

# UNESCO-IHE

## INSTITUTE FOR WATER EDUCATION



### **Adsorption of Copper and Cadmium from Urban Stormwater Runoff on Iron Oxide Coated Sand and Granular Ferric Hydroxide**

Mohammed Ahmed Abdullah Bakhamis

MSc Thesis (MWI-2009/04)

27 May 2009

# **Adsorption of Copper and Cadmium from urban stormwater runoff on Iron Oxide based adsorbents**

Master of Science Thesis

by

**Mohammed Ahmed Abdullah Bakhamis**

Supervisors

**Prof. Gary Amy (UNESCO-IHE)**  
**Mentor**

**Dr. Branislav Petrusovski (UNESCO-IHE)**  
**Co-Mentor**

**Uwamariya Valentine (UNESCO-IHE)**

Examination committee

**Prof. Dr. Gary Amy (UNESCO-IHE), Chairman**  
**Dr. Branislav Petrusovski (UNESCO-IHE)**  
**Dr. Yness March Slokar**  
**Uwamariya Valentine (UNESCO-IHE)**

This research is done for the partial fulfilment of requirements for the Master of Science degree at the

UNESCO-IHE Institute for Water Education, Delft, the Netherlands

**Delft**

**May 2009**

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.

## Acknowledgements

My sincere and deeply gratitude should first go to the GOD Almighty for giving me the strength and good health in the whole period of my studies and with his grace I was able to accomplish this piece of work.

Secondly, to my supervisor, Professor G.L Amy and Associate professor Dr. Branislav Petrusovski for their continuous guidance and follow up during all the preparation of this M.Sc thesis report. Their unparalleled guidance and close supervision and encouragement were the key to the successful completion of this thesis.

I also would like to thank my co-mentor Uwamariya Valentine and Dr. Mariska Ronteltap for their insightful comments. This report would not have been possible without their technical backstopping.

I would like to thank the entire laboratory staff for their tireless support during my lab work. Fred, Frank, Don, Peter, Ferdi and Lyzette all deserve the acknowledgement.

I also would like to thank my organization 'Qatar General Electricity & Water Corporation' for financial support and providing me an opportunity to study here in Netherlands. My Family, friends and colleagues have technically and morally supported me. I would also like to thank all my friends at UNESCO-IHE for continuous support and making my life easier, here in Netherlands

Last but not the least I would like to thank Embassy of Qatar here in Netherlands for their continuous support and making my life easier.

## Abstract

Stormwater generated by runoff from roads and highways contains metals. These metals are either dissolved or bound to particulates in the stormwater. Hence, urban stormwater runoff is considered as a substantial source of pollutants to receiving water bodies. Consequently, these heavy metals should be treated very well prior to being discharged into mains natural water courses.

Several methods are used to treat heavy metals such as chemical precipitation, coagulation and flocculation, reverse osmosis, ion exchange, nanofiltration and ultrafiltration. But these treatments have limitations such as high investment cost; generation of toxic sludge which requires further treatment, as well as difficulty in concisely reaching very low metal levels as required by standards.

This study investigated the stability of selected dissolved heavy metals such as copper and cadmium as a function of pH and calcium concentration, as well as the effect of pH and calcium concentration on adsorption of copper and cadmium on Iron Oxide Coated Sand (IOCS) and Granular Ferric Hydroxide (GFH). Firstly, the stability of copper as a function of pH and calcium concentration showed that pH had a significant influence on copper stability, and that pH can be used to remove copper through 5% precipitation at pH6 and 85% at pH 8. There was a small effect of calcium concentration on copper stability. In contrast, it was found that pH had a small effect on cadmium stability through precipitation at pH 6 (5%) and pH 8 (15%). Therefore, pH can not be used to remove cadmium. Similarity to copper, there was a small effect of calcium concentration on cadmium stability.

Secondly, copper can be effectively removed by IOCS. There was no significant effect of  $\text{Ca}^{2+}$  concentration on the adsorption efficiency. IOCS showed very poor adsorption at pH 6 but higher removal at pH 7 and 8.

GFH showed potential to remove copper at pH7 and 8, however, there was no clear effect of calcium concentration on copper adsorption on GFH. The increase in adsorption capacity at pH 8 could be explained by the effect of GFH surface charge.

Cadmium can also be effectively adsorbed by IOCS. It was found that an increase in calcium resulted in a slight reduction of adsorption efficiency, while an increase in pH from 6 to 8 resulted in increased adsorption efficiency. Overall, the results obtained from batch isotherm of cadmium on IOCS at pH 8 fit reasonably with freundlich isotherm.

GFH demonstrated poor cadmium removal on GFH and there was no removal at pH 6 but increased at pH 7 and 8 however very limited efficiency. No clear trend was observed on calcium concentration on removal efficiency. As with copper, the Improved of adsorption from pH 6 to 8 could be explained by the effect of GFH surface charge.

Therefore, IOCS can be used effectively to remove copper and cadmium, while pH control can be used to remove copper from urban stormwater runoff.

**Key words:** Storm water, urban-runoff, stability, adsorption, heavy metals, pH, calcium, copper and cadmium removal, GFH, IOCS.

## Table of contents

CHAPTER 1. INTRODUCTION .....	7
1.1 Background .....	12
1.2 Problem statement.....	13
1.3 Goal and objectives.....	13
CHAPTER 2. LITERATURE REVIEW .....	15
2.1 Introduction.....	15
2.2 Occurrence, impacts and source of pollutants in urban stormwater runoff .....	15
2.3 Chemistry, environment and health impact of heavy metals .....	18
2.3.1 Copper.....	18
2.3.2 Cadmium.....	21
2.3 Removal of heavy metals.....	23
2.3.1 Chemical precipitation .....	23
2.3.2 Coagulation – flocculation .....	23
2.3.3 Membrane filtration technology:.....	24
2.3.4 Ion Exchange .....	25
2.3.5 Adsorption treatment.....	27
CHAPTER 3. METHODOLOGY .....	31
3.1 Introduction.....	31
3.2 Experimental materials .....	31
3.3 Experimental methods/Procedure .....	36
CHAPTER 4. RESULTS AND DISCUSSION .....	37
4.1 Stability of copper and cadmium .....	37
4.1.1 Stability of copper.....	37
4.1.2 Stability of Cadmium .....	42
4.2.1 Adsorption on IOCS.....	47
4.2.2 Adsorption on GFH.....	59
CHAPTER 5. CONCLUSION AND RECOMMENDATIONS .....	67
Conclusion .....	67
Recommendations.....	68

## List of Tables

Table 2. 1 Summary of Inorganic Contaminant Sources in Urban Runoff (Makepeace, 1995)...	16
Table 2. 2 Average heavy metals concentration of street runoff samples in Amman, Jordan (Anwar, 2000). .....	17
Table 2. 3 Pollutants and typical composition of: rainwater, runoff from roofs, and runoff from trafficked areas (Göbel a, 2006).....	18
Table 2. 4 Maximum contaminant level of copper in surface water and their toxicities.(Tonni, 2006). .....	21
Table 2. 5 Maximum contaminant level of cadmium in surface water and their toxicities (Tonni, 2006). .....	22
Table 2. 6 Cadmium and copper removal using chemical precipitation (Tonni, 2006). .....	23
Table 2. 7 Summarize all the treatability of physico-chemical treatments for urban stormwater runoff.....	26
Table 2. 8 Physiochemical characteristic of IOCS .....	28
Table 2. 9 Physiochemical characteristics of GFH.....	30
Table 3. 1 High and low standard concentration of copper .....	34
Table 3. 2 Water quality matrix .....	34
Table 4. 1 Saturation index of copper based on Phreeqc calculation. (Model water: demineralized water with $\text{Ca}^{2+}$ (20, 40 and 60 mg/l), $\text{HCO}_3^-$ (20 mg/l), pH=6 and initial Cu (II) concentration = 4 mg/l. ....	38
Table 4. 2 Saturation index of copper based on Phreeqc calculation. (Model water: demineralized water with $\text{Ca}^{2+}$ (20, 40 and 60 mg/l), $\text{HCO}_3^-$ (20 mg/l), pH=7 and initial Cu (II) concentration = 4 mg/l. ....	40
Table 4. 3 Saturation index of copper based on Phreeqc calculation. (Model water: demineralized water with $\text{Ca}^{2+}$ (20, 40 and 60 mg/l), $\text{HCO}_3^-$ (20 mg/l), pH=8 and initial Cu (II) concentration = 4 mg/l. ....	41
Table 4. 4 Cadmium speciation percentage based on Phreeqc calculations at pH=6. ....	43
Table 4. 5 Cadmium speciation percentage based on Phreeqc calculations at pH=7. ....	45
Table 4. 6 Cadmium speciation percentage based on Phreeqc calculations at pH=8. ....	46

## List of Figures

Figure 2. 1 Copper Solubility diagram (source: Stum and Morgan, 1981) .....	20
Figure 2. 2 Aqueous speciation of cadmium as a function of pH. ( Yongjie Xue, Hou, Zhu 2008). .....	21
Figure 2. 3 Coating composition of IOCS samples (source: Restofenunie project report, 2006). 29	
Figure 3. 1 Atomic Absorption Spectrometer (AAS-Flame) used for analysis of copper.....	32
Figure 3. 2 Atomic Absorption Spectrometer - Graphite furnace used for analysis of cadmium. 33	
Figure 3. 3 GFL-Shaker 3019 .....	35
Figure 3. 4 Schematic diagram of procedure followed during batch adsorption experiments. ....	36
Figure 4. 1: (a) Effect of contact time and $\text{Ca}^{2+}$ concentration on Cu solubility at $\text{pH}=6\pm0.2$ . Model water: demineralized water with $\text{Ca}^{2+}$ (20, 40 and 60 mg/l), $\text{HCO}_3^-$ (20 mg/l) and initial Cu (II) concentration = 4 mg/l, samples filtered through $0.45\mu\text{m}$ . (b) Speciation of Cu based on Phreeqc calculation under same experimental conditions. ....	37
Figure 4. 2: (a) Effect of contact time and $\text{Ca}^{2+}$ concentration on Cu solubility at $\text{pH}=7\pm0.2$ . Model water: demineralized water with $\text{Ca}^{2+}$ (20, 40 and 60 mg/l), $\text{HCO}_3^-$ (20 mg/l) and initial Cu (II) concentration = 4 mg/l, samples filtered through $0.45\mu\text{m}$ . (b) Speciation of Cu based on Phreeqc calculation under same experimental conditions. ....	39
Figure 4. 3: (a) Effect of contact time and calcium concentration on Cu solubility at $\text{pH}=8\pm0.2$ . Model water: demineralized water with $\text{Ca}^{2+}$ (20, 40 and 60 mg/l), $\text{HCO}_3^-$ (20 mg/l) and initial Cu (II) concentration = 4 mg/l, samples filtered through $0.45\mu\text{m}$ . (b) Speciation of Cu based on Phreeqc calculation under same experimental conditions. ....	40
Figure 4. 4: (a) Effect of contact time and calcium concentration on Cd solubility at $\text{pH}=6\pm0.2$ . Model water: demineralized water with $\text{Ca}^{2+}$ (20, 40 and 60 mg/l), $\text{HCO}_3^-$ (20 mg/l) and initial Cd (II) concentration = 100 $\mu\text{g/l}$ , samples filtered through $0.45\mu\text{m}$ . (b) Speciation of Cd based on Phreeqc calculation under same experimental conditions. ....	42
Figure 4. 5: (a) Effect of contact time and calcium concentration on Cd solubility at $\text{pH}=7\pm0.2$ . Model water: demineralized water with $\text{Ca}^{2+}$ (20, 40 and 60 mg/l), $\text{HCO}_3^-$ (20 mg/l) and initial Cd (II) concentration = 100 $\mu\text{g/l}$ , samples filtered through $0.45\mu\text{m}$ . (b) Speciation of Cd based on Phreeqc calculation under same experimental conditions. ....	44
Figure 4. 6: (a) Effect of contact time and $\text{Ca}^{2+}$ concentration on Cd solubility at $\text{pH}=8\pm0.2$ . Model water: demineralized water with $\text{Ca}^{2+}$ (20, 40 and 60 mg/l), $\text{HCO}_3^-$ (20 mg/l) and initial Cd (II) concentration = 100 $\mu\text{g/l}$ , samples filtered through $0.45\mu\text{m}$ . (b) Speciation of Cd based on Phreeqc calculation under same experimental conditions. ....	45
Figure 4. 7: Effect of contact time and calcium concentration on Cu adsorption on IOCS at $\text{pH}=6\pm0.2$ . Model water: demineralized water with $\text{Ca}^{2+}$ (20, 40 and 60 mg/l), $\text{HCO}_3^-$ (20 mg/l)	

and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L. (a) Concentration of Cu in solution.  
 (b) Rate of Cu precipitation and adsorption on IOCS..... 47

Figure 4. 8: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on IOCS at  $\text{pH}=7\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L. (a) Concentration of Cu in solution.  
 (b) Rate of Cu precipitation and adsorption on IOCS..... 49

Figure 4. 9: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on IOCS at  $\text{pH}=8\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L. (a) Concentration of Cu in solution.  
 (b) Rate of Cu precipitation and adsorption on IOCS..... 50

Figure 4. 10: Effect of pH on Cu adsorption on IOCS. Model water: demineralized water with  $\text{Ca}^{2+}$  (20mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L. .... 51

Figure 4. 11: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on IOCS at  $\text{pH}=6\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . IOCS = 0.1 g/L. (a) Concentration of Cd in solution.  
 (b) Rate of Cd precipitation and adsorption on IOCS after 24 hours of CT..... 52

Figure 4. 12 Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on IOCS at  $\text{pH}=7\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . IOCS = 0.1 g/L. (a) Concentration of Cd in solution.  
 (b) Rate of Cd precipitation and adsorption on IOCS..... 53

Figure 4. 13: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on IOCS at  $\text{pH}=8\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . IOCS = 0.1 g/L. (a) Concentration of Cd in solution.  
 (b) Rate of Cd precipitation and adsorption on IOCS..... 54

Figure 4. 14: Effect of pH on Cd adsorption on IOCS. Model water: demineralized water with  $\text{Ca}^{2+}$  (20mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . IOCS = 0.1 g/L. ... 55

Figure 4. 15: (a) cadmium removal as a function of contact time and IOCS dose at  $\text{pH}=8\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 2.80 mg/l. IOCS dose: 0.1-0.9 g/l in pulverized form. (b) Cd adsorbed per mass of IOCS. .... 56

Figure 4. 16 Freundlich isotherm for Cd adsorption on IOCS at  $\text{pH}= 8 \pm 0.2$ . (Model water: demineralized water with  $\text{Ca}^{2+}$  (20 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 2.8 mg/l. .... 57

Figure 4. 17: (a) Kinetic model: Pseudo first. (b) pseudo second order adsorption kinetics (0.1 g/l). .... 58

Figure 4. 18: Effect of contact time and  $\text{Ca}^{2+v}$  concentration on Cu adsorption on GFH at  $\text{pH}=6\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l)

and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L. (a) Concentration of Cu in solution.  
 (b) Rate of Cu precipitation and adsorption on GFH..... 59

Figure 4. 19: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on GFH at  $\text{pH}=7\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L. (a) Concentration of Cu in solution.  
 (b) Rate of Cu precipitation and adsorption on GFH..... 60

Figure 4. 20: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on GFH at  $\text{pH}=8\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L. (a) Concentration of Cu in solution.  
 (b) Rate of Cu precipitation and adsorption on GFH..... 61

Figure 4. 21: Effect of pH on Cu adsorption on GFH. Model water: demineralized water with  $\text{Ca}^{2+}$  (20mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L. .... 62

Figure 4. 22: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on GFH at  $\text{pH}=6\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . of GFH = 0.1 g/L..... 63

Figure 4. 23: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on GFH at  $\text{pH}=7\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . GFH = 0.1 g/L. (a) Concentration of Cd in solution.  
 (b) Rate of Cd precipitation and adsorption on GFH..... 64

Figure 4. 24: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on GFH at  $\text{pH}=8\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . GFH = 0.1 g/L. (a) Concentration of Cd in solution.  
 (b) Rate of Cd precipitation and adsorption on GFH..... 65

Figure 4. 25: Effect of pH on Cd adsorption on GFH. Model water: demineralized water with  $\text{Ca}^{2+}$  (20mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . GFH = 0.1 g/L. .... 66

## List of symbols, Acronyms and Abbreviations

AAS: Atomic absorption spectrophotometer  
Ca: calcium  
Cd: Cadmium  
Conc: Concentration  
Cu: Copper  
CuO: Tenorite  
 $\text{Cu}_2(\text{OH})_2(\text{CO}_3)$ : Malachite  
 $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ : Azurite  
Cr: Chromium  
CSO: combined sewer overflow  
GFH: Granular ferric hydroxide  
Hg : Mercury  
IOCS: Iron oxide coated sand  
MOH: Mineral oil hydrocarbons  
MCL: Maximum Contamination Level  
mg/l: milligram per liter  
mg/g: milligram per gram  
 $\mu\text{g/g}$ : microgram per liter  
NURP: Nation wide urban runoff Program  
PAH: Polycyclic aromatic hydrocarbons  
Pb: Lead  
Rpm : revolution per minute  
USEPA: United States Environmental Protection Agency  
WHO: World health Organization  
Zn: Zinc

# CHAPTER 1. INTRODUCTION

## 1.1 Background

In recent years a lot of concern has been raised on urban stormwater runoff due to the presence of pollutants. Therefore, urban stormwater is considered as one of the major source of receiving water body degradation (USEPA, 1984).

Urban stormwater runoff is defined as rain water that is not filtered into the ground or evaporated and while its flow all pollutants are washed out and end up in receiving water.

There are two source of pollutants in urban stormwater first from point source such as industrial, wastewater treatment discharge and non point source like from development (construction site) building, motor way road, roofs of building, industrial buildings, scour and erosion and atmosphere scrubbing and end up into nearest receiving water body without any treatment (Mungur et al., 1995; Vassilios A. et al., 1996). Thus, regulation has been issued to abatement of pollution by wet weather discharges. Moreover the pollutant levels are associated with more intensive development (Livingstone, 1989).

Many research showed that the impact of urban runoff pollutants in the receiving water quality may vary from one site to another site. For instance, the type of the pollutants in the receiving water which is closed to industrial site is different from the pollutants that are closed to high way road, thus the water quality is different and the impact will be varied as well.

Moreover, some of the pollutants are transferred along the river to another site and gradually these pollutants may settle down results in slow dissolving toxic substances such as heavy metals and PCBs (Gjessing et al., 1984).

There are different type of pollutants frequently found in urban stormwater runoff such as heavy metals, suspended solids, chlorides, oils and grease. Each of these pollutants has different type of impact. For instance, copper and zinc are toxic to aquatic life, lead bioaccumulation on the bottom and reduce photosynthesis, cadmium and chromium could be mutagenic and carcinogenic, oil and grease from garages as well as due to an improper disposal is toxic and has adverse impact on receiving water quality (Pitt and Bozeman, 1980; Ferrara, 1986; Schueler, 1987).

Therefore, there is an essential need to remove theses pollutants prior stormwater to be discharge into the receiving water. There are several types of treatment methods to remove heavy metals from urban stormwater runoff such as Chemical precipitation, coagulation-flocculation, Ion exchange, Membrane filtration treatment.

But each of this treatment technology has disadvantageous. For instance, in chemical precipitation and coagulation-flocculation treatment a large volume of sludge and waste is generated that can cause a lot of problem to environment due to its high content of toxic and

hazard material. Thus, further treatment requires in handling this sludge/waste. In advanced technologies such as ultra filtration, nanofiltration, ion exchange and reverse osmosis are associated with high capital and operational cost prone to fouling problem and high energy consumption as well as large volume of waste water is generated which need further treatment

Adsorption technology has many advantageous such as simple design, sludge free and low cost investment (Viraraghven and Dronamraju, 1993).

Recently, many research revealed that effective removal of heavy metals such as cadmium, chromium, copper and lead can be conducted by using different iron oxide based adsorbents like iron oxide coated sand (IOCS) and granular ferric hydroxide (GFH) (Benjamin, 1982; Petrusevski, 2000; Yadav, 2007).

## **1.2 Problem statement**

Heavy metals such as chromium, iron, manganese, copper, nickel, lead and cadmium are present in urban stormwater in elevated levels (Anwar, 2001).

Yadav (2007) reported that pH can play an important in controlling adsorption treatment. At pH 6, copper can be removed effectively with GFH and IOCS adsorbents but cadmium can be removed only with IOCS adsorbent. Further on, the mechanism of Cu removal with GFH at pH of 6.0 could not be explained on the basis of electrostatic attraction and the effect of water quality matrix on adsorption was not studied as well. (Yadav, 2007).

Therefore, further study needs to be done to assess the effect of water quality matrix (which are consider as controlling variables such as pH and  $\text{Ca}^{2+}$ ) on IOCS and GFH adsorption efficiency. Hence, more study needs to be done in order to better understand the removal mechanisms.

## **1.3 Goal and objectives**

The main goal of this study is to assess the suitability of adsorptive removal of IOCS and GFH under selected water quality condition.

The research had the following specific objectives:

- To review options available for removal of metal from urban storm water.
- To assess the effect of various concentration of pH and  $\text{Ca}^{2+}$  on copper and cadmium stability in the water.
- To find out the adsorption efficiency of GFH to remove cadmium and copper at different pH value and calcium concentration in adsorption batch experiments.

- To find out the adsorption efficiency of IOCS to remove cadmium and copper at different pH values and calcium concentrations in adsorption batch experiments.
- To establish adsorption isotherm of cadmium adsorption on IOCS at pH 8 and calcium concentration of 20 mg/l.
- To feed obtained result in different adsorption kinetic models.

## **CHAPTER 2. LITERATURE REVIEW**

### **2.1 Introduction**

Urban stormwater is defined as runoff from urban areas that is not percolated or evaporated and while it flows all this industrial, agriculture, highway road waste are washed out and transported into either in drainage system or water body. Stormwater runoff is classified by EPA as runoff from impervious surface including streets, buildings, lawns, and other paved areas that enter a sewer, pipe, or ditch before discharging into surface waters (U.S. EPA, 1994; U.S. EPA, 1994; U.S. EPA, 2002a).

Stormwater run off is considered as one of the main sources of water quality impairment in water bodies across the United States as reported by the United States Environmental Protection Agency (EPA) due to its contents of pollutants from oils, heavy metals, greases to nutrients and sediments.

As part of this study there is a necessity to understand the occurrence of these metals like copper and cadmium in high level in urban stormwater runoff. If copper and cadmium exceed WHO guidelines, they can cause many health problems. Hence, it is crucial to understand the natural occurrence, chemical speciation and mineral forms of copper and cadmium in the environment and in urban storm water as well.

This chapter gives an insight of an urban stormwater and the occurrence of copper and cadmium in stormwater and various removal technologies that are used to remove copper and cadmium from urban stormwater runoff before its being discharged to receiving water body.

Moreover, this chapter introduces an overview of the adsorption process by using Iron Oxide Coated Sand (IOCS) and Granular Ferric Hydroxide (GFH) adsorbents.

### **2.2 Occurrence, impacts and source of pollutants in urban stormwater runoff**

During the year, rain water falls on the ground and encounters various contaminants sources, these contaminants sources for example can be from residential, commercial, industrial, highway, educational institutions, parks and open spaces. These are considered as non point sources.

There are many factors affecting urban runoff quality and quantity such as rainfall volume and intensity, land use, traffic volume and maintenance practices. The rainfall intensity and runoff volume during rainfall period affect the intensity and the transportation of these contaminants to the receiving water body. In the case of highway runoff, maintenance practice and high way road waste and contaminants accumulation on the roadside and wash off by stormwater. Land activities such as construction or agricultural lands, leaching of metals from solid dumping sites would increase the level of heavy metals in urban stormwater runoff. (Chui, 1982; Boyd and Gardner, 1990; Gupta, Agnew and Kobringer, 1981).

A combined sewer overflow (CSOs) do not cause environmental problems for nearby waterways, but during intense rainfall events water flow in CSOs may exceed the wastewater treatment plant's capacity (Slone and Evans, 2003; Bas and Baskaran, 2003 ;Moran,2004). As a result of the CSO, raw, untreated human waste is emptied into nearby waterways.

The most abundant heavy metals found in urban runoff are copper (Cu), cadmium (Cd), lead (Pb), zinc (Zn), chromium (Cr), mercury (Hg), in addition polycyclic aromatic hydrocarbons (PAH), mineral oil hydrocarbons (MOH), and readily soluble staff in runoff are partly regarded as hazardous to aquatic life in water body (Pit et al., 1994).

Specific sources for several chemical classes are listed and summarized in tables 2.1, The water quality characteristics of urban runoff in the United States for the median urban site reported total metals in the following concentrations: zinc (160 µg/l), lead (144 µg/l), copper (34 µg/l) (Ellis, 1988). Mercury concentrations typically range from 0.05 to 67 (µg/l) (Makepeace, 1995).

Table 2. 1 Summary of Inorganic Contaminant Sources in Urban Runoff (Makepeace, 1995).

Contaminants	Reported range (mg/l)	Typical sources
arsenic	0.001 to 0.21	Industrial emissions, fossil fuel combustion, smelting, laundry products, pesticides, weed killers, defoliants, preservatives
cadmium	0.00005 to 13.73	Combustion, wear of tires and brake pads, combustion of lubricants oil, metal-finishing industrial emissions, agricultural use of sludge, fertilizers and pesticides, and corrosion of galvanized metals
copper	0.00006 to 1.41	Wear of tires and brake linings, combustion of lubricants oils, corrosion of building materials, wear of moving parts in engines, smelter activity , metallurgical and other industrial emission, algicides, fungicides, pesticides.
lead	0.00057 to 26.00	Emissions from gasoline –powered vehicles, gasoline additives.
nickel	0.001 to 49.00	Corrosion of welded metal plating, wear of moving parts in engines, electroplating and alloy manufacturing, activity of smelters, food production.
zinc	0.0007 to 22.0	wear from tires, brake pads, combustion of lubrication oils, activity of smelters, corrosion of building materials and metal objects.

Heavy metals are non biodegradable and tend to accumulate in living organisms. Consequently, heavy metals may end up in human been through the food chain.

Several investigations have been carried out to evaluate heavy meals in street runoff in most industrial cities which show high levels of heavy metals table 2,2. (Anwar, 2000).

Table 2. 2 Average heavy metals concentration of street runoff samples in Amman, Jordan (Anwar, 2000).

Ionic species	November			December			January		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
Cd (ppm)	2	11	7	1	12	4	0.2	6	1.9
Cr (ppm)	6	75	23.5	3	23	15	1	56	14.9
Cu (ppm)	58	271	110.3	27	101	59	10	40	17.9
Fe (ppm)	1404	11403	5520.6	715	7500	3228	250	5870	1548.3
Mn (ppm)	200	1714	732.1	132	925	425	29	670	249.8
Ni (ppm)	10	77	28.3	2	66	20	3	65	23.8
Pb (ppm)	10	55	41.1	12	57	46	42	48	44.7

It can be seen from table 2.2 the high concentration of metals in urban stormwater. Different samples were collected during three months, in November, the minimum concentration of cadmium was 2 ppm and the maximum concentration was 11 ppm. In December, the minimum concentration of cadmium was 1 ppm and the maximum concentration was 12 ppm and in January, the minimum concentration of cadmium was 0.2 ppm and the maximum concentration was 6 ppm. All samples show high level of cadmium which exceeds WHO guideline as well as copper concentration was very high which exceeds WHO guideline.

Bauske and Goetz (1993) reported that suspended solids, Pb, Cd and Zn concentrations increases in winter due to the use of chloride-based deicing salts, which generate supply and corrison phenomena. Gobel (2006) reported that street runoff is considered one of the major sources.

Table 2. 3 Pollutants and typical composition of: rainwater, runoff from roofs, and runoff from trafficked areas (Göbel a, 2006).

Parameter		Unit	Roofs		Trafficked areas		Trafficked areas	
					with low		with high	
					density		density	
			Min.	Max.	Min.	Max.	Min.	Max.
pH		-	4.7	6.8	6.4	7.9	6.4	7.9
EC		µS/cm	23	269	n.a.	n.a.	108	2436
Heavy metals	Cd	µg/l	0.2	1	0.2	0.5	0.3	13
	Zn	µg/l	24	4880	15	1420	120	2000
	Cu	µg/l	6	3.416	21	140	97	104
	Pb	µg/l	2	493	98	170	11	525
	Ni	µg/l	2	7	n.a.	n.a.	4	70
	Cr	µg/l	2	6	n.a.	n.a.	6	50
Main ions	Na	mg/l	n.a.	n.a.	n.a.	n.a.	5	474
	Mg	mg/l	n.a.	n.a.	n.a.	n.a.	1	1.4
	Ca	mg/l	1	1900	n.a.	n.a.	13.7	57
	K	mg/l	n.a.	n.a.	n.a.	n.a.	1.7	3.8
	SO4	mg/l	n.a.	n.a.	n.a.	n.a.	5.1	139
	Cl	mg/l	n.a.	n.a.	n.a.	n.a.	3.9	669

Note: n.a.: not available.

Ball (2000) reported that copper (Cu), lead (Pb) and Zinc (Zn) show the most significant concentration among the heavy metals present in urban storm water run-off.

In conclusion, the quality and quantity of urban stormwater runoff basically depend on the characteristic of land, traffic intensity, rainfall intensity, on which the runoff takes place.

The main heavy metals present in urban stormwater are zinc (Zn), lead (Pb), copper (Cu), chromium (Cr) and cadmium (Cd) as well as the main ions present are  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$ .

## 2.3 Chemistry, environment and health impact of heavy metals

This section presents insight about the chemistry, environment and health impact of Copper and Cadmium.

### 2.3.1 Copper

Copper is frequently found in urban stormwater runoff in elevated level and any metal exceeded certain limit considered as pollutants. Any metal exceed certain level then it becomes risky to aquatic life and human health. Consequently, it considered as pollutants.

Metallic copper is malleable, ductile and a good thermal and electrical conductor. It has many commercial uses because of its versatility. Copper is used to make electrical wiring, pipes, valves, fittings, coins, cooking utensils and building materials. It is present in munitions, alloys (brass, bronze) and coatings. Copper compounds are used as or in fungicides, algicides, insecticides and wood preservatives and in electroplating, azo dye manufacture, engraving, lithography, petroleum refining and pyrotechnics. Copper compounds can be added to fertilizers and animal feeds as a nutrient to support plant and animal growth (Landner & Lindestrom, 1999; ATSDR, 2002). Copper compounds are also used as food additives (e.g., nutrient and/or colouring agent) (US FDA, 1994).

### **2.3.1.1 Chemistry of copper**

The symbol of copper is Cu, atomic number is 29, atomic weight is 63.55, atomic mass is 58 and electro negativity is 1.75.

Copper is categorized as heavy metal with a density greater than  $5\text{gcm}^{-3}$ . Copper is a transition metal with three oxidation states; zero ( $\text{Cu}^0$ , solid metal); plus one ( $\text{Cu}^+$ , cuprous ion); and plus two ( $\text{Cu}^{2+}$ , cupric ion).

There are basically three processes that control levels of copper in solution, its conversion into various forms, its mobility in aquatic environments:

1) Complexation, which controls the form (species) and concentration of the dissolved Cu. The main two major inorganic complexing ligands in most natural water, are the hydroxyl ( $\text{OH}^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) ions. The predominant inorganic Cu complexes include Cu hydrolysis products ( $\text{CuOH}^+$ ,  $\text{Cu}(\text{OH})_2^0$ ,  $\text{Cu}_2(\text{OH})_2^{2+}$ ) and basic carbonate complex ions ( $\text{CuCO}_3$ ,  $\text{Cu}(\text{CO}_3)_2^{2-}$ ) (Sylva, 1976; Stiff, 1971a).

