**Figure 2.3:** Eh-pH diagram of As species in water in a system containing As and NaCl at 20°C and 1 bar total pressure (Smedley, 2006).



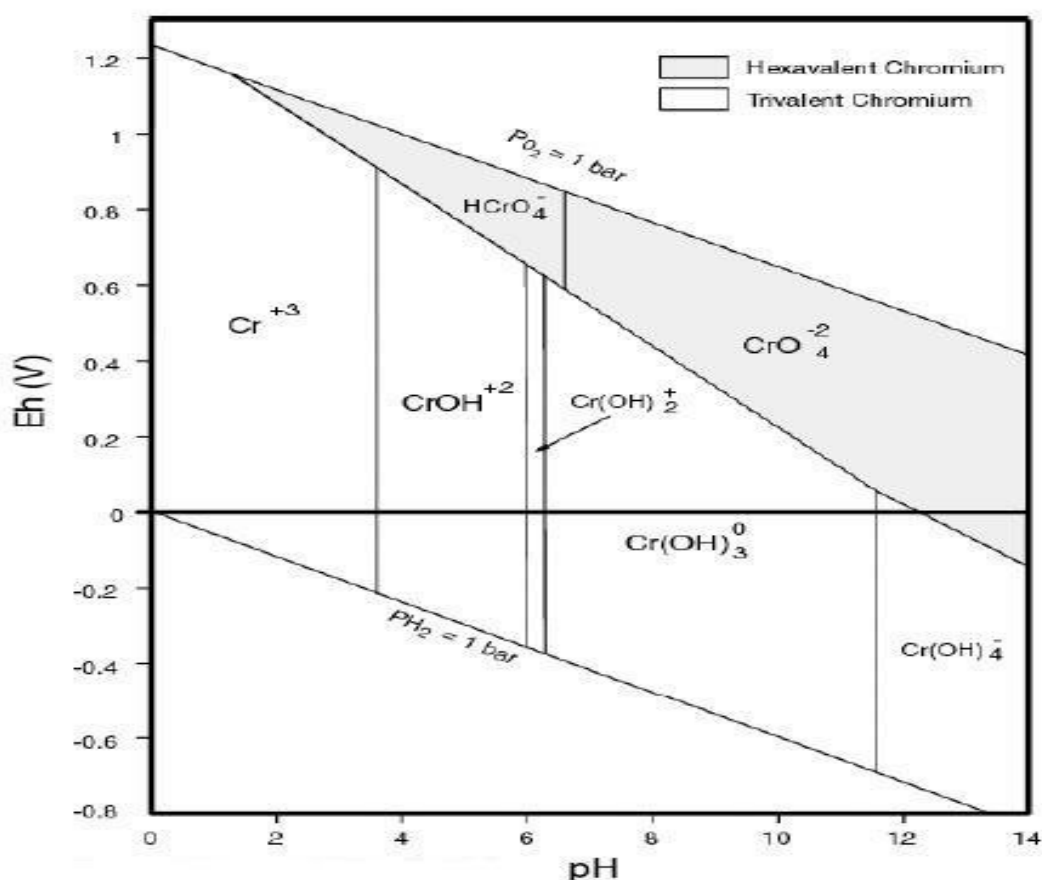


## 2.2 Chemistry and Toxicity of Chromium

Chromium with the atomic symbol **Cr** is a transition metal with the atomic number 24, atomic weight 52 and part of group VIB in the periodic table. Chromium exist in oxidation states ranging from +6 to -2: however, only the hexavalent Cr(VI) and trivalent Cr(III) are commonly encountered in the aquatic environment. Not only the toxicity of chromium but also its aqueous concentration and its mobility in different geologic environment are dependent on its oxidation state (Rai, et al., 1989).

The Cr(III) oxidation state is its most stable form and considerable energy would be required to convert it to lower or higher states. Cr(III) presence, concentration and forms in a given environment depend on different chemical and physical processes, such as hydrolysis, complexation, redox reactions and adsorption. Cr(VI) in acidic solution demonstrates a very high positive redox potential, which denotes that it is strongly oxidizing and unstable in the presence of electron donors. There are several form of Cr(VI), the relative proportions of which depend on both pH and total Cr(VI) concentration (Kotas, et al., 2000). In general, Cr(VI) salts are more soluble than those of Cr(III), making Cr(VI) relatively mobile (Sharma, et al., 2008).

The distribution of compounds containing Cr(III) and Cr(VI) depends on the redox potential (pE) and pH. The presence of oxidizing or reducing compounds, the kinetics of the redox reactions and the formation of Cr(III) complexes or insoluble Cr(III) are shown in the figure 2.5.



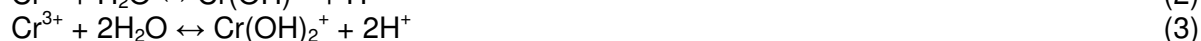
**Figure 2.5:** Eh-pH diagram of aqueous Cr species (USEPA, 2000).

Cr(VI) is readily hydrolysed in water. The dominant Cr(VI) species at total chromium concentrations below 500 mg/L are the oxyanions  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ . The equilibrium equation between the two species is highly dependent on pH.



At low pH the concentration of  $\text{H}^+$  ions is high, so the reaction lies to the left, and  $\text{HCrO}_4^-$  is dominant species. While at higher pH, the concentration of  $\text{H}^+$  ions is lower, the reaction lies to the right and  $\text{CrO}_4^{2-}$  predominates.  $\text{Cr}_2\text{O}_7^{2-}$  is predominate under acidic environment at Cr(VI) concentration higher than 500 mg/L.

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



Cr(III) as a  $\text{Cr}(\text{OH})_2^+$  is dominant at pH value between 6 and 8, while  $\text{Cr}(\text{OH})^{2+}$  and  $\text{Cr}^{3+}$  predominate in more acidic conditions below pH 4.  $\text{Cr}(\text{OH})_4^-$  and  $\text{Cr}(\text{OH})_{3(s)}$  are most likely to be found in alkaline water.

Chromium experiences redox reaction in certain condition:



The reduction of Cr(VI) to Cr(III) requires  $\text{H}^+$  ions to force the reaction (Selomulya, et al., 1999).

Chromium compounds are found in the environment, due to erosion of chromium-containing rocks and can also be distributed by volcanic eruptions. The concentration range in soil is between 1 and 3000 mg/kg, in sea water 5 to 800  $\mu\text{g/l}$ , and in rivers and lakes 26  $\mu\text{g/l}$  to 5.2 mg/l (Kotas, et al., 2000). Chromium is widely distributed in the earth's crust, in the form of steel-grey metallic element (Sharma, et al., 2008). In water, Cr(III) occurs as a cation that forms aqueous complexes and hydroxide precipitates. In surface waters, the ratio of Cr(III) to Cr(VI) varies widely, and relatively high concentrations of the latter can be found locally.

Chromium as a chromium amino acid chelate is an essential nutrient required for normal sugar and fat metabolism. Insufficient dietary chromium is associated with maturity-onset diabetes and/or cardiovascular diseases and also it was reported to be responsible for the control of glucose and lipid metabolism in mammals (Anderson, 1989). The National Academy and Science (NAS) of USA estimates a safe and adequate intake of 50 to 200  $\mu\text{g/day}$ .

Chromium toxicity is dependent on chemical speciation and thus associated health effects are influenced by chemical forms of exposure. Cr(VI) compounds are much more soluble than Cr(III) and are much more toxic (mutagenic and carcinogenic) to microorganisms, plants, animals and humans. In contrast, Cr(III) has relatively low toxicity and is immobile under moderately alkaline to slightly acidic conditions (Sharma, et al., 2008). Cr(VI) exerts toxic effects on biological systems. It was found that occupational exposure to Cr(VI) compounds leads to a variety of clinical problems. Inhalation and retention of Cr(VI) containing materials can cause perforation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of the larynx and liver, and increased incidence of bronchogenic carcinoma. Skin contact with Cr(VI) compounds can induce skin allergies, dermatitis, dermal necrosis and dermal corrosion (Kotas, et al., 2000). Cr(VI) has been shown to cause cancer in humans and animals through inhalation exposure, but has not been shown to be carcinogenic through ingestion exposure. The toxicological

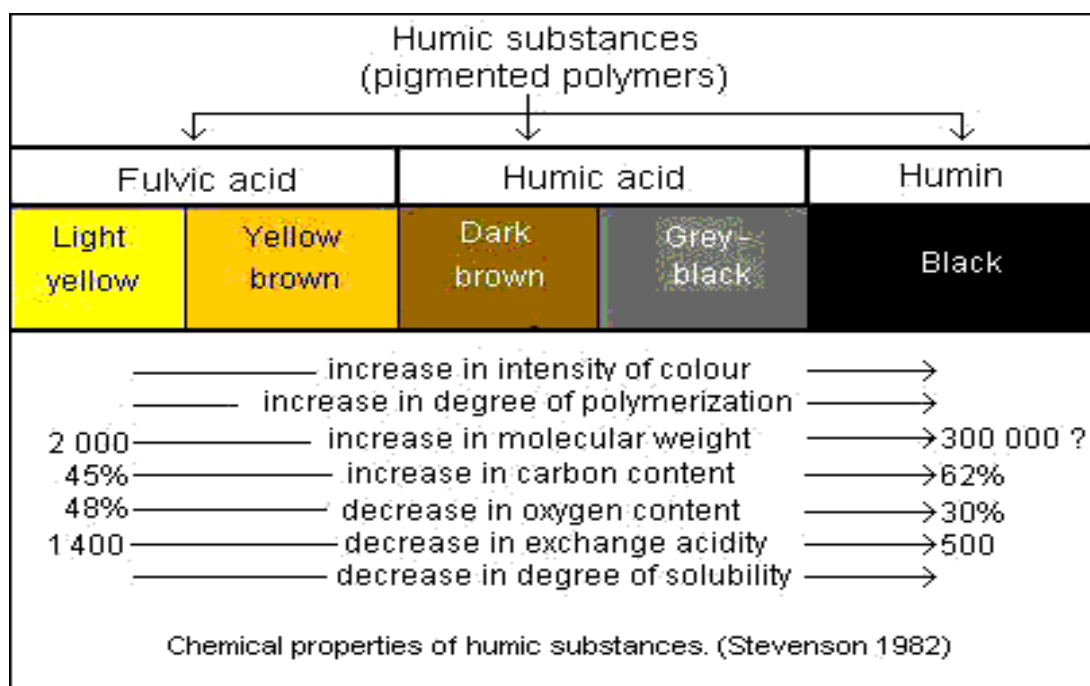
impact of Cr(VI) originates from the action of this form itself as an oxidizing agent, as well as from the formation of free radicals during the reduction of Cr(VI) to Cr(III) occurring inside the cell.

## **2.3 Natural Organic Matter in Water**

Natural Organic Matter (NOM) is generally used to describe the organic compounds found in water bodies. Aquatic NOM is present in all groundwater around the world, the concentration being between 0.5 to 10 mg/l of organic carbon. In general, NOM can be divided into two groups, humic and nonhumic fraction. The humic fraction is more hydrophobic in character and comprises humic and fulvic acid. The nonhumic fraction is less hydrophobic in character and comprises hydrophilic acids, proteins, amino acids, and carbohydrates (Owen, et al., 1995).

Most dissolved humic substances are thought to have molecular weight of few hundred to a few thousand atomic mass units (amu) (Thurman, et al., 1982). Humic substance have been considered the most important part of NOM in term of chemical properties and importance for water treatment (Owen, et al., 1995). In most natural waters, humic substance usually dominate the NOM, contributing from 50 to > 90% of the dissolve organic carbon (DOC) which varies related to its biological activities and seasonal cycles (Croue, et al., 2000). Humic molecules contain aromatic, carbonyl, carboxyl, methoxyl, and aliphatic units. Phenolic and carboxylic functional groups provide most of the protonation and metal complexation sites.

Other source mentions that humic substances are divided into three groups, which are humic acid, fulvic acid and humin. Humic acid are the fraction of humic substances that is not soluble in water under acidic conditions ( $\text{pH} < 2$ ) but is soluble at higher pH values. Humic acid can be extracted from soil by various reagents and they are the main extractable element of soil humic substances (Theng, et al., 1967). Humic acid can be identified from its color which is dark brown to black. Fulvic acid is the part of humic substances that is soluble in water under all pH conditions, they remain in solution after removal of humic acid by acidification. Differ with humic acid, fulvic acid has light yellow to yellow-brown in color. On the other hand, humin is the fraction of humic substances that is not soluble in water at any pH value which can be differentiated from its black color (Weber, 2009). Low concentrations of organics in natural waters make the determination of humic substances difficult, especially in neutral pH when both fulvic and humic acid are very soluble in water (Jucker, et al., 1994). Figure 2.6 shows the differentiation of humic substance and it is chemical properties.



**Figure 2.6:** Chemical properties of humic substances (Weber, 2009).

Basically, NOM considered non toxic but gives groundwater unwelcome color. Elevated color levels of groundwater have direct effect on taste and odor of water and can cause several problems during treatment and distribution of such groundwater. Another indirect, but considered very important effect is the formation of potentially harmful disinfection by-products and/or biological re-growth in the distribution systems (Genz, et al., 2008).

### 2.3.1 Means of Natural Organic Matter Characterization

Concentration of NOM is quantified as the amount of carbon in its molecules, and is measured as dissolved organic carbon (DOC) or particulate organic carbon (POC). Because of the complexity and multi-dimensional nature of NOM, various analytical techniques have are to characterize it. The characterization of NOM is important in order to understand treatment behavior and to compare different results. The main characteristics of NOM are molecular weight (MW), functional groups, hydrophobicity and charge (Schafer, 2001).

Generally, there are four steps to characterize NOM. First step focuses on the chemical identities of individual species included in the NOM group, such as amino acids and carbohydrates. Second step addresses the nature and abundance of structural units in the NOM molecules. The methods associated with the first two steps are able to provide specific chemical information but require complicated sample preparation, thus cannot be used in-situ. Third step addresses issues related to the chemical behavior of NOM, especially on the polymeric nature of NOM molecules. The final step comprises methods that do not clearly probe the chemical identities of functional groups and molecules, but measure a spectral signature of NOM, for example UV adsorbance and fluorescence spectroscopy (Croue, et al., 2000).

For NOM characterization the following techniques are commonly used:

- Color determination, used as substitute parameter of DOC.  
Color in water is caused by dissolved or colloiddally dispersed substances absorbing certain wavelength of the normal "white" light. Color of water that contains suspended matter is

defined as “apparent color” while color of water which particulate matter has been removed is defined as “true color”. Color in drinking water may occur for several reasons, such as the presence of colored organic substances originating from decay or aqueous extraction of natural vegetation, presence of metals, which are common in nature, or the presence of colored industrial waste. The color in groundwater is usually due to its colored mineral content.

- Measurement TOC/DOC, is indirect measure of  $\text{CO}_2$  produced by UV-oxidation or combustion of organic matter in a water sample.

Organic carbon (OC) is a sum parameter for organic matter concentration measurement. It can be expressed in terms of TOC (total organic carbon) or DOC, depending on the available carbon analyzer and the purpose of the test. In general, TOC is the sum of DOC and POC and is relatively easy to measure directly by carbon analyzer. On the other hand, if mixed organic substances are used, the method does not give any information about the humic substance content. The DOC measurement procedure requires that the sample be passed through a 0.45  $\mu\text{m}$  membrane filter prior to analysis to remove particulate OC from the sample.

- Specific UV-adsorption (SUVA), which is defined as the UV absorbance at 254 nm divided by the concentration of dissolved organic carbon.

The value of SUVA at 254 nm (SUVA<sub>254</sub>) is also often calculated and used as an indicator of the aromatic, hydrophobic character of the NOM (Croue, et al., 2000). The SUVA is highly effective measuring method for water containing humic acid, because double bonds in aromatic structure have a large impact on UV light absorbance (Michel, 1999). In terms of NOM, low SUVA values (in the range 1-2 L/m-mg) indicate non-humic substances such as proteins and high SUVA values (>4 L/m-mg) indicate more humic NOM (Mazola, 2008). According to the relatively high extinction coefficient, absorbance at these wavelengths can be measured directly, i.e., without pre concentration in most aqueous samples (Frimmel, et al., 1998).

- Fluorescence excitation-emission matrix (EEM)

Fluorescence happens when optically-excited molecules release light whose wavelength is longer than that of the excitation energy. In organic molecules the emission occurs in functional groups known as fluorophores (Croue, et al., 2000). The application of EEM is important to differentiate between the different fractions of NOM, the isolates obtained by different methods and the fractions of the samples from different origin and age (Frimmel, et al., 1998).

### **2.3.2 Fulvic acid**

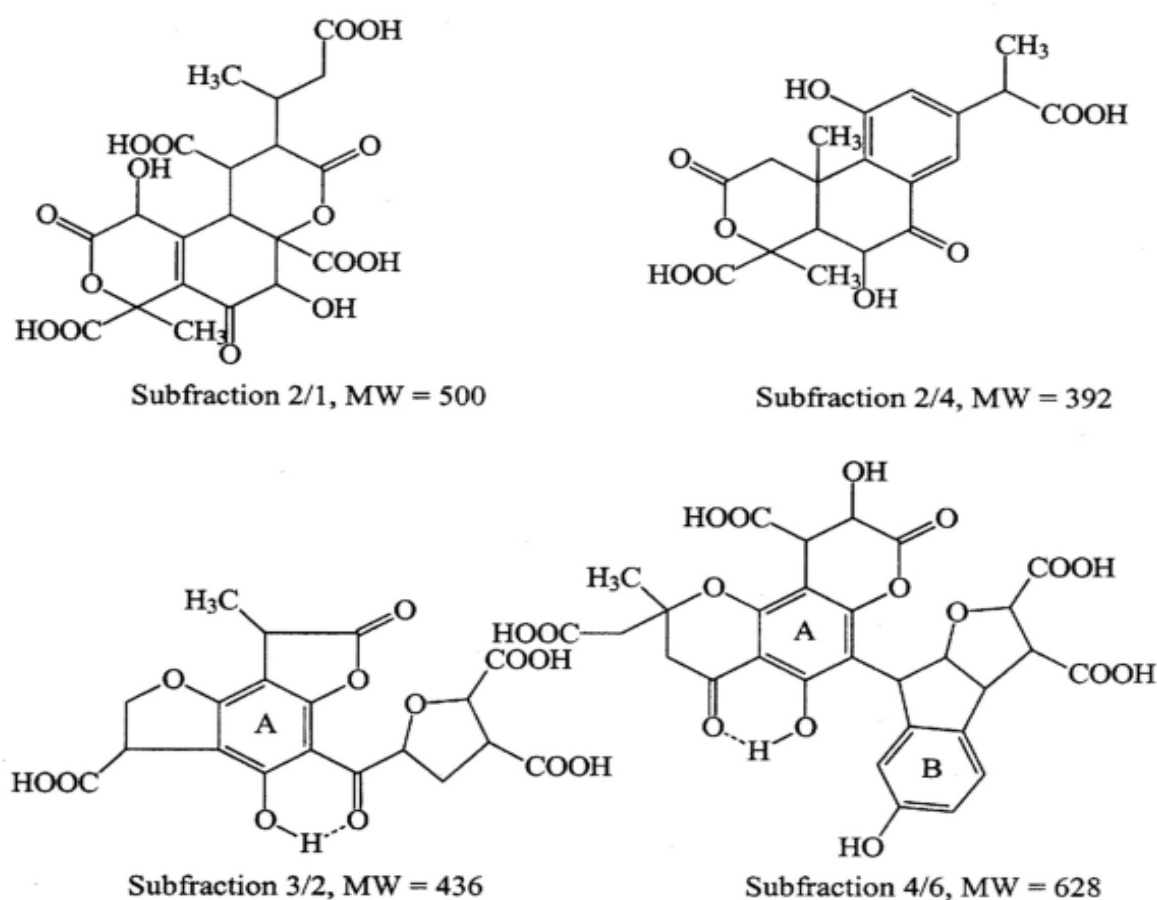
Fulvic acid are the part of humic substances that is soluble in water at all pH conditions. Fulvic acid are more soluble, smaller in average molecular weight between 500 to 2.000 Dalton (Thurman, 1985) - and more highly charged than humic acid. As stated by (Collins, et al., 1986) fulvic acid are more difficult to destabilize by aluminum coagulation dosages commonly applied in water treatment.

Fulvic acid is colored and polyelectrolytic, non-volatile organic acids. They are most soluble group of organic matter and account for 90% of the dissolved humic material in natural waters. Their presence gives color to water. Fulvic acid contain aliphatic and aromatic components, especially carboxylic and phenolic functional groups, which provide protonation and



complexation sites. As illustrated on figure 2.7, is recognized that the structure of fulvic acid contains not only a large proportion of aromatic moieties with  $-OH$ ,  $-COOH$  and other oxygen-rich groups, but also a portion of aliphatic groups. All these functional groups may result in different hydrophobicity, aromaticity and polarity of fulvic acid. The variety of interaction taking place on mineral surfaces is largely determined by the differences in the amount and reactive ability of functional groups (Li, et al., 2008).

Several studies found that negative charge of fulvic acid will increase with increasing pH (Filius, et al., 2000). This fact influences the processes of adsorption removal that highly dependent on the pH.



**Figure 2.7:** Molecular structure of Fulvic acid Suwannee River.

## 2.4 Technologies for Arsenic and Chromium Removal from Water

There are several approaches for removal of arsenic and chromium from aqueous solution and drinking water. This chapter will summarize some of the techniques that are recognized as the best available technologies for removal of arsenic and chromium.

### 1. Coagulation-Filtration

This method is known as a part of conventional water treatment processes. Coagulation with alum and Fe(III) is effective for removal of Cr(III). For removal of Cr(VI), Fe(II) is commonly used. Enhanced coagulation by addition of Fe and Al salts leads to adsorption of arsenic onto formed Fe/Al precipitates. Sedimentation/filtration is effective method for removal of As(V) and partly As(III) (Petrusevski, 2009).

### 2. Ion Exchange

Ion exchange substances are insoluble granular resins which have in their molecular structure acidic or basic radical that can be exchanged. The ions attached on these (positive or negative) radicals are replaced by ions in solution when in contact with them. For arsenic removal, strong base resin is preferable. Ion charges of resin are important on the removal processes. In the term of chromium removal, cation exchange resins are preferable for Cr(III) removal, while anion exchange resins are applied for Cr(VI).

### 3. Membrane Technologies

Membrane technologies, especially reverse osmosis, are considered as one of the best technologies for chromium removal (Sharma, et al., 2008). Reverse osmosis is carried out by applying a pressure to a concentrated solution, thus forcing water to flow across a semi permeable membranes to the dilute side.

With this technology, arsenic concentrations in the water can be reduced to 60%–90%. Effectiveness of reverse osmosis for Cr(VI) removal is classified as good (60-90% removal) to excellent (90-100% removal), and for Cr(III) it is considered as excellent (90-100% removal) (Tessema, 2004).

### 4. Adsorption

Adsorption is the binding of chemical species at the phase boundary, such as the surface of suspended particles. It has been known for a long time that if the adsorbent (solid surface) is chosen carefully and the solution chemistry is adjusted appropriately, adsorption-based processes are capable of removing metals over a wider pH range and to much lower levels than processes based on precipitation.

For arsenic and chromium removal from water, adsorption involves the use of granular adsorptive media. The processes can be carried out with or without pH adjustment and with or without spent media regeneration. Several granular adsorptive filter media have shown high effectiveness in arsenic and chromium removal from water (e.g. iron oxide coated sand, granular ferric hydroxide, activated alumina, manganese greensand etc.).



## 2.5 Adsorption Processes

Adsorption may be defined as “the process by which atom, molecules, or ions are taken up from the aqueous or gas phase and retained on the surface of solids by chemical or physical binding” (Jenne, 1998).

Adsorption processes have been known for a long time, and they are increasingly utilized to perform desired bulk separation or purification purposes. The main part of an adsorption process is usually a porous solid medium. The use of porous solid is to provide a very high surface area or high micropore volume and it is this high surface area or micropore volume that enables high adsorptive capacities of the media.

Adsorption is a process in which matter is extracted from one phase and concentrated at the surface of a second, and is properly termed a surface phenomena. Adsorption involves the inter-phase accumulation or concentration of substance at a surface or interface. The process itself 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 called adsorbate and the adsorbing phase is termed as adsorbent.

Adsorption from solution onto a solid phase occurs as the result of one of the two characteristic properties for a given solvent-solute-solid system. The driving force of adsorption may be a consequence of lyophobic (solvent-disliking) character of the solute or a high affinity of the solute for the solid. Usually on water and waste water treatment system, adsorption results from a combined action of the two forces (Sharma, 2007).

