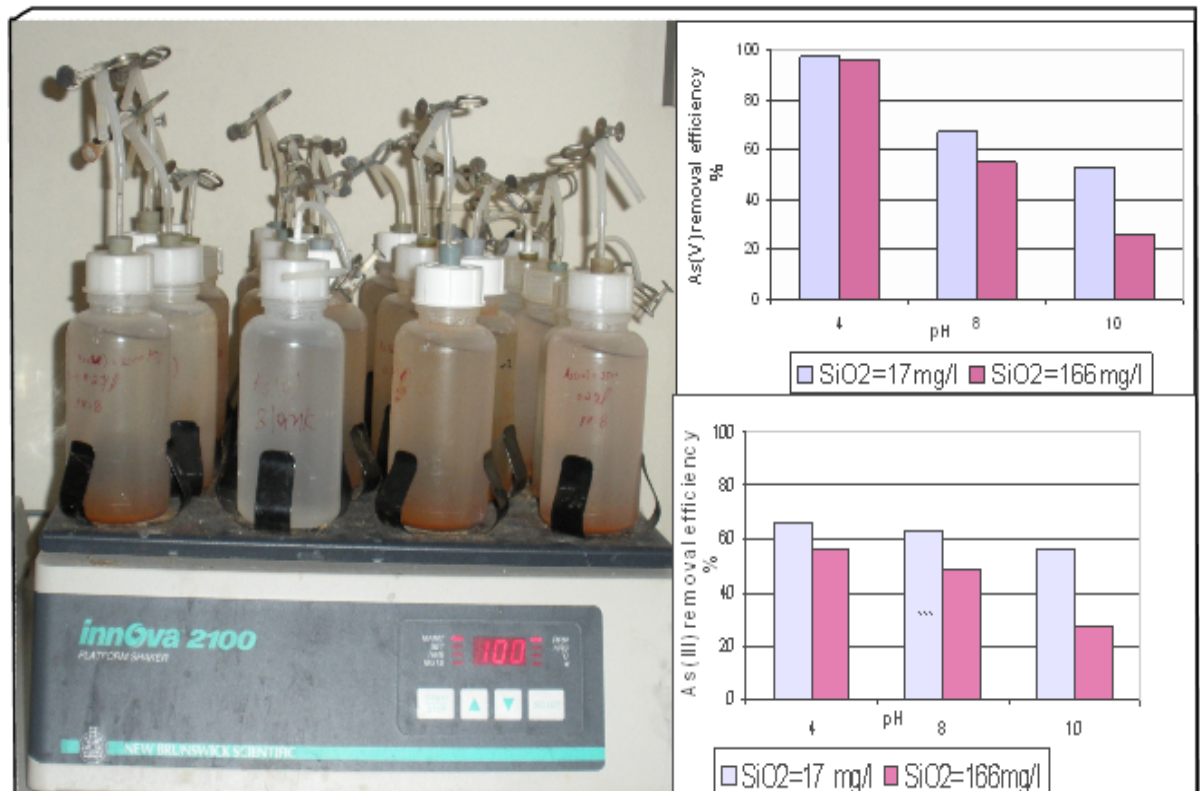


UNESCO-IHE INSTITUTE FOR WATER EDUCATION



Effect of Silica and pH on Arsenic Removal by Iron-Oxide Coated Sand

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Effect of Silica and pH on Arsenic Removal by Iron-Oxide Coated Sand

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

Abstract

Arsenic in drinking water is a global problem affecting many countries distributed overall five continents. The presence of arsenic in drinking water has serious adverse effects on human health. Symptoms of acute arsenic poisoning include: vomiting, diarrhea, muscle cramps, heart problems, and poor appetite. Long-term exposure to low arsenic concentration in drinking water is associated with human carcinogen risks like skin cancer and several internal cancers. The only way to avoid the toxicity of arsenic from drinking water is to use arsenic-free water source or to remove the arsenic from drinking water

A number of arsenic removal technologies from drinking water have been made available for removal of arsenic present in ground water. Some of these technologies are enhanced coagulation, lime softening, reverse osmosis, nanofiltration, in-site sub-surface arsenic removal, and adsorption by iron-oxide coated composites. The adapted arsenic removal technology should preferably remove the arsenic effectively, efficiently, cheaply, with suitability for central and point of use, and should be simple to use. Iron oxide-coated sand (IOCS) is one of arsenic adsorbents introduced by IHE that show high removal efficiency of arsenic. Arsenic removal technology based on use of IOCS is cheap, and it is suitable for both centralized and point of use applications. The removal of arsenic by IOCS is, however, strongly affected by composition of ground water. Among other compounds presence of silica in ground water depend on pH could cause reduction of arsenic adsorption capacity of IOCS.

The objective of this study is to assess the effect of silica and pH on arsenic removal by IOCS. Effect of silica and pH on arsenic adsorption on IOCs was investigated in batch adsorption experiments. This research presents detailed results, related discussion of results from experiments conducted to study effects of silica and pH on arsenic removal by IOCS. In addition a conceptual model describing effect of silica on arsenic adsorption on IOCS is proposed.

The chemistry of dissolved silica is very complex. Silica in water exists in the form of monomers, polymers, as colloidal and soluble silicate. Silica in all forms can adsorb on IOCS. The adsorption affinity of silica to IOCS increased with increased the pH of the water. The presence of silica in water affects the adsorption of arsenic on IOCS, the effect depends on silica concentration and pH of the water.

The study results show that the removal efficiency of As(V) and As(III) in the presence of silica decreased with increasing levels of silica and increasing pH of the model water. As a consequence of an increase of silica concentration from 4.5 to 33 mg/l at pH 8, the removal efficiency of As(V) and As(III) decreases by 40% and 20%, respectively. In silica (17mg/l) containing model water, removal efficiency of As(III) decreased by 10% and As(V) by 44% with pH increase from 4 to 10.

When designing arsenic removal process based on adsorption on IOCS, effect of silica and pH should be considered. The removal efficiency of arsenic in the presence of silica by IOCS decrease with increase pH level of the model water. The removal of arsenic from the water that contains high silica concentration could increase by decreasing pH level of the water.

Key words: Arsenic, adsorption, adsorption isotherm, IOCS, silica, pH

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Acronyms

IOCS	Iron oxide-coated sand
As	Arsenic
As(III)	Arsenite
As(V)	Arsenate
Fe	Iron
Si	Silicon
SiO ₂	Silica
AAs-GF	Atomic adsorption spectrometer perklin Elmer 200 with furnace
ICP	Inductively coupled plasma perklin Elmer 3000
AAS- flame	Atomic adsorption spectrometer perklin Elmer 200 with flame
μm	Micrometer

Chapter 1-INTRODUCTION

1.1 Background

Many countries in the world use ground water as a source of drinking water. About 2 billion people in the world use drinking water produced from ground water. Ground water has generally good quality and is safe compared to surface water. However, ground water is occasionally naturally contaminated with Fe, Mn, As and other impurities. Anthropogenic activities could introduce pesticides, nitrites, arsenic and other impurities. The presence of contaminants in the ground water has an adverse effect on health and on the aesthetic value of drinking water. Arsenic is one of the known toxic elements found in ground water in many parts of the world (Petrusevski et al, 2007).

Arsenic is a metalloid chemical element found in rocks, the atmosphere, soil, natural organisms, and waters distributed in many parts of the earth's crust. The presence of arsenic in ground water is due to the geological composition of soils and rocks and arsenic is introduced to ground water through the dissolution of minerals. Arsenic in drinking water is a global problem affecting many countries distributed over the entire world (Mirna et al, 2007).

Arsenic in ground water is found in organic and inorganic forms. The organic form of arsenic is found in combination with carbon, oxygen, and nitrogen, while the inorganic form is present in pyrite sulphide. The inorganic form of arsenic is widely distributed and is more toxic than the organic form. The two common form of arsenic in ground water are As(III) and As(V). The pentavalent arsenate species are AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- and the trivalent arsenites include $\text{As}(\text{OH})_3$, $\text{As}(\text{OH})_4^-$, $\text{As}(\text{OH})_2^-$ and AsO_3^- . Arsenate species predominate and are stable in oxygen rich aerobic while arsenites predominate in moderately reducing anaerobic ground water (Mohan et al, 2007).

The toxicity of arsenic at high concentration has been known for centuries. However the presented arsenic is difficult to establish, because it cannot be detected by odour or taste, and has no visible appearance in the water (Petrusevski et al, 2007). Acute arsenic poisoning causes vomiting, oesophageal and abdominal pain, and bloody "rice water" diarrhoea. The long-term exposure to arsenic in drinking water causes skin, lung, bladder, and kidney cancers, pigmentation changes, and skin thickening (hyperkeratosis), neurological disorder muscular weakness, loss of appetite and nausea (Mohan et al, 2007).

The presence of arsenic in drinking water has serious adverse effects on human health and other living organisms. Arsenic in drinking water is a global problem occurring in many countries around the world. The issue concerning arsenic presence in drinking water will increase in coming years. Arsenic contamination of ground water will be found in the near future in many parts of the world including Central and Eastern Europe and the developing world (Petrusevski et al, 2007)

The only ways to avoid the toxicity of arsenic present in drinking water is to use arsenic-free water source or to remove the arsenic from drinking water. The World Health Organization (WHO) guideline for acceptable arsenic concentration in drinking water is 10 μ l (WHO,

2006). Nevertheless in many parts of the world the concentration of arsenic is greater still than the WHO guideline. Many people living in West Bengal, India, and East Bangladesh were diagnosed with arsenic poisoning from arsenic present in water and food. Many of them are seriously and irreversibly ill from various maladies. In Bangladesh about 10-20 million people are considered to be at risk unless an alternative way of supplying arsenic free water is provided (Siegel, 2002).

There are many techniques for arsenic removal from drinking water. Among these techniques are enhanced coagulation, lime softening, reverse osmosis, nano filtration, in-situ sub-surface arsenic removal, adsorption by activated alumina, ion exchange, and adsorption by iron oxide coated sand, granular ferric hydroxide and other adsorbents (Petrusevski et al, 2008). The choice of an appropriate arsenic removal technique depends on the removal effectiveness, efficiency, cost, suitability for central and point of use, and simplicity of technique.

The IHE Arsenic removal technology based on arsenic adsorption on iron-oxide coated sand (IOCS) or other iron oxide coated filter materials, shows high efficiency for removal of both As(III) and As(V), and is suitable for centralized and point of use applications. The adsorbent used for arsenic removal is a by-product of the drinking water industry. The IHE arsenic removal family filter technique does not require electricity or chemicals, and therefore is simple and affordable for rural communities and very cheap compared to other techniques.

1.2 Problem identification

This study is a part of ongoing research being carried out by UNESCO-IHE staff and participants to further optimize performance of arsenic removal by IOCS. The removal of As(III) and As(V) by IOCS is strongly affected by ground water quality. A lot of the research was carried out using model water in single ion systems. However, in natural groundwaters arsenic is always accompanied by other (multi) ions. The presence of other compounds like silica, phosphate, calcium, and sulphate in ground water could cause a reduction of arsenic adsorption capacity of IOCS. Moreover, arsenic adsorption capacity of IOCS could be affected by pH of the water.

It is very important to understand the silica interference on arsenic adsorption on IOCS, since the economy of adsorptive arsenic removal can be significantly affected by silica presence in water to be treated. The concentration of silica in ground water can vary in wide ranges from 5-50 mg/l and could be as high as 100mg/l. Similarly the pH of ground water ranges from 5.5-8.5. It has been found adsorption capacity of IOCS could be strongly affected by silica concentration and pH of water. pH is one of the most important controls on adsorption of As(III), As(V) and silica. pH has a major influence on aqueous arsenic speciation, silica speciation and on the composition of surface functional groups. At pH values less than point zero charge of an adsorbent (solid), the net charge becomes positive and facilitates adsorption of anions. Limited research has been done on the effect of silica and pH on arsenic removal by other commercial adsorbents, but no research was done with IOCS. Therefore, research is needed to better understand the effect of silica and pH on arsenic adsorption by IOCS.

1.3 Research Goal and Objectives

The goal of this study was to analyse the effect of silica and pH on the removal of As(III) and As(V) by IOCS.

The specific objectives of the research:

- To analyse the chemical composition of IOCS including possible presence of silica in the IOCS coating
- To screen the effect of pH on As(III) and As(V) adsorption by IOCS
- To establish adsorption isotherms for As(III) and As(V) adsorption on IOCS for a few pH values selected based on screening experiments
- To screen the effect of silica concentration and form in which silica is present on As(III) and As(V) adsorption efficiency by IOCS
- To establish adsorption isotherms for As(III) and As(V) adsorption on IOCS for different silica concentrations selected based on screening experiments
- To propose a conceptual model that will explain the effect of pH and silica on arsenic adsorption of IOCS.

Chapter 2 - Literature review

2.1 The source and release of arsenic in ground water

Arsenic is a semi-metallic element and ranks 20th in natural abundance of the earth crust. It consists of about 0.0005% of the earth's crust. The concentration of arsenic in most rock ranges from 0.5 to 2.5 g/kg and higher concentration are found in finer grained argillaceous sediments and phosphate (Mohan et al, 2007).

Arsenic is released to ground water under natural conditions by weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities like mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants additional inputs (Mohan et al, 2007). Understanding of arsenic release into the ground water helps to identify the safe drinking water resources and to evaluate treatment methods to apply for contaminated waters. Arsenic in ground water significantly increases due to human activities, the use of ground water for the agriculture activities in West Bengal, India and east Bangladesh increases arsenic concentration in ground water. This is due to increasing agricultural activities in the area. Seasonal withdrawal of high amounts of water lowers the ground water table and aerated the strata comprising the aquifer which were not exposed to oxidation before the water demand increased in the area. The strata aerated which contain arsenian pyrite (FeS_2 , containing arsenic in trace to atom percent levels), decomposition of the arsenian pyrite released arsenic into the aquifer (Siegel, 2002).

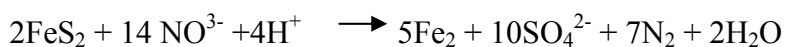
The release of arsenic via sulphide oxide, arsenian pyrite oxidation, can follow several reaction pathways.

The first is the chemical oxidation of pyrite by oxygen.

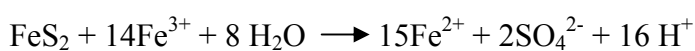
The first is the chemical oxidation of arsenian pyrite by oxygen.



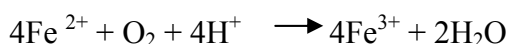
The second possible pathway is the oxidation of arsenian pyrite by nitrate



Pyrite can also be oxidized by Fe(III)



Fe(III) is regenerated by oxidation of Fe(II)



The majority of Fe (III) that bearing arsenic in waters that having near neutral pH existed in solid or colloidal phase. The colloidal forms that bearing arsenic cause transports or release to aquifer (Welch, 2003).

Arsenic releases to the ground water from the arsenic bearing rocks. The mechanisms of arsenic releasing from sediment into ground water in Bangladesh explained by Appelo (2005). The release of arsenic to the ground water due to reduction, oxidation, and displacement of arsenic bearing iron shows below.

1.Reduction of Fe (OH)₃

The reduction of iron (III) to iron (II) releases arsenic to the aquifer

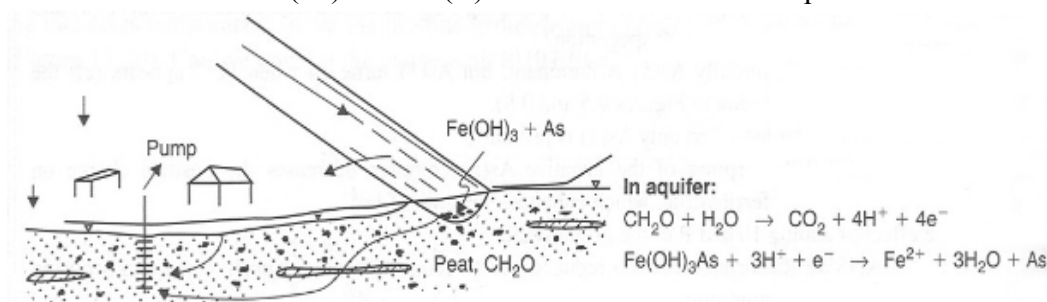


Figure 2-1 Iron-oxyhydroxide is reduced by organic matter causing As releases

2.Oxidation of pyrite in unsaturated zone Fes

Aerating of pyrite decomposes and the arsenic removes

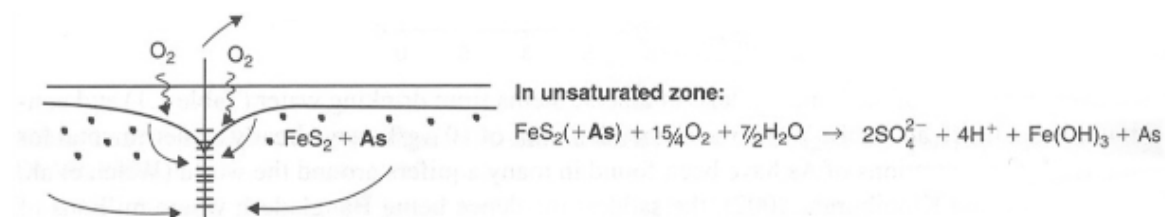


Figure 2-2 Ground water drawdown facilitates access of oxygen to arsenian pyrite.

3. Displacement of arsenic by HCO₃⁻

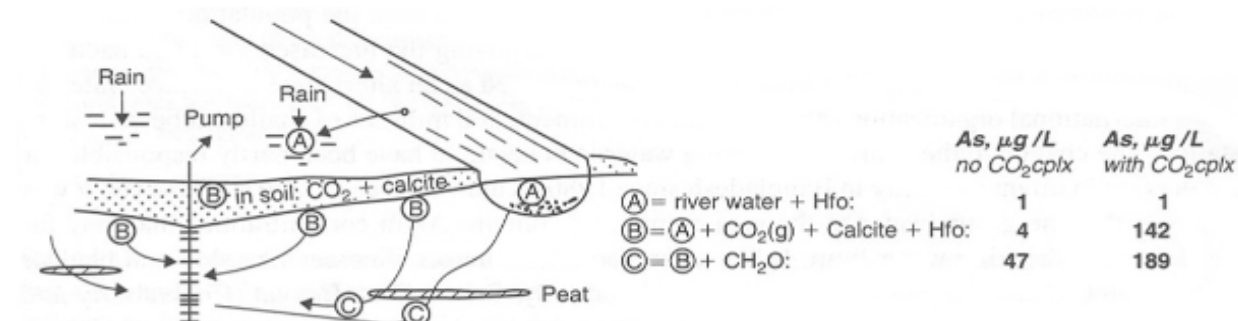


Figure 2-3 Change in HCO₃⁻ concentration displaces As from iron-oxyhydroxide

Arsenic is found in ground water in many parts of the world such as in south east Asia: Bangladesh, Vietnam, West Bengal-India, Nepal, Cambodia, Mongolia, China, Thailand, Pakistan, and Taiwan; in central and south America: Mexico, Chile and Argentina, and in North America (USA and Canada), in Australia, and in Europe: Finland, Hungary, Germany, Croatia, Romania, Italy, Spain and Greece (Biterna et al, 2007). The shaded part in figure 2-4 shows the distribution of Arsenic over the world.



Figure 2-4: The distribution of Arsenic over the world.
(Petrusevski et al, 2007)

2.2 Chemistry and occurrence of arsenic in ground water

Arsenic in natural ground water is mainly found in the inorganic form. Arsenic exists in the oxidation states of -3, 0, -3 and 5. The common arsenic species in ground water occurs in inorganic form as As(V) and As(III). Understanding of arsenic speciation in water is important in determining the extent of As(III) and As(V) reactions in solid phase. The most common forms of arsenic in ground water are H_2AsO_4^- , HAsO_4^{2-} , H_3AsO_3 and H_2As_3^- depending on redox potential and pH of water (Mirna et al, 2007).

The normal arsenic concentration in ground water is $1\text{--}2\mu\text{g/l}$, and extremely high concentrations of arsenic about $15,000\mu\text{g/l}$ were detected in domestic wells, monitoring wells, and public supply wells in USA. Arsenite and Arsenate both in water form protonated oxyanions in aqueous solutions the degree of formation depend on pH. arsenite and arsenate. Arsenite and Arsenate are stable in moderately reducing and oxidizing environments respectively (Welch, 2003).

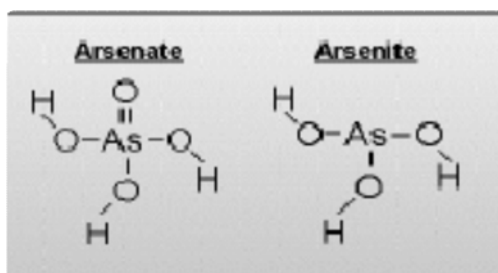


Figure 2-5 Common Species of Arsenic in Ground water
(Petrusevski et al, 2008)

Arsenite species are dominant over a wide range of pH, because it adsorbs weaker and much more soluble than arsenate. The predominate As(V) species in ground water is H_2AsO_4^- between pH 2.2 and 6.9, and HAsO_4^{2-} between pH 6.9 and 11.5. As(III) species H_3AsO_3^0 is predominates up to pH 9.2, while H_2AsO_3^- is predominant from pH 9.2 to 12 (Welch, 2003).

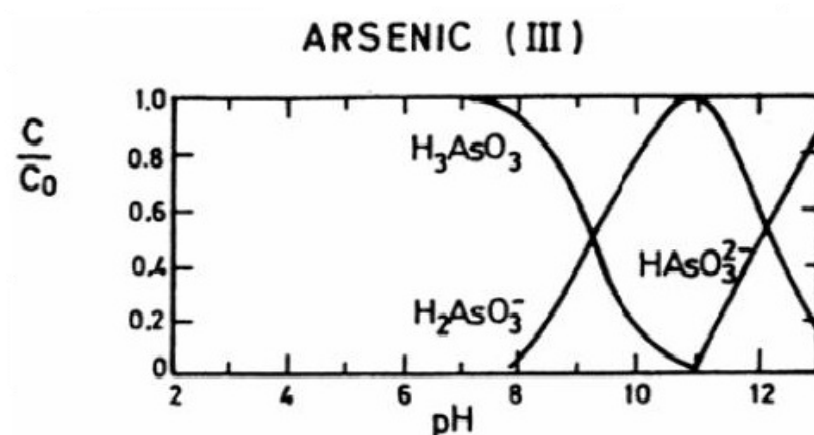


Figure2-6 The stability and dominant As(III) species at different pH levels

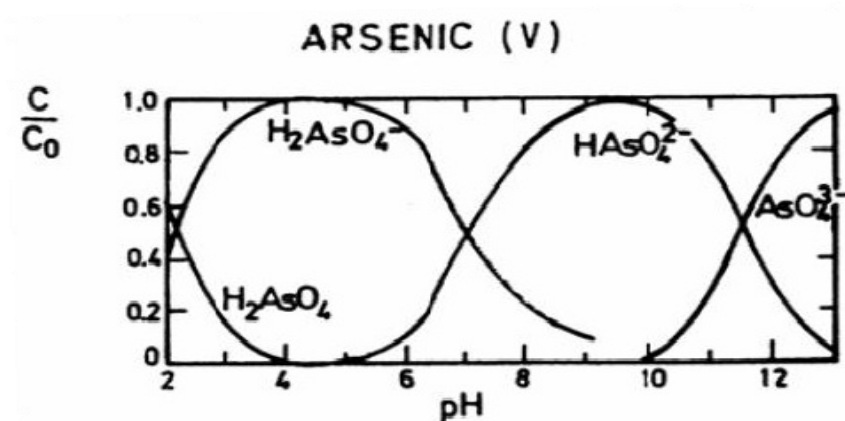


Figure 2-7 The stability and dominant As(V) species at different pH levels
(Mirna et al, 2007).

2.3 Health effect

Arsenic is an acute toxic compound that affects humans and all life. It has no test, smell and is not visible in water. People take arsenic by drinking; cooking with arsenic contaminated water, and by eating food grown in area with arsenic contaminated ground water. Arsenic-containing water does not negatively affect human health through hand-washing, bathing, and laundry (WHO, 1999).

The toxicity of arsenic in water depends on the form, type of compound, and concentration in water. The presence of inorganic arsenic is more toxic than organic arsenic.

The chronic exposure of arsenic to human being could cause several carcinogen risks like skin cancer and internal cancers such as: lungs, urinary bladder and others. It might follow some steps to develop the diseases, the first symptoms exposure to long term arsenic concentration in drinking water is the hardening palms and soles called **keratosis**. It is abnormal black brown skin pigmentation. If intake arsenic continued causes skin depigmentation, palms and soles to thicken, and painful cracks to emerge; these symptoms are called **hyperkeratosis**. These lead to stop blood flowing, the flesh starts to decay inside the body and causing gangrene of the lower extremities. The symptoms caused by long term ingestion arsenic are called arsenicosis. The diseases have not universally described and it could take ten years to develop (Petrusevski et al, 2008).