2) Precipitation is the second mechanism that responsible for the partitioning of Cu in natural waters, precipitation has been considered as one of the major reason in the reduction of soluble copper levels in natural waters (Elder and Horne, 1978; Stiff, 1971b). the most likely Cu precipitates form in natural waters as  $\text{Cu}(\text{OH})_2$  (copper hydroxide) and ultimately CuO (tenorite),  $\text{Cu}_2(\text{OH})_2(\text{CO}_3)$  (malachite) (Stiff, 1971b, Sylva, 1976) and  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$  (azurite) (Sylva, 1976).

3) Adsorption which controls dissolved copper levels in natural waters. Copper adsorption to living and non living particulate matter is significant in the removal of dissolved copper from polluted surface waters (Ramamoorthy and Kushner, 1975b) and ultimately into sediments (Jackson, 1978; Ramamoorthy and Rust, 1978). The predominant hydroxyl or carbonate Cu species in the natural environment depends on the concentrations of  $\text{OH}^-$  (pH) and carbonate ions present (Flemming and Trevors, 1989).

pH is considered as one of the important factor that controlling copper solubility and speciation in the water.

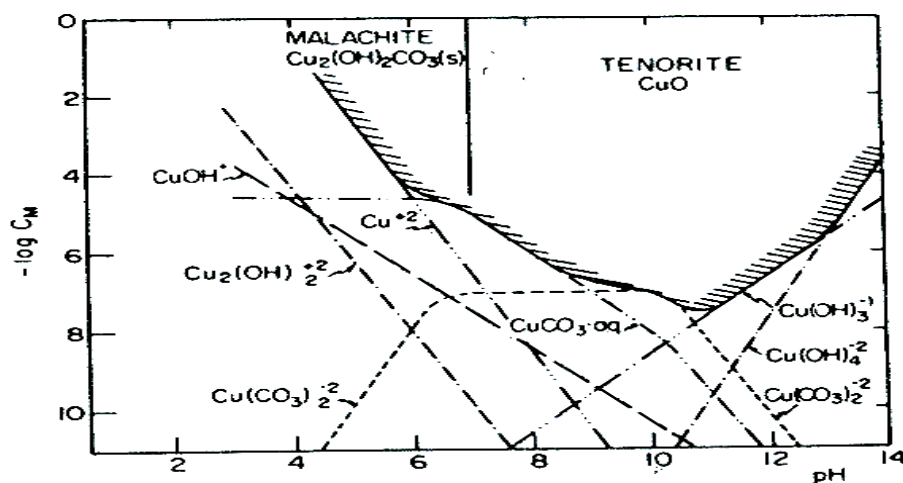


Figure 2. 1 Copper Solubility diagram (source: Stum and Morgan, 1981)

It can be seen from the figure 2.1 that up to pH 6.96 Cu (+2) ion is the major species in water which is controlled by the formation of insoluble malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s})$ ). Above pH 7 the solubility is controlled by the solubility of CuO (tenorite). The predominant species with increasing pH are  $\text{Cu}^{2+}$ ,  $\text{CuCO}_3(\text{aq})$ ,  $\text{Cu}(\text{CO}_3)_2^{2-}$ , and hydroxo copper (II) anions.

### 2.3.1.2 Environment and health impact of copper

Copper is an essential metal for natural environment and human health, it can come in water bodies from rock weathering, corrosion of brass and copper pipes and industrial waste such as electroplating, copper mining and smelting.

The particulate form of copper tends to become bound up in sediment where it may not be bioavailable, and therefore not toxic, to organisms, at least temporarily.

The various copper species present in water, and thus toxic to aquatic life, is affected by factors such as pH, alkalinity, and the presence of organic ligands. For example, toxicity decreases with increased organic carbon and alkalinity.

At lower doses, copper ions can cause symptoms typical of food poisoning (headache, nausea, vomiting, diarrhoea) Records from case-study reports of gastrointestinal illness induced by copper from contaminated water or beverages plus public health department reports for 68 incidents indicate an acute onset of symptoms. Symptoms generally appear after 15–60 min of exposure; nausea and vomiting are more common than diarrhoea (Wyllie, 1957; Spitalny et al., 1984; US EPA, 1987; Knobeloch et al., 1994; Low et al., 1996; Stenhammar, 1999).

Copper has significant impact in drinking water in terms of taste, odor and human health when it is exceeding WHO Guidelines value of 2 mg/l (WHO 2004), it is mostly that increases of copper level in drinking water as a result of the corrosion of interior copper plumbing and the USEPA has proposed as 0.25 mg/l a safe concentration in urban storm water discharge (Table 2.4).

Table 2. 4 Maximum contaminant level of copper in surface water and their toxicities.(Tonni, 2006).

Heavy metal	Toxicities	Maximum effluent discharge standards (mg/l)		
		EPA <sup>a</sup> (The USA)	EPD <sup>b</sup> (Hong Kong SAR)	PCD <sup>c</sup> (Thailand)
Copper	Liver damage, Wilson diseases, insomina	0.25	0.05-4.0	2.00

## 2.3.2 Cadmium

Cadmium is rare element (0.2 mg/kg in the earth crust) and is not found in the pure state in the nature. Cadmium metal is widely used in the steel industry, plastics and batteries

### 2.3.2.1 Chemistry of cadmium

The symbol of cadmium is Cd, the atomic number is 48, the atomic weight 112.41 and it's in the periodic table in group IIb along with zinc and mercury. It has relatively low melting (320.9 °C) and boiling (765°C) points and a relatively high vapour pressure. Figure 3 shows cadmium species as a function of pH.

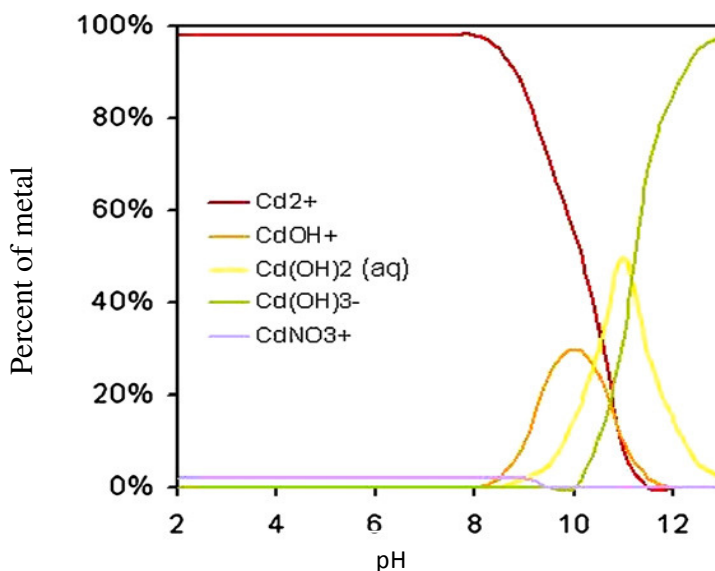


Figure 2. 2 Aqueous speciation of cadmium as a function of pH. ( Yongjie Xue, Hou, Zhu 2008).

pH is playing an important role on cadmium species in the solution, Cadmium appears predominantly as Cd<sup>2+</sup> species over pH 2–9. At pH 10, concentration of CdOH<sup>+</sup> reaches

maximum 30%, whereas the concentration of  $\text{Cd}(\text{OH})_2(\text{aq})$  and  $[\text{Cd}(\text{OH})_3]^-$  increases with the decrease of concentration of  $\text{Cd}^{2+}$  and  $\text{CdOH}^+$  at higher pH.

### 2.3.2.2 Environment and health impact of cadmium

Cadmium is widely used in industries, Hence, it released to the environment in wastewater, and diffuse pollution that is caused by contamination from fertilizers and local air pollution.

Exposure to cadmium may cause health problem to human, for instance Cadmium Poisoning in Jintisu River in Japan, This caused a painful skeletal disease diagnosed in 1947 and which later came to be known as itai-itai (ouchouch). Cadmium contamination of the aquatic environment was confirmed to be the cause in 1968 (Förstner and Wittmann, 1981).

The two main storage sites for cadmium in the body are the liver and the kidney. Hence, exposing to low levels of cadmium for long period may incur kidney damage and lung, bone, cardiovascular system, liver and reproductive system damage (Hrudey, 1995; USEPA, 1992).

Therefore, for safe drinking water, WHO has set guideline value of 0.003 mg/l in drinking water (WHO, 2004). The USEPA has set guideline value of 10  $\mu\text{g/l}$  as a safe concentration in urban storm water run-off (Table 2.5) (USEPA 1999a).

Table 2. 5 Maximum contaminant level of cadmium in surface water and their toxicities (Tonni, 2006).

Heavy metal	Toxicities	Maximum effluent discharge standards (mg/l)		
		EPA <sup>a</sup> (The USA)	EPD <sup>b</sup> (Hong Kong SAR)	PCD <sup>c</sup> (Thailand)
Cadmium	Kidney damage, renal disorder, Itai-Itai, probable human carcinogen	0.01	0.001-0.2	0.03

## 2.3 Removal of heavy metals

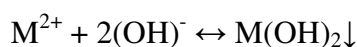
This section provides an insight in several removal technologies that are used in removing copper and copper from urban stormwater runoff.

In last two decades, a lot of research has been conducted to develop suitable techniques to remove heavy metals that are released from the urban storm water and are affecting receiving water.

### 2.3.1 Chemical precipitation

It is widely used for heavy metal removal from effluent/urban stormwater runoff. The concept is all heavy metals is precipitated at pH 11 along with proper dosage of precipitant agent such as lime all heavy metal is converted to insoluble solid phase and in the form of metal hydroxide.

The mechanism removal of chemical precipitation can be expressed as follow:



Where  $M^{2+}$  stand for metal ions,  $2(OH)^-$  stand for precipitant and  $M(OH)_2$  is the insoluble solid phase.

Table 2. 6 Cadmium and copper removal using chemical precipitation (Tonni, 2006).

Species	Precipitant	Initial metal conc. (mg/l)	Optimum pH	Removal efficiency	References
Cd (II)	Ca(OH) <sub>2</sub>	150	11	99.67	(L.Charentanyarak, 1999)
Cu (II)	Mg(OH) <sub>2</sub>	16	9.5	80	(O. Tunay, 1994)

The disadvantageous of this method is the treated effluent does not meet the USEPA standard limit which is lower than 1 mg/l as well as sludge disposal problem (USEPA, 1980).

### 2.3.2 Coagulation – flocculation

Coagulation is used worldwide in removing heavy metal from inorganic solution and effluent. Theoretically, coagulation process destabilize colloidal particles by adding a coagulant and results in sedimentation. In order to increase the particle size, coagulation process is followed by the flocculation of the unstable particles into bulky flocs. The concept for this technique involves pH adjustment and include the addition of ferric/alum salts as the coagulant to

overcome the repulsive forces amongst particles (Shammas, 2004; Semerjian, 2003; Licsko, 1997).

The advantageous of this method can be used to remove heavy metal with concentration less than 100 mg/l and the best removal efficiency can be achieved within pH range from 11 to 11.5. On the other hand, the disadvantages of this method that it generates big volume of sludge which require further treatment along with high operational cost.

### **2.3.3 Membrane filtration technology:**

Membrane technology is increasingly used recently for the treatment of inorganic effluent particularly heavy metals.

The concept is that the pressure is applied to push water through membrane that retain water on one side and allows pure water to pass through other side.

There are several type of membrane filtration such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). These technologies have been used in Tiwan and South Korian to remove Cd (II) from ions from contaminated wastewater.

Ultrafiltration (UF) technology utilizes permeable membrane of the pore size (5 – 20 nm) and molecular weight of the separating compounds (1000-100,000 Da) to separate heavy metals, macromolecules and suspended solids from effluent (Vigneswaran, 2004).

UF technology has removal efficiency more than 90% in removing metals concentration ranging from 10 to 12 mg/l at pH ranging from 5 to 9.5 and at par presuure 2-5.

The advantageous of this technique is requiring a small space due to its high packing density. On the other hand, the disadvantageous is high operational cost(Choi, 2005).

Nanofiltration (NF): In this separation technique involves steric (sieving) and electrical (Donnan) effects. A Donnan potential is occurred among the charged anions in the NF membrane and the co-ions in the effluent to reject the latter (Bruggen, 2003).

Reverse osmosis (RO): This technology is increasingly used in Malaysia and Spain due to strict environmental legislation, the RO membrane pore size has been developed to down  $10^{-4}$   $\mu\text{m}$  (Ujang, 1996; Benito, 2002; Bohdziewicz, 1999).

In general, RO is more effective for removing heavy metals than UF and NF, RO treatment can meet the environmental legislation, moreover, it works at a wide pH range from 3 to 11 and pressure bar of 4.5 to 15 bar, in fact RO system is mainly relying on pressure instead of pH in chemical precipitation, the more pressure the more removal efficiency results in higher energy consumption (Ujang, 1996).

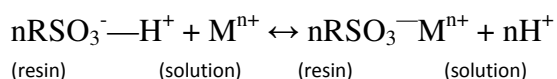
### 2.3.4 Ion Exchange

It is the most applied treatment worldwide for the removal of heavy metals from effluent laden with heavy metals.

Ion exchange technique involves an interchange of ions amongst the solid and liquid phase, where the resins remove ions from an electrolytic solution and free other ions of like charge in a chemically equivalent amount without any change in resin structure (Vigneswaran, 2004; Rengaraj, 2001).

Ion exchange is considered one of the methods that can be used to recover heavy metals from effluent.

The removal mechanism of ion exchange can be expressed as follow:



(-RSO<sub>3</sub><sup>-</sup>) and M stand for the anionic group attached to the resin and the metal cation, respectively.

The advantageous of this technique is proved to be an effective removal of heavy metals within range of 10 – 100 mg/l or below 10 mg/l or higher than 100 mg/l. It works with the acidic condition on pH from 2 to 6. Unlike, chemical precipitation method, there is no any sludge disposal problem. This method can be used for field work because the equipment can be carried anywhere (portable) and its very easy to handle.

While, the disadvantageous such as the ion exchange requires a pretreatment/secondary treatment to remove solid/small particles prior to ion exchange treatment as well as the capital and operational cost is very high (S. Ahmed, 1998).

Table 2. 7 Summarize all the treatability of physico-chemical treatments for urban stormwater runoff.

Type of treatment	Taget of removal	Advantages	Disadvantages	Reference
Chemical Precipitation	Copper/cadmium, divalent metals	Low capital cost, simple operation	Sludge generation, extra operational cost for sludge disposal	( Wang, 2004; Bose, 2002; Wingenfelder, 2005)
Coagulation-flocculation	Cu/Cd and suspended solids	Shorter time to settle out suspended solids, improved sludge settling	Sludge production, extra operational cost for sludge disposal	( Shammass, 2004; D 1996)
Ion Exchange	Cd, Cu, cations/anions, dissolved compounds.	No sludge generation, less time consuming	Not all ion exchanger resin is suitable for metal removal, high capital cost	(Vigneswaran, 2004;Rengaraj, 2001)
UF	Cu, Cd, high molecular weight compounds (1000-10000Da)	Smaller space requirement	High operational cost, prone to membrane fouling	(Vigneswaran, 2004;Aliane, 2001)
NF	Cu, Cd, Sulphate salts and hardness ions such as Ca (II) and Mg (II)	Lower pressure than RO(7-30 bar)	Costly, prone to membrane fouling	(Ahn, 1999)
RO	Cd, Cu, organic and inorganic compounds	High rejection rate, able to withstand high temperature	High energy consumption due to high pressure required (20-100 bar), susceptible to membrane fouling	(Vigneswaran, 2004;Bohdziewicz, 1999)
Adsorption	Cd and Cu	Low capital cost, simple operation	High cost of commercial adsorbent product, disposal of saturated solid waste and competitive with other compounds in water	(Yadav, 2007)

### 2.3.5 Adsorption treatment

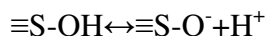
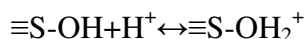
As stated earlier adsorption is one of the treatment that can be used to remove heavy metals. Adsorption is the process where the substance is transferred from the liquid phase to the solid surface. Adsorption involves the inter-phase accumulation or concentration of substances at a surface or interface and this process occurs at an interface between any two phases, such as liquid-liquid, gas-liquid, or liquid-solid interface.

There are three types of adsorption; ion exchange or exchange adsorption, physical and chemical adsorption.

Exchange or ion exchange adsorption is a process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface.

Physical adsorption (physisorption) is not site specific and is due to weak forces of attraction between molecules (van der Waals forces).

Chemical adsorption or chemisorption takes place as a result of chemical bond being formed between the molecule of the solute and the adsorbent, comparable with those leading to the formation of chemical compounds (Sharma, 2007). Davis & Leckie (1978) reported that the adsorption on hydrous metal oxide include surface ionization and surface complexation of metal ions with the hydrous metal oxide. An acid base equilibrium including the hydroxylated oxide surface is established as follows:



Where  $\equiv\text{S-OH}_2^{+}$ ,  $\equiv\text{S-OH}$  and  $\equiv\text{S-O}^{-}$  stand for positively, negatively and neutral charged surface hydroxyl respectively and neutral charged surface represent the point of zero charge ( $P_{zc}$ ) (Buamah, 2008).

There are many factors affecting adsorption such as nature of the adsorbent, nature of the adsorbate, nature of the solvent and others.

In adsorption modeling, the distribution of adsorbate between the two phases (the bulk solution and the adsorbent) is often described in terms of isotherm. The presentation of amount of solute adsorbed per unit of adsorbent ( $q$ ) as a function of the equilibrium concentration of the solute in the bulk ( $C_e$ ) at a constant temperature is called the adsorption isotherm.

$$Q = f(C_e) \dots\dots\dots (1)$$

Moreover, the most equations are most commonly used in adsorption modeling is Freundlich, Langmuir isotherm.

Adsorption processes are capable of removing metals if the adsorbent (solid surface) is selected carefully and the solution chemistry is controlled as well (Dugger et al., 1964; James and Healy, 1972; Kinniburgh et al., 1976; Schindler et al., 1976; Benjamin, 1983).

Adsorption on a surface or interface is occurred due to the binding force between the individual atoms, ions of the adsorbate and the surface. This binding force can be divided into two forces; short and long range forces. Thus, four principles have been introduced due to these adhesive forces: ion exchange, chemical adsorption, physical adsorption and specific adsorption (Yang,1999).

Several adsorbents have been used to remove heavy metals, but in our study two adsorbents will be used namely iron oxide coated sand (IOCS) and granular ferric hydroxide (GFH).

### **Iron oxide coated sand**

IOCS is obtained from the Dutch ground water treatment plant as a byproduct in the treatment of ground water that contains iron.

Iron oxide coated evolved under various condition which might have several physiochemical characteristic and therefore, different adsorption capacities. The surface characteristics of IOCS are physically and chemically heterogeneous and are expected to change with time. *Sharma* (2001) reported that IOCS (which collected from twelve different ground water treatments plants) has a very high porosity (110 times) and very large specific surface area (5-200 times) compared to new virgin sand. The range of Iron content of the coating was found from 27% to 45%, in addition, the coatings develop was not uniform and different region of the coating might have different composition and surface characteristics. IOCS contains silica and manganese and point of zero charge of these materials are at 2.0 and in between 2.0-4.5 respectively This is most likely to be the reason of low point of zero charge of IOCS which is 3.0-3.5. The table 2.8 shows the physiochemical characteristics and surface extractable content of IOCS.

Table 2. 8 Physiochemical characteristic of IOCS

<b>Grain size</b>	<b>Surface area</b>	<b>pH<sub>zpc</sub></b>	<b>Moisture content</b>	<b>Bulk Density</b>
1.8-4.0mm	201 m <sup>2</sup> /g	3.0-3.5	16.1%	2.360 g/cm <sup>3</sup>

Figure 2.3 shows the coating composition of IOCS samples and it can be seen that the Brucht water treatment plant sample has the highest concentration of Fe.

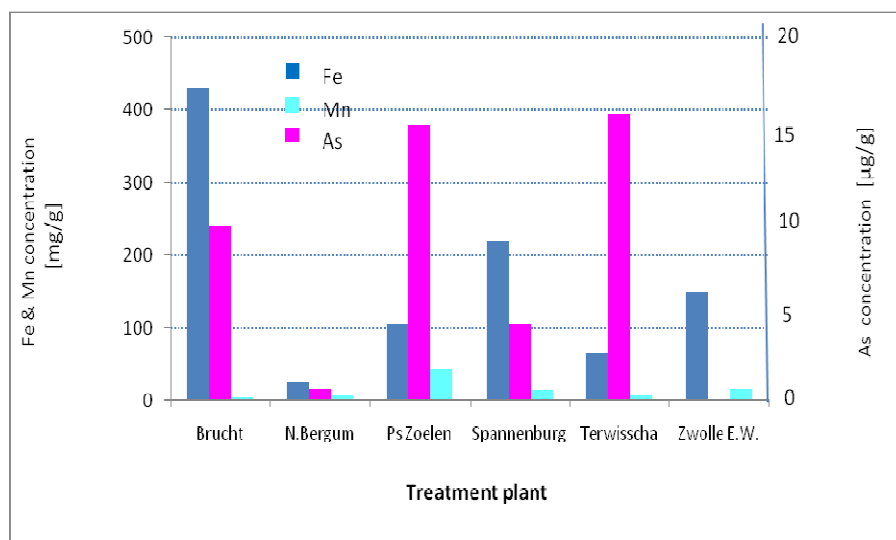


Figure 2. 3 Coating composition of IOCS samples (source: Restofenunie project report, 2006).

In general, iron oxide coating in iron removal plants is influenced by the raw water quality for instance pH,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Ca^{2+}$ , TOC etc that is being treated by the treatment plant. It also depends upon the process condition applied for example filtration rate, depth of media, back wash condition.

Many research have been conducted at UNESCO-IHE on adsorption of heavy metals by IOCS. IOCS has proved to be promising technology in removing heavy metals such as Mn, Ar, Cr, Cu and Cd.

Jens (2002) showed that IOCS can be used in removing Cu, Zn and Pb from urban stormwater runoff (Jens, 2002).

Yadav (2007) reported that IOCS can be used to remove Cr (III), Cu, Cd and Cr (VI), the adsorption capacity decreases in the order of Cr (III) > Cu > Cd > Cr (VI). The removal mechanism of copper and cadmium is likely due to electrostatic attraction, because Cu and Cd species at pH 6 have positive charge and IOCS surface charge is negative.

Another research showed that the equilibrium of copper on IOCS was reached in less than 24 hours as well as copper adsorption is varied from 10% below pH 4 to 90% above pH 6 (Sutha, 1999) and the adsorption removal efficiency increases as IOCS dose is increased due to the increasing in the surface area where the adsorption takes place. (Boujelben, 2008).

In another study, Hulya (2006) showed contradict results which is likely due to different experimental condition applied. The  $\text{pH}_{\text{pzc}}$  of IOCS was 9 and the average surface charge was positive at the experimental pH (7.5). Hence, IOCS has low affinity for copper and cadmium, on the other hand, IOCS attracted negative charged anions such as Arsenic and chromium.

Reviewing the performance of IOCS in various studies, IOCS can be used as an effective media for removing heavy metals from urban stormwater.

## Granular ferric hydroxide

Many studies show that GFH is adsorbents that have high affinity for arsenic and copper adsorption. It is a new granular commercially available adsorbent in the market. It has relatively high surface area (250-300  $\text{m}^2/\text{g}$ ) porosity of 75-80% and water saturated bulk density of  $1.32\text{g}/\text{cm}^3$ . The point of zero charge is between 7.5 to 8.0. The typical grain size ranges from 0.2 to 2.0 mm in diameter (Sperlich *et al.*, 2005).

It has high tendency to stick together because all of the pores of the GFH are totally filled with water as well as no any drying procedures involves in its preparation. Moreover, it contains about 50% of moisture. Table 2.9 summarizes the physiochemical characteristics of GFH.

Table 2. 9 Physiochemical characteristics of GFH

Grain size	Surface area	$\text{pH}_{\text{zpc}}$	Porosity	Moisture content	Bulk Density
0.2-2.0mm	280 $\text{m}^2/\text{g}$	7.5-8.0	75-80%	43-48%	$1.32\text{g}/\text{cm}^3$

Recent studies have shown that it is also able to remove ortho-P due to its properties comparable with those that of arsenate. M. Badruzzaman *et al.*, (2004) showed in his study that Freundlich isotherm constant K (adsorption capacity) for mesh size of 100x 140 and 60x 80 were 3.60 and 4.45 and 1/n value were 0.36 and 0.28. High field (2002) also reported similar magnitude of K i.e. 3.67 and 1/n value of 0.33. Yadav, (2007) reported that Granular Ferric Hydroxide (GFH) is capable of removing copper, chromium (Cr(VI) and Cr (III)) except with cadmium at pH 6 but when pH increases from 6 to 7, 8 and 9 there was significant removal of cadmium. In addition, the GFH adsorption has adsorption capacity decreases in the order of  $\text{Cu} > \text{Cr (VI)} > \text{Cr (III)} > \text{Cd}$ . Moreover, Hulya (2006) showed that GFH had medium efficiency removal for As at pH value 7.5, but GFH was the second most effective sorbent for Cr, Cd, Ni and Zn.

## CHAPTER 3. METHODOLOGY

### 3.1 Introduction

This chapter presents materials and methodologies that were used along with analytical techniques and experimental set up that was applied. In this study, the effect of selected water quality matrix on removal of selected heavy metals (cadmium and copper) with Iron Oxide Coated Sand (IOCS) and Granular Ferric Hydroxide (GFH) was studied.

First step was to find out the stability of copper and cadmium in the solution with different, pH(6-8) and calcium (20-60 mg/l) concentrations. Then, the short batch experiment was carried out to find out the effect of water quality matrix (pH and  $\text{Ca}^{++}$ ) and time on the adsorption of copper and cadmium on IOCS and GFH, based on the acquired result, the adsorption isotherm step was established.

### 3.2 Experimental materials

#### Chemicals and Reagents:

The following chemicals and reagents were used in the experiments:

- $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  : To prepare  $\text{Cu}^{2+}$  containing model water.
- $\text{CdCl}_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$  : To prepare  $\text{Cd}^{2+}$  containing model water.
- Sodium bicarbonate: For the buffering capacity of the solution.
- $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  : For the presence of  $\text{Ca}^{2+}$  in the model water.
- HCl and NaOH: For adjustment of pH.
- 65 %  $\text{HNO}_3$ : For the acidification of sample.
- Demineralised water : To prepare model water and chemical solutions

#### Apparatus

The following equipments are used in the experiments:

- Sieve analyzer
- Electronic balance
- Rotary mechanical shakers
- pH meter
- Polyethylene bottles (500 ml)
- Measuring cylinder
- Polyethylene syringes

- Filter head and filter paper of 45  $\mu\text{m}$  pore size
- Pipettes of various volumes
- Beaker, volumetric flask
- Fume cup board
- AAS – flame (figure 4)
- AAS – GF (figure 5)



Figure 3. 1 Atomic Absorption Spectrometer (AAS-Flame) used for analysis of copper.



Figure 3. 2 Atomic Absorption Spectrometer - Graphite furnace used for analysis of cadmium.

## **Preparatory work**

### **Adsorbents**

#### **IOCS**

IOCS is obtained from the Brucht ground water treatment plant as a byproduct in the treatment of ground water containing iron.

IOCS was pulverized with mortar and the sieving was done to get the required size fraction ( $<63 \mu\text{m}$ ). While grinding was done gently so that grinded fraction contains only coating but not the sand grains.

#### **GFH**

Granular ferric hydroxide (GFH) obtained from producer (GEH Wasserchemie Osnabruck) Germany has been used as an adsorbent in this study and was pulverized with grain size smaller than  $63 \mu\text{m}$ .

### **Equilibrium calculation**

Phreeqc-2 interactive software is used in this study in order to get the distribution of aqueous species and calculate saturation index and to predict the final concentration of metals that will be in solution at equilibrium.

### **Stock solution**

Stock solution of 1000 mg/l of Cu and Cd are prepared and certain volume is dosed to the model water according to the experiment procedure.

pH value for both stock solution (copper and cadmium) was 1.5.

### Standard solutions

Several concentration of Standard solution of Copper was prepared from (0.01-0.02-0.04-0.05-0.1-0.25-0.5-1-1.5 mg /l) (Table 3.1) and used for the measurement, calibration range and in the detection limit of AAS flame instrument.

Table 3. 1 High and low standard concentration of copper

Selected heavy metals	High concentration standard (mg/L)	Low concentration standard (mg/l)
Copper (Cu)	1.5	0.01

Standard solution of Cadmium was prepared from 10, 20 and 30  $\mu\text{g}$  /l and used for the measurement, calibration range and in the detection limit of AAS-GF instrument.

### Model water

Model water was prepared from several concentrations of  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$  and different value of pH to get the desired concentration of pH,  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  as per the experiment procedure (Table 3.2).

Table 3. 2 Water quality matrix

pH	$\text{HCO}_3^-$ (mg/l)	$\text{Ca}^{2+}$ (mg/l)	$\text{Na}^+$ (mg/l)	$\text{Cl}^-$ (mg/l)
6	20	20	7.5	35.5
6	20	40	7.5	71
6	20	60	7.5	106.5
7	20	20	7.5	35.5
7	20	40	7.5	71
7	20	60	7.5	106.5
8	20	20	7.5	35.5
8	20	40	7.5	71
8	20	60	7.5	106.5

### **pH control**

pH was adjusted and controlled during the experiments in order to avoid any fluctuation of pH, this was done by adding certain concentration of HCl (1 – 0.01 mole) to reduce pH value and NaOH (1 – 0.01 mole) was added to increase pH value.

### **Shaking speed**

Shaking speed was implemented in this experiment to make sure that all heavy metals ions will come in contact with all surface area during the experiments (Tekeste, 2003).



Figure 3. 3 GFL-Shaker 3019

### **Filtration of sample**

Sample was filtered in order to separate solid from the liquid by using 0.45  $\mu\text{m}$  whatman filter and acidified with  $\text{HNO}_3$ .

### **Analysis of samples**

Atomic Absorption Spectrophotometer – Graphite Furnace was used to determine the concentration of cadmium within  $\mu\text{g/l}$  concentration.

Atomic Absorption Spectrophotometer - Flam was used to determine the concentration of copper and calcium within  $\text{mg/l}$  concentration.

### 3.3 Experimental methods/Procedure

#### Stability of copper and cadmium Experiment

First step was to find out the effect of different calcium concentration (20-60mg/l), pH value (6-8) and time (0-24 hours) on copper and cadmium stability in the solution.

#### Short batch experiment

First step was short batch adsorption experiment. Short Batch adsorption experiment was carried out by using IOCS and GFH to assess which heavy metals could be affected by different value of pH (6-8), calcium concentration (20 – 60 mg/l) and time (0 – 24 hour).

Procedure:

- 1- 500 ml of model water (demineralized water with 20 mg/l of  $\text{HCO}_3^-$ , 20 mg/L of  $\text{Ca}^{2+}$  and 4 mg/l of copper at pH 6) was kept in 500 ml of Polyethylene bottle in which 0.05g of GFH or IOCS is dosed as well.
- 2- All samples were placed on GFL-Shaker (figure 8) on speed 100 rpm (figure 6).
- 3- Sampling was done at regular time intervals to analyze the residual concentration of metals.

The same procedure was done for copper but at pH 7 and 8.

The same procedure was done for cadmium but with 0.1 mg/l of cadmium concentration and at pH 6, 7 and 8.

#### Batch adsorption experiments

Batch adsorption isotherm experiment has been carried out as per the obtained result from the short batch experiment.

