NOVEL TREATMENT TECHNOLOGIES FOR ARSENIC REMOVAL FROM WATER

By

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CERTIFICATE

I certify that this thesis has not already been submitted for any degree and is not being submitted as part of candidature for any other degree.

I also certify that the thesis has been written by me and that any help that I have received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

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NOMENCLATURE

b	: constant related to the binding energy of adsorption (L/mg)
BV	: bed volume
C	: solute arsenic concentration (mg/L)
C_b	: desired concentration of adsorbate at breakthrough (mg/L)
C_e	: equilibrium concentration (mg/L)
C_{ef}	: effluent adsorbate concentration (mg/L)
C_{if}	: influent adsorbate concentration (mg/L)
C_o	: initial arsenic concentration (mg/L)
d	: depth of adsorbent's bed (m)
D_x	: dispersion coefficient in x direction (m^2/s)
EBCT	: empty bed contact time
IOCS-2	: Iron oxide coated sand 2
IOCSp	: Iron oxide coated sponge
k_1	: rate constant of BDST model (L/mg.h)
K_d	: linear equilibrium partitioning coefficient (L/mg)
k_F	: Freudlich constant indicative of the adsorption capacity
k_H	: Ho rate constant for adsorption (g/mg.min)
k_N	: mass transfer loss coefficient (1/s)
k_T	: Thomas rate constant (L/min.mg)
m	: amount of adsorbent (g)
n	: experimental constant indicative of the adsorption intensity
n_T	: effective porosity (dimensionless)

NZVI : nanoscale zero valent iron

p_s : solid density of the particles (mg/L)

q_t : amount of adsorbate at any time t, (mg/g)

q_e : amount of adsorbate at equilibrium (mg/g)

q_m : saturated maximum adsorption capacity (mg/g)

Q_v : volumetric flow rate (L/min)

r : correlation coefficient

S : amount sorbed onto porous medium (mg/mg)

SMZ/ZVI : surfactant modified zeolite – zero valent iron

t : service time of column (h)

T : temperature

u_x : velocity of water (m/s)

V : throughput volume (L)

w_a : mass of arsenic adsorbed after time t (mg)

w_a^0 : maximum adsorption capacity of filter (mg)

α : dispersivity (m)

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ABSTRACT

Arsenic is a toxic semi-metallic element that can be fatal to human health. It can have a significant adverse impact on the environment. Arsenic pollution in water has been found in many parts of the world, especially in developing countries such as Bangladesh, India, Nepal, and Vietnam. It is also detected in some areas of Australia. In rural area of Victoria, arsenic concentrations of up to 8 μg/L and 220 μg/L in groundwater and surface water have been reported. The arsenic contamination in water forced the water and health authorities to introduce stringent standards for arsenic levels in drinking water. World Health Organization (WHO) has recommended the arsenic level in drinking water to the stricter level to be 10 μg/L instead of 50 μg/L (since 1993). The U.S. Environmental Protection Agency (EPA) has lowered the maximum contaminant level (MCL) of arsenic from 50 μg/L to 10 μg/L. Rigorous criteria of arsenic level have been enforcing water authorities to identify and put into practice suitable and cost-effective arsenic removal technologies.

The main objectives of the research described in this thesis were to develop and assess the potential and effectiveness of a new adsorbent medium namely iron oxide coated sponge (IOCSp) in removing arsenite [As(III)] and arsenate [As(V)] to an acceptable level in drinking water supplies. Arsenite [As(III)] and arsenate [As(V)] are the two predominant arsenic species found in groundwater. Regeneration of the exhausted IOCSp was also investigated. In addition, two other adsorbents: iron oxide coated sand 2 (IOCS-2), and surfactant modified zeolite – zero valent iron (SMZ/ZVI) were evaluated and their efficiency were compared with that of IOCSp. Effectiveness of membrane and photocatalysis hybrid systems in removing arsenic was studied. In this study, tap water (Sydney, Australia and Regina, Saskatchewan, Canada) spiked with predetermined amounts of As(III) and As(V) was used in the batch, tray and column studies. Raw water containing arsenic from Kelliher, Saskatchewan and Van Phuc Village, Hanoi, Vietnam were also investigated in the study.

The research described below investigated optimised conditions for coating iron oxide on sponge by different coating conditions. Optimum conditions for coating the sponge with iron oxide were as follow: (i) pH value of coating condition of 4 (ii) time of contact between iron oxide and the sponge during coating of 10 hours; (iii) coating temperature of 110°C; and (iv) time of drying of sponge after the coating of 20 hours. The maximum adsorption capacities of IOCSp for As(III) and As(V) estimated by Langmuir, and Sips models were up to 4.18 and 4.6 mg/g of IOCSp, respectively. More than 92.4% of both As(III) and As(V) was removed after a contact period of 9 hours with the IOCSp (based on batch studies). The IOCSp adsorption equilibrium results with synthetic water fitted reasonably well with Freundlich, Langmuir, and Sips isotherms, indicating favourable adsorption.

The performance of the IOCSp column was experimentally evaluated with synthetic water spiked with arsenic. The results showed that the IOCSp column could maintain high arsenic removal efficiency even after a long filtration time without any need for regeneration. For example, a filter packed even with very small amount of 25 g IOCSp maintained a consistent arsenic removal efficiency of 95% from synthetic water containing arsenic concentration of as high as 1,000 μg/L. This produced a throughput volume of 153 and 178 L of water containing As(III) and As(V) respectively before any need for regeneration or disposal of IOCSp. A relatively small amount of IOCSp (8 g) could treat 42 – 63 L of arsenic contaminated groundwater (56 – 156 μg/L) in Kelliher (Canada) and in Hanoi (Vietnam) to a level of less than 20 μg/L. Studies showed that As(V) removal was better compared with As(III) removal.

The results showed that the performance of IOCSp was superior to than that of iron oxide coated sand (IOCS-2) and surfactant modified zeolite – zero valent iron (SMZ/ZVI) in terms of weight of media. The IOCSp, once exhausted, can be regenerated with a small amount of sodium hydroxide 0.3M. The regenerated IOCSp did not have any significant decrease in removal effectiveness as compared to the fresh IOCSp.

Photooxidation experimental results also showed that photooxidation of As(III) to As(V) with titanium dioxide (TiO_2) as photocatalyst is possible within minutes. Further, TiO_2 can also adsorb both As(III) and As(V) on its surface. Thus, the photocatalysis reaction with TiO_2 can reduce about 98% of arsenite from water containing 500 μg/L of arsenite. By adding nanoscale zero valent iron (nZVI) of 0.05 g/L in the photo reactor, arsenic removal can be significantly enhanced to a value less than 10 μg/L. The amount of TiO_2 used in this photocatalysis hybrid system was only 20% of normal photocatalysis operation.

Removal of arsenic by a membrane is highly dependent on the species of arsenic and the properties of membranes. About 57% of As(III) and 81% of As(V) removal from 500 μg/L arsenic solution could be achieved by nanofiltration (NF) of 700 molecular weight cutoff. This removal efficiency could be increased to more than 95% by an inline addition of 0.2 g/L of nZVI. This method is suitable when high quality effluent is required.

In summary, the study demonstrated conclusively that iron oxide coated sponge is an excellent media for reducing arsenic. IOCSp filter can be used as an effective and economical treatment system in removing arsenic from contaminated groundwater. The merits of the IOCSp filter process are the consistent removal efficiency, long life cycle, and simplicity in operation, regeneration and disposal.

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CHAPTER 1

INTRODUCTION

Chapter 1 Introduction

1.1 Introduction

Water is the essence of life and "Access to safe water is a fundamental human need and, therefore, a basic human right" (Kofi Annan, 2001). In many regions in the world, however, especially in developing countries, millions of people still suffer from the lack of access to safe drinking water. This harms people's health and can cause serious illnesses.

One of the problems in drinking water that raises concern over the world is that millions of people still have to use arsenic contaminated water. Medical research indicates that exposure to arsenic in drinking water causes urinary, bladder, lung and skin cancers, gastrointestinal disorders, muscular weakness, loss of appetite, nerve tissue injuries and blackfoot disease. Arsenic exists in several oxidation states (-III, 0, +III and +V) in the environment. However, in natural water, arsenic is mostly found in an inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. Arsenic occurs in extremely high quantities in groundwater in Bangladesh and in a number of other countries, such as India, Vietnam, Taiwan, Nepal, China, Mongolia, and America.

There are a number of studies using different treatment technologies such as coagulation, ion exchange, adsorption, and membrane processes that are used to remove arsenic from drinking water to produce water of a safe quality. The summary of the technologies that can be used in removing arsenic from drinking water is presented in Table 1.1.

Table 1.1. Characteristics of arsenic removal technologies (WHO, 2001)

Technology	Removal Efficiency		Characteristics
	As (III)	As (V)	
Salts	++	+++	Well proven at central level, piloted at community and household levels. Generates arsenic rich sludge. Relatively inexpensive.
Coagulation with alum	-	+++	Proven at central level, piloted at household levels. Optimal over a relatively narrow pH range. Generates arsenic - rich sludge. Relatively inexpensive
Ion exchange resins	-	+++	Tried in pilot scale in central and household systems, mostly in industrialized countries. High adsorption capacity. Moderately expensive. Regeneration produces arsenic - rich brine.
Lime softening	+	+++	Proven in laboratories and at pilot scale as an effective technology. Disadvantages include extreme pH and large volume of waste generated. Relatively inexpensive.
Adsorption on activated alumina	+/++	+++	Tried in pilot scale in community and household systems, both in industrialized and developing countries. Produces arsenic-rich waste. Moderately expensive.
Porous media sorbents (greensand, iron oxide coated sand, etc.)	+/++	++/+++	Shown effective from laboratory scale studies in both industrialized and developing countries. Need to be evaluated under different environmental conditions, and in field settings. Simple media are inexpensive; and advanced media can be relatively expensive.
Membrane methods	-/+++	+++	Shown effective in laboratory scale studies in industrialized countries. Pretreatment usually required. Relatively expensive.

Note: +++ Consistently > 90% removal
++ Generally 60 – 90% removal
+ Generally 30 – 60% removal
- < 30% removal

Since the majority of people affected by arsenic contamination worldwide live in developing countries and small communities, treatments need to be not only reliable but they also need to be simple and cost effective methods.

Since adsorption using a fixed bed treatment system is simple, in terms of operation and handling, has a good regeneration capacity and is a sludge free operation, this method has become very popular for arsenic removal in small-scale treatment systems. A number of absorbents such as iron oxide and aluminum oxide have been used to remove arsenic from water.

Sponge is an ideal material for adsorption as it is very porous and its large surface area facilitates arsenic absorption. In addition, sponge is inexpensive so it is appropriate for small communities, as well as in developing countries. To achieve high arsenic adsorption, sponge can be coated with iron oxide because arsenite and arsenate are strongly adsorbed on iron oxide. The disposal of media coated with arsenic is a problem. In the case of sponge, it can easily be disposed or regenerated with chemical solutions once adsorption of arsenic onto a sponge matrix is exhausted. Sponge can easily be squashed and incorporated into building materials such as concrete, making its disposal easier.

Another medium, namely surfactant modified zeolite – zero valent iron is seen to be a promising adsorbent due to its relative high surface area (28.2 m^2/g) and its composition (16% zeolite, 49% zero valent iron).

Nanoscale material such as nanoscale zero-valent iron (nZVI) has been demonstrated to have potential in environmental engineering applications due to the extremely small particle size, large surface area, and high in-situ reactivity. The combination of this material with advanced technologies, such as membrane or photocatalysis is believed can lead to very high treatment efficiency.

1.2 Objectives

The overall aim of the research described in this thesis was to develop and evaluate the potential and effectiveness of a new adsorbent medium namely iron oxide coated sponge (IOCSp) in removing arsenite [As(III)] and arsenate [As(V)] to an acceptable level in drinking water supplies.

The objectives of this research are as follows:

- Developing a new metal oxide coated sponge (IOCSp) with an appropriate coating method (Chapter 4).
- Investigating the capacity and the effectiveness of the metal oxide coated sponge in removing arsenic from drinking water (Chapter 4).
- Modelling the performance of IOCSp filter (Chapter 4).
- Comparing the applicability of IOCSp with 2 other adsorbents (IOCS-2 and SMZ/ZVI) in terms of arsenic removal capacity (Chapter 4).
- Evaluating the effectiveness of iron oxide coated sand 2 and surfactant modified zeolite/zero valent iron in removing arsenic (Chapter 5).
- Comparing the effectiveness of combinations of nZVI - photocatalysis and nZVI - membrane on arsenic removal (Chapter 6).

1.3 Structure of the study

This thesis has been divided into seven chapters and two appendices. Chapter I (Introduction) mainly deals with the problem of arsenic and an overview of solutions together with the objectives of study.

Chapter 2 (Literature review) presents recent works related to the arsenic problem including i) a detailed review of the occurrence, species and toxicity of arsenic in water, ii) the effect of arsenic on human health and drinking water standards for arsenic in water, iii) treatment technologies for arsenic removal, iv) a review of polyurethane sponge and its application in environment, and v) waste handling.

The experimental investigation is presented in Chapter 3. Materials used include iron oxide coated sponge, iron oxide coated sand 2, surfactant modified zeolite/zero valent iron, nanoscale zero valent iron, titanium dioxide, and membrane and treatment methodologies adopted in the study are described. The study parameters and analytical test methods are described in this chapter.

Chapter 4 presents the method of coating iron oxide on sponge and the effectiveness of sponge in removing arsenic. The experimental results presented in this chapter provide detailed information on kinetic and equilibrium results, column experiments with synthetic and natural water, and tray experiments with synthetic water. An adsorption model is believed to be useful in predicting the performance of fixed bed absorbers and helping for the design. A series of mathematical models was tested for the best in predicting the performance of fixed bed absorbers and helping for the design.

Iron based adsorbents could be used as efficient materials to remove arsenic from water. Chapter 5 presents the results with other adsorbents including iron oxide coated sand 2 and surfactant modified zeolite/zero valent iron. Both batch and column results are discussed.

It is important to evaluate the relative merits of different technologies. Chapter 6 presents details on the effect of nanoscale zero valent iron in removing arsenic by membrane and photocatalysis processes.

Chapter 7 presents the conclusions from the study with recommendations for the future work.

The simple designs for removing arsenic from water, and raw data are presented in appendices A and B.

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CHAPTER 2

LITERATURE REVIEW

Chapter 2 Literature review

2.1 History

Arsenic is a highly toxic semi-metallic element. Its name is derived from the Greek word arsenikon. Arsenic containing minerals have been known since ancient times. Arsenic sulphide mineral realgar, AsS, was possibly described in the 4th century BC by Greek philosopher Aristotle. The isolation of elemental arsenic was however first made possible by a German chemist Albertus Magnus in 1250 A.D (Vaughan, 2006).

2.2 Sources of arsenic

A number of natural and human activities are responsible for the arsenic contamination in groundwater sources. Arsenic contamination of the subsurface water is believed to be geological, and it may result from dissolution of or desorption from iron oxide, and the oxidation of As pyrites. The severity of arsenic pollution of groundwater in Bangladesh was first believed to be due to pyrite oxidation, but later it was discovered that it was due to the dissolution of As-rich Fe oxyhydroxide (Nickson et al., 2000; McArthur et al., 2001). Furthermore, the occurrence of arsenic in groundwater depends on factors such as redox conditions, ion exchange, precipitation, grain size, organic content, biological activity and characteristic of the aquifer (Robertson, 1989; McArthur et al., 2001). Arsenic is the major constituent in a number of minerals. These minerals are mainly ores containing sulfide, along with copper, nickel, lead, cobalt and other minerals (Pontius et al., 1994). The most common arsenic containing minerals are arsenic pyrites (FeAsS), realgar (AsS), lollingite ($FeAs_2$, $FeAs_3$ and $FeAs_5$) and orpiment (As_2S_3). The mining operations of coal containing arsenic increase the potential for soil contamination with arsenic. Arsenic is also widely used in pigment and dyes, preservatives of animal hides and wood, pulp and paper production, electro plating, battery plates, dye and soaps, ceramics and in the manufacture of semiconductors, glass and various pharmaceutical substances (Azcue and Nriagu, 1994; Welch et al., 1998). In USA alone, the chromate copper arsenate (CCA) (used to treat lumber) accounts for approximately 90% of the arsenic used annually by industry. The arsenic contamination can also be from mine tailings (wastewater from exploring for gold, copper and zinc ore, etc.), industrial waste discharges, fertilizers, pesticides/insecticide, smelting of metals, and burning of fossil fuels (Altundogan et al., 2000; Thirunavukkarasu et al., 2001). Arsenic can be also found in coal and coal combustion by-products. During combustion, arsenic is volatilized and may condense on the surface of the fly ash particles. Arsenic from coal combustion occupies approximately 23%, 14% by atmospheric fallout, 10% by mining tailing, 7% by smelters, 3% by agriculture and 2% by manufacturing, urban and forestry wastes (Bhumbla and Keefer, 1994).

2.3 Properties and toxicity of arsenic

Arsenic is a chemical element in the Nitrogen family, existing in both yellow and grey crystalline forms. Although some forms of the arsenic are metal-like, it is best classified as a semi-metallic element.

Arsenic can exist in several oxidation states (-III, 0, +III and +V) in the environment. However, in natural water, arsenic is mostly found in an inorganic form as oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). pH is the major factor controlling the differences in aqueous arsenic speciation in freshwater. The distributions of the species as a function of pH are presented in Figure 2.1.

In Figure 2.1, the domains of each species are defined by the solid lines. Two species have equal activities at the boundaries, while one species becomes increasingly dominant toward the interior of its domain. The diagram differs slightly depending on the conditions selected, but the major trends are consistent.

Figure 2.1 suggests that a decrease in pH should increase the occurrence of arsenite over the arsenate.

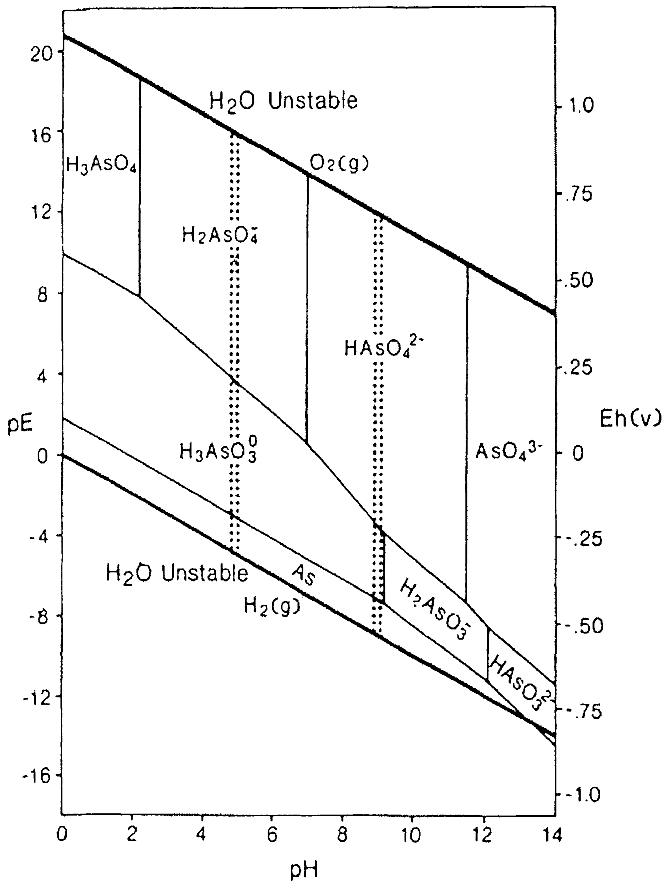


Figure 2.1. pE-pH diagram for the As–H_2O system at 25°C. Total dissolved As species set at 50 μg/L. The area within the vertical bars represents the common pE-pH domains for natural water (Cullen and Reimer, 1989)

Regardless of the specific pH, it is apparent that in oxygenated water, arsenic acid (As(V)) species: H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} are stable. Under slightly reducing conditions and/or lower pH, arsenous (As(III)) acid (mainly as neutral H_3AsO_3) becomes stable.

The pH range of natural water is mostly from 5 to 9 so As(V) should strongly dominate over As(III) in oxygenated water, at least on thermodynamic grounds. In fresh water of pH = 6, $H_2AsO_4^-$ becomes dominant (89% compares with 11% $HAsO_4^{2-}$ at pH = 14.6) (Cullen and Reimer, 1989).

The commonly found two organic species of arsenic are monomethyl arsenic acid (MMAA) and dimethyl arsenic acid (DMAA). Organic arsenic forms are produced by biological processes, mostly in surface waters, but are rarely quantitatively important. Organic forms are also synthesized for commercial use.

The toxicity of arsenic highly depends on its speciation. The toxicity of arsenite is 25 - 60 higher than that of arsenate and toxicity decreases in the order of arsine > inorganic As(III) > organic As(III) > inorganic As(V) > organic As(V) > arsonium compounds and elemental As (Subramanian, 1988).

2.4 Effect of arsenic on human health

Arsenic is a toxic and carcinogenic substance and is called the king of all poison. A fatal dose, which is sufficient for human death, is 125 mg (Dhaka Community Hospital, 2001). Arsenic enters the human body either from respiration or through the mouth.

The toxicity of arsenic depends on its speciation and concentration. Arsenic ranks 1,014 out of the 1,598 National priorities list hazardous waste sites in USA (ATSDR, 2000). Ingestion of inorganic arsenic can result in both cancer (skin, lung and urinary bladder) and non – cancer detrimental effects. In addition, inorganic arsenic in drinking water may affect many organs such as central and peripheral nervous systems, dermal, cardiovascular, gastrointestinal and respiratory systems. The most common ailments, such as keratoses and hyperpigmentation, may occur after 5 - 15 years of arsenic exposure equivalent to 700 μg/day for a 70 kg adult. A health effects study conducted by the National Academy of Sciences (NAS) (NAS, 1977) concluded that the cancer risk associated with arsenic exposure has been greatly underestimated by the United States Environmental Protection Agency. It was found that people who drink water with arsenic levels of 3 μg/L have a one in 1,000 risk of developing cancer. At 10 μg/L, the risk is three in 1,000. Non-cancer health effects include gangrene, limb loss, cardiovascular and pulmonary disease, endocrine and hematological disorders, and reproductive/developmental problems. In addition, arsenic is an "accumulative enabler," meaning people who are predisposed to various cancers, diabetes, high blood pressure and other ailments are more likely to fall ill. The World Health Organization (WHO) estimated that a lifetime exposure to arsenic in drinking water at a concentration of 200 μg/L might give a 5% risk of getting skin cancer (Chen et al., 1994). The United States Environmental Protection Agency

(USEPA) (USEPA, 1988) estimated that the lifetime risk of developing skin cancer as in 1 - 2% per 1,000 people/μg of inorganic As/Liter of drinking water. The National research council (NRC, 1999) states that the total cancer risk due to the consumption of drinking water with 50 μg/L As will be 1/100.

In Bangladesh, 1.2 million tube wells (29%) were found to be contaminated with arsenic. It is estimated that 85 million people at risk from arsenic (Hossain, 2006). In India, 200,000 people suffer from chronic poisoning from arsenic in well water (up to 1800 μg/L). An investigation of groundwater samples from private small scale tube-wells in Red River delta, Vietnam (over an area of 700 km^2) showed arsenic levels varying from 1 to 3,050 μg/L (Berg et al., 2001). Arsenic concentration was above 50 μg/L of 48% of samples analysed and above 150 μg/L of 20% of samples analysed. The average concentration of arsenic was 430 μg/L in highly affected rural areas. The United Nations Children's Fund (UNICEF) estimated that 17% of Vietnam's population is using groundwater for drinking purpose from private tubewells (UNICEF Vietnam, 2002). The high arsenic levels found in the tubewells indicate that several million people using untreated groundwater might be at significant risk of chronic arsenic poisoning. In the United States, about half of drinking water comes from groundwater. Smith et al. (1992) reported that 330,000 people supplied with water of more than 50 μg/L arsenic, the earlier US limit.

The high concentration of arsenic (671 ± 149 μg/L) in drinking water in southwest Taiwan is a cause of blackfoot disease (BFD) that makes skin gradually thicken, crack and ulcerate. Amputation of the affected extremities is often the final remedy to save BFD victims. In 1975, 1,141 BFD patients were identified in Taiwan (Chen et al., 1994). Hyperpigmentation was the most common ailment (183.5/1000) among the affected people in Taiwan. An investigation of a group of 40,421 showed hyperpigmentation in 18.4%, keratotic lesion in 7.1% and blackfoot disease in 0.9% (Tseng et al., 1968).

Arsenic in the water of the eastern area of Cordoba province, Argentina causes hyperpigmentation, keratosis and skin cancer (Bergoglio, 1964). Early 1960s, there were dermatologic manifestations and some deaths, particular among children due to water containing arsenic at 800 μg/L in Autofagasta, Chile. In northern Chile, nearly 7.3% of all deaths among those aged 30 years and over were due to internal cancers (bladder and lung cancer) caused by drinking arsenic contaminated water where people are exposed to a high level of As > 500 μg/L in drinking water (Smith et al., 1998). Dermatitis, a skin lession caused by arsenic, is prevalent in Bangladesh. A study conducted by the Dhaka Community Hospital servicing 80% of the total area of Bangladesh showed that people were affected with melanosis (93.5%), keratosis (68.3%), hyperkeratosis (37.6%), dipigmentation (39.1%) and cancer (0.8%). Data also showed that there is a dose-response relationship for ingested arsenic water and non-cancerous effects (NRC, 1999).