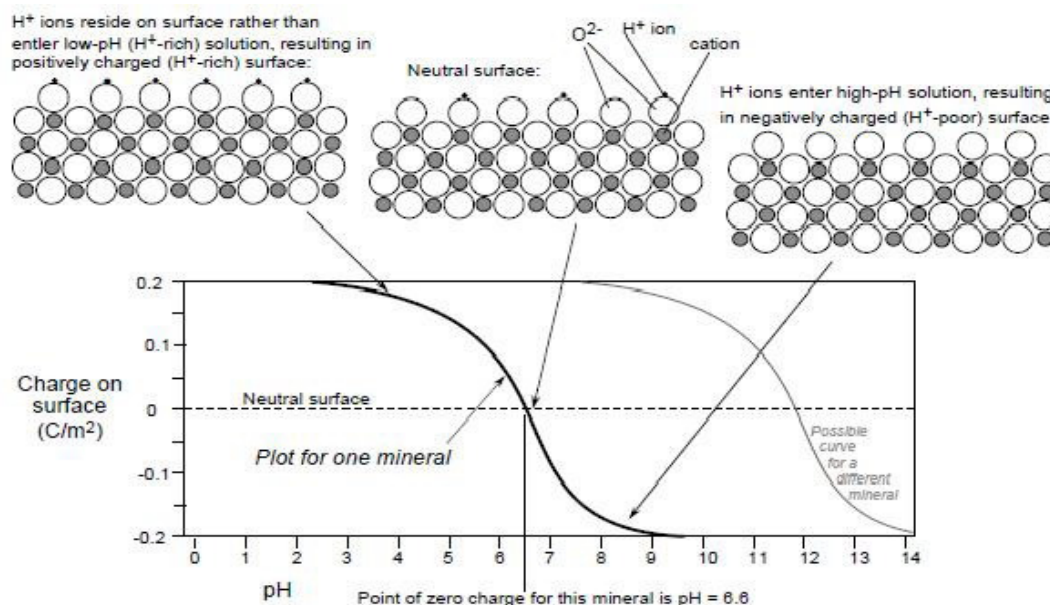
There are three types of adsorption are:

- ion exchange or exchange adsorption a process in which ions of one substance concentrate at surface of another substrate as a result of electrostatic attraction to charged sites at the surface;
- physical adsorption not site specific and it occurs due to weak forces of attraction between molecules (van der Waals forces);
- chemical adsorption a result of chemical bond that is being formed between the molecule of the solute and the adsorbent (this result in stronger bondage between molecules than is the case physical adsorption).

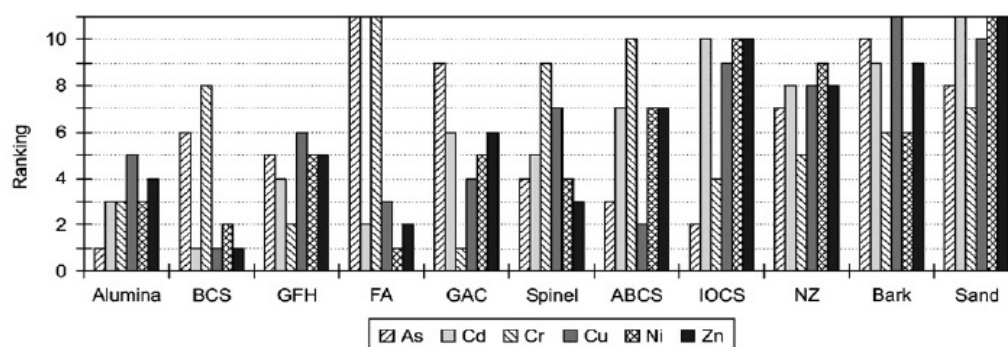
### 2.5.1 Adsorbents for Arsenic and Chromium Removal

Several types of adsorbent media have been developed to remove arsenic and chromium from water. Activated alumina, granular ferric hydroxide (GFH), iron oxide coated sand (IOCS), activated carbon, manganese-oxide coated sand, etc. are commonly used as adsorbents. Most of the solid phase in natural water contains oxide and hydroxides which will convert in to surface hydroxide groups. Most oxide found in water has a surface charge that highly influence by pH. Therefore, many of the oxides show acid-base activities thus the charge is pH dependent. Considering of the performance, cost-efficiency and availability, IOCS and GFH were selected for this research.

Furthermore, point of zero charge (pzc) of the adsorbent is an essential factor on the adsorption processes. The pH of point of zero charge is a perfect reference for predicting how the charge of adsorbent depends on pH. The pzc is the pH of the solution in chemical equilibrium with the surface in its neutralized state through adsorption of  $H^+$  and/or  $OH^-$  ions (Casamassima, et al., 1993). The processes of pzc on the adsorbent can be explained in the figure 2.8.



**Figure 2.8:** Example of point of zero charge for certain mineral.



**Ranking of the sorbents based on average  $K_d$  values (sorbents with lower rank are more effective).**

**Figure 2.9:** Ranking of the adsorbents based on average  $K_d$  values (Genç-Fuhrman, et al., 2007).

## Iron Oxide Coated Sand

Ferrihydrite (amorphous iron oxide) has been recognized as one of the most common adsorbents used in metal removal processes. IOCS is a by product from groundwater treatment plants treating water with high iron content. It is formed by coating quartz sand with ferric hydroxide, has proven to be effective for removal of chromium from wastewater effluent (Edward, et al., 1989). Figure 2.9 illustrate the virgin quartz sand and with iron oxide coating.

IOCS is formed under varying conditions, which might give it different physiochemical characteristics. As a consequence, it can have different adsorption efficiency. The characteristics of IOCS surface are physically and chemically heterogeneous and they are 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 2.1 (Bakhamis, 2009).

**Table 2.1:** 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

Several studies have proven that adsorption on IOCS is a promising method for chromium removal from drinking water (Das, 2004). IOCS shows very high removal efficiency for arsenic. The higher removal found on As(V) at low pH value (tested at pH 6) and decrease with the increases of pH value (Gebreyowhannes, 2009). The removal of arsenic shows promising with IOCS attracted negative charged anions such as arsenic and chromium. On the other hand, IOCS has low attraction for non-charged species such as nickel, zinc, copper and cadmium (Genç-Fuhrman, et al., 2007). Previous statement is supported by experiment which revealed the use of IOCS is advantageous for treatment of cadmium on urban storm water run-off (Yadav, 2007). Furthermore, IOCS can be chemically regenerated several times and reused without any significant loss of efficiency of the treatment, which makes it attractive removal method also from the costs point of view.

Chemical composition of IOCS is important to understand and predict the chemical reactions that might take place during experiments between ions and IOCS at different pH levels. The adsorption capacity of the IOCS mainly depends on the amount of iron. Adsorption capacity of the IOCS is increase dramatically with the development of iron oxide coating on the media (Sharma, 2001). Higher iron concentration in the IOCS commonly shown on the thickness of the coating. Figure 2.10 illustrate the virgin quartz sand and with coating.

**Figure 2.10:** Iron oxide coated sand and fresh sand without iron oxide coating.

## Granular Ferric Hydroxide

GFH is the most common (commercially available) ferric hydroxide filter. It is produced by neutralization and precipitation of ferric chloride. It has grain sizes between 0.2-2.0 mm, high porosity and high surface area (table 2.2). GFH was reported to be efficient adsorbant for arsenic removal, its adsorption capacities ranging between 1-10 g As/kg adsorbent. It also has 5-20 times longer life time in comparison to activated alumina, which makes is costly-wise attractive (Petrusevski, 2009). Figure 2.11 shows physical appearance of GFH.

**Table 2.2:** Example of physiochemical characteristics of GFH

Grain size (mm)	Surface area (m <sup>2</sup> /g)	pH <sub>zpc</sub>	Porosity (%)	Moisture content (%)	Bulk density (g/cm <sup>3</sup> )
0.2-2.0	280	7.5-8.0	75-80	43-48	1.32

Experiments have been carried out to learn about GFH performance in the adsorption processes. Batch adsorption results showed that Cr(III), Cr(VI) and Cu can be removed effectively with GFH. It was found that GFH is more efficient for Cr(VI) removal than Cr(III). Removal of Cu with GFH is more effective than with IOCS. On the other hand, there was no removal of Cd with GFH, whereas it can be removed with IOCS (Yadav, 2007). Similar result showed on the experiment on the removal Cu and Cd from urban storm water. Cd poorly adsorbed by GFH, but better removal showed on Cu (Bakhamis, 2009). GFH is the second most effective sorbent for Cr, out-performed only by GAC, but it is also effective for Ni and Zn removal. GFH is the third most effective sorbent when ranked according to average  $K_d$  values (Genç-Fuhrman, et al., 2007) see above figure 2.9 in page 15.



**Figure 2.11:** Granular Ferric Hydroxide (GFH).



### 2.5.2 Adsorption Isotherm

In adsorption modeling, the distribution of adsorbate between the two phases (the bulk solution and the adsorbent) is often described in terms of isotherms. The presentation of amount of solute adsorbed per unit adsorbent as a function of the equilibrium concentration of the solute in the bulk solution, at a constant temperature is called the adsorption isotherm (Sharma, 2007). It can be expressed as:

$$q = f(C_e) \quad (8)$$

Where:

$q$  ..... amount of adsorbate per unit of adsorbent

$C_e$  ..... equilibrium concentration of the solute in the bulk solution

The most common isotherms are Freundlich, Langmuir, and BET (developed by Brunauer, Emmet and Teller) isotherm.

#### Freundlich Isotherm

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energy (Faust, et al., 1998). This isotherm equation widely used mathematical description of adsorption in aqueous system, describe as:

$$x/m = KC_e^{1/n} \quad (9)$$

Where:

$x$  ..... amount of solute adsorbed

$m$  ..... the weight of adsorbent

$C_e$  ..... equilibrium concentration of the solute ( $\text{g/m}^3$ )

$K, 1/n$  ..... isotherm constant ( $K$  = adsorption capacity and  $1/n$  = adsorption intensity)

On linearisation, the equation takes the form:

$$\log q = \log K + 1/n \log C_e \quad (10)$$

As the Freundlich equation indicates, the adsorptive capacity  $x/m$  is a function of the equilibrium concentration of the solute. Therefore, higher capacities are obtained at higher equilibrium concentrations (Faust, et al., 1998). The Freundlich isotherm has advantages because of its characteristics as an empirical expression, mathematical description of adsorption in aqueous system, also in the reasons of heterogeneity and therefore it is more applicable to the real systems. This equation is applicable for multi layer adsorption.

#### Langmuir Isotherm

This isotherm assumes that maximum adsorption corresponds to a saturated monolayer of the solute on the adsorbent surface, that the adsorption energy is similar at all the sites, and that there is no transmigration of adsorbate in the plane of surfaces (Sharma, 2007) or interaction with neighboring molecules (Faust, et al., 1998). The Langmuir adsorption isotherm is expressed as:

$$X = X_m b C_e / (1 + b C_e) \quad (11)$$

Where:

$X$  .....  $x/m$ , the amount of solute adsorbed ( $x$ ) per unit weight of adsorbent ( $m$ )

$C_e$  ..... equilibrium concentration of the solute ( $\text{g/m}^3$ )

$X_m$ ..... amount of solute adsorbate per unit weight of adsorbent required for monolayer capacity

$b$  ..... a constant related to the heat of adsorption  $Q$

The monolayer capacity  $X_m$  determined from the Langmuir isotherm defines the total capacity of the adsorbent for a specific adsorbate. Also, it might be used to determine the specific surface area of the adsorbent by utilizing a solute of known molecular area (Faust, et al., 1998).

### **BET Isotherm**

As mentioned above, Langmuir isotherm is valid for single layer. Brunauer, Emmet and Teller extended the Langmuir model from monolayer to include multiplayer adsorption phenomena. It can be used for the same phase adsorption process (Sharma, 2007). BET isotherm can be expressed:

$$q/q_m = BC_e / ((C_e - C_0)[(1 + (B - 1)(C_e/C_s))]) \quad (12)$$

Where:

$q_m$  ..... maximum adsorption capacity (g/g)

$B$  ..... a dimensionless constant

$C_e$  ..... equilibrium concentration of the solute (g/m<sup>3</sup>)

$C_s$  ..... saturation concentration of the adsorbate

BET isotherm can be linearized as:

$$C_e / (C_s - C_e)q = 1/Bq_m + [(B - 1/Bq_m) (C_e/C_s)] \quad (13)$$

To explain the isotherm, it can be simply by considering that the free energy of adsorption increases lineary with the (log of the) concentration of adsorbate (Morel, 1983).

### **2.5.3 Kinetic Adsorption**

Regardless adsorption isotherm, there is another approach to describe the adsorption rate and confirm the reaction mechanism of heavy metals on adsorbents. Adsorption mechanisms involving kinetics-based models have been reported, numerous kinetic models have described the reaction order of adsorption systems based on solution concentration. Two kinetic models can be applied to the experimental data is Pseudo-first order equation proposed by Lagergren and Ho's second order expression. Lagergren's first order rate equation is the earliest known one describing the adsorption rate based on the adsorption capacity. It can be expresses to a linear form (Ho, 2006):

$$\log(q_e - q_t) = \log q_e - K_t/2.303 \quad (14)$$

Where:

$q_e$  ..... the mass of metal adsorbed at equilibrium (mg/g)

$q_t$  ..... the mass of metal adsorbed at any time  $t$  (mg/g)

$K_t$  ..... rate constant (mg/g-d)

The simple linear equation of a pseudo-second order (PSO) model for the analysis of adsorption kinetic data has been deduced by Ho and McKay (Wu, et al., 2009). The rate of pseudo-second order may be dependent on the amount of metals in the solution and amount metal ions adsorbed at equilibrium. It expressed as in equation below.

$$t/q_t = 1/h + t/q_e \quad (15)$$

$$h = k_2 q_e^2 \quad (16)$$

Where:

$h$  ..... initial rate of adsorption as  $t$  approaches zero (mg/g-d)

$q_e$  ..... amount of metal ion adsorbed at equilibrium (mg/g)

$q_t$  ..... amount of metal ion adsorbed at any time  $t$  (mg/g)

$k_2$  ..... pseudo-second order rate constant (g/mg hr)

The rate of a reaction is described as the change in concentration of a product per unit time. The pseudo-second order model constants can be determined experimentally by plotting  $t/q_t$  against  $t$ . Nevertheless, the pseudo-second order equation has advantage which is does not have a difficulties to assigning on the effective adsorption capacity. It mean, by using this model is that there is no need to know the equilibrium capacity from the experiments, as it can be calculated from the model (Ho, 2006). As stated by Wu et al., 2009, the pseudo-second order model was suitable for the adsorption of lower molecular-weight adsorbates on smaller adsorbent particles (Wu, et al., 2009).

## 2.5.4 Competitive Adsorption

The adsorption of arsenic and chromium is a complicated process of the interrelationship between ions, pH, the concentration of arsenic, concentration of chromium, and the presence of competing ions in the water. The presence of other (competitive) ions in water should be considered during the removal of arsenic and chromium from water because they may influence the adsorption efficiency. For simplicity, research has been mainly carried out on singles single ion systems, but arsenic contaminated water always contain more ions (multi component system), that are likely to affect the efficiency of adsorption (Mohan, et al., 2007).

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. The presence of phosphate, sulphate, carbonate, silica, and other ions have been shown to decrease adsorption of arsenic to varying degree depend on pH and their concentration presence in water. The presence of calcium and sulfate ions decreases adsorption of both As(III) and As(V). Adsorption capacity of arsenic decreases significantly in the presence of calcium and sulfate ions in higher and lower pH respectively (Gebreyowhannes, 2009).

The molecular weight (MW) of NOM constituents is a critical property that affects the competition between NOM and trace compounds. NOM components of different MW have been shown to have different effects on trace organic compound adsorption (Li, et al., 2003). Different effects of NOM components are related to the pore size distribution of the carbon. This was explained by the experiment that was carried out with 4 types of activated carbon fibers with different pore size distributions. From the research it was found that the molecular size of competing compounds relative to the pore size distribution of activated carbon determined whether and how the competing compounds affected the adsorption (Pelekani, et al., 1999). Direct site competition only happens in pores that are accessible to both NOM and the trace organic compound (Li, et al., 2003). Different fractions of NOM (with varying molecular weight and hydrophobicity) are adsorbed by iron oxide with different affinity and capacity (Gu, et al., 1995).

Furthermore, apart from competitive adsorption, preloading is known as an important factor in the adsorption process especially on activated carbon. Preloading identified to cause a decrease in adsorption capacity and the mass transfer rates (external and internal) of adsorbate on and into adsorbent. The reduces of external mass transfer could be caused by: (i) a formation of a zone on the external surface of adsorbent that has high resistance to the rate of transport of adsorbate or (ii) reduction of effective external surface area of adsorbent available for adsorbate (Orlandini, 1999). Previous research has shown that the adsorption capacity of preloaded GAC for a target compound is lower than the adsorption capacity of fresh GAC, time of preloading determine the its adsorption capacity (Knappe, et al., 1997). Orlandini (1999) showed that, preloading with background organic matter (BOM) from pretreated Rhine River water was shown to speed up the breakthrough of atrazine, but at the same time reduces the adsorption capacity of the adsorbent (Orlandini, 1999).

There are studies reported about the effect of fulvic acid on the adsorption processes. For mercury and cadmium adsorption on goethite, the presence of fulvic acid increased mercury adsorption substantially in the whole pH range studied. On the other hand, for cadmium it was found that the presence of fulvic acid can either increase or decrease its adsorption, depending on the pH range (Bäckström, et al., 2003). But, generally the adsorption is lower when fulvic acid is present compared to when fulvic acid is absent (Filius, et al., 2000).



### 3. MATERIALS AND METHODS

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

#### 3.1 Materials

##### 3.1.1 Adsorbent

For this research, iron oxide coated sand and granular ferric hydroxide were used as adsorption material.

- Iron Oxide Coated Sand (IOCS) was obtained from the Brucht groundwater treatment plants.
- Granular ferric hydroxide (GFH) was obtained from producer (GEH Wasserchemie Osnabruck) Germany.

For batch adsorption experiments, pulverized IOCS and GFH with grain size  $<63\ \mu\text{m}$  were used. After grinding, bulk adsorbent was sieved to get the required fraction. On this research, total weight of IOCS was used rather than total volume. Grinded fraction of IOCS, contains all of the IOCS components including the sand grain. Especially for IOCS, sieving and grinding also helps to homogenize the adsorbents since IOCS is not as homogenous as GFH.

##### 3.1.2 Chemicals

For research purposes, the composition of model water will be adjusted to meet specific parameter. The following table shows chemicals and reagents used in this research:

**Table 3.1:** Chemical and reagents used for the research.

Chemical	Concentration	Experiment
Standard As (V) solution	1000 mg/l	Individual and/or combination adsorption of As(V)+FA
Potassium dichromate ( $\text{K}_2\text{CrO}_7$ ) solution	100 mg/l	Individual and/or combination adsorption of Cr(VI)+FA, colorimetric method for determination of Cr(VI)
Fulvic acid solution (Suwannee river)	100 mg/l	Combination and/or Individual adsorption of FA
Sodium bicarbonate ( $\text{NaHCO}_3$ )	100 mg/l	All experiments except characterization of IOCS
Sodium hydroxide (NaOH) solution	1 M	All experiments except characterization of IOCS
Nitric acid ( $\text{HCO}_3$ ) solution	1 M	All experiments except characterization of IOCS
Nitric acid conc.	65-70% $\text{HNO}_3$	Stabilization, adsorption experiments (acidify)
Nickel nitrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$	-	Matrix modifier for As(V) analysis by AAS-GF
Magnesium nitrate $[\text{Mg}(\text{NO}_3)_2]$ in 1% $\text{HNO}_3$	-	Matrix modifier for Cr(VI) analysis by AAS-GF
Diphenylcarbazide solution	5 g/l of acetone	Reagent for colorimetric method for determination of Cr(VI)

Chemical	Concentration	Experiment
Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution	0.1 M	Colorimetric method for determination of Cr(VI)
Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) conc.	-	Colorimetric method for determination of Cr(VI)
Demineralized water	-	All experiments

### 3.1.3 Model water

Model water was prepared by mixing demineralized water and the required amount of sodium bicarbonate ( $\text{NaHCO}_3$ ) to get the presence of 100 mg/l of  $\text{HCO}_3^-$ . For the adsorption isotherm experiment, the initial arsenic, chromium and FA concentration is described in Table 3.2.

**Table 3.2:** Composition of model water.

Parameters	Model water	Unit
Temperature	20	$^{\circ}\text{C}$
pH	6, 7, 8	-
As (V)	0.2 and 2	mg/l
Cr (VI)	0.2 and 2	mg/l
Fulvic acid	0, 2, 5	mg/l
Bicarbonates	100	mg/l
Sodium	37	mg/l

### 3.1.4 Stock solutions

Stock solution containing 100 mg/l of Cr(VI) was prepared from potassium dichromate ( $\text{K}_2\text{CrO}_7$ ). Stock solution for FA was prepared from powdered Suwannee River fulvic acid with concentration 100 mg/l. For pH adjustment, 1 M of  $\text{HNO}_3$  were prepared from conc.  $\text{HNO}_3$  solution (contain 65-70% of  $\text{HNO}_3$ ) and 1 M NaOH from powdered NaOH ( $M=40$  gr/mol).

### 3.1.5 Equipment

Water quality analysis can be done by measurement of several parameters with specific tool. The following table describe the equipments were used for laboratory analysis:

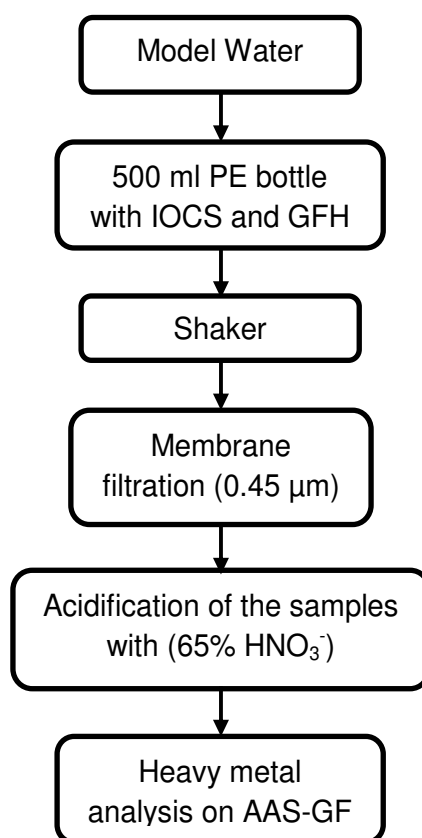
**Table 3.3:** List of equipments used for the research.

Equipment	Utility
Atomic Absorption Spectrometer- Flame (AAS-Flame)	Measurement of Fe, PO, Mn etc.
Atomic Absorption Spectrometer- Graphite Furnace (AAS-GF)	Measurement As(V) and Cr(VI)
Electronic balance	Weighting the chemical used
Erlenmeyer glass	Characterization of IOCS
Magnetic stirrer	Preparing model water
Measuring silinder	Preparing model water
Membranes filters 0.45 $\mu\text{m}$ sizes & holder	Sampling and separation of solid-liquid
pH meter	pH measurement

Equipment	Utility
Polyethylene bottles of 500 ml capacity	Batch experiments
Rotary mechanical shaker	Batch experiment
Sieve (Frisch analysette 3pro)	Sieve analysis
Spectrophotometer	Measurement organic matter
Total organic carbon analyzer	Measurement organic matter
Various sizes of pipettes	Preparing model water, dilution
Volumetric flask/beakers	Preparing model water, dilution

### 3.2 Experimental Methods (Screening Experiments)

This section describes the experimental methods in the study. Separate set of batch adsorption screening experiment was done using IOCS and GFH to assess the effectiveness As(V) and Cr(VI) removal by selected adsorbent at a pH of 6, 7 and 8. Figure 3.2 describes how the experiment was conducted.



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

### **3.2.1 Stability of Cr(VI)**

The objective of the experiment was to verify whether Cr(VI) is stable or will reduce to Cr(III) in the absence and present of fulvic acid. This experiment was carried out simply by preparing model water containing Cr(VI) with and without fulvic acid at pH 6, 7, 8 than kept it in the 500 ml PE bottles. The bottles were put on the shaker and sampling was done at 0, 2, 4, 6, 8 and 24 hours. Samples for measurement Cr(VI) by AAS-GF were immediately acidified with concentrated HNO<sub>3</sub>. Analysis for total Cr and Cr(VI) concentration with proposed equipment was conducted immediately to prevent changes in the chemical composition. Reduction of Cr(VI) to Cr(III) was determine by calculating the differences of measured total Cr and Cr(VI) concentration.

### **3.2.2 Short-Term Batch Experiments**

The purpose of the experiment was to investigate the effect of FA and pH on the As(V) and Cr(VI) removal by IOCS and GFH after 24 hour contact time. Demineralized water was used for the experiment with addition of certain chemical compounds (see tables 3.1, 3.2, 3.4). Sampling was done with syringe combined with 0.45 µm membrane filter at time intervals 0, 2, 4, 6, 8 and 24 hours. For metal adsorption, samples were immediately acidified and samples for FA adsorption were kept at low temperature in the refrigerator.

### **3.2.3 Long-Term Batch Experiments (adsorption isotherm)**

The purpose of the experiment was to examine the effect of FA in the adsorption capacity of the adsorbent for As(V) and Cr(VI). Experiments were carried out for several days to weeks until the equilibrium concentrations were reached. Demineralized water was used for the experiment with addition of certain chemical compounds (see tables 3.1-3.2 and 3.4).