Procedure:

- 1- Adsorption isotherm experiment have been carried out for cadmium with IOCS.
- 2- Model water was prepared in polyethylene bottles with fixed amount of cadmium besides two bottles as blank bottle without any adsorbents (to monitor the stability of the copper and cadmium in model water).
- 3- Varied amount of IOCS was added to the model water and kept at the top of mechanical round shaker and at room temperature of 20 (+/-2) till the equilibrium was reached.

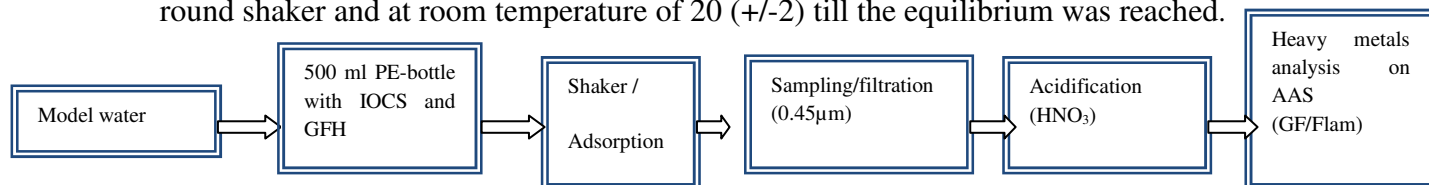


Figure 3. 4 Schematic diagram of procedure followed during batch adsorption experiments.

## CHAPTER 4. RESULTS AND DISCUSSION

This chapter presents results of experiments carried out to determine influence of pH, Ca concentration and contact time on:

1. stability of Cu and Cd; and
2. adsorption of Cu and Cd on two different adsorbents.

### 4.1 Stability of copper and cadmium

Prior to assess the effect of pH, calcium concentration and contact time on IOCS and GFH adsorption efficiency for copper and cadmium removal, stability of these metals in the model water was studied within pH(6-8) and calcium concentration (20-60 mg/l).

#### 4.1.1 Stability of copper

Figure 4.1 shows the concentration of dissolved Cu as a function of contact time and  $\text{Ca}^{2+}$  concentration at pH= 6.

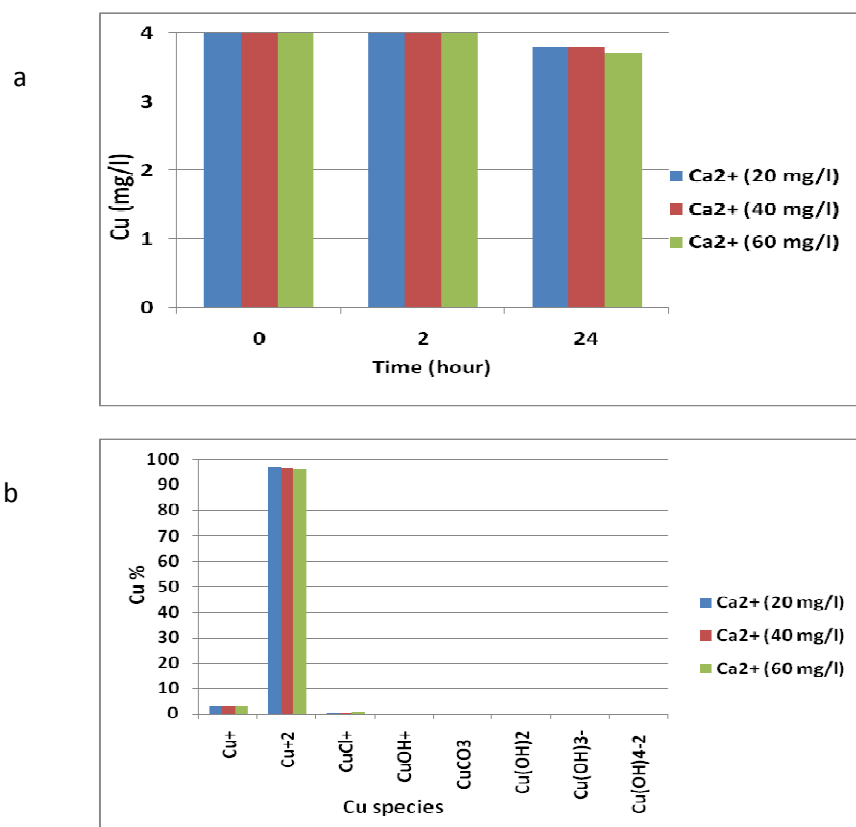


Figure 4. 1: (a) Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu solubility at pH=6 $\pm$ 0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l, samples filtered through 0.45 $\mu\text{m}$ . (b) Speciation of Cu based on Phreeqc calculation under same experimental conditions.

Obtained results show that there is no significant reduction in dissolved Cu concentration at pH=6 which confirmed that up to pH 6.9  $\text{Cu}^{2+}$  is predominant (Stum, Morgan 1981).

It can be seen from figure 4.1 (a) that there is small reduction of dissolved Cu concentration of about 5% in the solution. This reduction of dissolved Cu concentration in the solution was observed only after 24 hour of contact time. Based on Phreeqc calculations this reduction is likely caused by precipitation of  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  and  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$  compounds. Increase in calcium concentration resulted in further reduction of dissolved copper concentration.

Table 4. 1 Saturation index of copper based on Phreeqc calculation. (Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l), pH=6 and initial Cu (II) concentration = 4 mg/l.

Precipitating compound	$\text{Ca}^{2+}$ (20 mg/l)	$\text{Ca}^{2+}$ (40 mg/l)	$\text{Ca}^{2+}$ (60 mg/l)
$\text{Cu}_2(\text{OH})_2\text{CO}_3$	38.99	39.00	39.02
$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	52.04	52.06	52.08

Based on Phreeqc calculation (Table 4.1)  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  and  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$  are present in the solution in the form of precipitating compounds.

In general, the reduction of dissolved copper concentration of about 5% after 24 hours of contact time at pH=6, Yadav (2007) reported that the reduction of about 1% of dissolved Cu concentration was observed after 19 hours from 3 mg/l to 2.97 mg/l after 19 hours of contact time in the solution.

Figure 4.2 shows the concentration of copper as a function of time and calcium concentration at pH= 7±0.2.

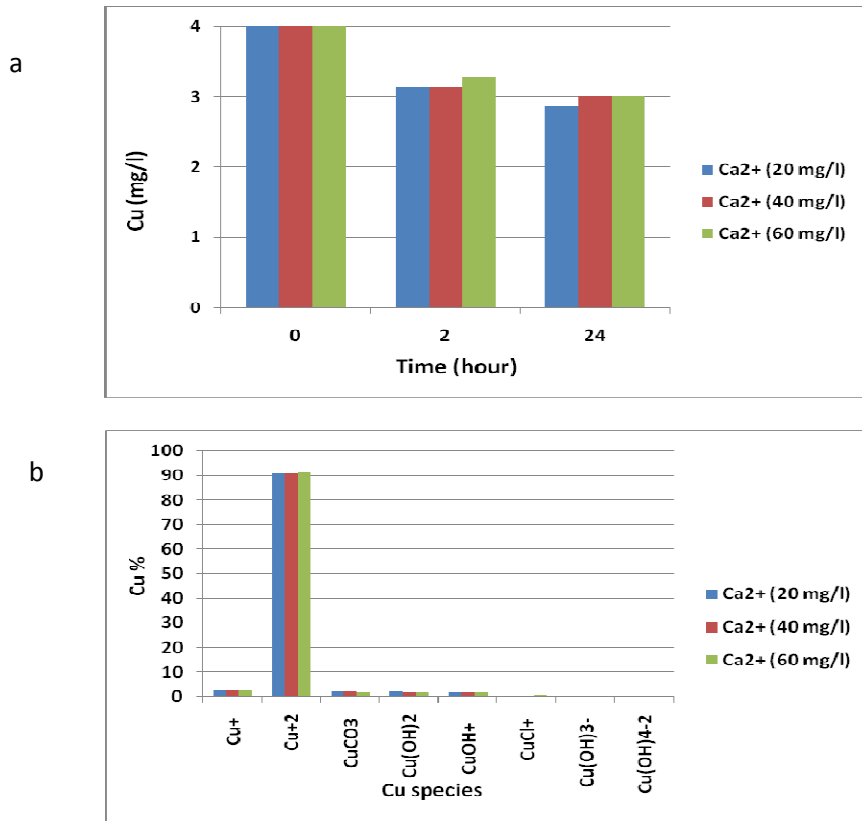


Figure 4. 2: (a) Effect of contact time and Ca<sup>2+</sup> concentration on Cu solubility at pH=7±0.2. Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup> (20 mg/l) and initial Cu (II) concentration = 4 mg/l, samples filtered through 0.45µm. (b) Speciation of Cu based on Phreeqc calculation under same experimental conditions.

Figure 4.2 (a) shows significant reduction in dissolved copper concentration at pH=7±0.2. The reduction of dissolved copper concentration was observed after 2 hours of contact time of about 18 % to 20%. Cu precipitation largely occurred after 2 hour of contact time. Further increase of contact time to 24 hours did not show significant reduction of dissolved Cu concentration. It was observed that there is no significant influence of Ca<sup>2+</sup> concentration in stability of Cu in the solution at pH=7±0.2

Based on Phreeqc calculations this reduction is likely due to the precipitation of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, Cu<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> and CuO (table 4.2).

Table 4. 2 Saturation index of copper based on Phreeqc calculation. (Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l), pH=7 and initial Cu (II) concentration = 4 mg/l.

Precipitating compound	$\text{Ca}^{2+}$ (20 mg/l)	$\text{Ca}^{2+}$ (40 mg/l)	$\text{Ca}^{2+}$ (60 mg/l)
$\text{Cu}_2(\text{OH})_2\text{CO}_3$	45.71	45.66	45.61
$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	62.02	61.94	61.88
CuO	0.14	0.12	0.10

The explanation of table 4.2 is the same as the one given at pH=6 including CuO.

Figure 4.3 shows the concentration of dissolved Cu as a function of contact time and  $\text{Ca}^{2+}$  concentration at pH=  $8 \pm 0.2$ .

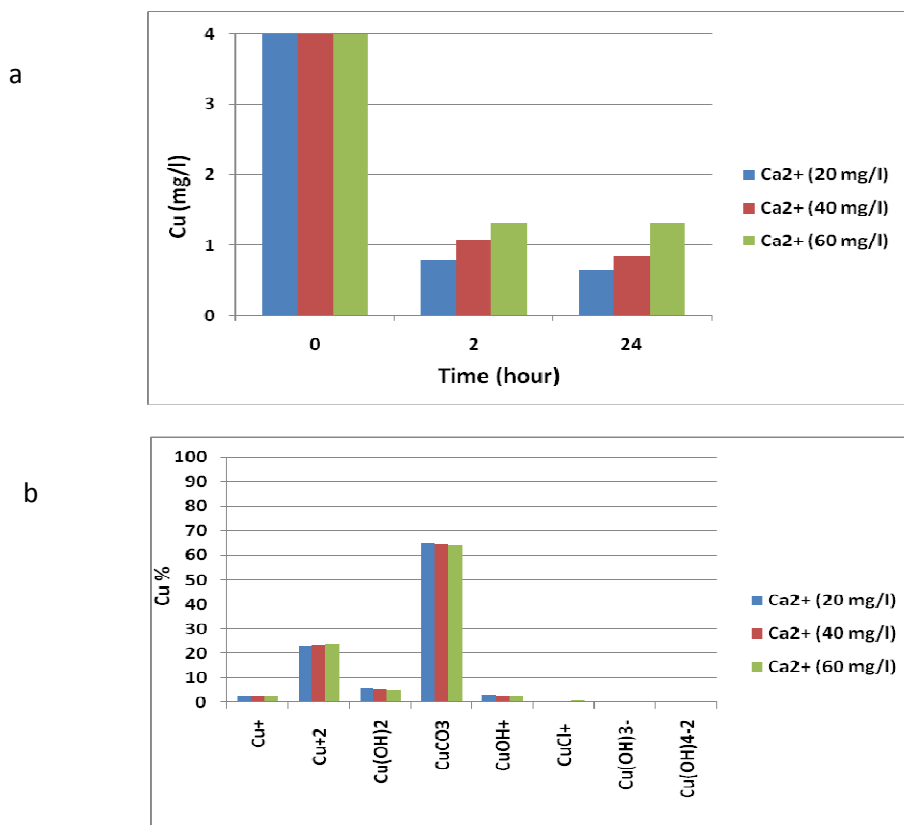


Figure 4. 3: (a) Effect of contact time and calcium concentration on Cu solubility at pH= $8 \pm 0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l, samples filtered through 0.45 $\mu\text{m}$ . (b) Speciation of Cu based on Phreeqc calculation under same experimental conditions.

Figure 4.3 (a) shows that there is a significant reduction in dissolved Cu concentration at pH 8 of about 65% to 85% after 2 hours and the same after 24 hours of contact time. Increase in  $\text{Ca}^{2+}$  concentration resulted in less reduction of dissolved Cu concentration.

Table 4. 3 Saturation index of copper based on Phreeqc calculation. (Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l), pH=8 and initial Cu (II) concentration = 4 mg/l).

Precipitating compound	$\text{Ca}^{2+}$ (20 mg/l)	$\text{Ca}^{2+}$ (40 mg/l)	$\text{Ca}^{2+}$ (60 mg/l)
$\text{Cu}_2(\text{OH})_2\text{CO}_3$	46.53	46.48	46.45
$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	63.20	63.13	63.08
$\text{CuO}$	0.60	0.58	0.57

Based on phreeqc calculation all precipitating compounds are nearly the same which is in contrast with figure 4.3 (a) due to the equilibrium here reached after long time more than 24 hours of contact time.

Therefore, copper solubility is affected by pH,  $\text{Ca}^{2+}$  concentration and contact time. pH increased can be used to remove Cu through 5% precipitation at pH6 and 85% at pH 8.

In addition, the stability of dissolved Cu concentration is more decreased with increasing of contact time from 2 hour to 24 hour. In contrast, increase in calcium concentration at pH 7 and 8 resulted in increase in copper stability.

Consequently, pH control (an increase to alkaline level) can be used to remove copper from urban stormwater runoff and softening of water should be done after Cu removal (Benjamin, 1996).

### 4.1.2 Stability of Cadmium

In this section the results of Cd stability as a function of contact time and  $\text{Ca}^{2+}$  concentration and pH are shown.

Figure 4.4 shows the concentration of Cd as a function of contact time and  $\text{Ca}^{2+}$  concentration at  $\text{pH} = 6 \pm 0.2$ .

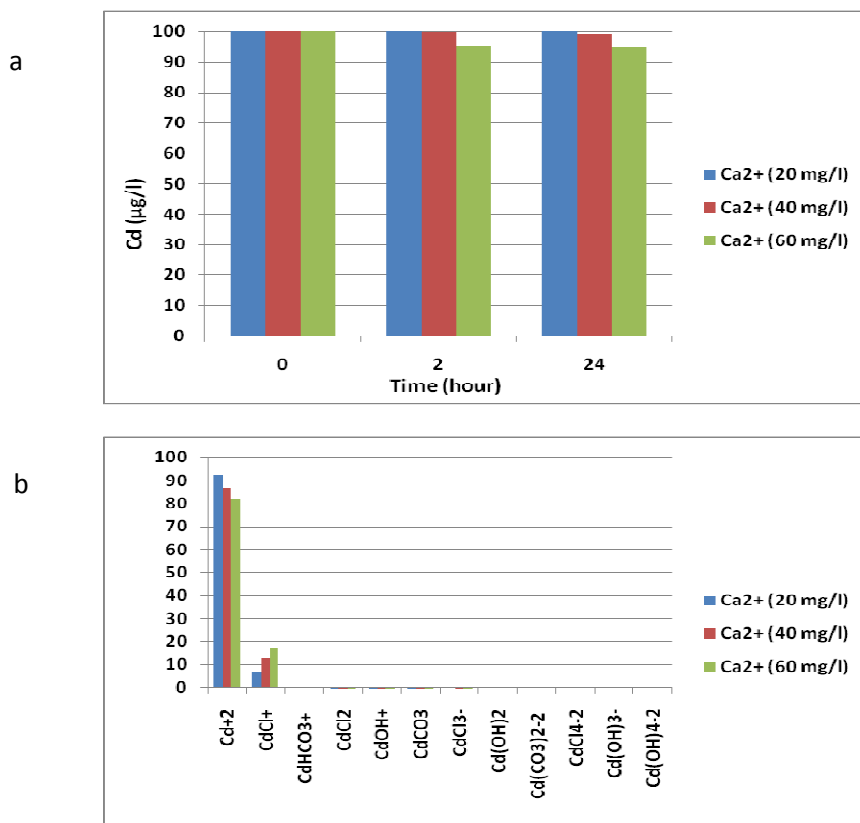


Figure 4. 4: (a) Effect of contact time and calcium concentration on Cd solubility at  $\text{pH} = 6 \pm 0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration =  $100 \mu\text{g/l}$ , samples filtered through  $0.45 \mu\text{m}$ . (b) Speciation of Cd based on Phreeqc calculation under same experimental conditions.

Figure 4.4 reveal that there is a small reduction of dissolved Cd concentration of about 5% in the solution. This reduction of dissolved Cd concentration in the solution was observed after 2 hours of contact time. Further increase in contact time to 24 hours did not show significant reduction of Cd concentration in the solution. Increase in  $\text{Ca}^{2+}$  concentration resulted in further reduction of Cd concentration in the solution.

Table 4. 4 Cadmium speciation percentage based on Phreeqc calculations at pH=6.

Cadmium species	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
Cd <sup>2+</sup>	92.37	86.73	82.09
CdCl <sup>+</sup>	7.35	12.94	17.51
CdHCO <sup>+</sup>	0.24	0.22	0.20
CdCl <sub>2</sub>	0.03	0.10	0.19
CdOH <sup>+</sup>	0.01	0.01	0.01

Table 4.4 shows that most of Cd species present as Cd<sup>2+</sup>, CdCl<sup>+</sup>, CdHCO<sup>+</sup>, CdCl<sub>2</sub> and CdOH<sup>+</sup>. Increase in calcium concentration resulted in further reduction of dissolved Cd concentration and further increase in CdCl<sup>+</sup> and CdCl<sub>2</sub> species.

Figure 4.5 shows the concentration of dissolved Cd as a function of contact time and calcium concentration at pH= 7±0.2.

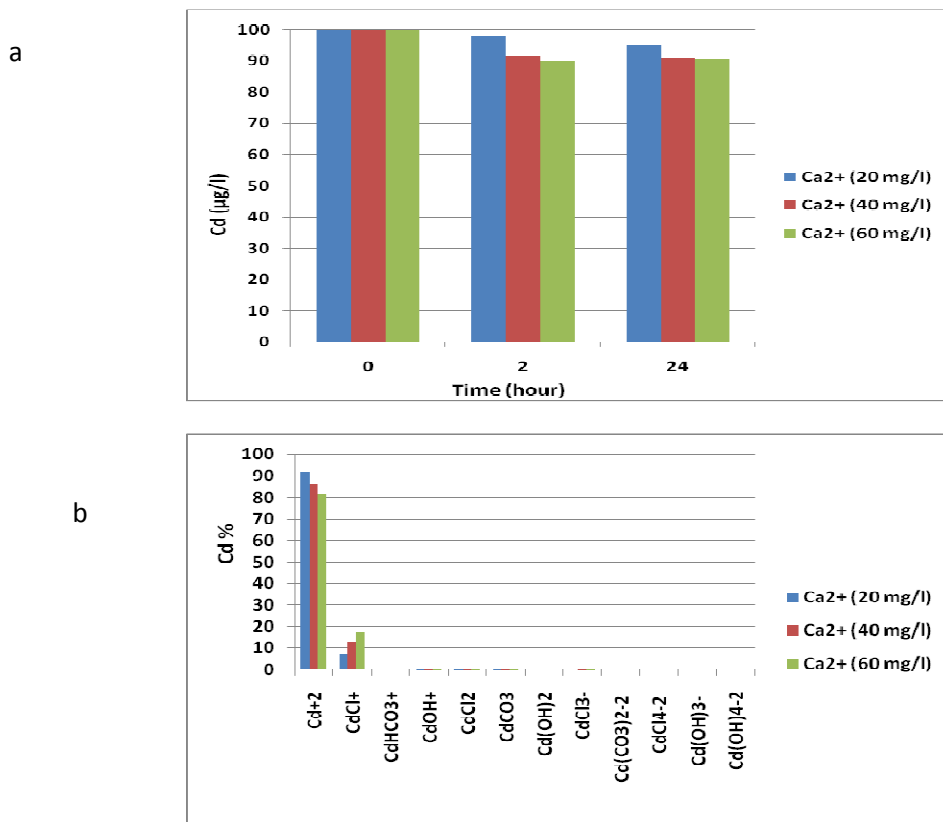


Figure 4. 5: (a) Effect of contact time and calcium concentration on Cd solubility at pH=7±0.2. Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cd (II) concentration = 100 µg/l, samples filtered through 0.45µm. (b) Speciation of Cd based on Phreeqc calculation under same experimental conditions.

Figure 4.5 reveal that there is a small reduction of dissolved Cd concentration of about 2% to 10% in the solution. This reduction of dissolved Cd concentration in the solution was observed after 2 hours of contact time. Further increase of contact time to 24 hours did not show significant reduction of dissolved Cd concentration in the solution. Increase in Ca<sup>2+</sup> concentration resulted in further reduction of dissolved Cd concentration in the solution.

Table 4. 5 Cadmium speciation percentage based on Phreeqc calculations at pH=7.

Cadmium species	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
Cd <sup>2+</sup>	91.98	86.41	81.83
CdCl <sup>+</sup>	7.29	12.86	17.41
CdHCO <sup>+</sup>	0.64	0.56	0.51
CdCl <sub>2</sub>	0.03	0.09	0.19
CdOH <sup>+</sup>	0.06	0.06	0.05

The explanation of table 4.5 is the same as the one given at pH 6.

Figure 4.6 shows the concentration of dissolved Cd concentration as a function of contact time and Ca<sup>2+</sup> concentration at pH= 8±0.2.

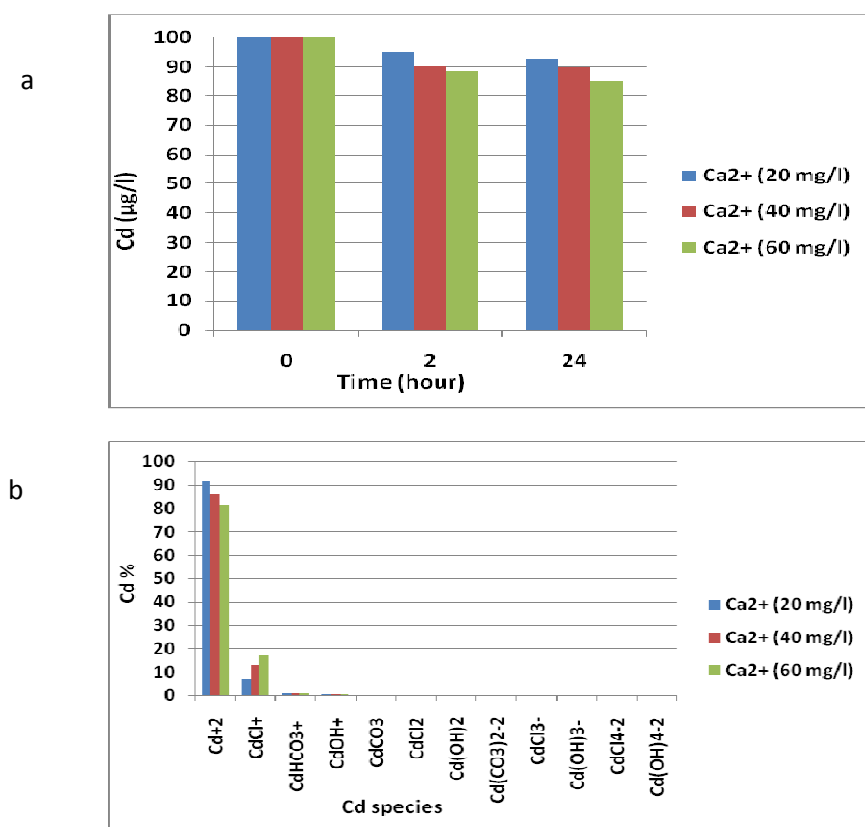


Figure 4. 6: (a) Effect of contact time and Ca<sup>2+</sup> concentration on Cd solubility at pH=8±0.2. Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup> (20 mg/l) and initial Cd (II) concentration = 100 µg/l, samples filtered through 0.45µm. (b) Speciation of Cd based on Phreeqc calculation under same experimental conditions.

Figure 4.6 reveal that there is a small reduction of dissolved Cd concentration of about 5% to 11% in model water. This reduction of dissolved Cd concentration in the solution was observed after 2 hours of contact time. Further increase of contact time to 24 hours did not show significant reduction of dissolved Cd concentration in the solution. Increase in  $\text{Ca}^{2+}$  concentration resulted in further reduction of dissolved Cd concentration in the solution.

Table 4. 6 Cadmium speciation percentage based on Phreeqc calculations at pH=8.

Cadmium species	$\text{Ca}^{2+}$ (20 mg/l)	$\text{Ca}^{2+}$ (40 mg/l)	$\text{Ca}^{2+}$ (60 mg/l)
$\text{Cd}^{2+}$	91.44	85.96	81.43
$\text{CdCl}^+$	7.24	12.78	17.32
$\text{CdHCO}^+$	0.75	0.66	0.60
$\text{CdCl}_2$	0.03	0.09	0.19
$\text{CdOH}^+$	0.47	0.43	0.40
$\text{CdCO}_3$	0.06	0.05	0.05

The explanation of table 4.6 is the same as the one given at pH 6.

In general, Removal of Cd increased under condition applied due to the precipitation at pH 6 (5%) and pH 8 (15%). Increase in  $\text{Ca}^{2+}$  concentration resulted in further reduction of dissolved Cd concentration in the solution. These results are in agreement with results reported by Chin (2002). Moreover, the reduction of cadmium in the solution at pH 7 and 8 is most likely due to the precipitation of otavite ( $\text{CdCO}_3$ ) which is confirmed by Phreeqc calculations. Under condition tested, pH cannot be used to remove Cd.

## 4.2 Adsorption experiments

Batch adsorption experiments were conducted to assess the effect of pH, calcium concentration and contact time on adsorption of copper and cadmium on IOCS and GFH adsorbents.

### 4.2.1 Adsorption on IOCS

In this section, the results of copper and cadmium adsorption on IOCS adsorbent are presented.

#### 4.2.1.1 Adsorption of copper on IOCS as a function of pH and $\text{Ca}^{2+}$ concentration

##### (i) pH 6

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on IOCS at pH= 6.

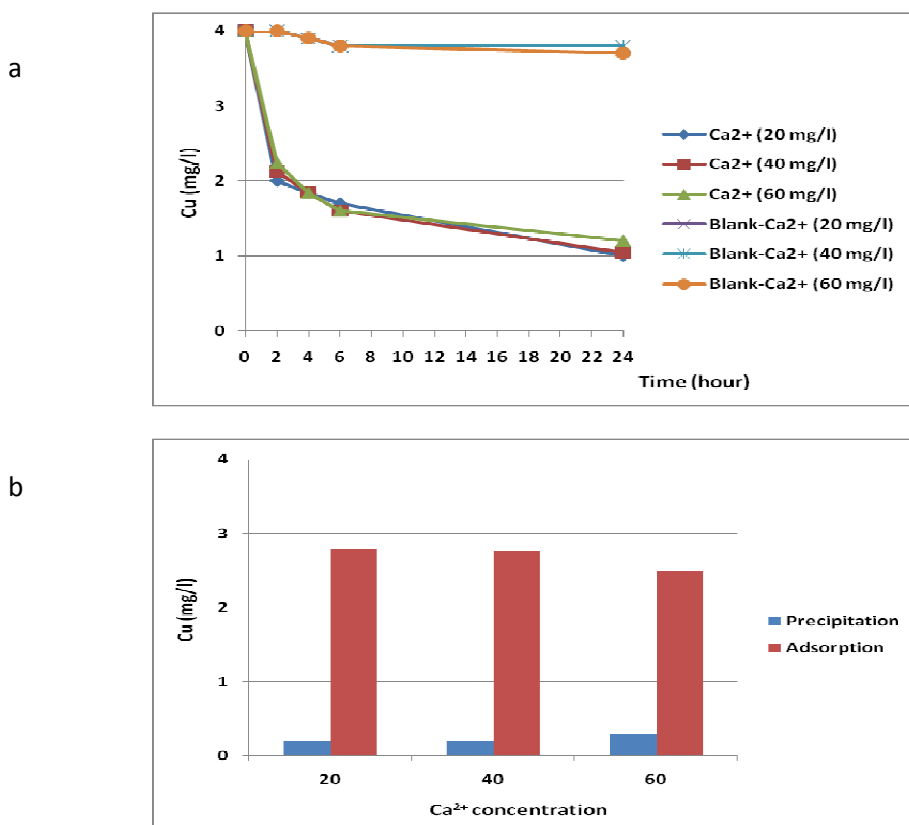


Figure 4. 7: Effect of contact time and calcium concentration on Cu adsorption on IOCS at pH=6±0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L. (a) Concentration of Cu in solution. (b) Rate of Cu precipitation and adsorption on IOCS.

Figure 4.7 show that there is adsorption of copper on IOCS which corresponds with Yadav's study (Yadav, 2007). It can be seen that within  $\text{Ca}^{2+}$  concentration tested (20, 40 and 60 mg/l)

does not have that much effect on copper adsorption with IOCS. Moreover, it was observed that adsorption rate was very fast in the first two hours. This resulted in the reduction of dissolved copper concentration around 50%, then adsorption rate was very slow after 2 hours resulting in the reduction of copper concentration around 5%. Even after 24 hours the adsorption rate was very slow till 24 hours which is not similar to Yadavs study in terms of contact time when he reported that there was reduction of about 33.3% of dissolved Cu concentration within 19 hours. The difference could be explained in terms of different experimental conditions.

At  $\text{pH}=6\pm 0.2$  the IOCS surface site is negatively charged and the major species of copper in the solution are  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{CuOH}^+$  and  $\text{CuCl}^+$  with percentage distribution of 2.8, 96.8, 0.035 and 0.28 respectively (calculated with Phreeqc at the same conditions as the experiment was carried out).

Therefore, it is most likely that the adsorption occurred due to electrostatic attraction between copper and IOCS surface.

## (ii) pH 7

This experiment was conducted to assess the effect of time and calcium concentration on Cu adsorption on IOCS at pH 7.