Figure 2- 8 Hardening of the sole of the patient's feet (Keratosis)

Continual ingestion of arsenic in water can primary lead to problems of kidney and liver function, and then to harm of the internal organs like lungs, kidney, liver and bladder. It can disturb the peripheral vascular system leading to gangrene in the legs (Petrusevski et al, 2008).



Figure 2-9 The patient has lost his left limb due to development of gangrene caused by arsenic poisoning

The acute arsenic toxition affects are vomiting, diarrhoea, muscle cramps, heart complex, and poor appetite. Acute toxicity of arsenic can be measured by LD₅₀ (Lethal dose 50) and determined within 4 days (96 hours) of exposure to arsenic-containing drinking water. Arsenic in the form of Sodium Arsenite, Arsenic trioxide, Calcium Arsenate and Arsenobetane has an LD₅₀ of 15-40, 34, 20-80, and >10,000 mg/kg of body weight, respectively (Petrusevski et al, 2007). According to toxicology, arsenic in the form of Sodium Arsenite, and Arsenic Trioxide describes as “**very toxic**” (Buitmen, 2008).

Diseases caused by arsenic poisoning from drinking water can not be treated medically and the only prevention is providing arsenic-free drinking water (Petrusevski et al, 2007).

2.4 Arsenic removal technologies

Controls of arsenic releases from rocks to ground water are complex and difficult. Alternative arsenic free sources such as rain water and treated surface water could use for drinking and cooking. If not available, it must remove arsenic from the drinking water. There is several arsenic removal technologies from ground water adapted, all arsenic removal technologies almost based on a few basic chemical processes which are presented below (Johnston et al, 2001).

1. Oxidation/ reduction
2. Precipitation
3. Adsorption and ion exchange
4. Solid/liquid separation
5. Physical exclusion
6. Biological remove process

The arsenic removal technology should preferably remove the arsenic effectively, efficiently, cheaply, with suitability for central and point of use, and should be simple to use. For applying of technology the community should involve in all stages from selection to operation and maintenance. For choice of the technology a wide range of optional information is required. The arsenic removal technologies have their own advantages and disadvantages, the selected technologies are shown in table 2-1.

Table 2-1 Summary of advantages and disadvantages of arsenic removal technologies

Technology		Advantages	Disadvantages
Oxidation/precipitation		It is capable of successfully treating wide range for removal of A(V) contaminates to achieve standards	-It requires skilled operators - more cost for operation
Coagulation	Alum	High removal efficiency for As(III) and As(V)	-Effective in very narrow pH(5.5-6) - Toxic waste generation
	Iron	More efficient than alum on wet basis	--Medium removal of As(III) - Toxic waste generation
	Lime softening	Most common chemicals	-Readjustment of pH is needed - Toxic waste generation
Sorption and Ion-exchange Technologies	Activated alumna	-Relatively well-known -Commercially available	-Readjustment of pH is needed
	Iron coated sand	-Expected to be cheap	-Need to be standardized -Regeneration
	Ion exchange resin	-easily regenerated by flushing with concentrated salt solutions	-High cost medium and tech. O&M, -maximum capacity is about 315 mg As/g. - Can't remove As(III)
Membrane Technologies	Nano filtration	-Well defined performance and high removal efficiency	-High running costs -High investment costs
	Reverse osmosis	-No solid waste and less space requirement	-High tech O &M -Toxic wastewater
	Electro dialysis	-Capable of removal of other contaminants	-Readjustment of water quality is required -membrane does not withstand oxidizing agents -Low recovery



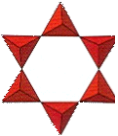

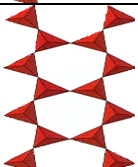
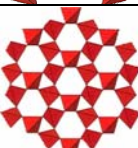
2.5. Silica

2.5.1 Introduction

The mineral silicates are the largest group of minerals, constituting more than 90% of the earth's crust distributed over the whole world. Silicates are the predominant minerals in igneous rocks and in most metamorphic and sedimentary rocks (Johnsen, 2002).

The basic arrangement of silicate structure is in tetrahedron (SiO_4). The silicon atom surrounded by four oxygen atom, the bond between silicon atom and oxygen is strong. Naturally silicates are classified in to six according to their arrangement (Table-2).

Table 2-2 Naturally silicate groups

Group	SiO_4 arrangement	The sil part of form	Example	Structure
1.Nesosilicates	-Isolated, no linked to other tetrahedra	Simple case SiO_4	Olivine, (Mg,Fe) 2SiO_4	
2.Sorosilicates	-Linked to form pairs by sharing one corner	Si_2O_7	hemimorphite, $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$	
3.Cyclosilicates	-Linked to form pairs by sharing one corner	Si_nO_{3n} (n is number tetrahedral in the ring)	Berly, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	
4.Inosilicates	-Form infinite chains	Si_2O_6	Diopside, $\text{CaMgSi}_2\text{O}_6$	
5.Phylosilicate	-Share corners with three others, thus forming infinite	Si_2O_5 ,	Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	
6.Tectosilicates	Share all four corners with others to form a three dimension framework	SiO_2	-Quartz, SiO_2 -Orthoclase, KAlSi_3O_8 (Al replacing one Si)	

Source: adapted from Johnsen (2002)

The most common elements in silicates are oxygen(O), silicon(Si), aluminium(Al), iron(Fe), calcium(Ca),sodium(Na), potassium(K), and magnesium(Mg). The source of silicate in ground water is by weathering of silicate rocks, amorphous silicate residues dissolved (Johnsen, 2002).

The sources of silicate in ground water are weathering and dissolution of silicate minerals from silicate rocks, amorphous silicate residues dissolved. Silica is found commonly in ground water; the typical concentration ranges are 5-50mg/l and the silica concentration could be as high as 100 mg/l. The soluble silica in ground water is mainly derived from dissolution of alumino-silicate rocks such as feldspars (Iler, 1979).

The chemistry of dissolved silicate is **complex** and **complicated** due to the conversion of monomeric to multimolecular polymeric and vice versa depending on the concentration of silica, pH, temperature and the presence of other cations.

2.5.2 Chemistry and occurrence of silica in ground water

Silica is the major component of the earth's solid surface and is referred to as silica (SiO_2) in all forms of its crystalline, amorphous, and hydrated or hydroxylated. The element silicon is the second abundant element in the earth's surface. Silica (SiO_2) includes for most beach sands, quartz, flint, and opal. The complex oxysilicates found with iron, aluminium, magnesium, and other metals refers for particularly known of all rocks, clays and soils. The most common form of silica in ground water is SiO_2 . Generally silica in water exists in the following three different forms:

1. Soluble (reactive, monomer),
2. Colloidal (polymer),
3. Suspended (granular, sand).

The reactive form is being that portion of the total dissolved silica that readily reacted with the standard molybdate colorimetric test. The colloidal and polymerize silica being that which not react with molybdate. The colloidal species is generally thought to be either silicon that has polymerized with multiple units of silicon dioxide, or silicon that has formed loose bonds with complex compounds usually forms with aluminium and calcium oxides structures (Iler, 1979). The concentration of monomer and polymer silica in the solution depends on pH and the amount present. With increasing the pH the amount of polymeric silica increases (Moller, 2008). Table 2-3 shows the concentration of monomer and polymer of silica at different pH levels.

Table 2-3 The polymer and monomeric silica concentration at different pH levels.

Silica dose(mg/l)	pH	Total Si(mg/l)	Monomeric Si(mg/l)	Polymeric Si(mg/l)
30	4.5	34	29.4	4.6
80	4.5	89.7	79.2	10.5
200	4.5	227	189	38
500	4.5	514	448	66
30	6.5	34	29.5	4.5
80	6.5	91.4	78.8	12.6
200	6.5	214	189	25
500	6.5	496	188	308
30	10	38.7	29.9	8.8
80	10	99.7	77.8	21.9
200	10	207	185	21.7
500	10	494	430	64.3
30	13	35.1	<0.2	35
80	13	94.2	75.1	19.1
200	13	202	192	9.6
500	13	482	436	45.5

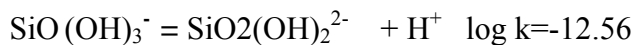
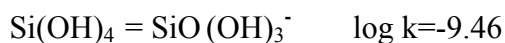
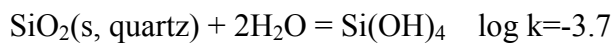
Source (Amy et al, 2005)

Silicon has four electrons in the outer energy level. Like carbon, silicon forms covalent bonds where electrons are shared with other atoms to achieve the energetically favourable eight-electron outer shell. The smaller carbon atom forms multiple bonds but the larger silicon atom forms only single bonds and, preferentially, with oxygen over hydrogen and other silicon atoms (Iler, 1979).

Solubility of silica

The dissolved silica in water is known as solubility of amorphous silica, the remaining silica polymerizing and tends to form a colloidal form in the solution. The dissolved silicate is capable of reacting more efficiently than polymerize silicates. The significant amount of silicate species found in water below pH 8 is silicic acid Si(OH)_4 . The silica reacting in water and the solubility is constant at 0.002 molar (Williams et al, 1999).

The solubility of silica in aqueous may be characterized by the following equilibrium



Where the equilibrium constants are for 25 °C.

The quartz solid form phase exist in solution is the most stable silica form in the solution. At the low temperature and pressure the kinetics of quartz formation are very slow, but the amorphous silica precipitates from supersaturated silica solution. The dissolved silica (Si(OH)_4) known as silicic acid, monosilicic acid, reactive silica, soluble silica, monomer, and hydrated silica(SiO_2).The solubility of silica refers to the amorphous silica. The solubility of silica in the solution can be affected by silica concentration, pH, temperature, the presence of catalytic species and residence times.

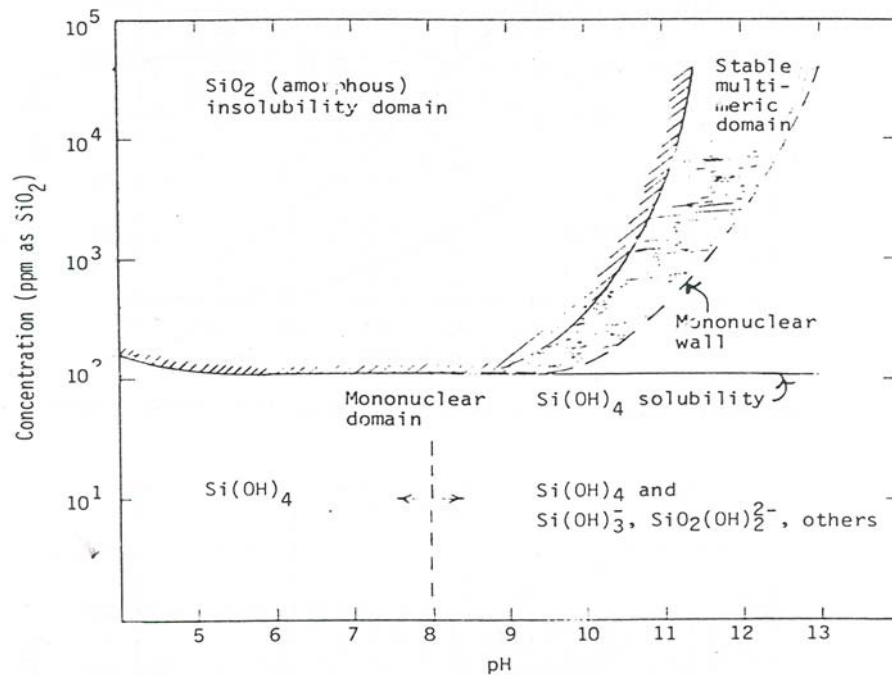


FIGURE 2-10 Amorphous silica species in equilibrium at different pH levels (25°C) (Micael C., 1981)

From the above figure 2-9 the upper shaded line represents the maximum soluble silica. The mononuclear wall indicates the lower monomeric silica concentration, below which the polynuclear species is not stable. The concentration of Si(OH)_4 is constant up to 8 pH, then the mononuclear negative charge silica species increases with increasing pH above pH 8. The above the solubility the supersaturating monomeric silica domains are the SiO_2 (amorphous) precipitates and the multimeric silica domain are the silicon polyanions both stable at stable. The common monomeric domain mononuclear silicon species of Si(OH)_4 , SiO(OH)_3^- and Si(OH)_2^{2-} (Micael C., 1981).

Effects of temperature on solubility of silica

Generally the solubility of SiO_2 increases with increasing of temperature; this can be expressed by the following equation

$$\text{Log}(\text{SiO}_2) = -0.599 - 588/T$$

Where T is given in $^{\circ}\text{K}$. The solubility of amorphous and quartz silica as function of temperature shows in figure 2-10.

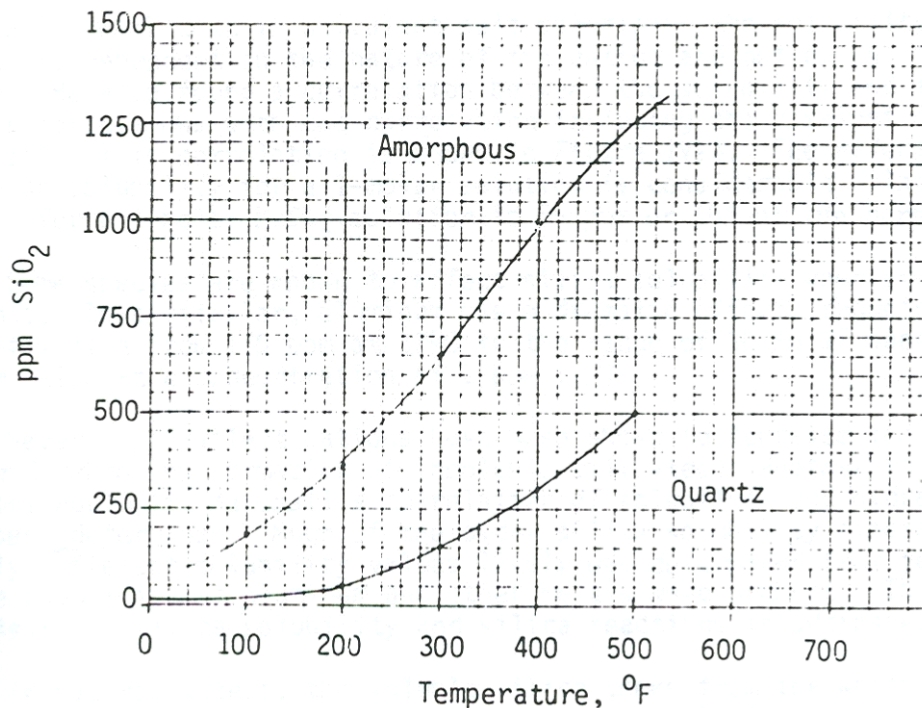
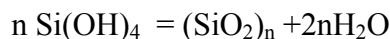


Figure 2-11 Solubility of silica as function of temperature (Micael C., 1981)

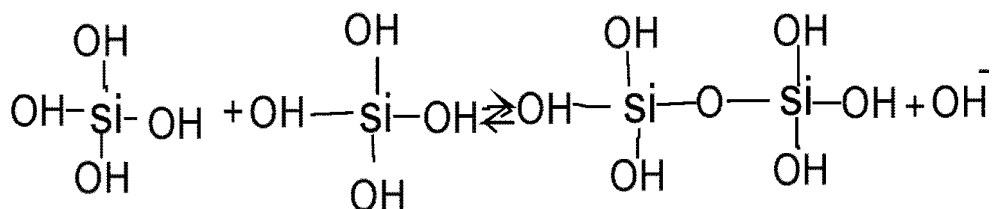
The figure shows the solubility of silica amorphous and quartz (ppm) verse temperature. Increasing temperature of the solution by a few degrees increased the solubility of silica. The increasing of temperature from 70 to 90 °F, the solubility of silica increases by around 10%.

Polymerization of silica

Polymerization of silica takes place in supersaturated silica solutions. The reaction is one of condensation.



The reaction takes place between an ionized silanol (SiOH) group and a unionized silnol group, as follows



The polymerization of silica is significantly occurs above pH 7, the particles growth continuously up to large diameter. Increasing the hydroxide (OH⁻) concentration will shift the reaction to the left. The reaction catalyzed by hydroxide ion with the reaction rate being first order in the hydroxide concentration from pH 2 to 7. Silicic acid is neutral at lower pH values and becomes negatively charged as ionization and forms extremely small and stops to grow above the size of 2-3nm (Iler, 1979). The first dissociation constant for silicic acid has a

pK value of 9.46 at 25°C, at this pH 50% of the acid is dissociated. At a pH of 8 around 3.5% is dissociated. When polymer grows the surface of silanol groups of a polymer have a higher acidity than the corresponding group in the monomer (Micael C., 1981).

The polymer grows to three or four linear silica (SiO_2) units, it takes on cyclic or ringed forms and eventually will crosslink internally, as well as grows in size by adding new monomer units. The bulk of the polymer part will have few silanol groups, whereas the surface will have many. The number of Si-O-Si bonds, or siloxane bridges, will be increased. The surface silanol groups of polymer silica have a higher acidity than the corresponding group in the monomer silica. Instead of a pK value of 9.46, the surface groups of the polymer have a pK value about (James J., 1970). The polymerization of silica from monomer to large particles and gels represented in figure (Iler, 1979).

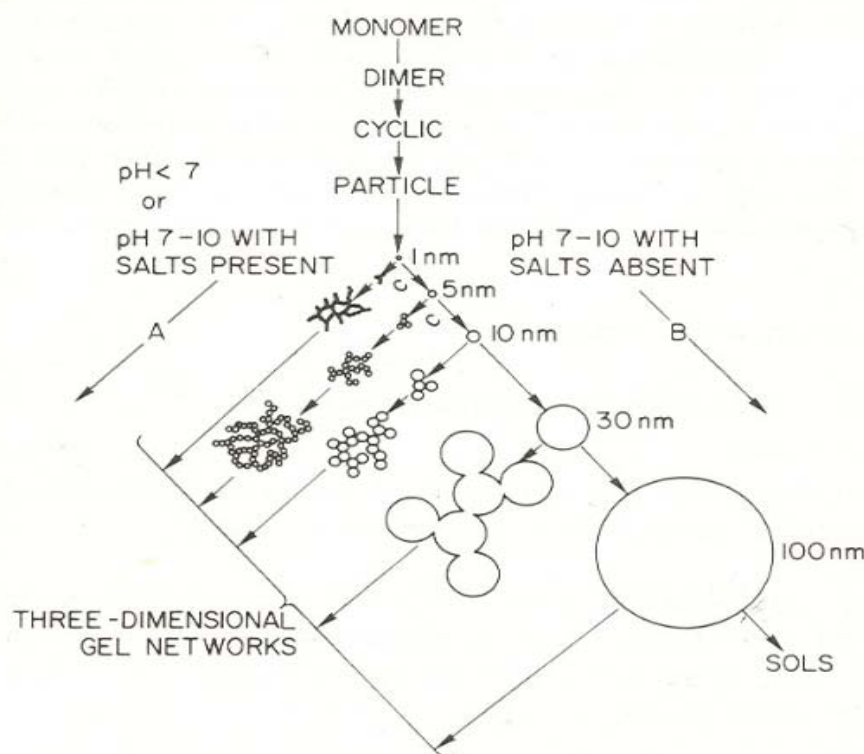


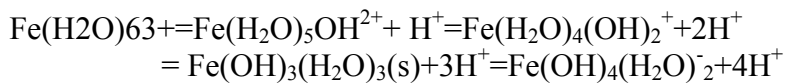
Figure 2- 12: Polymerization of silica in solution

The polymer may grow to colloidal dimensions with the number of polymers and sizes of the colloidal depend on the pH and concentration (rate of reaction), the greater is the tendency for more and smaller colloids to form. (Iler, 1979).

2.5.2 Silica and metal complexes

Metal ions like iron in water provide with the subject matter for field of coordination chemistry with silica or other anions. The reactions are exchange reactions with a group (neutral or negatively charged) being exchanged for another group. Most metal ions in solution are complex; the metals form aquo complexes with water molecules. When the pH water increases hydrogen ions are not existing in which giving rise to hydro(OH) and

finally(O) complexes. The hydrolysis sequence from Fe^{3+} takes in the following reaction forms.



The above reactions shows the simplified, besides this a polymeric and multinuclear hydrolysis species also commonly formed along with these species. The existence of metal ions as function of pH shows in figure 2-12.

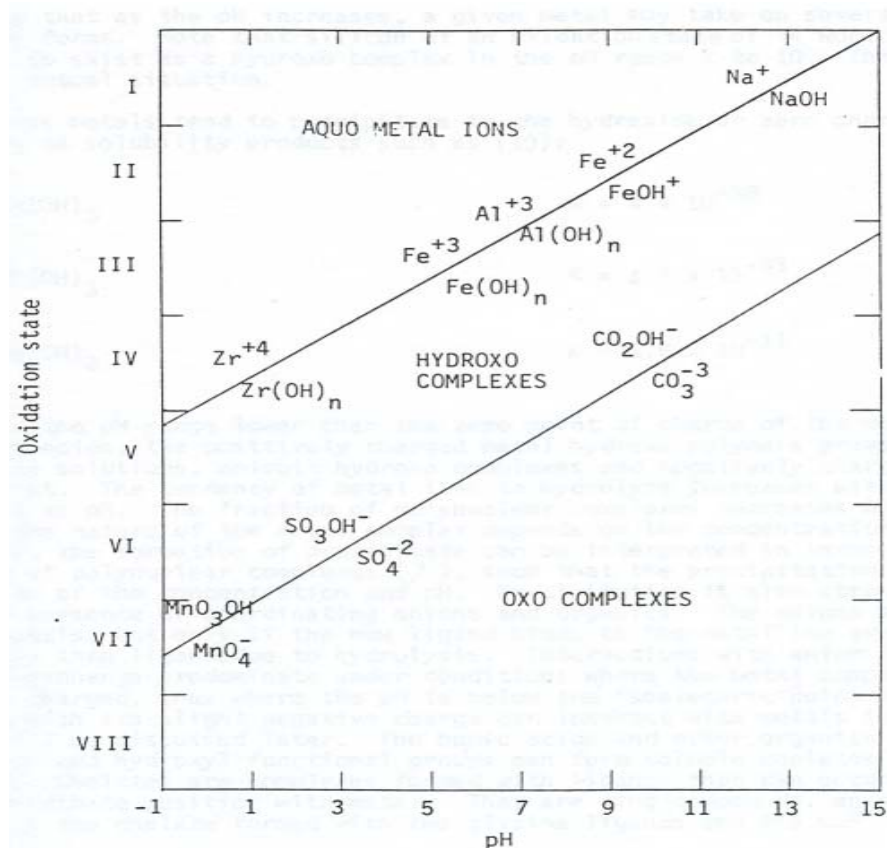


Figure 2-13 Predominant pH ranges for the occurrence of aquo, Hydro-oxo and Oxo complexes for various oxidation states (Micael C., 1981)

The above figure shows the occurrence of aquo, hydroxo and hydroxo-oxo and oxo complexes at predominant pH range for various oxidation states. This indicates simplification as the factors of atom size and electron distribution also affect the acidity of metal ions. When pH increases a given metal may take on several different complex forms. Silicon at an oxidation state of +4 would be predicted to exist as a hydroxo complex in the pH range of 1 to 10.

Polymeric metal ions like iron can adsorb **monomer**, **polymer**, and **colloidal** and **soluble silicate** forms of silica. Adsorption of iron appears to begin when pH is raised to within one to two pH units of the pH at which the polyvalent iron hydroxide would be precipitated if silica were not present. Precipitation can happen at low pH values where the silica surface silanol groups ($-\text{Si}-\text{OH}$) are not ionized. This is the case with the metal ions includes UO_2^{2+} ,

Fe^{3+} , Al^{3+} , and Cr^{3+} . At low pH values, the metal ions are polymerized in varying degrees and exist as extremely small positively charged colloidal oxide particles or polybasic cations. Adsorption of silica on the metals increases as the pH is increased. It is observed that a mixture of polyvalent metal silica co precipitates as the pH is raised to just below the pH at which the metal hydroxide would be precipitated. There are variations of these events dependent on the form of silica present. For instance, polymeric and colloidal silica begin to be adsorbed at lower pH values than does monomeric silica. Occurrence of adsorption seems to be favoured by both the silica and the iron ions being polymerized as opposed to being monomer units. Also the combining capacity of silica for iron ion may promote deposition of colloidal silica on external surfaces already covered with silica while a large concentration of iron ion may coagulate the colloidal silica particles in suspension (Iler, 1979).

The tendencies of various metal ions to form complexes correlated with their tendencies to react with the hydroxyl ion. The environment of the oxygen atom of $-\text{SiO}-$ and aqueous $-\text{OH}-$ are comparable enough that the reaction of each with metal ions is similar. (Micael C., 1981).