2.5 Standards for arsenic in water

The arsenic standard concentration limit set by different health and quality controlling organizations varies. In response to concerns about the cancer risk from arsenic contaminated drinking water, WHO revised its guideline from 50 to 10 μg/L in 1993. Table 2.1 shows the national standards for arsenic in drinking water in some countries.

Table 2.1. The national standards for arsenic in drinking water (WHO, 2001)

Standard (μg/L)	Countries
7	Australia
10	European Union, Japan, Jordan, Laos, Mongolia, Namibia, Syria, Vietnam
25	Canada
50	Bahrain, Bangladesh, Bolivia, China, Egypt, India, Indonesia, Oman, Philippines, Saudi Arabia, Sri Lanka, Zimbabwe

In Australian drinking water guideline, arsenic value of 7 μg/L has been estimated using the Provisional Tolerable Intake of 1 mg/kg/day derived by Di Marco and Buckett (1996) and the formula and assumptions of 2 L of water per day is consumed by a 70 kg adult used by NHMRC/ARMCANZ.

2.6 Treatment technologies for arsenic removal

Different treatment technologies are reported in the literature for arsenic removal. USEPA suggested ion exchange, activated alumina, reverse osmosis, modified coagulation/filtration and modified softening as best available technologies (BAT) (USEPA, 1999). Other technologies emphasized are: iron based coagulation assisted microfiltration, iron oxide coated sand, manganese greensand filtration and granular ferric hydroxide (GFH). Appropriate treatment depends on many factors, for example, concentration of arsenic, water composition, pH and cost effectiveness. In contrast to cyanide, arsenic cannot be destroyed. It can only be converted into different forms or transformed into insoluble compounds in combination with other elements, for example iron.

2.6.1 Coagulation/Filtration

Coagulation/filtration is the most commonly used technology in water treatment. In this process, the physical or chemical properties of dissolved colloidal or suspended matter are altered by the addition of coagulants such that the resulting particles (flocs) are large enough to settle out of solution by gravity or can be removed by filtration. The most commonly used coagulants are aluminium salts and ferric salts. Ferrous sulfate has also been used, but is less effective (Jekel, 1994; Hering et al., 1996; Hering et al., 1997). Sometimes polymers or colloidal substances such as clays are added to improve flocculation and sedimentation (Gulledge and O'Connor, 1973). The addition of 2 - 4 mg/L of cationic polymer allows the coagulant dose to be reduced by two-thirds while retaining good arsenic removal. Thus polymers or clays can be used to improve arsenic removal efficiency, and to reduce the volume of sludge generated. Cheng et al. (1994) showed that ferric or aluminium salts could remove over 99% arsenic under optimal conditions in the laboratory. The removal efficiency from full - scale plants was lower, from 50% to over 90%. In this process, mainly aluminium sulphate (alum) and iron salts are used. Iron coagulation is more effective than alum. Ferric chloride produces the best arsenic removal compared with ferrous and alum. Gulledge and O'Connor (1973) achieved more than 90% removal of As(V) with a 30 mg/L dose of ferric sulphate at pH 5 - 7 with an initial arsenic concentration in water of 300 μg/L.

The arsenic removal efficiency is influenced by a number of factors such as coagulant types, coagulant dose, coagulant pH, initial As(III)/As(V) concentration and co-occurring inorganic salts. Many studies have been carried out to investigate the effects of these factors. Adjustment of pH will often result in greater improvements in efficiency than increasing coagulant dose (Sorg and Logsdon, 1978; Edwards, 1994; Hering et al., 1996). Relatively few studies have examined the effects of inorganic salts. Some anions will lower removal rates by competing with arsenic for sorption sites and lowering the surface charge. Cations, in contrast, can increase the positive surface charge, and enhance arsenic adsorption. If the source water has high levels of phosphate or silicate, coagulation may be less effective. However, sulfate, carbonate, and chloride have little effect on removal rates. Meng et al. (2000) reported a decline in arsenite removal rate from 95% to 50% with the addition of 18 mg/L Si. Similarly, sulfate and carbonate can slightly decrease arsenite removal and have little effect on arsenate removal.

2.6.2 Ion exchange resins

Ion exchange is a physical-chemical process in which an ion on the solid phase (a synthetic resin) is exchanged for an ion in the feed water. In this process, feed water is continuously passed through a bed of ion exchange resin beads in a downflow or upflow mode until the resin is exhausted. The resin is then regenerated by rinsing the column with a regenerant. The factors that can affect the removal efficiency of the ion exchange process are the water quality parameters such as pH, competing ions, alkalinity, and influent arsenic concentration. The other factors that can affect the efficiency of the system are resin type, affinity of the resin for arsenic, spend regenerant, resin disposal requirements, and operating parameters.

Ion exchange resins are used in packed beds or columns, most often with an empty bed contact time (EBCT) of 1.5 to 3 minutes. A bed can typically treat several hundred to a thousand bed volumes before the resin needs to be regenerated. Typically 300 to 60,000 bed volume (BV) can be treated before regeneration is required. Resins can not adsorb iron, so if the raw water contains high levels of dissolved iron, the iron can precipitate out and clog the filter. Many types of strong-base anion exchange resins are commercially available which can successfully remove arsenate from solution. Conventional sulfate - selective resins are particularly appropriated for arsenate removal. Resins are used to be pretreated with hydrochloric acid to create chloride ions at the surface, which are easily replaced by arsenic (Ghurye et al., 1999).

Arsenate removal efficiency is strongly affected by competing anions, especially sulfate. However, pH has little effect on the arsenate removal. The USEPA recommends that ion exchange resins can not be used in waters containing more than 120 mg/L sulfate or more than 500 mg/L TDS (total dissolved solids). This method is most effective in waters with sulfate concentration lower than 25 mg/L (USEPA, 2000b). In waters containing low sulfate concentration, over 95% of arsenate could be removed by ion exchange resin and more than one thousand bed volumes could be achieved.

The disadvantage of ion exchange is that exhausted resins have chromatographic properties such that they can discharge nearly all the previously removed arsenic over a few bed volumes, leading to 'arsenic peaking' with concentrations several times higher than the influent (Ghurye et al., 1999). Another disadvantage of the ion exchange method is that resins can be fouled by precipitation of iron or manganese oxides. These metal oxides can decrease flow rates, and prevent contact between arsenic and the resin (Fox, 1989). These metal oxides themselves may adsorb arsenic, but this does not make use of the ion-exchange properties of the resin. In addition, colloidal iron may pass through the resin bed and can bring adsorbed arsenic, causing significant leakage through the bed (Ghurye et al., 1999).

Chitosan and chitin are natural polyaminosaccharides that have good ion exchange properties. A mixture of chitosan and chitin was found to have a low arsenic removal capacity of 10 µg As/g (Elson et al., 1980). Luong and Brown (1984) found that shellfish wastes containing chitosan could be used to remove arsenic from water contaminated by mining wastes.

A similar material has been produced out of ground rice husks, which are modified with an ammonium treatment to produce 'quaternized rice husk'. Arsenate removal from highly concentrated solutions (100,000 - 600,000 μg/L) was good, but dependent on pH, with maximum removal of about 80% from pH 6 through 10 (Baes et al., 1997; Lee et al., 1999).

Greensand is a granular material composed of the mineral glauconite and has strong ion exchange properties. As greensand surface is strongly oxidizing, it could remove both As(III) and As(V). Viraraghavan et al. (1999) showed that greensand could remove about 40% arsenite from 200 μg/L arsenic solution in the absence of iron.

2.6.3 Adsorption process

Adsorption is a physical-chemical process by which the adsorbates (ions of targeted solutes) are adsorbed to the surface of the adsorbent. Activated alumina (AA) is commonly used to remove arsenic. Activated alumina is a granulated form of aluminium oxide (Al_2O_3) with very high internal surface area, in the range of 200 - 300 m^2/g. Activated alumina works best in slightly acidic waters (pH 5.5 to 6) and adsorption of arsenate is faster than that of arsenite (Sorg and Logsdon, 1978).

Activated alumina is used in packed beds, with Empty Bed Contact Time (EBCT) about 5 to 8 minutes. Activated alumina beds usually have much longer run times than ion exchange resins, typically several tens of thousands of beds can be treated before arsenic breakthrough. The number of bed volumes that can be treated at optimal pH before arsenate breakthrough is mainly controlled by the influent arsenic concentration (Ghurye et al., 1999). For the best results, raw water containing arsenite is normally oxidized before treatment. Arsenic removal efficiency is typically more than 95%, but arsenic capacity varies significantly, and is controlled primarily by pH and influent arsenic concentration and speciation. The highest arsenate removal capacity is achieved in the narrow range from pH 5.5 to 6.0. (Trussell et al., 1980; Rosenblum and Clifford, 1984; Clifford, 1999).

Activated alumina is typically regenerated by a solution of 2 - 5% sodium hydroxide, followed by flushing with acid. However, regeneration is less complete (50 - 80%) than with ion exchange resins (Clifford, 1986). After regeneration, the bed volume is decreased as some of the arsenic remains irreversibly bound to the alumina and the caustic and acid treatment dissolves some of the alumina. As a result, after a certain number of regeneration cycles, fresh activated alumina must be added to make up for the lost media.

Activated carbon in particle form as GAC and in powder form as PAC is widely used as adsorbent for purifying purpose a long time ago. It can remove a number of dissolved compounds such as phenolic compounds, benzene, heavy metals and industry solvents. Activated carbon may remove arsenic for a short time, but as the surface is not very selective for arsenic, the overall capacity for arsenic removal is low (Sorg and Logsdon, 1978).

Fly ash, a by-product of coal combustion in power stations, has a very strong affinity for arsenate. Diamadopoulos et al. (1993) found that a lignite-based fly ash can remove 80% arsenate from solution, with an optimal pH of 4. Desorption studies showed that very little arsenic can be removed from the fly ash, indicating that chemisorption rather than ion exchange is the likely removal mechanism. One drawback of using of fly ash is that when As-rich coal is combusted, the resulting fly ash can have very high concentrations of arsenic, up to 47% by weight (Dutre and Vandecasteele, 1998).

Bajpai and Chaudhuri (1999) showed that manganese dioxide coated sand could remove both arsenite as well as arsenate. The manganese dioxide coated sand was able to remove 80% of a 1,000 µg/L solution of arsenite within two hours, but slightly less than 70% of an equivalent solution of arsenate.

2.6.4 Iron/Manganese oxidation

Iron/Manganese oxidation is a commonly used technique to treat groundwater. In this process, hydroxides of metals are formed during the oxidation process that can remove soluble arsenic by a subsequent precipitation or adsorption process. Edwards (1994) reported a significant removal of arsenic during the iron precipitation process. Removal of 2 mg/L of iron can remove 92.5% of As(V) from a 10 μg/L As(V) initial concentration by adsorption alone. The mechanisms involved are the same as in coagulation and filtration.

Shen et al. (1973) attempted to remove arsenic from groundwater through simple aeration and sedimentation. Arsenic concentration was reduced from 800 μg/L by only 9% after one full day of settling. After 15 days, the removal efficiency was 50%. Poor arsenic removal may be related to poor iron level in the water. Clifford and Lin (1991) showed that 60% arsenate was removed by oxidative precipitation from 188 μg/L arsenate influent. Iron concentration was elevated at 2 mg/L.

In Bangladesh and West Bengal, arsenic contaminated groundwater often contains high concentrations of iron and manganese. A survey found that over 80% of arsenic affected tubewells (>50 μg/L) in Bangladesh also contained at least 2 mg/L of iron (DPHE/BGS/MML, 1999). Due to the link between arsenic and iron levels, and the affinity of arsenic for iron hydroxides, a simple solution for arsenic removal is proposed as follows: simple storage of pumped water to allow iron to settle out, scavenging arsenic in the process. However, successful application of the "passive Fe-Mn oxidation" is not easy due to the following reasons:

(i) iron removal is not always easily accomplished;

(ii) without a filtration step, iron can remain suspended as colloidal matter;

(iii) arsenic removal will be less efficient if the water contain mostly arsenite; and

(iv) a high risk of bacterial contamination when water is stored in household containers.

Therefore, careful pilot studies using the local waters and local storage conditions should be carried out to assess the effectiveness of this technique, and the possibility of pathogenic contamination. The addition of chlorine would not only improve oxidation of both iron and arsenic but also provide protection against bacterial growth. However, it is difficulties in ensuring the accurate dose, and the potency of the chlorine agent at the household level.

2.6.5 Membrane technology

Membrane filtration is becoming a common technology used to treat municipal drinking water. It can remove a number of contaminants from water, including bacteria and other microorganisms, heavy metals, particulate material, and natural organic material, which can cause color, taste, and odor problems in drinking water. Membranes are basically a selective barrier, allowing some constituents to pass while blocking the passage of others. Separation of ionic species by a membrane strongly depends on the membrane properties (Tsuru et al., 1991a, 1991b). A membrane with smaller pores is better able to retain ionic species (Deen, 1987; Bowen et al., 1997).

When membranes were first evaluated for arsenic removal in the 1980s, cellulose - acetate reverse osmosis (RO) membranes were operated at high pressures (typically 2,758 kPa), and more than 90 % arsenate rejection was reported (Schneiter and Middlebrooks, 1983; Clifford, 1986).

In the mid-90s, (nano-filtration) NF membranes, which are more permeable and can be operated at pressures less than 689 kPa, were also found effective for arsenic removal (Legault et al., 1993; Waypa et al., 1997). One disadvantage of both RO and NF membranes is that only a small amount of the raw water (10 - 15%) passes through the membrane as permeate. Multiple membrane units in series are needed to achieve higher recovery rates (80 to over 90%).

In recent years, new generation of RO and NF membranes that are less expensive and operate at lower pressures have been developed. Waypa et al. (1997) showed that some of the new membranes, operated at pressures ranging from 276 -2,758 kPa, are able to reject from 96 - 99% of both arsenate and arsenite in spiked natural waters. They attributed this rejection of arsenite to the relatively large molecular weight of arsenate and arsenic, rather than charge repulsion. Due to its high arsenic rejection capacity, membrane filtration can produce extremely low arsenic concentrations in treated water. The performance of the NF membrane was comparably good with RO membranes; even though the operating pressure was much lower (276 - 827 kPa, compared to 1,379 – 2,758 kPa for RO).

The performance of the membrane processes is summarized in Table 2.2.

Table 2.2. Arsenic removal by UF at pilot scale; NF membranes; and RO at bench scale (USEPA, 2000b)

Membrane type	MWCO	Membrane charge	Water type	Arsenic species	pH	Total arsenic rejection (%)
UF membranes at pilot scale						
Desal GM2540F	8,000		High DOC GW	Total As		70
Desal GM2540F	8,000		Low DOC GW	Total As		30
			Finished SW	As(V)		47
				As(III)		10
NF membranes						
Single element						
NF 45-2540	300	(-)	DI	As(V)	6.7	85
NF 45-2540	300	(-)	Lake	As(V)	6.9	89
NF 45-2540	300	(-)	DI	As(III)	6.9	12
Flat sheet						
NF 45-2540	300	(-)	DI	As(V)	NA	90
RO at bench scale						
Single element						
DK2540F	180		DI	As(V)	6.8	96
DK2540F	180		Lake	As(V)	6.9	96
DK2540F	180		DI	As(III)	6.8	5
DK2540F	180		Lake	As(III)	6.8	5
Flat sheet						
DK2540F	180		DI	As(V)		88

MWCO: Molecular weight cutoff

GW: groundwater; SW: surface water DI: deionised water; NA: not available

DOC: Dissolved Organic Carbon

2.6.6 Photo oxidation

Arsenite [As(III)] is present in uncharged form at pH values typical of drinking water. Therefore, this form of arsenic is more difficult to be removed from water than arsenate [As(V)]. As(III) is typically removed by first oxidizing it to As(V) and then arsenate is removed using adsorption, precipitation, or ion exchange processes. Khoe et al. (1997) claimed that photo-assisted oxidation using UV light effectively oxidizes As(III) to As(V). However, a pilot study conducted with a 200 nm UV light indicated that UV oxidation was only effective at extremely high UV intensities (7000 times the UV dose required than for *E. coli* inactivation) (Ghurye and Clifford, 2001). Even though Khoe et al. (1997) claimed that UV oxidation is effective at higher wavelengths (>300 nm), Bissen et al. (2001) reported that only 54% of As(III) could be oxidized in 45 minutes.

Researchers from the Australian Nuclear Science and Technology Organisation (ANSTO) evaluated both UV lamp reactors and sunlight-assisted-photo-oxidation. Tests demonstrated that almost complete oxidation of As(III) is possible using photochemical process, preferably in the presence of excess of dissolved Fe(II) (iron to arsenic mole ratio: 22:1). Emett et al. (2001) also showed that ultraviolet radiation could catalyse the oxidization of arsenite in the presence of ferric iron by several orders of magnitude. The process can be described via a free radical mechanism in which the rate of photon absorption by dissolved Fe (III)-chloro and Fe (III)-hydroxo species determine the rate of initial reaction. Multivalent Fe(III)-complexants such as arsenate and sulphate do not participate in the photo-chemical reactions so the addition of sulphate or arsenate ions leads to lower quantum efficiencies for the arsenic photo-oxidation process. The overall photo-chemical reaction, in the absence of dissolved oxygen, leads to the oxidation of one mole of As(III) per two moles of Fe(III) reduced. In this case, dissolved Fe (II) is a significant inhibitor of the reaction. However, under oxic condition, both As(III) and Fe(II) can be oxidised simultaneously and the photon efficiency is increased by the presence of Fe(II) and by reducing pH of the solution. Hug et al. (2001) investigated thermal and photochemical As(III) oxidation, and found that dissolved oxygen and micromolar hydrogen peroxide did not oxidize As(III) on a time scale of hours. In solutions containing 0.06 - 5 mg/L Fe(II, III), over 90% of As(III) could be oxidized photochemically within 2 - 3 hours by illumination with 90 W/m^2 UV-A light. Citrate (in the form of lemon or lime juice), a strongly Fe(III) complexing ligand, strongly speeded up As(III) oxidation. The photoproduct of citrate (3-oxoglutaric acid) also increased flocculation and precipitation of Fe(III). In laboratory tests, after adding 50 μM citrate, illuminating for 2 - 3 hours and precipitation, 80 - 90% of total arsenic in water was removed. In the first field trials in Bangladesh, 45 - 78 % of total arsenic was removed by the same procedure. Kocar et al. (2003) investigated the photochemical oxidation of As(III) in irradiated ferrioxalate solutions and found that the rate of this oxidation decreased with increasing pH (from 255 ± 16 μM/h at pH = 3.0 to 14 μM/h at ph = 7.0). The results also suggested that OH* is the important free radical responsible for As(III) oxidation. When doing experiments with the natural water sample containing DOC, they also found that the rate of photoinduced oxidation of As(III) was significant. This indicates that photochemical oxidation of As(III) may contribute to arsenic cycling in natural waters.

TiO_2 - catalysed photooxidation of As(III) to As(V) has been studied (Bissen et al, 2001; Lee and Choi, 2002). UV oxidation occurs when the energy from the UV light source is transferred directly to the reaction. TiO_2 photooxidation utilizes a semiconducting photocatalyst in which, the photocatalytic TiO_2 absorbs light that has energy greater than the band gap energy of the TiO_2 (about 3.2 eV or 380 nm light), producing electrons and holes on the surface of the oxide. The strongly oxidizing holes can convert As(III) to As(V). Lee and Choi (2002) observed that photooxidation by suspensions of TiO_2 effectively oxidizes As(III) to As(V). Bissen et al. (2001) demonstrated that nanoparticulate suspensions of TiO_2 illuminated with UV light could oxidize As(III) to As(V) in less than three minutes. Here, no reverse reaction takes place as the photocatalytic reduction of As(V) is much slower than the photocatalytic oxidation of As(III). One of the disadvantages of this method is that it can be difficult to separate the treated solution and the particulate TiO_2 photocatalyst (Lee and Choi, 2002).

This technology however is still in an experimental phase and needs further evaluation before it can be recommended for use in practice.

2.6.7 Arsenic removal by adsorption on material containing iron

Several proprietary iron-based adsorption materials have been developed. These materials generally have high removal efficiency and capacity. Iron oxide coated sand (IOCS), sulphur modified iron (SMI), granular ferric hydroxide (GFH), and iron filings (IF) are some of the methods that can be used to treat arsenic rich water. The application of granular ferric hydroxide (GFH) has been demonstrated in column studies to remove As(III) and As(V) to a level less than 5 µg/L at pH 7.6 level in drinking water with high bed volumes (1,260 and 1,140) up to a breakthrough concentration of 5 µg/L were achieved (Thirunavukkarasu, 2003a). Granular ferric hydroxides are being used in full scale systems in Germany (Driehaus et al., 1998).

2.6.7.1 Zero valent iron

Zero valent iron (ZVI) is an inexpensive and moderately strong reducing agent (Genin et al., 1998). It is used as a catalyst in the chemical synthesis in industrial applications and is capable of removing many common environmental contaminants, such as Cr(VI), Se, and NO_3 (Campbell, 1988; Powell et al., 1995; Huang et al., 1998; Farrell et al., 1999; Alowitz and Scherer, 2002).

Several researchers have investigated the removal of arsenic using zero valent iron - Fe(0). Lackovic et al. (2000) showed that zero valent iron filings could be used either in situ or ex situ to remove arsenate, and produce ferrous iron, which eventually precipitates out. Arsenite is removed either through coprecipitation or adsorption onto pyrite. The drawback of zero valent iron is that the treated water contains very high ferrous iron. Therefore, another removal treatment process is needed to remove the ferrous iron.

A simple arsenic removal system, namely "three kolshi filter" using metal iron filings has been developed and tested in Bangladesh (DPHE/UNICEF/BRAC, 2000). One system costs about $5, and flow rates average 2.6 to 2.9 liters per hour. The three kolshi filter system can remove arsenic from groundwater containing a wide range of arsenic concentrations (80 to over 1,000 μg/L). Generally, high removal efficiency was achieved with 5 - 30 μg/L arsenic was found in treated water. In some cases, arsenic removal exceeded 99%. However, the disadvantage of this system is that dissolved iron concentrations are increased and become unacceptably high if batches are left for long times (Ramaswami et al., 2000).

The arsenic removal mechanism is mainly due to spontaneous adsorption and coprecipitation of arsenic with iron(II) and iron(III) oxides/hydroxides, which form in-situ during ZVI oxidation (corrosion) (Lackovic et al., 2000; Farrell et al., 2001; Su and Puls, 2001; Manning et al., 2002). The oxidation of ZVI by water and oxygen is as follows (Ponder et al., 2000):

$$Fe^0 + 2H_2O \rightarrow 2Fe^{2+} + H_2 + 2OH^- \tag{1}$$

$$Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{2}$$

Fe(II) further reacts to give magnetite (Fe_3O_4), ferrous hydroxide ($Fe(OH)_2$), and ferric hydroxide ($Fe(OH)_3$) depending upon redox conditions and pH.

$$6Fe^{2+} + O_2 + 6H_2O \rightarrow 2Fe_3O_4(s) + 12H^+ \tag{3}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2(s) \tag{4}$$

$$6Fe(OH)_2(s) + O_2 \rightarrow 2Fe_3O_4(s) + 6H_2O \tag{5}$$

$$Fe_3O_4(s) + O_2(aq) + 18H_2O \leftrightarrow 12Fe(OH)_3(s) \tag{6}$$

Heterogeneous reactions at the corroding ZVI surface are complex and result in a variety of potential adsorption surfaces for As(III) and As(V). Despite this complexity, studies using X-ray absorption spectroscopy showed that the products after reaction of As(III) and As(V) with ZVI were innersphere As(III) and As(V) surface complexeson iron(III) oxides/hydroxide corrosion products (Farrell et al., 2001; Manning et al., 2002).

To improve the adsorption capacities, ZVI has been modified in various ways such as coating iron with Pd, Pt, Ni, and Cu (Liang et al., 1997; Gui et al., 2000; Li and Farrell, 2000).

2.6.7.2 Nanoscale zero valent iron nZVI

The versatility of nanometer-scale zero valent iron (nZVI) material has been demonstrated for potential use in environmental engineering. Due to the extremely small particle size, large surface area, and high in-situ reactivity, these materials have great potential in a wide array of environmental applications such as in soil, sediment, and groundwater remediation (Wang and Zhang, 1997; Lien and Zhang, 1999). In addition, due to small size and capacity to remain in suspension, nZVI can be transported effectively by groundwater and can be injected as sub-colloidal metal particles into contaminated soils, sediments, and aquifers (Lien and Zhang, 1999; Zhang, 2003). Shushil et al. (2005) found that the particle sizes of nZVI ranged from 10 to 100 nm. Arsenic(III) adsorption kinetics were rapid and occurred in minutes following a pseudo first order rate expression with observed reaction rate constants of 0.07 - 1.3 min^{-1}, about 1,000 higher than that of micron size ZVI. The maximum As(III) adsorption capacity was 3.5 mg of As(III)/g of nZVI.