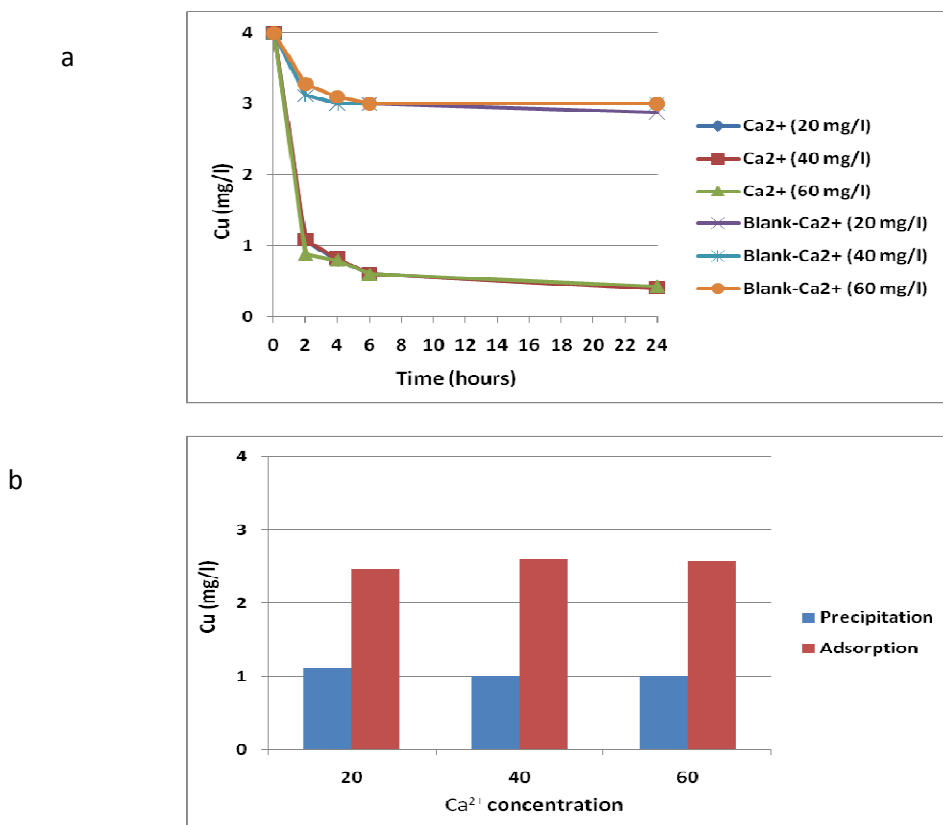


Figure 4. 8: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on IOCS at  $\text{pH}=7\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L. (a) Concentration of Cu in solution. (b) Rate of Cu precipitation and adsorption on IOCS.

Figure 4.8 show that there is no any effect of  $\text{Ca}^{2+}$  concentration on adsorption of copper with IOCS. Moreover, it was observed that the adsorption rate was very fast after 2 hours of contact time in the solution resulting in the reduction of about 66.6% of dissolved Cu concentration. Further increase of contact time to 24 did not show significant reduction of dissolved Cu concentration in the solution.

Copper is highly adsorbed on IOCS due to electrostatic attraction between positive charge of copper species and negative charge of IOCS surface. Moreover, 90.83 % of copper as  $\text{Cu}^{2+}$ , 0.26 % as  $\text{CuCl}^+$ ,  $\text{CuOH}^+$  as 1.8% and 2.82% as  $\text{Cu}^+$  (based on Phreeqc calculations, at pH 7 with  $\text{Ca}^{2+}$  concentration 20 mg/l in the solution) resulted in enhancing the adsorption process.

Removal efficiency of dissolved Cu concentration increases when pH increases from pH 6 to 7 because the precipitation and adsorption processes were taking place.

### (iii) pH 8

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on IOCS at pH 8.

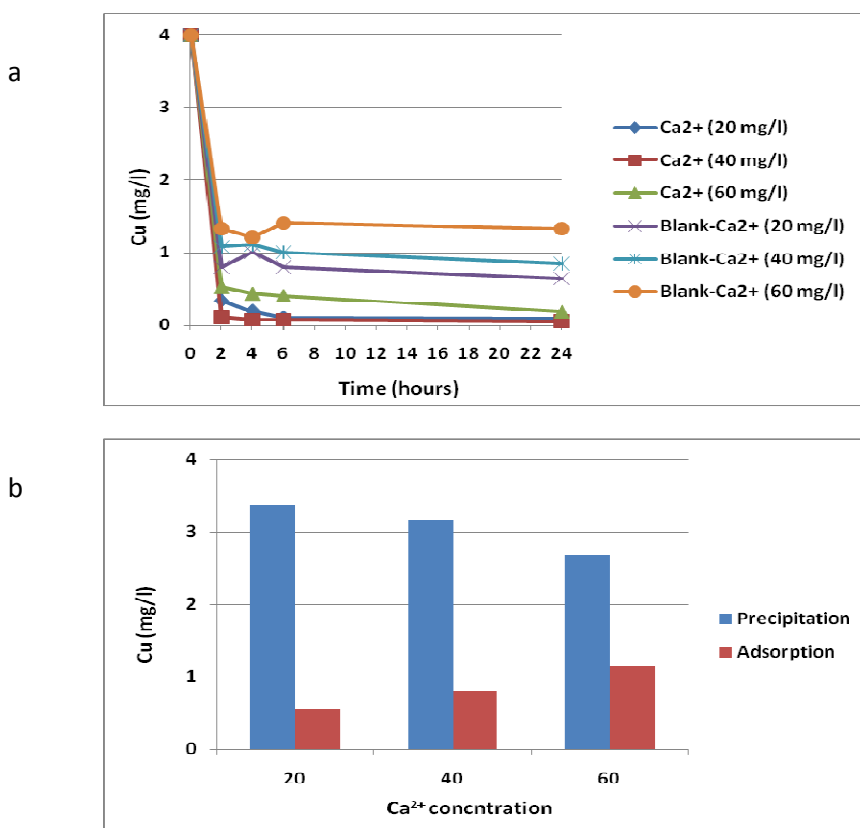


Figure 4. 9: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on IOCS at pH8=±0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L. (a) Concentration of Cu in solution. (b) Rate of Cu precipitation and adsorption on IOCS.

It can be seen that there is no significant effect of  $\text{Ca}^{2+}$  concentration on the adsorption. Moreover, it is observed that adsorption rate was very fast after 2 hours of contact time.

Copper is highly adsorbed on IOCS which is most likely due to low  $P_{zc}$  of IOCS. Therefore, electrostatic attraction between positive charge of copper species (which presents 2.82% as  $\text{Cu}^+$ , 23.04 as  $\text{Cu}^{2+}$ , 0.24 % as  $\text{CuCl}^+$ ,  $\text{CuOH}^+$  as 3% and 64.9 % as  $\text{CuCO}_3$  - based on Phreeqc

calculations, at pH 8 with calcium concentration of 20 mg/l in the solution) and negative surface charge of IOCS could be possibly occurred in the solution.

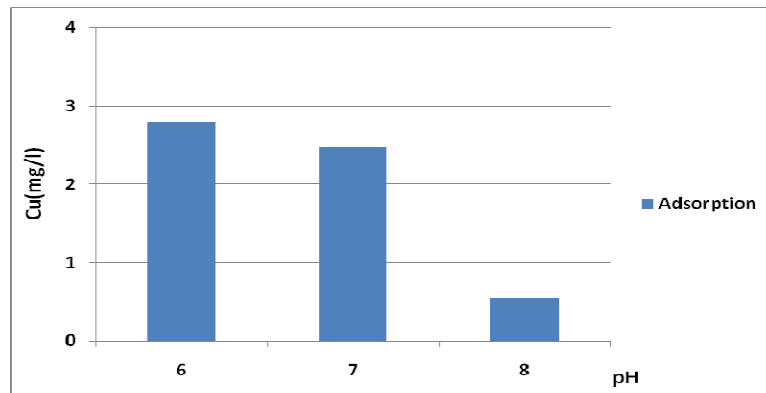


Figure 4. 10: Effect of pH on Cu adsorption on IOCS. Model water: demineralized water with  $\text{Ca}^{2+}$  (20mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L.

Increase in pH can be used to remove Cu through 5% precipitation at pH=6 and 85% at pH=8. The most removal efficiency was observed at pH=8 and achieved through precipitation and adsorption.

Hence, pH is playing an important role in copper solubility which is used as removal technology (such as chemical precipitation technology in treatemnt plants (Tonni.2006).

#### 4.2.1.2 Adsorption of cadmium on IOCS as a function of pH and $\text{Ca}^{2+}$ concentration

##### (i) pH 6

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on IOCS at pH= 6.

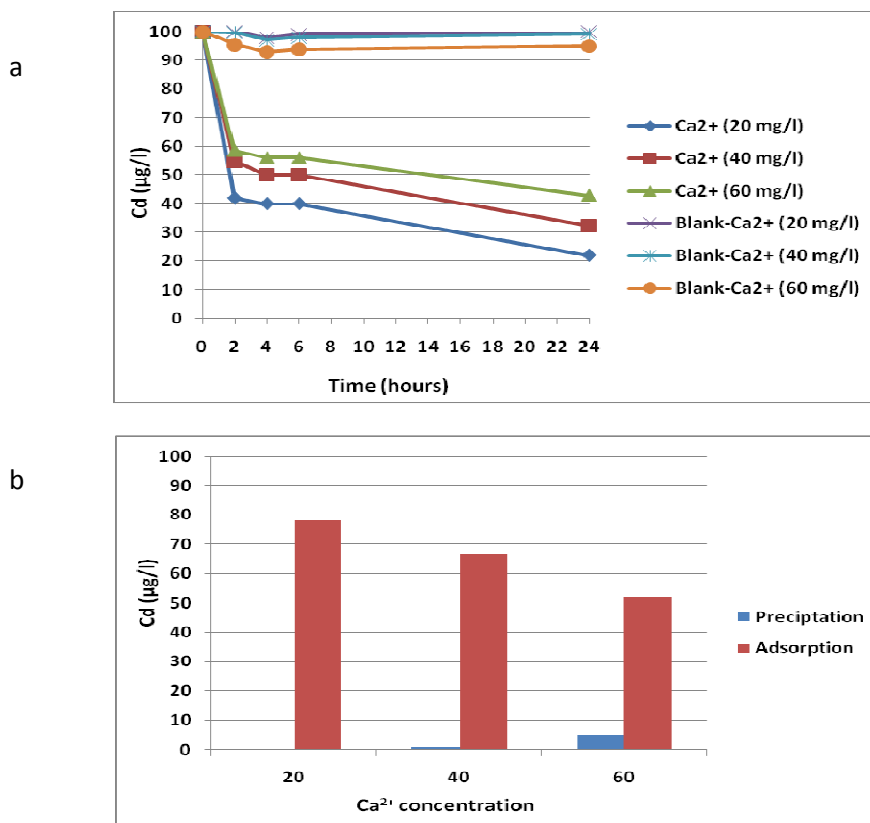


Figure 4. 11: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on IOCS at pH=6±0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100 µg/l. IOCS = 0.1 g/L. (a) Concentration of Cd in solution. (b) Rate of Cd precipitation and adsorption on IOCS after 24 hours of CT.

Figure 4.11 shows that the adsorption efficiency of Cd was affected by  $\text{Ca}^{2+}$  concentration and contact time. The adsorption was observed after 2 hours of contact time of about 42% to 58%. Further increase of contact time to 24 hours did not show significant reduction of dissolved Cd concentration in the solution. Increase in  $\text{Ca}^{2+}$  concentration resulted in less reduction of dissolved Cd concentration which is probably due to  $\text{Ca}^{2+}$  diminishing the number of adsorption sites on IOCS, which result in lower removal of cadmium (Zasoki and Bureau, 1988).

Cadmium is highly adsorbed with IOCS which is most likely due to the low of  $P_{zc}$  of IOCS. Hence, electrostatic attraction between positive charge of cadmium species (which presents 92.37% as  $\text{Cd}^{2+}$ , 7.35 as  $\text{CdCl}^+$ , 0.24 % as  $\text{CdHCO}^+$ ,  $\text{CdOH}^+$  as 0.01% and 0.03 % as

$\text{CdCl}_2$  - based on Phreeqc calculations, at pH 6 with  $\text{Ca}^{2+}$  concentration of 20 mg/l in the solution) and negative surface charge of IOCS could be probably occurred in the solution.

In general, Cd and  $\text{Ca}^{2+}$  are in cationic form. So, most likely the removal occurs due to electrostatic attraction with IOCS. Moreover, the efficiency of cadmium removal decreases while increasing calcium concentration.

## (ii) pH 7

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on IOCS at pH= 7.

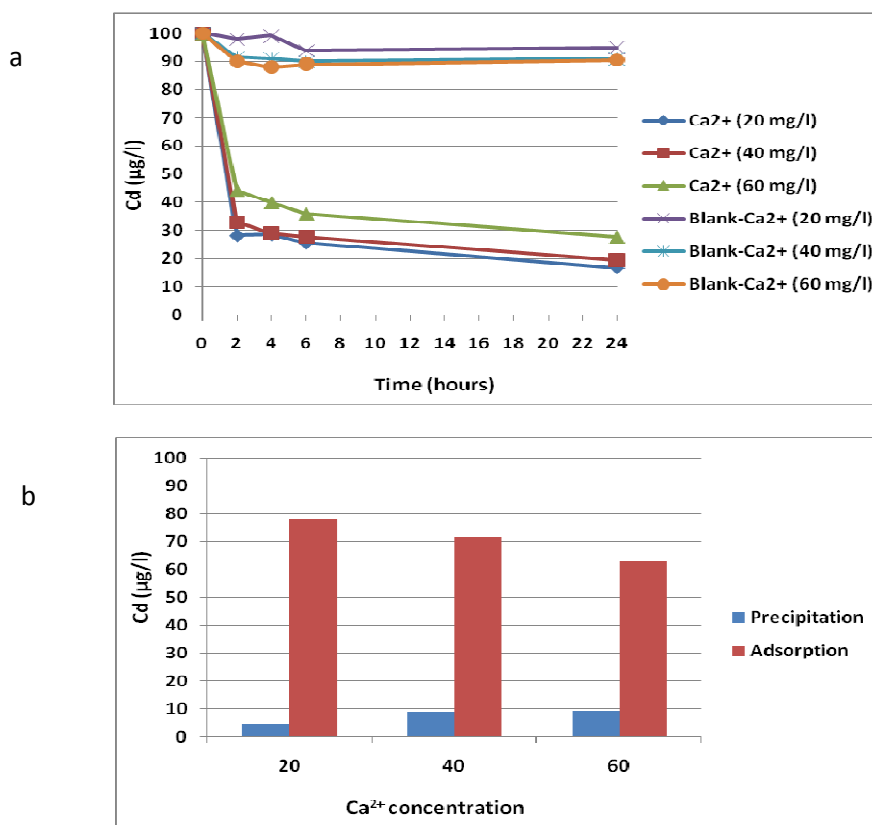


Figure 4. 12 Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on IOCS at pH=7±0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100 µg/l. IOCS = 0.1 g/L. (a) Concentration of Cd in solution. (b) Rate of Cd precipitation and adsorption on IOCS.

Adsorption rate of cadmium with IOCS increase while increasing pH value from 6 to 7, The adsorption was observed after 2 hours of contact time of about 55% to 72%. Further increase of contact time to 24 hours did not show significant reduction of dissolved Cd concentration in the solution. Increase in  $\text{Ca}^{2+}$  concentration resulted in less reduction of dissolved Cd concentration.

Based on Phreeqc calculations Cd presents 91.98% as  $\text{Cd}^{2+}$ , 7.29 as  $\text{CdCl}^+$ , 0.64 % as  $\text{CdHCO}^+$ ,  $\text{CdOH}^+$  as 0.06% and 0.03 % as  $\text{CdCl}_2$  at pH 7 with calcium concentration of 20 mg/l

in the solution. This reduction in dissolved Cd concentration from pH 6 to 7 in the solution is most likely due to the presence of  $\text{CdCO}_3$ .

### (iii) pH 8

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on IOCS at pH=8.

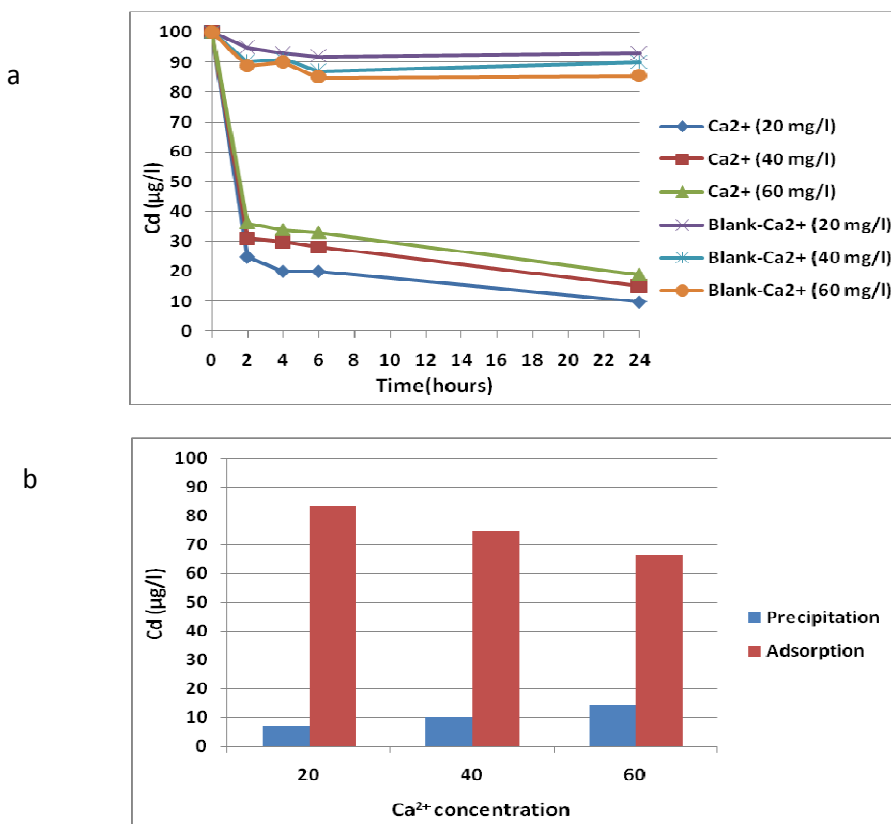


Figure 4. 13: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on IOCS at pH=8±0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100 µg/l. IOCS = 0.1 g/L. (a) Concentration of Cd in solution. (b) Rate of Cd precipitation and adsorption on IOCS.

Adsorption rate of Cd on IOCS increase while increasing pH value from 7 to 8, The adsorption was observed after 2 hours of contact time of about 65% to 75%. Further increase of contact time to 24 hours show a small reduction of dissolved Cd concentration in the solution of about 80% to 90%. Increases in  $\text{Ca}^{2+}$  concentration resulted in less reduction of dissolved Cd concentration.

Based on Phreeqc calculations cadmium presents 91.44% as  $\text{Cd}^{2+}$ , 7.24 as  $\text{CdCl}^+$ , 0.75 % as  $\text{CdHCO}^+$ ,  $\text{CdOH}^+$  as 0.47%, 0.03 % as  $\text{CdCl}_2$  and  $\text{CdCO}_3$  as 0.06% at pH 8 with calcium

concentration of 20 mg/l in the solution. The reduction in cadmium species from pH 7 to 8 in the solution is most likely due to the presence of  $\text{CdCO}_3$ .

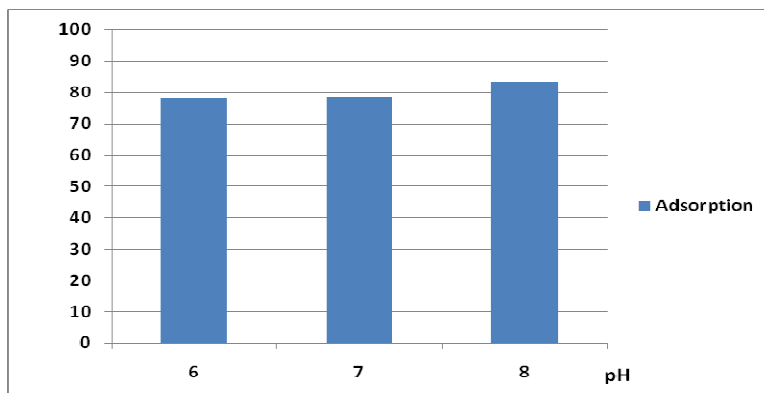


Figure 4. 14: Effect of pH on Cd adsorption on IOCS. Model water: demineralized water with  $\text{Ca}^{2+}$  (20mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . IOCS = 0.1 g/L.

Cd can be effectively adsorbed by IOCS. Increased in pH resulted in increase on removal efficiency. Increase in  $\text{Ca}^{2+}$  resulting in slight reduction of adsorption efficiency. Increase in pH from 6 to 8 resulted in increased adsorption efficiency.

#### 4.2.1.3 Freundlich isotherm for adsorption of cadmium on IOCS

Separate set of batch adsorption experiments were carried out to study the kinetics of adsorption and to establish Freundlich isotherm for Cd adsorption on IOCS. Experiments were carried out at pH=8±0.2.

Figure 4.15 shows the extent of cadmium removal as a function of IOCS concentration (0.1 to 0.9 g/l).

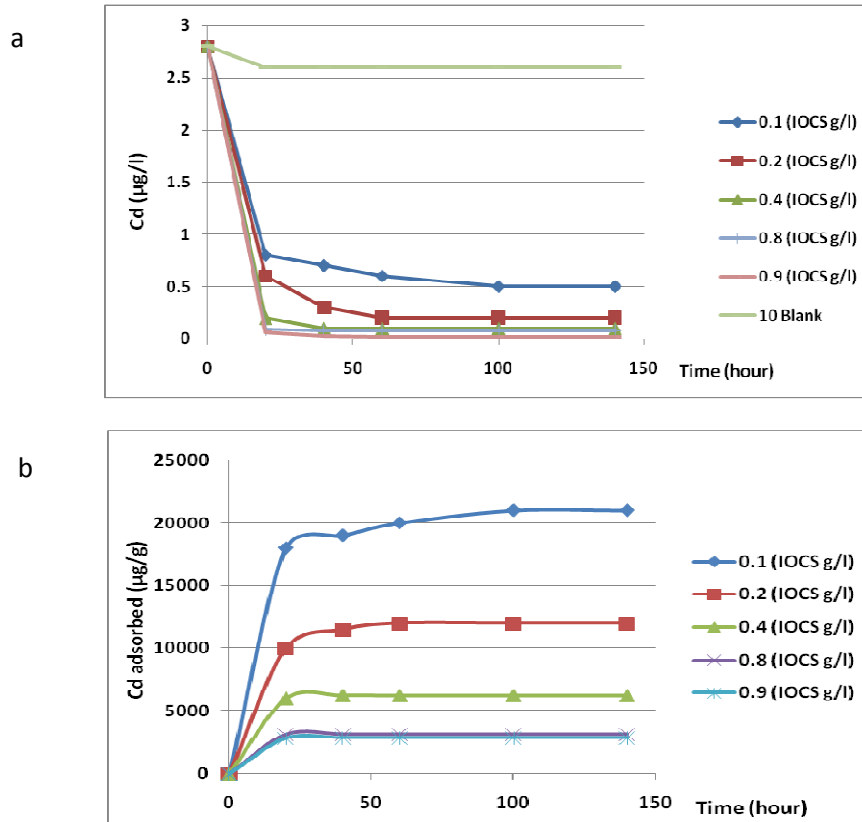


Figure 4. 15: (a) cadmium removal as a function of contact time and IOCS dose at pH=8±0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 2.80 mg/l. IOCS dose: 0.1-0.9 g/l in pulverized form. (b) Cd adsorbed per mass of IOCS.

After 6 days of contact time the equilibrium was reached, Dissolved cadmium in blank was reduced from 2.8 to 2.6 mg/l which is probably due to the precipitation of otavite ( $\text{CdCO}_3$ ) (calculated by Phreeqc).

At the equilibrium, cadmium uptake by IOCS varied from 80.76% to 99.23% for IOCS dosage of 0.1g/l and 0.9 g/l, respectively.

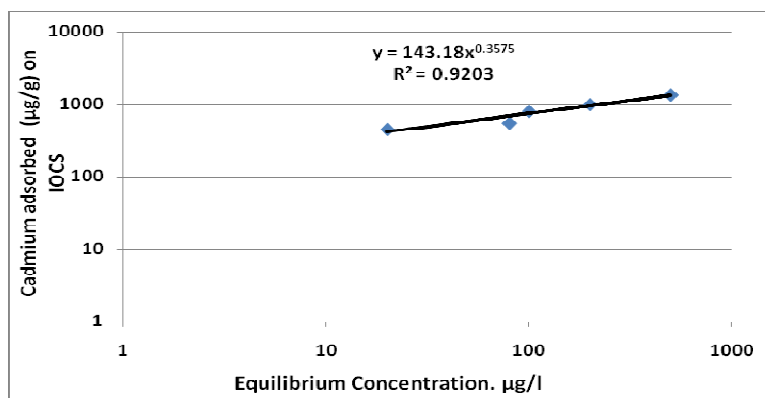


Figure 4. 16 Freundlich isotherm for Cd adsorption on IOCS at pH=  $8 \pm 0.2$ . (Model water: demineralized water with  $\text{Ca}^{2+}$  (20 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration =2.8 mg/l).

The amount of cadmium adsorbed has been plotted against the equilibrium cadmium concentration in solution. Correlation coefficient suggests that the data fits reasonably with Freundlich isotherm model.

The Freundlich isotherm constants K (in mg/g) was found to be 143.18 which suggest that the adsorption is favorable and Cd adsorbed is bonded to IOCS (figure 4.16). Yadav (2007) reported that the Freundlich isotherm constant K for Cd adsorption on IOCS at pH (6) was found to be 2.017.

## Adsorption Kinetic

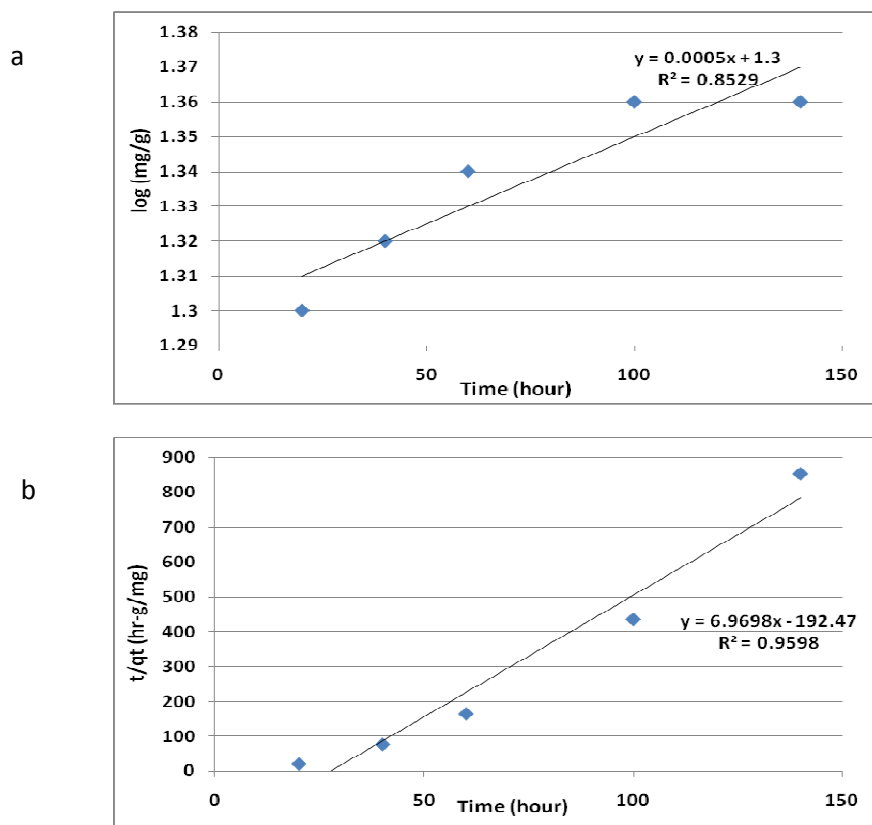


Figure 4. 17: (a) Kinetic model: Pseudo first. (b) pseudo second order adsorption kinetics (0.1 g/l).

Figure 4.17 shows the first and second order removal of Cd seems to follow second order adsorption kinetics. The result is also in line with the result reported by Yadav (2007) on the adsorption mechanism of cadmium on IOCS at pH= 6.

## 4.2.2 Adsorption on GFH

### 4.2.2 .1 Adsorption of copper on GFH as a function of pH and Ca concentration

#### (i) pH 6

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on GFH at pH= 6.

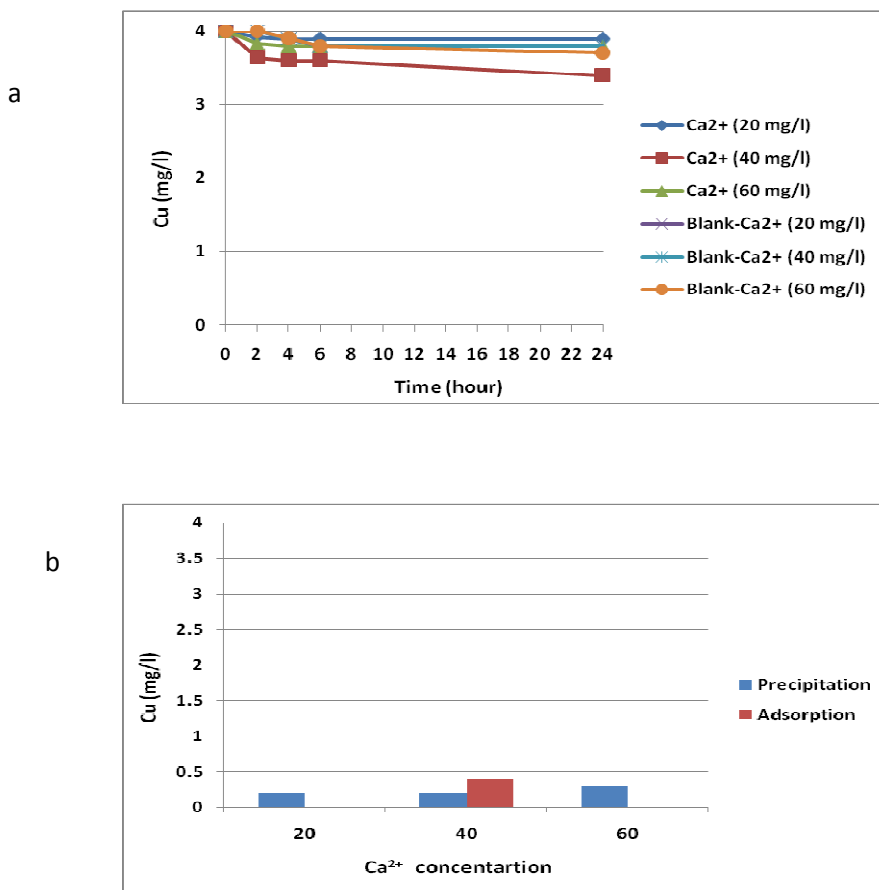


Figure 4. 18: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on GFH at pH=6±0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L. (a) Concentration of Cu in solution. (b) Rate of Cu precipitation and adsorption on GFH.

It can be clearly seen from Figure 4.18 that there is no adsorption of copper with GFH which is in contradiction with Yadav study, 2007.

At pH 6 the GFH surface site is positively charge ( $\text{Pzc} < 7.8$ ) and the major species of Cu in the solution are  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{CuOH}^+$  and  $\text{CuCl}^+$  with percentage distribution of 2.8, 96.8, 0.035 and 0.28 respectively (Calculated with phreeqc - Experimental condition: batch adsorption (Model water: demineralized water with  $\text{Ca}^{2+}$  (20 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and Initial Cu (II) concentration (4 mg/l) , GFH (0.1 g/l) and contact time (0-24 hour)).

Therefore, it seems to be that the adsorption process is not occurred. On the other hand, Yadav reported that copper can be adsorbed with GFH at pH 6. (Yadav, 2007).

## (ii) pH 7

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on copper adsorption on GFH at pH= 7.