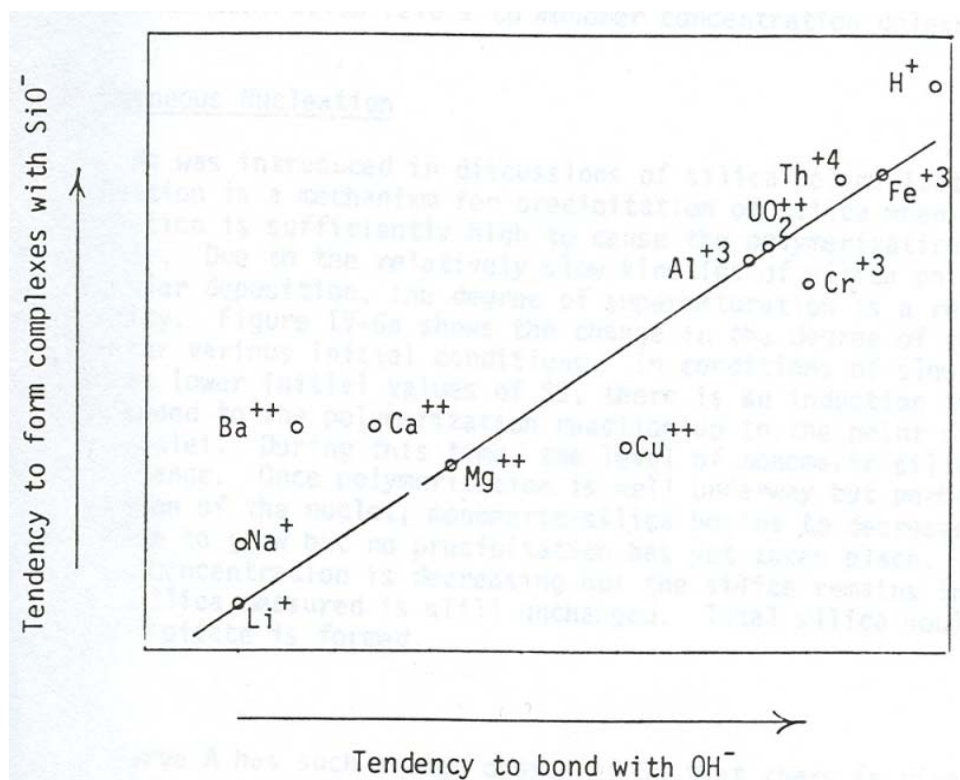


Figure 2-14 Tendency of metal ions to form complexes with amorphous silica (Micael C., 1981)

The above figure shows the metal ions most tending to form complexes with silica are in the upper right portion of the figure. Most other common metals **iron** and **aluminium** ions interact with silica in the pH range of 4 to 8.

2.6 Competitive adsorption

The adsorption of arsenic is a complex function of the interrelationship between ions, pH, the concentration of arsenic, arsenic speciation and the presence of competing ions in the water. The presence of other ions in water should be very competitive during the removal of arsenic from drinking water. The presence of other ions in water affects the adsorption degree of effects depend on the ionic radii, electro negativity, pH, and the availability of active sites. Most research was carried out on single ion systems, but arsenic contaminant water always occurred with other ions (multicomponent), that affects efficient adsorption of arsenic (Mohan et al, 2007).

The presence of phosphate, Sulphate, carbonate, silica, and other ions have been shown to decrease adsorption of arsenic to varying degree depend on pH and their concentration presence in water. The presence of calcium and sulfate ions decreases adsorption of both As(III) and As(V). Adsorption capacity of arsenic decreases significantly in the presence of calcium and sulfate ions in higher and lower pH respectively. Anions such as NO_3^- , SO_4^{2-} , and Br^- have no significant effect in adsorption of As(III). The adsorption of As(V) is slightly lower than phosphates at equal concentration. High concentration of phosphate (10times higher than As) greatly decreases As(V) adsorption.(Mohan et al, 2007).

The experimental result of (Ramadan, 2002) shows that the presence of phosphate (mg/l) concentration from 0-6 decreases the removal efficiency of arsenic by 51%. The presence of phosphate (mg/l) 2, 3, and 4 in water shows the efficiency removal reduces by 41%, 39%, and 28% respectively.

The competition adsorption of silica and arsenic strongly depend on the pH and concentration in the solution. When pH levels of the water increases, the polymerization of silica, and negative silica species increased, and highly compete for the available surface with arsenic (Welch, 2003). The competitive adsorption of silica and arsenic also depend on the availability surface charge of the adsorbent. Surface charge, based on ferric adsorbent media used for removal of arsenic depends on pH. In general ferric adsorbent media are useful over wide pH range of 4 to 11(Blau et al, 1940). The solubility equilibrium of amorphous iron ions under hydration in aqueous as function of pH shown in figure 2-15.

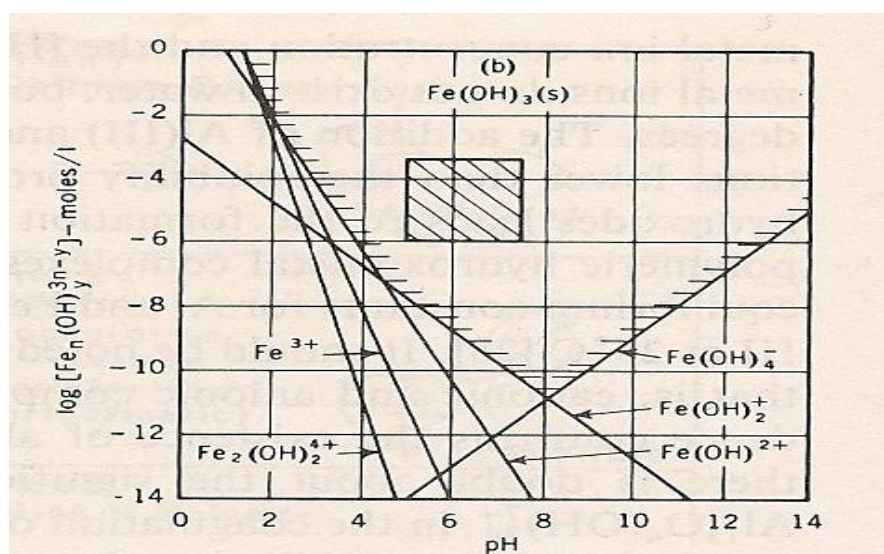


Table 2- 15 Solubility equilibria of amorphous $\text{Fe(OH)}_3(\text{s})$ (Faust, 1983)

The experiment on effect of silica and pH on As(V) adsorption by resin/iron oxide hybrid media were done by Moller(2007). The adsorbent media used for the experiment was npRio and ArsenX^{np}. Both types of the adsorbent media contains iron oxides, npRio adsorbent produced by precipitation of iron hydroxide into the pores of the bead used NaOH and ArsenXnp formed by contact resin with a solution of iron(II) salt and precipitation of iron hydroxide in situ. The batch experiments were done with the model water with silica ranges 0-70mg/l, at pH 7(figures 2-16 and 2-17) and, at silica 30mg/l in pH ranges of 7.18 to 8.9(figures 2-18 and 2-19). The result from the experiment show that the adsorption of As(V) decreases with increasing silica concentration and pH of the solution. The experimental result of this adsorbent media show in figure 20 and 31.

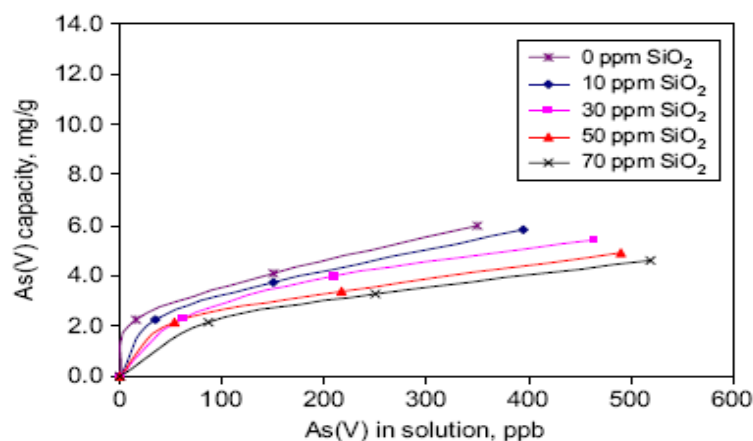


Table 2- 16 Effect of silica concentration on As(V) sorption on Arsen Xnp at pH 7.

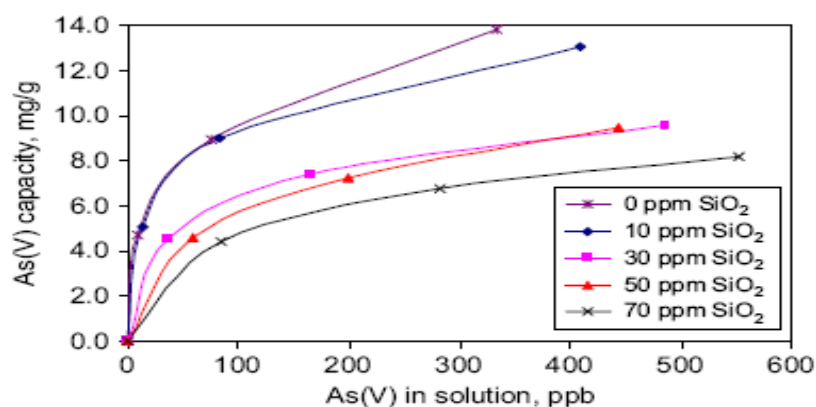


Table 2- 17 Effect of silica concentration on As(V) sorption on npRio(type 1) at pH 7

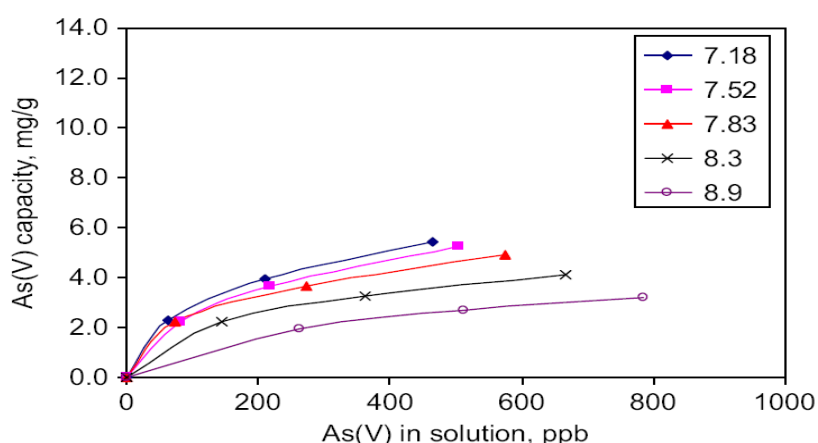


Table 2- 18 Effect of pH on As(V) capacity in the presence of 30ppm silica for ArsenXnp

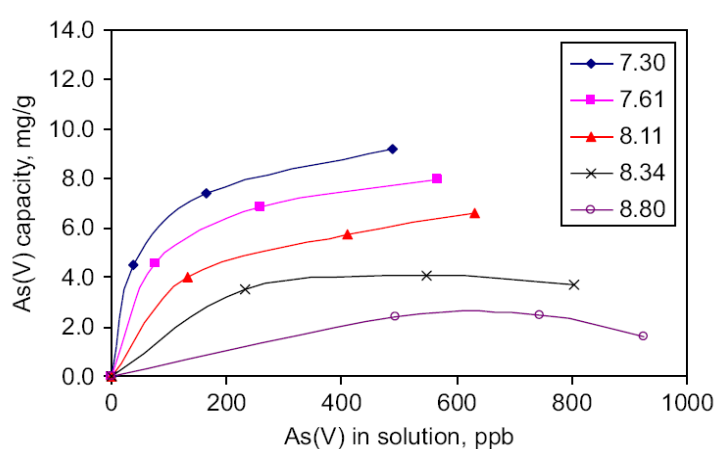


Table 2- 19 Effect of pH on As(V) capacity in the presence of 30ppm silica for npRIO.

Similar batch experiment was done by Smith (2005) on effect of silica, calcium, and pH on arsenate sorption to oxide surfaces. The adsorbent media used for the experiment was amorphous iron hydroxide in the pH range of 7-12, with silica concentration 40mg/l, and calcium 10 mg/l (figure 2-20). The adsorption of arsenic decreased with increase pH of the solution. The adsorption of silica was highest, but significantly decreased with the presence of silica. While, the presence of calcium with silica slightly increased the adsorption of arsenic on the media. The result presented in Figure 2-20.

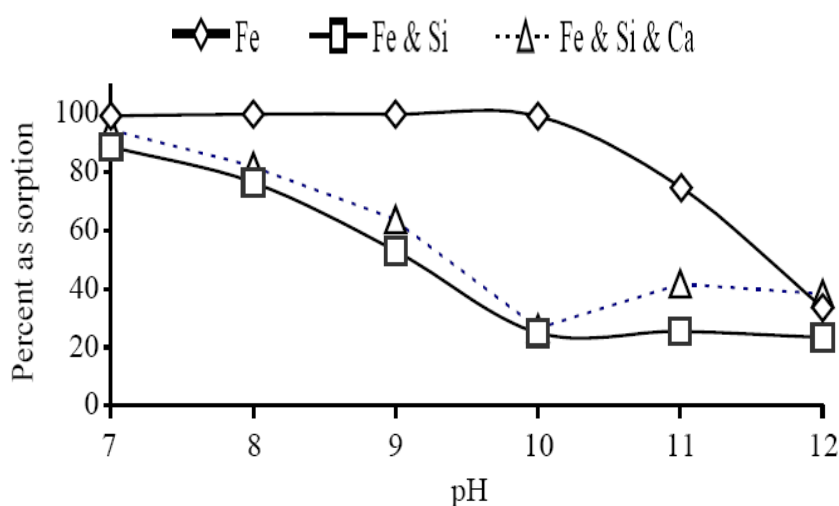


Table 2- 20 Equilibrium sorption after 1368hr, initial As=100ppb; Fe=20mg/l; SiO₂=40 mg/l; Ca=10mg/l

In figure 2-21, At pH 8 almost all As(V) was adsorbed to iron, when the silica present in the model water with iron, the arsenic removal decreased due to the competition with silica. On the other hand when calcium was present with silica initially the adsorption of As(V) higher but decreases with time. The calcium influence adsorption of arsenic in short time but no effect at long contact time.

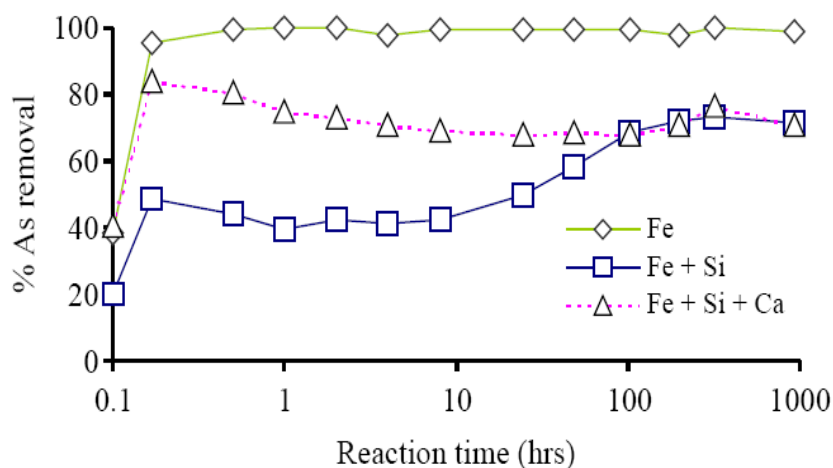


Table 2- 21 Percent arsenic removal over time with amorphous Fe(OH)₃, pH=8.5; initial As=100ppb; Fe=20mg/l; SiO₂=40mg/l; Ca=10 mg/l

2.7. Adsorption process

Adsorption is the process in which matters is extracted from one phase and concentrate at the solid surface, adsorption involves the inter-phase accumulation or concentration of substances at a surface or interface. The material being concentrated or adsorbed is adsorbate and the adsorbing phase is termed as adsorbent. Adsorption from the solution onto solid occurs due to the primary driving force for the adsorption and high affinity of the solute for the solid. Interaction between adsorbate and adsorbent consists of molecular forces embracing permanent dipole, induced dipole and quadruple electrostatic effects, and waal's forces. The preferential concentration of molecules in the proximity of a surface arises because the surface forces of an adsorbent solid are unsaturated. Both short range (repulsive) and longer range (attractive) forces between adsorbate and adsorbent become balanced when adsorption occurs (Duong C., 1998).

2.7.1 Adsorption isotherm

Isotherm model describes the distribution of adsorbate between the bulk solution and the media adsorbent. It expresses the amount of solute adsorbed per unit of adsorbent (q) as a function of the equilibrium concentration of the solute in the bulk solution (C_e), at constant temperature, expressed by:

$$q = f(C_e)$$

The most commonly used isotherm equations for calculation of adsorption capacity are Freundlich, Langmuir and BET isotherms (Sharma, 2008).

(A) Freundlich Adsorption Isotherm

The model used in the description of an aqueous system; the most and widely used equation. The empirical expression for calculation of the amount of solute adsorbed per unit weight adsorbent.

$$q = kC_e^{1/n}$$

Where: q = mass adsorbed per unit mass of adsorbent, (mg/g)

C_e = concentration in the bulk solution, (mg/l)

K and n = empirical constants

The equation is purely an empirical expression that encompasses the heterogeneity of the surface and exponential distribution sites and assumes that the adsorption of energy decreases logarithmically with adsorption density (Duong C., 1998). The Freundlich equation can be written in the logarithmic form. The linearization equation of Freundlich isotherm is expressed: (Sharma, 2008).

$$\log q = \log k_f + 1/n \log C_e$$

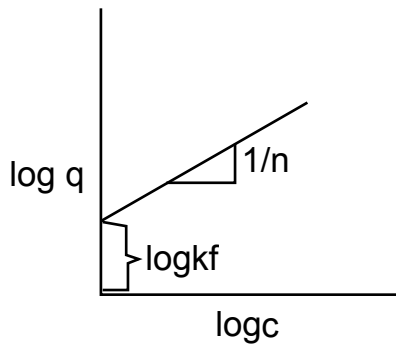


Figure 2-22 linear schematic representation of Freundlich Isotherm

(B) Langmuir isotherm

The Langmuir adsorption is based on the single layer adsorption in which the monolayer solute and saturated on the adsorbent surface at maximum level; the energy is the same in all sites.

The saturated maximum adsorption capacity (q_m) is expressed by:

$$Q = \frac{b q_m C_e}{1 + b C_e}$$

Where: Q = the amount of solute adsorbed per unit weight

C_e = amount of solute adsorbed per unit weight of adsorbent required for monolayer capacity

b = Langmuir isotherm constant

The linearization equation takes the form of

$$1/q = 1/q_m + 1/b q_m C_e$$

This yields a straight line with a slope of $1/b q_m$ and an intercept of $1/q_m$

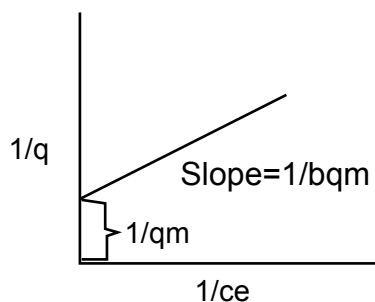


Figure 2-23 linear schematic of Langmuir isotherm

The assumptions of Langmuir model are:

- The surface is homogeneous, that is adsorption energy is constant over all sites
- Adsorption on surface is localized,
- Each site can accommodate only one molecule or atom, all adsorption sites have equal affinities for molecules or atoms of the adsorbate. (Duong C., 1998).

Chapter 3 - Materials and methods

3.1 Introduction

This study is continuation of the previous research done on arsenic removal at UNESCO-IHE. The materials and methods used in this study were similar to the previous research. This chapter includes analytical techniques, experiment equipment and procedure applied in the study.

3.2 Experiment materials

The following chemicals and reagents were used in the experiments:

- IOCS: Adsorbent media
- Standard As(III) solution(1000 mg/l): to prepare As(III) containing model water
- Standard As(V) solution(1000 mg/l): to prepare As(V) containing model water
- $\text{NaSiO}_3 \cdot \text{H}_2\text{O}$: To prepare SiO_2 containing model water
- 6M HCl: Preparation of combined reagents for monosilica analysis
- Ammonium Molybdate ($(\text{NH}_4)_6 \text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$): Preparation of combined reagents for monosilica analysis
- Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$): Preparation of combined reagents for monosilica analysis
- Nickel Nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$): Matrix modifier for arsenic analysis
- Delft tap water: to prepare model water
- De-mineralized water: to dilute and prepare chemical solutions
- Milli-Q water: to dilute and prepare for standard and samples for monosilica analysis
- Nitric acid: to preserve samples and prepare solutions
- NaOH and HCl: for pH adjustment

The following Experimental equipment were used in the experiments

- Sieve analyzer(Frrisch analysette 3pro)
- Electronic balance
- Mixer
- Rotary mechanical shaker
- pH meter
- Polyethylene syringes
- Polyethylene bottles of 500 ml capacity
- Pipettes of various sizes
- Mesearing cylinder
- Beakers, volumetric flasks etc
- Membrane filters 0.45 μm sizes
- AAs-GF Gf-95
- ICP
- Spectrometer
- AAS- flame

3.3 Experimental setup and operational procedures

3.3.1 Model water

The model of water for this study prepared from delft tap water in which certain parameters were adjusted such as pH, arsenic, and silicon. The initial arsenic concentration in the model water were around 240mg/l for As(III) and As(V). For the adsorption isotherm experiment the initial arsenic concentration was around 3300 mg/l for As(III) and As(V). The silica concentration for the experiment prepared in the range of 4.5-250 mg/l and the pH range was between 4 and 10. Table 1 shows a summary of delft tap water composition and composition of model water.

Table3-1 Water compositions of delft tap water and model water

parameter	unit	Delft tap water	Model water
Temperature	°C	16	25
O ₂	mg/l	10.5	10.5
pH	mg/l	8.1	6-8
Ca ²⁺	mg/l	53	53
Mg ²⁺	mg/l	7.9	7.9
HCO ₃ ⁻	mg/l	129	275
CO ₃ ²⁻	mg/l	0	0
CO ₂	mg/l	1.5	77
TOC	mg C/l	1.5	1.5
Kmn ₄ cons	mgO ₂ /l	4.9	4.9
Colour	Mg Pt/l	3	3
SiO ₂	mg/l	4.5	4.5-250
Iron	mg/l	0.03	0.03
Mn ²⁺	mg/l	0.005	0.005
SO ₄ ²⁻	mg/l	81	81
PO ₄ ³⁻	mg/l	0.03	0.03
P	mg/l	-	-
Cl ⁻	mg/l	61	125
Na ⁺	mg/l	40	134
As(III) or As(V)	µg/l	0	0-3500

(Source, Shahidullah(2000), Omeroglu(2001))

3.3.2 Iron oxide-coated sand (IOCS)

Iron oxide coated sand was used for adsorbent of arsenic in this study. IOCS have high removal capacity for both As(III) and As(V). In this study the source of IOCS was from the by-product of **Brucht** ground water treatment found in Dutch. Table: 2 and 3 shows the physical characteristics and the grain size distribution of Brucht coating samples of IOCS respectively.