2.6.7.3 Surfactant modified zeolite – zero valent iron

Zeolites are naturally occurring minerals with a crystalline structure characterized by large internal pore spaces. Therefore, they have very large surface areas, and high cation exchange capacities (CECs). A natural zeolite has a particle size of less than 0.4 mm (-40 mesh), BET surface area of 15.1 m^2/g, and an internal CEC of 800 meq/kg and an external (non-zeolitic) CEC of 100 meq/kg. The zeolite consists of approximately 74% clinoptilolite, 10% feldspar, 10% quartz and cristobalite, 5% smectite, and 1% iolite. Their rigid, three - dimensional structures make them free of the shrink/swell behaviour associated with smectite clays. For these reasons, zeolites can offer superior sorption and hydraulic properties and have found use as molecular sieves and sorbents in wastewater treatment (Breck, 1974; Barrer, 1978). Zeolites have been particularly useful in removing cationic species such as ammonium and some heavy metals from water. Natural zeolite minerals such as clinoptilolite and chabazite have a strong affinity for both As(III) and As(V). A chabazite filter could perform over 235 bed volumes before arsenic was detected in the effluent (Bonnin, 1997).

The cation exchange properties of natural zeolites can be exploited to modify their surface chemistries. A surfactant modified zeolite is capable of sorbing non - polar organic contaminants such as chlorinated ethylene, ionizable organics such as phenol and aniline, and inorganic anions such as nitrate and chromate (Li and Bowman, 1998; Li et al., 1998; Li et al., 2000)

A new material that combines ZVI with surfactant modified zeolite (SMZ) in a pelletized form showed encouraging results in removing contaminants from water. This material has a high hydraulic conductivity (9.7 cm/s), high surface area (28.2 m^2/g) and has 16% zeolite, 49% ZVI, 0.7% HDTMA-Cl, and 34% glass foam (by weight). The reduction rates of perchloroethylene (PCE) with the surfactant modified pellets were three times higher than the reduction rates with the unmodified pellets (Zhang et al., 2002). The surfactant modified zeolite – zero valent iron (SMZ/ZVI) pellets had the chromate removal capacity about 80% higher to SMZ pellets, due to the combined effects of sorption by SMZ and reduction by ZVI. The pseudo first order reduction constant of chromate and perchloroethylene (PCE) also increased by a factor of 3 and 9 for PCE and chromate respectively by surfactant modification (Li et al., 1999). Burt et al. (2005) showed that SMZ/ZVI could use as permeable reactive barriers (PRBs) material for groundwater remediation with PCE distribution coefficient (K[d]) of 3.0 L/kg. The enhanced contaminant reduction capacity of SMZ/ZVI pellets lead to a decrease in the amount of material required to achieve a given level of contaminant removal.

2.6.7.4 Iron oxide coated sand

Quartz is very poor at removing arsenic under most environmental conditions, because the mineral surface is negatively charged above a pH of 2. However, quartz sand can be made highly sorptive by coating the grains with metal oxides.

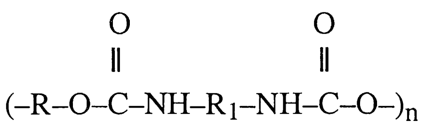
Vaishya and Agarwal (1993) found that sand from the Ganga River, India, which presumably is rich in iron coating, could remove arsenite with a capacity of 0.024 mg/g sand. The removal efficiency of this material depended on the pH and the highest removal efficiency was achieved in the pH range of 7 - 9. Viraraghavan et al. (1999) showed that addition of iron with the ratio of 20:1 in manganese greensand filtration system could reduce the arsenite concentration from 200 μg/L to below 25 μg/L.

Iron oxide coated sand (IOCS) was found to be able to remove both arsenite and arsenate. Joshi and Chaudhuri (1996) showed that a simple fixed bed unit packed with 75 g of IOCS was able to treat 163 - 184 and 149 - 165 bed volumes of groundwater spiked with 1,000 μg/L arsenite and arsenate respectively before arsenic reached 10 μg/L in the effluent. After breakthrough, iron oxide coated sand can be regenerated by flushing with sodium hydroxide. Other batch studies have been performed using iron oxide coated sand and ferrihydrite with natural water containing 325 μg/L arsenic, and the removal of 90% of the arsenic was observed (Thirunavukkarasu et al., 2001). Beside arsenic, iron oxide coated sand also can be used to remove other heavy metals in water such as cadmium, copper, nickel, and chromium (Khaodhiar et al., 2000).

2.7 Polyurethane sponge

Polyurethane is a polymer consisting of a chain of organic units joined by urethane links. It was invented in Germany during the 1930s as a result of research efforts to develop new polymeric fibre material. Generally, the characteristics of polyurethane depend on the manufacturing method and the starting chemicals used. As a result, polyurethane sponge can be flexible (for example sponge used in furniture cushions) or rigid (for example sponge used in construction panels). Flexible polyurethane are made from polyols of moderately high molecular weight and low degree of branching, whereas rigid polyurethane are prepared from highly branched resins of low molecular weight (Braun et al., 1985). Other properties of polyurethane (PU) such as foam density, cell structure, rate of wetting, and water retention vary depending on the ratio of polymer to cross - linking agent, foaming temperature, pH, and the type and amount of additives (Havens and Rase, 1993).

The simplest formula for PU is linear and represented by



$$(-R-O-\overset{\overset{O}{\|}}{C}-NH-R_1-NH-\overset{\overset{O}{\|}}{C}-O-)_n$$

Where n is the number of repetitions and R_1 is the hydrocarbon chain. R represents a hydrocarbon containing the OH group. Di-isocyanates are usually employed in PU production reactions because they react with any compound containing active hydrogen.

Commercial polyurethanes are composed of segments with the structure – (O-R’-O) – (CONH-R-NH-CO) – (O-R”-O) – (CO-NH-R-NH-CO) –, with organic groups R, R’, R”. They can be composed from (i) a di-isocynate OCN-R-NCO such as MDI (diphenylmethane di-isocyanate) or TDI (toluene di-isocynate), (ii) a polyol (or polyether) or polyester HO-R’-OH such as polypropylene glycol (PPG) or polytetramethylene glycol (PTMG), or polycaprolactone (PCL) or polybutylene adipate (PBA), and (iii) small - molecule chain extenders (OH-R”-OH) like 1,4-butanediol (BDO) or 1,6-hexanediol (HDO), linking di-isocyanates in “hard segments” (Lattimer et al., 1998).

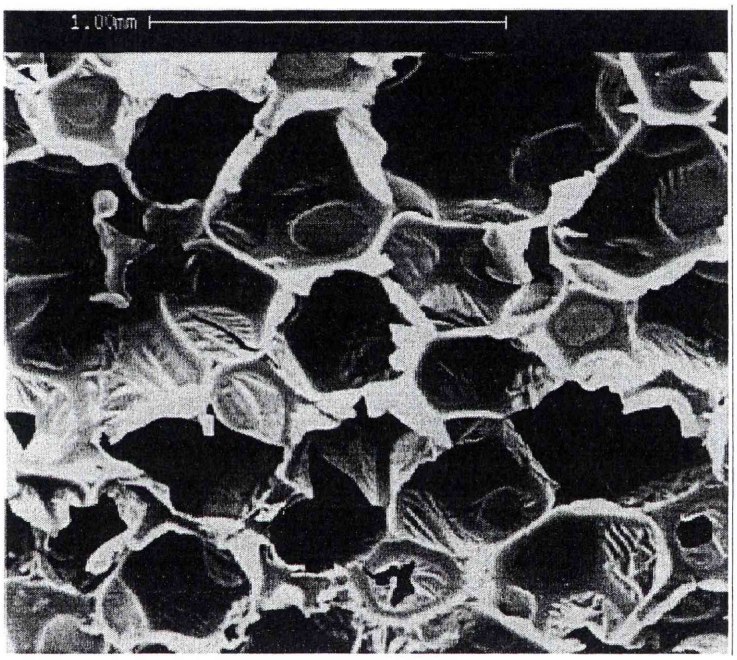


Figure 2.2. Scanning electron microscope (SEM) photo of commercial rigid PU foam with density 38 kg/m^3 (Branca et al., 2003)

Typical characteristics of polyurethane determined through experiments by Moe and Irvine (2000a) are presented in Table 2.3.

Table 2.3. Characteristics of polyurethane sponge (Moe and Irvine, 2000a; 2000b)

Property	Foam formulation (surfactant concentration)	
	10 g/L	20 g/L
Dry density (kg/m^3)	84	84
Density at 65% moisture content (kg/m^3)	117	113
Swelling in vertical direction when at 65% moisture content (%)	24	24
Swelling in horizontal direction when at 65% moisture content (%)	29	31
Swelling in volume when at 65% moisture content (%)	105	113
Porosity at 65% moisture content	0.85	
Average pore area (mm^2)	1.0	
Surface area (m^2/m^3)	620	
Head loss through 1m depth at surface loading of 60 m^3/m^2/hr (mm water)	2	

Chemical component of polyurethane is presented in Table 2.4.

Table 2.4. Chemical properties of polyurethane (Font et al., 2001)

Property	Value (%)
C	63.9
H	8.3
N	1.6
S	0
O	26.2

C: Carbon, H: Hydrogen, N: Nitrogen, S. Sulphur, O: Oxygen

There are a number of studies conducted using polyurethane sponges in environmental applications. Polyurethane foam was used as the support medium in an air biotrickling filter (Devinny et al., 1999). Loy and Flauger (1997) reported the use of polyurethane foam cubes as the support medium for biofilters treating industrial waste gases. Moe and Irvine (2000b) used a polyurethane medium as a biofilter which was able to remove over 99% of the influent toluene when fed at a concentration of 200 mg/L to remove waste stream containing toluene. This system operated for more than 300 days with empty bed residence times (EBRTs) ranging from one to four minutes.

To increase the effectiveness of sponge, many researchers have incorporated additives into polyurethane sponge. Brookes et al. (1987), Hu et al. (1994) have put living microorganisms into polyurethane foam matrices as a method of immobilization and used these sponges as biofilter media to remove phenols from wastewater. Other researchers (Wood et al., 1982; Havens and Rase, 1993) have immobilized active enzymes in the foam and used such materials in biological waste-gas treatment system. Additionally, Lupton and Zupancic (1991) used polyurethane foam containing PAC and immobilized microorganisms for the treatment of wastewater containing phenol. Al-Marzouqi et al. (2001) reported that low density polyurethane sponge (13 kg/m^3) has the highest capacity for absorbing oil (0.06 m^3 oil/kg sponge after one minute) in cooperation with palm trunk, pin fish fiber, rice bag, feathers, and PP pad sponge.

Another kind of sponge (Forage sponge) was studied to remove metals (including arsenic) from water. Forage sponge is an open-celled cellulose sponge incorporating an amine-containing chelating polymer that selectively absorbs dissolved heavy metals. The results from the demonstration indicated a reduction of Cu by 97%, lead by 97%, chromium by 32%, and arsenic by 7% from groundwater containing copper (917 µg/L), lead (578 µg/L), chromium (426 µg/L), and arsenic (47.7 µg/L) (USEPA, 1995).

2.8 Disposal

Management of arsenic residual is a major public concern and challenge. Different treatment processes such as coagulation, flocculation, adsorption or membrane processes that are often used to treat arsenic contaminated water, cannot destroy arsenic completely, rather all these processes convert arsenic into different forms or transformit into insoluble compounds in combination with other elements, such as iron. Safe disposal of arsenic wastes poses several problems.

There are three options available for dealing with arsenic waste streams: (i) recovery and reuse, (ii) dilution and dispersion, and (iii) encapsulation of the material through solidification/stabilization techniques. The cost and the safety are the two major issues associated with the first option. Due to a very limited market for the recovered arsenic, there is little commercial interest to recover arsenic and its compounds. Additionally, there are safety concerns for storing arsenic. Therefore, encapsulation of arsenic through solidification/stabilization techniques is the most attractive solution associated with the disposal of the arsenic residuals.

Solidification/stabilization (S/S) is a technology used to transform potentially hazardous liquid or solid wastes into less hazardous or nonhazardous solids before disposal, thus preventing the waste from entering the environment. Solidification refers to processes that encapsulate a waste to form a solid material and to restrict contaminant migration by declining the surface area exposed to leaching and/or by coating the waste with low-permeability materials. Stabilization refers to processes that involve chemical reactions that reduce the leachability of a waste (USEPA, 2000a).

A number of researchers have investigated arsenic solidification/stabilization processes using different solidifying materials: Portland cement (Akhter et al., 1990; Buchler et al., 1996), Portland cement and iron (II) and (III) (Taylor and Fuessle, 1994), Portland cement and lime (Dutre and Vandecasteele, 1998), Portland cement, iron and lime (Palfy et al., 1999), Portland cement and fly ash (Chu et al., 1991; Akhter et al., 1997), Portland cement and silicates (Chu et al., 1991). Some studies have also been conducted on the safe disposal of arsenic wastes by incorporation into slag and encapsulation using polymers (Twidwell and Mehta, 1985; Carter et al., 1995; De Villiers, 1995).

Akhter et al. (1990) investigated various methods for the immobilization of arsenic, cadmium, chromium and lead in contaminated soil with arsenic concentration of 12,200 mg/L. They tested various combinations of Portland cement, fly ash, blast furnace slag, lime and silica fume, and the only sample showing reasonable leaching performance was that using Portland cement alone, at a dosage of 1 part soil in 0.44 part cement.

The arsenic compound in the waste has a strong effect on the successfulness of S/S process (Buchler et al., 1996). By the Toxic Characteristic Leaching Procedure (TCLP), leachate concentrations varied from 510 to 1.7 mg/L. The experimental results showed that the wastes containing either sodium arsenate or sodium arsenite were better treated by S/S than the one containing arsenilic acid. The arsenic in leachate concentrations was 1.7 and 2.1 mg/L for sodium arsenate and arsenite respectively in comparison with 510 mg/L for arsenilic acid.

To increase the effectiveness of the solidification/stabilization process, a number of additives were used in the cementation process. The use of iron appears to be the most preferred option. The research of Taylor and Fuessle (1994) showed that the success of using iron is highly dependent upon the oxidation states of both the iron and arsenic. The use of iron (II) is preferred for arsenic stabilization over the longer term than iron (III). The use of iron (III) is not recommended for arsenate stabilization, because the fresh cement mix adsorbs ferric ions and does not allow adequate solidification/stabilization until long cure times hace elapsed. The effective conversion of arsenite to arsenate can be accomplished by the addition of hydrogen peroxide at stoichiometric dosages with adequate mixing (Taylor and Fuessle, 1994).

Dutre and Vandecasteele (1995) investigated solidification/stabilization of an industrial waste containing large amount of arsenic (42% arsenic). The waste was treated using S/S with cement and pozzolanic materials. Solidification with cement and lime was found very suitable technique to reduce the leachability of arsenic from the stabilised waste. A more recent work by Dutre and Vandecasteele (1998) examined the S/S of a waste fly ash from the metallurgical industry containing arsenic concentrations ranging from 23% to 47%. The optimum solidification/stabilization formulation consisted of 8 g of lime, 6 g of cement and 20 mL of water per 10 g of waste material. The solidification process was capable of reducing the leachate concentration from 5 g/L to approximately 5 mg/L. The extraction test used consisted of agitating 100 g of the treated material with 1L of distilled water for 24 h. The reduction in the arsenic concentration was due to the formation of $CaHAsO_3$ in the leachate, in the presence of $Ca(OH)_2$.

Palfy et al. (1999) studied the stabilization of a waste material arising from the carbon dioxide scrubbing in the Vetrocoke technology, where As_2O_3 solution is the activator. The aim of the fixation process was to embed calcium and ferric arsenates/arsenites in a cement matrix. The optimum process utilized a Ca:As ratio of 8 (ratios greater than 8 did not lead to a significant reduction in the residual concentration of arsenic in the solution) and a Fe:As mole ratio of 6. After the stabilisation process, the leachate concentration was 0.823 mg/L compared to 6,430 mg/L for the untreated waste. Leaching tests were conducted in distilled water at 25^0C with a solid-to-liquid ratio of 1:10 and a mixing speed of 150 rpm.

Twidwell and Mehta (1985) investigated the stabilization of arsenic in copper smelter flue dust. The stabilization process involved converting the arsenic oxide contained in the flue dust to calcium arsenate and arsenite by low temperature air roasting in the presence of lime. The calcium arsenate and arsenite were then dissolved in a molten iron silicate slag matrix. The incorporation of up to 23.5% arsenic into the slags was investigated. All slags passed the USEPA Extraction Procedure (EP) Toxicity Test.

The potential for encapsulation of the arsenic waste by combination with two commodity polymers was elevated by Carter and other (1995). They used recycled high density polyethylene HDPE and solprene 1204 a random styrene butadiene copolymer with 25% styrene content. They concluded that As_2O_3 could not be suitably bound into HDPE, because the processing temperatures generally employed approach the sublimation temperature, which made the process inefficient and hazardous. When As_2O_3 was stabilized with calcium oxide, volatility was decreased, and arsenic loadings of 17 wt. % were possible.

There are difficulties in comparing the results obtained by the a number of researches and drawing any firm conclusions on which S/S processes are the most efficient and effective. The first reason is that there were difference results between studies using different leaching tests. When using the Toxicity Characteristic Leaching Procedure (TCLP) test, the treatment using metal hydroxides appeared slightly better than the treatment that utilized either silicates or cement/fly ash. The results were 0.02, 0.03 and 0.09 mg/L arsenic, respectively. However, when the same samples were subjected to the Waste Extraction Test (WET) tests, the treatment using silicates yielded significantly better results than those obtained using metal hydroxides or cement/fly ash. The results obtained were: silicates, 3.2 mg/L arsenic; metal hydroxides, 17 mg/L arsenic; and cement/fly ash, 24 mg/L arsenic (Chu et al., 1991). Another reason that made difficult in comparison is that the diversity of arsenic compounds and oxidation states. Johnson et al. (1980) investigated the stabilization of three different arsenic wastes. Waste No. 1 (contained approximately 2% organic arsenicals) composed mostly of sulfate and chloride salts. The second material, Waste No. 2 (containing 0.9% arsenic in the form of As_2S_3) was a yellow, damp, 37% moisture acidic filter cake while Waste No. 3 (containing 90% As_2O_3) was a fine white powder. Each waste was subjected to several identical fixation processes. The three wastes were quite different in their response to fixation attempts, with Waste No. 1 by far performing the worst. Even after fixation, Waste No. 1 still leached an average of 78% whereas waste No. 3 performed significantly better than Waste No. 1, leaching less than 12% arsenic, and Waste No. 2 performed the best, leaching less than 2% arsenic.

2.9 Adsorption modelling

2.9.1 Adsorption kinetics and equilibrium

To assess the adsorption capacity and the kinetics of adsorbents such as iron oxide coated sponge, iron oxide coated sand 2, surfactant modified zeolite – zero valent iron, adsorption isotherms and adsorption kinetics equations are important.

2.9.1.1 Ho kinetics

In adsorption studies, process kinetics describe the rate at which the species are transferred from the solution to the pores of an adsorbent. The rate of adsorption determines the equilibrium condition and the detention time required for treatment (adsorption).

Ho et al. (1996) presented a pseudo second-order reaction rate model to describe the adsorption kinetics of metals on peat, as shown below:

$$\frac{t}{q_t} = \frac{1}{2k_H q^2} + \frac{t}{q} \qquad (7)$$

Where: k_H : Ho rate constant for adsorption, function of temperature (g/mg.min);

q: the amount of adsorbate at equilibrium (mg/g); and

q_t : the amount of adsorbate at any time t, (mg/g).

Ho pseudo second order kinetic model was used to simulate a number of sorption systems (Azizian, 2004). Ho's pseudo second order model presents the experimental kinetic data for the entire sorption period for most of the systems better than other models. This model has been used extensively by a lot of researchers as it could simulate excellent and fit experimental kinetic data for the entire sorption period (Kumar and Sivanesan, 2006).

To fit the data obtained from the kinetic studies, the equation (7) can be rearranged as follows:

$$q_t = \frac{2k_H q^2 t}{1 + 2k_H q\, t} \qquad (8)$$

2.9.1.2 The Langmuir isotherm

A number of models are used to describe the adsorption data in water treatment. In particular, the Langmuir and Freundlich isotherms are those most commonly used for single solute adsorption (Snoeyink and Summers, 1999).

The Langmuir model is the simple theoretical model for monolayer adsorption. The Langmuir model is developed based on the following underlying assumptions (Weber, 1972; Faust and Aly, 1987; Cooney, 1999):

- the molecules are adsorbed on definite sites on the surface of the adsorbent;
- each site can bind only one molecule of the adsorbing species (monolayer);
- the adsorption energy is the same at all sites; and
- there are no forces of interaction between adjacently adsorbed molecules.

The Langmuir isotherm is described as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \qquad (9)$$

Where C_e : the equilibrium concentration (mg/L),

b : a Langmuir constant related to the binding energy of adsorption (L/mg),

q_m: the saturated maximum monolayer adsorption capacity (mg/g).

2.9.1.3 The Freundlich isotherm

The Freundlich isotherm is an empirical equation developed based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites, and each site can be modeled by the following equation:

$$q_e = K_F . C_e^{\frac{1}{n}} \qquad (10)$$

Where K_F: a Freundlich constant indicative of the adsorption capacity of the adsorbent

n: an experimental constant indicative of the adsorption intensity of the adsorbent.

2.9.1.4 Toth isotherm

While the Langmuir and the Freundlich isotherm equations are by far the most common single solute expressions used, there are other single solute expressions that are sometimes employed. One of these is the three parameter isotherm proposed by Toth (1971). The isotherm equation is as follows:

$$q_e = \frac{q_m C_e}{(1+(bC_e{}^n)^{\frac{1}{n}}} \tag{11}$$

The Langmuir and Toth models follows the Henry law at low sorbate concentrations, that is the linear dependence of sorbate concentration and bulk concentration.

2.9.1.5 Sips isotherm

The Sips model is a different empirical model representing equilibrium adsorption data. This isotherm model has the features of both the Langmuir and Freundlich isotherm models. As a combination of the Langmuir and Freundlich isotherm models, the Sips model contains three parameters: q_m, b and n which can be evaluated by fitting the experimental data. For single solute equilibrium data, the Sips adsorption isotherm model can be written as follows:

$$q_e = \frac{q_m (bC_e)^{\frac{1}{n}}}{1+(bC_e)^{\frac{1}{n}}} \tag{12}$$

2.9.2 Fixed bed adsorption columns

Bohart and Adams (1920) proposed the bed depth service time (BDST) model that assumes that the adsorption rate is proportional to both the residual adsorbent capacity and the remaining adsorbate concentration. This model presents a linear empirical equation to predict the breakthrough time as a function of depth, flow rate, and inlet and outlet solute concentrations. The model is represented as follows:

$$\ln\left[\frac{c_{if}}{c_b}-1\right]=\ln\left[e^{k_1 n_0 \frac{d}{v_1}}-1\right]-k_1 C_{if} t \tag{13}$$

Where C_{if} : influent adsorbate concentration (mg/L)

C_b : desired concentration of adsorbate at breakthrough (mg/L)

k_1 : rate constant (L/mg.h)

n_o : adsorption capacity of the adsorbent (mg/L)

d : depth of the bed (m)

v_1 : flow velocity (mL/h)

t : service time of column (h)

The equation can be rearranged to yield an expression for service time t, as shown below:

$$t=\frac{n_o}{C_{if} v_1} d-\frac{1}{C_{if} k_1}\ln\left[\frac{c_{if}}{c_b}-1\right] \tag{14}$$

Hutchins (1973) proposed a linear relationship between the bed depth and service time, and the Bohart and Adams equation (14) is expressed as:

$$t = a x + b \tag{15}$$

Where: $a = \text{slope} = \frac{n_o}{C_{if} v_1}$, and

$$b = \text{intercept} = \frac{1}{C_{if} k_1}\ln\left[\frac{C_{if}}{C_b}-1\right]$$

The Thomas model is also easily applied to determine the adsorptive capacity of the adsorbent and to study the adsorption kinetics. Further, this model provides an approach for the design and projection of the performance of fixed bed absorbers without the need to conduct extensive experimental work and mathematical formulation.

The Thomas model as shown in Reynolds and Richards (1996) is as follows:

$$\frac{C_{ef}}{C_{if}} = \frac{1}{1 + \exp[\frac{k_T}{Q_v}(q_m m - C_o V)]} \qquad (16)$$

Where C_{ef}: effluent adsorbate concentration (mg/L)

C_{if} : influent adsorbate concentration (mg/L)

k_T : Thomas rate constant (L/min.mg)

q_m : maximum solid phase concentration of the solute (adsorption capacity) (mg/g)

m : mass of the adsorbent (g)

V : throughput volume (L)

Q_v : volumetric flow rate (L/min)

Nikolaidis et al. (2003) used another model to describe the transport of arsenic in the columns packed with zero valent iron. In this model, surface adsorption was assumed to be a fast reaction that reaches equilibrium in a fraction of the hydraulic detention time of the column. Arsenic precipitation and co-precipitation in solution or diffusion through the iron oxides (corrosion products) and surface precipitation are much slower processes and were modelled as a first-order-loss reaction.

$$\frac{\partial C}{\partial t} = -u_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t}\frac{\rho_s(1-n_N)}{n_N} - k_N C \qquad (17)$$

Where C : solute arsenic concentration (mg/L)

S : amount sorbed onto porous medium, = K_d C (mg/mg)

K_d : linear equilibrium partitioning coefficient (L/mg)

ρ_s : the solid density of the particles (mg/L)

n_N : the effective porosity, (dimensionless)

k_N : the first-order mass transfer loss coefficient (1/s)

D_x : dispersion coefficient in x direction (m^2/s) = α u_x

u_x : the velocity of water (m/s)

α : the dispersivity (m).

2.10 Conclusion

Arsenic is a very toxic chemical. It can exist in several oxidation states in the environment. However, in natural water, arsenic is mostly found in an inorganic form of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). The toxicity of arsenic depends on its speciation and concentration. Ingestion of inorganic arsenic can result in both cancer (skin, lung and urinary bladder) and non – cancer detrimental effects. The high concentration of arsenic was found in a number of countries such as Bangladesh, India, Taiwan, Vietnam, America, and Argentina.