Model water was kept in 500 ml PE bottles with fixed amount of studied heavy metal, well capped and placed on the mechanical shaker (circular movement) with varied amounts of IOCS and GFH. Sampling was done with syringe combined with 0.45 µm membrane filter for certain time interval until  $C_e$  was established. Concentrated HNO<sub>3</sub> was added to acidify the samples. On the other hand, for FA isotherm samples were kept under low temperature to prevent biological activity before measurement. All the experiments were done in duplicate at a room temperature of 20±2°C.

**Table 3.4:** Experimental set up for the batch experiment.

Component	Concentration [µg/l]	pH	FA (mg/l)	Absorbent	
				IOCS (g/l)	GFH (g/l)
Short Therm Batch Exp. Individually					
Cr(VI)	200	6,7,8	-	0.02	0.02
As(V)	200	6,7,8	-	0.02	0.02
Fulvic acid	2000	6,7,8	-	0.02	0.02
Short Therm Batch Exp. Combination					
Cr(VI)	2000	6,7,8	0, 2, 5	0.2	0.2
As(V)	2000	6,7,8	0, 2, 5	0.2	0.2
Long Therm Batch Exp. Adsorption Isotherm					
Cr(VI)	200	7	5	0.2, 0.5, 1, 2, 5, 10	0.2, 0.5, 0.75, 1, 1.5, 2
As(V)	200	7	5	0.2, 0.5, 1, 2, 5, 10	0.2, 0.5, 0.75, 1, 1.5, 2

### 3.2.4 Adsorption of metals with preloaded GFH with FA

The purpose of this experiment was to find out the performance of the adsorbent to remove metals after preloaded with 5 mg/l of FA for 24 days.

Demineralized water was used for the experiment with addition of certain chemical compounds. Experiment with duration of 24 hours using model water of FA adsorption isotherm experiment after the equilibrium concentration ( $C_e$ ) established. Model waters with initial FA concentration 5 mg/l at pH 7 and the dosage of adsorbent 20, 50, 75, 100, 150, and 200 mg/l were spiked with As(V) or Cr(VI) stock solution with concentration 0.2, 0.5, 0.75, 1, 1.5, and 2 mg/l respectively. Sampling was done at time intervals 0, 2, 4, 6, 8 and 24 hours to analyze the residual concentration of metals.

### 3.2.5 Sampling procedures

Appropriate amount of samples were collected by syringe through the prepared tubes at 500 ml PE bottles and were filtered through 0.45 µm Whatman membrane filter to separate solid from liquid (see figure 3.1). The sample was first drawn into the syringe using Silicon tubing. The silicon tubing was then removed and replaced with a filter holder in which a 0.45 µm filter was loaded. To rinse the filter, approximately 1 ml of the sample was passed through the filter and discarded. The remaining sample was passed through the filter directly into plastic sampling bottle. To maintain the heavy metal solution remain in the dissolved form, few drop of concentrated nitric acid ( $\text{HNO}_3$ ) was immediately added to acidify the samples.

For model water that contains fulvic acid, membranes must be soaked in the MilliQ water for > 24 hr and 3 times water changes to eliminate the influence of the membranes to the model water.



**Figure 3.2:** Syringe combined with filter holder and 0.45 µm filters.

### 3.2.6 Preserving the samples

On the metals adsorption, samples were immediately acidified for preservation purposes. Acidification were important to maintain metal in the solution remain in the dissolve form. After acidification, sample can be stored for months before measurement.

Different with the metal, organic matter cannot well preserved by acidification. Samples for FA adsorption were kept under low temperature in the refrigerator or freezer. In the refrigerator, sample can be preserved for a week before measurement. On the other hand, sample can be use after a months or even years under freezing temperature.

### 3.2.7 Preparation of samples for measurements

In some cases, samples could not be measured directly with the available equipment. Equipment used for this research has concentration detection limit. Therefore, before the measurement we have to know the approximate concentration of our samples. If expected concentration of measured samples is above the concentration limit we have to dilute the sample to get preferred concentration (below detection limit).

In this experiment, measurements were conducted for metals and organic matter. For metals, dilution was carried out with the mixture of certain amount of samples with acidified demineralized water to get the solution under  $\text{pH} < 2$  (as a requirement for the AAS-GF measurement). However, for the measurement of organic matter dilution was done simply by demineralized water.



### 3.2.8 Shaking Speed

Batch adsorption experiments were done using rotary mechanical shakers at shaking speed of 100 rpm as shown in figure 3.3. It was assumed that the applied shaking speed allows all the surface area of the adsorbent to come in contact with heavy metals ions during the experiments. For this research, sampling was carried out at appropriate time intervals to assess the adsorption processes during the time of the experiment.



**Figure 3.3:** Rotary mechanical shaker.

## 3.3 Analytical Methods

### 3.3.1 Equilibrium Calculation

Equilibrium calculations were done using PHREEQC-2 Interactive software for Windows. It is a computer program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations.

PHREEQC can be used as a speciation program to calculate saturation indices and the distribution of aqueous species. Analytical data for mole balances can be defined for any valence state or combination of valence states for an element. Distribution of redox elements among their valence states can be based on a specified  $pe$  or any redox couple for which data are available. PHREEQC allows the concentration of an element to be adjusted to obtain equilibrium (or a specified saturation index or gas partial pressure) with a specified phase. Solution compositions can be specified with a variety of concentration units (Parkhurst, et al.). In this study, equilibrium calculation, were performed with PHREEQC to predict the final concentration of metals that will be in solution at equilibrium. This program with the specific database was also used to predict species distribution in the solution, dominant complexed of metals formed and the saturation indices of the compounds formed in the model water.

### 3.3.2 Extraction of IOCS Coating

The purpose of this experiment is to find out the chemical composition of IOCS. The IOCS used for experiments was from the Brucht water treatment plant.

The following procedures were carried out:

1. 0.5 gm of IOCS sample was weighted.
2. Solution of 10 ml  $\text{HNO}_3$  and 40 ml demineralized water was prepared in 50 ml erlenmeyer flask.
3. Weighted IOCS was sample added to the solution.
4. Sample was mixed, then boiled at a temperature about  $250^\circ\text{C}$  for about 3 hours.
5. After cooling, the solution was diluted in the 100 ml vol. flask with demineralized water.
6. The solutions were kept for 24 hours for the settling of particles.
7. Standard solutions were prepared to establish calibration lines for the analysis.

Figure 3.4 shows several equipments used for the characterization of IOCS coating.



[A]



[B]



[C]



[D]

**Figure 3.4:** [A] AAS-Flame for measurement of Iron, Manganese, Magnesium, Calcium; [B] AAS-GF for Arsenic; [C] Inductively coupled plasma (ICP) for Silica; and [D] Spectrophotometer for Phosphate.



### 3.3.3 Metals analysis As(V) and Cr(VI)

For metals analysis, AAS-GF Perkin-Elmer 1100B with HGA 300 programmer was used (see figure 3.5). For As(V), the calibration line was in the range of 0-50  $\mu\text{g/l}$  and for Cr(VI) 0-30  $\mu\text{g/l}$ .



**Figure 3.5:** Atomic Adsorption Spectrometer-Graphite Furnace (AAS-GF).

### 3.3.3 NOM characterization

For NOM measurement, spectrophotometer (Perkin Elmer Lambda 20 1.11) and TOC analyzer (SHIMADZU TOC-VCN analyzer) were used as shown in figure 3.6. For samples measured with spectrophotometer, standard solutions were prepared to establish the calibration line (for this experiment in the range of 0-5 mg/l). On TOC analyzer, concentration of organic matter was measured directly.



[A]



[B]

**Figure 3.6:** [A] Spectrophotometer; [B] TOC Analyzer.



## 4. RESULTS AND DISCUSSION

This chapter presents the result of experiments carried out during the research.

### 4.1 Extraction of IOCS coating

The chemical composition of IOCS is presented in table 4.1.

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

Composition	Concentration	Unit	%
Arsenic	0.67	µg/g	0.07
Calcium	12.33	mg/g	1.23
Iron	324.50	mg/g	32.45
Magnesium	0.26	mg/g	0.03
Manganese	1.57	mg/g	0.16
Organic Matter	171.03	mg/g	17.10
Oxygen	182.53	mg/g	18.25
Phosphorus	19.48	mg/g	1.95
Sand	54.16	mg/g	5.42
Silica	2.17	mg/g	0.22
Other compounds	231	mg/g	23.10
<b>Total</b>	<b>1000</b>		<b>100</b>

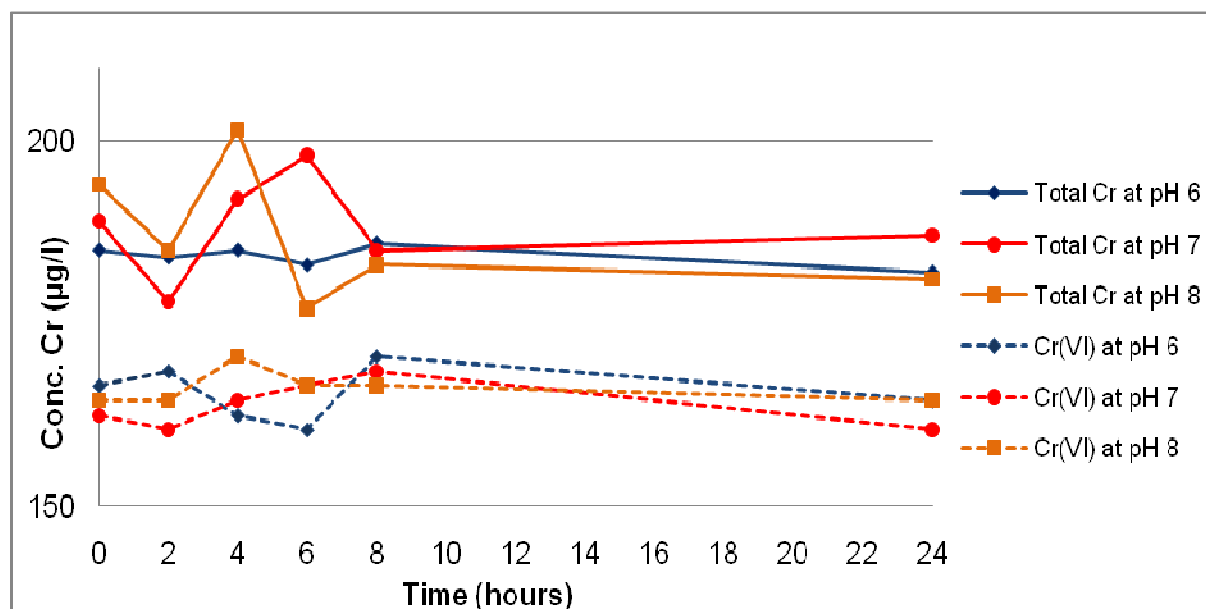
From the table 4.1 it can be seen that IOCS from WTP Brucht had a very high iron content of 324.5 mg/g IOCS, which is about 32% of the total IOCS composition. The second most dominant compound is oxygen with 182.5 mg/g of IOCS and followed by organic matter with 171 mg/g of IOCS. Concentration of oxygen in the IOCS was calculated by its chemical composition as FeOOH (goethite). Surprisingly, organic matter took a significant portion in the IOCS composition. It is likely that organic matter is present in the IOCS because IOCS was produced in the groundwater treatment plant which has high concentration of NOM. And this abundant amount of organic matter might be a result of intense contact time of IOCS with the groundwater which contains NOM (natural formation of IOCS takes years).

About 77% of the total composition of IOCS has been analyzed. There are several other compounds contained in the IOCS that were measured (table 4.1), but, there are also around 231 mg/g of IOCS of compounds that were not identified. It is quite difficult to get complete chemical composition of the IOCS, because it depends on several factors (such as contact time and the quality of treated groundwater), and can therefore differ for different IOCS samples.

## 4.2 Stability of Chromium (VI)

### 4.2.1. Stability of Cr(VI) in the absence of Fulvic acid

Figure 4.1 shows total chromium and Cr(VI) results as measured with GF-AAS and spectrophotometer, respectively, from the short-term batch experiment carried out to determine stability of Cr(VI) in the **absence** of fulvic acid.



**Figure 4.1:** Stability of Cr(VI) in the absence of fulvic acid at pH 6, 7, and 8. Model water: concentration of Cr(VI) = 200 µg/l,  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed: 100 rpm.

Figure 4.1 presents results obtained from the short batch experiment, and it shows that there are differences in the measured concentrations of total Cr and Cr(VI). Total Cr and Cr(VI) were measured on different machines and with different methods. Unlike total Cr measured on the AAS-GF, measurements of Cr(VI) on spectrophotometer involve addition of several chemical compounds. There is a possibility that Cr(VI) is not stable in the solution because of its solubility. Therefore, different concentration measured at 0 hr for each pH is possible. Those factors might be the reasons of the concentration differences. At 24 hrs experiment, the differences between total Cr and Cr(VI) are noticeable, namely 10%, 10%, 8% at pH 6, 7, and 8, respectively.

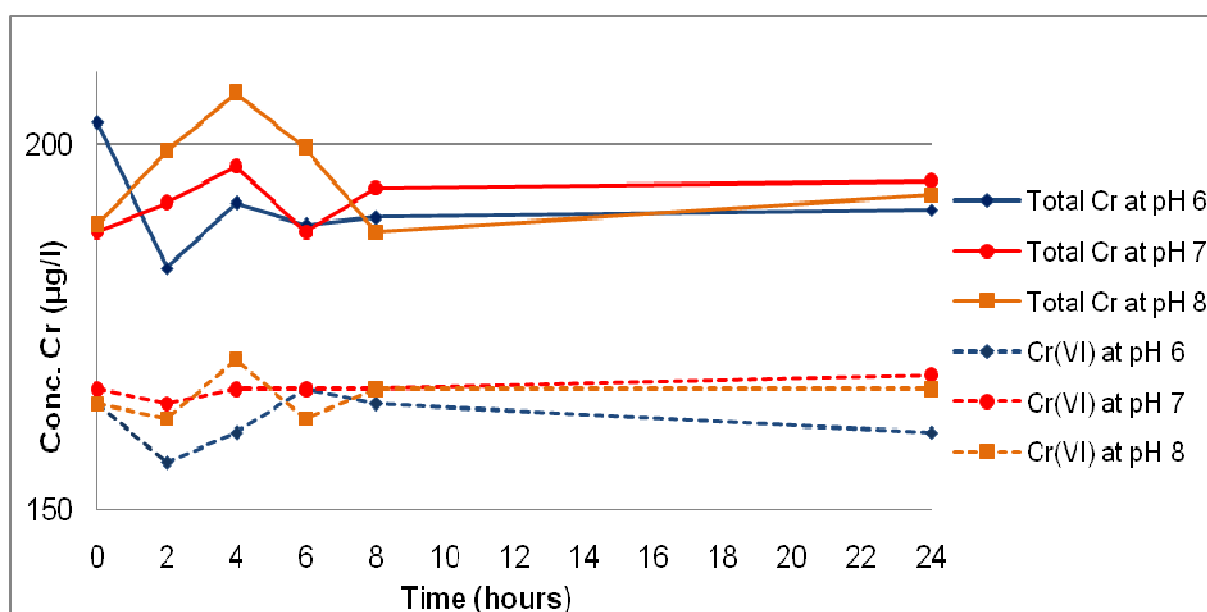
There are variations in concentrations of samples taken between 0 hr to 8 hr. Sampling was carried out at 0, 2, 4, 6, 8, and 24 hrs. Because of instability of Cr(VI) in the solution, the concentration of Cr(VI) might be varying during sampling periods. Mistakes during preparation of samples and execution of the measurement were likely to contribute to this occurrence.

AAS-GF measures all forms of Cr in the samples, whether it is Cr(III) or Cr(VI). Therefore, the concentrations of total Cr were supposed to be stable during 24 hr. As seen from the results, total Cr concentration is quite stable at all tested pH values, even though insignificant decreases are showing in the measurement. Possibility of precipitated Cr(VI) is overruled, which was confirmed with the results from PHREEQC computer program. Contamination or mistake during the preparation of the samples might be the reason for this occurrence.

From the results obtained, it cannot be concluded, that the difference between the concentration of total Cr and Cr(VI) is Cr(III). The assessment focuses on the established pattern in figure 4.1. The possibility of Cr(VI) to Cr(III) reduction was assessed simply by the concentration differences at 0 hr and 24 hr. From the result it can be seen that there are very slight differences of Cr(VI) measured at 0 hr and 24 hr, 1% at pH 6 and stable at pH 7-8. Thus, from this expression it is possible to assume that there is no reduction of Cr(VI) to Cr(III) during 24 hrs. Therefore, it is reasonable to conclude that Cr(VI) was stable as a function of pH and time in the absence of fulvic acid.

#### 4.2.2. Stability of Cr (VI) in the presence of Fulvic acid

Similar experiment as above was carried out also to determine stability of Cr(VI) in the **presence** of fulvic acid. Also in this case, total chromium and Cr(VI) from short-term batch experiment were measured with GF-AAS and spectrophotometer, respectively. Results are given in figure 4.2.



**Figure 4.2:** Stability of Cr(VI) in the presence of fulvic acid at pH 6, 7, and 8. Model water: concentration of Cr(VI) = 200 µg/l, fulvic acid = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed: 100 rpm.

Similar as the previous experiment, also the results shown in figure 4.2 show differences between the concentrations of total Cr and Cr(VI). Similar conclusions can be made also in this case. The differences could be due to instability of Cr(VI) in the solution and possibility of mistakes during the sampling and preparation for the measurement.

Different from the previous experiment are results of total Cr at pH 6, showing some reduction during 24 hrs. But, with the same reasons as earlier experiment, the concentration of total Cr should be constant during 24 hrs. Therefore, contamination of the sample and errors during the measurement might be the reasons of this happening. On the other hand, at pH 7 and 8 the concentration of total Cr seem to be stable during 24 hr experiment.

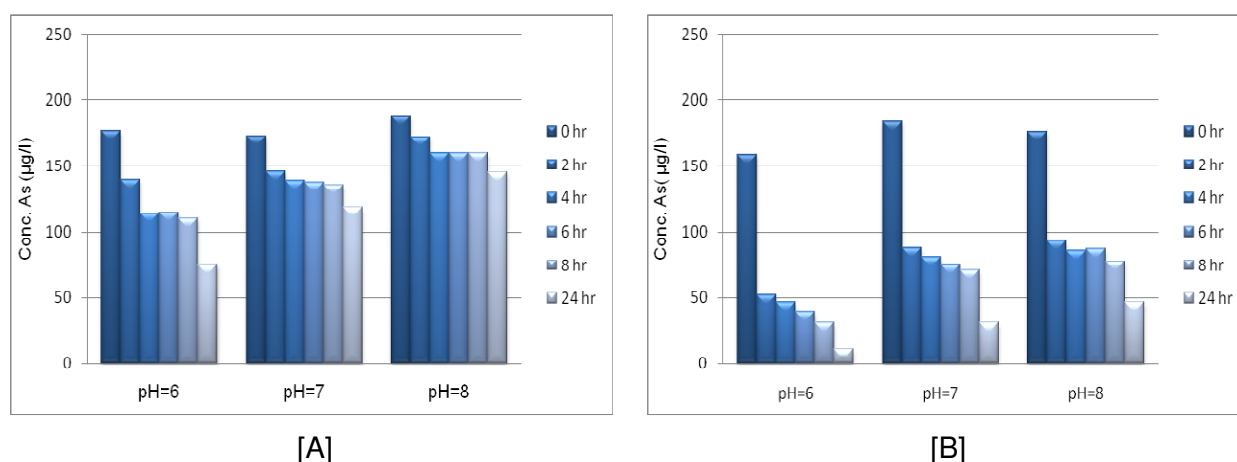
Different pattern was found for the measurement of Cr(VI). At all tested pH values, the concentration of Cr(VI) was relatively stable for 24 hrs of experiment duration. Small reduction only occurred at pH 6, the concentration of Cr(VI) was reduced 2% during 24 hrs, but stable at pH 7-8. From this result it can be assumed that at all tested pH value, the presence and absence of FA did not influence the reduction of Cr(VI) to Cr(III).

### 4.3 Short-term Batch Experiments

Batch experiments with iron oxide based adsorbents were carried out with model water containing either As(V), Cr(VI), FA, or a combination of either metal with FA.

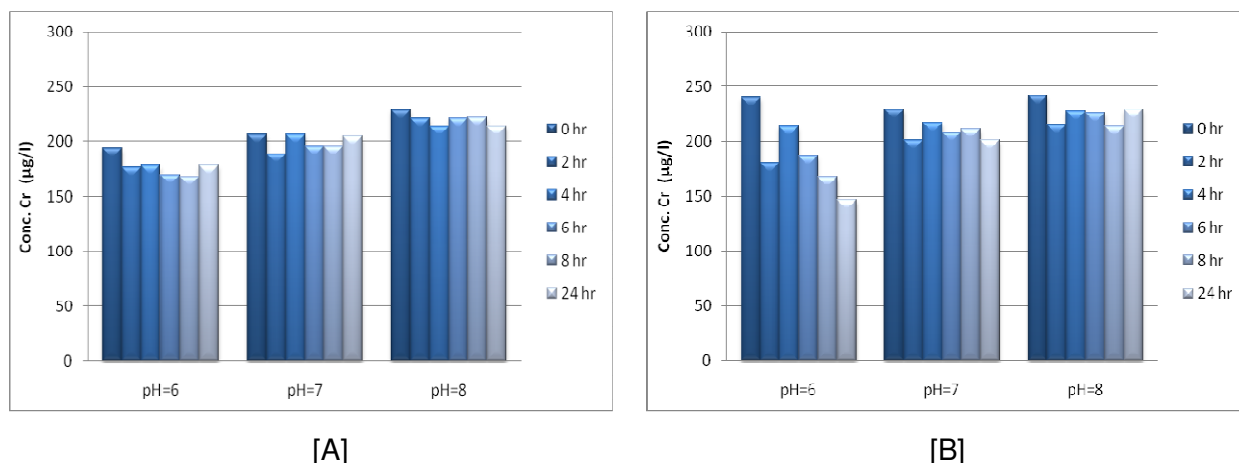
#### 4.3.1. Individual adsorption of Cr(VI), As(V), and FA by IOCS and GFH

Experiments with different types of model water containing As(V) or Cr(VI) and FA at pH 6, 7, and 8 were carried out. Adsorption efficiencies of IOCS and GFH for As(V), Cr(VI), and FA as a function of pH are shown in figures 4.3-4.5.



**Figure 4.3:** Removal of As(V) at pH 6, 7 and 8. Model water: initial conc. of As(V) = 200 µg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 20 mg/l. Shaker speed: 100 rpm. [A] Adsorption on IOCS; [B] adsorption on GFH.

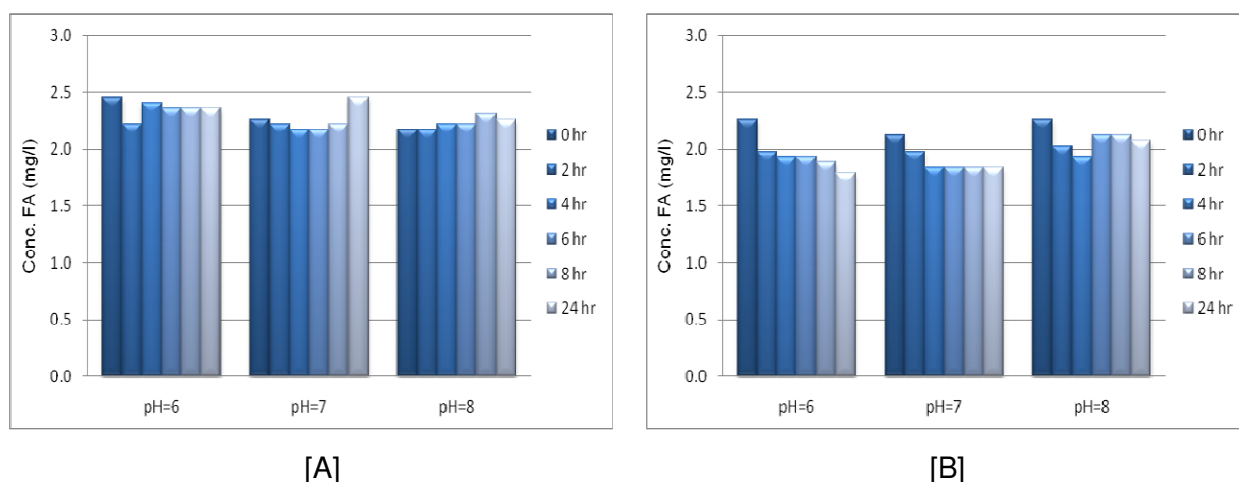
As seen from figure 4.3 IOCS seems to be less effective in the As(V) removal compared to GFH. Maximum adsorption of As(V) by IOCS was 57% and by GFH was 93%, both taking place at pH 6. This result was expected, because at this pH, As(V) is present as  $\text{H}_2\text{AsO}_4^-$  which is less negatively charged than  $\text{HAsO}_4^{2-}$  at pH 8. Under this condition, positive charge of the adsorbent surface at pH 6 will attract negatively charged  $\text{H}_2\text{AsO}_4^-$ . On the other hand, the surface charge of the adsorbent will be more negatively charged at higher pH, which is less attractive to  $\text{HAsO}_4^{2-}$ .