Table 3-2: Physical properties of IOCS samples from Brucht treatment plant

Parameter		Unit	Quantity
Bulk density,		g/L	1055.05
Particle density		g/L	222.22
Porosity		%	0.525
Particle properties	d_{avg}	mm	3.307
	d_{60}	mm	3.58
	d_{10}	mm	2.51
	Uniform coef.		1.43
	S_{sp}	m ² /L	0.861

(Petrusevski, 2008)

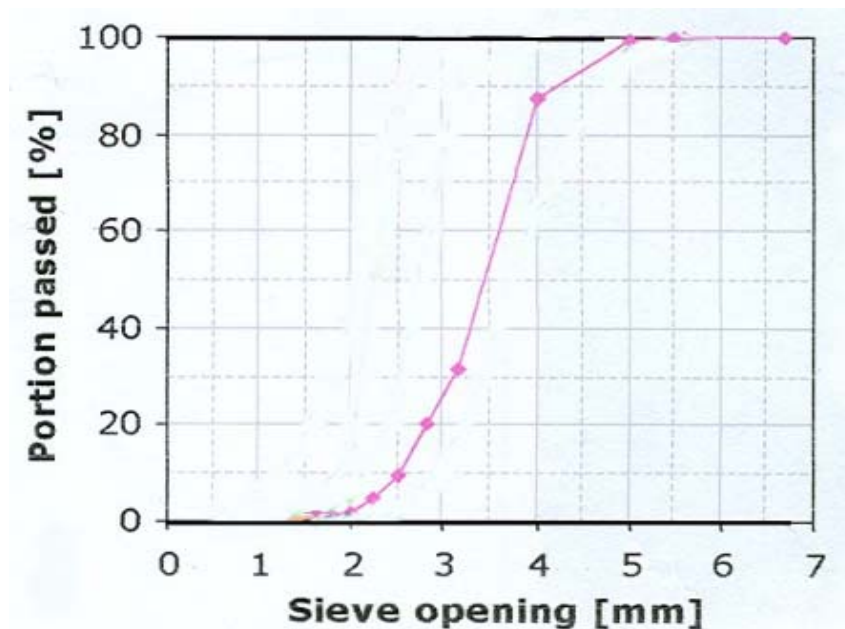


Figure 3-1 Grain size distribution curves of IOCS sample from Brucht treatment plant (Petrusevski, 2008)

3.3.3 Batch experiment

Several batch adsorption experiments were designed and conducted to investigate the effect of silica presence in ground water on arsenic removal. Table: 3 shows the summary of the experiment conditions applied in the batch experiment

Table 3-3 experimental conditions conducted in the batch experiment

Batch experiment	Form of As	Initial As c (μ/l)	Initial conc. SiO ₂ (mg/l)	Adsorbent dosage	pH	Contact time
Short batch (24 hr)	As(III)	240	4.5	0.2, 0.5, 1, 1.5, 2	8	24 hrs
	As(V)	230	4.5	0.2, 0.5, 1, 1.5, 2	8	24 hrs
	As(III)	260	4.5, 15, 30, 45, 60	0.2	8	24 hrs
	As(V)	240	4.5, 15, 30, 45, 60	0.2	8	24 hrs
	As(III)	250	30	0.2	6,7,8	24 hrs
	As(V)	250	30	0.2	6,7,8	24 hrs
	-	-	33	0.2,0.5, 1, 1.5, 2	8	24 hrs
	As(III)	240	15	0.2	4,8,10	24 hrs
	As(V)	230	15	0.2	4,8,10	24 hrs
	As(III)	240	160	0.2	4,8,10	24 hrs
	As(V)	230	160	0.2	4,8,10	24 hrs
	As(III)	3300	4.5	0, 0.2, 0.3, 0.6,0.8,1,1.5,2	8	21 days
Long batch	As(V)	3300	4.5	0, 0.2, 0.3, 0.6,0.8,1,1.5,2	8	s21 days
	As(III)	3300	20	0, 0.2, 0.3, 0.6,0.8,1,1.5,2	8	23 days
	As(V)	3300	20	0, 0.2, 0.3, 0.6,0.8,1,1.5,2	8	23 days
	As(III)	3300	50	0, 0.2, 0.3, 0.6,0.8,1,1.5,2	8	19 days
	As(V)	3300	50	0, 0.2, 0.3, 0.6,0.8,1,1.5,2	8	19 days
	As(III)	3300	4.5	0.2	6,7,8	14 days
	As(V)	3300	4.5	0.2	6,7,8	14 days
	As(III)	3300	20	0.2	6,7,8	14 days
	As(V)	3300	20	0.2	6,7,8	14 days
	As(III)	3300	50	0.2	6,7,8	14 day
	As(V)	3300	50	0.2	6,7,8	14 day
	As(III)	3300	250	0.2	6,7,8	14 day
	As(V)	3300	250	0.2	6,7,8	14 days

Two types of batch adsorption experiment were conducted

1.Short batch experiment with duration of 24-48 hours using model water containing As(III) and As(V) with different concentration of silica at different pH levels.

2.Long batch experiment with duration of 14-23 days to establish adsorption isotherm and to assess the effect of pH and silica using model water containing As(III) and As(V)

3.4 Analytical methods

3.4.1 Chemical composition of the IOCS

The chemical composition of the IOCS concentration might be important to analyze the chemical reaction and the effect of the specific element for assessing suitability of IOCS adsorbent for arsenic removal at different silica concentration and different pH levels. The following chemical composition elements were analyzed: Fe, Si, Mg, Mn, PO₄ –P, As and Ca.

The following procedure was followed:

- 3 gm IOCS sample was weighed
- 10 ml HNO₃ and 40 ml demineralized water solution was prepared
- IOCS sample added to the solution
- The sample was mixing and boiling at a temperature of about 250°C for about 3 hours
- After cooling, the solution was diluted to the 50 ml with demineralized water
- The solution was kept for 24 hours for settling the sand
- Fe, Mg, Mn, and Ca standard solution were prepared for analysis with the AAS-flame instrument

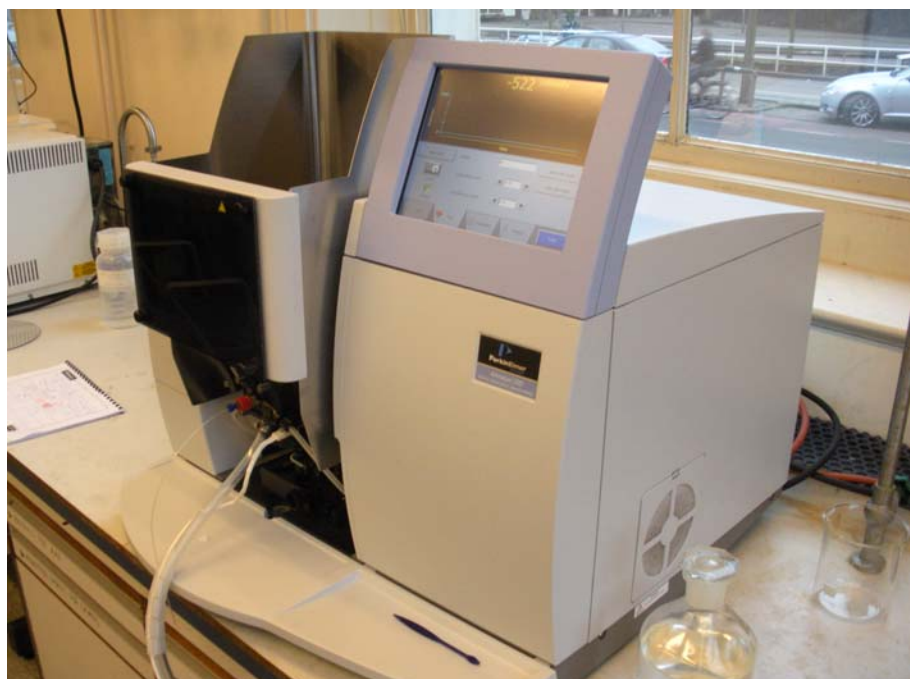


Figure 2 Atomic adsorption spectrometer perkin Elmer 200 with flame (AAS-flame)

3.4.1 Arsenic analysis

Atomic adsorption spectrometer (AAS) perkin-elmer 1100B with graphite furnace (GF) and HGA300 programmer was used for arsenic analysis. The samples taken by syringe and filtered by 0.45 μm membrane filter and acidified the samples by 65% HNO_3 in order to decreases the pH level below 2 to keep the arsenic dissolved. AAs-GF was calibrated before starting measuring the samples by using standard solutions in the range between 0-50mg/l.



Figure 3: Atomic adsorption spectrometer GF-95(AAS-GF)

3.4.2 Analyzing of silica

(A) Introduction

Silica presented in the batch experiment as monomer, polymer, colloidal and complex with metal silica(adsorbed silica). Measurements of polymer, colloidal and adsorbed silica were difficult. The monomeric silica were measured by molybdsilicate method and the total silica measured by ICP.

(B) Total silica

The total silica concentration was determined by inductively coupled plasma (ICP). The samples taken by syringe were filtered through 0.45 mm membrane filter to remove the iron and adsorbed silica. The samples were acidified with nitric acid to keep the silicon dissolved.

ICP was calibration before starting measuring the samples by using standard solution in the range of 1-30mg/l of silicon.



Figure 4: Inductively coupled plasma(ICP) perkin Elmer 3000

(C) Analyzing of silica by molybdosilicate method

The monomeric silica was measured as the molybdenum reactive silica. The monomeric reactive silica reacts at pH 1.2 with molybdenum complex to form silicic acids as well as phosphoric acids, which will have a yellow color (Kruis, 2007)

For measuring, the samples were transferred to 50 ml volumetric flask. Added 6m HCl to bring the pH 1.2 and also ammonium molybdate added to react with monosilicate. Finally the Oxalic acid added and the phosphoric acid destroyed, the silicic acids measured the absorbance at 410 nm in a 1 cm cell by spectrometer.



Figure 5: Spectrometer

Calibration curve

Calibration curve was made always before sample analysis. Standard silica solution was prepared from diluting the stock solution of 1000 mg/l Si concentration. Standard silica solutions were prepared in the concentration range of 0-1.711 mg SiO₂/50 ml. There is linear relation between sample and its concentration. The following calibration curve was used to get the actual silica concentration in the sample.

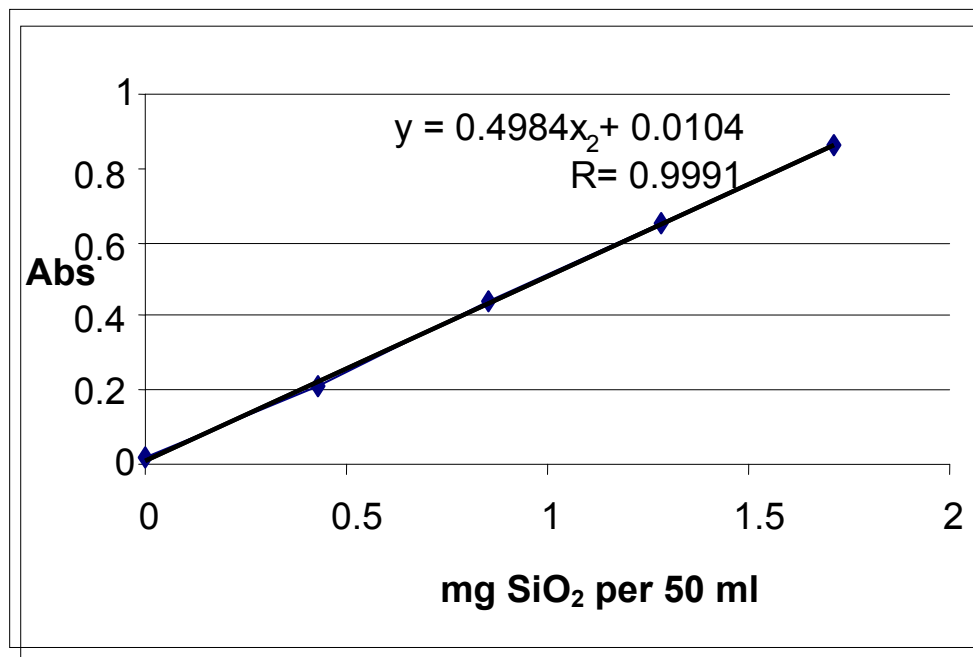


Figure 3-2 Typical monosilica calibration curve

The monomeric silica were calculated from the graph by using the following formula

$$\text{SiO}_2 = \frac{\text{mg SiO}_2 / 50\text{ml (from graph)} \times 100}{V}$$

V= ml sample volume

Stability calibration curve with time

The yellow color produced by the Molibdosilicate method has a limited stability, it depreciates with time. Figure 7 shows the stability of calibration curve of monomeric silica.

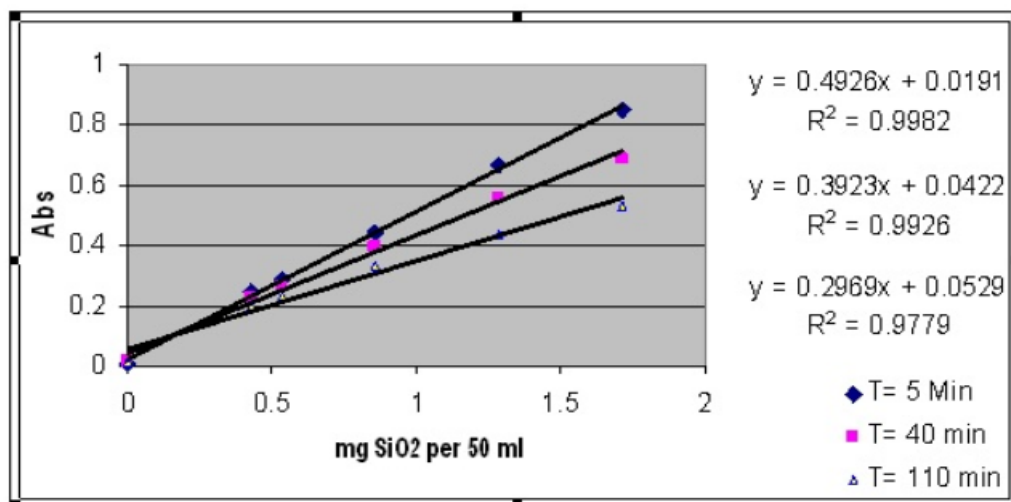


Figure 3-4 Calibration curve of the monemeric silica from standard solution with time

After 5 minutes the color of the solution started to decrease. So, it is necessary to measure the standards and the samples after mixed with oxalic acid before 5 minutes

Chapter 4 -Results and Discussion

In this chapter the results of the experiment conducted to analyze the chemical composition of IOCS, screening experiments designed to study adsorption of arsenic on IOCS in model water with and without silica at different pH levels. Based on screening experiments to establish adsorption isotherms for arsenic and silica at different SiO_2 concentration and pH levels will be presented and discussed.

4.1 Chemical composition of Iron-Oxide Coated Sand (IOCS)

The IOCS used for experiments conducted in this study was from the Dutch water treatment plant Brucht. Knowing the chemical composition of IOCS could help to understand and predict the chemical reactions that take place between ions and adsorption capacity of IOCS at different pH levels in solution. The chemical composition of IOCS is presented in table 4-1.

Table 4-1 Chemical composition of IOCS from WTP Brucht

Composition	Units	concentration
Iron	mg/g IOCS	333.65
Silicon	mg/g IOCS	23.4
Magnesium	mg/g IOCS	0.164
Manganese	mg/g IOCS	0.108
Sand	mg/g IOCS	44.11
Arsenic	$\mu\text{g/g}$ IOCS	≤ 3
PO_4 -P	mg/g IOCS	9.5
Calcium	mg/g IOCS	1.47

IOCS had a very high iron concentration of 333.65 mg Fe/g IOCS, which is about 33% of the total IOCS composition of the sample. The second most abundant compound is quartz sand with approximately 44.11 mg/g IOCS. The third is silicon that constitutes 23.4 mg/g of the IOCS sample. The adsorption capacity of the IOCS mainly depends on the concentration of iron. A high iron concentration might be a preliminary indication that the IOCS from the Brucht plant treatment could have a good adsorption capacity for arsenic and other anions

4.2 Batch screening experiments for arsenic and silica

Batch isotherm experiments with IOCS media were carried out with model water containing either arsenic, silica, or a mixture of both compounds. The objective of the experiment was to investigate the effect of silica and pH on arsenic removal by IOCS. The model water (Delft tap water) used for the experiment had 4.5mg/l of silica, which is similar to the actual lowest silica concentration (5mg/l) found in ground water.

4.1.1 Adsorption of As(III), As(V), and silica on IOCS

Two different types of model water containing As(III) or As(V) and silica without arsenic at different IOCS dosage were used. Figure 4-1 shows the adsorption efficiencies of IOCS for As(III) and As(V) as a function of IOCS dosage. The total silica removal by IOCS (in non filtered samples and in samples filtered through 0.45 μ m membrane filter) is shown in Figure 4-2.

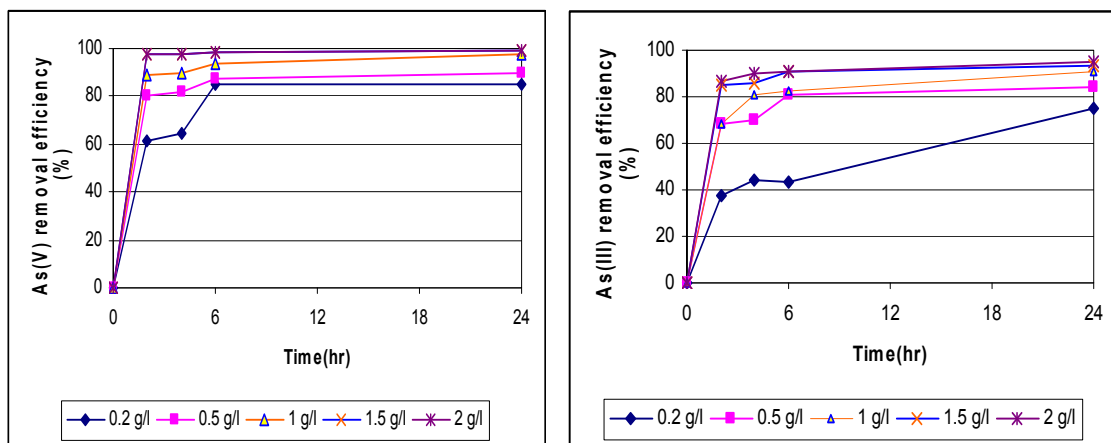


Figure 4- 1 Arsenic removal efficiency versus time at different IOCS dosages, model water with initial As(V) concentration 230 μ g/l, and As(III) concentration 240 μ g/l, pH=8.0 \pm 0.2.

IOCS shows a very high removal efficiency for As(III) and As(V) (Fig 4- 2) . The results of the experiment are similar to results from previous related research at IHE. As(V) was removed above 85% at IOCS dosage of 0.2 g/l and 0.3 g/l. The removal efficiency of As(V) was higher than 97% removed at the dosages of 1, 1.5, and 2g/l after contact time of 24 hours. As(III) removal efficiency was higher than 75% at IOCS dosage of 0.2 g/l and 0.3 g/l and above 90% at IOCS dosages of 1.0, 1.5, and 2.0 g/l. The removal efficiency of As(V) was found to be higher than As(III). The results indicate that IOCS has potential to effectively remove both As(III) and As(V) from drinking water.

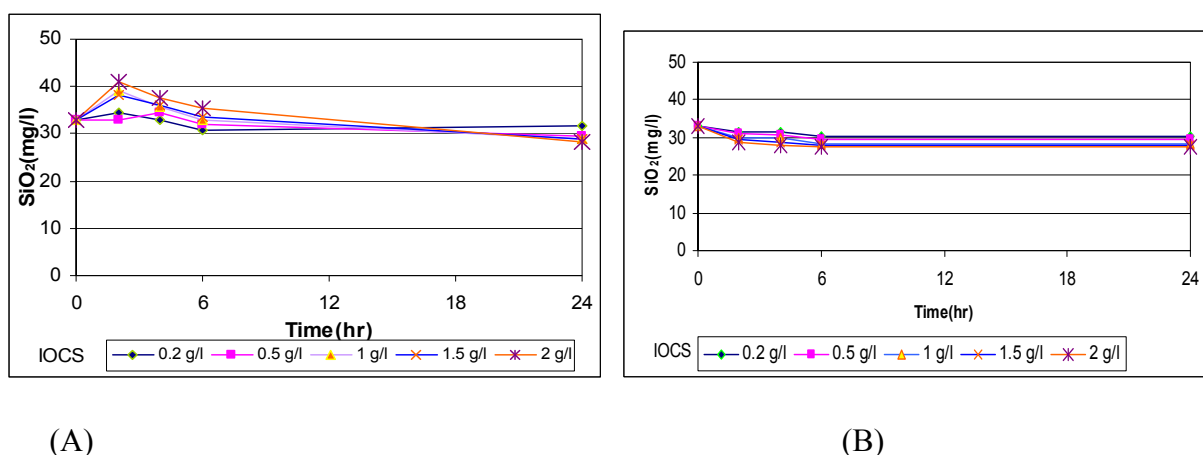


Figure 4-2 Total silica removal versus time at different IOCS dosages; initial $\text{SiO}_2 = 33\text{mg/l}$, model water without arsenic, $\text{pH}=8.0 \pm 0.2$, total silica was measured before filtering (A) and after filtering (B) through a $0.45\mu\text{m}$ membrane filter.

Figure 4-2 illustrates the removal of total silica at different IOCS dosages. Figures 4-2A and 4-2B show the silica (mg/l) concentration measured before and after filtering of a sample through a $0.45\mu\text{m}$ membrane filter, respectively. Figure 4-2 (A) shows that the total silica increased at the beginning of the experiment and reached levels above the initial concentration. After two hours the silica concentration started to decrease. This is probably due to the release of silica from the IOCS to the solution. However, the total silica concentration measured after filtering through $0.45\mu\text{m}$ membrane filter (Fig. 4-2 B) showed a slight decrease with time. The total silica removal from the model water increased with an increase of IOCS dosage and silica reached concentrations below the initial at all IOCS dosages tested ($0.2\text{-}2\text{g/l}$) after 24 hours. This result confirmed that silica can be adsorbed onto IOCS.

4.1.2 The effect of pH on As (III) and As(V) adsorption by IOCS

Batch experiments were conducted with model water containing As(III) or As(V) at pH 6, 7, and 8. The model water contained 4.5 mg/l of silica, initial As(III) was $265\mu\text{g/l}$ and As(V) was $250\mu\text{g/l}$. The results are presented in figure 4-3

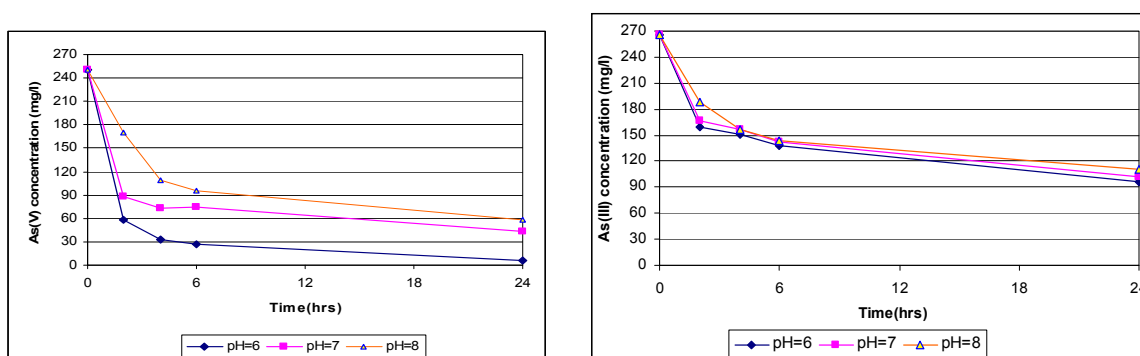


Figure 4-3 Effect of pH on As(III) and As(V) removal by IOCS, initial As(V) concentration $250\mu\text{g/l}$, As(III)= $265\mu\text{g/l}$, IOCS dosage 0.2g/l , $\text{pH}=6, 7, \text{ and } 8 \pm 0.2$ and contact time 24hours.

Figure 4-3 shows As(V) and As(III) removal by IOCS with time at pH levels of 6, 7, and 8. It is clear that the removal of As(III) and As(V) decreases with increasing pH value of the model water. As(V) removal was most efficient at lowest pH tested of 6.0 and removal efficiency decreased at pH of 7.0 and 8.0. This might be due to the presence of a more positively charged surface of IOCS and negatively charged HAsO_4^{-1} , at lower pH. Dominant arsenic species above 6.9 is HAsO_4^{-2} , however at this pH IOCS surface charge is less positive and the adsorption was, consequently less favorable.

IOCS showed a higher removal efficiency for As(V) than for As(III) at all pH values tested (6, 7, and 8). The removal efficiency of As(V) was significantly affected with an increase of pH from 6 to 8. The dominant As(III) species at $\text{pH} < 9.2$ is HAsO_3^0 and due to this the results show that As(III) removal efficiency was only slightly affected by an increase in pH from 6 to 8.

4.1.3 The effect of silica on As(V) and As(III) removal by IOCS

Batch adsorption experiments were conducted at different silica concentration with model water containing either As(V) or As(III). The initial concentration of As(III) and As(V) were 230 and 260 $\mu\text{g/l}$ respectively, and silica concentrations were 4.5, 17.0, 33.0, 45.0, and 65.0 mg/l . Experiments were conducted at $\text{pH} = 8 \pm 0.2$. The effect of silica concentration on As(V) and As(III) removal by IOCS is shown in figure 4-4 (see annex A table 7).

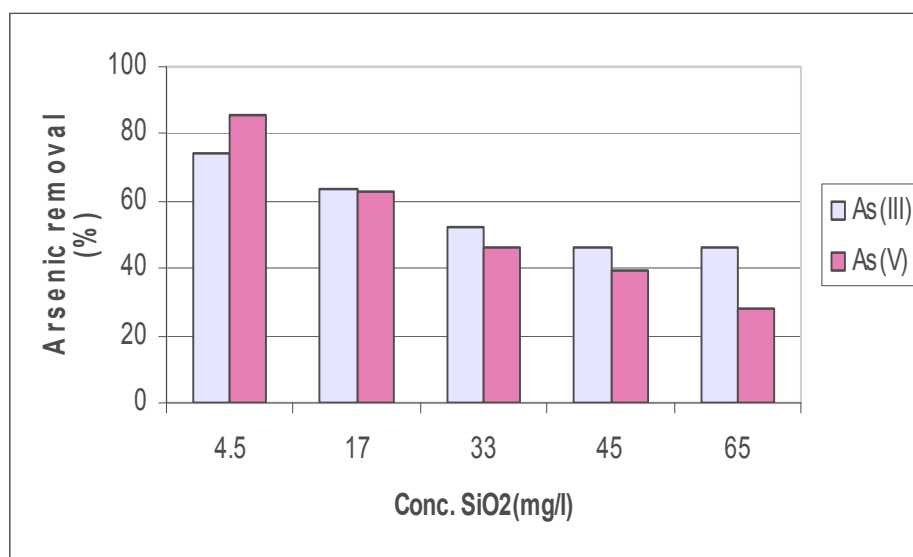


Figure 4-4 Arsenic removal efficiency versus silica concentration, Model water: As(V) = 240 $\mu\text{g/l}$, As(III) = 260 $\mu\text{g/l}$, $\text{pH} = 8 \pm 0.2$; IOCS = 0.2 g/l , contact time 24 hours

From figure 4-4 it is clear that the presence of silica significantly affects the removal efficiency of As(III) and As(V). Increasing the silica concentration in the model water resulted in a significant reduction in As(V) removal efficiency, as the removal efficiency of As(V) at silica concentrations of 17, 33, 45, and 65 mg/l were reduced by 25%, 30%, 40%, and 50 %, respectively. In the case of As(III), the removal efficiency at silica concentration of 17 mg/l was reduced by 10% and at 33 mg/l by 20%. Further increases of silica concentration caused a less marked reduction in As(III) removal efficiency (23%) at 45 mg/l .