Different treatment technologies such as ion exchange, adsorption, membrane, coagulation/filtration can be used to remove arsenic from water. A number of iron-based adsorption materials have been developed.

After treatment, the management of arsenic residual is also a major public concern and challenge. Encapsulation of arsenic through solidification/stabilization techniques shows the attractive solution for this matter.

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CHAPTER 3

EXPERIMENTAL INVESTIGATION

Chapter 3 Experimental investigation

3.1 Introduction

This chapter gives a detailed description of materials and methods used in this study to achieve the objectives outlined in Chapter 1. The experimental material, experimental set-up, and analysis methods adopted are discussed in this chapter.

3.2 Experimental materials

3.2.1 Water

In this study, two kinds of water were used. In the majority of experiments concerning the process development, synthetic water was used. In order to evaluate the effectiveness of iron oxide coated sponge in practice; the real groundwater samples from Kelliher in Canada and Hanoi in Vietnam were employed.

3.2.1.1 Synthetic groundwater

The majority of experiments using synthetic water were conducted at the University of Technology, Sydney (UTS), Australia. Synthetic water was prepared by adding arsenic stock solution (1 g/L) in tap water to obtain a predetermined concentration of arsenic. This synthetic water used for dynamic experiments represents arsenic contamination in water with different levels, from low concentration of 145 μg/L to high concentration of 1,000 μg/L. These concentrations are representative of different concentrations of water contaminated with arsenic found in the field. To investigate the kinetics and equilibrium adsorption of adsorbents, predetermined arsenic concentrations in synthetic water used for batch experiments were varied in a wide range of 260 μg/L to 30,000 μg/L. The experiments were conducted at different pH values from 2 to 10. Solutions 1M HNO_3 and NaOH were used to adjust the pH. The composition of the synthetic water used in this study is presented in Table 3.1.

3.2.1.2 Real groundwater

Real groundwater was drawn from the Kelliher Water Treatment Plant, Kelliher, Saskatchewan, Canada and a well in Vanphuc Village, Hanoi, Vietnam. Water was collected from wells using 20 L low density polyethylene containers and used in the studies immediately upon arrival in the laboratory. The arsenic concentrations in groundwater were of low levels, from 56 μg/L to 156 μg/L. The characteristics of the groundwater used are presented in Table 3.1.

Table 3.1. Water quality parameters

Parameters	Concentration		
	Synthetic water	Kelliher groundwater	Hanoi groundwater
Arsenic	0.145 – 30	0.056	0.156
Iron	0.016 - 0.09	2.1	6.2
Manganese	0.004 - 0.02	1.2	1.5
Nitrate	0.74 - 2	2.9	N/A
Turbidity (NTU)	0.15 - 0.28	N/A	N/A
Copper	0.001 – 0.049	0.04	0.08
Zinc	< 0.005	0.01	0.01
Lead	< 0.002	0.002	N/A
Cadmium	< 0.001	< 0.001	N/A
Chromium	< 0.001	0.001	N/A
Phosphate	0.004	N/A	1.5
Silicate	0.8	N/A	15

Note: All parameters except pH and turbidity are in mg/L N/A: Not available

(Source: Sydney Water, Saskatchewan Environment, and based on the analysis)

3.2.2 Standards and reagents

All chemicals used in the studies were reagent grade, and were used without any purification.

Arsenate [As(III)] stock solution (1,000 mg/L) was prepared by dissolving 1.3223 g of oxide arsenite (As_2O_3, Ajax Chemical) into 1 L distilled water. One mg/L of As(III) was prepared by pipetting 1 mL of stock solution into 1 L volumetric flask, and then the solution was made up to 1 L with distilled water.

Arsenate [As(V)] stock solution (1,000 mg/L) was prepared by dissolving 4.164 g of sodium arsenate ($Na_2HAs0_4.7H_20$, Sigma – Aldrich) into 1 L distilled water and was preserved with 0.5% HNO_3 (trace metal grade). One mg/L of As(V) was prepared by pipetting 1 mL of stock solution into 1 L volumetric flask, and then the solution was made up to 1 L with distilled water.

The required working standards were prepared daily from the corresponding stock solution for the studies. All glassware and sample bottles (200 mL HDPE bottles; National Measurement Institute, Australia) were washed with a detergent solution, rinsed with tap water, soaked in 10% nitric acid for at least 12 hours, and finally rinsed with distilled water three times.

Distilled (double) deionized water and milli Q water were used in the preparation of standard solutions and for dilution purposes.

3.2.3 Adsorbents

3.2.3.1 Preparation of iron oxide-coated sponge (IOCSp)

The principal method for preparation of IOCSp is as follows:

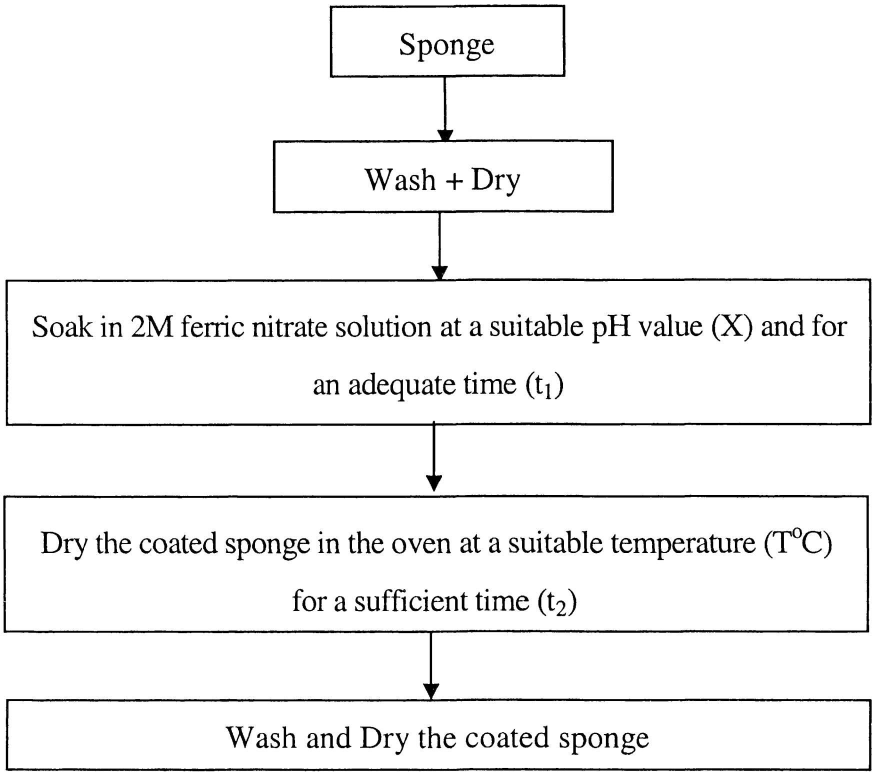


Figure 3.1. Procedure of coating of the sponge with iron oxide

The experiments were conducted at various operating conditions to find the optimum condition for iron oxide coating of the sponge. The conditions studied were: (i) pH value of coating solution (pH from 1, 2 ... to 12); (ii) time of contact between iron oxide and the sponge t_1 (5, 10, 15, 20, 30 minutes and up to 15 hours); (iii) coating temperature T^0C (110°C, 220°C); and (iv) time of drying of sponge after the coating t_2 (8, 12, 14, 18, 20 and up to 34 hours). After determining the optimum coating conditions for preparing IOCSp, the IOCSp was prepared at optimal conditions for all the experiments in the subsequent batch and column studies.

3.2.3.2 Preparation of iron oxide coated sand 2 (IOCS-2)

The capacity of IOCS-2 in removing arsenic was studied and compared with that of IOCSp.

In IOCS-2 preparation, the coating of iron oxide was achieved on the redflint filter sand obtained from Watergroup Canada Ltd., Regina, Saskatchewan. Initially, the sand was sieved to a geometric mean size of 0.6 mm to 0.8 mm, acid washed (pH 1; 24 h), rinsed with deionized distilled water three times, and dried at 100^0C for 20 hours before use. IOCS-2 was prepared by a two-step process developed by Thirunavukkarasu (Thirunavukkarasu et al., 2003b). In step 1, the solution containing a mixture of 80 mL of 2M $Fe(N0_3)_3.9H_20$ and 1 mL of 10 M NaOH was poured over 200 g of dried sand placed in a heat resistant dish. After gentle agitation, the mixture was heated for 4 hours at 110^0C and then at 550^0C for 3 hours. Upon cooling, the coated sand was washed with deionized distilled water until the black coloured fraction washed away. In step 2, the solution containing the same mixture of $Fe(N0_3)_3.9H_20$ and NaOH was poured over 100 g of the coated sand from step 1, and heated for 20 hours at 110^0C. After cooling, the sand was broken mechanically to separate the grains, and sieved. When exposed to room temperature (20^0C), the coated sand became moist, and this was overcome by drying it for 4 hours at 110^0C followed by 20 hours at 20^0C (five cycles). Finally, the iron oxide coating on the sand was found to be dry and stable in a strong base solution, and it was then stored in capped bottles. In a high temperature coating process, the attachment strength between the sand surface and the iron oxide becomes stronger, and there is an increase in specific surface area and number of pores (Lo et al., 1997).

3.2.3.3 Preparation of nanoscale zero valent iron (nZVI)

Nanoscale zero valent iron was prepared as per Sherman et al. (2000). 10.00 g of $FeSO_4.7H_2O$ was dissolved in 100 mL of 30% technical grade ethanol, and 70% deionized water (v/v) under non oxygen environment. The pH was adjusted to about 6.8 with 3.8 M NaOH. $NaBH_4$ powder (1.8 g) was added incrementally to the mixture, allowing the foaming to subside between increments. After addition of all of the $NaBH_4$, the mixture was stirred for 20 minutes. The solid was washed twice with technical grade ethanol, effectively substituting ethanol for the water in the mixture. This step helps to prevent immediate rusting as the filtration process is completed.

3.2.3.4 Preparation of surfactant modified zeolite - zero valent iron (SMZ/ZVI)

Surfactant modified zeolite - zero valent iron (SMZ/ZVI) obtained from Douglas Wolf, University of Dayton Research Institute, Ohio, America was used to study its capacity in removing arsenic. SMZ/ZVI was produced by coating a homogeneous slurry (by weight) of zeolite powder (14.5%), iron powder (43.5%), water (42.0%) and surfactant onto a glass foam substrate (Cell-Pore). After this procedure, the dried SMZ/ZVI slabs were broken into 2.5 cm cubes. The final cubes consisted of approximately 16.5% zeolite, 49.5% iron, and 34.0% silica foam substrate (determined by the mass fraction). For the laboratory column experiments, zeolite/ZVI cubes were crushed to smaller sized pellets (with a longest dimension of 0.5 cm).

3.2.4 Membranes

The membranes used in this study were NTR 729HF (NF) (Nitto Denko Corp., Japan) and Poly Vinyl Alcohol (MF) (PVA, MF, Pure-Envitech, Korea). These membranes were used for the (i) nanofilter and microfilter and (ii) nanofilter – nanoscale zero valent iron and microfilter – nanoscale zero valent iron hybrid systems to study the effectiveness of these processes in arsenic removal. Both membranes used in this study were made from polymer. The detailed characteristics of this membrane are presented from Tables 3.2 to 3.4. Figure 3.2 presents the SEM image of these membranes.

Table 3.2. Skin-layer functional groups of NTR729HF membrane (Thanuttamavong, 2002)

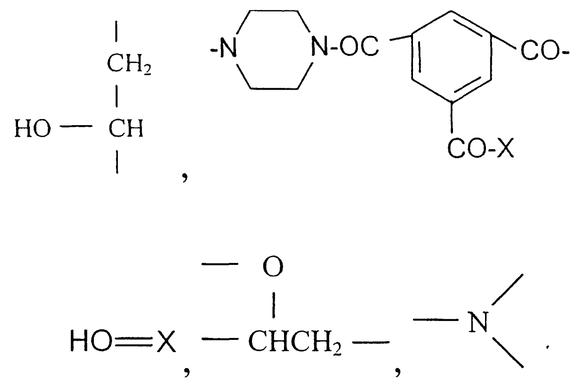
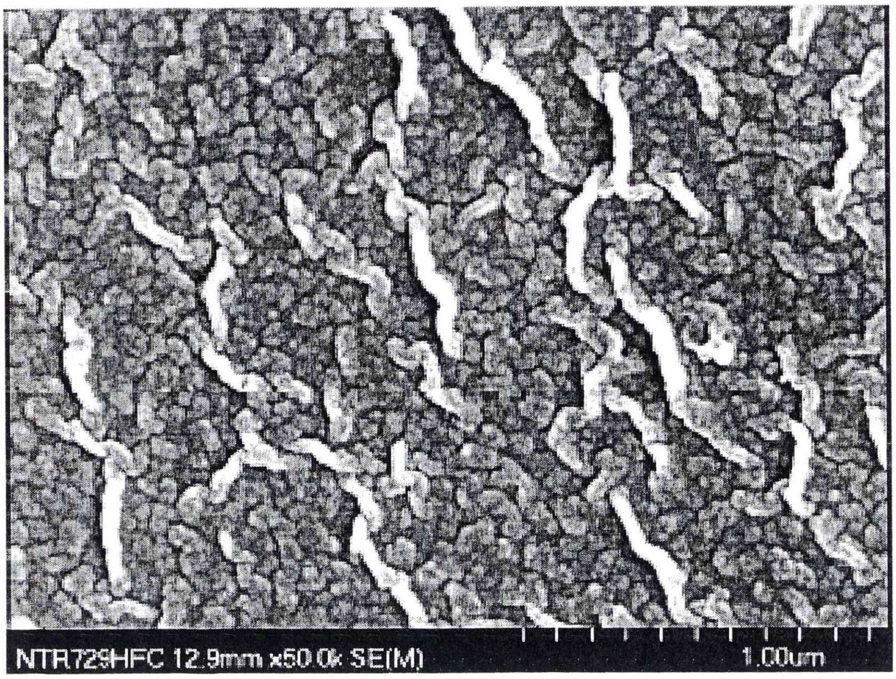
Code	Material	Skin-layer materials
NTR 729 HF	Polyvinylalcohol/ polyamides	

Table 3.3. Specification of NTR729HF membrane obtained from the manufacturer (Nitto Denko Corp., Japan)

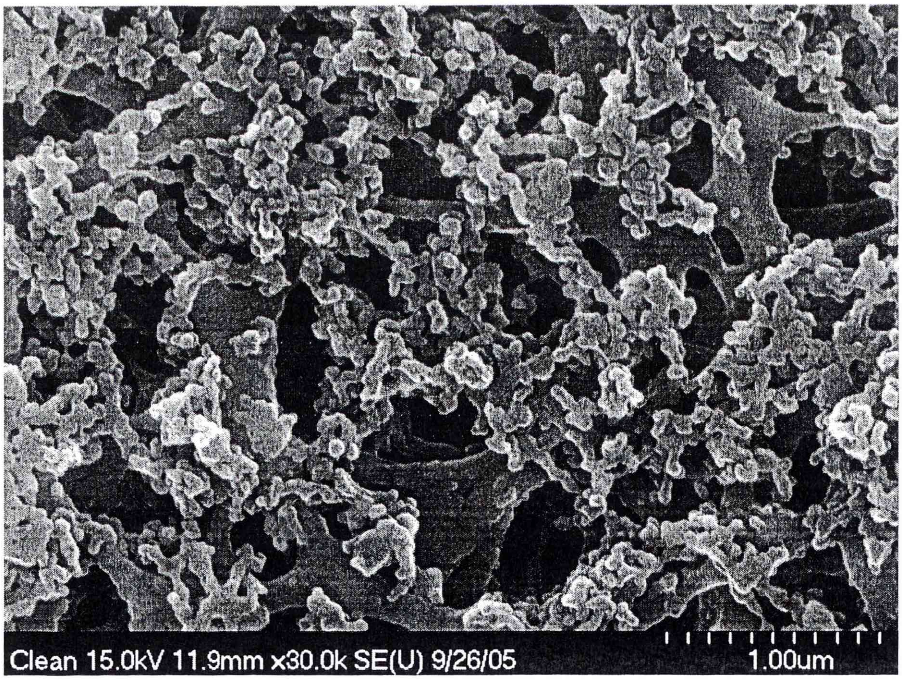
Membrane		NTR 729HF
NaCl rejection		92
Condition	Concentration (%)	0.15
	Pressure (MPa)	1.0
	Temperatute (°C)	25
	Recovery (%)	10-20
	pH	6.5
Range	Maximum temperature (^{0}C)	40
	pH	2-8
	Maximum pressure (MPa)	2.9
	Chlorine (mg/L)	<1

Table 3.4. Specification of PVA membrane obtained from the manufacturer (Pure-Envitech, Korea)

Membrane	MF
Material	Poly vinylidene fluoride
Pore size (μm)	0.4
Contact angle (°)	94
Pure water permeability (L/m^2.h) at 30 kPa	3300



(b) NTR 729HF



(b) PVA

Figure 3.2. SEM images of membranes

3.2.5 Titanium dioxide

The characteristics of titanium dioxide TiO_2 (P25 Degussa) powder used as catalyst in the photocatalytic experiments are shown in Table 3.5. The effectiveness of TiO_2 photocatalysis system in oxidizing As(III) into As(V) was studied.

Table 3.5. Characteristics of P25 Degussa photocatalytic TiO_2

Specification	P25 Degussa TiO_2
Structure	Non-porous
Components	65% anatase, 25% rutile, 0.2% SiO_2, 0.3% Al_2O_3, 0.3% HCl, 0.01% Fe_2O_3
Average aggregate particle diameter	Non-porous
Primary crystal size	3 μm
Mean pore diameter	6.9 nm
Band gap	3.03 (from 500 to 300 nm) with UV-Vis
Apparent density	130 kg/m^3
Surface area	42.32 ± 0.18 m^2/g
Type	Powdered
Product code	Degussa P25, Frankfurt am Main, Germany

3.3 Experimental studies

3.3.1 Batch kinetic studies

The adsorbents, namely IOCSp, IOCS-2, and SMZ/ZVI, were used in the batch kinetic studies. These experiments were conducted to remove both As(III) and As(V) from synthetic water spiked with arsenic. The effect of pH (on the time required to reach the adsorption equilibrium) was also studied. IOCSp and IOCS-2 kinetic studies were conducted at pH levels of 6, 7 and 8, whereas, for SMZ/ZVI, arsenic [As(III) and As(V)] removal was studied only in the pH 7. In the kinetic experiments using IOCSp, IOCS-2, and SMZ/ZVI, the initial concentrations of As(III) and As(V) were maintained at 260, 260 and 1,000 μg/L respectively. In these studies, the mass of IOCSp, IOCS-2, and SMZ/ZVI, was kept at 0.15, 1, and 2 g, respectively.

In the kinetic studies, 100 mL arsenic solutions were transferred to 250 mL Erlenmeyer flasks containing the adsorbent, and the flasks were sealed with parafilm. The samples were placed on a mechanical shaker and shaken at 130 - 175 rpm. A portable bench top platform shaker (Ratex Instrument Co., and New Brunswick Scientific Co. Inc.) was used to conduct the batch studies. Samples were collected at regular time intervals and analysed for residual arsenic using hydride generation atomic absorption spectrometry (HGAAS) or graphite furnace atomic absorption spectrometry (GFAAS).

3.3.2 Batch equilibrium studies

Equilibrium studies were conducted at the pH level of 7 using IOCSp, IOCS-2, SMZ/ZVI, and tap water spiked with required concentrations of As(III) and As(V). In the equilibrium experiments, the initial concentrations of As(III) and As(V) were varied in the range 260 – 30,000 μg/L. Equilibrium studies were conducted at the room temperature of 22^0C. In these experiments, the predetermined mass of adsorbent was transferred to 250 mL Erlenmeyer flasks containing 100 mL of the sample, and the flasks with samples were placed on the shaker and shaken at 130 – 175 rpm. After completion of the equilibrium time, samples from each flask were decanted and analyzed for residual arsenic. Data from the equilibrium studies were used to evaluate the coefficients in Langmuir, Freundlich, and Sips equilibriums.

3.3.3 Column studies

Column studies were conducted using IOCSp, IOCS-2, SMZ/ZVI. In the case of IOCSp, experiments were conducted to study the removal of As(III) and As(V) from groundwater and synthetic water. Different dimensions of glass columns were used in the studies. In the column studies using IOCS-2 and SMZ/ZVI, glass columns of 16 mm diameter and 450 mm height were used. In the case of IOCSp, bigger columns (20 mm diameter x 700 mm height, and 45 mm diameter x 940 mm) were used. All column experiments were conducted at the normal pH. A schematic diagram of the column setup is shown in Figure 3.3. The column was packed with a sufficient volume of the adsorbent, ensuring enough headspace to allow for expansion of the media during regeneration and backwashing. The columns were first flushed with distilled (double) deionized water for at least 30 minutes prior to the injection of contaminated water. Samples from the column tests were collected at regular time intervals and analysed for residual arsenic. In the studies using IOCSp and IOCS-2, the media were regenerated with NaOH 0.3M at the end of each cycle, and backwashed with deionized water.

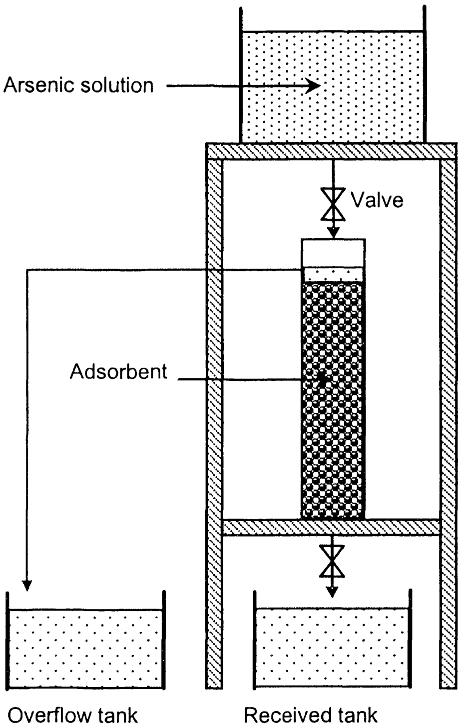


Figure 3.3. Schematic of the column setup

In the case of long term experiments using IOCSp and SMZ/ZVI, the synthetic water with the As(III) or As(V) concentrations of 1,000 µg/L was pumped through the packed columns in the upflow direction using a peristaltic pump (model # 75521 - 47, Cole Parmer Instrument Company) at predetermined flow rates.

3.3.3.1 Column studies with iron oxide-coated sponge (IOCSp)

Iron oxide coated sponge (IOCSp) (prepared through the process described in section 3.2.3.1) was used in the column study to assess its effectiveness and suitability. Column experiments were conducted both with synthetic water and natural groundwater.

a. Synthetic water

Short term and long term column experiments were carried out. Glass columns of 20 mm diameter, 700 mm height and 45 mm diameter, 940 mm height were used in the short term and long term studies respectively.

In the short term experiments, column experiments of only one cycle were conducted to study the removal of arsenic from synthetic water containing an initial concentration of 260 μg/L. The column (20 mm diameter x 700 mm long) was packed with 10 g of IOCSp (which corresponds to a volume of 204 mL). The flow rates through the column were kept at 8 and 15.6 mL/min (which correspond to 1.5 and 3 m/h respectively). This is equivalent to an empty bed contact time (EBCT) between 13 to 26 minutes. Effluent samples were analysed for residual arsenic.

In the long term experiment, synthetic water with higher concentrations of As(III) and As(V) (1,000 μg/L) was pumped through the packed column with a peristaltic pump at a flow rate of 4.5 mL/minute (0.17m/h). The column was packed with 25 g (1,240 mL) of the IOCSp. After 43 days running, the IOCSp was regenerated with 12 L of 0.3M NaOH and backwashed with deionized water until the pH of the effluent was equal to the pH of the influent. Then the columns were run again until the effluent arsenic level reached 300 μg/L.

b. Groundwater

Column tests were also conducted with Kelliher (Canada) and Hanoi (Vietnam) groundwater. Columns of 20 mm diameter, 700 mm height were used in the study with groundwater. The columns were packed with different weight of IOCSp (6 g, 8 g and 10 g). The column tests were conducted in the down-flow mode and with a normal pH of water between 6.7 - 7.6. The water was allowed to flow through the packed column at a filtration velocity from 8 and 15.6 mL/min (which correspond to 1.5 and 3 m/h).

3.3.3.2 Column studies with iron oxide-coated sand (IOCS-2)

A dynamic column study was also conducted using IOCS-2 to compare its performance with that of IOCSp in removing arsenic from synthetic water with an initial As(III) concentration of 260 μg/L. In the first set of experiments, the column (16 mm diameter x 450 mm height) was filled with 90 g of IOCS-2, and synthetic water containing arsenic was pumped through the packed column. The packed volume of IOCS-2 in the column was 57 mL and the flow rate was kept at 15.6 mL/min (4.6 m/h). This yielded an empty bed contact time (EBCT) of 3.65 minutes. The column was run for 129 hours, and samples were collected at regular intervals and analysed for residual arsenic. After that, the media was regenerated with 4 L of 0.3M NaOH and than deionized water until the effluent arsenic reached a level that was less than 10 μg/L. The flow rate during the regeneration operations was also kept at 13.5 mL/min (4 m/h). After regeneration, the column experiment was continued with the same flow rate of 15.6 mL/min.