**Figure 4.4:** Removal of Cr(VI) at pH 6, 7 and 8. Model water: initial conc. of Cr(VI) = 200  $\mu\text{g/l}$ ,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 20 mg/l. Shaker speed: 100 rpm. [A] Adsorption on IOCS; [B] adsorption on GFH.

Figure 4.4 shows the result of Cr(VI) adsorption by IOCS and GFH at pH 6, 7, and 8. Unlike the result of the adsorption of As(V), Cr(VI) seem to be quite difficult to be adsorbed by both IOCS and GFH. Even though adsorption by GFH is better compared to that by IOCS, the difference is insignificant. Similar as the removal of As(V), highest adsorption occurred at pH 6 which is 39% for GFH and 8% for IOCS, after 24 hrs. This is supported by the result from previous study of the adsorption of Cr(VI) on activated carbon where the maximum adsorption occurs at pH 6 (Lach, et al., 2008). At this pH, Cr(VI) is present mostly in the form of  $\text{HCrO}_4^-$  and at pH >6.5 Cr(VI) is present as  $\text{CrO}_4^{2-}$  anion which will influence the charge at the surface of the adsorbent.

Similarly, as with the adsorption of As(V),  $\text{pH}_{\text{pzc}}$  of the adsorbent is likely an important factor in this experiment. At high pH, which was higher than  $\text{pH}_{\text{pzc}}$ , the surface charge of the adsorbent will be more negative. At this state, negative charge of Cr(VI) which is present as  $\text{CrO}_4^{2-}$  will be less adsorbed by the adsorbents.



**Figure 4.5:** Removal of fulvic acid at pH 6, 7 and 8. Model water: initial conc. of fulvic acid = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 20 mg/l. Shaker speed: 100 rpm. [A] Adsorption on IOCS; [B] adsorption on GFH.



Figure 4.5 is displaying the results of the adsorption of FA by IOCS and GFH at pH 6, 7, and 8. The results show that FA is poorly adsorbed by IOCS and GFH. Better performance showed on GFH especially at pH 6 with 21% removal, then 13% at pH 7 and 8% at pH 8. FA is hardly adsorbed on IOCS, at pH 6 only 4% removal was found.

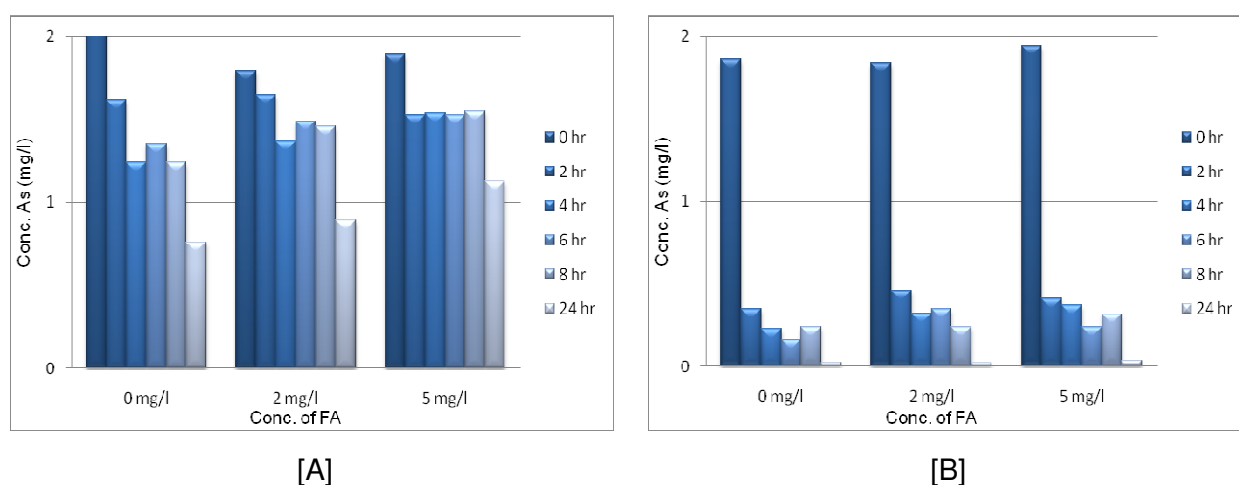
Similar situation as found with As(V) and Cr(VI) result might be the case in this experiment, as well. At lower pH FA has less negative charge than at higher pH. At pH 6 when the surface of GFH has positive charge, negatively charged FA will be adsorbed by the adsorbent. In contrast, at higher pH, more negatively charged FA will be less adsorbed by negative surface of adsorbent and reduce its performance. The performance of the adsorbent is influenced by its point of zero charge ( $pH_{pzc}$ ). The surface of the adsorbent will be negatively charge at  $pH > pH_{pzc}$ . For GFH,  $pH_{pzc}$  is 7.5-8, thus at pH 8 which is higher than its  $pH_{pzc}$ , the surface charge of GFH will likely be negative. Under this condition, negatively charged of  $HAsO_4^{2-}$ ,  $CrO_4^{2-}$ , and FA at pH 8 will be less favorable. Nevertheless,  $pH_{pzc}$  of IOCS coating (iron oxide) is around 7, but  $pH_{pzc}$  of silica sand is about 2-4.5. Therefore, it is possible that the  $pH_{pzc}$  of IOCS is below its natural  $pH_{pzc}$  which would lead to the negative charge at working pH of this experiment. It might explain the poor performance of IOCS with the metals and FA removal. More positively charged adsorbent would increase adsorption capacity.

Supportive to above conclusion is experiment carried out to study the adsorption of fulvic acid by boehmite (aluminum oxyhydroxide). As reported, the adsorption was better at low pH value and decreased as pH was increasing (Yoon, et al., 2004).

### 4.3.2. Competitive adsorption of metals and FA by IOCS and GFH

#### 4.3.2.1 Adsorption of As(V) in the presence of FA by IOCS and GFH

Model water containing As(V) in the presence of FA at pH 6, 7, and 8 was used. Following figures show the adsorption efficiencies of IOCS and GFH for As(V) adsorption in the presence of FA as a function of pH (figures 4.6-4.8). The measurements were focused only on the adsorption of metals (and not FA).

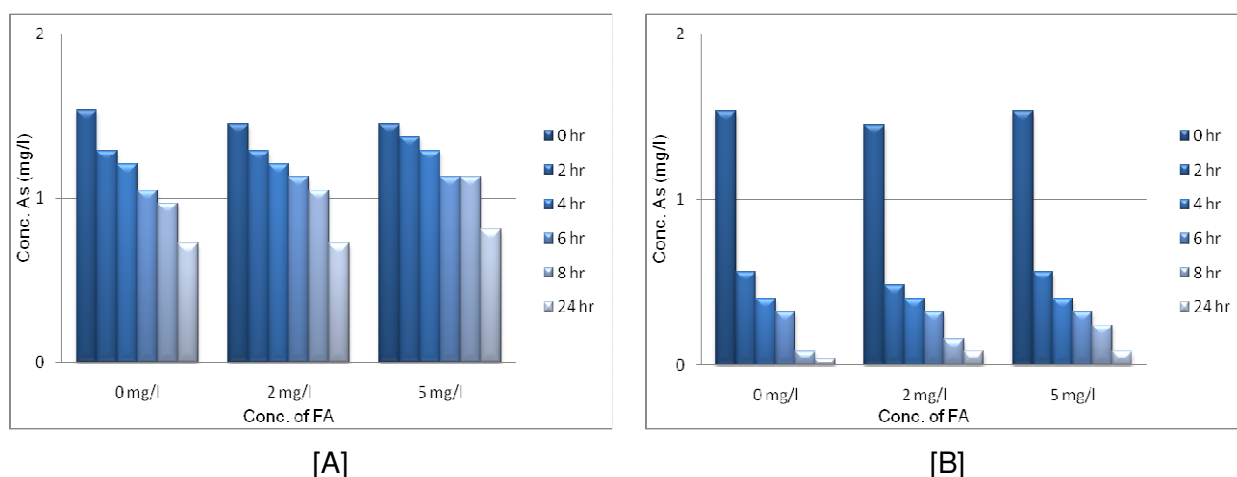


**Figure 4.6:** Removal of As(V) at pH 6 with various amount of fulvic acid. Model water: initial conc. of As(V) = 2 mg/l,  $HCO_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l, conc. of FA 0, 2, and 5 mg/l. Shaker speed: 100 rpm. [A] Adsorption on IOCS; [B] adsorption on GFH.



Role of FA in the adsorption of As(V) is better observed on IOCS, compared to GFH. As shown in figure 4.6 [A], the adsorption of As(V) by IOCS decreases with the increase of the concentration of FA. In the absence of FA, 63% of As(V) was removed during 24 hrs contact time, and the value decreases to 50% at 2 mg/l and 40% at 5 mg/l of FA. In contrast with the performance of IOCS, GFH seem to perform fine on the removal of As(V). At 24 hrs contact time, with 0 mg/l and 2 mg/l of FA, the removal of As(V) is 99% and slightly decreases to 98% at 5 mg/l of FA. Therefore, presence of FA did not influence As(V) adsorption by GFH.

In the adsorption of As(V) by IOCS, FA might act as competitive ion and reduce the adsorption capacity of the adsorbent. Presence of FA might create a complex and change the behavior of the species in the solution. Furthermore, negatively charged FA might influence the natural charge of IOCS. Consequently, with the increasing concentration of FA species in the solution metals will be less attracted to more negatively charged adsorbent. Figure 4.7 shows the performance of the adsorbent (IOCS and GFH) to adsorb the metal at pH 7.

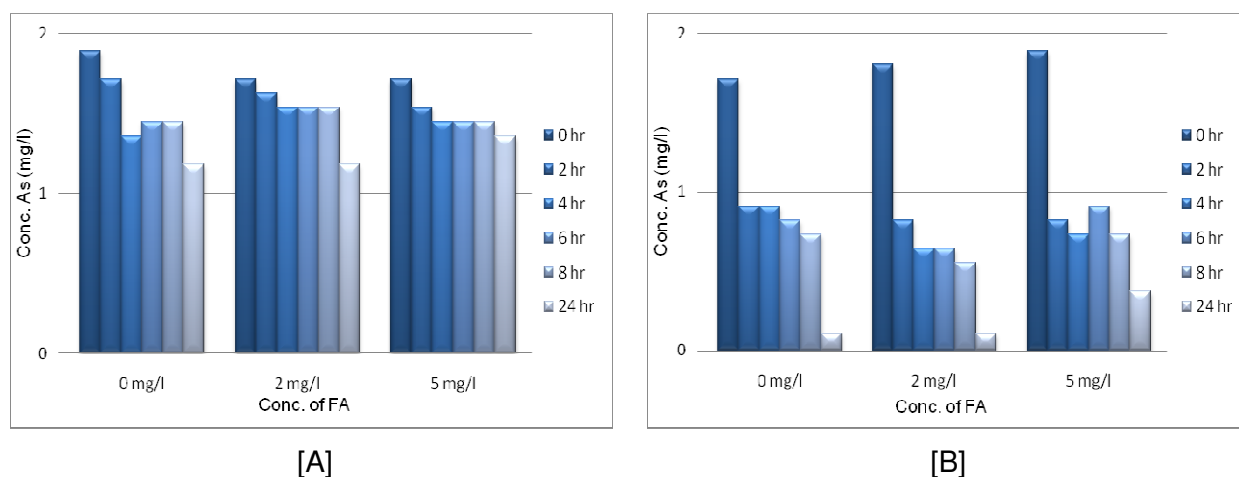


**Figure 4.7:** Removal of As(V) at pH 7 with various amount of fulvic acid. Model water: initial conc. of As(V) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l, conc. of FA 0, 2, and 5 mg/l. Shaker speed: 100 rpm. [A] Adsorption on IOCS; [B] adsorption on GFH.

Speed of As(V) adsorption by IOCS is slightly faster in the absence of FA and slower with the increase of FA concentration. But, at the end of the experiment (24 hrs) the adsorptive removal of As(V) was relatively similar in the absence and presence of FA (see figure 4.7 [A]). For adsorption of As(V) by GFH, similar pattern as at pH 6 was found in this case as well. As shown on figure 4.7 [B], 97% of As(V) was removed by GFH in the absence of FA. Adsorbance slightly decreases to 95% at 5 mg/L of FA.

From this values it can be concluded, at pH 7 performance of GFH was better than IOCS on the As(V) removal. Presence of FA did not influence the adsorption of As(V) by IOCS and GFH. Nevertheless, the removal efficiency at pH 7 is lower compared to that at pH 6. This result is expected due to the fact that at  $\text{pH} > 6.8$  As(V) has more negative charge and is thus less favorable for more negatively charged adsorbent.

The last assessment of the influence of FA on the adsorptive removal of As(V) was carried out at  $\text{pH} = 8$ . Results are shown in figure 4.8.



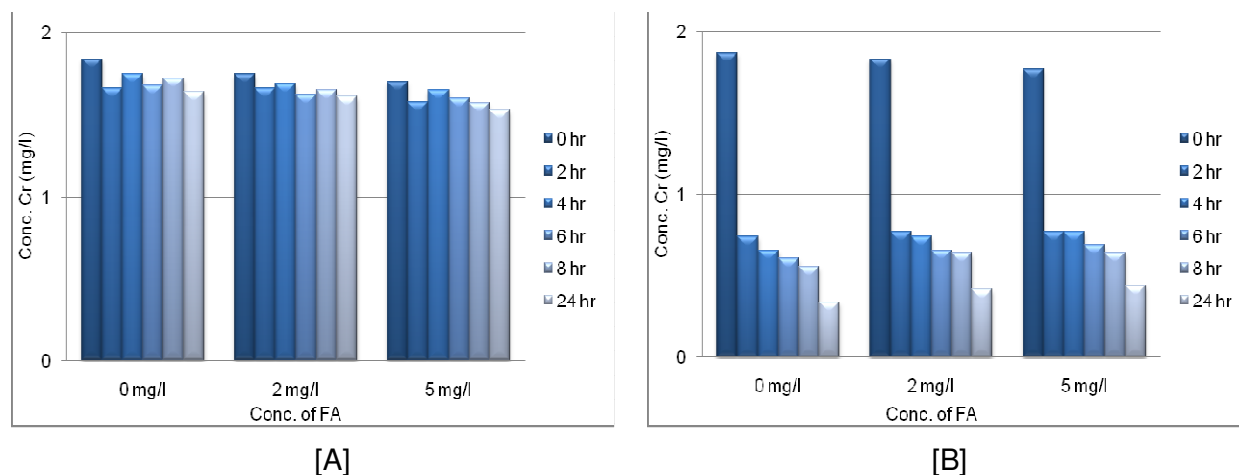
**Figure 4.8:** Removal of As(V) at pH 8 with various amount of fulvic acid. Model water: initial conc. of As(V) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l, conc. of FA 0, 2, and 5 mg/l. Shaker speed: 100 rpm. [A] Adsorption on IOCS; [B] adsorption on GFH.

The efficiency of adsorbents seems to decrease by increasing pH. In contrast with the previous experiments, more pronounced pattern of the influence of different concentration of FA on the adsorptive removal of As(V) was observed at this pH. With IOCS, in the absence of FA, only 37% of As(V) had been removed and removal decreases significantly to 21% in the presence 5 mg/l of FA. This trend is also found with the GFH as the adsorbent. In this experiment, with 0 mg/l of FA in the model water, 93% of As(V) had been adsorbed by GFH, and adsorption was decreased to 80% with 5 mg/l of FA present.

Compared to the previous experiments, the influence of FA of both adsorbents at pH 8 on the adsorptive removal of As(V) is relatively higher. The reason for this might be related to complexation in the solution due to FA presence and more negatively charges adsorbent at higher pH. However, at this pH complexation between As(V) and FA might appear as more negatively charged species. Thus, the species will be less adsorbed with negatively charged of adsorbent surface. As a conclusion, in the presence of FA the adsorption of As(V) will decrease with the increases of the pH due to more negative charge of the adsorbent.

#### 4.3.2.2 Adsorption of Cr(VI) in the presence of FA by IOCS and GFH

Model water containing Cr(VI) in the presence of FA, at pH 6, 7, and 8 were used in this experiment. Following figures show the adsorption efficiencies of IOCS and GFH for Cr(VI) adsorption in the presence of FA as a function of pH (figure 4.9-4.11). The measurements were focused only on the adsorption of metals (and not FA).



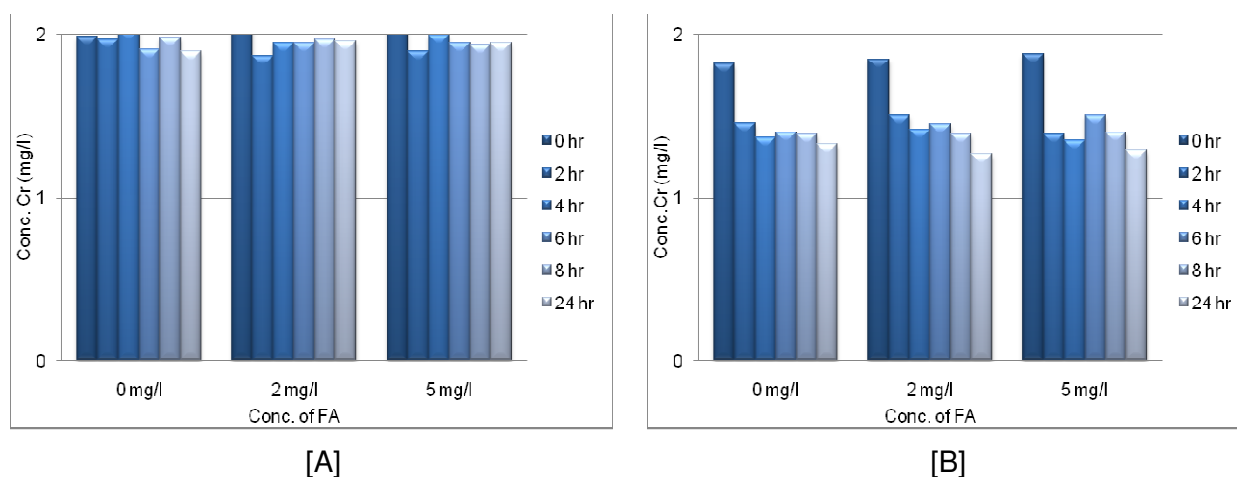
**Figure 4.9:** Removal of Cr(VI) at **pH 6** with various amount of fulvic acid. Model water: initial conc. of Cr(VI) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l, conc. of FA = 0, 2, and 5 mg/l. Shaker speed: 100 rpm. [A] Adsorption on IOCS; [B] adsorption on GFH.

Compared with the adsorptive removal of As(V), Cr(VI) appears to be less adsorbed either by IOCS or GFH. As shown in figure 4.9, hardly any Cr(VI) was adsorbed by IOCS during 24 hr contact time. In the absence of FA, 11% of Cr(VI) is able to be removed and adsorption slightly decreases to 10% in the presence 5 mg/l of FA. In these experiments, the FA did not appear as a competitive ion because of the poor performance of IOCS on the adsorption of Cr(VI). Nevertheless, GFH shows better performance in the removal of Cr(VI). In the absence of FA, 82% of Cr(VI) had been adsorbed, 77% at 2 mg/l concentration of FA and 75% at 5 mg/l concentration of FA in the model water.

From these results it can be concluded that the influence of FA is insignificant in the adsorption of Cr(VI) by IOCS and GFH. With GFH, even though adsorption at 24 hrs is relatively equal, the adsorption rate is slightly lower with the increases of FA concentration.

At the same pH and similar concentration of metal and FA, the result of the adsorption of Cr(VI) cannot be compared to the adsorption of As(V). The efficiency of the adsorbent is considerably different, Cr(VI) was less adsorbed by IOCS and GFH. At this pH, there was no indication of significant removal of Cr(VI) by IOCS, although some of it is adsorbed by GFH.

Figures 4.10 showed the Cr(VI) removal by IOCS and GFH at pH 7.

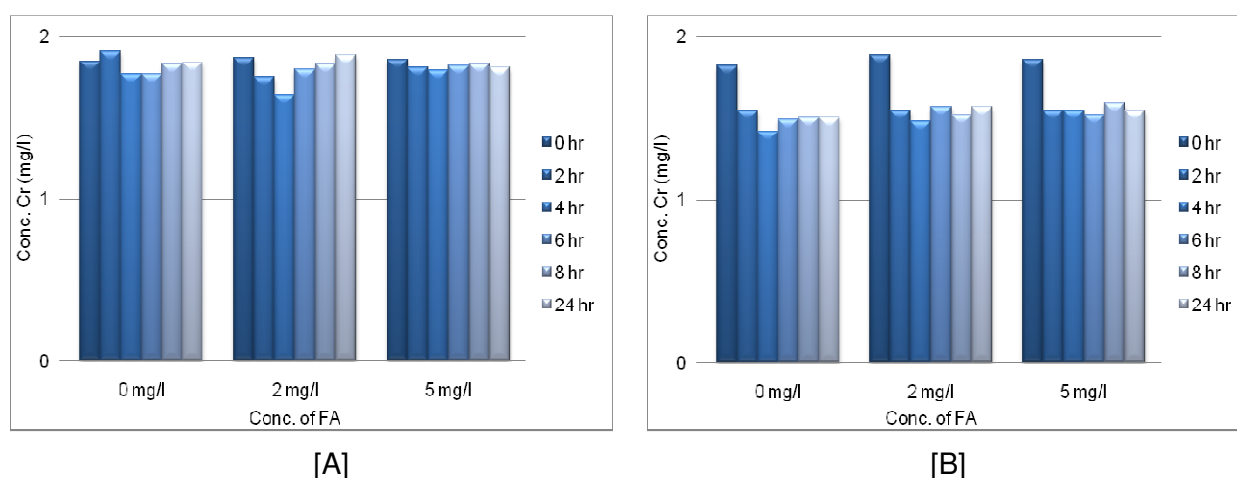


**Figure 4.10:** Removal of Cr(VI) at **pH 7** with various amount of fulvic acid. Model water: initial conc. of Cr(VI) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l, conc. of FA 0, 2, and 5 mg/l. Shaker speed: 100 rpm. [A] Adsorption on IOCS; [B] adsorption on GFH.

At this pH, the removal of Cr(VI) with IOCS was around 4% at all FA concentrations. Therefore, after 24 hrs of experiment around 1.95 mg/l of Cr(VI) was still present in the solution from its initial concentration 2 mg/l. If we compare this with the results from the previous experiment (at pH 6), there are slight differences in the performance of GFH. Cr(VI) removal seem to be better by the GFH. At 0 mg/l of FA, 27% Cr(VI) removal is noted and surprisingly increases at 2 and 5 mg/l of FA with 32% Cr(VI) removal. The result is quite out of the pattern of this experiment. It might be able to be an indicator that at this pH, the presence of FA does not influence the performance of the GFH and the difference in end concentrations is only due to error of analytical method.

Decreases of adsorbent efficiency on the adsorption of Cr(VI) at this pH seem to be influenced by the charge of Cr(VI) and FA. Negative charge of those species causes them to be less adsorbed by less positively charged adsorbent.

Figure 4.11 shows the performance of the adsorbent (IOCS and GFH) to adsorb Cr(VI) at pH 8.



**Figure 4.11:** Cr(VI) removal at **pH 8** by **IOCS** [A] and **GFH** [B] with various amount of FA. Model water: initial conc. of Cr(VI) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l, conc. of FA 0, 2, 5 mg/l. Shaker speed: 100 rpm. [A] Adsorption on IOCS; [B] adsorption on GFH.

As shown in figure 4.11, the result at pH 8 is comparable with the result at pH 7. Poor Cr(VI) removal by IOCS was found, the range was 1% and 3% at 0 mg/l and 5 mg/l of FA, respectively. Although the removal was not as good as the removal at lower pH, the adsorptive removal with GFH is slightly better, with 17% removal at all FA concentrations. In this case, negative charge of the species present in the solution and negative charge of the adsorbent seem to be responsible for this occurrence. At this pH, negatively charged Cr(VI) will be less favourable for negatively charged adsorbent.

Additional conclusions can be gathered from the presented results of the adsorptive removal of metals combined with FA at pH 6, 7 and 8.

The results show that pH plays an important role on the adsorptive removal of As(V) and Cr(VI) either by IOCS and GFH. The established patterns showed that by increasing the pH, the performance of the adsorbent decreases. The pH might highly influence the surface charge of adsorbent (Stumm, et al., 1981). And the pH dependence is self related to type and ionic state of the functional group present in the adsorbent and also to the metal chemistry in the solution (Gupta, et al., 2001).

As shown in the result of adsorption of As(V) and Cr(VI) in the presence of FA by IOCS and GFH, it was found that the performance of the GFH is generally better than the performance of IOCS at all pH values. This result is in agreement with the previous experiment carried out by Yadav, where GFH had higher adsorption capacity than IOCS for the removal of Cr(VI) (Yadav, 2007). On the other hand, different results are obtained in the removal of As(V) by GFH. Genç-Fuhrman et al, stated that in the removal of As(V), the performance of IOCS was better than GFH (Genç-Fuhrman, et al., 2007). It is possible that the observed low adsorption of As(V) onto GFH may be due to differences in experimental conditions.