SiO₂). There was no further reduction in As(III) removal efficiency when silica was increased from 45 to 65 mg/l.

Adsorption of As(V) on IOCS decreased more significantly with increasing silica concentrations in the model water as compared to As(III). By increasing the silica concentration in the model water from 4.5 to 65 mg/l, As(V) removal efficiency was reduced from 85% to 35% and As(III) from 75% to 50%. This could be because of the presence of the dominant As(V) species pH 8 which was HAsO_4^{2-} . Therefore the surface charge become less positive and adsorption was less favorable, and easily affected by the presence of Silica. Incase of As(III), dominant species in solution in pH < 9.2 was HAsO_3^0 is neutral and has less affected with increasing silica solution.

4.1.3 The effect of silica concentration at different pH levels on arsenic removal by IOCS

(a) The effect of silica concentration on As(V) and As(III) adsorption at pH 6, 7, and 8

Batch experiments were carried out with the model water with initial As(III) concentration of 3200 µg/l, or 3600 µg As(V) /l and silica concentration of 4.5, 20, 50, or 250 mg/l, at pH 6, 7, and 8. The experiments were run for 14 days. Figures 4-5 and 4-6 show arsenic removal after 14 days.

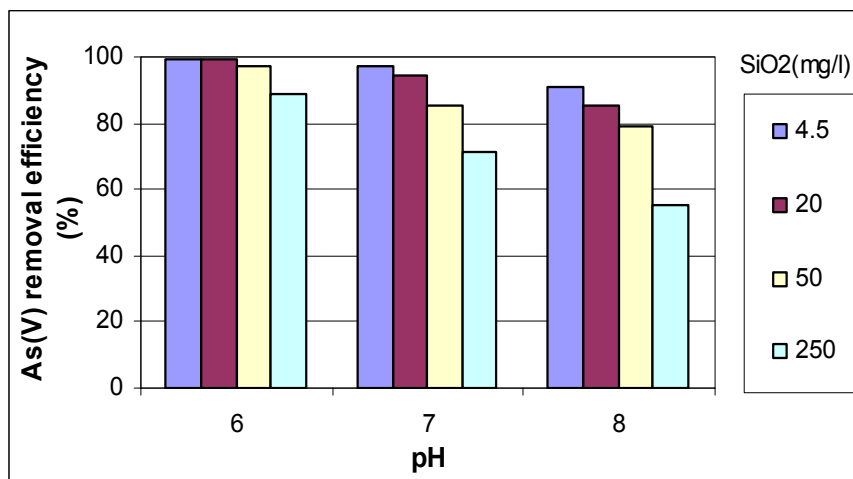


Figure 4-5 Effect of silica concentration on As(V) removal efficiency at pH of 6, 7, and 8; initial As(V) concentration 3600 µg/l, IOCS dosage 0.2 g/l, contact time 14 days.

Figure 4-5 shows the effect of silica concentrations 4.5, 20, 50, and 250 mg/l on As(V) removal efficiency by IOCS. From Figure 4.5 at pH 6, the removal efficiency of As(V) was not significantly affected by the silica concentration. The removal efficiency of As(V) was, however, significantly affected by an increasing silica concentration at pH 7 and 8. The removal efficiency of As(V) at a silica concentration of 50mg/l decreased by 12% and 15% at pH 7 and 8 respectively. From these results it is clear that the negative effect of silica presence at a higher concentration on As(V) removal efficiency increased at a higher pH of model water

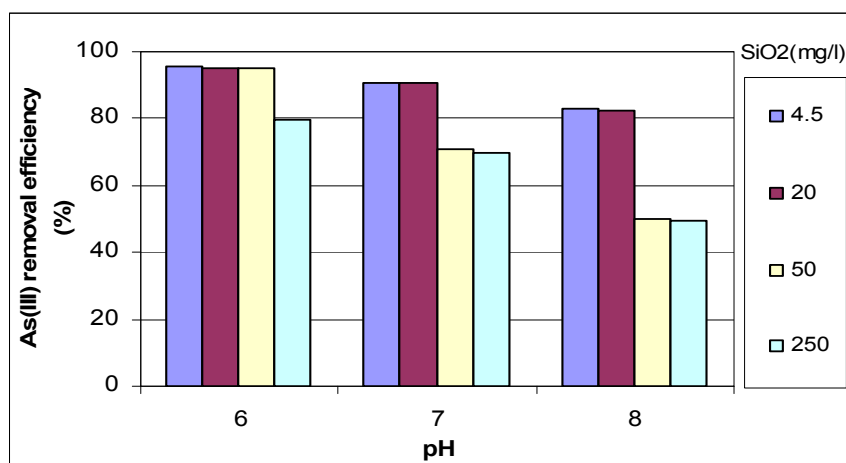
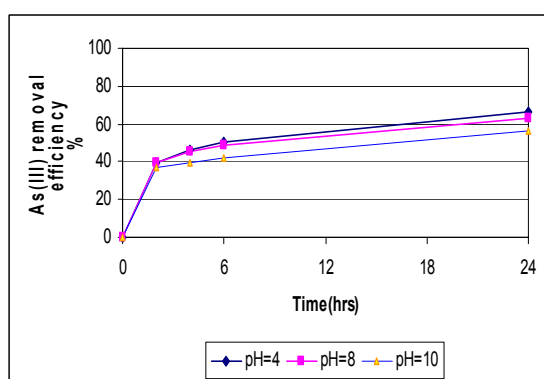


Figure 4-6 Effect of silica concentration on As(III) removal efficiency at pH of 6, 7, and 8; initial As(III) concentration 3600 $\mu\text{g/l}$, IOCS dosage 0.2 g/l, contact time 14 days

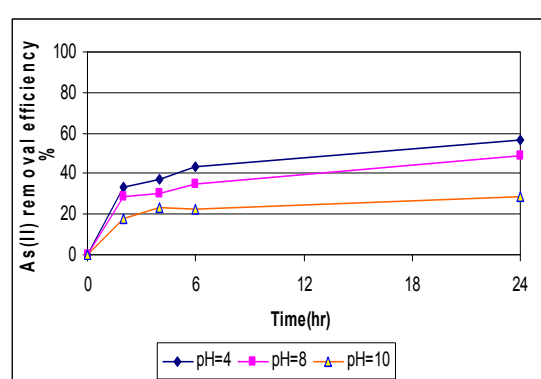
Figure 4-6 shows the removal efficiency of As(III) at different pH levels with initial silica concentration of 4.5, 20, 50, and 250 mg/l. The presence of silica ($\leq 50\text{mg/l}$) in the model water did not show a significant effect on As(III) removal efficiency at pH 6. The removal efficiency of As(III) was not affected markedly at a silica concentration from 4.5 to 20 mg/l at pH 6, 7 and 8. With an increasing silica concentration (50 mg/l) in the model water, adsorption of As(III) was significantly reduced (at pH 7 21% reduction and at pH 8 30% reduction). There was no further pronounced reduction of As(III) removal efficiency with a further increase of silica concentration above 50 mg/l.

(b) The effect of silica concentration at pH 4, 8, and 10 on As(V) and As(III)

Batch adsorption experiments were conducted with the model water containing 17 and 166 mg/l of silica at pH levels of 4, 8, and 10. These experiments were done with model water with initial concentrations of 240 μg As(III) /l and 230 μg As(V) /l (Figures 4-7 and 4-8).



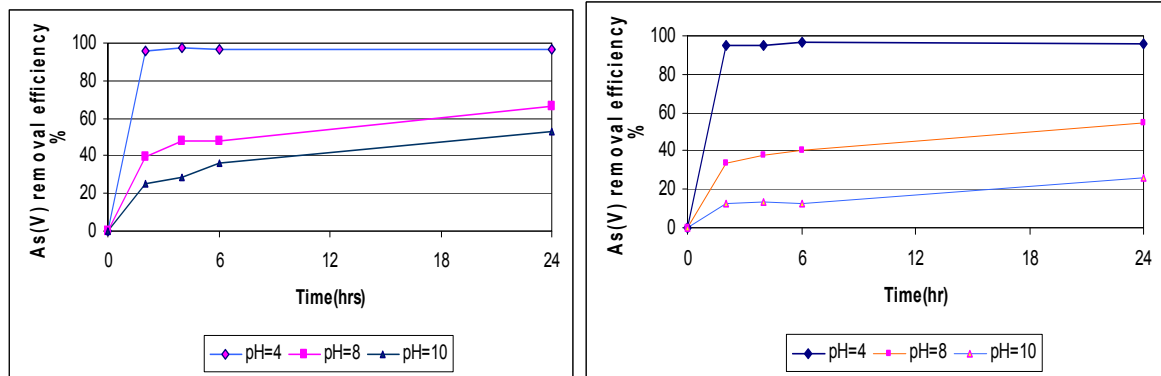
(a) 17 mg SiO_2/l



(b) 166 mg SiO_2/l

Figure 4-7 As(III) removal efficiency versus contact time at silica concentrations of 17 (a) and 166 mg/l (b), IOCS dosage 0.2 g/l, initial concentration of As(III)=240 $\mu\text{g/l}$, and contact time 24 hrs.

Figure 4-7 illustrates the effect of silica levels at 17 mg/l (a) and 166 mg/l (b) on As(III) removal, at pH levels of 4, 8, and 10, and contact time 24 hours. With increasing pH of the model water the removal efficiency of As(III) decreased at both silica concentrations tested (17mg/l and 166mg/l). The removal efficiency of As(III) at silica concentration 17mg/l and 166mg/l decreased by 10 % and 28 % with an increase in the pH from 4 to 10, respectively.



(a) 17 mg SiO₂/l

(b) 166 mg SiO₂/l

Figure 4-8 As(V) removal efficiency versus contact time at silica concentration of 17 mg/L (a) and 166 mg/l (b), IOCS dosage 0.2g/l, initial concentration of As(V)=230 µg/l, contact time 24 hrs

With increasing model water pH in figure 4-8, removal efficiency of As(V) strongly decreased at both 17(4-8(a)) and 166 mg/l (4-8(b)) silica concentration. In figure 4-8(a) the removal efficiency of As(V) decreased by 44% with an increase of pH from 4 to 10. In figure 4-8(b) the adsorption of As(V) decreased by 70% with an increase of pH from 4 to 10. From these results it can be concluded that removal of As(V) was significantly reduced with increased silica concentration.

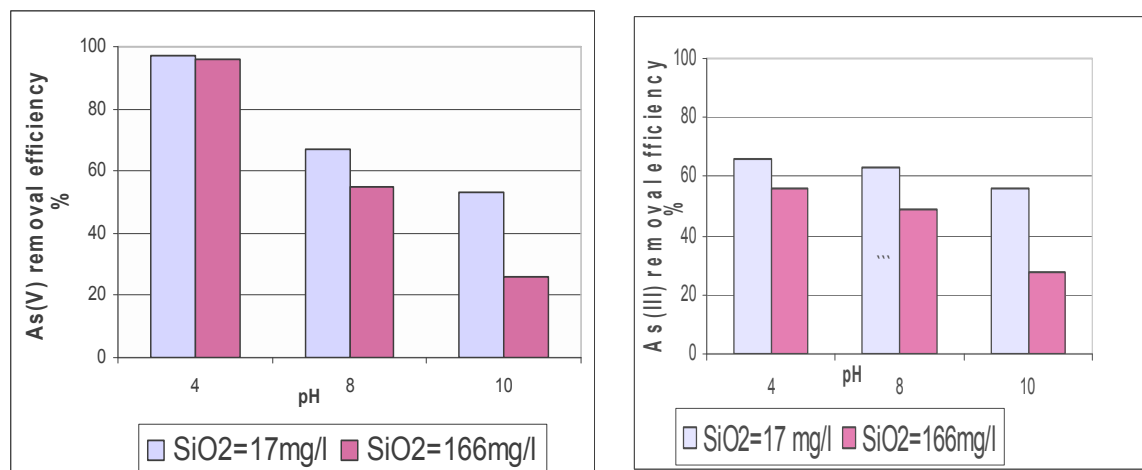


Figure 4-9 The removal efficiency of As(V) and As(III) as a function of pH and silica concentration; initial concentration of As(V) =230µg/l and As(III) =240µg/l; IOCS dosage 0.2g/l, SiO₂ concentration 17 mg/l (a) and 166 mg/l (b); contact time 24hrs

Figure 4-9 shows removal efficiency of As(V) and As(III) on IOCS in model water containing 17 and 166 mg/l of silica, at pH levels of 4, 8, and 10 after 24 hours contact time.

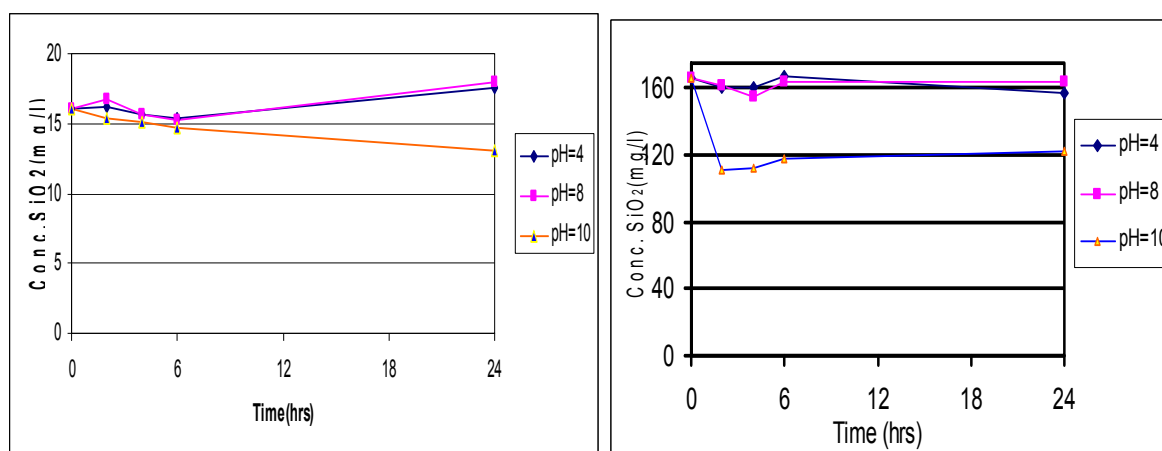
The removal efficiency of As(III) and As(V) decreased with increasing silica concentration and pH level of the solution. However, adsorption of As(V) was more significantly reduced with an increase in pH and silica concentration, as compared to As(III) removal. From these experimental results, it is clear that pH is the major influence on the adsorption of arsenic. pH influenced arsenic and silica speciation and the composition of functional groups through protonation and deprotonation reactions.

The predominant silica species at low pH is uncharged Si(OH)_4 . This form of silica was probably not strongly attracted to positively charged IOCS surfaces and consequently has only a minor effect on arsenic removal by IOCS. In addition polymer silica at low pH is not stable and has a very limited effect on arsenic adsorption on IOCS. At low pH value As(V) was more effectively removed than As(III) and there was almost no effect of silica present in the model water. As(V) adsorption was most effective at low pH values and decreased with increasing pH. This is mainly due to favorable adsorption energies between the more positively charged surface of IOCS and negatively charged H_2AsO_4^- , the predominant As(V) species within pH ranged from 2.2 to 6.9

However, as the pH of the solution increased with the same silica concentration, adsorption of As(V) decreased more significantly than adsorption of As(III). The effect was due to the prevailing As(V) species, and formation of different silica species. When the pH increased, the polymerization of silica increased as well, resulting in IOCS fouling and blocking of the access for As(V) to IOCS. In addition the oxygen atom of the polymer silica $-\text{SiO}-$ and aqueous $-\text{OH}-$ or Si(OH)O^- possibly reacted with iron oxide and consequently decreased the availability of adsorption sites for As(V). At a higher pH level, the dissociation of silica produce negatively charged species, such as Si(OH)_3^- , and $\text{SiO}_2(\text{OH})_5^-$.

The predominant As(III) species in solution at pH values below 9.2 is neutral H_3AsO_3^0 . At higher pH values, neutral H_3AsO_3^0 was more readily able to donate a proton to the surface OH group than the negatively charges As(V) species. At $\text{pH} > 9.2$ IOCS has a high adsorption capacity for As(III) due to negatively charged H_3AsO_3^- .

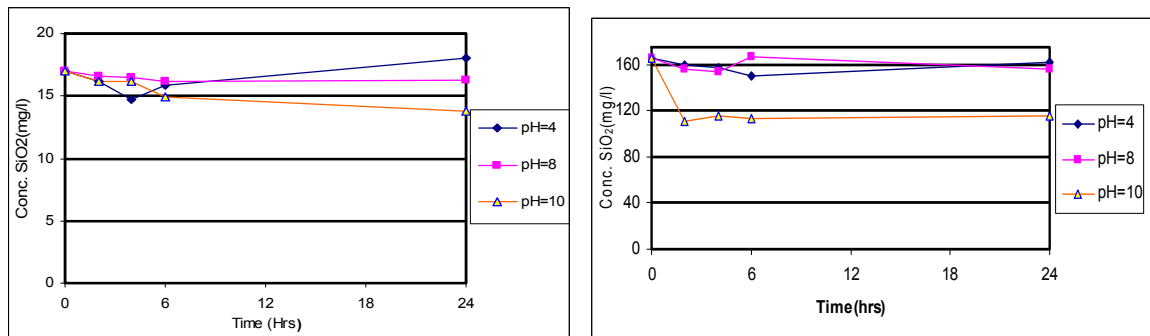
Besides the arsenic removal from the model water, the total silica removal over time was also monitored. Figures 4-10 and 4-11 show the removal of total silica over time in the presence of As(III) and As(V).



(a) 17 mg SiO₂/l

(b) 166 mg SiO₂/l

Figure 4-10 Removal of total silica as a function of time and pH; model water composition: As(III)=240 µg/l, initial total silica concentration 17 mg/l(a) and 166mg/l(b) pH 4, 8, and 10; IOCS dosage 0.2g/l



(a) 17 mg SiO₂/l

(b) 166 mg SiO₂/l

Figure 4-11 Removal of total silica as a function of time and pH; model water composition: As(V) =230 µg/l, initial total silica concentration 17 mg/l(a) and 166mg/l(b) pH 4, 8, and 10; IOCS dosage 0.2g/l

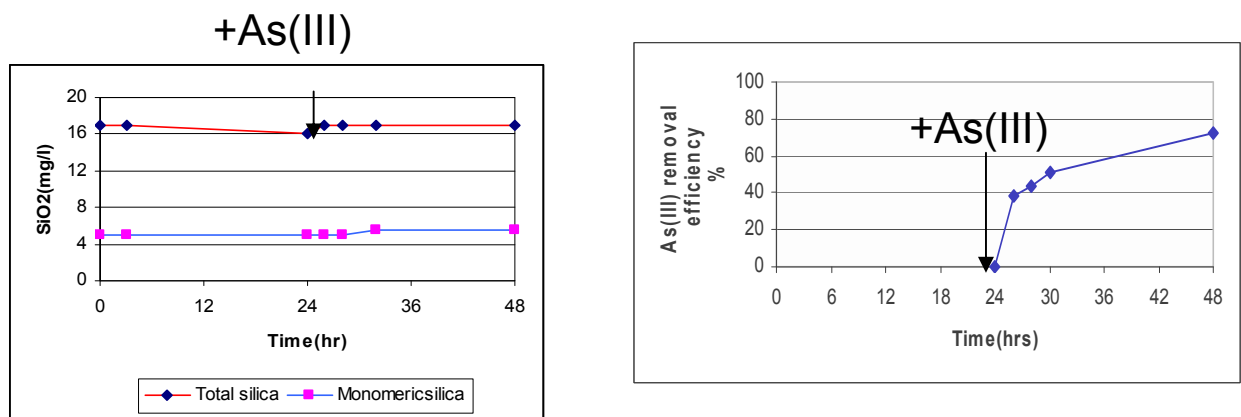
Figures 4-10 and 4-11 illustrate the removal of total silica from the model water in the presence of As(III) and As(V) over time. The removal of total silica concentration was not significantly affected by arsenic species (As(V) or As(III)). The total silica concentration from the model water decreases with an increasing pH value of the solution. The total silica concentration was decreased from 17 to 14mg/l, and 166mg/l to 115mg/l at pH 10. This might be due to the adsorption of negative silica species $\text{Si}(\text{OH})_3^-$, $\text{SiO}_2(\text{OH})_5^-$ and silica polymerization, and settling of silica polymerization or colloidal particles. These results confirm that silica removal is higher at a high pH of the solution.

4.5 Competitive adsorption

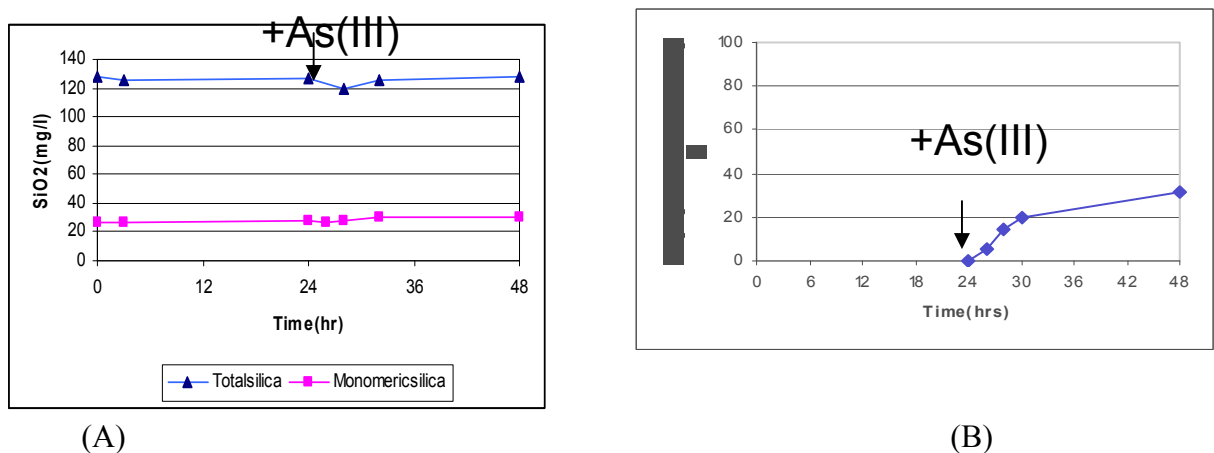
The separated batch experiments were conducted in order to assess adsorption of total and monomeric silica on IOCS, and to examine if replacement of already adsorbed silica by arsenic could take place.

(a) Competitive adsorption of silica and As(III) or As(V)

Two types of model water were prepared: one with a silica concentration of 17mg/l and of pH=4, and the second with 166 mg/l of silica and pH=10. In both cases, 0.2 mg/l of pulverized IOCS were applied and the contact time was 24 hours. Then As(III) or As(V) were added to observe if replacement of silica by arsenic would possibly take place. The samples were taken with and without filtration through a 0.45 μm membrane filter. Results from these experiments are shown in figures 4-12, 4-13, 4-14, 4-15, and in annex A table (15-16).



(A) (B)
Figure 4-12 Total (SiO_2) and monomeric (SiO_2) silica concentration versus time in the solution (A) Model water: initial total silica (SiO_2) 17mg/l and monomeric silica (SiO) 5mg/l, pH=4+, As(III) =250 $\mu\text{g/l}$ added after 24 hours of contact time (B); IOCS dosage 0.2g



(A) (B)
Figure 4-13 The total and monomeric silica concentration versus time in the solution The initial total concentration of SiO_2 =166mg/l, monomeric silica 5mg/l, pH=10, IOCS=0.2g/l and As(III) =250 $\mu\text{g/l}$ added (B) after 24 hours

Figures 4-12(A) and 4-13 (A) show the total and monomeric silica concentration in model water for 48 hours of contact time. The effect of adding As(III) after 24 hr can be seen in figures 4-12 (B) and 4-13 (B). The upper and the lower lines in figures 4-12 (A) and 4-13 (A) represent the total and monomeric silica concentration respectively. The purpose of the experiment was to investigate the possible adsorption of monomeric and total silica on IOCS, and possible replacement of silica by As(III), but the adsorption of silica was not shown to be significant. This could possibly be due to low dosage of IOCS that was insufficient to adsorb a high concentration of silica. As(III) removal efficiency in the presence of 17mg/l at pH 4 and at 166mg/l at pH 10 of silica were 72% and 33%, respectively after 24 hours of contact time. A similar experiment was done with As(V) presented in the figures 4-14 and 4-15.