3.3.3.3 Column studies with SMZ/ZVI

Glass column with 16 mm diameter and 450 mm height was used. Zeolite/ZVI cubes (2.5 cm cube in each dimension) were manually crushed to smaller sized pellets (0.5 cm, the longest dimension) and 68 g of SMZ – ZVI was packed into the column. As(III) and As(V) solutions with concentration 1,000 μg/L were continuously injected into the column in an upward-flow mode and the effluent concentration of As(III) and As(V) were monitored. The flow rate of the column was 4.4 mL/min (1.3 m/h) and it was kept constant throughout the course of the experiment. The column was run until the adsorbent was exhausted.

3.3.4 Tray study with IOCSp

A tray with IOCSp glued on to it was investigated as a continuous adsorption system. Here, the purpose was to provide a large sponge surface area to achieve high arsenic removal.

The laboratory - scale IOCSp tray experimental set-up is shown in Figure 3.4. This system consisted of a synthetic water feeding system and a tray with IOCSp glued on to it. The tray was designed to hold 10 rows of semi circular sponge. Each row of sponge had a length of 19.5 cm, diameter of 3 cm and weight about 1.92 g. The tray (L x W x H = 30 cm x 20 cm x 5 cm) was inclined at an angle of 10^0 to the horizontal to facilitate the water flow over the sponge under gravity. The tray had an influent collection basin, which helped to evenly distribute the water across the cross-section of the tray. In the first experiments with As(III), synthetic water spiked with the As(III) concentration of 145 μg/l was pumped over the tray using a peristaltic pump at a flow rate of 15.6 mL/min. The water at the outlet was sampled for arsenic analysis. After 5 hours of operation, IOCSp was regenerated by 4 L of 0.3M NaOH before running the second cycle with higher influent Arsenic (III) (260 μg/L) in order to study the effect influent concentration.

Similar experiments were conducted with As(V) solution with a determined As(V) concentration of 265 μg/L. In these experiments, the IOCSp was also regenerated with 4 L of 0.3M NaOH solution. In the experiments with As(V) solution, the tray contained only 7 rows of semi circular IOCSp. The angle of inclination of the tray was decreased to 6^0 in order to get a better contact between IOCSp and water when the water passes though each row of IOCSp.

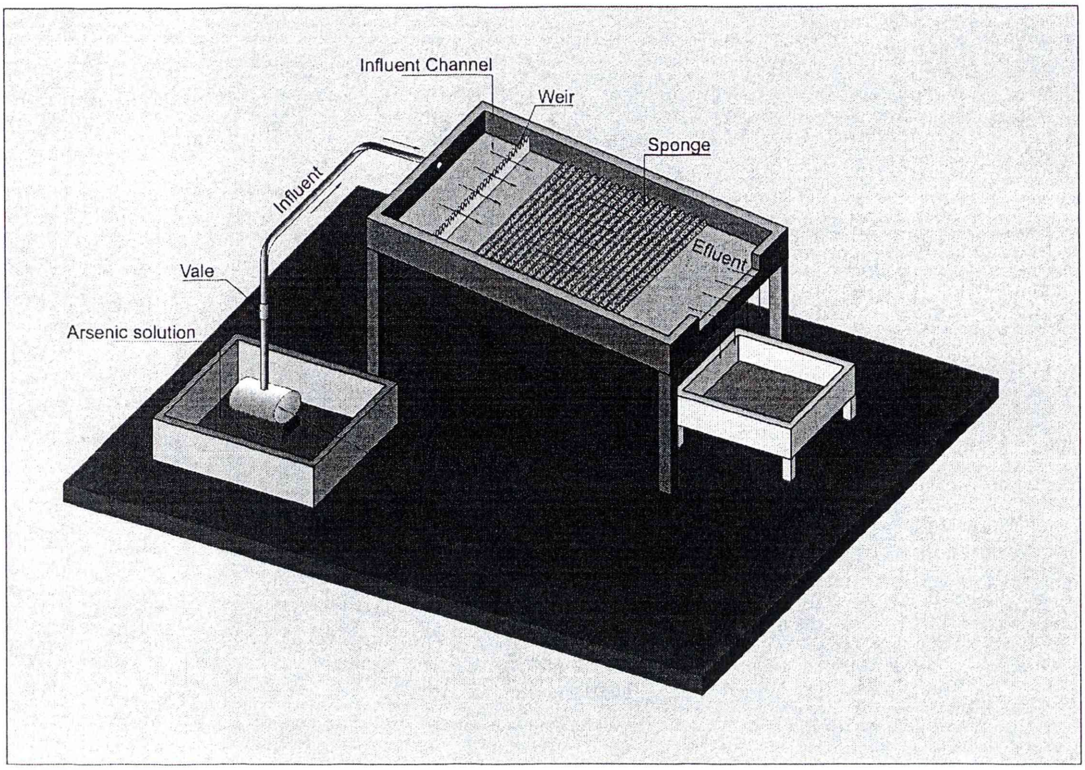


Figure 3.4. Schemetic of the IOCSp tray experiments

3.3.5 Photocatalytic set-up

Photocatalysis experiments were conducted with TiO_2 under UV light to study the efficiency of oxidation of As(III) to As(V).

Photocatalysis experiments were conducted with powdered P25 Degussa TiO_2 particles as a catalyst. The experiments were performed in a UV light. The characteristic of the UV lamp used in the experiment were as follows:

- Lamp current: 11 W, 0.33 A

- UV output (253.7 nm) = 8903 μw.sec/cm^2.

- Size: 38 mm diameter x 278 mm length

The initial concentration of As(III) was varied from 100 to 1,000 μg/L. The concentration of TiO_2 was also varied between 0.01 to 1 g/L. The samples were irradiated for different periods of time (10 to 240 minutes).

Schematic of the photocatalytic reactor is shown in Figure 3.5. The total surface area of the UV lamp was 332 cm^2. The total volume of the reactor was 63 mL. The volume of synthetic water in the feeding tank is 1 Litre. The flow rate of synthetic water through the column was 70 mL/min.

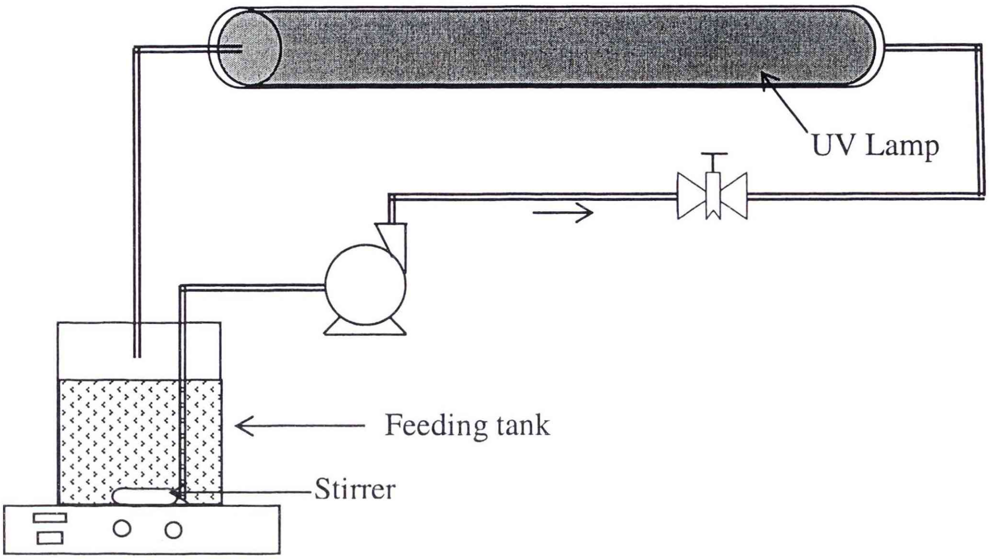


Figure 3.5. Schematic of the photocatalytic reactor

The same experiments were also carried out with the addition of nZVI of different concentration (0.05 to 0.2 g/L) to assess the effect of nZVI.

Finally, the adsorption of As(III) and As(V) on TiO_2 was quantified. Samples containing 100 µg/L, 500 µg/L, and 1,000 µg/L of As(III) and various concentrations of TiO_2 were stirred for 2 hours in a dark condition (without any UV/visible light) and then the samples were filtered and analysed for As(III) and As(V).

3.3.6 Crossflow membrane set-up

The removal efficiency of As(III) and As(V) by membrane filtration was also studied.

The membrane filtration experimental set-up is shown in Figure 3.6. The cross - flow membrane unit (Nitto Denko Corp.) was used to study the effect of different membranes on arsenic removal with and without in line addition of nZVI. The synthetic water (with an arsenic concentration of 500 µg/L) was pumped to a flat sheet membrane module with an effective membrane area of 0.006 m^2. The operating pressure and cross - flow velocity were controlled at 10 - 250 kPa by means of by-pass and regulating valves. New membranes were used in each experiment to avoid the effect of residual nZVI on membrane filtration and to compare the results obtained under different membrane operating conditions. Synthetic water, with and without adding nanoscale zero valent iron, was pumped into a flat sheet membrane module.

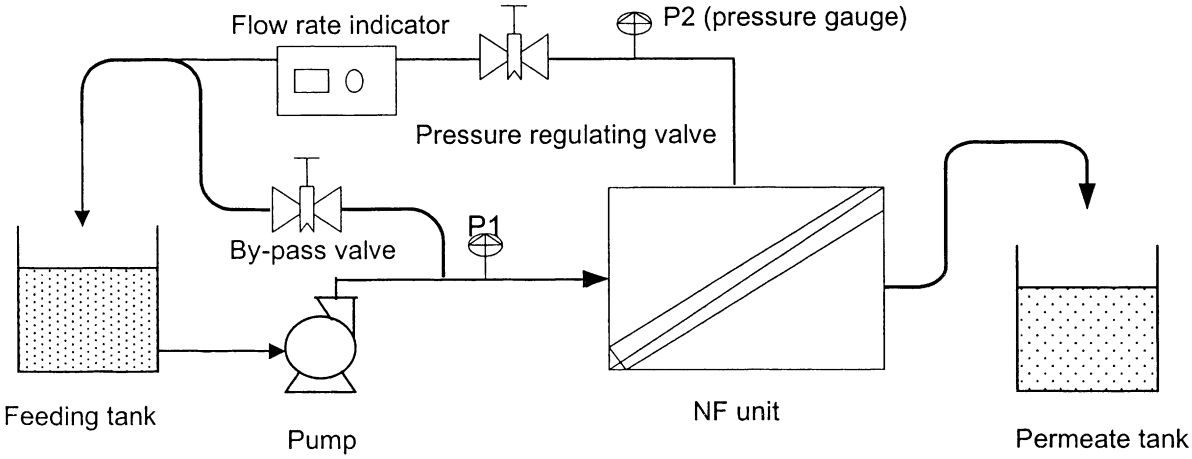


Figure 3.6. Schematic of the cross-flow unit

3.4 Analytical methods

3.4.1 Arsenic analysis

All samples were acidified with 0.3% $HN0_3$ (trace metal grade), and analysed for arsenic using a hydride generation atomic absorption spectrometry (HGAAS), model AAS 932 Plus and HGGBC 3000 and Varian type Spectr AA-600 Zeeman GFAAS equipped with a GTA 100-graphite tube atomizer. An arsenic hallow cathode lamp with an emitting wavelength of 193.7 nm was used. An external reference standard from the National Measurement Institute, Australia was used to verify the calibration.

To determine the arsenic species (As(III) and As(V)) in photocatalysis experiments, an anion-exchange cartridge method was used. The cation and anion-exchange cartridge retained organically complexed As and As(V) whereas As(III) was unretained. Retained As(V) was eluted with 1 M HCl to separate it from organically complexed As.

3.4.2 Iron content and surface area

The weight of iron oxide coated on sponge and sand (as dry weight) was calculated on a regular basis. Both coated and uncoated sponge were dried in an oven at 100°C for 24 hours and desiccated prior to the measurement of the total amount of coated iron oxide.

Morphological analysis of the IOCSp before and after the adsorption of arsenic was performed by field emission scanning electron microscopy (FE-SEM) using a Hitachi 4700 microscope (at 15 kV) with energy-dispersive X-ray (EDX) analyses.

University of Technology, Sydney

Faculty of Engineering

CHAPTER 4

ARSENIC REMOVAL BY IRON OXIDE COATED SPONGE

Chapter 4 Arsenic removal by iron oxide coated sponge

4.1 Introduction

Sponge is seen to be a promising material for adsorption because of the following characteristics. Sponge is non-toxic and has high internal porosity and specific surface that facilitate arsenic absorption. In addition, sponge can be easily compacted to a very small volume to facilitate disposal. Importantly, sponge is cost effective so it can be applied in small rural communities as well as in developing countries. To achieve high arsenic adsorption, sponge should be coated with metal oxide. After adsorption of arsenic onto a sponge matrix, the sponge can be directly disposed of or regenerated with chemical solutions. Therefore, polyurethane sponge was selected as the absorbent carrier in this study.

The main objectives of this chapter are to:

(1) Optimize the coating of iron oxide onto sponge, and

(2) Evaluate the adsorption capability of the new material (iron oxide coated sponge) in removing arsenic. The adsorption equilibrium and kinetics of the batch and dynamic columns, and tray systems are discussed.

The sponge which was used in this study is one kind of normal commercial polyurethane sponge. The dry density of polyurethane sponge is 28 kg/m^3, average pore area is 0.7 mm^2.

4.2 Capacity of uncoated sponge in removing arsenic

Firstly, the sponge was tested without any chemical coating to evaluate the arsenic removal efficiency of the sponge itself. The experimental results showed that uncoated sponge did not remove arsenic in any significant amount. The results from the batch adsorption study with the uncoated sponge showed only 10% arsenic removal where 0.18 g of uncoated sponge was soaked in 100 mL arsenic solution of

530 µg/L for 96 hours. This result was similar to the one of forager sponge (EPA, 1995).

4.3 Optimisation of preparation conditions of iron oxide coated sponge (IOCSp)

As discussed in Chapter 3, the experiments were conducted at various operating conditions of (i) pH value of coating solution (pH from 1, 2 ... to 12); (ii) time (t_1) of contact between iron oxide and the sponge (5, 10, 15, 20, 30 minutes and up to 15 hours); (iii) coating temperature T^0C (25°C, 75°C, 110°C, 220°C); and (iv) time (t_2) of drying of sponge after the coating (8, 12, 14, 18, 20 and up to 34 hours) to find the optimum condition for coating of iron oxide on sponge.

4.3.1 Effect of pH on coating

Experimental results showed that sponge could not be coated well at a pH above 5. The batch adsorption experiments conducted with the iron oxide coated sponge at pH of 1 to 4 showed that arsenic adsorption in this range improved with the increase of pH but this increase did not vary much (Table 4.1). As a result, pH of 4 was chosen in the subsequent experiments as it is the most closet to neutral conditions.

Table 4.1. Effect of IOCSp prepared at different pH in adsorbing As
(t_1 = 5 hours, T = 110^0C, t_2 = 18 hours, influent As(III) concentration = 500 µg/L, mass of sponge = 0.174 g, contact time of As solution with IOCSp = 4 hours, volume of As solution = 200 mL)

No	pH	Effluent As concentration (µg/L)
1	1	260
2	2.1	246
3	3	235
4	4	230
5	5 and above	Sponge was uncoated

4.3.2 Effect of contact time (t_1) and coating temperature (T)

Experimental results showed that sponge could not be coated in an adequate manner when the soaking time (t_1) was less than 1 hour. Results from batch adsorption experiments with iron oxide coated sponge showed that the increase of contact time from 1 hour to 10 hours (during the coating process) led to an increase in the arsenic removal by about 20%. However, there was only a marginal improvement in arsenic removal capacity when the contact time was increased beyond 10 hours (Table 4.2). Consequently, the contact time of 10 hours was used in the subsequent experiments.

Table 4.2. Effect of IOCSp prepared at different contact times in adsorbing As (pH = 4, T = 110^0C, t_2 = 18 hours, influent As(III) concentration = 500 μg/L, mass of sponge = 0.174 g, contact time of As solution with IOCSp = 4 hours, volume of As solution = 200 mL)

No	Contact time (hours)	Effluent As concentration (μg/L)
1	1	296
2	5	232
3	10	205
4	15	202

The experiments also showed that the sponge was coated well at a temperature of 110^0C but was damaged at a temperature of 220^0C and above and was uncoated at a temperature of 75^0C and below.

4.3.3 Effect of drying time (t_2)

Table 4.3 shows that when the drying time (t_2) was increased from 8 to 20 hours, the adsorption of arsenic improved but when t_2 was increased up to 34 hours, the sponge became damaged. Therefore, a drying time of 20 hours was used in the subsequent experiments.

Table 4.3. Effect of IOCSp prepared at different drying time in adsorbing As (pH = 4, T = 110^0C, t_1 = 10 hours, influent As(III) concentration = 500 μg/L, mass of sponge = 0.272 g, contact time of As solution with IOCSp = 90 hours, volume of As solution = 200 mL)

No	Drying time (h)	Effluent As concentration (μg/L)
1	8	7
2	12	3
3	18	1
4	20	Not detectable
5	34	Sponge was damaged

From these detailed studies, the following coating conditions were chosen as suitable and practical for coating the sponge with iron oxide: pH = 4, t_1 = 10 hours, T^0 = 110^0C and t_2 = 20 hours.

4.4 Properties of the adsorbent

The mass of iron oxide coated on sponge (as dry mass) was calculated on a regular basis. Both coated and uncoated sponges were dried in an oven at 100°C for 24 hours and desiccated prior to the measurement of the total amount of coated iron oxide.

It was difficult to assess the homogeneity of iron oxide coating on the sponge. However, preliminary experiments conducted with different sizes of IOCSp (0.5 – 2 cm) showed that a uniform amount of iron per volume of sponge. As such, one could assume a uniform coating. The weight measurement showed that 12% weight of IOCSp was iron oxide. An experimental study with the specific surface area (S_{BET}) of IOCSp was made to study the characteristic of IOCSp. The results were difficult to interpret due to the sample size. However, a previous study (Moe and Irvine, 2000) showed that the surface area of sponge was 620 m^2/m^3.

4.5 Removal mechanism of arsenic

The colour of iron oxide on the sponge was brown. Therefore, it may be assumed that the iron oxide on the sponge was probably a combination of goethite and haematite.

In this research study, the possible reactions that lead to the formation of both goethite ($\alpha FeOOH$) and haematite (α-Fe_20_3) in the preparation of IOCSp may be thought of as follows:

$$2\ Fe(N0_3)_3.9H_20 + 2H_20 \rightarrow 2Fe + 6\ HN0_3 + 17\ H_20 + 1.5\ O_2 \quad (18)$$

$$2\ Fe + 6\ HN0_3 + 17\ H_20 + 1.5\ 0_2 + 4\ NaOH \rightarrow 2\ Fe(OH)_2 + 2\ HN0_3 + 4\ NaN0_3 + 19\ H_20 + 0.5\ O_2 \quad (19)$$

$$2\ Fe(OH)_2 + 2\ HN0_3 + 4\ NaN0_3 + 19\ H_20 + 0.5\ O_2 \xrightarrow[\text{dehydroxylation}]{\text{dehydration}}$$

$$\alpha\text{-}Fe_20_3 + 2\ HN0_3 + 21\ H_20 + 4\ NaNO_3 \quad (20)$$

or

$$\alpha\text{-}FeOOH + 2\ HNO_3 + 20\ H_20 + 4\ NaN0_3 \quad (21)$$

As(V) and As(III) get adsorbed at the oxyhydroxide surfaces by forming complexes with the surface sites (Edwards, 1994). Specific adsorption involves direct coordination of the adsorbate in solution to the surface metal atom of the solid. The reactions between arsenite, arsenate and goethite and haematite may be represented as follows:

$$\alpha\text{-}FeOOH + H_2AsO_4^- + 3\ H^+ \rightarrow FeH_2AsO_4 + 2\ H_20 \quad (22)$$

$$\alpha\text{-}FeOOH + H_3AsO_3 + 2\ H^+ \rightarrow FeH_2AsO_3 + 2\ H_20 \quad (23)$$

4.6 Batch adsorption experiments

4.6.1 Effect of pH

The results showed that the arsenic removal efficiency of IOCSp did not depend on the pH, even when the pH of the solution was very low or high. This finding is different from earlier studies which showed the dependence on the pH of iron oxide coated sand or amorphous ferric hydroxide (Pierce and Moore, 1980; Wilkie and Hering, 1996). They noted that the adsorption of As(III) increased as the pH increased. Present results showed that even an effluent arsenic concentration of less than 22 μg/L could be achieved at low pH of 2 and a high pH of 10.2 from an arsenic solution of 1,000 μg/L. In the experiments, 0.5 g of IOCSp was soaked into an arsenic solution of 100 mL.

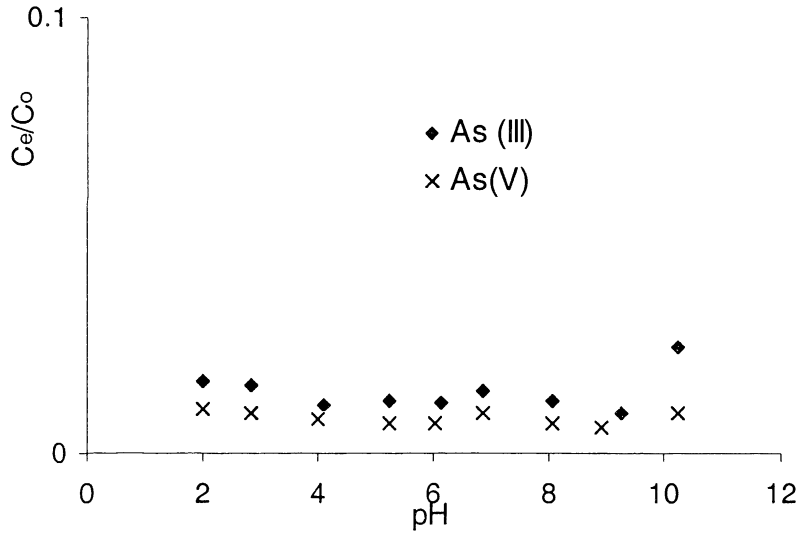


Figure 4.1. Removal efficiency of arsenic as a function of pH (Initial arsenic concentration = 1,000 μg/L; weight of IOCSp = 0.5 g, temperature = 22 ^{0}C, volume of arsenic solution = 100 mL)

4.6.2 Adsorption kinetics

The IOCSp adsorption capacity with time was investigated in adsorption kinetics experiments. The adsorption kinetics of IOCSp was evaluated at concentrations of 260 μg/L. The results of IOCSp adsorption kinetics of As(III) and As(V) are presented in Figures 4.2 to 4.3. Arsenic in the synthetic water was quickly adsorbed within the first 4 hours and then the arsenic adsorption rate by IOCSp increased slightly. The results show that IOCSp could remove 47.3% to 65% of As(III) and As(V) within a 1 hour of contact with IOCSp. After four hours, 81.4% to 88.7% of As(III) and As(V) were adsorbed. A nine hour - adsorption led to a very high amount of arsenic adsorption with 92.4 % to 96% of As(III) and As(V) respectively (less than 20 µg/L of As remaining in the water). In these experiments, 0.15 g of IOCSp was placed in a flask containing 100 mL of As solution. The results show that there were not much difference in removal efficiency between As(III) and As(V) as well as at different values of pH (6 to 8).