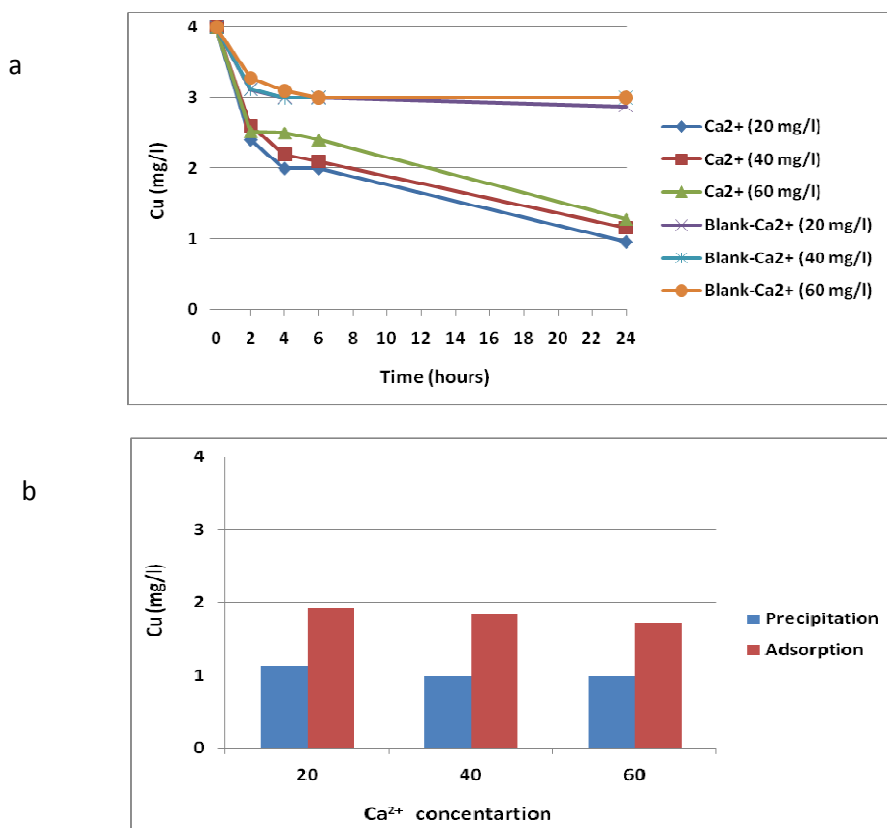


Figure 4. 19: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on GFH at pH=7±0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L. (a) Concentration of Cu in solution. (b) Rate of Cu precipitation and adsorption on GFH.

Adsorption rate of Cu on GFH increase while increasing pH value from 6 to 7, The adsorption was observed after 2 hours of contact time of about 40%. Further increase of contact time to 24 hours show reduction of dissolved Cd concentration in the solution of about 65% to 75%. Increase in  $\text{Ca}^{2+}$  concentration resulted in further reduction of Cu removal efficiency.

Mechanism of Cu removal with GFH cannot be explained on the basis of the electrostatic attraction over pH range applied in this study as major species of copper is in cationic form and

GFH is positively charged at a  $\text{pH} < 7.8$ . The major species of Cu in the solution are 90.8 % as  $\text{Cu}^{2+}$ , 0.26 % as  $\text{CuCl}^+$ ,  $\text{CuOH}^+$  as 1.8% and 2.82% as  $\text{Cu}^+$  (Based on Phreeqc calculations, at  $\text{pH}=7$  with  $\text{Ca}^{2+}$  concentration 20 mg/l in the solution) Under such condition, adsorption of positively charged Cu species must have occurred by chemical interaction with enough energy to overcome repulsive force between the positively charged Cu species and the GFH surface. In addition, the removal efficiency decreases while increasing the calcium concentration because in high calcium concentration, more positive charge was presented in the solution and the  $P_{\text{zc}}$  of GFH surface is positive as well at pH 7. Thus, the repulsive force is taking place.

In general, two processes were taking place here, adsorption and precipitation processes which playing an important role in Cu removal.

### (iii) pH 8

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on GFH at  $\text{pH}=8$ .

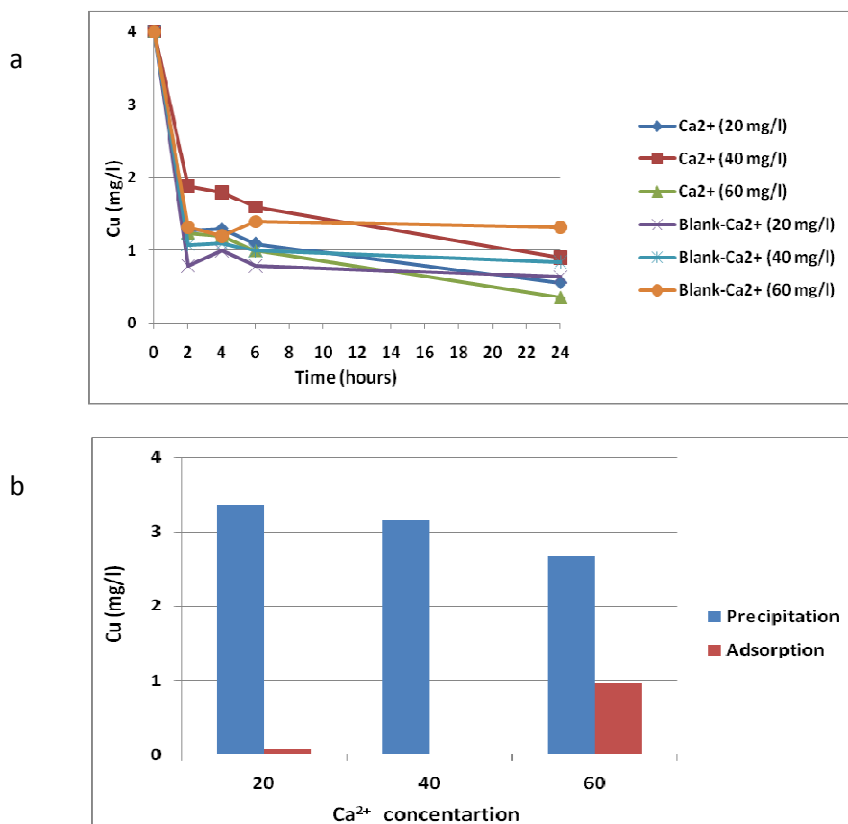


Figure 4. 20: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cu adsorption on GFH at  $\text{pH}=8\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L. (a) Concentration of Cu in solution. (b) Rate of Cu precipitation and adsorption on GFH.

It can be seen from figure 4.20 (a) that there is no clear effect on Cu adsorption by GFH within  $\text{Ca}^{2+}$  concentration tested (20 -60 mg/l).

Mechanism of Copper removal with GFH can be probably explained on the basis of the electrostatic attraction over pH range applied in this study as major species of copper is in cationic form and GFH surface charge becomes less in positively charge when pH is 8 and the  $\text{Pzc}$  of GFH < 7.8.

Hence, the major speciation of Cu in the solution are 23 % as  $\text{Cu}^{2+}$ , 0.24 % as  $\text{CuCl}^+$ ,  $\text{CuOH}^+$  as 3% and 2.82% as  $\text{Cu}^+$  (based on Phreeqc calculations, at pH 8 with  $\text{Ca}^{2+}$  concentration 20 mg/l in the solution). Under such conditions, adsorption of Cu on GFH could probably be explained by electrostatic attraction between the positively charged species of Cu and the GFH surface site.

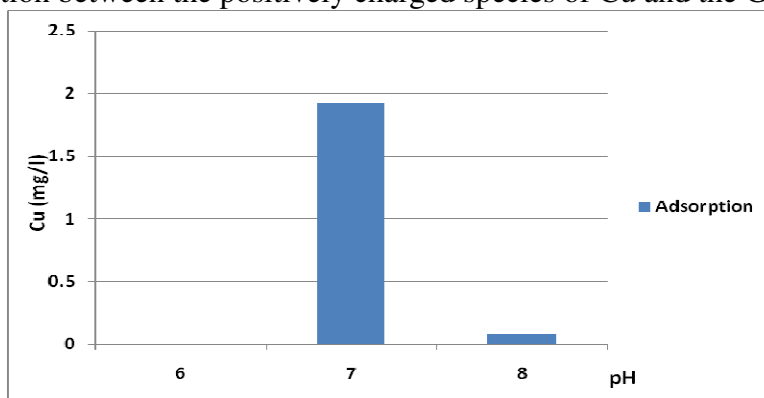


Figure 4. 21: Effect of pH on Cu adsorption on GFH. Model water: demineralized water with  $\text{Ca}^{2+}$  (20mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L.

In conclusion, GFH showed potential to remove Cu. Very poor adsorption at pH=6 but higher removal of Cd at pH=7 and 8 through precipitation and adsorption. Within  $\text{Ca}^{2+}$  concentration tested (20 -60 mg/l) there is no clear effect on Cu adsorption on GFH. Moreover, the most removal efficiency was observed at pH=8 and achieved through precipitation and adsorption.

#### 4.2.2 .2 Adsorption of cadmium on GFH as a function of pH and Ca concentration

##### (i) pH 6

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on GFH at pH= 6.

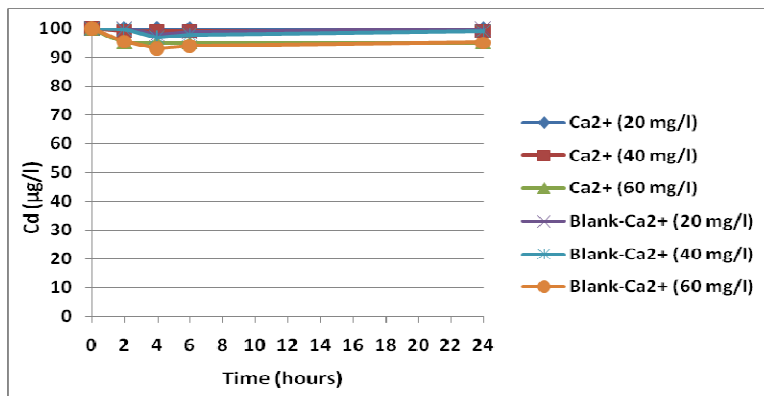


Figure 4. 22: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on GFH at pH=6±0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100 µg/l. of GFH = 0.1 g/L.

Figure 4.22 reveals that there is no adsorption of Cd on GFH at pH= 6 which confirmed by previous studies (Yadav, 2007). But many studies show that when the pH increases then the adsorption will start to occur and higher removal efficiency obtained at higher pH range (Lai *et al.*, 1995; Benjamin *et al.*, 1996). As the pH increased there was increase of concentration of hydroxyl which increases the negatively charged sites and enlarges the attraction force between metal cations and GFH.

## (ii) pH 7

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on GFH at pH 7.

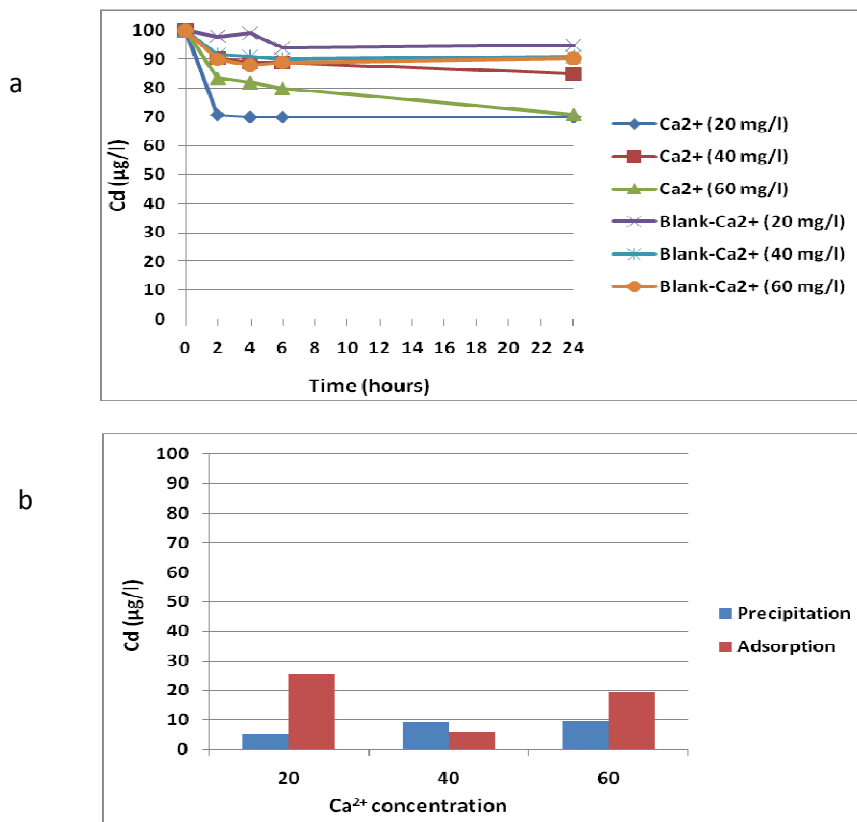


Figure 4. 23: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on GFH at  $\text{pH}=7\pm0.2$ . Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . GFH = 0.1 g/L. (a) Concentration of Cd in solution. (b) Rate of Cd precipitation and adsorption on GFH.

Adsorption rate of Cd on GFH increase while increasing pH value from 6 to 7. The adsorption was observed after 2 hours of contact time of about 10% to 30%. Further increase of contact time to 24 hours did not show significant reduction of dissolved Cd concentration in the solution. No clear trend was observed on  $\text{Ca}^{2+}$  concentration on removal efficiency.

### (iii) pH 8

This experiment was conducted to assess the effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on GFH at pH=8.

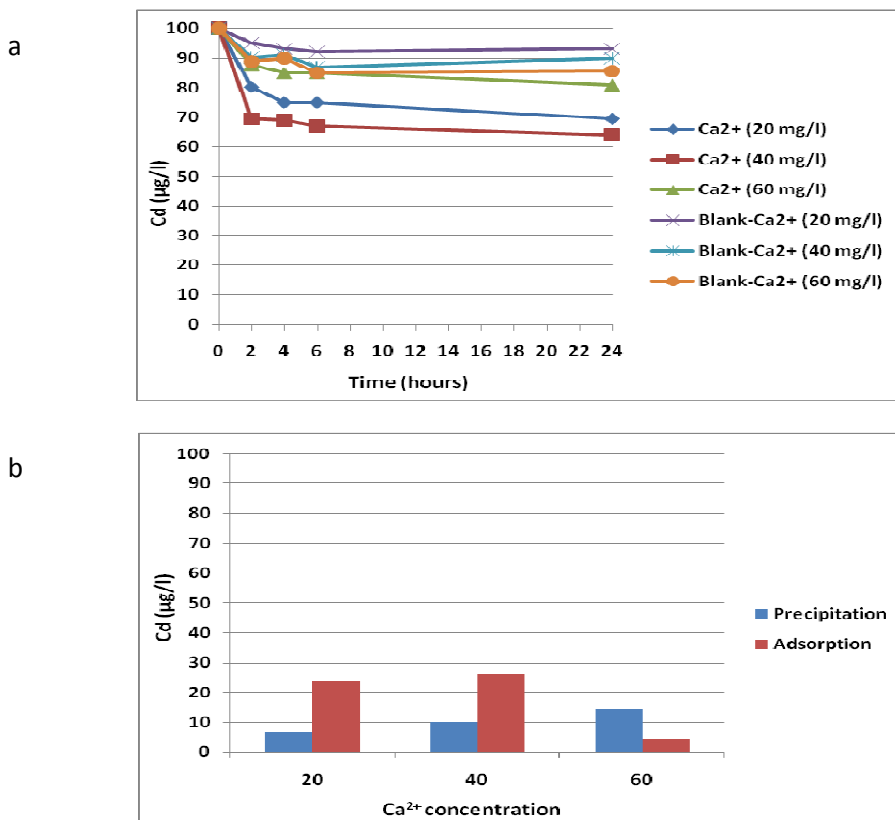


Figure 4. 24: Effect of contact time and  $\text{Ca}^{2+}$  concentration on Cd adsorption on GFH at pH=8±0.2. Model water: demineralized water with  $\text{Ca}^{2+}$  (20, 40 and 60 mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100 µg/l. GFH = 0.1 g/L. (a) Concentration of Cd in solution. (b) Rate of Cd precipitation and adsorption on GFH.

Adsorption rate of Cd on GFH increase while increasing pH value from 7 to 8. The adsorption was observed after 2 hours of contact time of about 12% to 30%. Further increase of contact time to 24 hours did not show significant reduction of dissolved Cd concentration in the solution. There is no clear effect of  $\text{Ca}^{2+}$  concentration on removal efficiency.

It was observed that the removal efficiency of cadmium on GFH at pH=8 increased. This could be explained by the Pzc which is less than 8 (Pzc = 7.8).

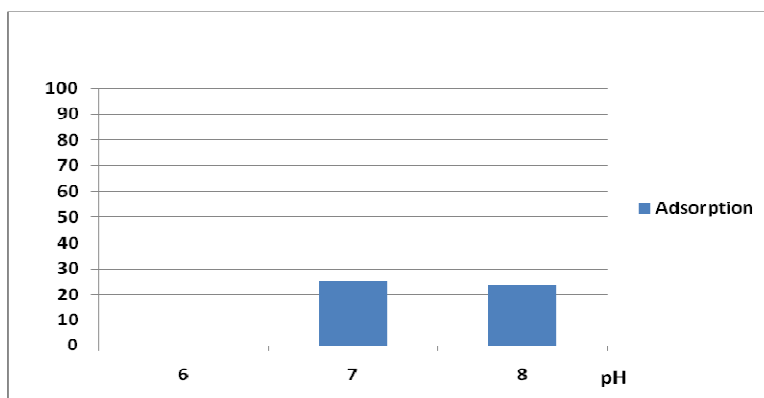


Figure 4. 25: Effect of pH on Cd adsorption on GFH. Model water: demineralized water with  $\text{Ca}^{2+}$  (20mg/l),  $\text{HCO}_3^-$  (20 mg/l) and initial Cd (II) concentration = 100  $\mu\text{g/l}$ . GFH = 0.1 g/L.

In conclusion, increased in pH from 6 to 8 resulted in increased adsorption efficiency, GFH demonstrated under condition tested poor Cd removal on GFH, there is no removal at pH 6 but increased at pH 7 and 8 however very limited, no clear trend was observed on  $\text{Ca}^{2+}$  concentration on removal efficiency and improvement of adsorption from pH 6 to 8 could be explained due to the effect of GFH surface charge.

## CHAPTER 5. CONCLUSION AND RECOMMENDATIONS

### Conclusion

This study was aimed to investigate the effect of pH, calcium concentration and time on adsorption of copper and cadmium on IOCS and GFH. The following conclusions were drawn on the basis of the result obtained from the experiment

#### Removal of copper

##### (i) IOCS

- Increase in pH can be used to remove Cu through 5% precipitation at pH 6 and 85% at pH 8.
- Cu can be effectively removed by IOCS.
- There is no significant effect of  $\text{Ca}^{2+}$  concentration on the adsorption efficiency.
- The most removal efficiency was observed at pH 8 and achieved through precipitation and adsorption.
- Increase in adsorption efficiency from pH 6 to 8 is possible due the low value of  $P_{zc}$  of IOCS, however, no measurement was done to confirm this.
- pH has pronounced effect on Cu removal.

##### (ii) GFH

- Very poor adsorption at pH 6 but higher removal at pH 7 and 8.
- GFH showed potential to remove Cu.
- Within  $\text{Ca}^{2+}$  concentration tested (20 -60 mg/l) there is no clear effect of  $\text{Ca}^{2+}$  on Cu adsorption by GFH.
- Increase in adsorption capacity of Cu at pH 8 could be probably explained by the effect of GFH surface charge.

#### Removal of cadmium

##### (i) IOCS

- Removal of Cd increased under condition applied due to the precipitation at pH 6 (5%) and pH 8 (15%).
- Under condition tested, pH can not be used to remove Cd.
- Cd can be effectively adsorbed by IOCS.
- Increase in pH resulted in increase on the removal efficiency.
- Increase in  $\text{Ca}^{2+}$  concentration resulted in slight reduction of adsorption efficiency.
- Obtained results from batch isotherm experiment of Cd on IOCS at pH 8 fit reasonably with freundlich isotherm.
- Increase in pH from 6 to 8 resulted in increase of adsorption efficiency.

**(ii) GFH**

- GFH demonstrated under condition tested poor Cd removal on GFH.
- There is no removal at pH 6 but increased at pH 7 and 8. However the adsorption was very limited .
- No clear trend was observed on  $\text{Ca}^{2+}$  concentration on the removal efficiency.
- Improvement of adsorption from pH 6 to 8 could be explained by the effect of GFH surface charge.

## **Recommendations**

The following has been recommended on the basis of the finding of this thesis.

- Use of IOCS for removal of Cu from urban stormwater runoff should be further studied in pilot scale experiment.
- Possible effect of GFH ageing on the adsorption efficiency should be further studied.
- Further research needs to be carried out on the competitive effects of Cu and Cd on IOCS.
- Surface charge on IOCS should be studied more in details.

## References

- 1) **Anwar. G. Jiries, Helmi. H. Hussein and Zeid Halaseh (2000)** *The quality of water and sediments of street runoff in Amman, Jordan.*
- 2) **ATSDR (2002)** *Toxicological profile for copper (draft for public comment).* Atlanta, GA, US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry (Subcontract No. ATSDR-205-1999-00024).
- 3) **Aydin. H., Bulut. Yasemin., Yerlikysys .C (2007)** *Removal of Copper (II) from aqueous solution by adsorption onto low-cost adsorbents.* (Available at [www.sciencedirect.com/science/](http://www.sciencedirect.com/science/)) (Accessed on 27 March 2007).
- 4) **Bauske b, Goetz D. (1993)** *Effect of deicing salts on heavy metals mobility.*  
a. Acta Hydrochim Hydrobiol, 21:38-42
- 5) **Boyd, G. and Gardner, N. (1990)** *Urban stormwater: An overview for municipalities,* Public Works, December, pp. 39–42.
- 6) **B. Bruggen, C. Vandecasteele (2003)** *Removal of pollutants from surface water and ground water by nanofiltration: overview of possible application in the drinking water industry,* Environ. Pollut. 122, 435-445.
- 7) **Chui, T. W., Mar, B. W. and Horner, R. R. (1982)** *A pollutant loading model for highway runoff,* J.Environ. Eng., ASCE **108**(6), 1193–1210.
- 8) **Ellis, J.B. (1988)** “Urban Discharges and Receiving Water Quality Impacts” Proceedings, IA WPRC 141h Biennial Conference, Brighton, UK, 18-21.
- 9) **Elder, J.F. and Horne, A. J. (1978)** Environ. Management 2, 17.
- 10) **Ferrara, R. A. (1986)** *Toxic Pollutants, Impact and Fate in Receiving Waters,* in H. C. Torno, J. Marsalek, and M. Desbordes, (eds.), NATO ASI Series, Vol. G10, urban Runoff Pollution, Springer-Verlag, Berlin, Heidelberg, pp. 423-435.
- 11) **Flemming C. A. and J. T. Trevors (1989)** *Copper toxicity and chemistry in the environment.*
- 12) **Forstner, U. and Wittmann, G. T. W (1981)** *Metal Pollution in the Aquatic Environment,* Springer-Verlage, Berlin-Heidelberg, New York.
- 13) **Gjessing, E., Lygren, E., Berglind, L., Gulbrandsenm T. and skaane, R. (1984)** *Effects of high way runoff on lake water quality,* Sci. tot. Environ. 33, 245-257.
- 14) **Gupta, M. K., Agnew, R. K. and Kobringer, N. P. (1981)** *Constituents of highway runoff,* Vol. I, FHWA/RD–81/042, Federal Highway Administration, Washington D.C., U.S.A.
- 15) **H. Choi, K. Zhang, D.D. Dionysion, D. B. Oerther, G. A. Sorial (2005)** *Effect of permeate flux and tangential flow on membrane fouling for wastewater treatment,* Sep, Purif. Tech. 45, 68-78.
- 16) **Hrudey, S. E, W. Chen and C. G. Rousseaux (1995)** *Bioavailability in environment risk assessment.* Lewis Publ., Boca Raton, FL.

- 17) **Hulya Genc-Fuhrman, Peter S. Mikkelsen, Anna Ledin (2006)** *Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater: Experimental comparison of 11 different sorbent.*
- 18) **Jackson, T. A. (1978)** *Environ. Geol.*2, 173.
- 19) **J. Bohdziewicz, M. Bodzek, E. Wasik (1999)** *The application of reverse osmosis and nanofiltration to the removal of nitrates from ground water*, *Desalination* 121, 139-147.
- 20) **Jens Moller, Anna Ledin and Peter Steen Mikkelsen (2002)** *Removal of dissolved heavy metals from pre-settled stormwater runoff by iron-oxide coated sand (IOCS)*, *Environ & Res. DTU*, Technical University of Denmark.
- 21) **Livingstone EH. (1989)** *Use of wetlands for urban stormwater management*. In: Hammer DA, editor. *Constructed wetlands for wastewater treatment-municipal*. Michigan: Industrial and Agricultural Lewis: 253-264.
- 22) **Knobeloch L et al. (1994)** *Gastrointestinal upsets associated with ingestion of copper-contaminated water. Environmental Health Perspectives*, 102(11):958–961.
- 23) **Landner L, Lindstrom L (1999)** *Copper in society and in the environment*. Vasteras, Swedish Environmental Research Group (MFG) (SCDA S-721 88).
- 24) **L. Semerjian, G. M. Ayoub (2003)** *High-pH mechanism coagulation-flocculation lation in wastewater treatment*, *Adv. Environ. Res.* 7, 389-403.
- 25) **I. Licsko (1997)** *Realistic coagulant mechanism in the use of aluminium and iron (III) salts*, *Water Sci. Technol.* 36 (4) 103-110.
- 26) **Low BA, Donohue JM, Bartley CB (1996)** *Backflow prevention failures and copper poisonings associated with post-mix soft drink dispensers*. Ann Arbor, MI, NSF International.
- 27) **Makepeace, D. K., D. W. Smith, and S. J. Stanley (1995)** *Environ. Sci Technol.*, 25(2), 93-139.
- 28) **Mungur AS, Shutes RBE, Revitt DM, House MA (1995)** *An assessment of high way runoff treatment by a natural wetland*. *Water Sci Technol* ;32:169-175.
- 29) **M. F. Schultz, M.M. Benjamin and J. F. Ferguson (1987)** *Adsorption and desorption of metals on ferrihydrite: reversibility of the reaction and sorption properties of the regenerated solid*, *Environ. Sci. Technol.* 21(9), 863-869.
- 30) **N. Boujelben, J. Bouzid, Z. Elouear (2008)** *Adsorption of nickel and copper onto natural iron oxide coated sand from aqueous solutions: Study in single and binary systems.*
- 31) **N. K. Shammas (2004)** *Coagulant and flocculation, Physiochemical Treatment Process*, Vol 3, Humana Press, New Jersey, pp. 103-140.
- 32) **P. Göbel, C. Dierkes, W.G. Coldewey (2006)** *Storm water runoff concentration matrix for urban areas.*
- 33) **Pitt, R and Bozeman, M (1980)** *Water quality and biological effects of urban runoff on Coyote Creek, Phase I – Preliminary Survey Report*, EPA – 600/2-80-104.

- 34) **Ramamoorthy, S. and Kushner, D. J. ( 1975) b**, *Nature* 256, 399.
- 35) **Ramamoorthy, S. and Rust, B. R. (1978)** *Environ. Geol.*2, 165.
- 36) **R. Buamah, B. Petrusevski and J. C. Schippers (2008)** *Adsorptive removal of manganese (II) from the aqueous phase using iron oxide coated sand*.
- 37) **Schueler, T. R. (1987)** **Controlling urban runoff: A practical manual for planning urban BMPs**, Washington Metropolitan Water Resources planning Board, July.
- 38) **Sharma, S.k (2007)** *Adsorption process*, IHE lecture Notes.
- 39) **Sperlich.A., Werner. A., Genz. A., Amy.G., Worch. E., Jekel. Martin (2005)** *Break through behavior of granular ferric hydroxide (GFH) fixed bed adsorption filters: modeling and experimental approaches*, *Water Research* 39 (6), 1190-1198
- 40) **Spitalny KC et al. (1984)** *Drinking-water-induced copper intoxication in a Vermont family. Pediatrics*, 74(6):1103–1106.
- 41) **Stenhammar L (1999)** *Diarrhoea following contamination of drinking water with copper*. *European Journal of Medical Research*, 4:217–218.
- 42) **Stiff, M. J. (1971) a**, *Water Res.* 5, 171.
- 43) **Stiff, M. J. (1971) b**, *Water Res.* 5, 585.
- 44) **Stumm W, Morgan JJ (1981)** *Aquatic chemistry*. New York, NY, Wiley Interscience.
- 45) **Sutha Khaodhiar, Mohammad F. Azizian, Khemarath Osathaphan and Peter O. Nelson (1999)** *Copper, chromium and arsenic adsorption and equilibrium modeling in an Iron-Oxide-coated-Sand*, Background Electrolyte system. Department of civil, Construction and Environmental Engineering, Oregon state University.
- 46) **Sylva, R. N. (1976)** *Water Res.* 10, 789.
- 47) **S.Ahmed, S. Chughtai, M.A. Keane (1998)** *The removal of cadmium and lead from aqueous solution by ion exchange with Na-Y zeolite*, *Sep. Purif. Technol.* 13, 57-64.
- 48) **S. Rengaraj, K.H. Yeon, S.H. Moon (2001)** *Removal of chromium from water and wastewater by ion exchange resins*, *J. Hazard. Mater.* B87, 273-287.
- 49) **S. Vigneswaran, H.H Ngo, D. S. Chaudhary, Y.T. Hung (2004)** *Physiochemical treatment process for water reuse*, in: L.K. Wang, Y.T Hung, N.K. Shammass (Eds), *Physiochemical treatment process*, vol3, Humana Press, New Jersey, pp. 635-676.
- 50) **Tonni Agustiono Kurniawan a, Gilbert Y. S. Chan, Wai-Hung Lo, Sandhya Babel (2006)** *Physico-chemical treatment techniques for wastewater laden with heavy metals*.
- 51) **USEPA (1992)** *Common chemicals found at Superfund sites*. EPA 540/R-94/044. U. S. Gov. Print. Office, Washington, DC.
- 52) **US EPA (1987)** *Drinking water criteria document for copper*. Cincinnati, OH, US Environmental Protection Agency, Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office.
- 53) **United States Environmental Protection Agency (1999a)**. *Preliminary data summary of urban storm water best management practices*. EPA 821/R-99/012. Office of Water, Washington, DC.

- 54) **US Environmental Protection Agency (1980)** *Control and treatment technology for the metal finishing industry, sulfide precipitation*, Summery report, USEPA, Washington D.C, (EPA-625/8-80/003).
- 55) **US Environmental Protection Agency (1984)** *Report to Congress: Nonpoint source pollution in the U.S.A.*, Office of the Water Program Operations, Water Planning Division, Washington D.C., U.S.A.
- 56) **US FDA (1994)** *Code of Federal Regulations*. Vol. 21. Food and Drugs Part 182, Substances Generally Recognized as Safe, pp. 399–418, and Part 184, Direct Food Substances Affirmed as Generally Regarded as Safe, pp. 418–432. Rockville, MD, US Food and Drug Administration.
- 57) **Vassilios A. Tsihrintzis and Rizwan Hamid (1996)** *Modeling and Management of Urban Stormwater Runoff Quality: A Review*. Feb 6<sup>th</sup>.
- 58) **WHO (2004)** *Guidelines for Drinking water quality*, Second edition Vol.2:Health Criteria and Other supporting information. World health organization.Geneva, Switzerland.
- 59) **Wyllie J (1957)** *Copper poisoning at a cocktail party. American Journal of Public Health*, 47:617.
- 60) **Yang, R. T (1999)** *Gas Separation by Adsorption Process- series on chemical Engineering*, (Vol 1). Publishers-Imperial College Press, London, UK.
- 61) **Yongjie Xue, Haobo Hou, Shujing Zhu (2008)** *Competitive adsorption of copper(II), cadmium(II), lead(II) and zinc(II) onto basic oxygen furnace slag*
- 62) **Y. Benito, M.I, Ruiz (2002)** *Reverse osmosis applied to metal finishing wastewater, Desalination* 142, 229-234.
- 63) **Z. Ujang, G.K. Anderson (1996)** *Application of low pressure reverse osmosis membrane for Zn<sup>2+</sup> and Cu<sup>2+</sup> removal from wastewater*, *Water Sci, Technol.* 34(9) 247-253.