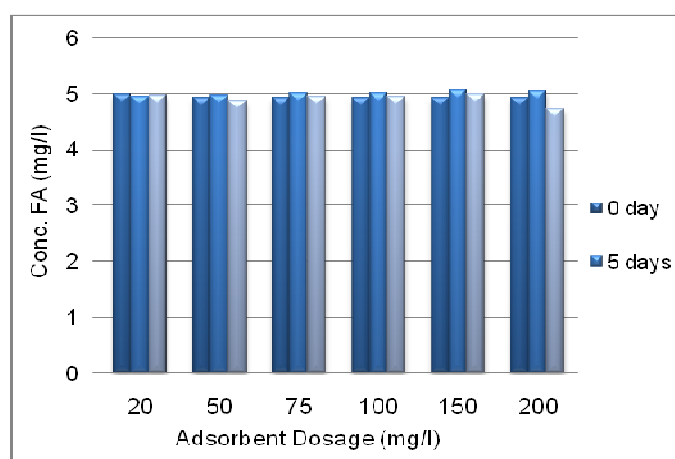
In our experiments, both adsorbents were pulverized to size  $<0.63\ \mu\text{m}$ . As oppose to pulverized GFH which contain 100% of active adsorbent, pulverized IOCS contains the sand grain apart from the iron oxide coating. Therefore, with the same weight GFH has higher adsorption surface than IOCS. This might be the reason for the lower adsorption capacity of IOCS compared to GFH in the removal of As(V) and Cr(VI).

## 4.4 Adsorption Isotherm (Long Term Batch Experiments)

Adsorption isotherms for both adsorbents were carried out with model water containing only FA and combination of As(V) with FA and combination of Cr(VI) with FA. Results of the experiment are presented in continuation.

### 4.4.1. Adsorption Isotherm of FA using IOCS as adsorbent

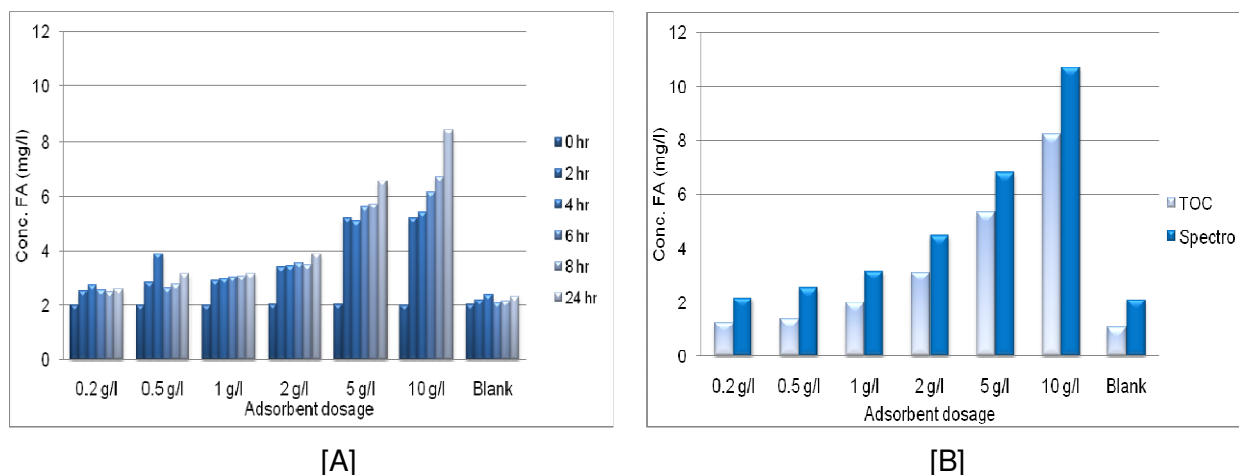
Following figures (figure 4.12-4.13) shows efficiency of IOCS for the adsorption of FA as a function of dosage of the adsorbent.



**Figure 4.12:** Adsorption of fulvic acid by IOCS at pH 7 as a function of different adsorbent dosages. Model water: initial conc. of FA = 5 mg/l,  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed: 100 rpm.

From figure 4.12 it can be seen that during the experiment time there was no adsorption of FA by IOCS. Concentration of FA stayed relatively stable for 10 days of the experiment. A slight decrease occurred after 10 days with the highest adsorbent dosage, but the change is insignificant compared to the initial concentration. This result might indicate that inadequate amount of IOCS was added to the model water or ineffectiveness of IOCS to remove FA regardless the concentration of adsorbent.

To identify the problem, another experiment needed to be carried out with different dosages of IOCS. The purpose of the experiment was to find out the capability of IOCS to remove FA at higher amounts of adsorbent with lower concentration of FA (figure 4.13).

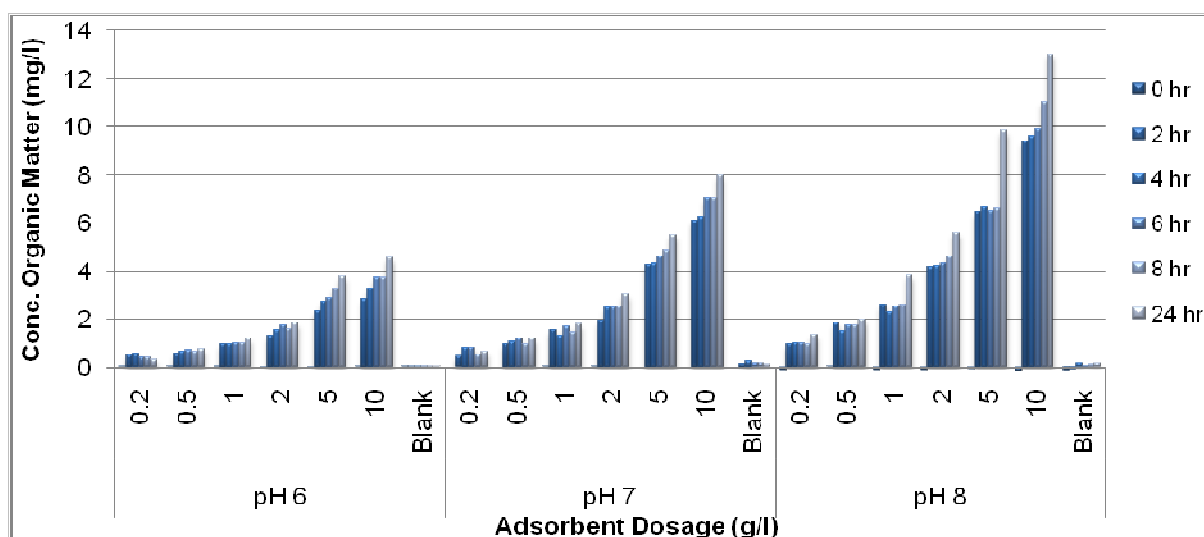


**Figure 4.13:** Adsorption of fulvic acid by IOCS at pH 7 as a function of different adsorbent dosage. Model water: initial conc. of FA = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed: 100 rpm. [A] Result after 24 hrs contact time as measured with spectrophotometer; [B] result after 5 days contact time as measure with spectrophotometer and TOC analyzer.

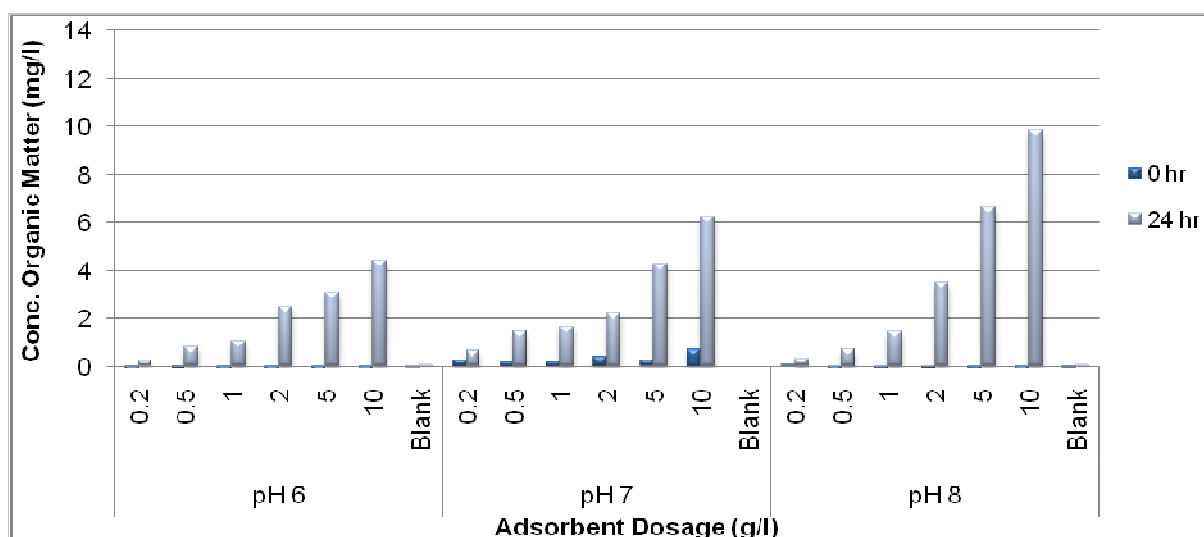
As shown in the figures above, over time FA concentration increases with the increase of adsorbent dosage. As shown in the figure 4.13 [A], concentration of FA increased 31%, 59%, 58%, 92%, 224%, and 328% with 0.2, 0.5, 1, 2, 5, and 10 g/l of IOCS, respectively. Furthermore, as illustrated in figure 4.13 [B], during 5 days experiment time, concentration of FA continued to increase 59%, 122%, 238%, and 443% with the adsorbent dosage of 1, 2, 5, and 10 g/l, respectively. However, at 5 days experiment time, lower concentration was found with adsorbent dosage 0.2 and 0.5 g/l, which might be due to the settlement of the adsorbent in the solution or error on the spectrophotometer measurement. The increases of FA concentration might still continue until it reaches the equilibrium concentration in the solution.

From figure 4.13 [B] it can be seen, that measurement with TOC analyzer were lower than those measured with spectrophotometer which varies from 22% to 50%. The reason behind these occurrences is not clear. Either TOC analyzer is unable to measure part of the organic matter that spectrophotometer can, or measurements are less accurate due to high detection limit of the machine. Similar pattern was found throughout the research, with the same samples (same concentration) being measured as containing less organic matter when analyzed by TOC analyzer than measured with spectrophotometer. However, the differences were varying due to the concentration or pH.

The following figures (4.14-4.15) are illustrating the leaching of organic matter into demineralized water as a function of time, pH, and adsorbent dosage.



**Figure 4.14:** Assessment of organic matter leaching from IOCS at pH 6, 7, and 8 as measured with spectrophotometer. Model water:  $\text{HCO}_3^- = 100$  mg/l. Shaker speed: 100 rpm.



**Figure 4.15:** Assessment of organic matter leaching from IOCS at pH 6, 7, 8 as measured with TOC analyzer. Model water:  $\text{HCO}_3^- = 100$  mg/l. Shaker speed: 100 rpm.

From figures 4.14 and 4.15 one can see that there is considerable leaching of organic matter from IOCS in the demineralized water. The pH seems to influence the leaching rate of organic matter. With the increase of the pH, the concentration of organic matter increases as well (measured either with spectrophotometer or TOC analyzer).

This experiment shows evidence that increase of pH could be a dominant factor of the in releases of DOC from soil. Any chemical process that increases pH might take a role with the solubilization of the organic matter (Grybos, et al., 2009). Similar processes may be occurring in these presented experiments. With the increase of the pH, the organic matter in the IOCS is more soluble, the easier the release of it is.



Concentration of organic matter in the demineralized water after 24 hrs seems not to be the maximum possible concentration. Table 4.1 at page 30, showed that amount of organic matter is 171.03 mg/g of IOCS. Therefore, from this experiment we can calculate the approximate amount and proportion of organic matter that leached for each dosage of IOCS (table 4.2).

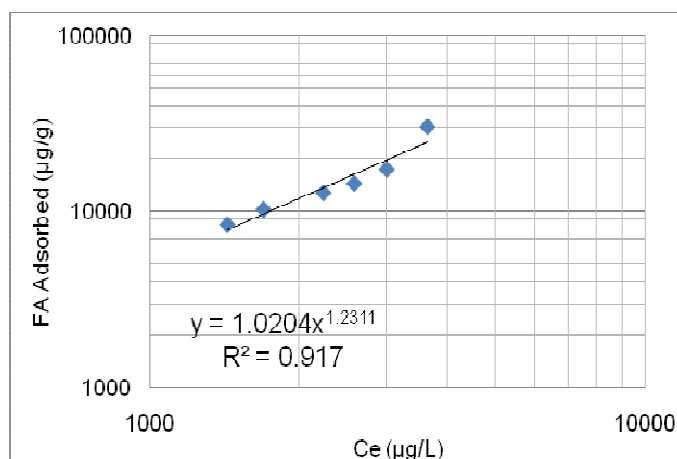
**Table 4.2:** Approximate amount of leached organic matter from IOCS in the demineralized water. Model water contained  $\text{HCO}_3^- = 100 \text{ mg/l}$ .

IOCS dosage (g/l)	c(NOM) per IOCS dosage (mg/l)	c(NOM) leached (mg/l)			Portion of (NOM) leached (%)		
		pH = 6	pH = 7	pH = 8	pH = 6	pH = 7	pH = 8
0.2	34	0.3	0.7	1.4	1.0	2.0	4.0
0.5	86	0.8	1.2	2.0	0.9	1.4	2.3
1	171	1.2	1.8	3.8	0.7	1.1	2.2
2	342	1.9	3.0	5.6	0.5	0.9	1.6
5	855	3.8	5.5	9.8	0.4	0.6	1.2
10	1710	4.6	8.0	13.0	0.3	0.5	0.8

As shown in table 4.2, with the increase of IOCS dosage, the concentration of leached NOM increased, but the portion of leached amount decreased. This is the indicator that the portion of NOM leaching was not linear with the increase of NOM concentration per IOCS dosage. There is a possibility that the rate of leaching is slower with the higher NOM concentration (IOCS dosage). In addition, pH values seem to be an important factor in this experiment. With the increase of the pH value, leached NOM was increased respectively with the increase of the IOCS dosage. As stated earlier, the increase of NOM solubility with the increase of pH value seem to be the reason for this occurrence. In the longer run time of the experiment, the concentration of organic matter measured in demineralized water might be considerably increased.

#### 4.4.2. Adsorption Isotherm of FA using GFH as adsorbent

For determination of adsorption isotherm of FA for GFH, buffered model water was used. The equilibrium concentration ( $C_e$ ) of FA was reached after 24 days. Figure 4.16 shows Freundlich adsorption isotherm obtained from the experimental result.



**Figure 4.16:** The Freundlich adsorption isotherm of fulvic acid using GFH as adsorbent. Model water: Initial FA conc.= 5 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 20, 50, 75, 100, 150 and 200 mg/l at pH 7. 24 days contact time, shaker speed: 100 rpm.

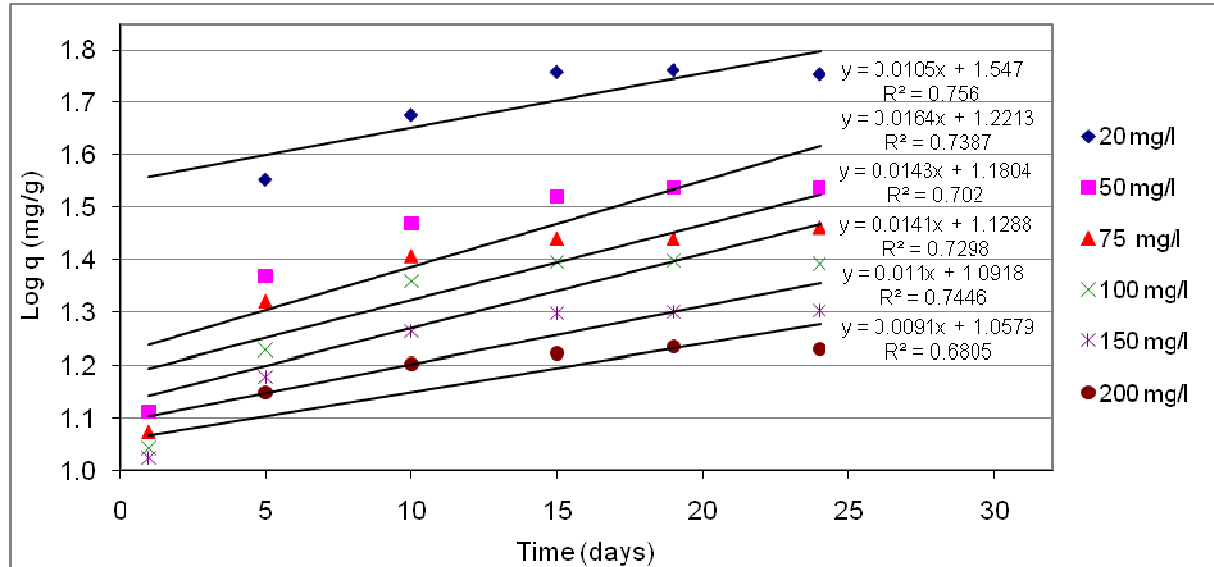
As shown in figure 4.16, the amount of FA adsorbed per unit mass of GFH has been plotted against the equilibrium concentration of FA in solution. Co-relation coefficient ( $R^2=0.9344$ ) implies that data fits well with the Freundlich isotherm model.

From the Freundlich isotherm, the adsorption capacity (K) found was to be 1.0204 mg of FA per 1 g of GFH and adsorption intensity ( $1/n$ ) value is 1.2311. K value obtained from the Freundlich isotherm is relatively small. The bigger the K value is, the more favorable the adsorption. Steep slope of isotherm line obtained in this experiment indicates that FA removal per unit weight of GFH is considerably changing with change of the equilibrium concentration of FA. Thus, we can assume that the decrease of adsorption capacity as function of adsorbent dosage might because of the heterogeneity of adsorbent on the surface.

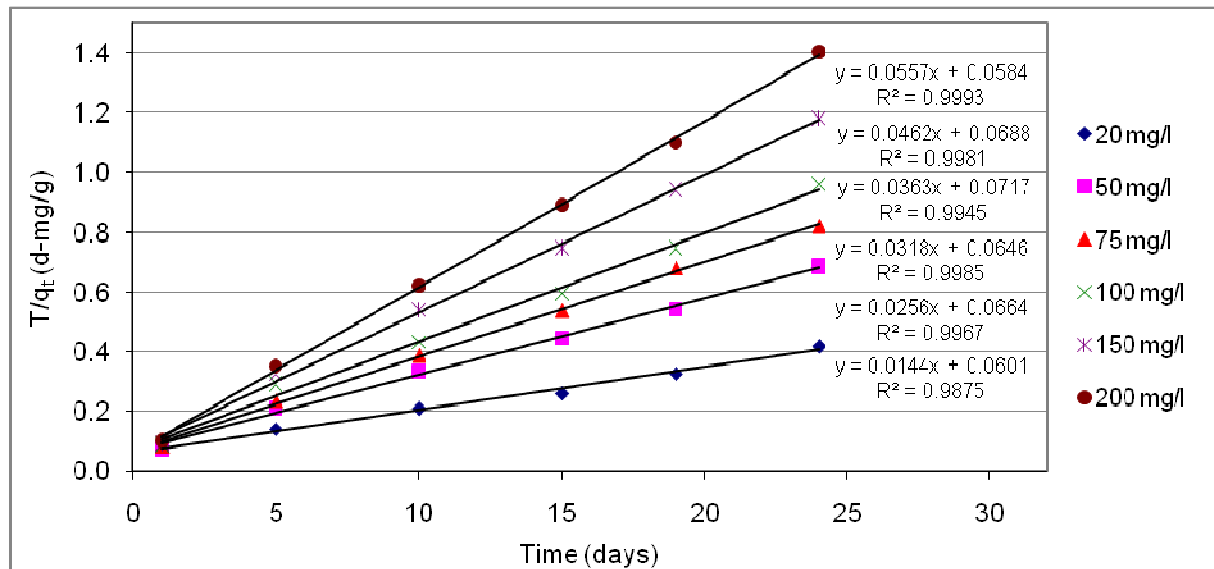
Negatively charged FA had to be easily attracted by positively charged GFH at pH 7. But, in this experiment, amount of adsorbed FA was not in line with the weight of the adsorbent, highest adsorption of FA was found at smallest adsorbent dosage.

#### 4.4.3. Adsorption Kinetic of FA on GFH

The behavior of adsorbate on the adsorption process can be determined by its kinetic order. Following figures shows kinetic order of FA adsorption isotherm using GFH as adsorbent.



**Figure 4.17:** First order reaction of FA adsorption isotherm. Model water:  $\text{HCO}_3^- = 100 \text{ mg/l}$ , dosage of adsorbent = 20, 50, 75, 100, 150 and 200 mg/l, pH 7. Shaker speed: 100 rpm.



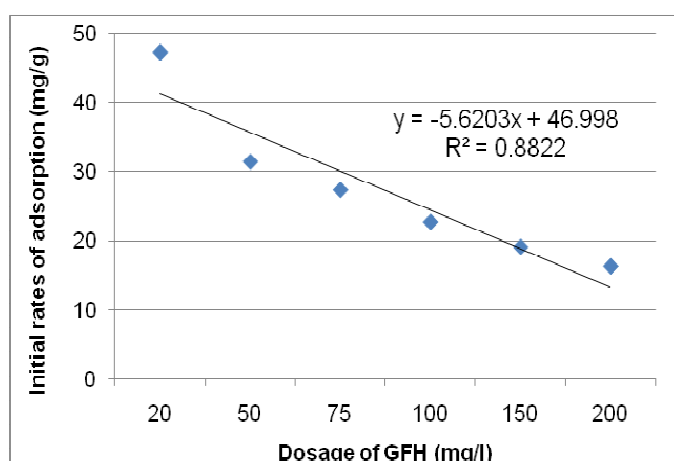
**Figure 4.18:** Second order reaction of FA adsorption isotherm. Model water:  $\text{HCO}_3^- = 100 \text{ mg/l}$ , dosage of adsorbent = 20, 50, 75, 100, 150 and 200 mg/l, pH 7. Shaker speed: 100 rpm.

Figures 4.17 and 4.18 show the results obtained from FA adsorption isotherm experiments being fitted to pseudo-first order kinetic model and pseudo-second order kinetic model. The figure clearly indicates that the pseudo second order rate equation yields the better fitting, suggesting that the kinetic of adsorption can be better described by the pseudo-second order rate equation. Table 4.3 shows kinetic order for FA adsorption isotherm on GFH.

**Table 4.3:** Pseudo-first order and pseudo-second order rate constants for FA adsorption isotherm on GFH.

Dosage of GFH (mg/l)	First order kinetic		Second order kinetic			
	R <sup>2</sup>	K (mg/g-d)	R <sup>2</sup>	K <sub>2</sub> (g/mg-d)	h (mg/g-d)	q <sub>e</sub> (mg/g)
20	0.756	1.05E-02	0.988	1.44E-02	47.26	57.287
50	0.739	1.64E-02	0.997	2.56E-02	31.41	35.027
75	0.702	1.43E-02	0.999	3.18E-02	27.32	29.312
100	0.730	1.41E-02	0.995	3.63E-02	22.66	24.987
150	0.745	1.10E-02	0.998	4.62E-02	19.04	20.301
200	0.681	9.10E-03	0.999	5.57E-02	16.27	17.090

The rate constant  $K_2$  varies from 1.44E-02 to 5.57E-02 g/mg-d, and the initial rate of adsorption reduces from 47.26 mg/g-d to 16.27 mg/g-d. The following figure shows correlation between initial rate of adsorption and dosage of adsorbent.

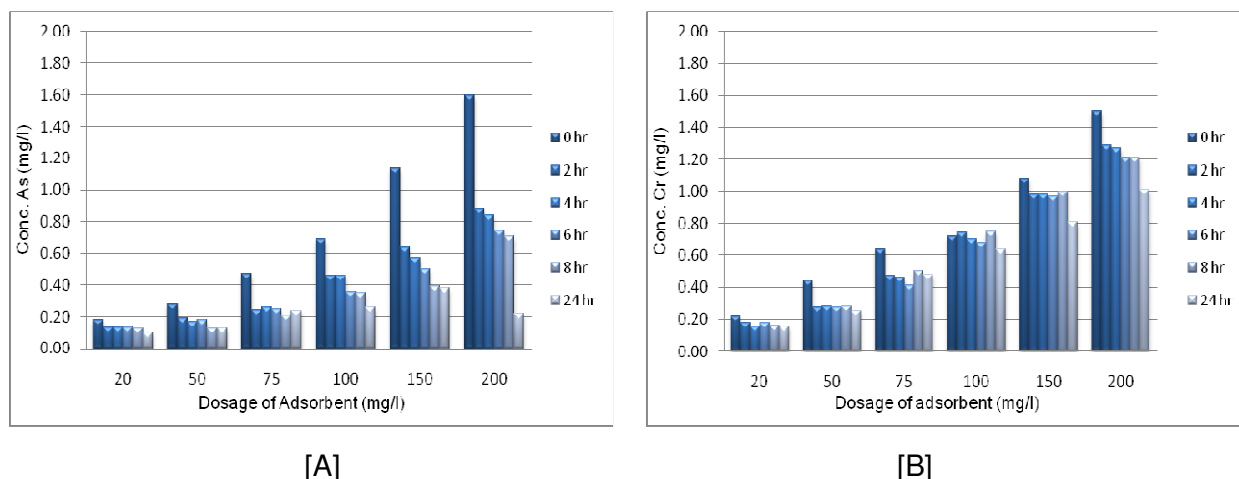


**Figure 4.19:** Co-relation between initial rate of FA adsorption and the dosage of GFH. Model water:  $\text{HCO}_3^- = 100$  mg/l, dosage of adsorbent = 20, 50, 75, 100, 150 and 200 mg/l, pH 7, and 24 days contact time. Shaker speed: 100 rpm.