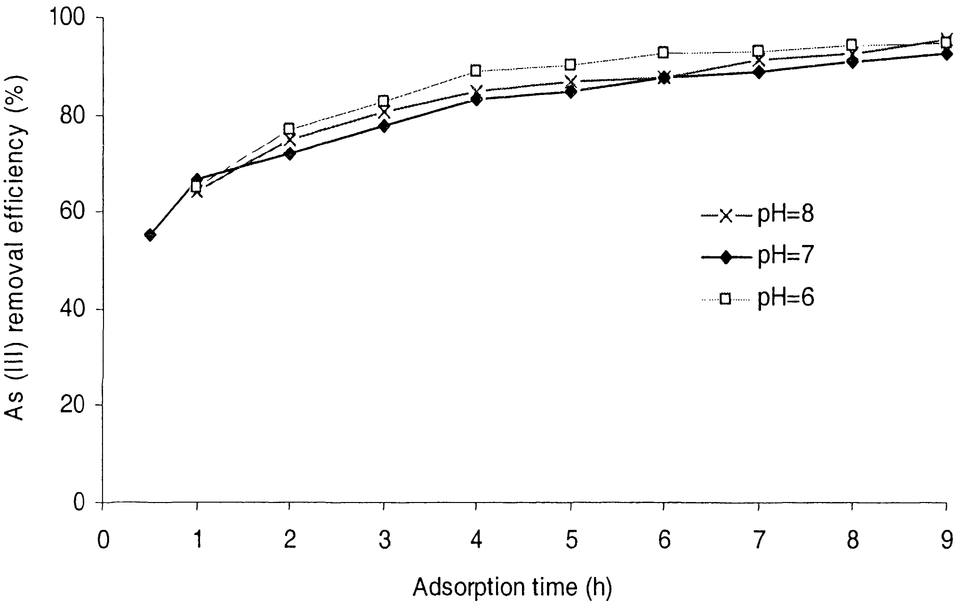


Figure 4.2. Removal efficiency of As(III) as a function of adsorption time (Initial As(III) concentration = 260 µg/L; weight of IOCSp = 0.15 g, volume of As solution = 100 mL, mixing rate = 175 rpm, temperature = 22^0C)

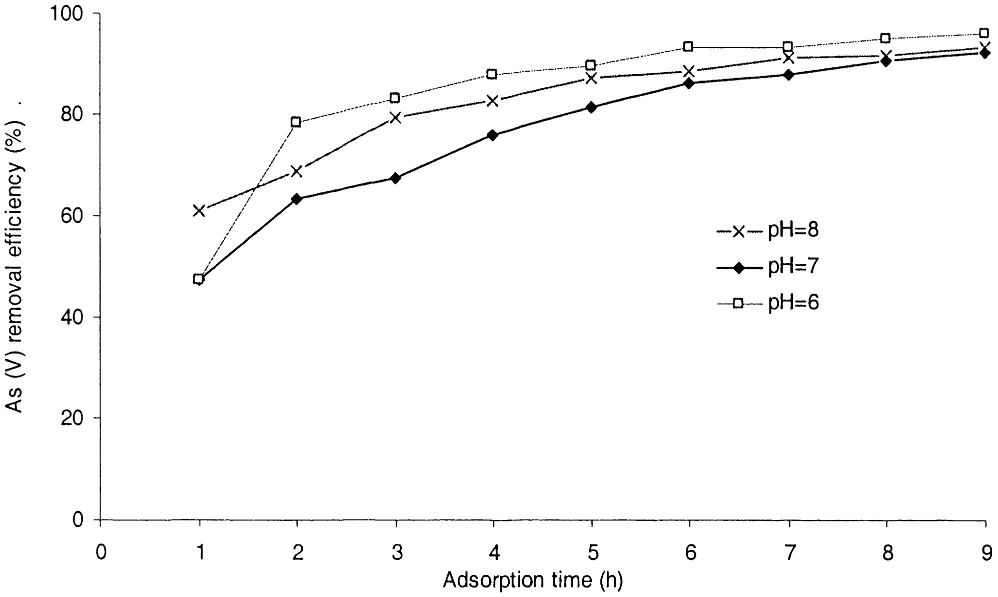


Figure 4.3. Removal efficiency of As(V) as a function of adsorption time (Initial As(V) concentration = 260 μg/L; weight of IOCSp = 0.15 g, volume of As solution = 100 mL, mixing rate = 175 rpm, temperature = 22^0C)

The detailed results of the kinetics of arsenic removal (for both As(III) and As(V)) are shown in Appendix B (Tables B1 to B2).

Kinetic adsorption of IOCSp with arsenic can be described by the Ho model. Ho model is a pseudo second order reaction rate model (Ho et al., 1996). With the q and K_H given in Table 4.4, the kinetic adsorption data of IOCSp with synthetic water was reasonable fitted to the Ho model (Figures 4.4 and 4.5).

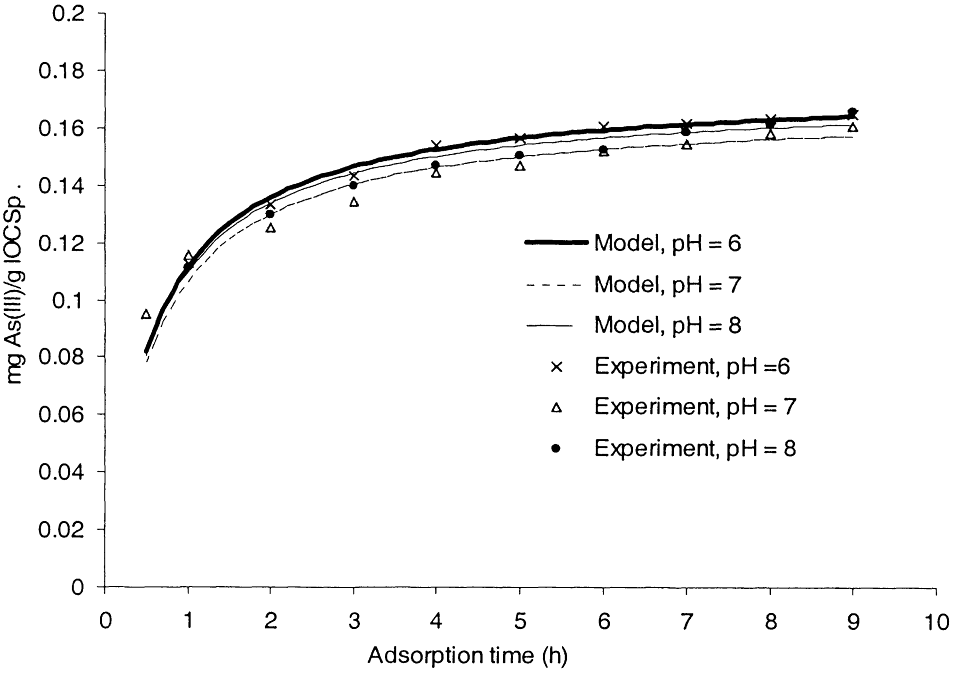


Figure 4.4. Prediction of adsorption kinetics of IOCSp with As(III) by the Ho model (Initial As(III) concentration = 260 μg/L; weight of IOCSp = 0.15 g, volume of As solution = 100 mL, mixing rate = 175 rpm, temperature = 22^0C)

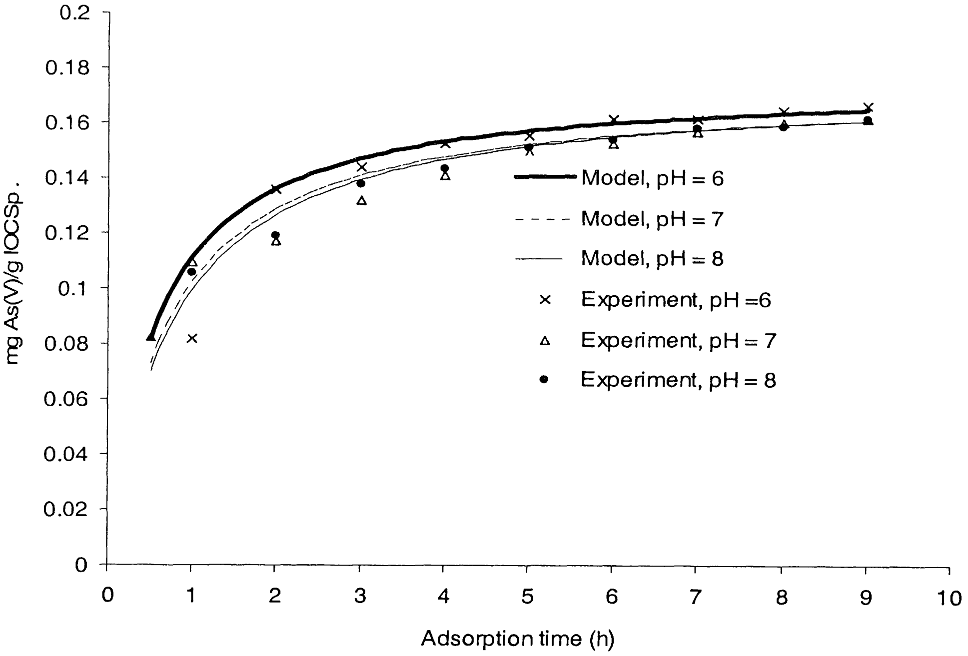


Figure 4.5. Prediction of adsorption kinetics of IOCSp with As(V) by the Ho model (Initial As(V) concentration = 260 μg/L; weight of IOCSp = 0.15 g, volume of As solution = 100 mL, mixing rate = 175 rpm, temperature = 22^0C)

Table 4.4. Kinetics adsorption parameters of Ho model for IOCSp adsorption

Arsenic species	pH	q	K_H	Equation	Correlation coefficient (r)
As(III)	6	0.174	5.13	$q_t = 0.311\ t/(1+1.79t)$	0.991
	7	0.167	5.26	$q_t = 0.293\ t/(1+1.76t)$	0.919
	8	0.171	5.25	$q_t = 0.307\ t/(1+1.8t)$	0.965
As(V)	6	0.175	5.01	$q_t = 0.307\ t/(1+1.75t)$	0.970
	7	0.173	4.22	$q_t = 0.253\ t/(1+1.46t)$	0.912
	8	0.174	3.85	$q_t = 0.233\ t/(1+1.34t)$	0.967

The correlation coefficient (r) for the modeled plots at all the pH level studied were more than 0.912, representing a good correlation of the observed data, and Ho model was found to provide a realistic description of the adsorption kinetics of arsenic.

4.6.3 Equilibrium adsorption experiments

Equilibrium adsorption studies were conducted at the normal pH level of 7 for the removal of both As(III) and As(V) (from synthetic water spiked with arsenic concentration of about 5,500 μg/L). Equilibrium experiments were conducted at a room temperature of 22^{O}C. In these experiments, different amounts of adsorbent (0.018 g to 1.296 g) was placed into 250 mL Erlenmeyer flasks containing 100 mL of the arsenic sample, and the samples were placed on the shaker and shaken at 130 rpm for 20 hours. After 20 hours of contact time, samples from each flask were decanted and analyzed for the residual arsenic in the solution.

The equilibrium results were than fitted with Langmuir, Freundlich, and Sips isotherm equations. The adsorption curves predicted by all of these models reasonable fitted with the observed values. The predicted and the experimental concentrations of remaining As(III) and As(V) are shown in Figures 4.6 and 4.7. The model equations and the isotherm parameters are shown in Table 4.5.

Table 4.5. Isotherm equations for arsenic removal using IOCSp

Parameters		Arsenic species	
		As(III)	As(V)
Langmuir	q_m	3.85	4.5
	b	0.95	0.7
	r	0.966	0.974
	Equation	$q_e = 3.66\ C$ $/ (1 + 0.95\ C)$	$q_e = 3.15\ C$ $/ (1 + 0.7\ C)$
Freudlich	k_F	1.97	1.9
	n	3.5	2.8
	r	0.985	0.990
	Equation	$q_e = 1.97\ C^{0.29}$	$q_e = 1.9\ C^{0.36}$
Sips	q_m	4.18	4.6
	b	0.91	0.74
	n	1.27	1.22
	r	0.965	0.972
	Equation	$q_e = 4.18\ (0.91\ C)^{0.79}$ $/ (1 + (0.91\ C)^{0.79})$	$q_e = 4.6\ (0.74\ C)^{0.82}$ $/ (1 + (0.74\ C)^{0.82})$

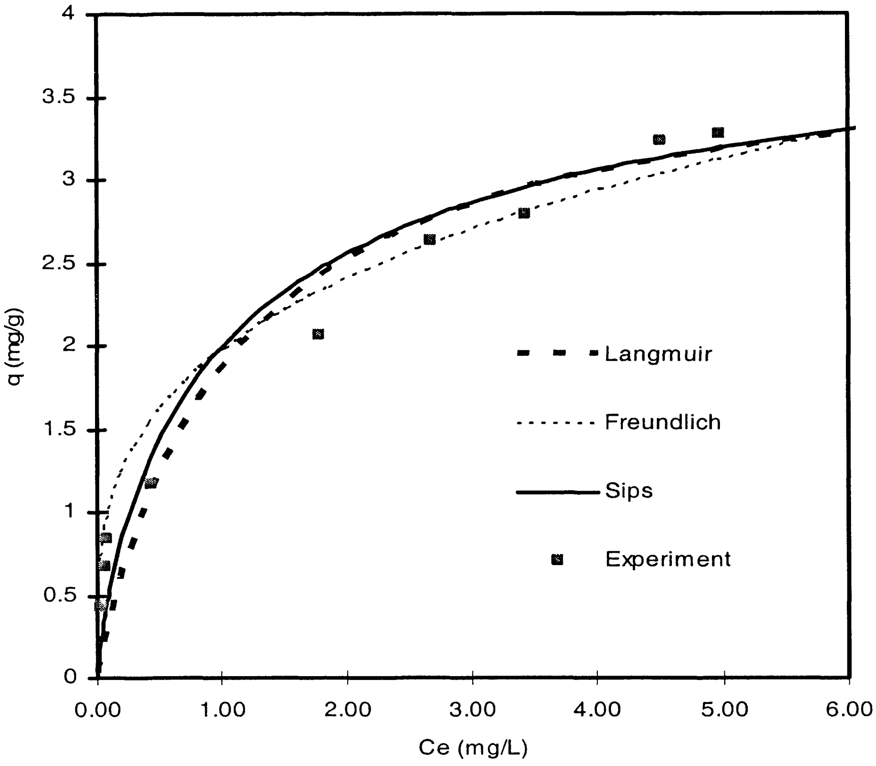


Figure 4.6. Prediction of equilibrium adsorption of As(III) by different adsorption models (contact time =20 hours, mixing rate = 130 rpm, temperature = 22^{0}C)

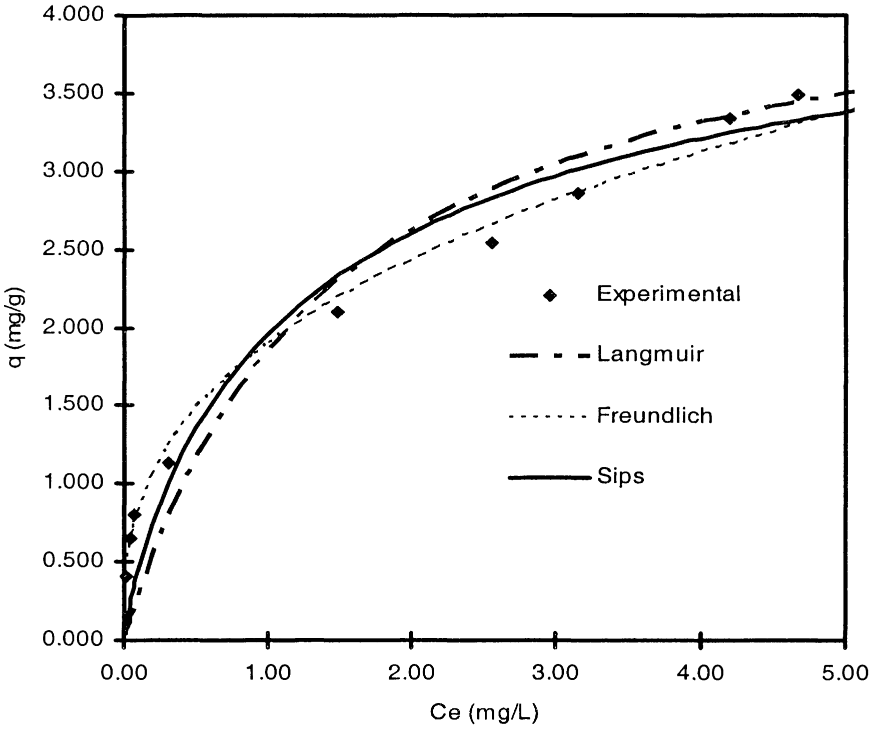


Figure 4.7. Prediction of equilibrium adsorption of As(V) by different adsorption models (contact time = 20 hours, mixing rate = 130 rpm, temperature = 22^{0}C)

It can be seen that the Langmuir and Sips models yielded the same values for arsenic adsorption capacity (q_m). The values were 3.85 – 4.18 mg As(III) / g IOCSp and 4.5 - 4.6 mg/g IOCSp respectively. The values of constant b for both models were almost same. It was in the range of 0.91 – 0.95 for As(III) and 0.7 - 0.74 for As(V). As a result, equilibrium adsorption curves of these models were almost the same (Figures 4.6 and 4.7). This prediction shows that there is not much difference between these two models in describing the adsorption of a single component system. In this study, the value of the adsorption capacity of IOCSp (q_m) is much higher than that with the other adsorbents (Table 4.6). This indicates that IOCSp has a superior arsenic adsorption capacity.

Table 4.6. Comparison of arsenic adsorption capacity of IOCSp with other adsorbents

Name of adsorbent	Adsorption capacity (mg/g)	References
Iron oxide coated sand	0.029	Gupta et al. (2005)
Granular ferric hydroxide	0.11	Thirunavukkarasu et al., (2003a)
Activated alumina	0.180	Singh and Pant (2004)
Red mud	0.66	Altudogan et al. (2000)
Ferruginous manganese ore	0.680	Chakravarty et al. (2002)
Iron oxide impregnated activated alumina	0.734	Kuriakose et al. (2004)
Activated red mud	0.87	Altudogan et al. (2002)
Nanoscale zero valent iron	3.5	Kanel et al. (2005)
Iron oxide coated sponge	*3.85 – 4.6*	

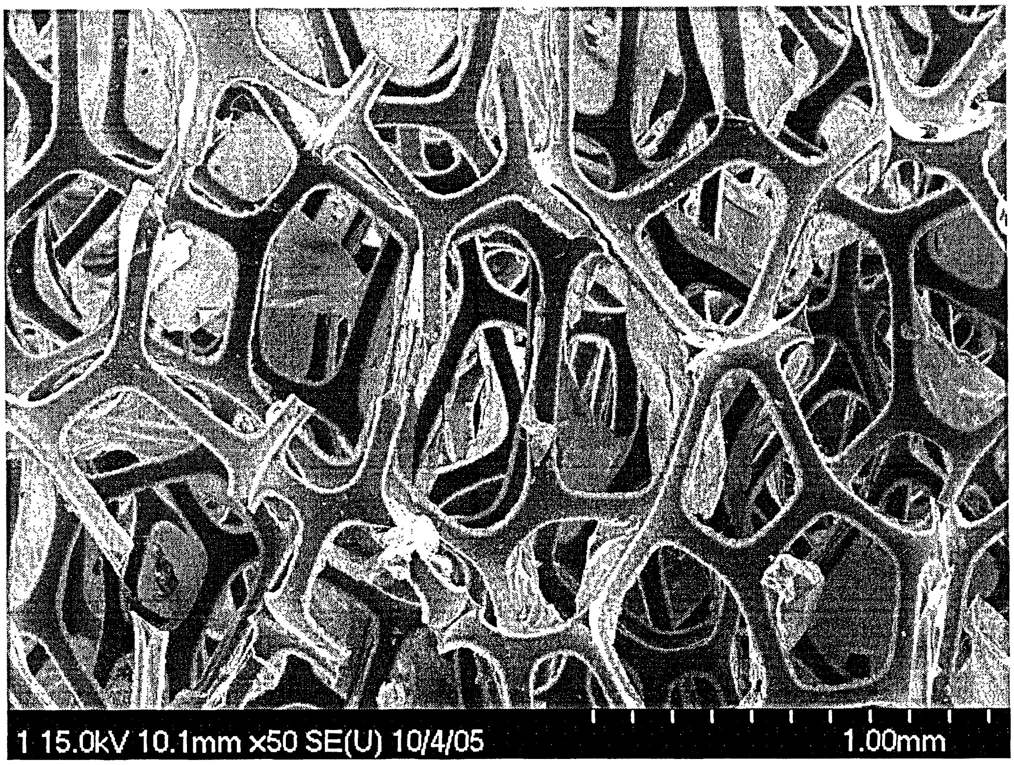
The low value of 1/n (< 0.36) in the Freundlich isotherm suggests that any large change in the equilibrium concentration of soluble arsenic would not result in a change in the amount of arsenic sorbed by the IOCSp.

The correlation coefficient (r) for all the isotherms ranged from 0.965 to 0.99, representing a good fit of the observed data.

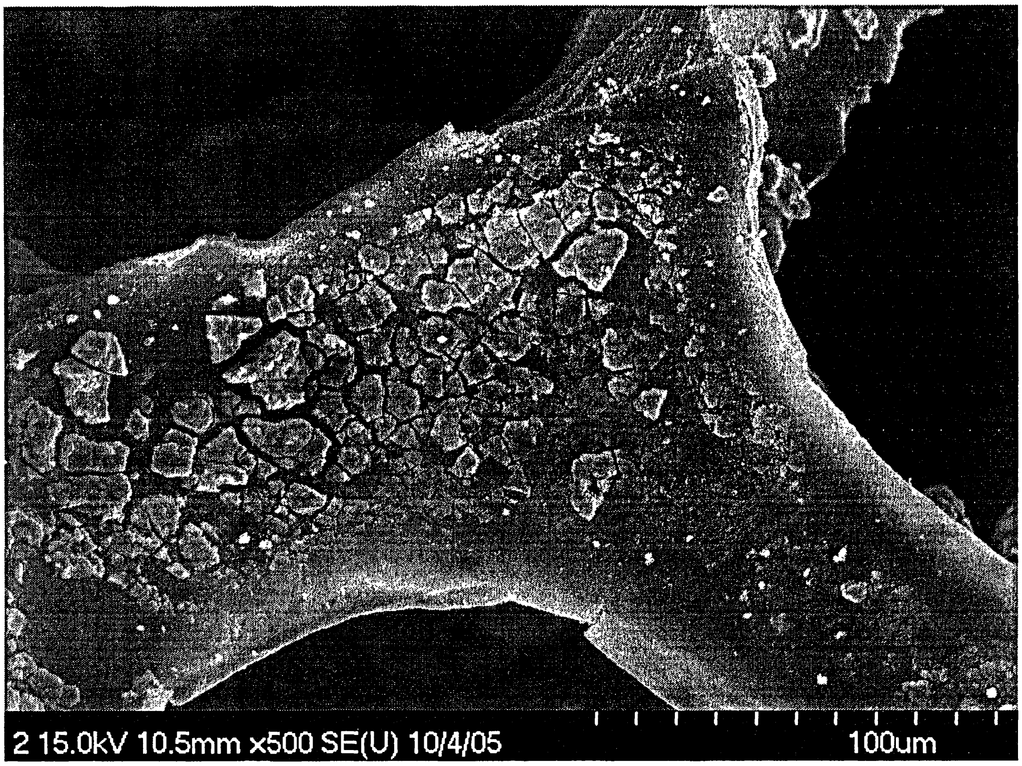
The results of the equilibrium experiments for the removal of both As(III) and As(V) using IOCS are shown in Appendix B (Tables B3 to B4).

4.7 Field emission scanning electron microscopy (FE-SEM) results

The FE-SEM analyses of blank sponge, iron oxide coated sponge before and after adsorption with arsenic were carried out to estimate the pore area and surface of sponge and IOCSp (Figure 4.8). The pore area of sponge was in the range of 0.1 to 0.5 mm^2. The size of iron particles attached onto the sponge was in the size range of 3 to 22 μm (Figure 4.8(b)) as measured by SEM. Adsorption of As caused increases in particle aggregation (Figures 4.8(c) and 4.8(d)).