## APPENDIX

- A. Stability of copper solution
- B. Stability of cadmium
- C. Equilibrium Calculation (Phreeqc interactive)
- D. Adsorption of copper
- E. Adsorption of cadmium

### Appendix A : Stability of copper solution

### Appendix B : Stability of cadmium solution

### Appendix C: Equilibrium calculation

Appendix C1: Equilibrium calculation of Cu

Appendix C2: Equilibrium calculation of Cd

### Appendix D: Adsorption of copper

Appendix D1: Adsorption of Cu on IOCS

Appendix D2: Adsorption of Cu on GFH

### Appendix E: Adsorption of cadmium

Appendix E1: Adsorption of Cd on IOCS

Appendix E2: Adsorption of Cd on GFH

### Appendix A : Stability of copper

**Table A1: Result of stability of copper at pH=6±0.2.**( Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cu (II) concentration = 4 mg/l)

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	4	4	4
2	4	4	4
24	3.8	3.8	3.7

**Table A2: Result of stability of copper at pH=7±0.2**(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cu (II) concentration = 4 mg/l).

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	4	4	4
2	3.12	3.12	3.28
24	2.88	3	3

**Table A3: Result of stability of copper at pH=8±0.2**(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cu (II) concentration = 4 mg/l).

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	4	4	4
2	0.8	1.08	1.32
24	0.64	0.84	1.32

## Appendix B : Stability of cadmium

**Table B1: Result of stability of cadmium at pH=6±0.2**(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cd (II) concentration = 100 µg/l).

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	100	100	100
2	100	99.75	95.5
24	100	99	95

**Table B2: Result of stability of cadmium at pH=7±0.2**(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cd (II) concentration = 100 µg/l).

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	100	100	100
2	98	91.5	90
24	95	91	90.5

**Table B3: Result of stability of cadmium at pH=8±0.2**(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cd (II) concentration = 100 µg/l).

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	100	100	100
2	95	90.25	88.75
24	93	90	85.5

## Appendix C: Equilibrium calculation

**Appendix C1:1 Equilibrium calculation of Cu at pH=6±0.2 within calcium concentration tested (20-60mg/l).  
Copper stability - pH 6, Ca 20 mg/l.**

-----  
Reading input data for simulation 1.  
-----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

SOLUTION 1

temp 25  
pH 6  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Na 0.327  
C(4) 0.327  
Ca 0.5  
Cl 1  
water 1 # kg

SOLUTION 2

temp 25  
pH 1.5  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Cu 15.73  
Cl 31.47  
water 1 # kg

MIX 1

1 0.996  
2 0.004

Phases

Fix\_H+

H+ = H+  
log\_k 0

EQUILIBRIUM\_PHASES 1

SELECTED\_OUTPUT

file copper 6.0 .out

reset false

ph true

alkalinity true

ionic\_strength true

totals Cu Cu(2) Na C(4) Ca

molalities Cu+2 Cu(OH)2 CuCl+ CuCO3  
CuOH+ Ca+2 CaCO3 CaHCO3+  
CaOH+ Na+ NaCO3- NaHCO3

activities Cu+2 Cu(OH)2 CuCl+ CuCO3  
CuOH+ Na+ NaCO3- NaHCO3  
Ca+2 CaCO3 CaHCO3+ CaOH+  
Cu3(OH)2(CO3)2

WARNING: Did not find species, Cu3(OH)2(CO3)2.  
-----

Beginning of initial solution calculations.

-----Distribution of species-----					
Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	5.024e-005	4.803e-005	-4.299	-4.318	-0.020
OH-	2.187e-010	2.084e-010	-9.660	-9.681	-0.021
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-47.204	-47.204	0.000
C(4)	3.257e-004				
CO2	3.225e-004	3.227e-004	-3.491	-3.491	0.000
HCO3-	3.132e-006	2.988e-006	-5.504	-5.525	-0.020
CaHCO3+	1.648e-008	1.572e-008	-7.783	-7.804	-0.020
CuCO3	7.388e-010	7.391e-010	-9.131	-9.131	0.000
NaHCO3	5.215e-010	5.218e-010	-9.283	-9.283	0.000
CO3-2	3.522e-012	2.917e-012	-11.453	-11.535	-0.082
CaCO3	2.020e-012	2.021e-012	-11.695	-11.694	0.000
NaCO3-	1.770e-014	1.687e-014	-13.752	-13.773	-0.021
Ca	4.980e-004				
Ca+2	4.980e-004	4.124e-004	-3.303	-3.385	-0.082
CaHCO3+	1.648e-008	1.572e-008	-7.783	-7.804	-0.020
CaCO3	2.020e-012	2.021e-012	-11.695	-11.694	0.000
CaOH+	1.495e-012	1.425e-012	-11.825	-11.846	-0.021
Cl	1.122e-003				
Cl-	1.122e-003	1.069e-003	-2.950	-2.971	-0.021
CuCl+	1.793e-007	1.709e-007	-6.747	-6.767	-0.021
Cu(1)	1.780e-006				
Cu+	1.780e-006	1.695e-006	-5.749	-5.771	-0.021
Cu(2)	6.114e-005				
Cu+2	6.094e-005	5.055e-005	-4.215	-4.296	-0.081
CuCl+	1.793e-007	1.709e-007	-6.747	-6.767	-0.021
CuOH+	2.205e-008	2.102e-008	-7.657	-7.677	-0.021
CuCO3	7.388e-010	7.391e-010	-9.131	-9.131	0.000
Cu(OH)2	4.575e-010	4.577e-010	-9.340	-9.339	0.000
Cu(OH)3-	6.024e-019	5.742e-019	-18.220	-18.241	-0.021
Cu(OH)4-2	2.889e-027	2.385e-027	-26.539	-26.622	-0.083
H(0)	1.334e-020				
H2	6.668e-021	6.671e-021	-20.176	-20.176	0.000
Na	3.257e-004				
Na+	3.257e-004	3.105e-004	-3.487	-3.508	-0.021
NaHCO3	5.215e-010	5.218e-010	-9.283	-9.283	0.000
NaOH	4.269e-014	4.271e-014	-13.370	-13.369	0.000
NaCO3-	1.770e-014	1.687e-014	-13.752	-13.773	-0.021
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-52.029	-52.028	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-6.58	-14.92	-8.34	CaCO3
Calcite	-6.44	-14.92	-8.48	CaCO3

CO2(g)	-2.02	-3.49	-1.47	CO2
Cu(OH)2	-4.36	-23.66	-19.30	Cu(OH)2
Cu2(OH)2CO3	38.99	5.19	-33.80	Cu2(OH)2CO3
Cu3(OH)2(CO3)2	52.04	6.04	-46.00	Cu3(OH)2(CO3)2
CuCO3	-6.23	-15.83	-9.60	CuCO3
Cuo	-3.31	4.34	7.65	CuO
Fix_H+	-4.32	-4.32	0.00	H+
H2(g)	-17.03	-20.18	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-8.06	-6.48	1.58	NaCl
O2(g)	-49.14	-52.03	-2.89	O2

End of run.

### Copper stability – pH 6, Ca 40 mg/l.

-----  
Reading input data for simulation 1.  
-----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

SOLUTION 1

temp 25  
pH 6  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Na 0.327  
C(4) 0.327  
Ca 1  
Cl 2  
water 1 # kg

SOLUTION 2

temp 25  
pH 1.5  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Cu 15.73  
Cl 31.47  
water 1 # kg

MIX 1

1 0.996  
2 0.004

Phases

Fix\_H+

H+ = H+

log\_k 0

EQUILIBRIUM\_PHASES 1

SELECTED\_OUTPUT

file copper 6.0 .out

reset false

ph true

alkalinity true

ionic\_strength true

totals Cu Cu(2) Na C(4) Ca

```

molalities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Ca+2 CaCO3 CaHCO3+
           CaOH+ Na+ NaCO3- NaHCO3
activities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Na+ NaCO3- NaHCO3
           Ca+2 CaCO3 CaHCO3+ CaOH+
           Cu3(OH)2(CO3)2
WARNING: Did not find species, Cu3(OH)2(CO3)2.
-----
Beginning of initial solution calculations.
-----
-----Distribution of species-----

```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	4.900e-005	4.624e-005	-4.310	-4.335	-0.025
OH-	2.307e-010	2.165e-010	-9.637	-9.665	-0.028
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-47.185	-47.185	0.000
C(4)	3.257e-004				
CO2	3.224e-004	3.226e-004	-3.492	-3.491	0.000
HCO3-	3.300e-006	3.103e-006	-5.481	-5.508	-0.027
CaHCO3+	3.275e-008	3.080e-008	-7.485	-7.512	-0.027
CuCO3	7.506e-010	7.512e-010	-9.125	-9.124	0.000
NaHCO3	5.334e-010	5.338e-010	-9.273	-9.273	0.000
CaCO3	4.109e-012	4.112e-012	-11.386	-11.386	0.000
CO3-2	4.027e-012	3.147e-012	-11.395	-11.502	-0.107
NaCO3-	1.909e-014	1.793e-014	-13.719	-13.747	-0.027
Ca	9.960e-004				
Ca+2	9.960e-004	7.779e-004	-3.002	-3.109	-0.107
CaHCO3+	3.275e-008	3.080e-008	-7.485	-7.512	-0.027
CaCO3	4.109e-012	4.112e-012	-11.386	-11.386	0.000
CaOH+	2.974e-012	2.792e-012	-11.527	-11.554	-0.027
Cl	2.118e-003				
Cl-	2.118e-003	1.987e-003	-2.674	-2.702	-0.028
CuCl+	3.188e-007	2.993e-007	-6.497	-6.524	-0.027
Cu(1)	1.780e-006				
Cu+	1.780e-006	1.669e-006	-5.749	-5.778	-0.028
Cu(2)	6.114e-005				
Cu+2	6.080e-005	4.763e-005	-4.216	-4.322	-0.106
CuCl+	3.188e-007	2.993e-007	-6.497	-6.524	-0.027
CuOH+	2.191e-008	2.057e-008	-7.659	-7.687	-0.027
CuCO3	7.506e-010	7.512e-010	-9.125	-9.124	0.000
Cu(OH)2	4.650e-010	4.653e-010	-9.333	-9.332	0.000
Cu(OH)3-	6.458e-019	6.063e-019	-18.190	-18.217	-0.027
Cu(OH)4-2	3.367e-027	2.616e-027	-26.473	-26.582	-0.110
H(0)	1.348e-020				
H2	6.740e-021	6.745e-021	-20.171	-20.171	0.000
Na	3.257e-004				
Na+	3.257e-004	3.059e-004	-3.487	-3.514	-0.027
NaHCO3	5.334e-010	5.338e-010	-9.273	-9.273	0.000
NaOH	4.367e-014	4.371e-014	-13.360	-13.359	0.000
NaCO3-	1.909e-014	1.793e-014	-13.719	-13.747	-0.027

O(0)	0.000e+000					
O2	0.000e+000	0.000e+000	0.000e+000	-52.038	-52.038	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-6.28	-14.61	-8.34	CaCO3
Calcite	-6.13	-14.61	-8.48	CaCO3
CO2(g)	-2.02	-3.49	-1.47	CO2
Cu(OH)2	-4.35	-23.65	-19.30	Cu(OH)2
Cu2(OH)2CO3	39.00	5.20	-33.80	Cu2(OH)2CO3
Cu3(OH)2(CO3)2	52.06	6.06	-46.00	Cu3(OH)2(CO3)2
CuCO3	-6.22	-15.82	-9.60	CuCO3
Cuo	-3.30	4.35	7.65	CuO
Fix_H+	-4.33	-4.33	0.00	H+
H2(g)	-17.02	-20.17	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.80	-6.22	1.58	NaCl
O2(g)	-49.15	-52.04	-2.89	O2

-----  
End of run.

**Copper stability – pH 6, Ca 60 mg/l.**

-----  
Reading input data for simulation 1.

-----  
DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

SOLUTION 1

temp	25
pH	6
pe	4
redox	pe
units	mmol/kgw
density	1
Na	0.327
C(4)	0.327
Ca	1.5
Cl	3
water	1 # kg

SOLUTION 2

temp	25
pH	1.5
pe	4
redox	pe
units	mmol/kgw
density	1
Cu	15.73
Cl	31.47
water	1 # kg

MIX 1

1	0.996
2	0.004

Phases

```

Fix_H+
  H+ = H+
  log_k      0
EQUILIBRIUM_PHASES 1
SELECTED_OUTPUT
file copper 6.0 .out
reset false
ph true
alkalinity true
ionic_strength true
totals Cu Cu(2) Na C(4) Ca
molalities Cu+2 Cu(OH)2 CuCl+ CuCO3
          CuOH+ Ca+2 CaCO3 CaHCO3+
          CaOH+ Na+ NaCO3- NaHCO3
activities Cu+2 Cu(OH)2 CuCl+ CuCO3
          CuOH+ Na+ NaCO3- NaHCO3
          Ca+2 CaCO3 CaHCO3+ CaOH+
          Cu3(OH)2(CO3)2
WARNING: Did not find species, Cu3(OH)2(CO3)2.
-----
Beginning of initial solution calculations.
-----
-----Distribution of species-----

```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	4.802e-005	4.488e-005	-4.319	-4.348	-0.029
OH-	2.406e-010	2.231e-010	-9.619	-9.652	-0.033
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-47.175	-47.174	0.000
C(4)	3.257e-004				
CO2	3.222e-004	3.226e-004	-3.492	-3.491	0.000
HCO3-	3.438e-006	3.197e-006	-5.464	-5.495	-0.032
CaHCO3+	4.896e-008	4.552e-008	-7.310	-7.342	-0.032
CuCO3	7.611e-010	7.620e-010	-9.119	-9.118	0.000
NaHCO3	5.431e-010	5.437e-010	-9.265	-9.265	0.000
CaCO3	6.257e-012	6.264e-012	-11.204	-11.203	0.000
CO3-2	4.469e-012	3.341e-012	-11.350	-11.476	-0.126
NaCO3-	2.027e-014	1.881e-014	-13.693	-13.726	-0.032
Ca	1.494e-003				
Ca+2	1.494e-003	1.116e-003	-2.826	-2.952	-0.127
CaHCO3+	4.896e-008	4.552e-008	-7.310	-7.342	-0.032
CaCO3	6.257e-012	6.264e-012	-11.204	-11.203	0.000
CaOH+	4.448e-012	4.128e-012	-11.352	-11.384	-0.032
Cl	3.114e-003				
Cl-	3.113e-003	2.887e-003	-2.507	-2.540	-0.033
CuCl+	4.477e-007	4.155e-007	-6.349	-6.381	-0.032
Cu(1)	1.780e-006				
Cu+	1.780e-006	1.648e-006	-5.749	-5.783	-0.034
Cu(2)	6.114e-005				
Cu+2	6.067e-005	4.551e-005	-4.217	-4.342	-0.125
CuCl+	4.477e-007	4.155e-007	-6.349	-6.381	-0.032
CuOH+	2.183e-008	2.026e-008	-7.661	-7.693	-0.032

CuCO3	7.611e-010	7.620e-010	-9.119	-9.118	0.000
Cu(OH)2	4.716e-010	4.721e-010	-9.326	-9.326	0.000
Cu(OH)3-	6.830e-019	6.338e-019	-18.166	-18.198	-0.032
Cu(OH)4-2	3.799e-027	2.818e-027	-26.420	-26.550	-0.130
H(0)	1.356e-020				
H2	6.780e-021	6.787e-021	-20.169	-20.168	0.000
Na	3.257e-004				
Na+	3.257e-004	3.025e-004	-3.487	-3.519	-0.032
NaHCO3	5.431e-010	5.437e-010	-9.265	-9.265	0.000
NaOH	4.447e-014	4.452e-014	-13.352	-13.351	0.000
NaCO3-	2.027e-014	1.881e-014	-13.693	-13.726	-0.032
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-52.044	-52.043	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-6.09	-14.43	-8.34	CaCO3
Calcite	-5.95	-14.43	-8.48	CaCO3
CO2(g)	-2.02	-3.49	-1.47	CO2
Cu(OH)2	-4.35	-23.65	-19.30	Cu(OH)2
Cu2(OH)2CO3	39.02	5.22	-33.80	Cu2(OH)2CO3
Cu3(OH)2(CO3)2	52.08	6.08	-46.00	Cu3(OH)2(CO3)2
CuCO3	-6.22	-15.82	-9.60	CuCO3
Cuo	-3.30	4.35	7.65	CuO
Fix_H+	-4.35	-4.35	0.00	H+
H2(g)	-17.02	-20.17	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.64	-6.06	1.58	NaCl
O2(g)	-49.15	-52.04	-2.89	O2

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

**Appendix C1:2 Equilibrium calculation of Cu at pH=7±0.2 within calcium concentration tested (20-60mg/l).  
Copper stability based on phreeqc pH 7, Ca 20 mg/l**

-----  
Reading input data for simulation 1.  
-----

```

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt
SOLUTION 1
  temp      25
  pH        7
  pe        4
  redox     pe
  units     mmol/kgw
  density   1
  Na        0.327
  C(4)      0.327
  Ca        0.5
  Cl        1
  water     1 # kg

```

```

SOLUTION 2
    temp      25
    pH        1.5
    pe        4
    redox     pe
    units     mmol/kgw
    density   1
    Cu        15.73
    Cl        31.47
    water     1 # kg
MIX 1
    1      0.996
    2      0.004
Phases
Fix_H+
    H+ = H+
    log_k    0
EQUILIBRIUM_PHASES 1
SELECTED_OUTPUT
file copper 6.0 .out
reset false
ph true
alkalinity true
ionic_strength true
totals Cu Cu(2) Na C(4) Ca
molalities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Ca+2 CaCO3 CaHCO3+
           CaOH+ Na+ NaCO3- NaHCO3
activities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Na+ NaCO3- NaHCO3
           Ca+2 CaCO3 CaHCO3+ CaOH+
           Cu3(OH)2(CO3)2
WARNING: Did not find species, Cu3(OH)2(CO3)2.
-----
Beginning of initial solution calculations.
-----
-----Distribution of species-----

```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	9.151e-007	8.747e-007	-6.039	-6.058	-0.020
OH-	1.201e-008	1.144e-008	-7.920	-7.941	-0.021
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-61.082	-61.082	0.000
C(4)	3.257e-004				
CO2	2.111e-004	2.112e-004	-3.675	-3.675	0.000
HCO3-	1.126e-004	1.074e-004	-3.948	-3.969	-0.021
CuCO3	1.367e-006	1.367e-006	-5.864	-5.864	0.000
CaHCO3+	5.911e-007	5.637e-007	-6.228	-6.249	-0.021
NaHCO3	1.874e-008	1.875e-008	-7.727	-7.727	0.000
CO3-2	6.958e-009	5.758e-009	-8.158	-8.240	-0.082
CaCO3	3.978e-009	3.980e-009	-8.400	-8.400	0.000
NaCO3-	3.493e-011	3.328e-011	-10.457	-10.478	-0.021

Ca	4.980e-004					
Ca+2	4.974e-004	4.115e-004	-3.303	-3.386	-0.082	
CaHCO3+	5.911e-007	5.637e-007	-6.228	-6.249	-0.021	
CaCO3	3.978e-009	3.980e-009	-8.400	-8.400	0.000	
CaOH+	8.192e-011	7.806e-011	-10.087	-10.108	-0.021	
Cl	1.122e-003					
Cl-	1.122e-003	1.069e-003	-2.950	-2.971	-0.021	
CuCl+	1.680e-007	1.601e-007	-6.775	-6.796	-0.021	
Cu(1)	1.780e-006					
Cu+	1.780e-006	1.695e-006	-5.749	-5.771	-0.021	
Cu(2)	6.114e-005					
Cu+2	5.718e-005	4.738e-005	-4.243	-4.324	-0.082	
CuCO3	1.367e-006	1.367e-006	-5.864	-5.864	0.000	
Cu(OH)2	1.293e-006	1.294e-006	-5.888	-5.888	0.000	
CuOH+	1.135e-006	1.082e-006	-5.945	-5.966	-0.021	
CuCl+	1.680e-007	1.601e-007	-6.775	-6.796	-0.021	
Cu(OH)3-	9.352e-014	8.912e-014	-13.029	-13.050	-0.021	
Cu(OH)4-2	2.465e-020	2.033e-020	-19.608	-19.692	-0.084	
H(0)	5.031e-024					
H2	2.515e-024	2.517e-024	-23.599	-23.599	0.000	
Na	3.257e-004					
Na+	3.257e-004	3.104e-004	-3.487	-3.508	-0.021	
NaHCO3	1.874e-008	1.875e-008	-7.727	-7.727	0.000	
NaCO3-	3.493e-011	3.328e-011	-10.457	-10.478	-0.021	
NaOH	2.344e-012	2.345e-012	-11.630	-11.630	0.000	
O(0)	0.000e+000					
O2	0.000e+000	0.000e+000	-45.182	-45.182	0.000	

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

Phase	SI	log IAP	log KT	
Aragonite	-3.29	-11.63	-8.34	CaCO3
Calcite	-3.15	-11.63	-8.48	CaCO3
CO2(g)	-2.21	-3.68	-1.47	CO2
Cu(OH)2	-0.91	-20.21	-19.30	Cu(OH)2
Cu2(OH)2CO3	45.71	11.91	-33.80	Cu2(OH)2CO3
Cu3(OH)2(CO3)2	62.02	16.02	-46.00	Cu3(OH)2(CO3)2
CuCO3	-2.96	-12.56	-9.60	CuCO3
Cuo	0.14	7.79	7.65	CuO
Fix_H+	-6.06	-6.06	0.00	H+
H2(g)	-20.45	-23.60	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-8.06	-6.48	1.58	NaCl
O2(g)	-42.29	-45.18	-2.89	O2

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

**Copper stability based on phreeqc pH 7, Ca 40 mg/l**

Reading input data for simulation 1.  
-----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

```

SOLUTION 1
  temp      25
  pH        7
  pe        4
  redox     pe
  units     mmol/kgw
  density    1
  Na        0.327
  C(4)      0.327
  Ca        1
  Cl        2
  water     1 # kg
SOLUTION 2
  temp      25
  pH        1.5
  pe        4
  redox     pe
  units     mmol/kgw
  density    1
  Cu        15.73
  Cl        31.47
  water     1 # kg
MIX 1
  1      0.996
  2      0.004
Phases
Fix_H+
  H+ = H+
  log_k      0
EQUILIBRIUM_PHASES 1
SELECTED_OUTPUT
file copper 6.0 .out
reset false
ph true
alkalinity true
ionic_strength true
totals Cu Cu(2) Na C(4) Ca
molalities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Ca+2 CaCO3 CaHCO3+
           CaOH+ Na+ NaCO3- NaHCO3
activities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Na+ NaCO3- NaHCO3
           Ca+2 CaCO3 CaHCO3+ CaOH+
           Cu3(OH)2(CO3)2
WARNING: Did not find species, Cu3(OH)2(CO3)2.
-----
Beginning of initial solution calculations.
-----
-----Distribution of species-----

```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	9.281e-007	8.756e-007	-6.032	-6.058	-0.025
OH-	1.219e-008	1.143e-008	-7.914	-7.942	-0.028

H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-60.943	-60.942	0.000
C(4)	3.257e-004				
CO2	2.098e-004	2.100e-004	-3.678	-3.678	0.000
HCO3-	1.134e-004	1.066e-004	-3.945	-3.972	-0.027
CuCO3	1.282e-006	1.283e-006	-5.892	-5.892	0.000
CaHCO3+	1.124e-006	1.056e-006	-5.949	-5.976	-0.027
NaHCO3	1.833e-008	1.834e-008	-7.737	-7.737	0.000
CaCO3	7.445e-009	7.450e-009	-8.128	-8.128	0.000
CO3-2	7.315e-009	5.712e-009	-8.136	-8.243	-0.107
NaCO3-	3.466e-011	3.253e-011	-10.460	-10.488	-0.027
Ca	9.960e-004				
Ca+2	9.949e-004	7.765e-004	-3.002	-3.110	-0.108
CaHCO3+	1.124e-006	1.056e-006	-5.949	-5.976	-0.027
CaCO3	7.445e-009	7.450e-009	-8.128	-8.128	0.000
CaOH+	1.568e-010	1.472e-010	-9.805	-9.832	-0.027
Cl	2.118e-003				
Cl-	2.118e-003	1.987e-003	-2.674	-2.702	-0.028
CuCl+	2.999e-007	2.815e-007	-6.523	-6.550	-0.027
Cu(1)	1.780e-006				
Cu+	1.780e-006	1.668e-006	-5.749	-5.778	-0.028
Cu(2)	6.114e-005				
Cu+2	5.725e-005	4.481e-005	-4.242	-4.349	-0.106
CuCO3	1.282e-006	1.283e-006	-5.892	-5.892	0.000
Cu(OH)2	1.220e-006	1.221e-006	-5.914	-5.913	0.000
CuOH+	1.089e-006	1.022e-006	-5.963	-5.990	-0.027
CuCl+	2.999e-007	2.815e-007	-6.523	-6.550	-0.027
Cu(OH)3-	8.951e-014	8.402e-014	-13.048	-13.076	-0.027
Cu(OH)4-2	2.466e-020	1.914e-020	-19.608	-19.718	-0.110
H(0)	5.457e-024				
H2	2.729e-024	2.731e-024	-23.564	-23.564	0.000
Na	3.257e-004				
Na+	3.257e-004	3.058e-004	-3.487	-3.514	-0.027
NaHCO3	1.833e-008	1.834e-008	-7.737	-7.737	0.000
NaCO3-	3.466e-011	3.253e-011	-10.460	-10.488	-0.027
NaOH	2.306e-012	2.308e-012	-11.637	-11.637	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-45.253	-45.253	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-3.02	-11.35	-8.34	CaCO3
Calcite	-2.87	-11.35	-8.48	CaCO3
CO2(g)	-2.21	-3.68	-1.47	CO2
Cu(OH)2	-0.93	-20.23	-19.30	Cu(OH)2
Cu2(OH)2CO3	45.66	11.86	-33.80	Cu2(OH)2CO3
Cu3(OH)2(CO3)2	61.94	15.94	-46.00	Cu3(OH)2(CO3)2
CuCO3	-2.99	-12.59	-9.60	CuCO3
Cuo	0.12	7.77	7.65	CuO
Fix_H+	-6.06	-6.06	0.00	H+
H2(g)	-20.41	-23.56	-3.15	H2

H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.80	-6.22	1.58	NaCl
O2(g)	-42.36	-45.25	-2.89	O2

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

### Copper stability based on phreeqc pH 7, Ca 60 mg/l

-----  
Reading input data for simulation 1.  
-----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

SOLUTION 1

temp 25  
pH 7  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Na 0.327  
C(4) 0.327  
Ca 1.5  
Cl 3  
water 1 # kg

SOLUTION 2

temp 25  
pH 1.5  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Cu 15.73  
Cl 31.47  
water 1 # kg

MIX 1

1 0.996  
2 0.004

Phases

Fix\_H+

H+ = H+  
log\_k 0

EQUILIBRIUM\_PHASES 1

SELECTED\_OUTPUT

file copper 6.0 .out

reset false

ph true

alkalinity true

ionic\_strength true

totals Cu Cu(2) Na C(4) Ca

molalities Cu+2 Cu(OH)2 CuCl+ CuCO3

CuOH+ Ca+2 CaCO3 CaHCO3+

CaOH+ Na+ NaCO3- NaHCO3

activities Cu+2 Cu(OH)2 CuCl+ CuCO3

CuOH+ Na+ NaCO3- NaHCO3

Ca+2 CaCO3 CaHCO3+ CaOH+  
 Cu3(OH)2(CO3)2

WARNING: Did not find species, Cu3(OH)2(CO3)2.