As seen from figure 4.19, low co-relation coefficient ( $R^2 = 0.88$ ) implies that initial rate of adsorption was not influenced significantly by the dosage of adsorbent. The initial rate of adsorption does not decrease linearly with the increase of the adsorbent dosage.

#### 4.5 Adsorption of Metals by Preloading GFH with FA

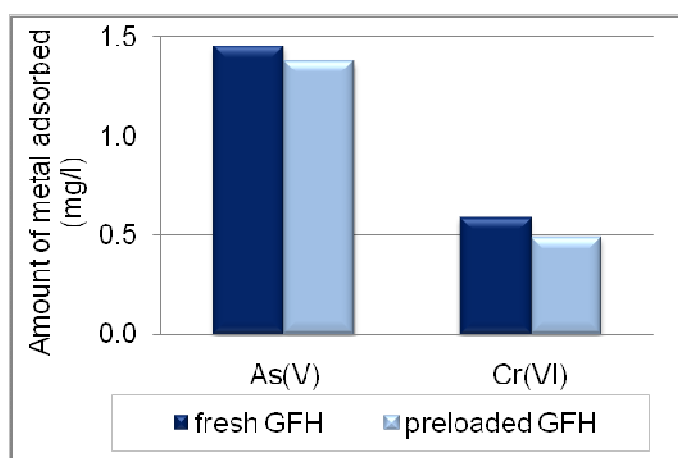
Figure 4.21 shows the results of the As(V) and Cr(VI) short-term adsorption on GFH preloaded with FA, at pH 7 and contact time of 24 hrs. Solutions used for this experiment were those that remained after adsorption isotherm for FA was determined. Estimated remaining volume was calculated based on the number of samples taken during the adsorption isotherm experiment.



**Figure 4.20:** Adsorption efficiency of GFH preloaded with FA. Model water:  $\text{HCO}_3^- = 100 \text{ mg/l}$ , initial metals concentration = 0.2, 0.5, 0.75, 1, 1.5, and 2 mg/l, dosage of adsorbent = 20, 50, 75, 100, 150, and 200 mg/l, respectively, pH 7. Shaker speed: 100 rpm. [A] Adsorption results for As(V), [B] adsorption results for Cr(VI).

As shown in figure 4.20, initial concentration of metals was less than what was aimed at. This might be because of (i) wrong estimation of the volume of solution remaining from the previous experiment, which influenced the calculation of stock solution that needed to be added, or (ii) small part of the metals already adsorbed by the adsorbent by the first sampling. This problem does not influence the purpose of the experiment - to find out the effect of preloaded GFH with FA on the removal of metals. The results can be compared with the similar experiments conducted earlier.

The following figures shows comparison of preloaded GFH and fresh GFH efficiency in the removal of As(V) and Cr(VI). The comparison taken from competitive adsorption experiment at pH 7, dosage of adsorbent (GFH) 200 mg/l, initial concentration of metals 2 mg/l, concentration of FA 5 mg/l, contact time 24 hrs. Shaker speed 100 rpm.



**Figure 4.21:** Amount of adsorbed metal after 24 hrs contact time, on fresh and preloaded GFH. Model water: initial conc. of metals = 2 mg/l,  $\text{HCO}_3^- = 100 \text{ mg/l}$ , dosage of adsorbent = 200 mg/l. Shaker speed: 100 rpm.

The differences of fresh and preloaded GFH efficiency for the removal of As(V) and Cr(VI) after 24 hours experiment is showed on Figure 4.21.

Amount of As(V) adsorbed with fresh GFH was 1.5 mg/l, while that of Cr(VI) was only 0.6 mg/l. Amount of adsorbed metals with preloaded GFH was slightly less, 1.4 mg/l and 0.5 mg/l for As(V) and Cr(VI), respectively. From this experiment we can make a conclusion that the effect of FA on the performance of GFH on the As(V) and Cr(VI) removal is relatively similar on the preloaded GFH with FA and fresh GFH with combined model water (metals and FA). Fresh GFH adsorbs slightly better than preloaded GFH.

## 5. CONCLUSIONS AND RECOMMENDATIONS

### 5.1 Conclusions

This study was carried out to investigate the influence of fulvic acid on adsorptive removal of As(V) and Cr(VI) by IOCS and GFH. The following conclusions were gathered on the basis of the result obtained from the experiments.

#### Stability of Cr(VI):

- As a function of pH and time, the concentration of total Cr and Cr(VI) was found to be stable during 24 hrs experiment in the absence **and** presence of fulvic acid. Therefore, influence of FA on the reduction of Cr(VI) to Cr(III) was not significant.

#### Short-term batch experiments:

- In the adsorption experiments with individual components, at pH 6, 7, and 8, As(V) removal by GFH was better than by IOCS. In the same range of pH, GFH performed slightly better than IOCS in the adsorptive removal of Cr(VI). FA was hardly adsorbed by either, IOCS or GFH. Slight removal was found at pH 6 by GFH. Negative charge of the metals at pH >6.8 and  $pH_{pzc}$  of the adsorbent seem to be the main reasons of this occurrence.
- In the adsorption experiments with simultaneous As(V) and FA presence, it was found that role of FA was insignificant almost at all pH values with either IOCS or GFH as adsorbent. Influence of FA was only detected in the removal of As(V) by IOCS at pH 6 and by GFH at pH 8. In the presence of FA, less negative charge of As(V) at this pH value might formed complex species. Highest As(V) removal (99%) occurred at pH 6 by GFH.
- In the adsorption experiments with simultaneous Cr(VI) and FA presence by IOCS and GFH at pH 6, 7, and 8, role of FA as a competitive ion seem to be undetectable with the poor performance of IOCS and GFH on the removal of Cr(VI). The highest Cr(VI) removal (82%) occurred at pH 6 by GFH.

#### Adsorption isotherm experiments:

- FA is poorly adsorbed by IOCS, so adsorption isotherm could not be determined under studied conditions.
- IOCS seems to be leaching organic matter. Amount of the leaching of organic matter from IOCS depends on time, adsorbent dosage and pH. During 24 contact time, <2% organic matter was released from total 171.03 mg NOM per gram of IOCS.
- The result of Freundlich isotherm showed that the adsorption capacity (K) is relatively low which could be an indicator of less efficient GFH as adsorbent for the adsorption of FA.
- The adsorption results fitted with the pseudo-second order rate equation rather than pseudo-first order rate.

#### Preloading:

- In the removal of both metals adsorption on preloaded GFH compared to fresh GFH in the presence of FA is slightly lower.

## 5.2 Recommendations

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

- To perform similar experiments as carried out for this research, but with different metals' concentration and adsorbent dosage.
- To perform experiments with IOCS coating only (as oppose to complete pulverized IOCS sample), to compare its performance with to that of GFH in the removal of As(V) and Cr(VI).
- To carry out the experiment with GFH for determination of competitive adsorption isotherm of As(V) and Cr(VI) in the presence of FA.
- Further studies need to be carried out to determine the effect of fulvic acid and pH on As(V) and Cr(VI) removal by IOCS and GFH on Rapid Small Scale Column Test (RSSCT).
- Further research is needed to characterize the NOM present in the IOCS.
- Further research could be conducted for the removal of other heavy metals combined with FA with varying concentrations, and as a function of pH.



## 6. REFERENCES

- Anderson RA (1989) Essentiality of chromium in humans. *Science of The Total Environment* 86: 75-81
- Bäckström M, Dario M, Karlsson S, Allard B (2003) Effects of a fulvic acid on the adsorption of mercury and cadmium on goethite. *The Science of The Total Environment* 304: 257-268
- Bakhamis MAA (2009) Adsorption of Copper and Cadmium from urban stormwater runoff on Iron Oxide based adsorbents. MSc. Thesis, UNESCO-IHE
- Casamassima M, Darque-Ceretti E, Etcheberry A, Aucouturier M (1993) Correlation between Lewis donor/acceptor properties determined by XPS and Brönsted acid/base properties determined by rest-potential measurements, for aluminium and silicon oxides. *Journal of Materials Science* 28: 3997-4002
- Collins MR, Amy GL, Steelink C (1986) Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: implications for removal during water treatment. *Environmental Science & Technology* 20: 1028-1032 DOI 10.1021/es00152a011
- Croue JP, Korshin GV, Benjamin M (2000) Characterization of natural organic matter in drinking water. AWWA Research Foundation and American Water Works Association
- Das S (2004) Adsorptive chromium removal using iron oxide coated sand. MSc. Thesis, UNESCO-IHE
- Edward M, Benjamin MM (1989) Adsorptive filtration using coated sand: a new approach for treatment of metal-bearing wastes. *Research Journal of the Water Pollution Control Federation* 61: 1523-1533
- Faust SD, Aly OM (1998) *Chemistry of water treatment-2nd edition*. Lewis publisher, Boca Raton
- Ferguson JF, Gavis J (1972) A review of the arsenic cycle in natural waters. *Water Research* 6: 1259-1274
- Filius JD, Lumsdon DG, Meeussen JCL, Hiemstra T, Van Riemsdijk WH (2000) Adsorption of fulvic acid on goethite. *Geochimica et Cosmochimica Acta* 64: 51-60
- Frimmel FH, Abbt-Braun G (1998) Basic characterization of reference NOM from Central Europe -- Similarities and differences. *Environment International* 25: 191-207
- Gebreyowhannes YB (2009) Effect of Silica and pH on Arsenic Removal by Iron-Oxide Coated Sand. MSc. Thesis, UNESCO-IHE
- Genç-Fuhrman H, Mikkelsen PS, Ledin A (2007) Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: Experimental comparison of 11 different sorbents. *Water Research* 41: 591-602
- Genz A, Baumgarten B, Goernitz M, Jekel M (2008) NOM removal by adsorption onto granular ferric hydroxide: Equilibrium, kinetics, filter and regeneration studies. *Water Research* 42: 238-248
- Grybos M, Davranche M, Gruau G, Petitjean P, Pédrot M (2009) Increasing pH drives organic matter solubilization from wetland soils under reducing conditions. *Geoderma* 154: 13-19
- Gu B, Schmitt J, Chen Z, Liang L, McCarthy JF (1995) Adsorption and desorption of different organic matter fractions on iron oxide. *Geochimica et Cosmochimica Acta* 59: 219-229
- Gupta VK, Shrivastava AK, Jain N (2001) Biosorption of Chromium(VI) From Aqueous solutions by green algae *spirogyra* species. *Water Research* 35: 4079-4085
- Ho Y-S (2006) Review of second-order models for adsorption systems. *Journal of Hazardous Materials* 136: 681-689

- Jenne EA (1998) Adsorption of Metals by Geomedia. Academic Press, San Diego
- Jucker C, Clark MM (1994) Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes. *Journal of Membrane Science* 97: 37-52
- Knappe DRU, Snoeyink VL, Roche P, Prados MJ, Bourbigot M-M (1997) The effect of preloading on rapid small-scale column test predictions of atrazine removal by GAC adsorbers. *Water Research* 31: 2899-2909
- Kotas J, Stasicka Z (2000) Chromium occurrence in the environment and methods of its speciation. *Environmental Pollution* 107: 263-283
- Lach J, Okoniewska E, Neczaj E, Kacprzak M (2008) The adsorption of Cr(III) and Cr(VI) on activated carbons in the presence of phenol. *Desalination* 223: 249-255
- Li A, Xu M, Li W, Wang X, Dai J (2008) Adsorption characterizations of fulvic acid fractions onto kaolinite. *Journal of Environmental Sciences* 20: 528-535
- Li Q, Snoeyink VL, Mariñas BJ, Campos C (2003) Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds. *Water Research* 37: 773-784
- Lindberg A, Vahter M (2006) Health effect of inorganic arsenic. Paper presented at the Arsenic in Groundwater - A World Problem, Utrecht, The Netherlands 2006
- Matsui Y, Fukuda Y, Inoue T, Matsushita T (2003) Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: characteristics and mechanism of competitive adsorption. *Water Research* 37: 4413-4424
- Mazola OJ (2008) Performance Evaluation of Slow Sand Filters: Removal of Natural Organic Matter Components and Characterization of Schmutzdecke. MSc. Thesis, UNESCO-IHE
- Michel P (1999) Characteristics of Natural Organic Matter Effecting Barium Sulphate Precipitation. MSc. Thesis, UNESCO-IHE
- Mohan D, Pittman JCU (2007) Arsenic removal from water/wastewater using adsorbents--A critical review. *Journal of Hazardous Materials* 142: 1-53
- Morel MMF (1983) Principles of Aquatic Chemistry A Wiley-Interscience publication New York
- Orlandini E (1999) Pesticide Removal by Combined Ozonation and Granular Activated Carbon Filtration.
- Owen DM, Amy GL, Chowdhury ZK, Paode R, McCoy G, Viscosil K (1995) NOM characterization and treatability. AWWA January
- Parkhurst DL, Appelo CAJ User's Guide to PHREEQC (Version 2)-A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations.
- Pelekani C, Snoeyink VL (1999) Competitive adsorption in natural water: role of activated carbon pore size. *Water Research* 33: 1209-1219
- Petrusevski B (2009) Module Groundwater Treatment and Resources. UNESCO-IHE.
- Rai D, Eary LE, Zachara JM (1989) Environmental chemistry of chromium. *Science of The Total Environment* 86: 15-23
- Schafer AI (2001) Natural Organics Removal Using Membranes. A Technomic Publishing Company Book, Lancaster, Pennsylvania
- Selomulya C, Meeyoo V, Amal R (1999) Mechanisms of Cr(VI) removal from water by various types of activated carbons. *Journal of Chemical Technology & Biotechnology* 74: 111-122
- Sharma SK (2001) Adsorptive Iron Removal from Groundwater. PhD Thesis, UNESCO-IHE
- Sharma SK (2007) Adsorption processes. UNESCO-IHE.
- Sharma SK, Petrusevski B, Gary A (2008) Chromium removal from water: a review. *Journal of Water Supply: research and Technology* 57: 541-553

- Smedley PL (2006) Sources and distribution of arsenic in groundwater aquifers. Paper presented at the Arsenic in Groundwater - A World Problem Utrecht, The Netherlands 2006
- Stumm W, Morgan JJ (1981) Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters Second Edition edn A Wiley-Interscience Publication
- Tessema BS (2004) Removal of chromium from groundwater using IOCS MSc. Thesis, UNESCO-IHE
- Theng BKG, Wake JRH, Posner AM (1967) THE HUMIC ACIDS EXTRACTED BY VARIOUS REAGENTS FROM A SOIL. European Journal of Soil Science 18: 349-363
- Thirunavukkarasu OS, Viraraghavan T, Subramanian KS, Tanjore S (2002) Organic arsenic removal from drinking water. Urban Water 4: 415-421
- Thurman EM (1985) Organic Geochemistry of Natural Waters. Martinus Nijhoff / DR W. Junk Publishers Dordrecht / Boston / Lancaster
- Thurman EM, Wershaw RL, Malcolm RL, Pinckney DJ (1982) Molecular size of aquatic humic substances. Organic Geochemistry 4: 27-35
- In situ* treatment of soil and groundwater contaminated with chromium (2000). Cited February 18, 2010
- Properties of humic substances (2009) <http://karnet.up.wroc.pl/~weber/kwasy2.htm>. Cited September, 28 2009
- Wu F-C, Tseng R-L, Huang S-C, Juang R-S (2009) Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: A mini-review. Chemical Engineering Journal 151: 1-9
- Xu H, Ephraim J, Ledin A, Allard B (1989) Effects of fulvic acid on the adsorption of Cd(II) on alumina. Science of The Total Environment 81-82: 653-660
- Yadav D (2007) Adsorptive Removal of Heavy Metals from Urban Storm Water Run-off. MSc. Thesis, UNESCO-IHE
- Yoon TH, Johnson SB, Brown GE (2004) Adsorption of Suwannee River Fulvic Acid on Aluminum Oxyhydroxide Surfaces: An In Situ ATR-FTIR Study. Langmuir 20: 5655-5658 DOI 10.1021/la0499214
- Zaporozec A (2004) Groundwater contamination inventory. UNESCO, Paris



## 7. APPENDIX

### Appendix A: Stability of Cr(VI)

Table 1: Stability of Cr(VI) as a function of Cr concentration with the **absence** of fulvic acid. Model water: Cr(VI) = 200 µg/l, HCO<sub>3</sub><sup>-</sup> = 100 mg/l.

Contact Time (hours)	Conc. of Total Cr (µg/l)			Conc. of [Cr(VI)] (µg/l)		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	185	189	194	166	162	164
2	184	178	185	168	160	164
4	185	192	202	162	164	170
6	183	198	177	160	166	166
8	186	185	183	170	168	166
24	182	187	181	164	160	164

Table 2: Stability of Cr(VI) as a function of Cr concentration with the **presence** of fulvic acid. Model water: Cr(VI) = 200 µg/l, HCO<sub>3</sub><sup>-</sup> = 100 mg/l.

Contact Time (hours)	Conc. of Total Cr (µg/l)			Conc. of [Cr(VI)] (µg/l)		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	203	188	189	164	166	164
2	183	192	199	156	164	162
4	192	197	207	160	166	170
6	189	188	200	166	166	162
8	190	194	188	164	166	166
24	191	195	193	160	168	166

### Appendix B: Short-term Batch Experiment

Table 3: Adsorption As(V) at pH 6, 7, and 8 by IOCS and GFH. Model water: initial conc. of As(V)= 200 µg/l, HCO<sub>3</sub><sup>-</sup> = 100 mg/l, dosage of adsorbent = 20 mg/l. Shaker speed: 100 rpm.

Contact Time (hours)	Conc. of [As(V)] (µg/l) by IOCS			Conc. of [As(V)] (µg/l) by GFH		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	177	173	188	159	184	176
2	140	146	172	52	88	93
4	114	139	160	47	81	86
6	115	138	160	39	75	87
8	110	136	160	31	71	78
24	75	119	145	11	31	47

Table 4: Adsorption Cr(VI) at pH 6, 7, and 8 by IOCS and GFH. Model water: initial conc. of Cr(VI)= 200 µg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 20 mg/l. Shaker speed: 100 rpm.

Contact Time (hours)	Conc. of [Cr(VI)] (µg/l) by IOCS			Conc. of [Cr(VI)] (µg/l) by GFH		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	194	207	228	240	229	242
2	177	189	221	180	201	215
4	178	207	214	214	217	228
6	170	196	221	187	208	226
8	168	196	222	168	212	214
24	178	205	214	147	201	229

Table 5: Adsorption FA at pH 6, 7, and 8 by IOCS and GFH. Model water: initial conc. of FA= 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 20 mg/l. Shaker speed: 100 rpm.

Contact Time (hours)	Conc. of FA (mg/l) by IOCS			Conc. of FA (mg/l) by GFH		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	194	207	228	240	229	242
2	177	189	221	180	201	215
4	178	207	214	214	217	228
6	170	196	221	187	208	226
8	168	196	222	168	212	214
24	178	205	214	147	201	229

Table 6: Adsorption of As(V) with 0 mg/l of FA at pH 6, 7, 8 by IOCS and GFH. Model water: initial conc. of As(V) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l. Shaker speed: 100 rpm.

Contact time (hours)	Conc. of [As(V)] (mg/l) by IOCS			Conc. of [As(V)] (mg/l) by GFH		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	2.06	1.53	1.89	1.86	1.53	1.71
2	1.61	1.29	1.71	0.35	0.56	0.91
4	1.24	1.21	1.36	0.23	0.40	0.91
6	1.36	1.05	1.45	0.16	0.32	0.82
8	1.24	0.97	1.45	0.24	0.08	0.73
24	0.76	0.73	1.18	0.02	0.04	0.11

Table 7: Adsorption of As(V) with 2 mg/l of FA at pH 6, 7, 8 by IOCS and GFH. Model water: initial conc. of As(V) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l. Shaker speed: 100 rpm.

Contact time (hours)	Conc. of [As(V)] (mg/l) by IOCS			Conc. of [As(V)] (mg/l) by GFH		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	1.79	1.45	1.71	1.84	1.45	1.80
2	1.65	1.29	1.63	0.46	0.48	0.82
4	1.37	1.21	1.54	0.32	0.40	0.64
6	1.49	1.13	1.54	0.35	0.32	0.64
8	1.46	1.05	1.54	0.24	0.16	0.55
24	0.89	0.73	1.18	0.02	0.08	0.11

Table 8: Adsorption of As(V) with 5 mg/l of FA at pH 6, 7, 8 by IOCS and GFH. Model water: initial conc. of As(V) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l. Shaker speed: 100 rpm.

Contact time (hours)	Conc. of [As(V)] (mg/l) by IOCS			Conc. of [As(V)] (mg/l) by GFH		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	1.89	1.45	1.71	1.95	1.53	1.89
2	1.53	1.37	1.54	0.41	0.56	0.82
4	1.54	1.29	1.45	0.37	0.40	0.73
6	1.53	1.13	1.45	0.24	0.32	0.91
8	1.55	1.13	1.45	0.32	0.24	0.73
24	1.13	0.81	1.36	0.04	0.08	0.38

Table 9: Adsorption of Cr(VI) with 0 mg/l of FA at pH 6, 7, 8 by IOCS and GFH. Model water: initial conc. of Cr(VI) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l. Shaker speed: 100 rpm.

Contact time (hours)	Conc. of [Cr(VI)] (mg/l) by IOCS			Conc. of [Cr(VI)] (mg/l) by GFH		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	1.84	1.99	1.85	1.87	1.82	1.82
2	1.66	1.97	1.91	0.74	1.46	1.55
4	1.75	2.03	1.77	0.66	1.37	1.42
6	1.68	1.91	1.77	0.61	1.40	1.49
8	1.72	1.98	1.83	0.56	1.39	1.50
24	1.64	1.90	1.84	0.34	1.33	1.50

Table 10: Adsorption of Cr(VI) with 2 mg/l of FA at pH 6, 7, 8 by IOCS and GFH. Model water: initial conc. of Cr(VI) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l. Shaker speed: 100 rpm.

Contact time (hours)	Conc. of [Cr(VI)] (mg/l) by IOCS			Conc. of [Cr(VI)] (mg/l) by GFH		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	1.75	2.06	1.87	1.87	1.85	1.89
2	1.66	1.87	1.75	0.74	1.50	1.55
4	1.69	1.95	1.64	0.66	1.42	1.48
6	1.62	1.95	1.80	0.61	1.45	1.57
8	1.65	1.97	1.83	0.56	1.39	1.52
24	1.61	1.96	1.89	0.34	1.27	1.57

Table 11: Adsorption of Cr(VI) with 5 mg/l of FA at pH 6, 7, 8 by IOCS and GFH. Model water: initial conc. of Cr(VI) = 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l, dosage of adsorbent = 200 mg/l. Shaker speed: 100 rpm.

Contact time (hours)	Conc. of [Cr(VI)] (mg/l) by IOCS			Conc. of [Cr(VI)] (mg/l) by GFH		
	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0	1.70	2.05	1.86	1.83	1.88	1.86
2	1.58	1.90	1.81	0.77	1.39	1.55
4	1.65	2.00	1.79	0.74	1.35	1.55
6	1.60	1.95	1.82	0.66	1.50	1.52
8	1.57	1.94	1.83	0.64	1.40	1.59
24	1.53	1.95	1.81	0.42	1.29	1.55

## Appendix C: Long Term Batch Experiment

Table 12: Adsorption isotherm of FA at pH 7 with various dosages of IOCS. Model water: initial conc. of FA= 5 mg/l,  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed: 100 rpm.

Contact time (day)	Conc. of FA with the dosage of adsorbent					
	20 (mg/l)	50 (mg/l)	75 (mg/l)	100 (mg/l)	150 (mg/l)	200 (mg/l)
0	4.989	4.934	4.934	4.934	4.934	4.934
5	4.938	4.962	5.010	5.010	5.057	5.033
10	4.968	4.878	4.946	4.946	4.991	4.721



Table 13: Adsorption of FA at pH 7 with higher dosages of IOCS. Model water: initial conc. of FA= 2 mg/l,  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed: 100 rpm.

Contact time (hours)	Conc. FA with the dosage of adsorbent						
	0.2 (g/l)	0.5 (g/l)	1 (g/l)	2 (g/l)	5 (g/l)	10 (g/l)	Blank
0	1.98	2.00	2.00	2.02	2.02	1.97	2.02
2	2.53	2.83	2.90	3.41	5.20	5.20	2.19
4	2.74	3.88	2.97	3.44	5.09	5.39	2.38
6	2.57	2.64	3.01	3.53	5.61	6.15	2.09
8	2.50	2.75	3.06	3.49	5.70	6.72	2.14
24	2.60	3.18	3.16	3.88	6.55	8.44	2.33

Table 14: Adsorption isotherm of FA at pH 7 by GFH. Model water: initial conc. of FA= 5 mg/l,  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed 100 rpm.