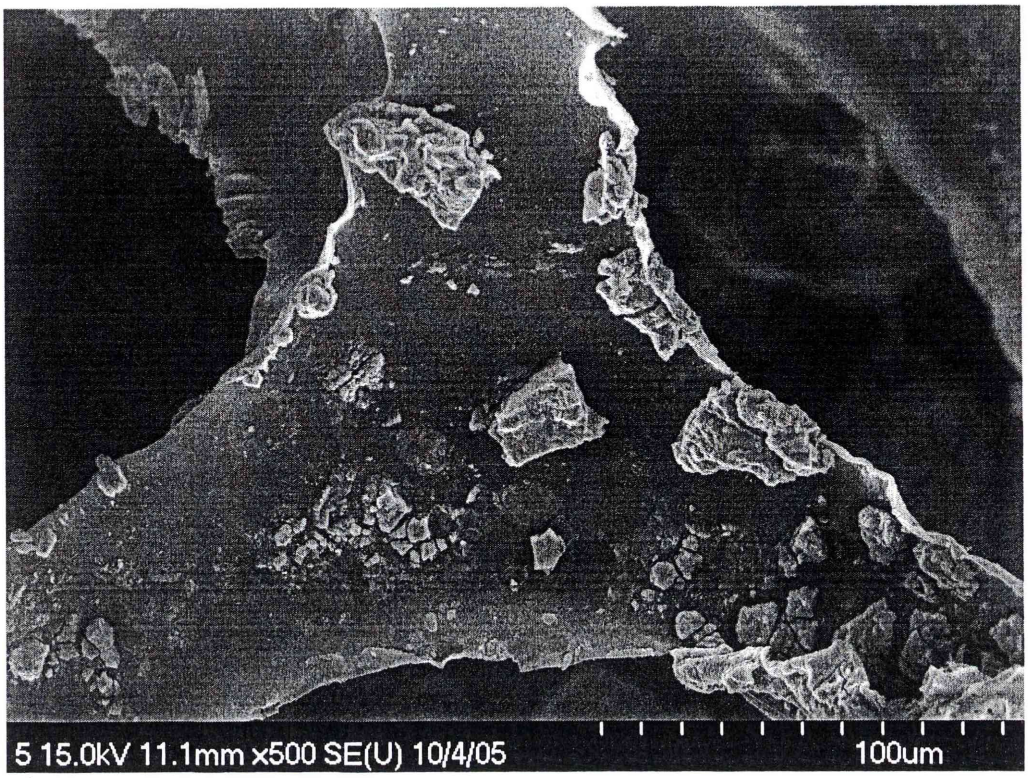


(a). SEM of blank sponge

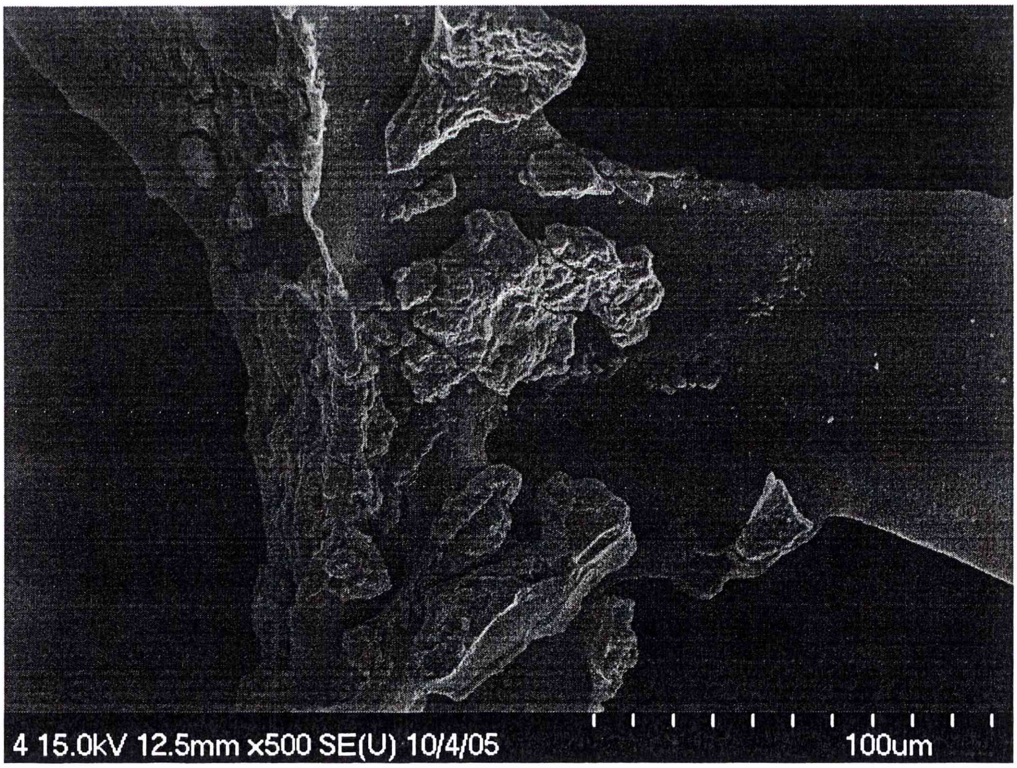


(b). SEM of iron oxide coated sponge

Figure 4.8. SEM of IOCSP before and after adsorption with arsenic



(c). SEM of As(III) absorbed iron oxide coated sponge



(d). SEM of As(V) absorbed iron oxide coated sponge

Figure 4.8. SEM of IOCSp before and after adsorption with arsenic

4.8 IOCSp column experiments

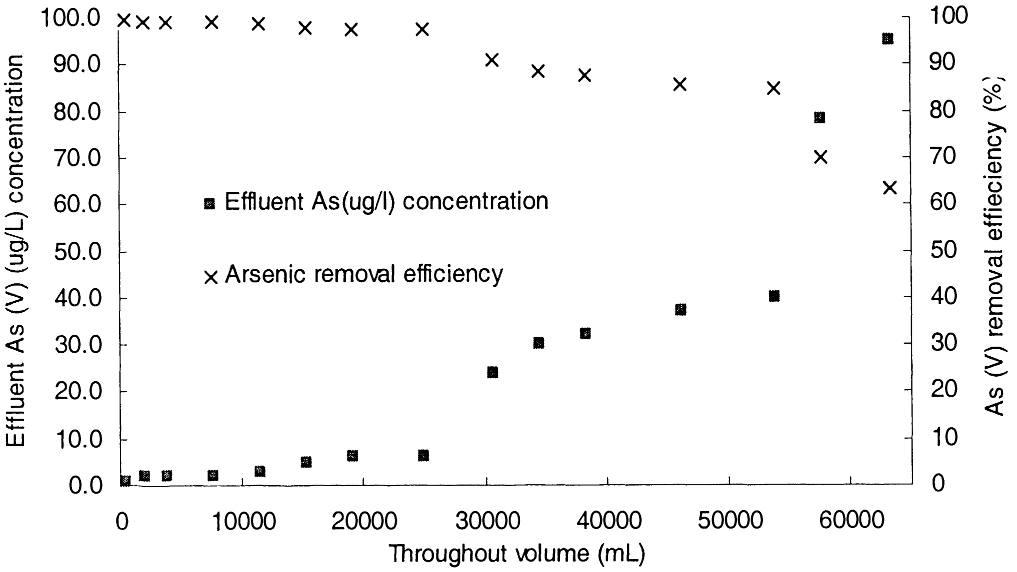
Following the favourable batch adsorption results of arsenic by IOCSp, a series of dynamic column experiments were conducted with filter columns packed with IOCSp. Both synthetic water and groundwater containing arsenic were used in this study.

4.8.1 Synthetic water

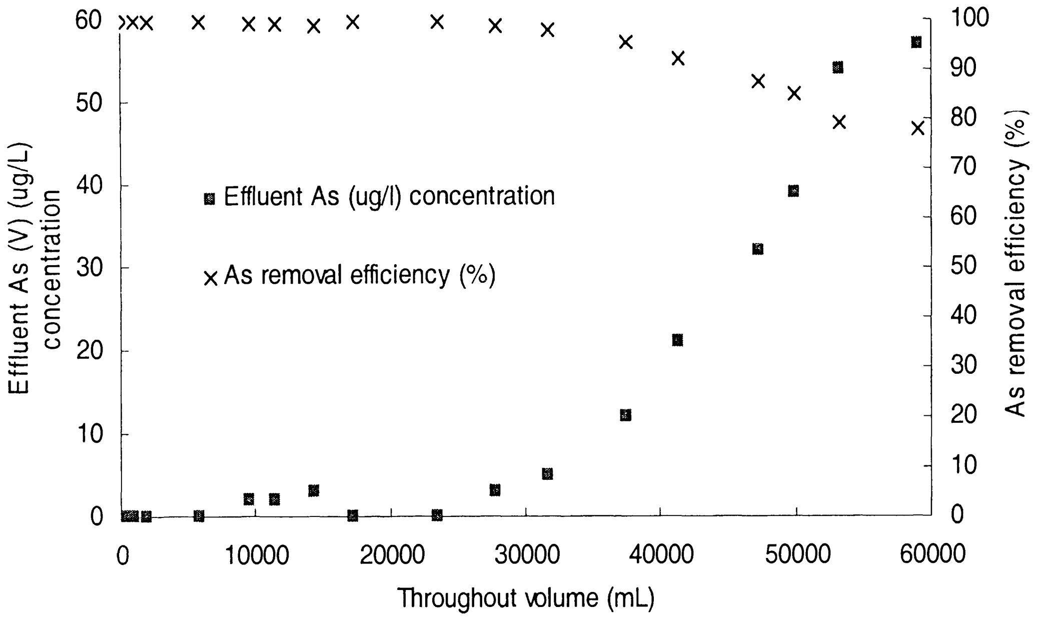
4.8.1.1 Short term experiment

In this study, the adsorption column experiments were conducted with throughput (filtration) rates of 1.5 m/h and 3 m/h. The filtration rate was kept constant during the experimental run using a constant head tank. The IOCSp medium of 0.5 cm in size length, width and height was used.

The results on the removal of arsenic from synthetic water using IOCSp column system are presented in Figure 4.9. For both filtration rates (1.5 and 3 m/h) employed in this study, the columns could be operated for a long time with an effluent As concentration of less than 50 μg/L of As(V). The number of bed volumes achieved was about 260 (which correspond to a throughput volume of more than 50 L). Here, the bed volume is defined as a ratio of throughput volume run through the reactor to volume of the reactor.



(a). Q = 1.5 m/h



(b). Q = 3 m/h

Figure 4.9. Removal of arsenate from synthetic water by IOCSp column (short term) (Initial As(V) concentration = 260 μg/L; weight of IOCSp = 10 g)

The results also showed that the effluent quality became inferior with the increase in filtration rates. However, the differences between the removal efficiencies at the two flow rates were not significant during the initial stage (Figure 4.10).

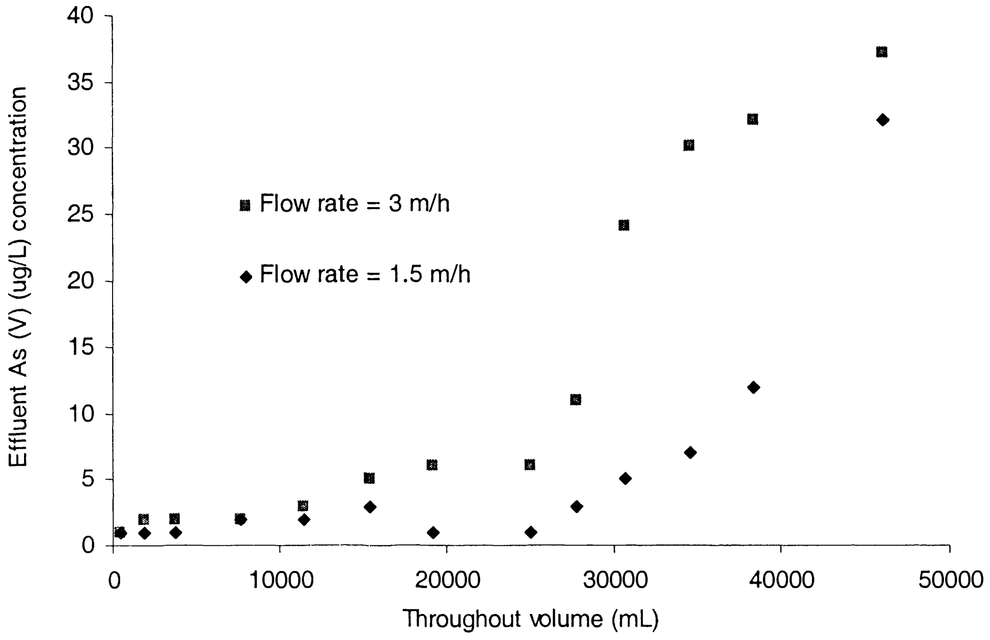


Figure 4.10. Effect of filtration rate on As(V) removal by IOCSp column (Initial As(V) concentration = 260 μg/L; weight of IOCSp = 10 g)

4.8.1.2 Long term performance of IOCSp with synthetic water

Larger columns with a diameter of 45 mm, and a height of 940 mm were used in the long term experiments. Each adsorption column was packed with 25 g IOCSp. The throughput (filtration) rate was maintained at 0.17 m/h. The results on the removal of arsenic from synthetic water are presented in Figure 4.11.

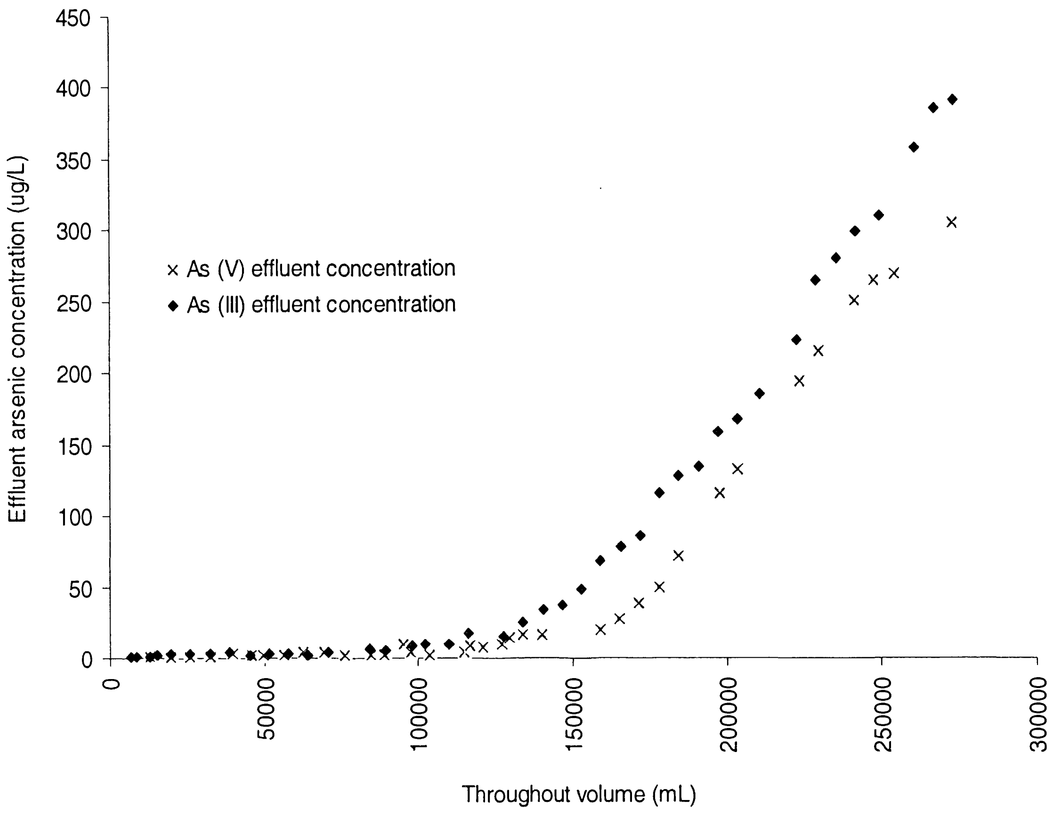


Figure 4.11. Removal of As from synthetic water by IOCSp column (long term) (Initial As concentration = 1,000 μg/L; weight of IOCSp = 25 g)

The columns could be operated for a long time with an effluent arsenic concentration of less than 50 μg/L even with a small volume of IOCSp of 25 g. The throughput volume of As(V) and As(III) was approximately 178 L and 153 L respectively (which correspond to bed volumes of 144 with As(V) and 123 with As(III)).

The results of the column studies showed that the bed column performed by IOCSp was smaller than that of iron oxide coated sand (IOCS) reported earlier by Joshi and Chaudhuri (1996). However, the density of IOCSp is much lower than that of IOCS. Thus, in term of the weight of adsorbent, the performance of IOCSp was much better than IOCS

Analysis of effluent samples collected during the column test experiment showed that the iron concentrations ranged between 0.03 – 0.1 mg/L, and were nearly the same as the concentrations in the influent. The weight measurements of IOCSp that was collected from the column after completion of long term experiments showed that the weight of IOCSp after experiments was also equal to the initial IOCSp's weight. Based on the calculation of weight of iron oxide coated on sponge (3 g) and the amount of arsenic adsorbed on sponge (about 0.25 g), it can be defined that about 8% was lost during the experiment and approximately 92% of the iron oxide coated on the sponge was firmly attached onto it.

4.8.1.3 Effect of regeneration on arsenic removal efficiency

After 43 days running with throughput volume of 280 Litre, IOCSp in the column was regenerated by 0.3M NaOH with flow rate of 4 mL/min (0.15 m/h) until the arsenic concentrations in the effluent were below 50 μg/L. The volume of NaOH needed for the regeneration was 12 Litre. The column was then washed again with DI water until the pH of the effluent was equal to the pH of the influent. After washing with DI water, the column was run again with the same flow rate of 4.4 mL/min (0.17 m/h). The results on the removal of arsenic from the regenerated column are presented in Figures 4.12 and 4.13.

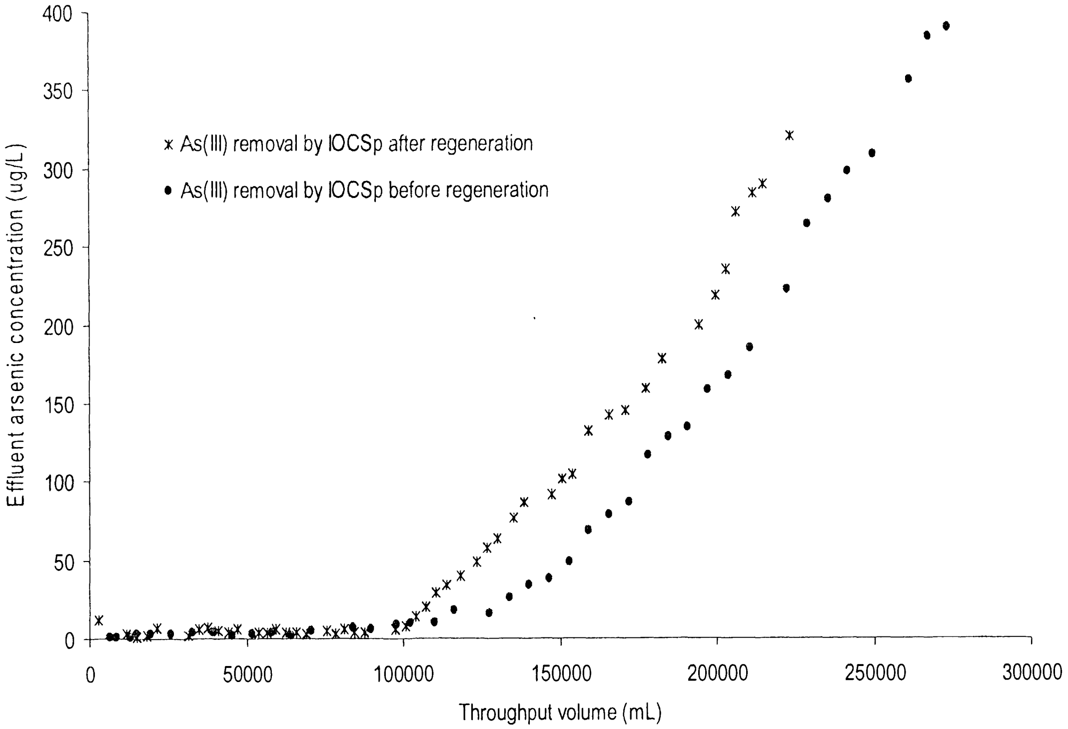


Figure 4.12. Removal of As(III) from synthetic water by regenerated IOCSp column (Initial As concentration = 1,000 μg/L; weight of IOCSp = 25 g)

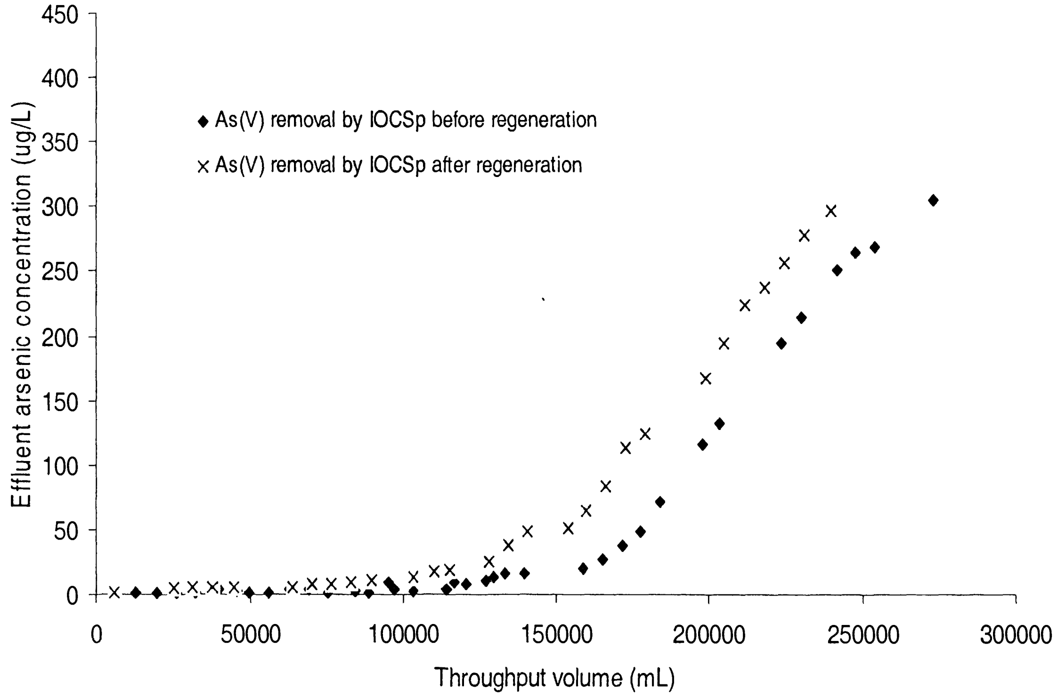


Figure 4.13. Removal of As(V) from synthetic water by regenerated IOCSp column (Initial As concentration = 1,000 μg/L; weight of IOCSp = 25 g)

After the regeneration of IOCSp by NaOH solution, the columns could remove both As(III) and As(V) to the value of less than 50 μg/L with the throughput volume approximately 124 L and 147 L respectively (which correspond to bed volumes of 100 with As(III) and 118 with As(V)). These values were about 82% in comparison with the original IOCSp. This showed that IOCSp could be regenerated and retains a high removal capacity.

4.8.2 Groundwater

4.8.2.1 Kelliher groundwater, Canada

The IOCSp column was tested with Kelliher groundwater in Canada. The arsenic removal efficiency of the Kelliher groundwater by the IOCSp column is shown in Figure 4.14. The arsenic concentration in the effluent increased gradually but still was less than 18 μg/L even after a continuous input of volume of more than 60 L (which corresponds to a bed volume of 310). Two different amounts of adsorption medium (IOCSp) of 6 g and 8 g were used in order to study the effect of filter medium amount (Figure 4.14). The results indicated that there was not much difference in removal efficiency when the weight of IOCSp was decreased from 8 g to 6 g during the experimental period.

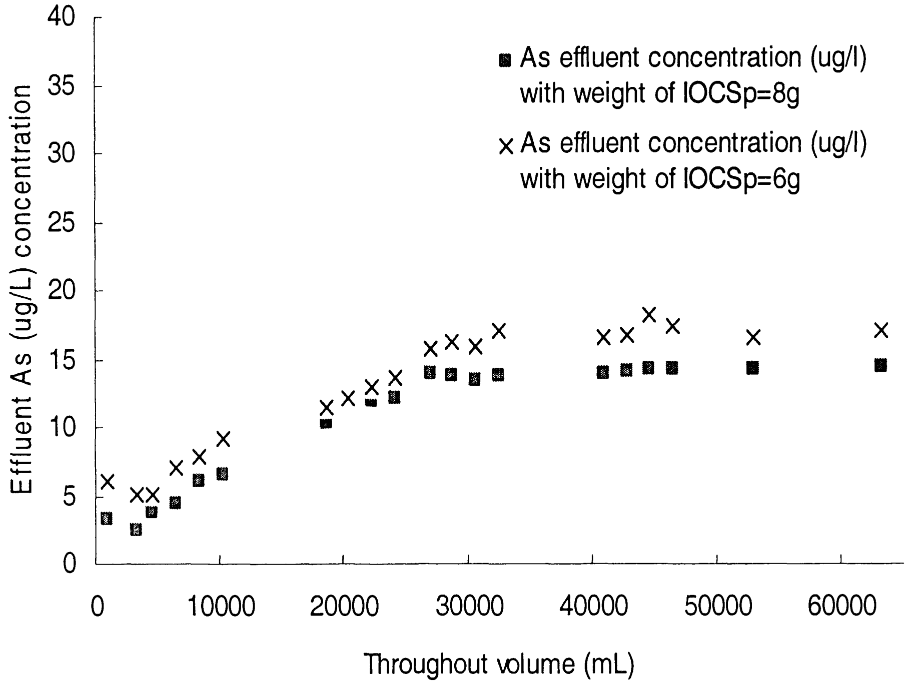


Figure 4.14. Effect of weight of IOCSp on As removal
(Initial As influent: 56 μg/L, filtration rate = 3 m/h)

4.8.2.2 Hanoi groundwater, Vietnam

The IOCSp column study was also carried out with a groundwater in Hanoi, Vietnam to evaluate the arsenic removal capacity of IOCSp. The columns were run at a filtration rate of 3 m/h. The performances of two IOCSp media sizes of 0.3 cm and 0.5 cm were compared.

During the initial stage, when the throughput volume was less than 22 L, the effluent arsenic concentration was less than 10 μg/L for both media sizes (Figures 4.15). After this stage, the arsenic concentration in the effluent increased slowly with the IOCSp media size of 0.3 cm but the effluent concentration was still lower than 50 μg/L even when the bed volume was about 370 (which corresponds to a throughput volume of 75 L). The results also showed that, with the increase in size of IOCSp, the arsenic removal became inferior, especially in the later stages of the experiment.

The improvement of the arsenic removal efficiency with the decrease in the IOCSp size was due to the increase in the surface area. This shows the importance of optimizing the size of IOCSp medium.

During the experiment with natural groundwater, arsenic was removed both by iron oxides incorporated in IOCSp and iron oxides formed from the naturally present Fe(II) existing in the natural groundwater.

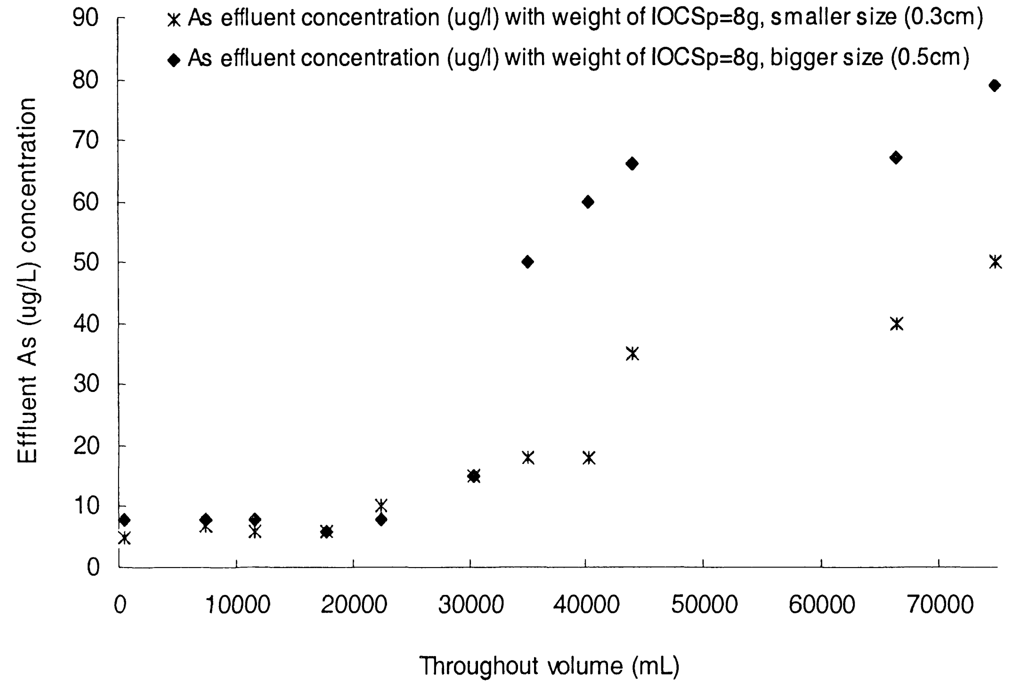


Figure 4.15. Effect of size of IOCSp on As removal
(Weight of IOCSp = 8 g, initial As influent: 156 μg/L, filtration rate = 3 m/h)

The column experimental conditions and results of removal arsenic by IOCSp column are presented in Table 4.7.