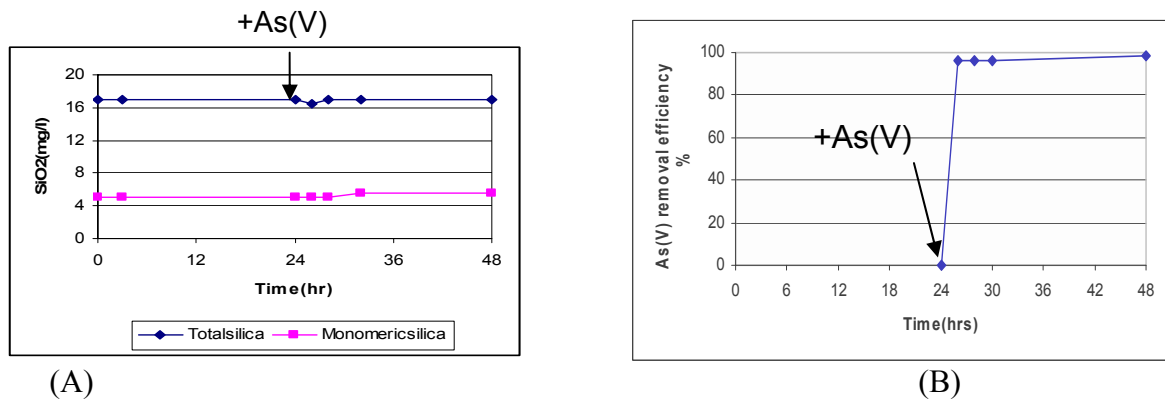


Figure: 4-14 The total and monomeric silica concentration versus time in the solution the initial total concentration of $\text{SiO}_2=17\text{mg/l}$, monomeric silica 5mg/l, pH=4, IOCS=0.2g/l and As(V) =250 $\mu\text{g/l}$ added after 24 hours

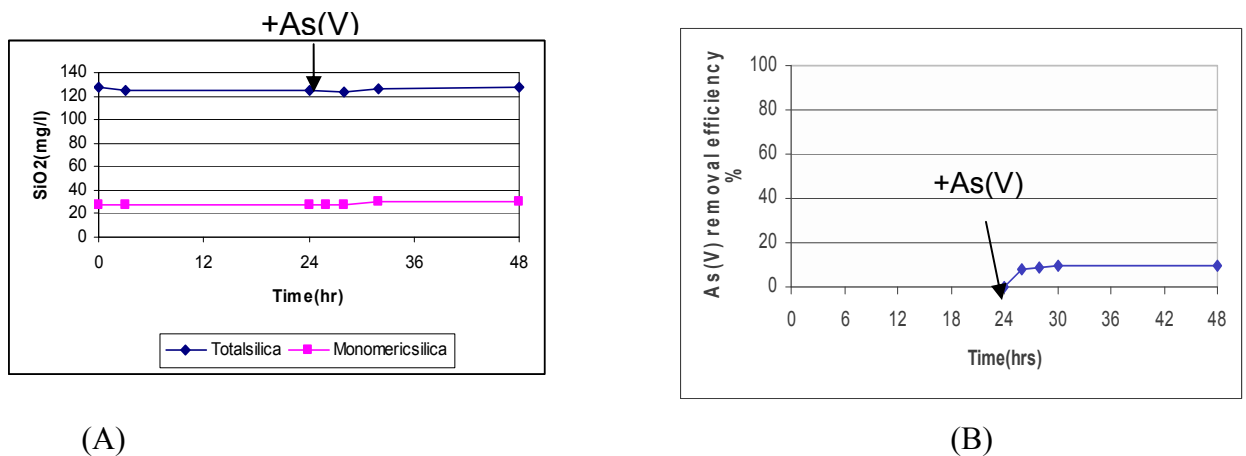


Figure 4-15 The total and monomeric silica concentration versus time in the solution for the initial total concentration of $\text{SiO}_2=166\text{mg/l}$, monomeric silica 5mg/l, pH=10, IOCS=0.2g/l and As(V) =250 $\mu\text{g/l}$ added after 24 hours

Figures 4-14A and 4-15A show the total and monomeric silica concentrations in the solution over 48 hours, together with the As(V) concentration (Figs 4-14 B and 4-15 B) that was added to the model water after 24 hours of contact time. Silica adsorption to IOCS was the same as in the experiment done with As(III). The removal efficiency of As(V) at silica concentrations of 17 mg/l and 166 mg/l concentration were 98 % and 10%, respectively

(b) Adsorption of total and monomeric silica and competitive arsenic and silica adsorption

Separated batch experiments were conducted at different pHs (4, 8 and 10) in order to assess the adsorption of total and monomeric silica on IOCS and to examine if the replacement of adsorbed silica by arsenic could take place. The model water was prepared with an initial total silica concentration of 41mg/l. The IOCS dosage applied was 4 g/l. After 48 hours As(III) or As(V) were added to observe if adsorbed silica could be replaced by arsenic. The samples were analyzed with and without filtering through a 0.45 μm membrane filter. Results from these experiments are shown in figures 4-16 and 4-17 shown

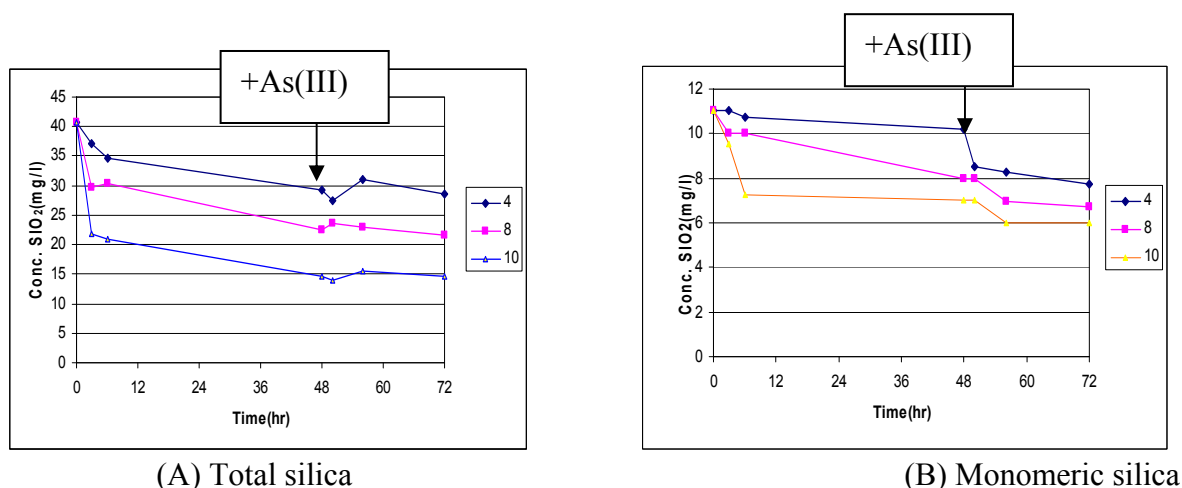


Figure: 4-16 Silica concentration versus time in the solution, at pH 4, 8, and 10; the initial $\text{SiO}_2=41\text{mg/l}$, $\text{IOCS}= 4\text{g/l}$, and $\text{As(III)}=7.2 \text{ mg/l}$ was added after 48 hours, contact time 72 hr.

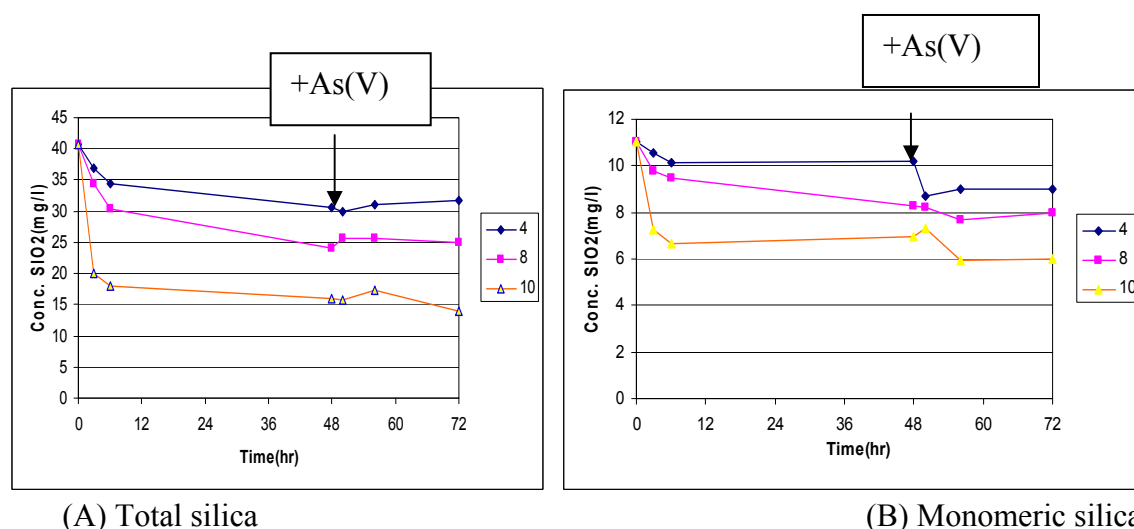


Figure: 4-17 Silica concentration versus time in the solution, at pH 4, 8, and 10, the initial $\text{SiO}_2=40\text{mg/l}$, $\text{IOCS}= 4\text{g/l}$, and $\text{As(V)} =8 \text{ mg/l}$ was added after 48 hours, and a contact time of 72 hours.

From the result in figures 4-16 and 4-17 it is clear that IOCS can remove the monomeric and the total (polymeric and monomeric) silica from the solution at pH 4, 8, and 10. The removal

efficiency of silica by IOCS increases with increased pH. The removal efficiency of total and monomeric is highest at pH 10. At higher pH levels, the dissociation of silica produces negatively charged species, such as $\text{Si}(\text{OH})_3^-$, and $\text{SiO}_2(\text{OH})_5^-$. The objective of arsenic addition to the model waters after 48 hour was to assess the replacement of silica by arsenic. However the concentration of silica did not show significant change in the model water. This might indicate that arsenic has a lower replacement capacity to silica (polymer and monomeric).

4.6 Batch adsorption isotherms for arsenite, arsenate, and silica

Batch adsorption isotherm experiments were conducted with model water containing As(III) or As(V), with and without the addition of silica at different pH using IOCS as an adsorbent. The objective of these experiments was to examine the effect of pH and silica concentration on adsorption capacity of IOCS for As(III) and As(V) removal.

4.6.1 Adsorption isotherm for As(III) and As(V) at pH 7 and 8.

This experiment was done jointly with MSc. participant Yasoda Shresta from Nepal and it addressed the effect of phospahte and pH on arsenic adsorption on IOCS. Batch adsorption isotherm experiments were carried out with model water containing of As(III) or As(V) at pH 7 and 8.

Adsorption of As(V) on IOCS at pH 7 and 8 as a function of time is shown in figures 4-18a and 4-20a respectively. Results obtained for As(III) adsorption are shown in figures 4-19a (pH=7) and 4-21a (pH=8). Data obtained at pH 7 fitted well with the Freundlich isotherm model presented in figures 4-18b (As(V)) and 4-20b (As(III)), and with the pH 8 Freundlich isotherm model presented in figures 4-19b(As(V)) and 4-21b(As(III)).

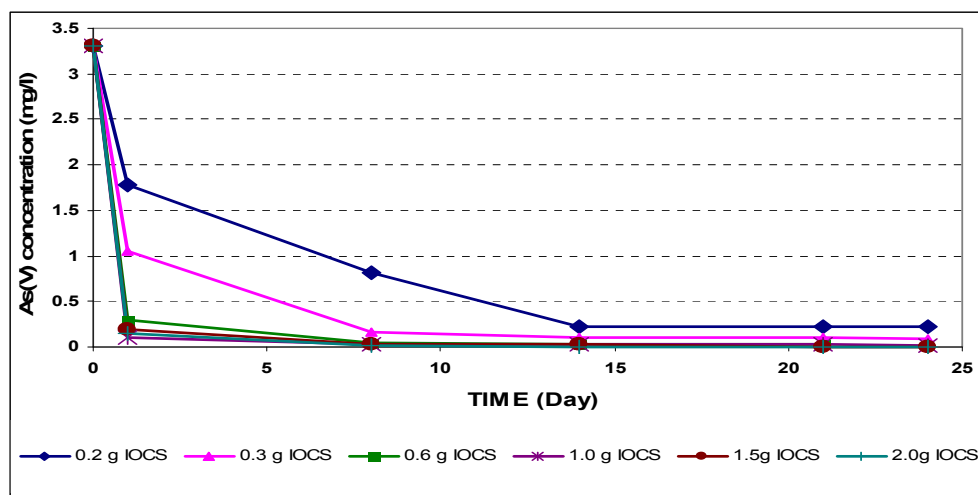


Figure 4-18a: As(V) concentration versus time at different IOCS dosage; initial As(V) concentration of 3300 $\mu\text{g/l}$, $\text{SiO}_2=4.5\text{mg/l}$, $\text{pH}=7+0.2$, $T=20^\circ\text{C}$; contact time 24 days (results from Y. Shresta's MSc thesis, 2009).

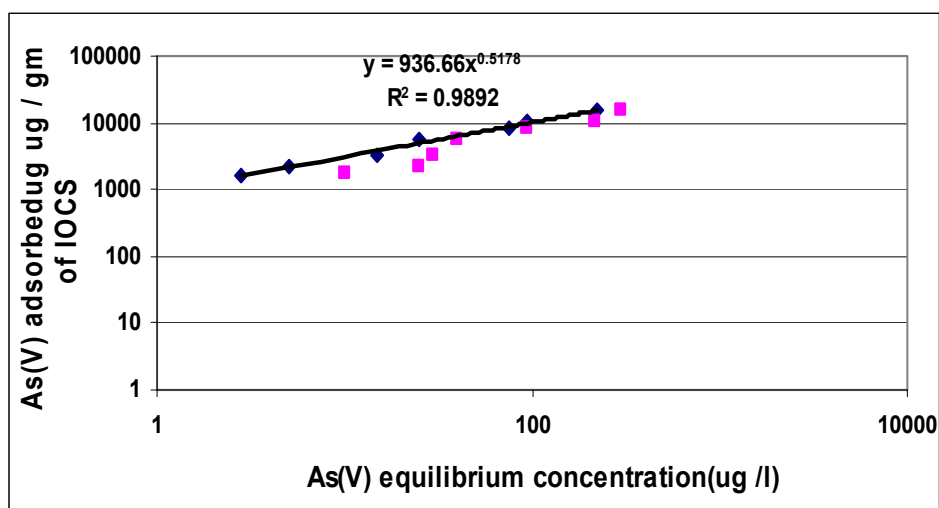


Figure 4-18b: Freundlich isotherm for As(V) adsorption on to IOCS; model water with initial As(V) 3300 μ g/l, silica concentration 4.5mg/l, pH=7.0 \pm 0.2, T=20°C, contact time 24 days (from Y. Shrestha's MSc thesis, 2009).

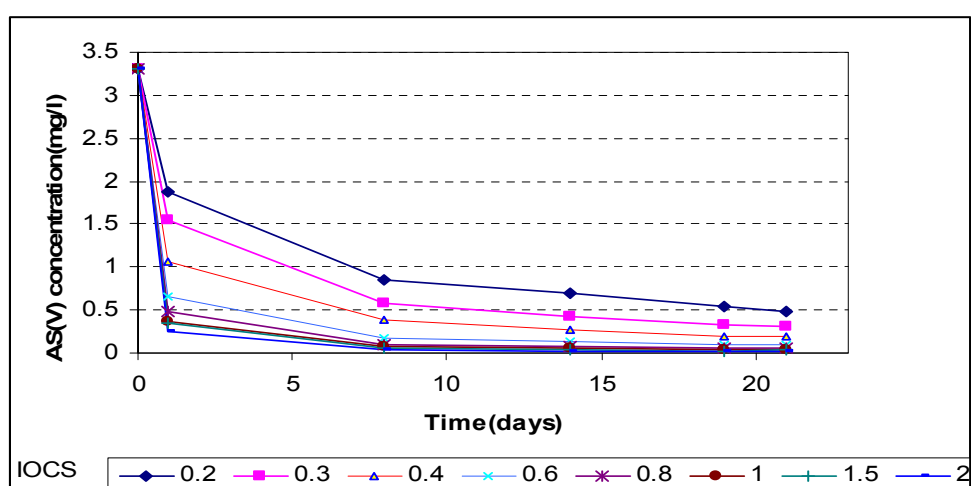


Figure 4-19a: As(V) concentration versus time at different IOCS dosage; initial As(V) concentration of 3400 μ g/l, SiO₂=4.5mg/l, pH=8 \pm 0.2, T=20°C; contact time 24 days

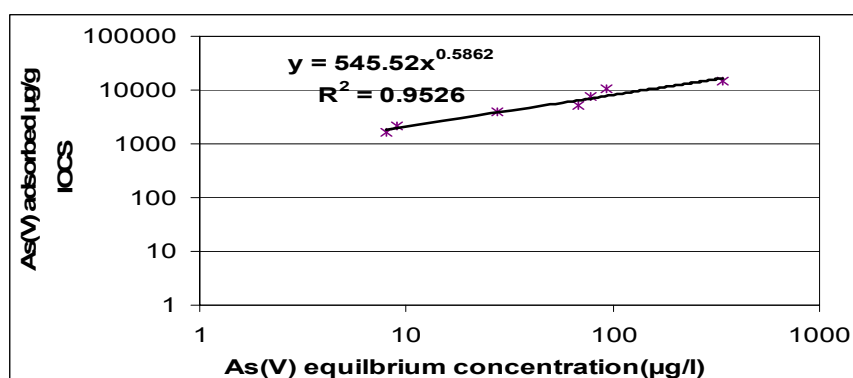


Figure 4-19b: Freundlich isotherm for As(V) adsorption on to IOCS; model water with initial As(V) 3400 $\mu\text{g/l}$, silica concentration 4.5mg/l, pH=8.0+0.2, T=20°C, contact time 24 days.

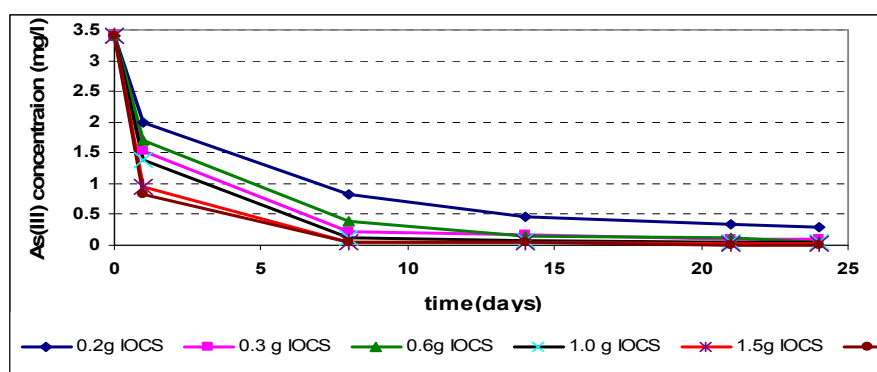


Figure 4-20a: As(III) concentration versus time at different IOCS dosage; initial As(III) concentration of 3300 $\mu\text{g/l}$, $\text{SiO}_2=4.5\text{mg/l}$, pH=7+0.2, T=20°C; contact time 24 days (results from Y. Shresta's MSc thesis, 2009).

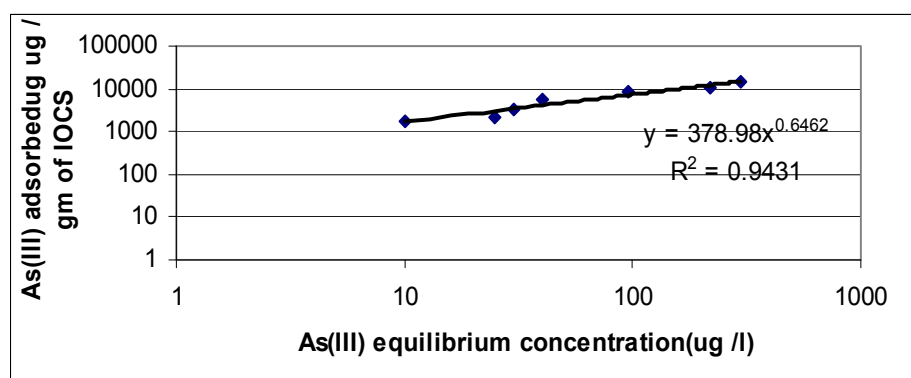


Figure 4-20b: Freundlich isotherm for As(III) adsorption on to IOCS; model water with initial As(III) 3300 $\mu\text{g/l}$, silica concentration 4.5mg/l, pH=7+0.2, T=20°C, contact time 24 days (From MSc thesis Y. Shresta 2009)

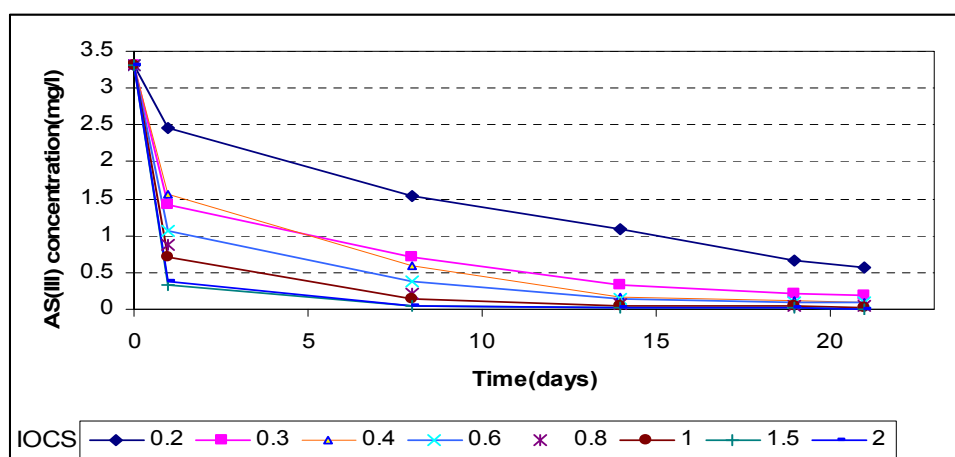


Figure 4-21a: As(V) concentration versus time at different IOCS dosage; initial As(V) concentration of 3300 $\mu\text{g/l}$, $\text{SiO}_2=4.5\text{mg/l}$, pH=8+0.2, T=20°C; contact time 24 days.

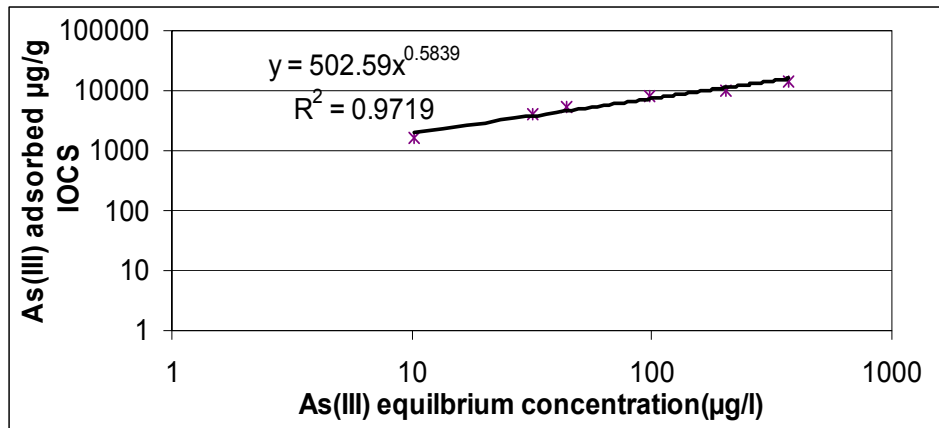


Figure 4-21b: Freundlich isotherm for As(III) adsorption on to IOCS; model water with initial As(III) 3300µg/l, silica concentration 4.5mg/l, pH=8.0±0.2, T=20°C, contact time 24 days

Table 4-2 Summary isotherm constants As(III) and As(V) on IOCS at pH 7 and 8

Type of arsenic	pH	K value	1/n value
As(V)	7	936	0.5178
As(V)	8	545	0.5862
As(III)	7	378	0.6462
As(III)	8	502	0.5839

From the above results it is clear that adsorption capacity of IOCS is higher for As(V) at pH 7 than at pH 8. This is mainly due to the predominant As(V) species in pH 7 namely H_2AsO_4^- , which is more favorable for adsorption on positively charged IOCS surfaces. At pH 8 the dominant As(V) species is HAsO_4^{2-} but the surface charge of IOCS became less positive, and adsorption was less favorable. The expected result was slightly to decrease the adsorption of As(III) at pH 8, but the result show that the adsorption capacity higher at pH 8 than 7.