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

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	9.383e-007	8.767e-007	-6.028	-6.057	-0.029
OH-	1.232e-008	1.142e-008	-7.910	-7.942	-0.033
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-60.835	-60.835	0.000
C(4)	3.257e-004				
CO2	2.088e-004	2.090e-004	-3.680	-3.680	0.000
HCO3-	1.140e-004	1.060e-004	-3.943	-3.975	-0.032
CaHCO3+	1.621e-006	1.507e-006	-5.790	-5.822	-0.032
CuCO3	1.219e-006	1.221e-006	-5.914	-5.913	0.000
NaHCO3	1.801e-008	1.803e-008	-7.745	-7.744	0.000
CaCO3	1.060e-008	1.062e-008	-7.975	-7.974	0.000
CO3-2	7.591e-009	5.671e-009	-8.120	-8.246	-0.127
NaCO3-	3.441e-011	3.193e-011	-10.463	-10.496	-0.033
Ca	1.494e-003				
Ca+2	1.492e-003	1.114e-003	-2.826	-2.953	-0.127
CaHCO3+	1.621e-006	1.507e-006	-5.790	-5.822	-0.032
CaCO3	1.060e-008	1.062e-008	-7.975	-7.974	0.000
CaOH+	2.273e-010	2.109e-010	-9.643	-9.676	-0.033
Cl	3.114e-003				
Cl-	3.113e-003	2.887e-003	-2.507	-2.540	-0.033
CuCl+	4.225e-007	3.920e-007	-6.374	-6.407	-0.033
Cu(1)	1.780e-006				
Cu+	1.780e-006	1.648e-006	-5.749	-5.783	-0.034
Cu(2)	6.114e-005				
Cu+2	5.728e-005	4.294e-005	-4.242	-4.367	-0.125
CuCO3	1.219e-006	1.221e-006	-5.914	-5.913	0.000
Cu(OH)2	1.166e-006	1.167e-006	-5.933	-5.933	0.000
CuOH+	1.054e-006	9.783e-007	-5.977	-6.010	-0.033
CuCl+	4.225e-007	3.920e-007	-6.374	-6.407	-0.033
Cu(OH)3-	8.643e-014	8.020e-014	-13.063	-13.096	-0.033
Cu(OH)4-2	2.462e-020	1.825e-020	-19.609	-19.739	-0.130
H(0)	5.811e-024				
H2	2.906e-024	2.909e-024	-23.537	-23.536	0.000
Na	3.257e-004				
Na+	3.257e-004	3.024e-004	-3.487	-3.519	-0.032
NaHCO3	1.801e-008	1.803e-008	-7.745	-7.744	0.000
NaCO3-	3.441e-011	3.193e-011	-10.463	-10.496	-0.033
NaOH	2.276e-012	2.279e-012	-11.643	-11.642	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-45.308	-45.308	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-2.86	-11.20	-8.34	CaCO3
Calcite	-2.72	-11.20	-8.48	CaCO3
CO2(g)	-2.21	-3.68	-1.47	CO2
Cu(OH)2	-0.95	-20.25	-19.30	Cu(OH)2
Cu2(OH)2CO3	45.61	11.81	-33.80	Cu2(OH)2CO3
Cu3(OH)2(CO3)2	61.88	15.88	-46.00	Cu3(OH)2(CO3)2
CuCO3	-3.01	-12.61	-9.60	CuCO3
Cuo	0.10	7.75	7.65	CuO
Fix_H+	-6.06	-6.06	0.00	H+
H2(g)	-20.39	-23.54	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.64	-6.06	1.58	NaCl
O2(g)	-42.42	-45.31	-2.89	O2

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

**Appendix C1:3 Equilibrium calculation of Cu at pH=8±0.2 within calcium concentration tested (20-60mg/l)  
 Copper stability based on phreeqc. pH 8, Ca 20 mg/l**

-----  
 Reading input data for simulation 1.  
 -----

```

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt
SOLUTION 1
  temp      25
  pH        8
  pe        4
  redox     pe
  units     mmol/kgw
  density   1
  Na        0.327
  C(4)      0.327
  Ca        0.5
  Cl        1
  water     1 # kg
SOLUTION 2
  temp      25
  pH        1.5
  pe        4
  redox     pe
  units     mmol/kgw
  density   1
  Cu        15.73
  Cl        31.47
  water     1 # kg
MIX 1
  1        0.996
  2        0.004
Phases

```

```

Fix_H+
  H+ = H+
  log_k      0
EQUILIBRIUM_PHASES 1
SELECTED_OUTPUT
file copper 6.0 .out
reset false
ph true
alkalinity true
ionic_strength true
totals Cu Cu(2) Na C(4) Ca
molalities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Ca+2 CaCO3 CaHCO3+
           CaOH+ Na+ NaCO3- NaHCO3
activities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Na+ NaCO3- NaHCO3
           Ca+2 CaCO3 CaHCO3+ CaOH+
           Cu3(OH)2(CO3)2
WARNING: Did not find species, Cu3(OH)2(CO3)2.
-----
Beginning of initial solution calculations.
-----
-----Distribution of species-----

```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	5.135e-007	4.907e-007	-6.289	-6.309	-0.020
OH-	2.142e-008	2.040e-008	-7.669	-7.690	-0.021
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-62.885	-62.885	0.000
C(4)	3.257e-004				
CO2	1.649e-004	1.650e-004	-3.783	-3.783	0.000
HCO3-	1.568e-004	1.495e-004	-3.805	-3.825	-0.021
CuCO3	4.086e-005	3.101e-006	-5.509	-5.508	0.000
CaHCO3+	8.223e-007	7.841e-007	-6.085	-6.106	-0.021
NaHCO3	2.609e-008	2.610e-008	-7.584	-7.583	0.000
CO3-2	1.728e-008	1.429e-008	-7.762	-7.845	-0.083
CaCO3	9.863e-009	9.867e-009	-8.006	-8.006	0.000
NaCO3-	8.668e-011	8.259e-011	-10.062	-10.083	-0.021
Ca	4.980e-004				
Ca+2	4.972e-004	4.110e-004	-3.303	-3.386	-0.083
CaHCO3+	8.223e-007	7.841e-007	-6.085	-6.106	-0.021
CaCO3	9.863e-009	9.867e-009	-8.006	-8.006	0.000
CaOH+	1.459e-010	1.390e-010	-9.836	-9.857	-0.021
Cl	1.122e-003				
Cl-	1.122e-003	1.068e-003	-2.950	-2.971	-0.021
CuCl+	1.536e-007	1.463e-007	-6.814	-6.835	-0.021
Cu(1)	1.780e-006				
Cu+	1.780e-006	1.695e-006	-5.749	-5.771	-0.021
Cu(2)	6.114e-005				
CuCO3	4.086e-005	3.101e-006	-5.509	-5.508	0.000
Cu+2	1.450e-005	4.330e-005	-4.282	-4.364	-0.082
Cu(OH)2	3.755e-006	3.756e-006	-5.425	-5.425	0.000

CuOH+	1.850e-006	1.762e-006	-5.733	-5.754	-0.021
CuCl+	1.536e-007	1.463e-007	-6.814	-6.835	-0.021
Cu(OH)3-	4.841e-013	4.612e-013	-12.315	-12.336	-0.021
Cu(OH)4-2	2.275e-019	1.875e-019	-18.643	-18.727	-0.084
H(0)	1.895e-024				
H2	9.477e-025	9.481e-025	-24.023	-24.023	0.000
Na	3.257e-004				
Na+	3.257e-004	3.104e-004	-3.487	-3.508	-0.021
NaHCO3	2.609e-008	2.610e-008	-7.584	-7.583	0.000
NaCO3-	8.668e-011	8.259e-011	-10.062	-10.083	-0.021
NaOH	4.177e-012	4.179e-012	-11.379	-11.379	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-44.334	-44.334	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-2.90	-11.23	-8.34	CaCO3
Calcite	-2.75	-11.23	-8.48	CaCO3
CO2(g)	-2.31	-3.78	-1.47	CO2
Cu(OH)2	-0.44	-19.74	-19.30	Cu(OH)2
Cu2(OH)2CO3	46.53	12.73	-33.80	Cu2(OH)2CO3
Cu3(OH)2(CO3)2	63.20	17.20	-46.00	Cu3(OH)2(CO3)2
CuCO3	-2.61	-12.21	-9.60	CuCO3
Cuo	0.60	8.25	7.65	CuO
Fix_H+	-6.31	-6.31	0.00	H+
H2(g)	-20.87	-24.02	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-8.06	-6.48	1.58	NaCl
O2(g)	-41.44	-44.33	-2.89	O2

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

#### Copper stability based on phreeqc pH8, Ca, 40

-----  
Reading input data for simulation 1.  
-----

```

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt
SOLUTION 1
  temp      25
  pH        8
  pe        4
  redox     pe
  units     mmol/kgw
  density   1
  Na        0.327
  C(4)      0.327
  Ca        1
  Cl        2
  water     1 # kg
SOLUTION 2

```

```

temp      25
pH        1.5
pe         4
redox     pe
units     mmol/kgw
density   1
Cu         15.73
Cl         31.47
water     1 # kg
MIX 1
  1      0.996
  2      0.004
Phases
Fix_H+
  H+ = H+
  log_k      0
EQUILIBRIUM_PHASES 1
SELECTED_OUTPUT
file copper 6.0 .out
reset false
ph true
alkalinity true
ionic_strength true
totals Cu Cu(2) Na C(4) Ca
molalities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Ca+2 CaCO3 CaHCO3+
           CaOH+ Na+ NaCO3- NaHCO3
activities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Na+ NaCO3- NaHCO3
           Ca+2 CaCO3 CaHCO3+ CaOH+
           Cu3(OH)2(CO3)2
WARNING: Did not find species, Cu3(OH)2(CO3)2.
-----
Beginning of initial solution calculations.
-----
-----Distribution of species-----

```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	5.192e-007	4.898e-007	-6.285	-6.310	-0.025
OH-	2.179e-008	2.044e-008	-7.662	-7.690	-0.028
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-62.773	-62.773	0.000
C(4)	3.257e-004				
CO2	1.633e-004	1.634e-004	-3.787	-3.787	0.000
HCO3-	1.579e-004	1.484e-004	-3.802	-3.829	-0.027
CuCO3	4.069e-005	2.929e-006	-5.534	-5.533	0.000
CaHCO3+	1.563e-006	1.469e-006	-5.806	-5.833	-0.027
NaHCO3	2.550e-008	2.552e-008	-7.594	-7.593	0.000
CaCO3	1.850e-008	1.852e-008	-7.733	-7.732	0.000
CO3-2	1.820e-008	1.421e-008	-7.740	-7.847	-0.108
NaCO3-	8.620e-011	8.091e-011	-10.064	-10.092	-0.028
Ca	9.960e-004				

Ca+2	9.944e-004	7.758e-004	-3.002	-3.110	-0.108
CaHCO3+	1.563e-006	1.469e-006	-5.806	-5.833	-0.027
CaCO3	1.850e-008	1.852e-008	-7.733	-7.732	0.000
CaOH+	2.801e-010	2.629e-010	-9.553	-9.580	-0.028
Cl	2.118e-003				
Cl-	2.118e-003	1.986e-003	-2.674	-2.702	-0.028
CuCl+	2.753e-007	2.584e-007	-6.560	-6.588	-0.028
Cu(1)	1.780e-006				
Cu+	1.780e-006	1.668e-006	-5.749	-5.778	-0.028
Cu(2)	6.114e-005				
CuCO3	4.069e-005	2.929e-006	-5.534	-5.533	0.000
Cu+2	1.479e-005	4.114e-005	-4.279	-4.386	-0.107
Cu(OH)2	3.580e-006	3.583e-006	-5.446	-5.446	0.000
CuOH+	1.787e-006	1.678e-006	-5.748	-5.775	-0.028
CuCl+	2.753e-007	2.584e-007	-6.560	-6.588	-0.028
Cu(OH)3-	4.696e-013	4.407e-013	-12.328	-12.356	-0.028
Cu(OH)4-2	2.314e-019	1.795e-019	-18.636	-18.746	-0.110
H(0)	2.026e-024				
H2	1.013e-024	1.014e-024	-23.994	-23.994	0.000
Na	3.257e-004				
Na+	3.257e-004	3.058e-004	-3.487	-3.515	-0.027
NaHCO3	2.550e-008	2.552e-008	-7.594	-7.593	0.000
NaCO3-	8.620e-011	8.091e-011	-10.064	-10.092	-0.028
NaOH	4.122e-012	4.125e-012	-11.385	-11.385	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-44.392	-44.392	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-2.62	-10.96	-8.34	CaCO3
Calcite	-2.48	-10.96	-8.48	CaCO3
CO2(g)	-2.32	-3.79	-1.47	CO2
Cu(OH)2	-0.46	-19.76	-19.30	Cu(OH)2
Cu2(OH)2CO3	46.48	12.68	-33.80	Cu2(OH)2CO3
Cu3(OH)2(CO3)2	63.13	17.13	-46.00	Cu3(OH)2(CO3)2
CuCO3	-2.63	-12.23	-9.60	CuCO3
Cuo	0.58	8.23	7.65	CuO
Fix_H+	-6.31	-6.31	0.00	H+
H2(g)	-20.84	-23.99	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.80	-6.22	1.58	NaCl
O2(g)	-41.50	-44.39	-2.89	O2

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

#### Copper stability based on phreeqc pH 8, Ca 60

-----  
Reading input data for simulation 1.  
-----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

```

SOLUTION 1
  temp      25
  pH         8
  pe         4
  redox      pe
  units      mmol/kgw
  density    1
  Na         0.327
  C(4)       0.327
  Ca         1.5
  Cl         3
  water      1 # kg
SOLUTION 2
  temp      25
  pH         1.5
  pe         4
  redox      pe
  units      mmol/kgw
  density    1
  Cu         15.73
  Cl         31.47
  water      1 # kg
MIX 1
  1      0.996
  2      0.004
Phases
Fix_H+
  H+ = H+
  log_k      0
EQUILIBRIUM_PHASES 1
SELECTED_OUTPUT
file copper 6.0 .out
reset false
ph true
alkalinity true
ionic_strength true
totals Cu Cu(2) Na C(4) Ca
molalities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Ca+2 CaCO3 CaHCO3+
           CaOH+ Na+ NaCO3- NaHCO3
activities Cu+2 Cu(OH)2 CuCl+ CuCO3
           CuOH+ Na+ NaCO3- NaHCO3
           Ca+2 CaCO3 CaHCO3+ CaOH+
           Cu3(OH)2(CO3)2
WARNING: Did not find species, Cu3(OH)2(CO3)2.
-----
Beginning of initial solution calculations.
-----
-----Distribution of species-----

```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	5.233e-007	4.889e-007	-6.281	-6.311	-0.030
OH-	2.209e-008	2.048e-008	-7.656	-7.689	-0.033

H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-62.688	-62.688	0.000
C(4)	3.257e-004				
CO2	1.619e-004	1.621e-004	-3.791	-3.790	0.000
HCO3-	1.586e-004	1.475e-004	-3.800	-3.831	-0.032
CuCO3	4.057e-005	2.804e-006	-5.553	-5.552	0.000
CaHCO3+	2.254e-006	2.095e-006	-5.647	-5.679	-0.032
CaCO3	2.643e-008	2.646e-008	-7.578	-7.577	0.000
NaHCO3	2.505e-008	2.507e-008	-7.601	-7.601	0.000
CO3-2	1.894e-008	1.415e-008	-7.723	-7.849	-0.127
NaCO3-	8.585e-011	7.965e-011	-10.066	-10.099	-0.033
Ca	1.494e-003				
Ca+2	1.492e-003	1.113e-003	-2.826	-2.953	-0.127
CaHCO3+	2.254e-006	2.095e-006	-5.647	-5.679	-0.032
CaCO3	2.643e-008	2.646e-008	-7.578	-7.577	0.000
CaOH+	4.074e-010	3.780e-010	-9.390	-9.423	-0.033
Cl	3.114e-003				
Cl-	3.113e-003	2.886e-003	-2.507	-2.540	-0.033
CuCl+	3.890e-007	3.609e-007	-6.410	-6.443	-0.033
Cu(1)	1.780e-006				
Cu+	1.780e-006	1.648e-006	-5.749	-5.783	-0.034
Cu(2)	6.114e-005				
CuCO3	4.057e-005	2.804e-006	-5.553	-5.552	0.000
Cu+2	1.498e-005	3.954e-005	-4.278	-4.403	-0.125
Cu(OH)2	3.452e-006	3.456e-006	-5.462	-5.461	0.000
CuOH+	1.741e-006	1.615e-006	-5.759	-5.792	-0.033
CuCl+	3.890e-007	3.609e-007	-6.410	-6.443	-0.033
Cu(OH)3-	4.591e-013	4.259e-013	-12.338	-12.371	-0.033
Cu(OH)4-2	2.346e-019	1.738e-019	-18.630	-18.760	-0.130
H(0)	2.131e-024				
H2	1.065e-024	1.067e-024	-23.972	-23.972	0.000
Na	3.257e-004				
Na+	3.257e-004	3.024e-004	-3.487	-3.519	-0.032
NaHCO3	2.505e-008	2.507e-008	-7.601	-7.601	0.000
NaCO3-	8.585e-011	7.965e-011	-10.066	-10.099	-0.033
NaOH	4.081e-012	4.086e-012	-11.389	-11.389	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-44.437	-44.436	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-2.47	-10.80	-8.34	CaCO3
Calcite	-2.32	-10.80	-8.48	CaCO3
CO2(g)	-2.32	-3.79	-1.47	CO2
Cu(OH)2	-0.48	-19.78	-19.30	Cu(OH)2
Cu2(OH)2CO3	46.45	12.65	-33.80	Cu2(OH)2CO3
Cu3(OH)2(CO3)2	63.08	17.08	-46.00	Cu3(OH)2(CO3)2
CuCO3	-2.65	-12.25	-9.60	CuCO3
Cuo	0.57	8.22	7.65	CuO
Fix_H+	-6.31	-6.31	0.00	H+
H2(g)	-20.82	-23.97	-3.15	H2

H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.64	-6.06	1.58	NaCl
O2(g)	-41.54	-44.44	-2.89	O2

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

## Appendix C2:1 Equilibrium calculation of Cd at pH=6±0.2 within calcium concentration tested (20-60mg/l)

### Cadmium stability based on phreeqc pH 6, Ca 20 mg/l

Reading input data for simulation 1.  
-----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

SOLUTION 1

temp 25  
pH 6  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Na 0.327  
C(4) 0.327  
Ca 0.5  
Cl 1  
water 1 # kg

SOLUTION 2

temp 25  
pH 1.5  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Cd 8.896  
Cl 17.79  
water 1 # kg

MIX 1

1 0.9999  
2 0.0001

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

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.099e-006	1.053e-006	-5.959	-5.978	-0.019
OH-	9.962e-009	9.511e-009	-8.002	-8.022	-0.020
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-121.060	-121.059	0.000
C(4)	3.270e-004				
CO2	2.263e-004	2.264e-004	-3.645	-3.645	0.000
HCO3-	1.001e-004	9.567e-005	-4.000	-4.019	-0.020

	CaHCO3+	5.321e-007	5.085e-007	-6.274	-6.294	-0.020
	NaHCO3	1.680e-008	1.680e-008	-7.775	-7.775	0.000
	CO3-2	5.109e-009	4.263e-009	-8.292	-8.370	-0.079
	CaCO3	2.982e-009	2.983e-009	-8.525	-8.525	0.000
	CdHCO3+	2.165e-009	2.068e-009	-8.664	-8.684	-0.020
	NaCO3-	2.596e-011	2.479e-011	-10.586	-10.606	-0.020
	CdCO3	2.314e-012	2.315e-012	-11.636	-11.636	0.000
	Cd (CO3) 2-2	3.751e-017	3.120e-017	-16.426	-16.506	-0.080
Ca		4.999e-004				
	Ca+2	4.994e-004	4.166e-004	-3.302	-3.380	-0.079
	CaHCO3+	5.321e-007	5.085e-007	-6.274	-6.294	-0.020
	CaCO3	2.982e-009	2.983e-009	-8.525	-8.525	0.000
	CaOH+	6.878e-011	6.569e-011	-10.163	-10.183	-0.020
Cd		8.896e-007				
	Cd+2	8.218e-007	6.835e-007	-6.085	-6.165	-0.080
	CdCl+	6.537e-008	6.242e-008	-7.185	-7.205	-0.020
	CdHCO3+	2.165e-009	2.068e-009	-8.664	-8.684	-0.020
	CdCl2	2.488e-010	2.489e-010	-9.604	-9.604	0.000
	CdOH+	5.656e-011	5.402e-011	-10.247	-10.267	-0.020
	CdCO3	2.314e-012	2.315e-012	-11.636	-11.636	0.000
	CdCl3-	1.572e-013	1.502e-013	-12.803	-12.823	-0.020
	Cd (OH) 2	2.755e-015	2.756e-015	-14.560	-14.560	0.000
	Cd (CO3) 2-2	3.751e-017	3.120e-017	-16.426	-16.506	-0.080
	CdCl4-2	3.444e-017	2.865e-017	-16.463	-16.543	-0.080
	Cd (OH) 3-	3.076e-022	2.938e-022	-21.512	-21.532	-0.020
	Cd (OH) 4-2	2.991e-030	2.488e-030	-29.524	-29.604	-0.080
Cl		1.002e-003				
	Cl-	1.002e-003	9.563e-004	-2.999	-3.019	-0.020
	CdCl+	6.537e-008	6.242e-008	-7.185	-7.205	-0.020
	CdCl2	2.488e-010	2.489e-010	-9.604	-9.604	0.000
	CdCl3-	1.572e-013	1.502e-013	-12.803	-12.823	-0.020
	CdCl4-2	3.444e-017	2.865e-017	-16.463	-16.543	-0.080
H (0)		5.008e-039				
	H2	2.504e-039	2.505e-039	-38.601	-38.601	0.000
Na		3.270e-004				
	Na+	3.270e-004	3.123e-004	-3.486	-3.505	-0.020
	NaHCO3	1.680e-008	1.680e-008	-7.775	-7.775	0.000
	NaCO3-	2.596e-011	2.479e-011	-10.586	-10.606	-0.020
	NaOH	1.960e-012	1.960e-012	-11.708	-11.708	0.000
O (0)		1.328e-015				
	O2	6.640e-016	6.642e-016	-15.178	-15.178	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-3.41	-11.75	-8.34	CaCO3
Calcite	-3.27	-11.75	-8.48	CaCO3
Cd (OH) 2	-7.86	5.79	13.65	Cd (OH) 2
CO2 (g)	-2.18	-3.65	-1.47	CO2
H2 (g)	-35.45	-38.60	-3.15	H2
H2O (g)	-1.51	-0.00	1.51	H2O
Halite	-8.11	-6.52	1.58	NaCl
O2 (g)	-12.29	-15.18	-2.89	O2

Otavite                    -2.44   -14.54   -12.10   CdCO3

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

**Cadmium stability based on phreeqc pH6, Ca 40 mg/l**

-----  
Reading input data for simulation 1.  
-----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

SOLUTION 1

temp            25  
pH              6  
pe              4  
redox          pe  
units          mmol/kgw  
density        1  
Na              0.327  
C(4)           0.327  
Ca              1  
Cl              2  
water        1 # kg

SOLUTION 2

temp            25  
pH              1.5  
pe              4  
redox          pe  
units          mmol/kgw  
density        1  
Cd              8.896  
Cl              17.79  
water        1 # kg

MIX 1

1            0.9999  
2            0.0001

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

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.114e-006	1.052e-006	-5.953	-5.978	-0.025
OH-	1.013e-008	9.515e-009	-7.994	-8.022	-0.027
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	2.179e-028				
CH4	2.179e-028	2.181e-028	-27.662	-27.661	0.000
C(4)	3.270e-004				
CO2	2.249e-004	2.250e-004	-3.648	-3.648	0.000
HCO3-	1.011e-004	9.513e-005	-3.995	-4.022	-0.026
CaHCO3+	1.011e-006	9.517e-007	-5.995	-6.022	-0.026
NaHCO3	1.644e-008	1.645e-008	-7.784	-7.784	0.000
CaCO3	5.581e-009	5.585e-009	-8.253	-8.253	0.000

	CO3-2	5.400e-009	4.240e-009	-8.268	-8.373	-0.105
	CdHCO3+	1.928e-009	1.813e-009	-8.715	-8.742	-0.027
	NaCO3-	2.583e-011	2.428e-011	-10.588	-10.615	-0.027
	CdCO3	2.028e-012	2.030e-012	-11.693	-11.693	0.000
	Cd(CO3)2-2	3.485e-017	2.722e-017	-16.458	-16.565	-0.107
Ca	9.999e-004					
	Ca+2	9.989e-004	7.841e-004	-3.000	-3.106	-0.105
	CaHCO3+	1.011e-006	9.517e-007	-5.995	-6.022	-0.026
	CaCO3	5.581e-009	5.585e-009	-8.253	-8.253	0.000
	CaOH+	1.316e-010	1.237e-010	-9.881	-9.908	-0.027
Cd	8.896e-007					
	Cd+2	7.716e-007	6.026e-007	-6.113	-6.220	-0.107
	CdCl+	1.151e-007	1.082e-007	-6.939	-6.966	-0.027
	CdHCO3+	1.928e-009	1.813e-009	-8.715	-8.742	-0.027
	CdCl2	8.478e-010	8.485e-010	-9.072	-9.071	0.000
	CdOH+	5.068e-011	4.764e-011	-10.295	-10.322	-0.027
	CdCO3	2.028e-012	2.030e-012	-11.693	-11.693	0.000
	CdCl3-	1.071e-012	1.007e-012	-11.970	-11.997	-0.027
	Cd(OH)2	2.430e-015	2.432e-015	-14.614	-14.614	0.000
	CdCl4-2	4.837e-016	3.777e-016	-15.315	-15.423	-0.107
	Cd(CO3)2-2	3.485e-017	2.722e-017	-16.458	-16.565	-0.107
	Cd(OH)3-	2.758e-022	2.593e-022	-21.559	-21.586	-0.027
	Cd(OH)4-2	2.813e-030	2.197e-030	-29.551	-29.658	-0.107
Cl	2.002e-003					
	Cl-	2.001e-003	1.881e-003	-2.699	-2.726	-0.027
	CdCl+	1.151e-007	1.082e-007	-6.939	-6.966	-0.027
	CdCl2	8.478e-010	8.485e-010	-9.072	-9.071	0.000
	CdCl3-	1.071e-012	1.007e-012	-11.970	-11.997	-0.027
	CdCl4-2	4.837e-016	3.777e-016	-15.315	-15.423	-0.107
H(0)	1.121e-015					
	H2	5.606e-016	5.611e-016	-15.251	-15.251	0.000
Na	3.270e-004					
	Na+	3.270e-004	3.075e-004	-3.486	-3.512	-0.027
	NaHCO3	1.644e-008	1.645e-008	-7.784	-7.784	0.000
	NaCO3-	2.583e-011	2.428e-011	-10.588	-10.615	-0.027
	NaOH	1.930e-012	1.931e-012	-11.715	-11.714	0.000
O(0)	0.000e+000					
	O2	0.000e+000	0.000e+000	-61.878	-61.878	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-3.14	-11.48	-8.34	CaCO3
Calcite	-3.00	-11.48	-8.48	CaCO3
Cd(OH)2	-7.91	5.74	13.65	Cd(OH)2
CO2(g)	-2.18	-3.65	-1.47	CO2
H2(g)	-12.10	-15.25	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.82	-6.24	1.58	NaCl
O2(g)	-58.99	-61.88	-2.89	O2
Otavite	-2.49	-14.59	-12.10	CdCO3

-----  
 End of run.

-----  
**Cadmium stability based on phreeqc pH 6, Ca 60 mg/l**  
 -----

-----  
 Reading input data for simulation 1.  
 -----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

SOLUTION 1

temp 25  
 pH 6  
 pe 4  
 redox pe  
 units mmol/kgw  
 density 1  
 Na 0.327  
 C(4) 0.327  
 Ca 1.5  
 Cl 3  
 water 1 # kg

SOLUTION 2

temp 25  
 pH 1.5  
 pe 4  
 redox pe  
 units mmol/kgw  
 density 1  
 Cd 8.896  
 Cl 17.79  
 water 1 # kg

MIX 1

1 0.9999  
 2 0.0001

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

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.125e-006	1.052e-006	-5.949	-5.978	-0.029
OH-	1.025e-008	9.517e-009	-7.989	-8.021	-0.032
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-120.168	-120.168	0.000
C(4)	3.270e-004				
CO2	2.237e-004	2.240e-004	-3.650	-3.650	0.000
HCO3-	1.018e-004	9.470e-005	-3.992	-4.024	-0.031
CaHCO3+	1.459e-006	1.358e-006	-5.836	-5.867	-0.031
NaHCO3	1.617e-008	1.619e-008	-7.791	-7.791	0.000
CaCO3	7.963e-009	7.972e-009	-8.099	-8.098	0.000
CO3-2	5.627e-009	4.223e-009	-8.250	-8.374	-0.125
CdHCO3+	1.753e-009	1.629e-009	-8.756	-8.788	-0.032
NaCO3-	2.573e-011	2.390e-011	-10.590	-10.622	-0.032

	CdCO3	1.822e-012	1.824e-012	-11.739	-11.739	0.000
	Cd (CO3) 2-2	3.271e-017	2.436e-017	-16.485	-16.613	-0.128
Ca	1.500e-003					
	Ca+2	1.498e-003	1.124e-003	-2.824	-2.949	-0.125
	CaHCO3+	1.459e-006	1.358e-006	-5.836	-5.867	-0.031
	CaCO3	7.963e-009	7.972e-009	-8.099	-8.098	0.000
	CaOH+	1.909e-010	1.773e-010	-9.719	-9.751	-0.032
Cd	8.896e-007					
	Cd+2	7.303e-007	5.439e-007	-6.136	-6.264	-0.128
	CdCl+	1.558e-007	1.447e-007	-6.808	-6.840	-0.032
	CdHCO3+	1.753e-009	1.629e-009	-8.756	-8.788	-0.032
	CdCl2	1.679e-009	1.681e-009	-8.775	-8.775	0.000
	CdOH+	4.630e-011	4.301e-011	-10.334	-10.366	-0.032
	CdCl3-	3.180e-012	2.954e-012	-11.498	-11.530	-0.032
	CdCO3	1.822e-012	1.824e-012	-11.739	-11.739	0.000
	CdCl4-2	2.205e-015	1.642e-015	-14.657	-14.785	-0.128
	Cd (OH) 2	2.193e-015	2.196e-015	-14.659	-14.658	0.000
	Cd (CO3) 2-2	3.271e-017	2.436e-017	-16.485	-16.613	-0.128
	Cd (OH) 3-	2.521e-022	2.342e-022	-21.598	-21.630	-0.032
	Cd (OH) 4-2	2.665e-030	1.985e-030	-29.574	-29.702	-0.128
Cl	3.001e-003					
	Cl-	3.001e-003	2.786e-003	-2.523	-2.555	-0.032
	CdCl+	1.558e-007	1.447e-007	-6.808	-6.840	-0.032
	CdCl2	1.679e-009	1.681e-009	-8.775	-8.775	0.000
	CdCl3-	3.180e-012	2.954e-012	-11.498	-11.530	-0.032
	CdCl4-2	2.205e-015	1.642e-015	-14.657	-14.785	-0.128
H (0)	8.384e-039					
	H2	4.192e-039	4.196e-039	-38.378	-38.377	0.000
Na	3.270e-004					
	Na+	3.270e-004	3.039e-004	-3.486	-3.517	-0.032
	NaHCO3	1.617e-008	1.619e-008	-7.791	-7.791	0.000
	NaCO3-	2.573e-011	2.390e-011	-10.590	-10.622	-0.032
	NaOH	1.907e-012	1.909e-012	-11.720	-11.719	0.000
O (0)	4.729e-016					
	O2	2.364e-016	2.367e-016	-15.626	-15.626	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-2.99	-11.32	-8.34	CaCO3
Calcite	-2.84	-11.32	-8.48	CaCO3
Cd (OH) 2	-7.96	5.69	13.65	Cd (OH) 2
CO2 (g)	-2.18	-3.65	-1.47	CO2
H2 (g)	-35.23	-38.38	-3.15	H2
H2O (g)	-1.51	-0.00	1.51	H2O
Halite	-7.65	-6.07	1.58	NaCl
O2 (g)	-12.73	-15.63	-2.89	O2
Otavite	-2.54	-14.64	-12.10	CdCO3

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

**Appendix C2:2 Equilibrium calculation of Cd at pH=7±0.2 within calcium concentration tested (20-60mg/l)**  
**Cadmium stability pH 7, Ca 20 mg/l.**

-----  
 Reading input data for simulation 1.  
 -----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

SOLUTION 1

temp 25  
 pH 7  
 pe 4  
 redox pe  
 units mmol/kgw  
 density 1  
 Na 0.327  
 C(4) 0.327  
 Ca 0.5  
 Cl 1  
 water 1 # kg

SOLUTION 2

temp 25  
 pH 1.5  
 pe 4  
 redox pe  
 units mmol/kgw  
 density 1  
 Cd 8.896  
 Cl 17.79  
 water 1 # kg

MIX 1

1 0.9999  
 2 0.0001

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

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.126e-007	1.077e-007	-6.948	-6.968	-0.019
OH-	9.742e-008	9.291e-008	-7.011	-7.032	-0.021
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-123.178	-123.178	0.000
C(4)	3.270e-004				
HCO3-	2.642e-004	2.523e-004	-3.578	-3.598	-0.020
CO2	6.109e-005	6.112e-005	-4.214	-4.214	0.000
CaHCO3+	1.396e-006	1.333e-006	-5.855	-5.875	-0.020
CO3-2	1.321e-007	1.098e-007	-6.879	-6.959	-0.080
CaCO3	7.638e-008	7.641e-008	-7.117	-7.117	0.000
NaHCO3	4.424e-008	4.426e-008	-7.354	-7.354	0.000
CdHCO3+	5.669e-009	5.408e-009	-8.247	-8.267	-0.020
NaCO3-	6.687e-010	6.379e-010	-9.175	-9.195	-0.020
CdCO3	5.911e-011	5.913e-011	-10.228	-10.228	0.000
Cd(CO3)2-2	2.479e-014	2.053e-014	-13.606	-13.688	-0.082