Bottle	Wt. of adsorbent (g)	Volume, V (L)	Initial conc., $C_o$ , ( $\mu\text{g/L}$ )	Final conc., $C_e$ , ( $\mu\text{g/L}$ )	Total amount of FA adsorbed, x, ( $\mu\text{g/L}$ )	Amount adsorbed FA per unit wt of GFH, q, ( $\mu\text{g/g}$ )
1	0.2	0.5	4789.474	1437.247	1676.11	8380.567
2	0.15	0.5	4767.544	1700.405	1533.57	10223.797
3	0.1	0.5	4789.474	2246.964	1271.26	12712.551
4	0.075	0.5	4745.614	2591.093	1077.26	14363.473
5	0.05	0.5	4745.614	3016.194	864.71	17294.197
6	0.02	0.5	4855.263	3643.725	605.77	30288.462

Table 15: Pseudo-first order kinetic adsorption isotherm of FA at pH 7 by GFH. Model water: initial conc. of FA= 5 mg/l,  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed 100 rpm.

Contact time (days)	Log q, with the dosage of GFH					
	20 mg/l	50 mg/l	75 mg/l	100 mg/l	150 mg/l	200 mg/l
1		1.112	1.073	1.042	1.023	0.985
5	1.553	1.368	1.320	1.228	1.179	1.149
10	1.676	1.469	1.406	1.359	1.264	1.203
15	1.758	1.521	1.440	1.395	1.298	1.222
19	1.761	1.537	1.440	1.399	1.300	1.234
24	1.754	1.537	1.461	1.392	1.303	1.229

Table 16: Pseudo-second order kinetic adsorption isotherm of FA at pH 7 by GFH. Model water: initial conc. of FA= 5 mg/l,  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed 100 rpm.

Contact time (days)	T/q <sub>(T)</sub> , with the dosage of GFH					
	20 mg/l	50 mg/l	75 mg/l	100 mg/l	150 mg/l	200 mg/l
1		0.076	0.083	0.089	0.094	0.102
5	0.139	0.211	0.236	0.291	0.328	0.352
10	0.209	0.334	0.387	0.432	0.539	0.621
15	0.259	0.445	0.537	0.595	0.747	0.891
19	0.326	0.542	0.679	0.748	0.942	1.099
24	0.419	0.685	0.819	0.961	1.182	1.404

#### Appendix D: Leaching of NOM from IOCS

Table 17: Leaching of NOM assessment at pH 6 with various dosages of IOCS. Model water:  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed 100 rpm.

Contact time (hours)	Dosage of adsorbent (g/l)						
	0.2	0.5	1	2	5	10	Blank
0	0.03	0.03	0.03	-0.01	-0.01	0.03	0.01
2	0.50	0.55	0.97	1.32	2.34	2.85	0.00
4	0.55	0.68	0.97	1.53	2.73	3.28	0.00
6	0.42	0.72	1.02	1.74	2.90	3.71	0.00
8	0.42	0.68	1.02	1.62	3.28	3.71	0.00
24	0.33	0.76	1.19	1.87	3.79	4.56	0.00

Table 18: Leaching of NOM assessment at pH 7 with various dosages of IOCS. Model water:  $\text{HCO}_3^-$  = 100 mg/l. Shaker speed 100 rpm.

Contact time (hours)	Dosage of adsorbent (g/l)						
	0.2	0.5	1	2	5	10	Blank
0	0.00	0.00	0.02	0.05	0.00	0.00	0.00
2	0.45	0.97	1.54	1.95	4.25	6.11	0.14
4	0.81	1.04	1.31	2.49	4.30	6.24	0.27
6	0.83	1.22	1.72	2.50	4.62	7.05	0.16
8	0.54	0.96	1.43	2.52	4.88	7.05	0.16
24	0.67	1.20	1.81	3.02	5.51	7.97	0.11

Table 19: Leaching of NOM assessment at pH 8 with various dosages of IOCS. Model water:  $\text{HCO}_3^- = 100 \text{ mg/l}$ . Shaker speed 100 rpm.

Contact time (hours)	Dosage of adsorbent (g/l)						
	0.2	0.5	1	2	5	10	Blank
0	-0.12	0.01	-0.12	-0.12	-0.08	-0.17	-0.14
2	0.97	1.83	2.57	4.18	6.44	9.40	-0.09
4	1.01	1.49	2.27	4.23	6.62	9.62	0.16
6	1.01	1.75	2.53	4.31	6.49	9.88	0.08
8	0.97	1.75	2.57	4.62	6.57	11.01	0.12
24	1.36	2.01	3.83	5.62	9.83	13.01	0.16

### Appendix E: Adsorption of metals by preloading GFH

Table 20: Adsorption of As(V) by preloading GFH. Model water:  $\text{HCO}_3^- = 100 \text{ mg/l}$  with initial metals concentration: 0.2, 0.5, 0.75, 1, 1.5, and 2 mg/l with the dosage of adsorbent: 20, 50, 75, 100, 150, and 200 mg/l respectively at pH 7. Shaker speed: 100 rpm.

Contact time (hours)	Conc. of As(V) (mg/l) with the dosage of adsorbent					
	20 mg/l	50 mg/l	75 mg/l	100 mg/l	150 mg/l	200 mg/l
0	0.181	0.280	0.470	0.690	1.140	1.600
2	0.134	0.190	0.240	0.460	0.640	0.880
4	0.131	0.170	0.260	0.460	0.570	0.840
6	0.135	0.180	0.250	0.360	0.500	0.740
8	0.129	0.130	0.210	0.350	0.390	0.710
24	0.099	0.130	0.237	0.260	0.380	0.220

Table 21: Adsorption of Cr(VI) by preloading GFH. Model water:  $\text{HCO}_3^- = 100 \text{ mg/l}$  with initial metals concentration: 0.2, 0.5, 0.75, 1, 1.5, and 2 mg/l with the dosage of adsorbent: 20, 50, 75, 100, 150, and 200 mg/l respectively at pH 7. Shaker speed: 100 rpm.

Contact time (hours)	Conc. of Cr(VI) (mg/l) with the dosage of adsorbent					
	20 mg/l	50 mg/l	75 mg/l	100 mg/l	150 mg/l	200 mg/l
0	0.216	0.441	0.641	0.720	1.080	1.500
2	0.181	0.273	0.473	0.740	0.980	1.290
4	0.159	0.284	0.462	0.700	0.980	1.270
6	0.179	0.273	0.410	0.680	0.970	1.210
8	0.161	0.284	0.504	0.750	1.000	1.210
24	0.154	0.252	0.483	0.640	0.810	1.010

**Appendix F: Standard deviation of the equipment**

Table 22: Standard deviation for spectrophotometer, assessed with standard solutions of Cr(VI).

Measurement	Absorbance (nm) at						
	0 mg/l	0.5 mg/l	1.0 mg/l	1.5 mg/l	2.0 mg/l	2.5 mg/l	3.0 mg/l
1	0.000	0.486	0.907	1.325	1.750	2.153	2.540
2	0.000	0.405	0.840	1.248	1.626	2.082	2.487
3	0.000	0.405	0.836	1.246	1.624	2.079	2.492
4	0.000	0.404	0.837	1.247	1.627	2.085	2.493
5	0.000	0.468	0.858	1.316	1.646	2.086	2.461
6	0.000	0.470	0.859	1.317	1.646	2.087	2.464
7	0.000	0.471	0.861	1.319	1.646	2.088	2.462
average	0.000	0.444	0.857	1.288	1.652	2.094	2.486
sd(standard deviation)	0.000	0.035	0.023	0.036	0.041	0.024	0.026
% of sd	0	7.79%	2.67%	2.78%	2.48%	1.15%	1.04%
2* $\sigma$	0.000	0.069	0.046	0.072	0.082	0.048	0.052
upper limit	0.000	0.513	0.903	1.360	1.734	2.143	2.537
lower limit	0.000	0.375	0.811	1.217	1.570	2.046	2.434

Table 23: Standard deviation for AAS-GF, assessed with standard solutions of Cr(VI).

Measurement	Absorbance (nm) at					
	0 $\mu$ g/l	5 $\mu$ g/l	10 $\mu$ g/l	15 $\mu$ g/l	20 $\mu$ g/l	30 $\mu$ g/l
1	0.057	0.189	0.326	0.438	0.510	0.744
2	0.038	0.103	0.173	0.242	0.266	0.412
3	0.101	0.189	0.273	0.366	0.410	0.607
4	0.075	0.212	0.334	0.452	0.506	0.765
5	0.095	0.266	0.468	0.595	0.660	0.974
6	0.124	0.224	0.337	0.442	0.489	0.759
7	0.088	0.221	0.387	0.510	0.589	0.878
8	0.075	0.197	0.337	0.446	0.506	0.770
9	0.047	0.131	0.213	0.318	0.335	0.510
10	0.079	0.151	0.196	0.316	0.412	0.566
average	0.078	0.188	0.304	0.413	0.468	0.699
sd(standard deviation)	0.025	0.046	0.087	0.098	0.110	0.163
% of sd	31.588%	24.319%	28.528%	23.813%	23.546%	23.390%
2* $\sigma$	0.049	0.092	0.174	0.196	0.221	0.327
upper limit	0.127	0.280	0.478	0.609	0.689	1.025
lower limit	0.029	0.097	0.131	0.216	0.248	0.372

Table 24: Standard deviation for AAS-GF, assessed with standard solutions of As(V).

Measurement	Absorbance (nm) at					
	0 µg/l	10 µg/l	20 µg/l	30 µg/l	40 µg/l	50 µg/l
1	0.008	0.037	0.071	0.108	0.129	0.161
2	0.006	0.033	0.062	0.087	0.117	0.149
3	0.012	0.033	0.073	0.093	0.117	0.147
4	0.008	0.037	0.073	0.099	0.144	0.162
5	0.013	0.036	0.065	0.102	0.128	0.159
average	0.009	0.035	0.069	0.098	0.127	0.156
sd(standard deviation)	0.003	0.002	0.004	0.007	0.010	0.006
% of sd	28.227%	5.207%	6.526%	7.413%	7.827%	4.056%
2*σ	0.005	0.004	0.009	0.014	0.020	0.013
upper limit	0.015	0.039	0.078	0.112	0.147	0.168
lower limit	0.004	0.032	0.060	0.083	0.107	0.143

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

### As(V) concentration 200 µg/l, at 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      20
  pH        6
  pe        4
  redox     pe
  units     mg/l
  density   1
  As(5)     0.2
  Na        37
  H(0)      1
  C         20
  O(0)      80
  water     1 # kg

```

Beginning of initial solution calculations.

Initial solution 1.

-----Solution composition-----					
Elements	Molality	Moles			
As (5)	2.670e-006	2.670e-006			
C	3.333e-004	3.333e-004			
H (0)	9.923e-004	9.923e-004			
Na	1.610e-003	1.610e-003			
O (0)	5.001e-003	5.001e-003			
-----Description of solution-----					
		pH	=	6.000	
		pe	=	4.000	
		Activity of water	=	1.000	
		Ionic strength	=	8.573e-004	
		Mass of water (kg)	=	1.000e+000	
		Total alkalinity (eq/kg)	=	9.976e-005	
		Total CO2 (mol/kg)	=	3.333e-004	
		Temperature (deg C)	=	20.000	
		Electrical balance (eq)	=	1.507e-003	
Percent error, 100*(Cat- An )/(Cat+ An )			=	87.94	
		Iterations	=	8	
		Total H	=	1.110152e+002	
		Total O	=	5.551284e+001	
-----Redox couples-----					
Redox couple	pe	Eh (volts)			
H (0) / H (1)	-5.9119	-0.3439			
O (-2) / O (0)	15.2078	0.8845			
-----Distribution of species-----					
Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.033e-006	1.000e-006	-5.986	-6.000	-0.014
OH-	7.088e-009	6.858e-009	-8.149	-8.164	-0.014
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
As (5)	2.670e-006				
H2AsO4-	2.386e-006	2.306e-006	-5.622	-5.637	-0.015
HAsO4-2	2.838e-007	2.477e-007	-6.547	-6.606	-0.059
H3AsO4	3.815e-010	3.816e-010	-9.418	-9.418	0.000
AsO4-3	9.466e-013	6.967e-013	-12.024	-12.157	-0.133
C (4)	3.333e-004				
H2CO3	2.328e-004	2.328e-004	-3.633	-3.633	0.000
HCO3-	1.004e-004	9.720e-005	-3.998	-4.012	-0.014
NaHCO3	9.357e-008	9.357e-008	-7.029	-7.029	0.000
CO3-2	4.699e-009	4.121e-009	-8.328	-8.385	-0.057
NaCO3-	1.420e-010	1.375e-010	-9.848	-9.862	-0.014
H (0)	9.923e-004				
H2	4.961e-004	4.962e-004	-3.304	-3.304	0.000
Na	1.610e-003				
Na+	1.610e-003	1.558e-003	-2.793	-2.808	-0.014
NaHCO3	9.357e-008	9.357e-008	-7.029	-7.029	0.000
NaCO3-	1.420e-010	1.375e-010	-9.848	-9.862	-0.014
O (0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000
-----Saturation indices-----					

Phase	SI	log IAP	log KT	
As2O5	-25.61	-18.84	6.77	As2O5
CH4(g)	-58.57	-100.38	-41.81	CH4
CO2(g)	-2.23	-20.38	-18.16	CO2
Natron	-12.49	-14.00	-1.51	Na2CO3:10H2O
O2(g)	-44.80	40.00	84.80	O2
Thermonatrite	-14.67	-14.00	0.67	Na2CO3:H2O

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

### As(V) concentration 200 µg/l, at pH 7

-----  
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 20  
pH 7  
pe 4  
redox pe  
units mg/l  
density 1  
As(5) 0.2  
Na 37  
H(0) 1  
C 20  
O(0) 80  
water 1 # kg

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

Initial solution 1.

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

Elements	Molality	Moles
As(5)	2.670e-006	2.670e-006
C	3.333e-004	3.333e-004
H(0)	9.923e-004	9.923e-004
Na	1.610e-003	1.610e-003

O(0) 5.001e-003 5.001e-003

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

pH = 7.000  
 pe = 4.000  
 Activity of water = 1.000  
 Ionic strength = 9.437e-004  
 Mass of water (kg) = 1.000e+000  
 Total alkalinity (eq/kg) = 2.723e-004  
 Total CO2 (mol/kg) = 3.333e-004  
 Temperature (deg C) = 20.000  
 Electrical balance (eq) = 1.335e-003  
 Percent error, 100\*(Cat-|An|)/(Cat+|An|) = 70.83  
 Iterations = 4  
 Total H = 1.110151e+002  
 Total O = 5.551284e+001

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-6.9119	-0.4020
O(-2)/O(0)	14.2078	0.8264

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.035e-007	1.000e-007	-6.985	-7.000	-0.015
OH-	7.099e-008	6.858e-008	-7.149	-7.164	-0.015
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
As(5)	2.670e-006				
HAsO4-2	1.454e-006	1.260e-006	-5.837	-5.900	-0.062
H2AsO4-	1.216e-006	1.173e-006	-5.915	-5.931	-0.016
AsO4-3	4.890e-011	3.545e-011	-10.311	-10.450	-0.140
H3AsO4	1.941e-011	1.942e-011	-10.712	-10.712	0.000
C(4)	3.333e-004				
HCO3-	2.703e-004	2.613e-004	-3.568	-3.583	-0.015
H2CO3	6.260e-005	6.260e-005	-4.203	-4.203	0.000
NaHCO3	2.512e-007	2.512e-007	-6.600	-6.600	0.000
CO3-2	1.271e-007	1.108e-007	-6.896	-6.955	-0.060
NaCO3-	3.818e-009	3.691e-009	-8.418	-8.433	-0.015
H(0)	9.923e-004				
H2	4.961e-004	4.963e-004	-3.304	-3.304	0.000
Na	1.610e-003				
Na+	1.609e-003	1.555e-003	-2.793	-2.808	-0.015
NaHCO3	2.512e-007	2.512e-007	-6.600	-6.600	0.000
NaCO3-	3.818e-009	3.691e-009	-8.418	-8.433	-0.015
O(0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000

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

Phase	SI	log IAP	log KT	
As2O5	-28.20	-21.42	6.77	As2O5
CH4(g)	-67.14	-108.96	-41.81	CH4
CO2(g)	-2.80	-20.96	-18.16	CO2
Natron	-11.06	-12.57	-1.51	Na2CO3:10H2O



O2(g)	-40.80	44.00	84.80	O2
Thermonatrite	-13.24	-12.57	0.67	Na2CO3:H2O

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

### As(V) concentration 200 µg/l, at pH 8

-----  
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      20
  pH         8
  pe         4
  redox      pe
  units      mg/l
  density    1
  As(5)      0.2
  Na         37
  H(0)       1
  C          20
  O(0)       80
  water      1 # kg

```

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

Initial solution 1.

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

Elements	Molality	Moles
As(5)	2.670e-006	2.670e-006
C	3.333e-004	3.333e-004
H(0)	9.923e-004	9.923e-004
Na	1.610e-003	1.610e-003
O(0)	5.001e-003	5.001e-003

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

pH	=	8.000
pe	=	4.000
Activity of water	=	1.000

```

          Ionic strength = 9.751e-004
        Mass of water (kg) = 1.000e+000
    Total alkalinity (eq/kg) = 3.306e-004
        Total CO2 (mol/kg) = 3.333e-004
        Temperature (deg C) = 20.000
        Electrical balance (eq) = 1.276e-003
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 65.72
          Iterations = 4
            Total H = 1.110150e+002
            Total O = 5.551284e+001

```

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-7.9119	-0.4602
O(-2)/O(0)	13.2078	0.7682

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	7.103e-007	6.858e-007	-6.149	-6.164	-0.015
H+	1.035e-008	1.000e-008	-7.985	-8.000	-0.015
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
As(5)	2.670e-006				
HAsO4-2	2.463e-006	2.130e-006	-5.608	-5.672	-0.063
H2AsO4-	2.057e-007	1.983e-007	-6.687	-6.703	-0.016
AsO4-3	8.310e-010	5.993e-010	-9.080	-9.222	-0.142
H3AsO4	3.282e-013	3.282e-013	-12.484	-12.484	0.000
C(4)	3.333e-004				
HCO3-	3.239e-004	3.130e-004	-3.490	-3.504	-0.015
H2CO3	7.497e-006	7.497e-006	-5.125	-5.125	0.000
CO3-2	1.526e-006	1.327e-006	-5.817	-5.877	-0.061
NaHCO3	3.006e-007	3.006e-007	-6.522	-6.522	0.000
NaCO3-	4.572e-008	4.418e-008	-7.340	-7.355	-0.015
H(0)	9.923e-004				
H2	4.961e-004	4.963e-004	-3.304	-3.304	0.000
Na	1.610e-003				
Na+	1.609e-003	1.554e-003	-2.793	-2.809	-0.015
NaHCO3	3.006e-007	3.006e-007	-6.522	-6.522	0.000
NaCO3-	4.572e-008	4.418e-008	-7.340	-7.355	-0.015
O(0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000

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

Phase	SI	log IAP	log KT	
As2O5	-31.74	-24.97	6.77	As2O5
CH4(g)	-76.06	-117.88	-41.81	CH4
CO2(g)	-3.72	-21.88	-18.16	CO2
Natron	-9.99	-11.49	-1.51	Na2CO3:10H2O
O2(g)	-36.80	48.00	84.80	O2
Thermonatrite	-12.16	-11.49	0.67	Na2CO3:H2O

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

Cr(VI) concentration 200 µg/l, at 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        20  
     pH          6  
     pe          4  
     redox       pe  
     units       mg/l  
     density     1  
     Cr(6)       0.2  
     Na          37  
     H(0)        1  
     C           20  
     O(0)        80  
     water       1 # kg

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

Initial solution 1.

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

Elements	Molality	Moles
C	3.333e-004	3.333e-004
Cr(6)	3.847e-006	3.847e-006
H(0)	9.923e-004	9.923e-004
Na	1.610e-003	1.610e-003
O(0)	5.001e-003	5.001e-003

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

pH	=	6.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	8.589e-004
Mass of water (kg)	=	1.000e+000
Total alkalinity (eq/kg)	=	1.005e-004
Total CO2 (mol/kg)	=	3.333e-004
Temperature (deg C)	=	20.000
Electrical balance (eq)	=	1.505e-003
Percent error, 100*(Cat- An )/(Cat+ An )	=	87.73
Iterations	=	8

Total H = 1.110152e+002  
Total O = 5.551285e+001

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-5.9119	-0.3439
O(-2)/O(0)	15.2078	0.8845

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.033e-006	1.000e-006	-5.986	-6.000	-0.014
OH-	7.088e-009	6.858e-009	-8.149	-8.164	-0.014
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	3.333e-004				
H2CO3	2.328e-004	2.328e-004	-3.633	-3.633	0.000
HCO3-	1.004e-004	9.720e-005	-3.998	-4.012	-0.014
NaHCO3	9.357e-008	9.357e-008	-7.029	-7.029	0.000
CO3-2	4.699e-009	4.121e-009	-8.328	-8.385	-0.057
NaCO3-	1.420e-010	1.375e-010	-9.848	-9.862	-0.014
Cr(6)	3.847e-006				
HCrO4-	2.854e-006	2.758e-006	-5.545	-5.559	-0.015
CrO4-2	9.854e-007	8.642e-007	-6.006	-6.063	-0.057
NaCrO4-	6.921e-009	6.689e-009	-8.160	-8.175	-0.015
Cr2O7-2	3.446e-010	3.007e-010	-9.463	-9.522	-0.059
H2CrO4	1.733e-012	1.733e-012	-11.761	-11.761	0.000
H(0)	9.923e-004				
H2	4.961e-004	4.962e-004	-3.304	-3.304	0.000
Na	1.610e-003				
Na+	1.610e-003	1.558e-003	-2.793	-2.808	-0.014
NaHCO3	9.357e-008	9.357e-008	-7.029	-7.029	0.000
NaCrO4-	6.921e-009	6.689e-009	-8.160	-8.175	-0.015
NaCO3-	1.420e-010	1.375e-010	-9.848	-9.862	-0.014
O(0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000

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

Phase	SI	log IAP	log KT	
CH4(g)	-58.57	-100.38	-41.81	CH4
CO2(g)	-2.23	-20.38	-18.16	CO2
CrO3	-14.87	-18.06	-3.19	CrO3
Na2Cr2O7	-19.78	-29.74	-9.96	Na2Cr2O7
Na2CrO4	-14.67	-11.68	2.99	Na2CrO4
Natron	-12.49	-14.00	-1.51	Na2CO3:10H2O
O2(g)	-44.80	40.00	84.80	O2
Thermonatrite	-14.67	-14.00	0.67	Na2CO3:H2O

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

Cr(VI) concentration 200 µg/l, at pH 7

-----  
 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      20  
   pH        7  
   pe        4  
   redox     pe  
   units     mg/l  
   density   1  
   Cr(6)     0.2  
   Na        37  
   H(0)      1  
   C         20  
   O(0)      80  
   water     1 # kg

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

Initial solution 1.

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

Elements	Molality	Moles
C	3.333e-004	3.333e-004
Cr(6)	3.847e-006	3.847e-006
H(0)	9.923e-004	9.923e-004
Na	1.610e-003	1.610e-003
O(0)	5.001e-003	5.001e-003

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	9.466e-004
Mass of water (kg)	=	1.000e+000
Total alkalinity (eq/kg)	=	2.738e-004
Total CO2 (mol/kg)	=	3.333e-004
Temperature (deg C)	=	20.000
Electrical balance (eq)	=	1.332e-003
Percent error, 100*(Cat- An )/(Cat+ An )	=	70.59
Iterations	=	4

Total H = 1.110151e+002

Total O = 5.551285e+001

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-6.9119	-0.4020
O(-2)/O(0)	14.2078	0.8264

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.035e-007	1.000e-007	-6.985	-7.000	-0.015
OH-	7.099e-008	6.858e-008	-7.149	-7.164	-0.015
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	3.333e-004				
HCO3-	2.703e-004	2.613e-004	-3.568	-3.583	-0.015
H2CO3	6.260e-005	6.260e-005	-4.203	-4.203	0.000
NaHCO3	2.511e-007	2.511e-007	-6.600	-6.600	0.000
CO3-2	1.271e-007	1.108e-007	-6.896	-6.955	-0.060
NaCO3-	3.818e-009	3.690e-009	-8.418	-8.433	-0.015
Cr(6)	3.847e-006				
CrO4-2	2.970e-006	2.588e-006	-5.527	-5.587	-0.060
HCrO4-	8.562e-007	8.261e-007	-6.067	-6.083	-0.016
NaCrO4-	2.073e-008	2.000e-008	-7.683	-7.699	-0.016
Cr2O7-2	3.112e-011	2.697e-011	-10.507	-10.569	-0.062
H2CrO4	5.191e-014	5.191e-014	-13.285	-13.285	0.000
H(0)	9.923e-004				
H2	4.961e-004	4.963e-004	-3.304	-3.304	0.000
Na	1.610e-003				
Na+	1.609e-003	1.555e-003	-2.793	-2.808	-0.015
NaHCO3	2.511e-007	2.511e-007	-6.600	-6.600	0.000
NaCrO4-	2.073e-008	2.000e-008	-7.683	-7.699	-0.016
NaCO3-	3.818e-009	3.690e-009	-8.418	-8.433	-0.015
O(0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000

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

Phase	SI	log IAP	log KT	
CH4(g)	-67.14	-108.96	-41.81	CH4
CO2(g)	-2.80	-20.96	-18.16	CO2
CrO3	-16.39	-19.59	-3.19	CrO3
Na2Cr2O7	-20.83	-30.79	-9.96	Na2Cr2O7
Na2CrO4	-14.19	-11.20	2.99	Na2CrO4
Natron	-11.06	-12.57	-1.51	Na2CO3:10H2O
O2(g)	-40.80	44.00	84.80	O2
Thermonatrite	-13.24	-12.57	0.67	Na2CO3:H2O

End of simulation.