4.6.2 Adsorption isotherm for As(III), As(V) and silica adsorption on IOCS

Additional batch adsorption experiments were carried out with the model water containing 23 and 58 mg/l of silica, in addition to As(III) or As(V) to quantify the adsorption capacity of IOCS for As(III) and As(V) in the presence of silica. It took approximately 19 days to reach equilibrium conditions. Results of these experiments are given in figures 4-22, 4-23, and 4-24.

4.6.2.1 Adsorption isotherm for As(III)

Batch adsorption isotherms were conducted the model water contain with initial silica concentration of 23, and 58 mg/l, As(III) at different IOCS dosage. Results obtained for As(III) adsorption on IOCS, at the silica concentrations 23 and 58 were found to fit the Freundlich adsorption isotherm experiment and are shown in figures 4-22b and 4-23b. Figures 4-22a and 4-23a show removal efficiency As(III) versus time at silica concentrations of 23 and 58 mg/l, respectively

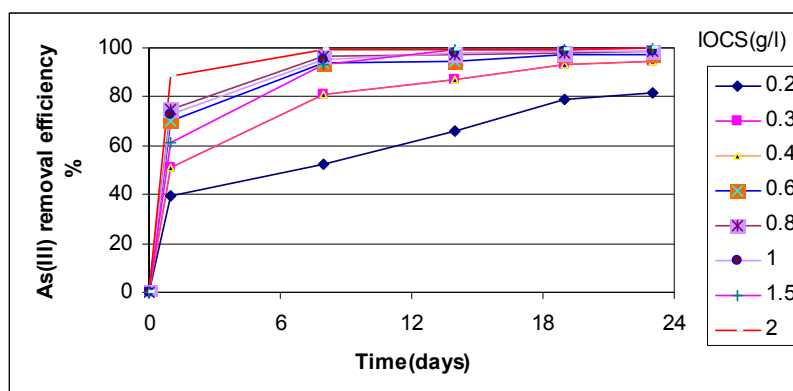


Figure 4-22a: As(III) removal efficiency versus time at different IOCS dosages, initial As(III) concentration of 2600 $\mu\text{g/l}$, $\text{SiO}_2=23\text{mg/l}$, $\text{pH}=8.0\pm0.2$, $T=20^\circ\text{C}$, contact time 23 days

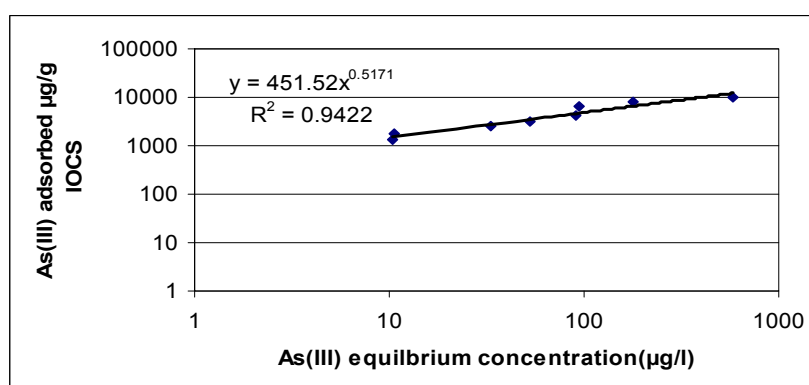


Figure 4-22b: Freundlich isotherm for As(III) adsorption on to IOCS; model water with initial As(III) =2600 $\mu\text{g/l}$, silica concentration 23mg/l, $\text{pH}=8.0\pm0.2$, $T=20^\circ\text{C}$, contact time is 23 days

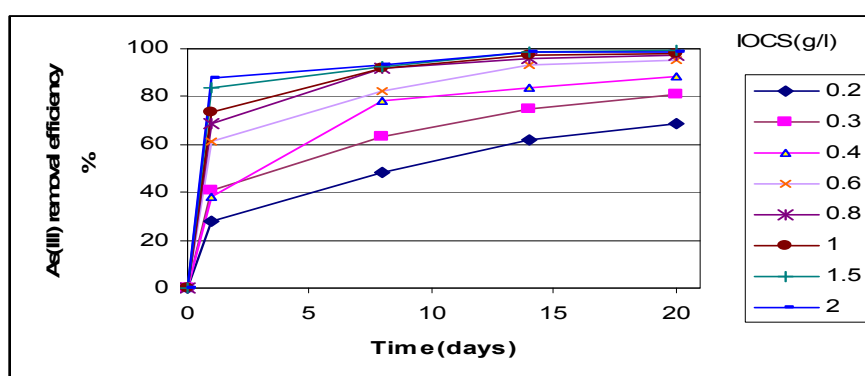


Figure 4-23a: As(III) concentration versus time at different IOCS dosage; initial As(III) concentration of 2600 $\mu\text{g/l}$, $\text{SiO}_2=58\text{ mg/l}$, $\text{pH}=8\pm0.2$, $T=20^\circ\text{C}$; contact time 21 days

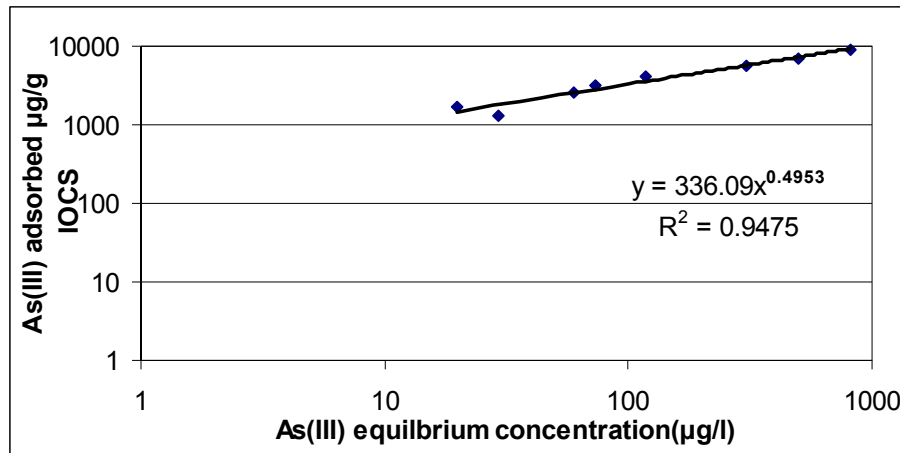


Figure 4-23b: Freundlich isotherm for As(III) adsorption on to IOCS; model water with initial As(III) 2600µg/l, silica concentration 58mg/l, pH=8.0±0.2, T=20°C, contact time 21 days

From figures 4-22b and 4-23b, it is clear that the adsorption of As(III) decreases with increasing silica concentration. The adsorption isotherm constant K , that indicates IOCS adsorption capacity for As(III), reduced from 451 to 336 with an increase silica from 23 mg/l to 58 mg/l.

4.6.2.2 Adsorption isotherm for As(V)

Similar batch adsorption experiments were conducted with model water containing As(V) with an initial silica concentration of 23 and 58 mg/l at different IOCS dosages. Results obtained for As(V) adsorption on IOCS in model water with silica concentration of 23 and 58 were found to fit the Freundlich adsorption isotherm well with a correlation coefficient (R^2) of 0.99 figure (4-24b) and 0.9 figure (4-25b) for As(V) in the presence of silica concentrations of 23 and 58 mg/l, respectively. Figures 4-25a and 4-26a show As(V) removal efficiency versus time, at silica concentrations of 23, and 58 mg/l, respectively.

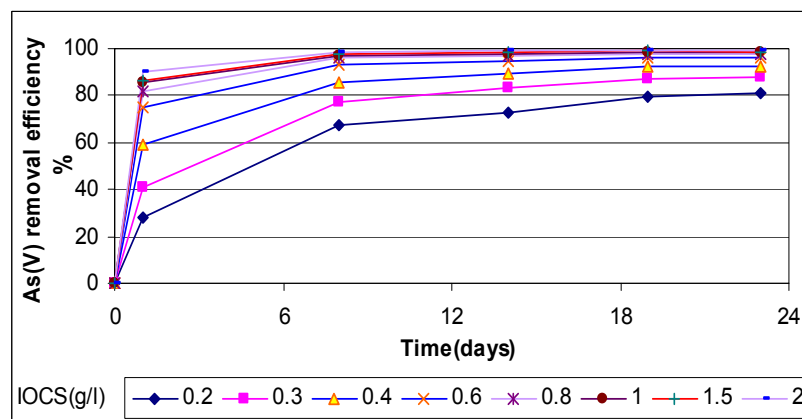


Figure 24a: As(V) removal efficiency versus time at different IOCS dosages; initial As(V) concentration 2600 µg/l, SiO₂=23mg/l, pH=8.0±0.2, T=20°C; contact time 23 days.

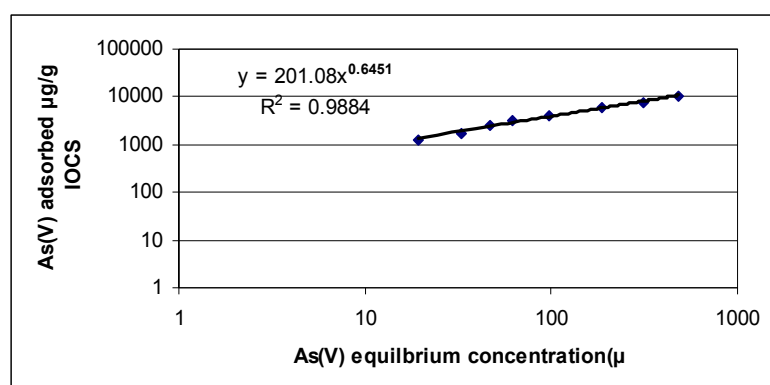


Figure 4-24b: Freundlich isotherm for As(V) adsorption on to IOCS; model water: initial As(V) =2600µg/l, silica concentration 23mg/l, pH=8.0±0.2, T=20°C, contact time 23 days.

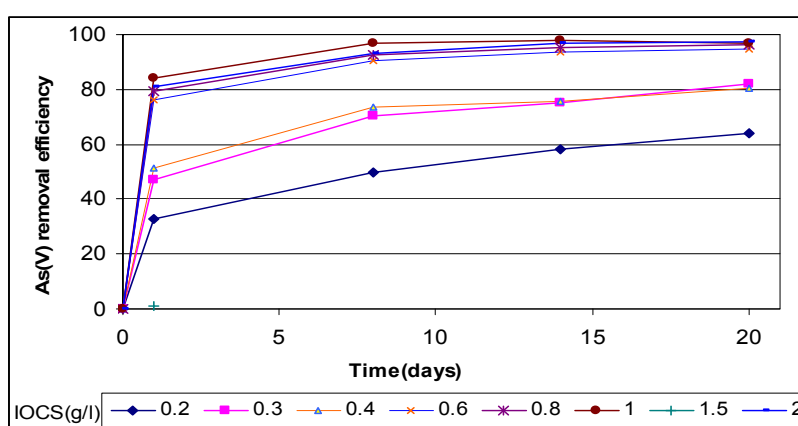


Figure 4-25a: As(V) concentration versus time at different IOCS dosages; initial As(V) concentration of 2600µg/l, SiO₂=58 mg/l, pH=8±0.2, T=20°C; contact time 20 days.

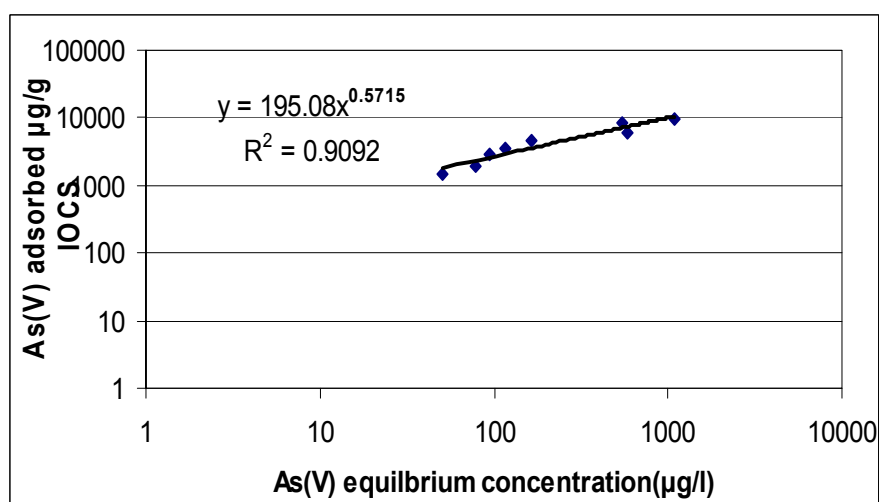


Figure 4-25b: Freundlich isotherm for As(V) adsorption on to IOCS; model water with initial As(V) 2600µg/l, silica concentration 58mg/l, pH=8.0±0.2, T=20°C, contact time 20days

From Figs 4-25a, 4-25b and 4-25b it is clear that the adsorption of As(V) significantly decreases when silica concentration increases. The adsorption isotherm constant K for As(V) adsorption on IOCS were 545, 201, and 195 with initial silica concentrations of 4.5, 23.0, and 58.0 mg/l, respectively.

4.6.2.3 Removal of total silica by IOCS in the presence of As(III) and As(V)

In previous batch adsorption experiments presented in section 4.6.2, besides the arsenic adsorption, removal of silica was also measured. The removal of total silica over time in the presence of As(III) or As(V) is shown in figures 4-26, 4-27 and 4-28.

(A) Initial silica concentration of (23mg/l)

The model water contains As(III), As(V), and the initial silica concentration of 23mg/l. The figure 4-27 shows the removal of silica over time

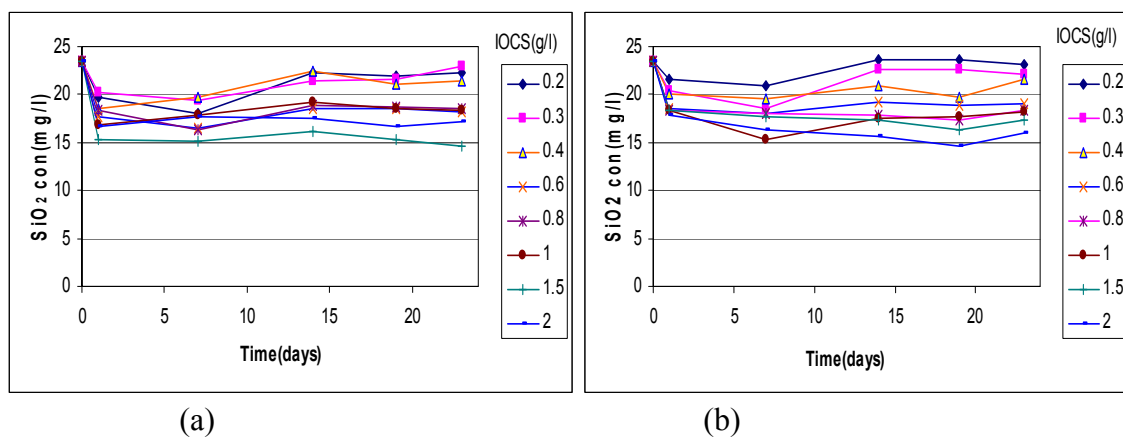


Figure 4-26 Total silica concentration versus contact time at different IOCS doses; initial SiO₂ concentration 23mg/l, initial arsenic concentration 2600 µg /l: As(III) graph (a) or As(V) graph (b), pH=8.0±0.2, T=20°C, contact time 21days

Figures 4-26 (a) and (b) show the removal of silica over time in the presence of As(III) and As(V). The removal of silica increased with increased IOCS dosage. The removal of silica was not significantly affected by the arsenic speciation in the model water. The increasing amount of silica in the model water after 7 days might be due to depolymerization. However, the final concentration of the silica is lower than the initial concentration of silica. This result is similar to the result obtained from the screen experiment. This confirmed that silica can be adsorbed to IOCS.

(B) Initial silica concentration of 58 mg/l

The model water contained As(III) or As(V), and initial silica concentration was 58mg/l. The figures 4-27 and 4-28 show removal of silica with time

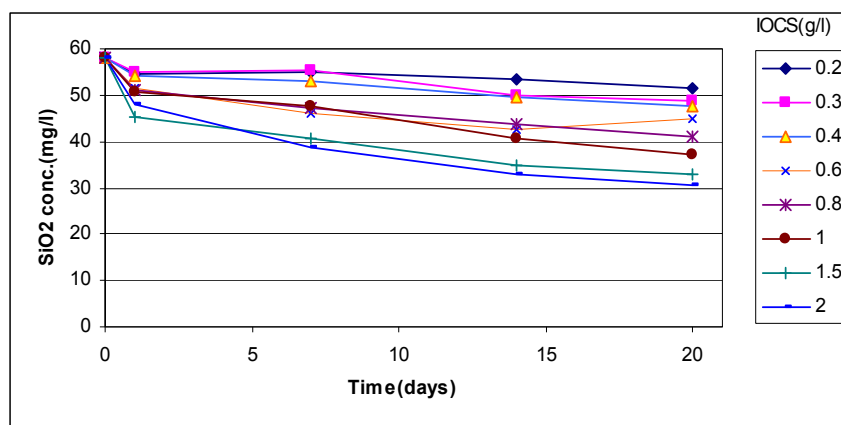


Figure 4-27a Total silica concentration versus contact time at different IOCS doses; initial SiO₂ concentration 58mg/l, As(V) = 2600 µg /l, and pH=8+0.2, T=20°C, and contact time is 20 days.

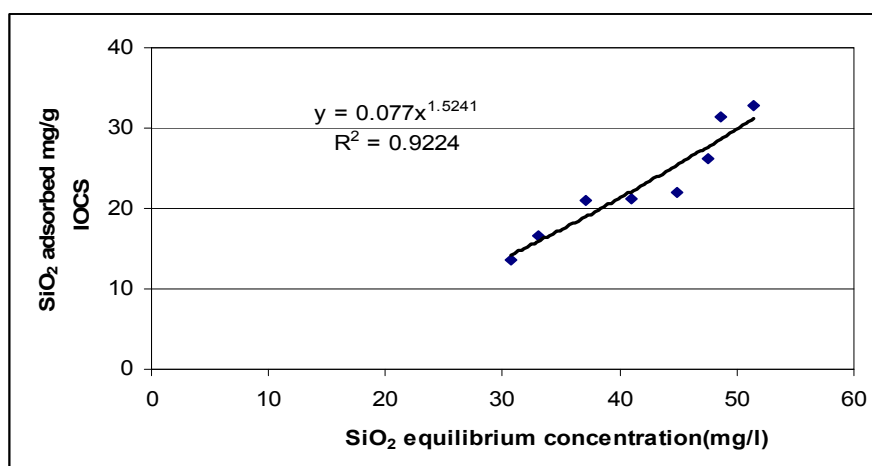


Figure 4-27b Freundlich isotherm for SiO₂ adsorption on to IOCS; model water: initial silica concentration 58mg/l, As(V) =2600µg/l, pH=8+0.2, and contact time is 20 days.

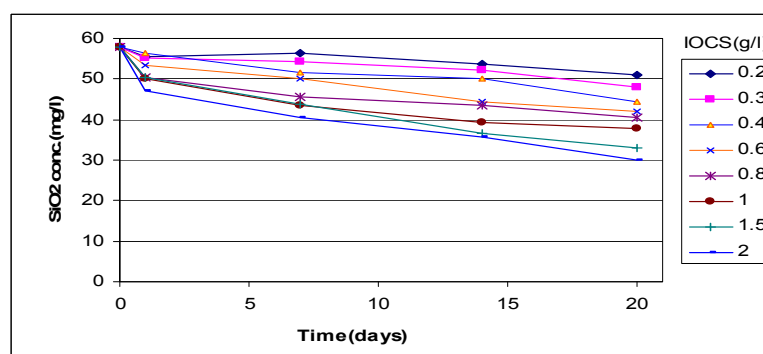


Figure 4-28a Total silica concentration versus contact time at different IOCS doses; initial SiO₂ concentration 58mg/l, As(III) = 2600 µg /l, and pH=8+0.2, T=20°C, and contact time is 20 days

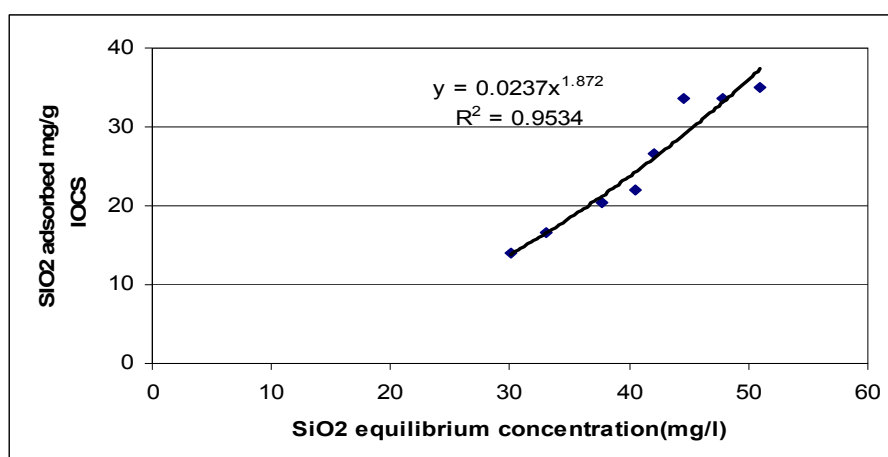


Figure 4-28b: Freundlich isotherm for silica adsorption on to IOCS; model water with 58mg/l, As(III) =2600μg/l, pH=8.0±0.2, T=20°C, and contact time is 20 days

Figures 4-27 (a) and 4-28 (a) show the removal of silica over time in the presence of As(III) and As(V). The concentration of silica decreased with time and with increased IOCS dosage. The removal of silica was not showing significantly difference by the arsenic speciation in the model water. The final concentration of the silica is lower than the initial concentration of silica. This result is similar to the result obtained from the screen experiment. This confirmed that silica can be adsorbed to IOCS.

4.6.2.4 Adsorption of As(III) and (V) at different silica concentrations

The figures 4-29 and 4-30 show the Freundlich adsorption isotherms for As(III) and As(V) adsorption on IOCS at different silica concentrations (4.5, 28.0 and 58.0 mg/l). The results presented in annex B.

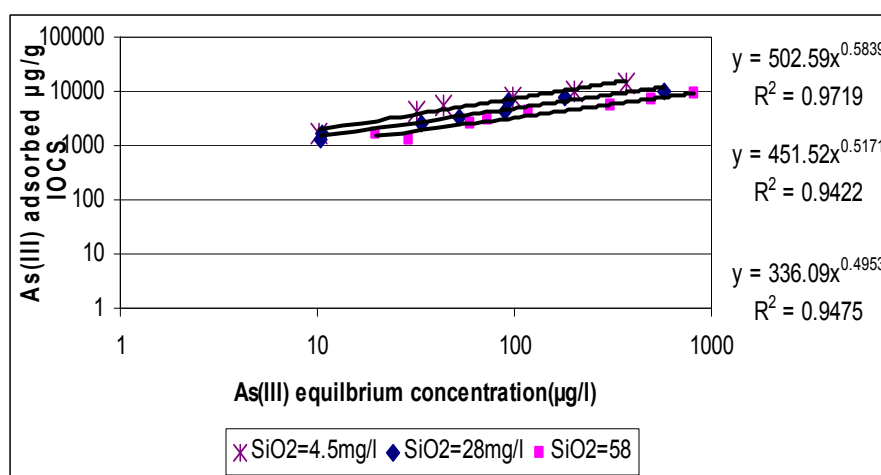


Figure 4-29: Freundlich isotherm for As(V) adsorption on to IOCS; three models of water prepared with initial silica concentrations of 4.5, 20, and 58mg/l As(V) =3300μg/l, pH=8.0±0.2, T=20°C, contact time is 20 to 24 days.