Ca	4.999e-004					
Ca+2	4.985e-004	4.142e-004	-3.302	-3.383	-0.080	
CaHCO3+	1.396e-006	1.333e-006	-5.855	-5.875	-0.020	
CaCO3	7.638e-008	7.641e-008	-7.117	-7.117	0.000	
CaOH+	6.687e-010	6.380e-010	-9.175	-9.195	-0.020	
Cd	8.896e-007					
Cd+2	8.183e-007	6.779e-007	-6.087	-6.169	-0.082	
CdCl+	6.482e-008	6.184e-008	-7.188	-7.209	-0.020	
CdHCO3+	5.669e-009	5.408e-009	-8.247	-8.267	-0.020	
CdOH+	5.485e-010	5.233e-010	-9.261	-9.281	-0.020	
CdCl2	2.462e-010	2.463e-010	-9.609	-9.609	0.000	
CdCO3	5.911e-011	5.913e-011	-10.228	-10.228	0.000	
Cd(OH)2	2.607e-013	2.608e-013	-12.584	-12.584	0.000	
CdCl3-	1.556e-013	1.485e-013	-12.808	-12.828	-0.020	
Cd(CO3)2-2	2.479e-014	2.053e-014	-13.606	-13.688	-0.082	
CdCl4-2	3.416e-017	2.830e-017	-16.467	-16.548	-0.082	
Cd(OH)3-	2.847e-019	2.716e-019	-18.546	-18.566	-0.020	
Cd(OH)4-2	2.712e-026	2.247e-026	-25.567	-25.648	-0.082	
Cl	1.002e-003					
Cl-	1.002e-003	9.553e-004	-2.999	-3.020	-0.021	
CdCl+	6.482e-008	6.184e-008	-7.188	-7.209	-0.020	
CdCl2	2.462e-010	2.463e-010	-9.609	-9.609	0.000	
CdCl3-	1.556e-013	1.485e-013	-12.808	-12.828	-0.020	
CdCl4-2	3.416e-017	2.830e-017	-16.467	-16.548	-0.082	
H(0)	2.052e-039					
H2	1.026e-039	1.026e-039	-38.989	-38.989	0.000	
Na	3.270e-004					
Na+	3.269e-004	3.120e-004	-3.486	-3.506	-0.020	
NaHCO3	4.424e-008	4.426e-008	-7.354	-7.354	0.000	
NaCO3-	6.687e-010	6.379e-010	-9.175	-9.195	-0.020	
NaOH	1.912e-011	1.913e-011	-10.718	-10.718	0.000	
O(0)	7.909e-015					
O2	3.955e-015	3.956e-015	-14.403	-14.403	0.000	

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

Phase	SI	log IAP	log KT	
Aragonite	-2.01	-10.34	-8.34	CaCO3
Calcite	-1.86	-10.34	-8.48	CaCO3
Cd(OH)2	-5.88	7.77	13.65	Cd(OH)2
CO2(g)	-2.75	-4.21	-1.47	CO2
H2(g)	-35.84	-38.99	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-8.11	-6.53	1.58	NaCl
O2(g)	-11.51	-14.40	-2.89	O2
Otavite	-1.03	-13.13	-12.10	CdCO3

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

**Cadmium stability-phreeqc pH 7, Ca 40 mg/l.**

-----  
 Reading input data for simulation 1.  
 -----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

SOLUTION 1

temp 25  
 pH 7  
 pe 4  
 redox pe  
 units mmol/kgw  
 density 1  
 Na 0.327  
 C(4) 0.327  
 Ca 1  
 Cl 2  
 water 1 # kg

SOLUTION 2

temp 25  
 pH 1.5  
 pe 4  
 redox pe  
 units mmol/kgw  
 density 1  
 Cd 8.896  
 Cl 17.79  
 water 1 # kg

MIX 1

1 0.9999  
 2 0.0001

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

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.142e-007	1.078e-007	-6.942	-6.967	-0.025
OH-	9.889e-008	9.284e-008	-7.005	-7.032	-0.027
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-123.111	-123.110	0.000
C(4)	3.270e-004				
HCO3-	2.639e-004	2.482e-004	-3.579	-3.605	-0.027
CO2	6.014e-005	6.018e-005	-4.221	-4.221	0.000
CaHCO3+	2.628e-006	2.472e-006	-5.580	-5.607	-0.027
CaCO3	1.415e-007	1.416e-007	-6.849	-6.849	0.000
CO3-2	1.379e-007	1.080e-007	-6.861	-6.967	-0.106
NaHCO3	4.286e-008	4.289e-008	-7.368	-7.368	0.000
CdHCO3+	5.003e-009	4.700e-009	-8.301	-8.328	-0.027
NaCO3-	6.576e-010	6.177e-010	-9.182	-9.209	-0.027
CdCO3	5.131e-011	5.135e-011	-10.290	-10.289	0.000
Cd(CO3)2-2	2.251e-014	1.753e-014	-13.648	-13.756	-0.109
Ca	9.999e-004				

Ca+2	9.971e-004	7.806e-004	-3.001	-3.108	-0.106
CaHCO3+	2.628e-006	2.472e-006	-5.580	-5.607	-0.027
CaCO3	1.415e-007	1.416e-007	-6.849	-6.849	0.000
CaOH+	1.279e-009	1.201e-009	-8.893	-8.920	-0.027
Cd	8.896e-007				
Cd+2	7.688e-007	5.988e-007	-6.114	-6.223	-0.109
CdCl+	1.144e-007	1.075e-007	-6.942	-6.969	-0.027
CdHCO3+	5.003e-009	4.700e-009	-8.301	-8.328	-0.027
CdCl2	8.412e-010	8.418e-010	-9.075	-9.075	0.000
CdOH+	4.917e-010	4.619e-010	-9.308	-9.335	-0.027
CdCO3	5.131e-011	5.135e-011	-10.290	-10.289	0.000
CdCl3-	1.063e-012	9.982e-013	-11.974	-12.001	-0.027
Cd(OH)2	2.299e-013	2.300e-013	-12.639	-12.638	0.000
Cd(CO3)2-2	2.251e-014	1.753e-014	-13.648	-13.756	-0.109
CdCl4-2	4.805e-016	3.743e-016	-15.318	-15.427	-0.109
Cd(OH)3-	2.548e-019	2.393e-019	-18.594	-18.621	-0.027
Cd(OH)4-2	2.540e-026	1.978e-026	-25.595	-25.704	-0.109
Cl	2.002e-003				
Cl-	2.001e-003	1.879e-003	-2.699	-2.726	-0.027
CdCl+	1.144e-007	1.075e-007	-6.942	-6.969	-0.027
CdCl2	8.412e-010	8.418e-010	-9.075	-9.075	0.000
CdCl3-	1.063e-012	9.982e-013	-11.974	-12.001	-0.027
CdCl4-2	4.805e-016	3.743e-016	-15.318	-15.427	-0.109
H(0)	2.141e-039				
H2	1.071e-039	1.071e-039	-38.970	-38.970	0.000
Na	3.270e-004				
Na+	3.269e-004	3.073e-004	-3.486	-3.512	-0.027
NaHCO3	4.286e-008	4.289e-008	-7.368	-7.368	0.000
NaCO3-	6.576e-010	6.177e-010	-9.182	-9.209	-0.027
NaOH	1.881e-011	1.883e-011	-10.726	-10.725	0.000
O(0)	7.256e-015				
O2	3.628e-015	3.631e-015	-14.440	-14.440	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-1.74	-10.07	-8.34	CaCO3
Calcite	-1.59	-10.07	-8.48	CaCO3
Cd(OH)2	-5.94	7.71	13.65	Cd(OH)2
CO2(g)	-2.75	-4.22	-1.47	CO2
H2(g)	-35.82	-38.97	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.82	-6.24	1.58	NaCl
O2(g)	-11.55	-14.44	-2.89	O2
Otavite	-1.09	-13.19	-12.10	CdCO3

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

**Cadmium stability-pH 7, Ca 60 mg/l.**

-----  
 Reading input data for simulation 1.  
 -----

DATABASE C:\Lab work.1\phreeqc.29.3.09.txt

SOLUTION 1

temp 25  
pH 7  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Na 0.327  
C(4) 0.327  
Ca 1.5  
Cl 3  
water 1 # kg

SOLUTION 2

temp 25  
pH 1.5  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Cd 8.896  
Cl 17.79  
water 1 # kg

MIX 1

1 0.9999  
2 0.0001

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

-----Distribution of species-----					
Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
H+	1.154e-007	1.079e-007	-6.938	-6.967	-0.029
OH-	1.000e-007	9.278e-008	-7.000	-7.033	-0.033
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	3.684e-024				
CH4	3.684e-024	3.688e-024	-23.434	-23.433	0.000
C(4)	3.270e-004				
HCO3-	2.634e-004	2.451e-004	-3.579	-3.611	-0.031
CO2	5.938e-005	5.945e-005	-4.226	-4.226	0.000
CaHCO3+	3.763e-006	3.500e-006	-5.424	-5.456	-0.031
CaCO3	2.001e-007	2.003e-007	-6.699	-6.698	0.000
CO3-2	1.422e-007	1.065e-007	-6.847	-6.973	-0.126
NaHCO3	4.181e-008	4.186e-008	-7.379	-7.378	0.000
CdHCO3+	4.515e-009	4.192e-009	-8.345	-8.378	-0.032
NaCO3-	6.489e-010	6.024e-010	-9.188	-9.220	-0.032
CdCO3	4.572e-011	4.577e-011	-10.340	-10.339	0.000
Cd(CO3)2-2	2.075e-014	1.542e-014	-13.683	-13.812	-0.129
Ca	1.500e-003				
Ca+2	1.496e-003	1.120e-003	-2.825	-2.951	-0.126
CaHCO3+	3.763e-006	3.500e-006	-5.424	-5.456	-0.031
CaCO3	2.001e-007	2.003e-007	-6.699	-6.698	0.000

CaOH+	1.855e-009	1.722e-009	-8.732	-8.764	-0.032
Cd	8.896e-007				
Cd+2	7.280e-007	5.410e-007	-6.138	-6.267	-0.129
CdCl+	1.549e-007	1.438e-007	-6.810	-6.842	-0.032
CdHCO3+	4.515e-009	4.192e-009	-8.345	-8.378	-0.032
CdCl2	1.668e-009	1.670e-009	-8.778	-8.777	0.000
CdOH+	4.491e-010	4.170e-010	-9.348	-9.380	-0.032
CdCO3	4.572e-011	4.577e-011	-10.340	-10.339	0.000
CdCl3-	3.159e-012	2.933e-012	-11.500	-11.533	-0.032
Cd(OH)2	2.073e-013	2.075e-013	-12.683	-12.683	0.000
Cd(CO3)2-2	2.075e-014	1.542e-014	-13.683	-13.812	-0.129
CdCl4-2	2.193e-015	1.630e-015	-14.659	-14.788	-0.129
Cd(OH)3-	2.325e-019	2.158e-019	-18.634	-18.666	-0.032
Cd(OH)4-2	2.399e-026	1.783e-026	-25.620	-25.749	-0.129
Cl	3.001e-003				
Cl-	3.001e-003	2.784e-003	-2.523	-2.555	-0.033
CdCl+	1.549e-007	1.438e-007	-6.810	-6.842	-0.032
CdCl2	1.668e-009	1.670e-009	-8.778	-8.777	0.000
CdCl3-	3.159e-012	2.933e-012	-11.500	-11.533	-0.032
CdCl4-2	2.193e-015	1.630e-015	-14.659	-14.788	-0.129
H(0)	1.783e-014				
H2	8.914e-015	8.924e-015	-14.050	-14.049	0.000
Na	3.270e-004				
Na+	3.269e-004	3.037e-004	-3.486	-3.518	-0.032
NaHCO3	4.181e-008	4.186e-008	-7.379	-7.378	0.000
NaCO3-	6.489e-010	6.024e-010	-9.188	-9.220	-0.032
NaOH	1.858e-011	1.860e-011	-10.731	-10.731	0.000
O(0)	0.000e+000				
O2	0.000e+000	0.000e+000	-64.282	-64.281	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-1.59	-9.92	-8.34	CaCO3
Calcite	-1.44	-9.92	-8.48	CaCO3
Cd(OH)2	-5.98	7.67	13.65	Cd(OH)2
CO2(g)	-2.76	-4.23	-1.47	CO2
H2(g)	-10.90	-14.05	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.65	-6.07	1.58	NaCl
O2(g)	-61.39	-64.28	-2.89	O2
Otavite	-1.14	-13.24	-12.10	CdCO3

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

### Appendix C2:3 Equilibrium calculation of Cd at pH=8±0.2 within calcium concentration tested (20-60mg/l)

#### Cadmium stability-phreeqc pH8, Ca 20 mg/l.

-----  
Reading input data for simulation 1.  
-----

DATABASE C:\Lab work.1\phreeqc.22.04.09.txt

SOLUTION 1

temp 25  
pH 8  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Na 0.327  
C(4) 0.327  
Ca 0.5  
Cl 1  
water 1 # kg

SOLUTION 2

temp 25  
pH 1.5  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Cd 8.896  
Cl 17.79  
water 1 # kg

MIX 1

1 0.9999  
2 0.0001

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

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	7.551e-007	7.199e-007	-6.122	-6.143	-0.021
H+	1.454e-008	1.391e-008	-7.838	-7.857	-0.019
H2O	5.551e+001	1.000e+000	1.744	-0.000	0.000
C(-4)	3.741e-025				
CH4	3.741e-025	3.742e-025	-24.427	-24.427	0.000
C(4)	3.270e-004				
HCO3-	3.140e-004	2.997e-004	-3.503	-3.523	-0.020
CO2	9.366e-006	9.370e-006	-5.028	-5.028	0.000
CaHCO3+	1.654e-006	1.579e-006	-5.781	-5.802	-0.020
CO3-2	1.217e-006	1.011e-006	-5.915	-5.995	-0.081
CaCO3	7.009e-007	7.012e-007	-6.154	-6.154	0.000
NaHCO3	5.254e-008	5.256e-008	-7.280	-7.279	0.000
CdHCO3+	6.688e-009	6.379e-009	-8.175	-8.195	-0.021
NaCO3-	6.154e-009	5.870e-009	-8.211	-8.231	-0.021
CdCO3	5.402e-010	5.404e-010	-9.267	-9.267	0.000
Cd(CO3)2-2	2.088e-012	1.727e-012	-11.680	-11.763	-0.082
Ca	4.999e-004				
Ca+2	4.976e-004	4.130e-004	-3.303	-3.384	-0.081
CaHCO3+	1.654e-006	1.579e-006	-5.781	-5.802	-0.020

	CaCO3	7.009e-007	7.012e-007	-6.154	-6.154	0.000
	CaOH+	5.168e-009	4.928e-009	-8.287	-8.307	-0.021
Cd		8.896e-007				
	Cd+2	8.135e-007	6.731e-007	-6.090	-6.172	-0.082
	CdCl+	6.437e-008	6.139e-008	-7.191	-7.212	-0.021
	CdHCO3+	6.688e-009	6.379e-009	-8.175	-8.195	-0.021
	CdOH+	4.221e-009	4.026e-009	-8.375	-8.395	-0.021
	CdCO3	5.402e-010	5.404e-010	-9.267	-9.267	0.000
	CdCl2	2.443e-010	2.444e-010	-9.612	-9.612	0.000
	Cd(OH)2	1.554e-011	1.555e-011	-10.808	-10.808	0.000
	Cd(CO3)2-2	2.088e-012	1.727e-012	-11.680	-11.763	-0.082
	CdCl3-	1.544e-013	1.473e-013	-12.811	-12.832	-0.021
	Cd(OH)3-	1.315e-016	1.255e-016	-15.881	-15.902	-0.021
	CdCl4-2	3.392e-017	2.806e-017	-16.470	-16.552	-0.082
	Cd(OH)4-2	9.718e-023	8.040e-023	-22.012	-22.095	-0.082
Cl		1.002e-003				
	Cl-	1.002e-003	9.550e-004	-2.999	-3.020	-0.021
	CdCl+	6.437e-008	6.139e-008	-7.191	-7.212	-0.021
	CdCl2	2.443e-010	2.444e-010	-9.612	-9.612	0.000
	CdCl3-	1.544e-013	1.473e-013	-12.811	-12.832	-0.021
	CdCl4-2	3.392e-017	2.806e-017	-16.470	-16.552	-0.082
H(0)		1.598e-014				
	H2	7.991e-015	7.994e-015	-14.097	-14.097	0.000
Na		3.270e-004				
	Na+	3.269e-004	3.119e-004	-3.486	-3.506	-0.020
	NaHCO3	5.254e-008	5.256e-008	-7.280	-7.279	0.000
	NaCO3-	6.154e-009	5.870e-009	-8.211	-8.231	-0.021
	NaOH	1.481e-010	1.482e-010	-9.829	-9.829	0.000
O(0)		0.000e+000				
	O2	0.000e+000	0.000e+000	-64.186	-64.186	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-1.04	-9.38	-8.34	CaCO3
Calcite	-0.90	-9.38	-8.48	CaCO3
Cd(OH)2	-4.11	9.54	13.65	Cd(OH)2
CH4(g)	-21.57	-24.43	-2.86	CH4
CO2(g)	-3.56	-5.03	-1.47	CO2
H2(g)	-10.95	-14.10	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-8.11	-6.53	1.58	NaCl
O2(g)	-61.29	-64.19	-2.89	O2
Otavite	1.53	-12.17	-13.70	CdCO3

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

**Cadmium stability-phreeqc pH8, Ca 40 mg/l.**

-----  
Reading input data for simulation 1.  
-----

DATABASE C:\Lab work.1\phreeqc.22.04.09.txt

SOLUTION 1

temp 25  
pH 8  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Na 0.327  
C(4) 0.327  
Ca 1  
Cl 2  
water 1 # kg

SOLUTION 2

temp 25  
pH 1.5  
pe 4  
redox pe  
units mmol/kgw  
density 1  
Cd 8.896  
Cl 17.79  
water 1 # kg

MIX 1

1 0.9999  
2 0.0001

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

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	7.802e-007	7.323e-007	-6.108	-6.135	-0.028
H+	1.448e-008	1.367e-008	-7.839	-7.864	-0.025
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	0.000e+000				
CH4	0.000e+000	0.000e+000	-121.386	-121.385	0.000
C(4)	3.270e-004				
HCO3-	3.122e-004	2.936e-004	-3.506	-3.532	-0.027
CO2	9.018e-006	9.025e-006	-5.045	-5.045	0.000
CaHCO3+	3.102e-006	2.917e-006	-5.508	-5.535	-0.027
CaCO3	1.317e-006	1.318e-006	-5.881	-5.880	0.000
CO3-2	1.287e-006	1.007e-006	-5.890	-5.997	-0.106
NaHCO3	5.068e-008	5.072e-008	-7.295	-7.295	0.000
NaCO3-	6.135e-009	5.762e-009	-8.212	-8.239	-0.027
CdHCO3+	5.884e-009	5.526e-009	-8.230	-8.258	-0.027
CdCO3	4.759e-010	4.762e-010	-9.323	-9.322	0.000
Cd(CO3)2-2	1.949e-012	1.517e-012	-11.710	-11.819	-0.109
Ca	9.999e-004				
Ca+2	9.955e-004	7.787e-004	-3.002	-3.109	-0.107
CaHCO3+	3.102e-006	2.917e-006	-5.508	-5.535	-0.027
CaCO3	1.317e-006	1.318e-006	-5.881	-5.880	0.000
CaOH+	1.006e-008	9.453e-009	-7.997	-8.024	-0.027
Cd	8.896e-007				

Cd+2	7.648e-007	5.952e-007	-6.116	-6.225	-0.109
CdCl+	1.137e-007	1.068e-007	-6.944	-6.971	-0.027
CdHCO3+	5.884e-009	5.526e-009	-8.230	-8.258	-0.027
CdOH+	3.855e-009	3.621e-009	-8.414	-8.441	-0.027
CdCl2	8.358e-010	8.364e-010	-9.078	-9.078	0.000
CdCO3	4.759e-010	4.762e-010	-9.323	-9.322	0.000
Cd(OH)2	1.421e-011	1.422e-011	-10.847	-10.847	0.000
Cd(CO3)2-2	1.949e-012	1.517e-012	-11.710	-11.819	-0.109
CdCl3-	1.056e-012	9.915e-013	-11.976	-12.004	-0.027
CdCl4-2	4.776e-016	3.717e-016	-15.321	-15.430	-0.109
Cd(OH)3-	1.243e-016	1.167e-016	-15.906	-15.933	-0.027
Cd(OH)4-2	9.780e-023	7.611e-023	-22.010	-22.119	-0.109
Cl	2.002e-003				
Cl-	2.001e-003	1.879e-003	-2.699	-2.726	-0.027
CdCl+	1.137e-007	1.068e-007	-6.944	-6.971	-0.027
CdCl2	8.358e-010	8.364e-010	-9.078	-9.078	0.000
CdCl3-	1.056e-012	9.915e-013	-11.976	-12.004	-0.027
CdCl4-2	4.776e-016	3.717e-016	-15.321	-15.430	-0.109
H(0)	9.288e-039				
H2	4.644e-039	4.648e-039	-38.333	-38.333	0.000
Na	3.270e-004				
Na+	3.269e-004	3.072e-004	-3.486	-3.513	-0.027
NaHCO3	5.068e-008	5.072e-008	-7.295	-7.295	0.000
NaCO3-	6.135e-009	5.762e-009	-8.212	-8.239	-0.027
NaOH	1.483e-010	1.485e-010	-9.829	-9.828	0.000
O(0)	3.856e-016				
O2	1.928e-016	1.930e-016	-15.715	-15.715	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-0.77	-9.11	-8.34	CaCO3
Calcite	-0.63	-9.11	-8.48	CaCO3
Cd(OH)2	-4.15	9.50	13.65	Cd(OH)2
CH4(g)	-118.53	-121.39	-2.86	CH4
CO2(g)	-3.58	-5.04	-1.47	CO2
H2(g)	-35.18	-38.33	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.82	-6.24	1.58	NaCl
O2(g)	-12.82	-15.71	-2.89	O2
Otavite	1.48	-12.22	-13.70	CdCO3

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

# **Cadmium stability-pH8, Ca 60 mg/l.**

Reading input data for simulation 1.

-----  
 DATABASE C:\Lab work.1\phreeqc.22.04.09.txt  
 SOLUTION 1  
     temp        25  
     pH          8

```

pe      4
redox   pe
units   mmol/kgw
density 1
Na       0.327
C(4)     0.327
Ca       1.5
Cl       3
water   1 # kg
SOLUTION 2
temp     25
pH       1.5
pe      4
redox    pe
units    mmol/kgw
density  1
Cd       8.896
Cl       17.79
water    1 # kg
MIX 1
1      0.9999
2      0.0001

```

-----Distribution of species-----					
Species	Molality	Activity	Log Molality	Log Activity	Log Gamma
OH-	8.009e-007	7.428e-007	-6.096	-6.129	-0.033
H+	1.442e-008	1.348e-008	-7.841	-7.870	-0.029
H2O	5.551e+001	9.999e-001	1.744	-0.000	0.000
C(-4)	3.027e-028				
CH4	3.027e-028	3.031e-028	-27.519	-27.518	0.000
C(4)	3.270e-004				
HCO3-	3.105e-004	2.888e-004	-3.508	-3.539	-0.031
CO2	8.742e-006	8.752e-006	-5.058	-5.058	0.000
CaHCO3+	4.426e-006	4.117e-006	-5.354	-5.385	-0.031
CaCO3	1.884e-006	1.886e-006	-5.725	-5.724	0.000
CO3-2	1.343e-006	1.005e-006	-5.872	-5.998	-0.126
NaHCO3	4.927e-008	4.932e-008	-7.307	-7.307	0.000
NaCO3-	6.122e-009	5.683e-009	-8.213	-8.245	-0.032
CdHCO3+	5.294e-009	4.914e-009	-8.276	-8.309	-0.032
CdCO3	4.291e-010	4.295e-010	-9.367	-9.367	0.000
Cd(CO3)2-2	1.838e-012	1.365e-012	-11.736	-11.865	-0.129
Ca	1.500e-003				
Ca+2	1.494e-003	1.117e-003	-2.826	-2.952	-0.126
CaHCO3+	4.426e-006	4.117e-006	-5.354	-5.385	-0.031
CaCO3	1.884e-006	1.886e-006	-5.725	-5.724	0.000
CaOH+	1.482e-008	1.376e-008	-7.829	-7.862	-0.032
Cd	8.896e-007				
Cd+2	7.245e-007	5.381e-007	-6.140	-6.269	-0.129
CdCl+	1.541e-007	1.430e-007	-6.812	-6.845	-0.032
CdHCO3+	5.294e-009	4.914e-009	-8.276	-8.309	-0.032
CdOH+	3.577e-009	3.321e-009	-8.446	-8.479	-0.032
CdCl2	1.658e-009	1.660e-009	-8.780	-8.780	0.000
CdCO3	4.291e-010	4.295e-010	-9.367	-9.367	0.000

	Cd(OH) 2	1.322e-011	1.323e-011	-10.879	-10.878	0.000
	CdCl3-	3.141e-012	2.916e-012	-11.503	-11.535	-0.032
	Cd(CO3) 2-2	1.838e-012	1.365e-012	-11.736	-11.865	-0.129
	CdCl4-2	2.181e-015	1.620e-015	-14.661	-14.791	-0.129
	Cd(OH) 3-	1.187e-016	1.101e-016	-15.926	-15.958	-0.032
	Cd(OH) 4-2	9.808e-023	7.284e-023	-22.008	-22.138	-0.129
Cl	3.001e-003					
	Cl-	3.001e-003	2.784e-003	-2.523	-2.555	-0.033
	CdCl+	1.541e-007	1.430e-007	-6.812	-6.845	-0.032
	CdCl2	1.658e-009	1.660e-009	-8.780	-8.780	0.000
	CdCl3-	3.141e-012	2.916e-012	-11.503	-11.535	-0.032
	CdCl4-2	2.181e-015	1.620e-015	-14.661	-14.791	-0.129
H(0)	2.740e-015					
	H2	1.370e-015	1.372e-015	-14.863	-14.863	0.000
Na	3.270e-004					
	Na+	3.269e-004	3.037e-004	-3.486	-3.518	-0.032
	NaHCO3	4.927e-008	4.932e-008	-7.307	-7.307	0.000
	NaCO3-	6.122e-009	5.683e-009	-8.213	-8.245	-0.032
	NaOH	1.487e-010	1.489e-010	-9.828	-9.827	0.000
O(0)	0.000e+000					
	O2	0.000e+000	0.000e+000	-62.655	-62.655	0.000

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

Phase	SI	log IAP	log KT	
Aragonite	-0.61	-8.95	-8.34	CaCO3
Calcite	-0.47	-8.95	-8.48	CaCO3
Cd(OH) 2	-4.18	9.47	13.65	Cd(OH) 2
CH4(g)	-24.66	-27.52	-2.86	CH4
CO2(g)	-3.59	-5.06	-1.47	CO2
H2(g)	-11.71	-14.86	-3.15	H2
H2O(g)	-1.51	-0.00	1.51	H2O
Halite	-7.65	-6.07	1.58	NaCl
O2(g)	-59.76	-62.65	-2.89	O2
Otavite	1.43	-12.27	-13.70	CdCO3

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

## Appendix D: Adsorption of copper

### Appendix D1: Adsorption of Cu on IOCS

**Table D1:1 Adsorption of Cu on IOCS at pH=6±0.2(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L).**

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	4	4	4
2	2	2.12	2.24
4	1.84	1.84	1.84
6	1.7	1.6	1.6
24	1	1.04	1.2

**Table D1:2 Adsorption of Cu on IOCS at pH=7±0.2(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L).**

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	4	4	4
2	1.07	1.08	0.88
4	0.8	0.83	0.8
6	0.6	0.6	0.6
24	0.41	0.4	0.43

**Table D1:3 Adsorption of Cu on IOCS at pH=8±0.2(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cu (II) concentration = 4 mg/l. IOCS = 0.1 g/L).**

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	4	4	4
2	0.33	0.11	0.52
4	0.19	0.07	0.43
6	0.1	0.07	0.4
24	0.09	0.05	0.18

#### Appendix D2: Adsorption of Cu on GFH

**Table D2:1 Adsorption of Cu on GFH at pH=6±0.2(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L).**

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	4	4	4
2	3.92	3.64	3.84
4	3.9	3.6	3.8
6	3.9	3.6	3.8
24	3.9	3.4	3.8

**Table D2:2 Adsorption of Cu on GFH at pH=7±0.2(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L).**

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	4	4	4
2	2.4	2.6	2.52
4	2	2.2	2.5
6	2	2.1	2.4
24	0.96	1.16	1.28

**Table D2:3 Adsorption of Cu on GFH at pH=8±0.2(Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup>(20 mg/l) and initial Cu (II) concentration = 4 mg/l. GFH = 0.1 g/L).**

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	4	4	4
2	1.28	1.88	1.24
4	1.3	1.8	1.2
6	1.1	1.6	1
24	0.56	0.9	0.36

## Appendix E: Adsorption of cadmium

**Table E1:1 Adsorption of Cd on IOCS at pH=6±0.2 (Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup> (20 mg/l) and initial Cd (II) concentration = 100 µg/l. IOCS = 0.1 g/L).**

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	100	100	100
2	42	54.75	58.5
4	40	50	56
6	40	50	56
24	22	32.25	43

**Table E1:2 Adsorption of Cd on IOCS at pH=7±0.2 (Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup> (20 mg/l) and initial Cd (II) concentration = 100 µg/l. IOCS = 0.1 g/L).**

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	100	100	100
2	28.25	33	44.25
4	28.5	29	40
6	25.5	27.75	36
24	16.75	19.5	27.75

**Table E1:3 Adsorption of Cd on IOCS at pH=8±0.2 (Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup> (20 mg/l) and initial Cd (II) concentration = 100 µg/l. IOCS = 0.1 g/L).**

Time (hour)	Ca <sup>2+</sup> (20 mg/l)	Ca <sup>2+</sup> (40 mg/l)	Ca <sup>2+</sup> (60 mg/l)
0	100	100	100
2	24.75	31	36.25
4	20	30	34
6	20	28	33
24	9.75	15	19

**Table E1: 4 Heavy metal removal kinetics in batch adsorption experiment of cadmium without IOCS and with varying dose of IOCS, initial pH=8±0.2 and grain size < 63 µm, Ca<sup>2+</sup>=20 mg/l, Cd(II)=2.8mg/l and contact time of 140 hrs.**

Dose of IOCS (g/l)	0 hrs	20 hrs	40 hrs	60 hrs	100 hrs	140 hrs	Removal %
	C <sub>0</sub> (mg/l)	C <sub>e</sub> (mg/l)	C <sub>e</sub> (mg/l)	C <sub>e</sub> (mg/l)	C <sub>e</sub> (mg/l)	C <sub>e</sub> (mg/l)	
0	2.8	2.6	2.6	2.6	2.6	2.6	7.14
0.1	2.8	0.8	0.7	0.6	0.5	0.5	80.76
0.2	2.8	0.6	0.3	0.2	0.2	0.2	92.3
0.4	2.8	0.2	0.1	0.1	0.1	0.1	96.15
0.8	2.8	0.1	0.08	0.08	0.08	0.08	96.92
0.9	2.8	0.06	0.03	0.02	0.02	0.02	99.23

**Appendix E2: Adsorption of Cd on GFH****Table E2:1 Adsorption of Cd on GFH at pH=6±0.2 (Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup> (20 mg/l) and initial Cd (II) concentration = 100 µg/l. GFH = 0.1 g/L).**

Time (hour)	Ca2+ (20 mg/l)	Ca2+ (40 mg/l)	Ca2+ (60 mg/l)
0	100	100	100
2	100	99	95
4	100	99	95
6	100	99	95
24	100	99	95

**Table E2:2 Adsorption of Cd on GFH at pH=7±0.2 (Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup> (20 mg/l) and initial Cd (II) concentration = 100 µg/l. GFH = 0.1 g/L).**

Time (hour)	Ca2+ (20 mg/l)	Ca2+ (40 mg/l)	Ca2+ (60 mg/l)
0	100	100	100
2	70.75	90.5	83.5
4	70	89	82
6	70	89	80
24	70	85	71

**Table E2:3 Adsorption of Cd on GFH at pH=8±0.2 (Model water: demineralized water with Ca<sup>2+</sup> (20, 40 and 60 mg/l), HCO<sub>3</sub><sup>-</sup> (20 mg/l) and initial Cd (II) concentration = 100 µg/l. GFH = 0.1 g/L).**

Time (hour)	Ca2+ (20 mg/l)	Ca2+ (40 mg/l)	Ca2+ (60 mg/l)
0	100	100	100
2	80.25	69.5	87.75
4	75	69	85
6	75	67	85
24	69.5	64	81