Cr(VI) concentration 200 µg/l, at pH 8

-----  
 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        20  
     pH          8  
     pe          4  
     redox       pe  
     units       mg/l  
     density     1  
     Cr(6)       0.2  
     Na          37  
     H(0)        1  
     C           20  
     O(0)        80  
     water       1 # kg

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

Initial solution 1.

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

Elements	Molality	Moles
C	3.333e-004	3.333e-004
Cr(6)	3.847e-006	3.847e-006
H(0)	9.923e-004	9.923e-004
Na	1.610e-003	1.610e-003
O(0)	5.001e-003	5.001e-003

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

pH	=	8.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	9.775e-004
Mass of water (kg)	=	1.000e+000
Total alkalinity (eq/kg)	=	3.318e-004
Total CO2 (mol/kg)	=	3.333e-004
Temperature (deg C)	=	20.000
Electrical balance (eq)	=	1.274e-003
Percent error, 100*(Cat- An )/(Cat+ An )	=	65.51
Iterations	=	3

Total H = 1.110150e+002  
Total O = 5.551285e+001

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-7.9119	-0.4602
O(-2)/O(0)	13.2078	0.7682

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	7.103e-007	6.858e-007	-6.149	-6.164	-0.015
H+	1.036e-008	1.000e-008	-7.985	-8.000	-0.015
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	3.333e-004				
HCO3-	3.239e-004	3.130e-004	-3.490	-3.504	-0.015
H2CO3	7.497e-006	7.497e-006	-5.125	-5.125	0.000
CO3-2	1.526e-006	1.327e-006	-5.816	-5.877	-0.061
NaHCO3	3.006e-007	3.006e-007	-6.522	-6.522	0.000
NaCO3-	4.572e-008	4.417e-008	-7.340	-7.355	-0.015
Cr(6)	3.847e-006				
CrO4-2	3.714e-006	3.230e-006	-5.430	-5.491	-0.061
HCrO4-	1.069e-007	1.031e-007	-6.971	-6.987	-0.016
NaCrO4-	2.587e-008	2.494e-008	-7.587	-7.603	-0.016
Cr2O7-2	4.858e-013	4.200e-013	-12.314	-12.377	-0.063
H2CrO4	6.478e-016	6.478e-016	-15.189	-15.189	0.000
H(0)	9.923e-004				
H2	4.961e-004	4.963e-004	-3.304	-3.304	0.000
Na	1.610e-003				
Na+	1.609e-003	1.554e-003	-2.793	-2.809	-0.015
NaHCO3	3.006e-007	3.006e-007	-6.522	-6.522	0.000
NaCO3-	4.572e-008	4.417e-008	-7.340	-7.355	-0.015
NaCrO4-	2.587e-008	2.494e-008	-7.587	-7.603	-0.016
O(0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000

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

Phase	SI	log IAP	log KT	
CH4(g)	-76.06	-117.88	-41.81	CH4
CO2(g)	-3.72	-21.88	-18.16	CO2
CrO3	-18.30	-21.49	-3.19	CrO3
Na2Cr2O7	-22.64	-32.60	-9.96	Na2Cr2O7
Na2CrO4	-14.10	-11.11	2.99	Na2CrO4
Natron	-9.99	-11.49	-1.51	Na2CO3:10H2O
O2(g)	-36.80	48.00	84.80	O2
Thermonatrite	-12.16	-11.49	0.67	Na2CO3:H2O

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



As(V) concentration 2 mg/l, at 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        20  
     pH          6  
     pe          4  
     redox       pe  
     units       mg/l  
     density     1  
     As(5)       2  
     Na          37  
     H(0)        1  
     C           20  
     O(0)        80  
     water       1 # kg

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

Initial solution 1.

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

Elements	Molality	Moles
As(5)	2.670e-005	2.670e-005
C	3.333e-004	3.333e-004
H(0)	9.923e-004	9.923e-004
Na	1.610e-003	1.610e-003
O(0)	5.001e-003	5.001e-003

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

pH	=	6.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	8.731e-004
Mass of water (kg)	=	1.000e+000
Total alkalinity (eq/kg)	=	1.023e-004
Total CO2 (mol/kg)	=	3.333e-004
Temperature (deg C)	=	20.000
Electrical balance (eq)	=	1.481e-003
Percent error, 100*(Cat- An )/(Cat+ An )	=	85.07
Iterations	=	8

Total H = 1.110153e+002  
Total O = 5.551294e+001

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-5.9119	-0.3439
O(-2)/O(0)	15.2078	0.8845

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.034e-006	1.000e-006	-5.986	-6.000	-0.014
OH-	7.090e-009	6.858e-009	-8.149	-8.164	-0.014
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
As(5)	2.670e-005				
H2AsO4-	2.385e-005	2.305e-005	-4.622	-4.637	-0.015
HAsO4-2	2.840e-006	2.476e-006	-5.547	-5.606	-0.060
H3AsO4	3.814e-009	3.814e-009	-8.419	-8.419	0.000
AsO4-3	9.489e-012	6.964e-012	-11.023	-11.157	-0.134
C(4)	3.333e-004				
H2CO3	2.328e-004	2.328e-004	-3.633	-3.633	0.000
HCO3-	1.004e-004	9.719e-005	-3.998	-4.012	-0.014
NaHCO3	9.354e-008	9.354e-008	-7.029	-7.029	0.000
CO3-2	4.704e-009	4.121e-009	-8.328	-8.385	-0.057
NaCO3-	1.420e-010	1.374e-010	-9.848	-9.862	-0.014
H(0)	9.923e-004				
H2	4.962e-004	4.963e-004	-3.304	-3.304	0.000
Na	1.610e-003				
Na+	1.610e-003	1.557e-003	-2.793	-2.808	-0.014
NaHCO3	9.354e-008	9.354e-008	-7.029	-7.029	0.000
NaCO3-	1.420e-010	1.374e-010	-9.848	-9.862	-0.014
O(0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000

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

Phase	SI	log IAP	log KT	
As2O5	-23.61	-16.84	6.77	As2O5
CH4(g)	-58.57	-100.38	-41.81	CH4
CO2(g)	-2.23	-20.38	-18.16	CO2
Natron	-12.49	-14.00	-1.51	Na2CO3:10H2O
O2(g)	-44.80	40.00	84.80	O2
Thermonatrite	-14.67	-14.00	0.67	Na2CO3:H2O

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

As(V) concentration 2 mg/l, at pH 7

-----  
 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      20  
   pH       7  
   pe       4  
   redox     pe  
   units     mg/l  
   density   1  
   As(5)     2  
   Na       37  
   H(0)      1  
   C        20  
   O(0)      80  
   water     1 # kg

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

Initial solution 1.

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

Elements	Molality	Moles
As(5)	2.670e-005	2.670e-005
C	3.333e-004	3.333e-004
H(0)	9.923e-004	9.923e-004
Na	1.610e-003	1.610e-003
O(0)	5.001e-003	5.001e-003

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	9.754e-004
Mass of water (kg)	=	1.000e+000
Total alkalinity (eq/kg)	=	2.854e-004
Total CO2 (mol/kg)	=	3.333e-004
Temperature (deg C)	=	20.000
Electrical balance (eq)	=	1.298e-003
Percent error, 100*(Cat- An )/(Cat+ An )	=	67.53
Iterations	=	4

Total H = 1.110151e+002

Total O = 5.551294e+001

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-6.9119	-0.4020
O(-2)/O(0)	14.2078	0.8264

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.035e-007	1.000e-007	-6.985	-7.000	-0.015
OH-	7.103e-008	6.858e-008	-7.149	-7.164	-0.015
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
As(5)	2.670e-005				
HAsO4-2	1.455e-005	1.258e-005	-4.837	-4.900	-0.063
H2AsO4-	1.215e-005	1.171e-005	-4.916	-4.931	-0.016
AsO4-3	4.908e-010	3.540e-010	-9.309	-9.451	-0.142
H3AsO4	1.938e-010	1.939e-010	-9.713	-9.712	0.000
C(4)	3.333e-004				
HCO3-	2.704e-004	2.612e-004	-3.568	-3.583	-0.015
H2CO3	6.257e-005	6.257e-005	-4.204	-4.204	0.000
NaHCO3	2.509e-007	2.509e-007	-6.600	-6.600	0.000
CO3-2	1.273e-007	1.108e-007	-6.895	-6.956	-0.061
NaCO3-	3.816e-009	3.687e-009	-8.418	-8.433	-0.015
H(0)	9.923e-004				
H2	4.962e-004	4.963e-004	-3.304	-3.304	0.000
Na	1.610e-003				
Na+	1.609e-003	1.554e-003	-2.793	-2.808	-0.015
NaHCO3	2.509e-007	2.509e-007	-6.600	-6.600	0.000
NaCO3-	3.816e-009	3.687e-009	-8.418	-8.433	-0.015
O(0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000

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

Phase	SI	log IAP	log KT	
As2O5	-26.20	-19.42	6.77	As2O5
CH4(g)	-67.14	-108.96	-41.81	CH4
CO2(g)	-2.80	-20.96	-18.16	CO2
Natron	-11.07	-12.57	-1.51	Na2CO3:10H2O
O2(g)	-40.80	44.00	84.80	O2
Thermonatrite	-13.24	-12.57	0.67	Na2CO3:H2O

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

As(V) concentration 2 mg/l, at pH 8

-----  
 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        20  
     pH          8  
     pe          4  
     redox        pe  
     units        mg/l  
     density      1  
     As(5)        2  
     Na          37  
     H(0)         1  
     C            20  
     O(0)         80  
     water        1 # kg

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

Initial solution 1.

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

Elements	Molality	Moles
As(5)	2.670e-005	2.670e-005
C	3.333e-004	3.333e-004
H(0)	9.923e-004	9.923e-004
Na	1.610e-003	1.610e-003
O(0)	5.001e-003	5.001e-003

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

pH	=	8.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	1.020e-003
Mass of water (kg)	=	1.000e+000
Total alkalinity (eq/kg)	=	3.528e-004
Total CO2 (mol/kg)	=	3.333e-004
Temperature (deg C)	=	20.000
Electrical balance (eq)	=	1.230e-003
Percent error, 100*(Cat- An )/(Cat+ An )	=	61.87
Iterations	=	4

Total H = 1.110150e+002  
Total O = 5.551294e+001

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-7.9119	-0.4602
O(-2)/O(0)	13.2078	0.7682

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	7.108e-007	6.858e-007	-6.148	-6.164	-0.016
H+	1.036e-008	1.000e-008	-7.985	-8.000	-0.015
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
As(5)	2.670e-005				
HAsO4-2	2.464e-005	2.124e-005	-4.608	-4.673	-0.065
H2AsO4-	2.052e-006	1.977e-006	-5.688	-5.704	-0.016
AsO4-3	8.346e-009	5.974e-009	-8.079	-8.224	-0.145
H3AsO4	3.271e-012	3.272e-012	-11.485	-11.485	0.000
C(4)	3.333e-004				
HCO3-	3.240e-004	3.128e-004	-3.490	-3.505	-0.015
H2CO3	7.492e-006	7.492e-006	-5.125	-5.125	0.000
CO3-2	1.529e-006	1.326e-006	-5.815	-5.877	-0.062
NaHCO3	3.002e-007	3.002e-007	-6.523	-6.523	0.000
NaCO3-	4.569e-008	4.411e-008	-7.340	-7.355	-0.015
H(0)	9.923e-004				
H2	4.962e-004	4.963e-004	-3.304	-3.304	0.000
Na	1.610e-003				
Na+	1.609e-003	1.553e-003	-2.793	-2.809	-0.015
NaHCO3	3.002e-007	3.002e-007	-6.523	-6.523	0.000
NaCO3-	4.569e-008	4.411e-008	-7.340	-7.355	-0.015
O(0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000

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

Phase	SI	log IAP	log KT	
As2O5	-29.74	-22.97	6.77	As2O5
CH4(g)	-76.06	-117.88	-41.81	CH4
CO2(g)	-3.72	-21.88	-18.16	CO2
Natron	-9.99	-11.50	-1.51	Na2CO3:10H2O
O2(g)	-36.80	48.00	84.80	O2
Thermonatrite	-12.16	-11.50	0.67	Na2CO3:H2O

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

Cr(VI) concentration 2 mg/l, at 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        20  
     pH          6  
     pe          4  
     redox       pe  
     units       mmol/kgw  
     density     1  
     Cr(6)       1.4  
     Na          37  
     H(0)        1  
     C           20  
     O(0)        80  
     K           0.6  
     water       1 # kg

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

Initial solution 1.

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

Elements	Molality	Moles
C	2.000e-002	2.000e-002
Cr(6)	1.400e-003	1.400e-003
H(0)	1.000e-003	1.000e-003
K	6.000e-004	6.000e-004
Na	3.700e-002	3.700e-002
O(0)	8.000e-002	8.000e-002

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

pH	=	6.000
pe	=	4.000
Activity of water	=	0.998
Ionic strength	=	2.330e-002
Mass of water (kg)	=	1.000e+000
Total alkalinity (eq/kg)	=	7.012e-003
Total CO2 (mol/kg)	=	2.000e-002
Temperature (deg C)	=	20.000
Electrical balance (eq)	=	2.919e-002

Percent error,  $100 * (Cat - |An|) / (Cat + |An|) = 63.86$   
Iterations = 7  
Total H = 1.110490e+002  
Total O = 5.565239e+001

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-5.9147	-0.3440
O(-2)/O(0)	15.5098	0.9021

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.157e-006	1.000e-006	-5.937	-6.000	-0.063
OH-	7.964e-009	6.847e-009	-8.099	-8.164	-0.066
H2O	5.551e+001	9.983e-001	1.744	-0.001	0.000
C(4)	2.000e-002				
H2CO3	1.344e-002	1.344e-002	-1.872	-1.872	0.000
HCO3-	6.452e-003	5.610e-003	-2.190	-2.251	-0.061
NaHCO3	1.104e-004	1.104e-004	-3.957	-3.957	0.000
CO3-2	4.264e-007	2.379e-007	-6.370	-6.624	-0.253
NaCO3-	1.866e-007	1.622e-007	-6.729	-6.790	-0.061
Cr(6)	1.400e-003				
HCrO4-	8.652e-004	7.245e-004	-3.063	-3.140	-0.077
CrO4-2	4.069e-004	2.270e-004	-3.391	-3.644	-0.253
NaCrO4-	4.290e-005	3.592e-005	-4.368	-4.445	-0.077
Cr2O7-2	4.226e-005	2.077e-005	-4.374	-4.682	-0.308
KCrO4-	5.218e-007	4.369e-007	-6.282	-6.360	-0.077
H2CrO4	4.553e-010	4.553e-010	-9.342	-9.342	0.000
H(0)	1.000e-003				
H2	5.000e-004	5.027e-004	-3.301	-3.299	0.002
K	6.000e-004				
K+	5.995e-004	5.181e-004	-3.222	-3.286	-0.063
KCrO4-	5.218e-007	4.369e-007	-6.282	-6.360	-0.077
Na	3.700e-002				
Na+	3.685e-002	3.184e-002	-1.434	-1.497	-0.063
NaHCO3	1.104e-004	1.104e-004	-3.957	-3.957	0.000
NaCrO4-	4.290e-005	3.592e-005	-4.368	-4.445	-0.077
NaCO3-	1.866e-007	1.622e-007	-6.729	-6.790	-0.061
O(0)	8.000e-002				
O2	4.000e-002	4.022e-002	-1.398	-1.396	0.002

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

Phase	SI	log IAP	log KT	
CH4(g)	-56.81	-98.62	-41.81	CH4
CO2(g)	-0.46	-18.62	-18.16	CO2
CrO3	-12.45	-15.64	-3.19	CrO3
K2Cr2O7	-8.37	-25.86	-17.48	K2Cr2O7
K2CrO4	-9.65	-10.22	-0.57	K2CrO4
Na2Cr2O7	-12.32	-22.28	-9.96	Na2Cr2O7
Na2CrO4	-9.63	-6.64	2.99	Na2CrO4
Natron	-8.12	-9.62	-1.51	Na2CO3:10H2O
O2(g)	-44.80	40.00	84.80	O2
Thermonatrite	-10.29	-9.62	0.67	Na2CO3:H2O

End of simulation.



Cr(VI) concentration 2 mg/l, at pH 7

-----  
 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        20  
     pH          7  
     pe          4  
     redox       pe  
     units       mg/l  
     density     1  
     Cr(6)       1.4  
     Na          37  
     H(0)        1  
     C           20  
     O(0)        80  
     K           0.6  
     water       1 # kg

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

Initial solution 1.

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

Elements	Molality	Moles
C	3.333e-004	3.333e-004
Cr(6)	2.693e-005	2.693e-005
H(0)	9.923e-004	9.923e-004
K	1.535e-005	1.535e-005
Na	1.610e-003	1.610e-003
O(0)	5.001e-003	5.001e-003

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

pH	=	7.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	9.925e-004
Mass of water (kg)	=	1.000e+000
Total alkalinity (eq/kg)	=	2.918e-004
Total CO2 (mol/kg)	=	3.333e-004
Temperature (deg C)	=	20.000
Electrical balance (eq)	=	1.306e-003

Percent error,  $100 \cdot (\text{Cat} - |\text{An}|) / (\text{Cat} + |\text{An}|) = 67.22$   
Iterations = 4  
Total H = 1.110151e+002  
Total O = 5.551294e+001

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-6.9119	-0.4020
O(-2)/O(0)	14.2078	0.8264

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.036e-007	1.000e-007	-6.985	-7.000	-0.015
OH-	7.105e-008	6.858e-008	-7.148	-7.164	-0.015
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	3.333e-004				
HCO3-	2.704e-004	2.612e-004	-3.568	-3.583	-0.015
H2CO3	6.256e-005	6.256e-005	-4.204	-4.204	0.000
NaHCO3	2.508e-007	2.508e-007	-6.601	-6.601	0.000
CO3-2	1.275e-007	1.107e-007	-6.895	-6.956	-0.061
NaCO3-	3.815e-009	3.685e-009	-8.419	-8.434	-0.015
Cr(6)	2.693e-005				
CrO4-2	2.080e-005	1.807e-005	-4.682	-4.743	-0.061
HCrO4-	5.982e-006	5.767e-006	-5.223	-5.239	-0.016
NaCrO4-	1.447e-007	1.395e-007	-6.840	-6.855	-0.016
Cr2O7-2	1.522e-009	1.314e-009	-8.818	-8.881	-0.064
KCrO4-	1.032e-009	9.946e-010	-8.986	-9.002	-0.016
H2CrO4	3.624e-013	3.624e-013	-12.441	-12.441	0.000
H(0)	9.923e-004				
H2	4.962e-004	4.963e-004	-3.304	-3.304	0.000
K	1.535e-005				
K+	1.535e-005	1.482e-005	-4.814	-4.829	-0.015
KCrO4-	1.032e-009	9.946e-010	-8.986	-9.002	-0.016
Na	1.610e-003				
Na+	1.609e-003	1.554e-003	-2.793	-2.809	-0.015
NaHCO3	2.508e-007	2.508e-007	-6.601	-6.601	0.000
NaCrO4-	1.447e-007	1.395e-007	-6.840	-6.855	-0.016
NaCO3-	3.815e-009	3.685e-009	-8.419	-8.434	-0.015
O(0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000

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

Phase	SI	log IAP	log KT	
CH4(g)	-67.14	-108.96	-41.81	CH4
CO2(g)	-2.80	-20.96	-18.16	CO2
CrO3	-15.55	-18.74	-3.19	CrO3
K2Cr2O7	-15.66	-33.14	-17.48	K2Cr2O7
K2CrO4	-13.83	-14.40	-0.57	K2CrO4
Na2Cr2O7	-19.14	-29.10	-9.96	Na2Cr2O7
Na2CrO4	-13.35	-10.36	2.99	Na2CrO4
Natron	-11.07	-12.57	-1.51	Na2CO3:10H2O
O2(g)	-40.80	44.00	84.80	O2
Thermonatrite	-13.24	-12.57	0.67	Na2CO3:H2O

End of simulation.

Cr(VI) concentration 2 mg/l, at pH 8

-----  
 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        20  
     pH          8  
     pe          4  
     redox       pe  
     units       mg/l  
     density     1  
     Cr(6)       1.4  
     H(0)        1  
     C           20  
     O(0)        80  
     Na          37  
     K           0.6  
     water       1 # kg

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

Initial solution 1.

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

Elements	Molality	Moles
C	3.333e-004	3.333e-004
Cr(6)	2.693e-005	2.693e-005
H(0)	9.923e-004	9.923e-004
K	1.535e-005	1.535e-005
Na	1.610e-003	1.610e-003
O(0)	5.001e-003	5.001e-003

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

pH	=	8.000
pe	=	4.000
Activity of water	=	1.000
Ionic strength	=	1.030e-003
Mass of water (kg)	=	1.000e+000
Total alkalinity (eq/kg)	=	3.543e-004
Total CO2 (mol/kg)	=	3.333e-004
Temperature (deg C)	=	20.000
Electrical balance (eq)	=	1.244e-003

Percent error,  $100 \cdot (\text{Cat} - |\text{An}|) / (\text{Cat} + |\text{An}|) = 62.03$   
Iterations = 3  
Total H = 1.110150e+002  
Total O = 5.551294e+001

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

Redox couple	pe	Eh (volts)
H(0)/H(1)	-7.9119	-0.4602
O(-2)/O(0)	13.2078	0.7682

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	7.109e-007	6.858e-007	-6.148	-6.164	-0.016
H+	1.036e-008	1.000e-008	-7.984	-8.000	-0.016
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(4)	3.333e-004				
HCO3-	3.240e-004	3.127e-004	-3.490	-3.505	-0.015
H2CO3	7.490e-006	7.490e-006	-5.125	-5.125	0.000
CO3-2	1.530e-006	1.326e-006	-5.815	-5.877	-0.062
NaHCO3	3.001e-007	3.001e-007	-6.523	-6.523	0.000
NaCO3-	4.568e-008	4.409e-008	-7.340	-7.356	-0.015
Cr(6)	2.693e-005				
CrO4-2	2.600e-005	2.253e-005	-4.585	-4.647	-0.062
HCrO4-	7.465e-007	7.191e-007	-6.127	-6.143	-0.016
NaCrO4-	1.804e-007	1.738e-007	-6.744	-6.760	-0.016
KCrO4-	1.287e-009	1.239e-009	-8.891	-8.907	-0.016
Cr2O7-2	2.373e-011	2.044e-011	-10.625	-10.690	-0.065
H2CrO4	4.519e-015	4.519e-015	-14.345	-14.345	0.000
H(0)	9.923e-004				
H2	4.962e-004	4.963e-004	-3.304	-3.304	0.000
K	1.535e-005				
K+	1.535e-005	1.481e-005	-4.814	-4.830	-0.016
KCrO4-	1.287e-009	1.239e-009	-8.891	-8.907	-0.016
Na	1.610e-003				
Na+	1.609e-003	1.553e-003	-2.793	-2.809	-0.016
NaHCO3	3.001e-007	3.001e-007	-6.523	-6.523	0.000
NaCrO4-	1.804e-007	1.738e-007	-6.744	-6.760	-0.016
NaCO3-	4.568e-008	4.409e-008	-7.340	-7.356	-0.015
O(0)	5.001e-003				
O2	2.500e-003	2.501e-003	-2.602	-2.602	0.000

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

Phase	SI	log IAP	log KT	
CH4(g)	-76.06	-117.88	-41.81	CH4
CO2(g)	-3.72	-21.88	-18.16	CO2
CrO3	-17.45	-20.65	-3.19	CrO3
K2Cr2O7	-17.47	-34.95	-17.48	K2Cr2O7
K2CrO4	-13.74	-14.31	-0.57	K2CrO4
Na2Cr2O7	-20.95	-30.91	-9.96	Na2Cr2O7
Na2CrO4	-13.25	-10.27	2.99	Na2CrO4
Natron	-9.99	-11.50	-1.51	Na2CO3:10H2O
O2(g)	-36.80	48.00	84.80	O2
Thermonatrite	-12.16	-11.50	0.67	Na2CO3:H2O

End of simulation.