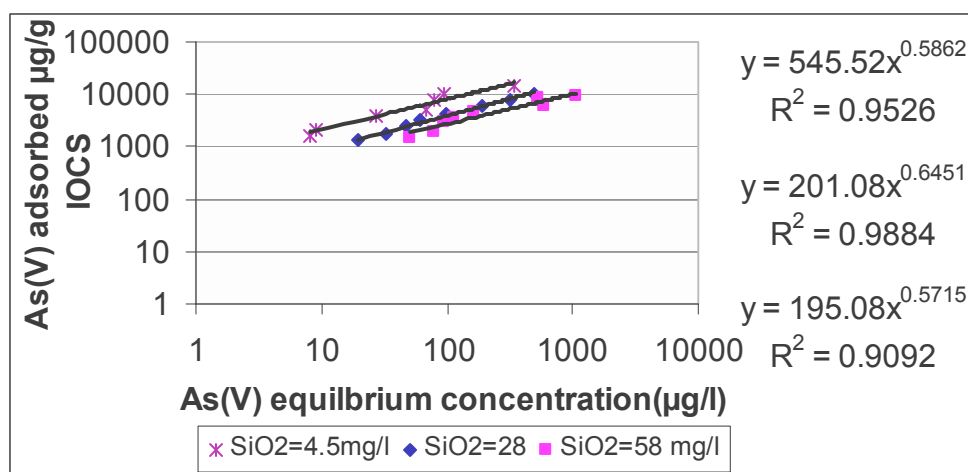


Figure 4-30: Freundlich isotherm for As(V) adsorption on to IOCS; three model water at initial silica concentration 4.5, 20, and 58mg/l As(V) =3300µg/l, pH=8.0±0.2, T=20°C, contact time is 20-24 days

Table 4-3 Freundlich adsorption isotherm coefficients for As(III) and As(V) adsorption on IOCS at different silica concentrations at pH=8.0±0.2

Arsenic speciation	SiO ₂ (mg/l)	K value	1/n value	R ²
As(V)	4.5	502.59	0.5839	0.9719
As(V)	23	451.52	0.5171	0.9422
As(V)	58	336.09	0.4953	0.9475
As(III)	4.5	545.52	0.5862	0.9526
As(III)	23	201.08	0.6451	0.9884
As(III)	58	195.08	0.5715	0.92

From the results presented in the table 3 and in figures 4-29 and 4-30 it is clear that the removal efficiency of As(V) and As(III) decreases with increasing of silica concentration. The removal efficiency of As(V) is higher at low silica concentration, but it decreases significantly with the increasing of silica concentration compare to As(III). This is mainly due to the presence of the dominant As(V) species in pH 8.0 is HAsO_4^{2-} surface charge became less positive with increasing silica concentration. In the case of As(III), the dominant As(III) species at pH=8.0 is H_3AsO_3^0 , and consequently the As(III) adsorption on IOCS is less affected by the increasing silica concentration in the model water as compared to As(V).

Chapter 5 - Conclusions and Recommendations

This chapter includes conclusions of the research and recommendations for further related studies.

5.1 Conclusions

- The chemical composition of IOCS from one of the Dutch iron removal plants has high silicon (approximately 23 mg/g IOCS) and high iron (333.3mg/gIOCS) concentrations. Composition of filter material tested confirmed that silica can be adsorbed on IOCS.
- IOCS has high adsorption capacity for As(III) and As(V). Similarly to arsenic, IOCS can effectively remove silica from a solution.
- IOCS can adsorb both monomer and polymer silica; adsorption of silica (monomer and polymers) increases as pH of the model water increases.
- The removal efficiency of As(V) by IOCS decreased with pH increase of model water from 6 to 8 . IOCS As(V) adsorption capacity is high at pH 6, but was significantly reduced with increasing pH to 8. This is mainly due to the presence of dominant As(V) species H_2AsO_4^- within the pH ranges of 2.2 to 6.9; H_2AsO_4^- is negatively charged and has more favorable adsorption energy to positively charge surface of IOCS. Above pH 6.9, the dominant As(V) species became less positive, and adsorption is less favorable.
- Removal efficiency of As(III) was only slightly reduced with an increase of pH from 6 to 8. However, the predominant As(III) species in model water at pH values of less than 9.2 is neutral H_3AsO_3^0 and is consequently less affected by an increase of pH from 6 to 8.
- As(V) capacity IOCS decreased significantly as the concentration of silica increased from 4.5 to 65mg/l in model water at pH 8, while As(III) adsorption efficiency decreased only slightly. Due to silica level increased(4.5 to 65 mg/l) the removal efficiency As(V) and As(III) were decreased by 50 and 25%, respectively
- In silica (17mg/l) containing model water, removal efficiency of As(III) decreased by 10% and As(V) by 44% with pH increase from 4 to 10. The removal efficiency of As(III) and As(V) at silica concentration of 166 mg/l decreased by 28% and 70% with an increase in the pH from 4 to 10 respectively
- The effect of silica on arsenic adsorption on IOCS depends on the silica concentration and pH. The removal efficiency of As(V) and As(III) in silica containing water decreases with increasing pH. Removal efficiency of arsenic was found to be low at a high pH 10. This is mainly due to:
 - Polymer silica that physically fouls IOCS and blocks sites for arsenic adsorption.
 - Dissociation of silica at high pH that produces negatively charged species, such as $\text{Si}(\text{OH})_3^-$, $\text{SiO}_2(\text{OH})_5^-$, and $\text{SiO}_2(\text{OH})_2^{2-}$ which are strongly attracted to IOCS.
 - Reaction of oxygen atom of the polymer silica $-\text{SiO}-$ and aqueous $-\text{OH}-$ with IOCS.

- The removal efficiency of As(III) and As(V) is less affected by the presence of silica at low pH (e.g. pH=4). This is mainly due to
 - The predominant uncharged silica form (Si(OH)_4) at a low pH that is not attracted to positively charged IOCS surface.
 - The polymers silica that is unstable and exist in very small size (2-3nm) at pH <7 and has very low effect on arsenic removal by IOCS.
- Reduction of pH should be considered when removing arsenic from groundwater with high silica concentration,.

5.2 Recommendations

- The effect of silica and pH on arsenic removal by IOCS should be further studied with the help of RSSCT and a pilot plant.
- Further studies are required to determine the removal capacity of IOCS for silica adsorption by IOCS
- Further study should be conducted on the effect of other ions in presence of silica on arsenic removal by IOCS.

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Appendix

Appendix A: Silica Species

Table: 1 Total, polymer and monomeric silica at different pH levels, the model water measured by ICP and spectrometer.

pH	Silica dose (mg/l)	Total silica measured by ICP	Silica measured by Spectrometer		Silica measured by ICP	
			Monomersilica	Polymersilica	Silica conc. (Size <0.1 μm)	Silica conc. (Size >0.1 μm)
4	10	12	10	2	11	1
	30	33	14	19	27	5
	50	52	18	33	43	7
	200	208	32	176	157	51
6	10	12	10	2	12	0
	30	33	14	18	30	2
	50	53	19	33	46	6
	200	208	32	177	158	50
7	10	12	10	2	12	0
	30	33	14	18	32	1
	50	53	19	34	50	3
	200	218	32	186	170	48
8	10	12	10	2	12	0
	30	33	15	18	32	1
	50	53	19	34	51	2
	200	220	31	189	189	31
10	10	12	10	2	12	0
	30	33	15	18	32	1
	50	52	23	28	51	1
	200	221	40	181	200	21

Appendix B: Screen batch experiment

Table:1 Batch experiment result of As(III) adsorption on IOCS, initial As(III) concentration 240 $\mu\text{g/l}$, pH 8 \pm 0.2, contact time 24 hr, 100 rpm

Time(hrs)	Adsorbent dose of IOCS (g/l)				
	2	1,5	1	0,5	0,2
0	240	240	240	240	240
2	149	76	75	35	31.5
4	134	71	46	33	23.2
6	136	45	42	21	21
24	59	38	21	15	11

Table: 2 Batch experiment result of As(V) adsorption on IOCS, initial As(V) concentration 230 μ g/l , pH 8 \pm 0.2, contact time 24 hour, 100 rpm

Time(hrs)	Adsorbent dose of (g/l)				
	2	1,5	1	0,5	0,2
0	230	230	230	230	230
2	88	45	26	5	5
4	82	41	23	5	5
6	35	29	15	3	3
24	34	24	6	2	2

Table: 3 Batch experiment result of Silica adsorption on IOCS, initial silica concentration 33mg/l , pH 8 \pm 0.2, contact time 24 hour, 100 rpm, with out filtering

Time(hrs)	240 μ g/l , pH 8 \pm 0.2 IOCS(g/l)				
	0.2	0.5	1	1.5	2
0	33	33	33	33	33
2	35	33	39	38	41
4	33	34	36	36	38
6	31	32	33	33	35
24	32	30	29	29	28

Table: 4 Batch experiment result of Silica adsorption on IOCS, initial silica concentration 33mg/l, contact time 24 hour, 100 rpm, filtered through 0.45 membrane filter.

Time(hrs)	Dosage of IOCS(g/l)				
	0.2	0.5	1	1.5	2
0	33	33	33	33	33
2	31	31	30	30	29
4	31	31	30	29	28
6	30	30	28	28	28
24	30	30	28	28	28

Table:5 Batch experiment result of As(III) adsorption on IOCS, initial As(III) concentration 265 $\mu\text{g/l}$, pH 6,7, and 8, contact time 24 hr, 100 rpm

Time(hr)	pH		
	6	7	8
0	265	265	265
2	160	167	188
4	151	157	157
6	138	142	144
24	97	103	110

Table: 6 Batch experiment result of As(V) adsorption on IOCS, initial As(V) concentration 250 $\mu\text{g/l}$, pH 6,7, and 8, contact time 24 hr, 100 rpm

Time(hr)	pH		
	6	7	8
0	250	250	250
2	57.5	88.5	169.5
4	33	73.5	108.5
6	27	74.5	96
24	6	43	58

Table: 7 Batch experiment result of As(III) adsorption on IOCS in presence of initial silica concentrations(mg/l) (4.5, 17, 33, 45, and 65), initial As(III) concentration 260 $\mu\text{g/l}$, pH 8 \pm 0.2, contact time 24 hr, 100 rpm

Time(hr)	SiO ₂ (mg/l)				
	4.5	17	33	45	65
0	260	260	260	260	260
2	148.5	160	175	188	190
4	140	150	155	163	165
6	135.5	137.5	143	160	162
24	58.7	84.5	109.5	124.5	123

Table: 8 Batch experiment result of As(V) adsorption on IOCS in presence of initial silica concentrations(mg/l) (4.5, 17, 33, 45, and 65), initial As(V) concentration 240 $\mu\text{g/l}$, pH 8 \pm 0.2, contact time 24 hr, 100 rpm

Time(hr)	SiO ₂ (mg/l)				
	4.5	17	33	45	65
0	240	240	240	240	240
2	87.5	122	168	188	190
4	81.5	116.5	176	186	188.5
6	34.8	102	152.5	172.5	183.5
24	33.6	85	123.5	139	166

Table:9 Batch experiment result of As(III) adsorption on IOCS in presence of initial silica concentrations(mg/l), initial As(III) concentration 3200 $\mu\text{g/l}$, pH 6, 7, and 8, contact time 14 days, and 100 rpm

pH	SiO ₂ (mg/l)				Time(days)
	4.5	20	50	250	
6	3200	3200	3200	3200	0
	1580	1655	1750	1765	1
	590	645	520	1242.5	7
	135	160	155	657.5	14
7	3200	3200	3600	3200	0
	1535	1750	1565	2045	1
	800	1135	910	1282.5	7
	295	305	678.15	962.5	14
8	3200	3200	3200	3200	0
	1335	1795	2000	2055	1
	1160	1290	1980	1372.5	7
	550	560	1925	1072.5	14

Table: 10 Batch experiment result of As(V) adsorption on IOCS in presence of initial silica concentrations(mg/l), initial As(V) concentration 3600µg/l , pH 6, 7, and 8, contact time 14 days, and 100 rpm

pH	SiO ₂ (mg/l)				Time(days)
	4.5	20	50	4.5	
6	3600	3600	3600	3600	0
	500	620	630	1030	1
	55	115	325	530	7
	23.75	30	107.5	523.05	14
7	3600	3600	3600	3600	0
	925	920	1065	1565	1
	380	570	1160	910	7
	105	192.5	530	678.15	14
8	3600	3600	3600		0
	1110	1470	1650	2270	1
	845	1400	1745	1117.5	7
	322.5	522.5	765	1070.85	14

Table:11 Batch experiment result of As(III) adsorption on IOCS, initial As(III) concentration 240µg/l, SiO₂ 17mg/l, pH 4, 8, and 10, contact time 24 hr, and 100 rpm

Time(hr)	pH		
	4	8	10
0	240	240	240
2	145	145	151
4	128.5	130.5	148
6	118.5	124	138.5
24	81	89	105.5

Table:12 Batch experiment result of As(III) adsorption on IOCS, initial As(III) concentration 240 μ g/l, SiO₂ 166mg/l, pH 4, 8, and 10, contact time 24 hr, and 100 rpm

Time(hr)	pH		
	4	8	10
0	240	240	240
2	160	171	197
4	151.5	167.5	185
6	135.5	156	185.5
24	105	123.5	172

Table:13 Short batch experiment result of As(V) adsorption on IOCS, initial As(V) concentration 230 μ g/l, SiO₂ 17mg/l, pH 4, 8, and 10, contact time 24 hr, and 100 rpm

Time(hr)	pH		
	4	8	10
0	230	230	230
2	9.5	139	172
4	6.5	120.5	165
6	8	120.5	146
24	8	76.5	108

Table:14 Batch experiment result of As(V) adsorption on IOCS, initial As(V) concentration 230 μ g/l, SiO₂ 166mg/l, pH 4, 8, and 10, contact time 24 hr, and 100 rpm

Time(hr)	pH		
	4	8	10
0	230	230	230
2	11.5	152.5	201.5
4	12	142.5	200
6	8.1	137.5	200.5
24	10.1	104	170.5

Table:15 Batch experiment result of total silica removal, of initial As(III) concentration 7.2mg/l added after 48 hr, IOCS 4mg/l, SiO₂ 41mg/l, pH 4, 8, and 10, contact time 72 hr, and 100 rpm

Time(hr)	pH		
	4	8	10
0	41	41	41
3	37	34	20
6	34	30	18
48	31	24	16
50	30	26	16
56	31	26	17
72	32	25	14

Table:16 Batch experiment result of total monosilica removal, of initial As(III) concentration 7.2mg/l added after 48 hr, IOCS 4mg/l, SiO₂ 11mg/l, pH 4, 8, and 10, contact time 72hr, and 100 rpm

Time(hr)	pH
----------	----

	4	8	10
0	11	11	11
3	11	10	10
6	11	10	7
48	10	8	7
50	9	8	7
56	8	7	6
72	8	7	6

Table:17 Batch experiment result of total silica removal, of initial As(V) concentration 8mg/l added after 48 hr, IOCS 4mg/l, SiO₂ 41mg/l , pH 4, 8, and 10, contact time 72 hr, and 100 rpm

Time(hr)	pH		
	4	8	10
0	37	30	22
3	35	30	21
6	29	23	15
48	27	24	14
50	31	23	16
56	28	22	15
72	41	41	41

Table:18 Batch experiment result of total monosilica removal, with initial As(V) concentration 8mg/l added after 48 hr, IOCS 4mg/l, SiO₂ 11mg/l , pH 4, 8, and 10, contact time 72hr, and 100 rpm

Time(hr)	pH		
	4	8	10
0	11	11	11
3	11	10	7
6	10	9	7
48	10	8	7
50	9	8	7
56	9	8	6
72	9	8	6

Appendix C: Batch adsorption isotherms for arsenic and silicaTable 1a: Batch experiment result for As(III) adsorption on IOCS; initial As(III) concentration of 3300 µg/l, SiO₂=4.5mg/l, pH=8+0.2; contact time 24 days, rpm 100

IOCS(g/l)	Days					
	0	1	8	14	19	24
0.2	3300	1575	930	480.96	681	373
0.3	3300	1270	495	283.9	215	200
0.4	3300	990	322.5	118.57	96	81
0.6	3300	775	151.97	56.78	46.5	36
0.8	3300	655	95.19	33.4	31	20
2	3300	300	25.05	5.01	13.4	10

Table: 1b: As(III) isotherm adsorption on IOCS; model water with initial silica concentration 4.5mg/l, pH=8.0+0.2, contact time 24 days

Adsorbent dose(g/l)	Co	Ce	Amount adsorbed in mg/l	X/M in mg/l
0.2	3300	373	2928	14638
0.3	3300	202	3098	10327
0.4	3300	98	3202	8005
0.6	3300	44	3256	5427
0.8	3300	32	3268	4085
2	3300	10	3290	1645

Table: 2a Batch experiment result for As(V) adsorption on IOCS; initial As(V) concentration of 3300 µg/l, SiO₂=4.5mg/l, pH=8+0.2; contact time 24 days, rpm 100

IOCS(g/l)	Days					
	0	1	8	14	19	21
0.2	3400	1240	482.5	399.13	340	338
0.3	3400	1240	282.5	101.87	93.5	93
0.4	3400	610	145.29	101.87	85	79
0.6	3400	575	155.31	76.82	75	68
0.8	3400	355	61.79	38.41	43	28
2	3400	16.25	20.04	16.7	9	8

Table: 2b: As(III) isotherm adsorption on IOCS; model water with initial silica concentration 4.5mg/l, pH=8.0+0.2, contact time 24 days

Adsorbent dose(g/l)	Co	Ce	Amount adsorbed in mg/l	X/M in mg/l
0.2	3400	338	2863	14313
0.3	3400	93	3107	10357
0.4	3400	79	3121	7803
0.6	3400	68	3133	5221
0.8	3400	28	3173	3966
1.5	3400	9	3191	2127

2	3400	8	3192	1596
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Table: 3a Batch experiment result for As(V) adsorption on IOCS; initial As(V) concentration of 2600 µg/l, SiO₂=23mg/l, pH=8+0.2; contact time 23 days, rpm 100

IOCS(g/l)	Days					
	0	1	8	14	19	23
0.2	2600	2460	1532.5	1077	666	579
0.3	2600	1420	717.5	333	218	180
0.4	2600	1550	601.25	165	112	94
0.6	2600	1075	377.5	148	92.5	90
0.8	2600	865	213.75	71	55	53
1	2600	705	141.25	48	39.5	34
1.5	2600	325	39.2	20	14.7	11
2	2600	380	45.3	16	12.1	10

Table: 3b: As(III) isotherm adsorption on IOCS; model water with initial silica concentration 23mg/l, pH=8.0+0.2, contact time 23 days

Adsorbent dose(g/l)	Co	Ce	Amount adsorbed in mg/l	X/M in mg/l
0.2	2600	579	2021	10105
0.3	2600	180	2420	8067
0.4	2600	94	2507	6266
0.6	2600	90	2510	4183
0.8	2600	53	2548	3184
1	2600	34	2567	2567
1.5	2600	11	2590	1726
2	2600	10	2590	1295

Table: 4a Batch experiment result for As(V) adsorption on IOCS; initial As(V) concentration of 2600 µg/l, SiO₂=23mg/l, pH=8+0.2; contact time 23days, rpm 100

As(V) concentration		Time(days)				
IOCS	0	1	8	14	19	23
0.2	3300	1870	855	700	534	486
0.3	3300	1540	587.5	433	333	313
0.4	3300	1060	380	278	194.5	189
0.6	3300	650	167.5	128	98	97
0.8	3300	480	105.21	71	64	62
1	3300	365	75	55	43	47
1.5	3300	345	66.8	37	27.5	33
2	3300	255	48	26	18.2	19

Table: 4b: As(III) isotherm adsorption on IOCS; model water with initial silica concentration 23mg/l, pH=8.0+0.2, contact time 23 days

Adsorbent dose(g/l)	Co	Ce	Amount adsorbed in mg/l	X/M in mg/l
0.2	2600	486	2114	
0.3	2600	313	2287	
0.4	2600	189	2412	
0.6	2600	97	2503	
0.8	2600	62	2539	
1	2600	47	2554	
1.5	2600	33	2567	
2	2600	19	2581	

Table: 5a Batch experiment result for As(III) adsorption on IOCS; initial As(III) concentration of 2600 µg/l, SiO₂=58mg/l, pH=8+0.2; contact time 19 days, rpm 100

IOCS	Time(days)				
	0	1	8	14	20
0.2	2600	1880	1350	995	815
0.3	2600	1545	952.5	655	500
0.4	2600	1615	565	422.5	305
0.6	2600	1005	452.5	172.5	118.5
0.8	2600	815	212.5	105	73.5
1	2600	690	110	72.5	59.5
1.5	2600	430	195	40	19.8
2	2600	313	210	35	29.3

Table: 5b: As(III) isotherm adsorption on IOCS; model water with initial silica concentration 58mg/l, pH=8.0+0.2, contact time 20 days

Adsorbent dose(g/l)	Co	Ce	Amount adsorbed in mg/l	X/M in mg/l
0.2	2600	815	1785	8925
0.3	2600	500	2100	7000
0.4	2600	305	2295	5738
0.6	2600	118.5	2482	4136
0.8	2600	73.5	2527	3158
1	2600	59.5	2541	2541
1.5	2600	19.8	2580	1720
2	2600	29.3	2571	1285

Table: 6a Batch experiment result for As(V) adsorption on IOCS; initial As(V) concentration of 2600 µg/l, SiO₂=58mg/l, pH=8+0.2; contact time 20 days, rpm 100

IOCS	Co	Time(days)			
		1	8	14	20
0.2	3000	2020	1500	1260	1080
0.3	3000	1585	890	740	540
0.4	3000	1460	800	732.5	584
0.6	3000	715	292.5	197.5	166
0.8	3000	625	227.5	147.5	115
1	3000	470	92.5	65	94
1.5	3000	575	200	97.5	78
2	3000	190	40	25	51

Table: 6b: As(V) isotherm adsorption on IOCS; model water with initial silica concentration 58mg/l, pH=8.0±0.2, contact time 20 days

Adsorbent dose(g/l)	Co	Ce	Amount adsorbed in mg/l	X/M in mg/l
0.2	3000	1080	1920	9600
0.3	3000	540	2460	8200
0.4	3000	584	2416	6040
0.6	3000	166	2834	4723
0.8	3000	115	2885	3606
1	3000	94	2906	2906
1.5	3000	78	2922	1948
2	3000	51	2949	1475

Table: 7a Total silica concentration; initial SiO₂ concentration 58mg/l, As(III) = 2600mg/l, and pH=8±0.2, T=20°C, and contact time is 20 days.

0	1	7	14	20
58	54.6	54.8	53.6	51.4
58	55.1	55.2	50	48.6
58	54.3	53	49.6	47.5
58	51.6	46.2	42.6	44.8
58	51	47.3	43.6	41
58	50.6	47.7	40.5	37.1
58	45.4	40.8	34.8	33.1
58	48.1	38.6	33.1	30.7

Table: 7b Freundlich isotherm for SiO₂ adsorption on to IOCS; model water: initial silica concentration 58mg/l, As(III) =2600µg/l, pH=8±0.2, and contact time is 20 days.

Adsorbent dose(g/l)	Co	Ce	Amount adsorbed in mg/l	X/M in mg/l
0.2	58	51	7	33
0.3	58	49	9	31
0.4	58	48	10	26
0.6	58	45	13	22
0.8	58	41	17	21
1	58	37	21	21
1.5	58	33	25	17
2	58	31	27	14

Table: 8a Total silica concentration; initial SiO₂ concentration 58mg/l, As(V) = 2600mg/l, and pH=8±0.2, T=20°C, and contact time is 20 days.

0	1	7	14	20
58	55.6	56.3	53.8	51
58	55.4	54.3	52.2	47.9

58	56.4	51.5	50	44.5
58	53.3	50	44.5	42
58	50.3	45.7	43.4	40.5
58	50.1	43.5	39.5	37.7
58	50.3	43.9	36.6	33
58	47.1	40.4	35.8	30

Table: 8b Freundlich isotherm for SiO₂ adsorption on to IOCS; model water: initial silica concentration 58mg/l, As(V) =2600μg/l, pH=8+0.2, and contact time is 20 days.

Adsorbent dose(g/l)	Co	Ce	Amount adsorbed in mg/l	X/M in mg/l
0.2	58	51	7	35
0.3	58	48	10	34
0.4	58	45	13	34
0.6	58	42	16	27
0.8	58	40	18	22
1	58	38	20	20
1.5	58	33	25	17
2	58	30	28	14

Table: 9 Total silica concentration; initial SiO₂ concentration 23mg/l, As(III) = 2600mg/l, and pH=8+0.2, T=20oC, and contact time is 21 days.

0	1	7	14	19	23
23	19.8	18.1	22.2	21.9	22.2
23	20.2	19.4	21.4	21.5	23
23	18.5	19.8	22.5	21.1	21.5
23	17.7	16.6	18.5	18.6	18.1
23	18.4	16.3	18.9	18.8	18.5
23	16.9	17.8	19.3	18.6	18.4
23	15.3	15.1	16.2	15.3	14.6
23	16.6	17.7	17.4	16.7	17.1

Table: 10 Total silica concentration; initial SiO₂ concentration 23mg/l, As(V) = 2600mg/l, and pH=8+0.2, T=20oC, and contact time is 21 days.

0	1	7	14	19	23
23	21.5	20.9	23.6	23.7	23.1
23	20.4	18.5	22.6	22.6	22.1
23	20.1	19.6	21	19.8	21.6
23	18.5	18	19.3	18.9	19.1
23	18.4	18	17.8	17.4	18.4
23	18.4	15.3	17.6	17.6	18.2
23	18.4	17.7	15.6	14.6	17.1
23	17.8	16.3	17.4	16.3	17.3