Table 4.7. Filter columns and operational conditions

Filter columns	Initial As concentration (µg/L)	Column height (mm)	Column diameter (mm)	Mass of IOCSp (g)	Filtration rate (m/h)	Arsenic in effluent (µg/L)	throughput volume (L)
Synthetic water	260	700	20	10	1.5-3	40	50 - 54
Synthetic water	1,000	940	45	25	0.17	48	153 - 178
Kelliher groundwater, Canada	56	700	20	6-8	3	18	63
Hanoi groundwater, Vietnam	156	700	20	8	3	50	75

4.8.3 Mathematical modelling of IOCSp filter

In the column packed with IOCSp, adsorption is the main phenomena to remove arsenic. Thus, the filtration modellings used in this study could be based on the Thomas and Nikolaidis adsorption models

4.8.3.1 Thomas Model

Figures 4.16 and 4.17 present the experimental bed volume dependent breakthrough curves and model simulations. The data fitted quite well with the simulated data of Thomas model. The parameters of the model are presented in Table 4.8.

Table 4.8. Parameters of Thomas model

No	Parameters	Unit	Fresh IOCSp		Regenerated IOCSp	
			As(III)	As(V)	As(III)	As(V)
1	q_m	mg/g	11.08	11.6	10.08	10.4
2	k_T	L/min.mg	1.06x10^{-7}	1.09x10^{-7}	1.04x10^{-7}	1.07x10^{-7}
5	r		0.976	0.959	0.983	0.993

The maximum solid phase concentration (q_m) for regenerated IOCSp was about 90% in comparison with fresh IOCSp (10.08 mg As(III) and 10.4 mg As(V) for a gram of regenerated IOCSp). It confirmed that regenerated IOCSp did not have any significant decrease in removal as compared to the fresh IOCSp.

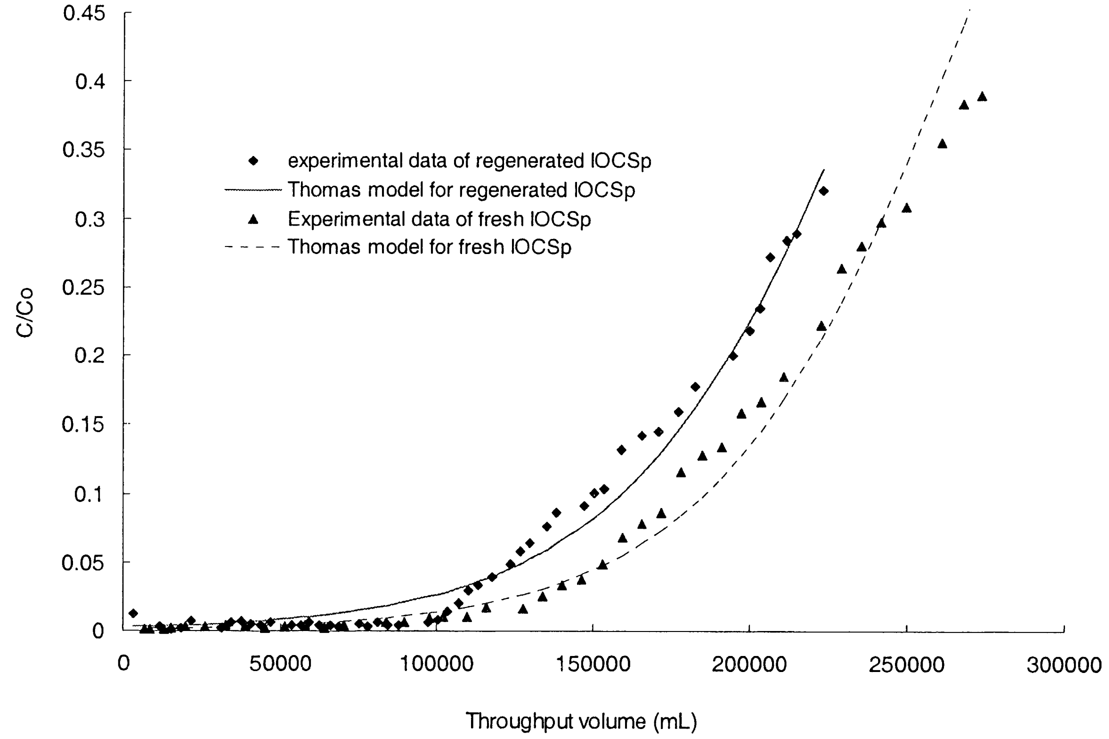


Figure 4.16. Experimental and simulated As(III) profiles by the Thomas model in the IOCSp column studies

(Initial As concentration = 1,000 μg/L; IOCSp' weight =25 g, IOCSp depth = 0.78 m)

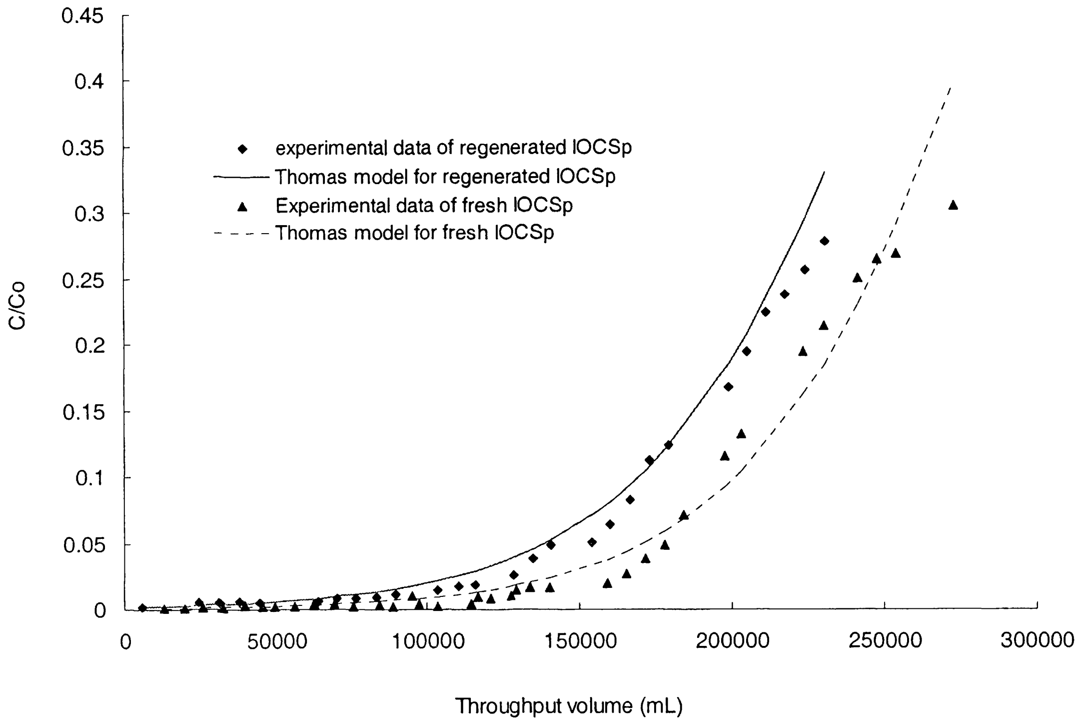


Figure 4.17. Experimental and simulated As(V) profiles by the Thomas model in the IOCSp column studies

(Initial As concentration = 1,000 μg/L; IOCSp' weight =25 g, IOCSp depth = 0.78 m)

The results showed that there was not much difference between the breakthrough times calculated from the Thomas model and from experimental data for fresh IOCSp and regenerated IOCSp (Table 4.9). Here, the breakthrough time is corresponding to effluent concentration 50 μg/L.

Table 4.9. Comparison of the theoretical service times from the Thomas approach with the experimental time

Species	Breakthrough time of fresh IOCSp (hour)		Breakthrough time of regenerated IOCSp (hour)	
	Experimental	Theoretical	Experimental	Theoretical
As(III)	580	584	467	480
As(V)	673	647	551	519

As is evident from Table 4.9, the theoretical and experimental values are well comparable with each other.

4.8.3.2 Nikolaidis modified Model

Nikolaidis et al. (2003) formulated a model to describe the transport of arsenic in the columns packed with zero valent iron. The model is represented as follows:

$$\frac{\partial C}{\partial t} = -u_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t} \frac{\rho_s (1 - n_N)}{n_N} - k_N C$$

The above model was modified to imitate the performance of IOCSp filter. The modified model can be written as follows:

$$\frac{\partial C}{\partial t} = -u_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - k_d C(1 - \frac{w_a}{w_a^0}) - k_N C$$

Where C : solute arsenic concentration (mg/m^3)

K_d : linear equilibrium partitioning coefficient (m^3/mg) to account for adsorption

k_N : the first-order mass transfer loss coefficient (1/s) to account for precipitation

u_x : velocity of water (m/s)

D_x : dispersion coefficient in x direction, (m^2/s)

w_a : mass of arsenic adsorbed after time t (mg)

w_a^0 : maximum adsorption capacity of filter (mg) = q_m x m

q_m : Maximum adsorption capacity of adsorbent (mg/g)

m : amount of adsorbent in filter (g)

S : amount sorbed onto porous medium = K_d x C (mg/g)

n_N : effective porosity (dimensionless)

ρ_s : solid density of the particles (mg/m^3)

The experimental bed volume dependent breakthrough curves and model simulations for As(III) and As(V) are presented in Figures 4.18 and 4.19. The parameters of model are presented in Table 4.10.

Table 4.10. Parameters of Nikolaidis modified model

No	Parameters	Unit	Fresh IOCSp		Regenerated IOCSp	
			As(III)	As(V)	As(III)	As(V)
1	q_m	mg/g	12.27	12.27	11.48	11.48
2	k_N	1/s	$7x10^{-5}$	$7x10^{-5}$	$7x10^{-5}$	$7x10^{-5}$
3	K_d	m^3/mg	$8x10^{-4}$	$8x10^{-4}$	$8x10^{-4}$	$8x10^{-4}$
4	D_x	m^2/s	$3x10^{-6}$	$1.9x10^{-6}$	$4x10^{-6}$	$2.5x10^{-6}$
5	r		0.987	0.991	0.983	0.980

The model simulated the column experimental data reasonably well. The maximum adsorption capacities (q_m) estimated from the model for fresh IOCSp and regenerated IOCSp were 12.27 mg/g and 11.48 mg/g respectively. This value was nearly the same as the value calculated by Thomas model.

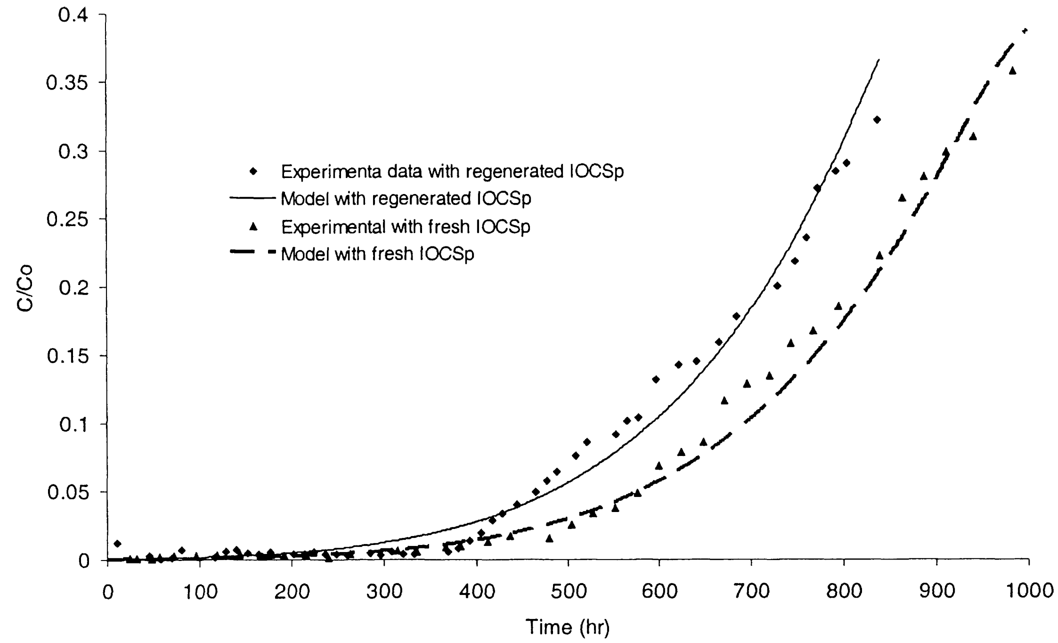


Figure 4.18. Experimental and simulated As(III) values by the Nikolaidis modified model in the IOCSp column studies

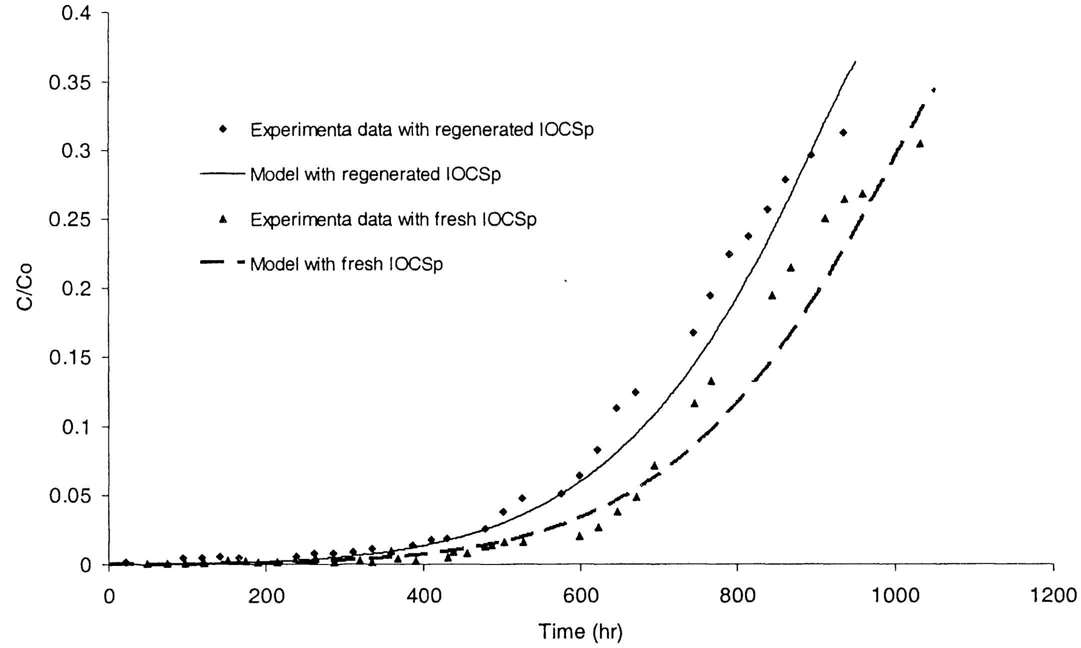


Figure 4.19. Experimental and simulated As(V) values by the Nikolaidis modified model in the IOCSp column studies

Table 4.11 shows the breakthrough times for fresh IOCSp and regenerated IOCSp calculated from the Nikolaidis modified model and obtained experimentally.

Table 4.11. Comparison of the theoretical service times from the Nikolaidis modified model with the experimental time

Species	Breakthrough time of fresh IOCSp (hour)		Breakthrough time of regenerated IOCSp (hour)	
	Experimental	Theoretical	Experimental	Theoretical
As(III)	580	593	467	482
As(V)	673	675	551	572

As is evident from Table 4.11, the theoretical and experimental values were well comparable with each other. In addition, the correlation coefficients (r) values of this model were more than 0.98, representing a good correlation of the simulated data with observed data. The model is relatively simple but does simulate the adsorption process of arsenic on IOCSp reasonably well. The Nikolaidis model was developed for arsenic removal by zero valent iron but in this study, IOCSp, a very high porosity material which a specific surface area was used. Therefore, the accuracy of the model could be improved further if these factors are incorporated and taken into account in the Nikolaidis modified model so that it can simulate better the adsorption process of arsenic on IOCSp.

4.9 IOCSp tray experiments

The inclined tray fitted with IOCSp was used as continuous adsorption system to remove arsenic from water. The experimental details of the tray system are explained in section 3.3.4 of Chapter 3. After cycle 1, the IOCSp was regenerated by 4 L of 0.3M NaOH. The details of tray operation conditions are shown in Table 4.12.

Table 4.12. Tray operational conditions

Experiment		Initial arsenic concentration (μg/L)	Time of operation (h)	Flow rate (mL/minute)	Weight of IOCSp glued on tray (g)	Angle of inclination (°)
As(III)	Cycle 1	145	4	15.6	19.2	10
	Cycle 2	260	30	15.6	19.2	10
As(V)	Cycle 1	265	28	15.6	13.4	6
	Cycle 2	265	6	15.6	13.4	6

Note: Cycle 1: run with fresh IOCSp
Cycle 2: run with regenerated IOCSp

The experimental results on As(III) and As(V) removal by IOCSp tray are presented in Figures 4.20 to 4.21.

In the experiment with As(III), the results of the first cycle showed that high removal efficiency (more than 96%) was observed during 4 hours of operation. After IOCSp in the tray was regenerated with 4 L of 0.3M NaOH, IOCSp was able to treat nearly 10 L of As(III) of 260 μg/L to a value less then 50 μg/L. After 30 hours of running with 28 L of arsenic solution, the arsenic removal efficiency decreased gradually to an effluent arsenic concentration of 124 μg/L (Figure 4.20).

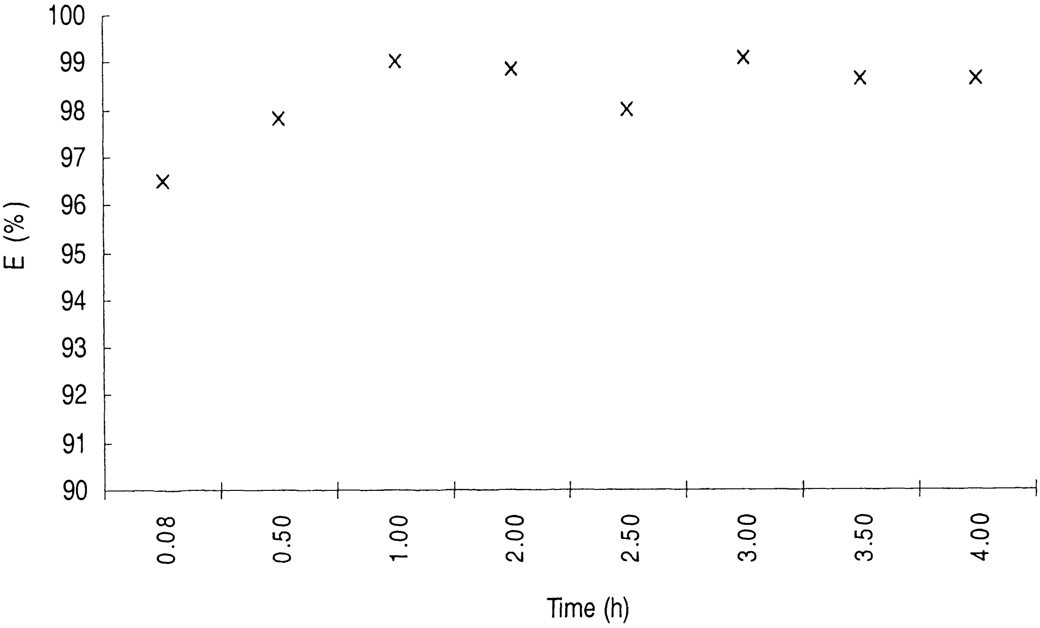


Figure 4.20. Removal of As(III) by IOCSp tray, cycle 1
(Initial As(III) concentration = 145 μg/L; IOCS'p weight = 19.2 g)

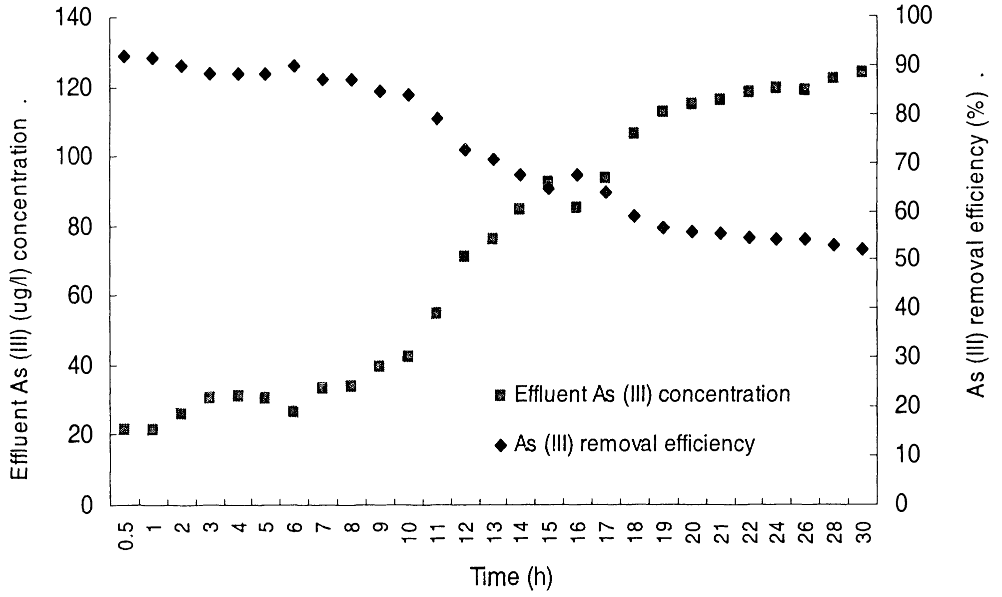


Figure 4.21. Removal of As(III) by IOCSp tray, cycle 2
(Initial As(III) concentration = 260 μg/L; weight of sponge = 19.2 g)

When As(V) was used as a feed solution, after 6 hours (which corresponds to a throughput volume of nearly 6 L) of running the tray adsorption experiments, As(V) concentration in the effluent reached to the value of 49.2 μg/L. The effluent concentration increased to 110 μg/L after 28 hours of running (Figure 4.22).

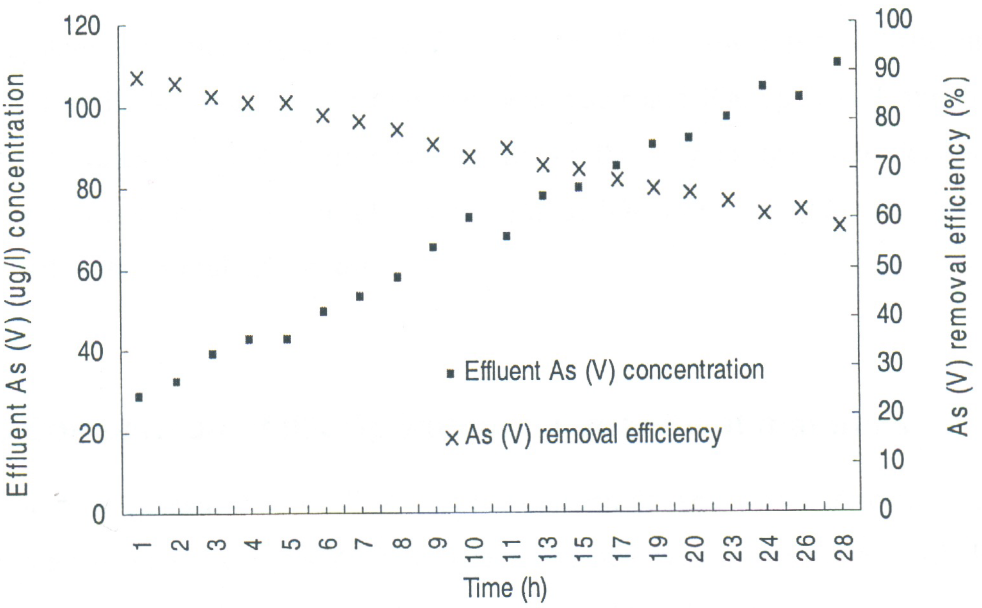


Figure 4.22. Removal of As(V) by IOCSp tray, cycle 1
(Initial As(V) concentration = 265 µg/L; weight of sponge = 13.4 g)

After IOCSp in the tray was regenerated by 4 L of 0.3M NaOH, IOCSp continued to adsorb As(V) to a value of less than 20 µg/L even after 6 hours of running time (Figure 4.23).

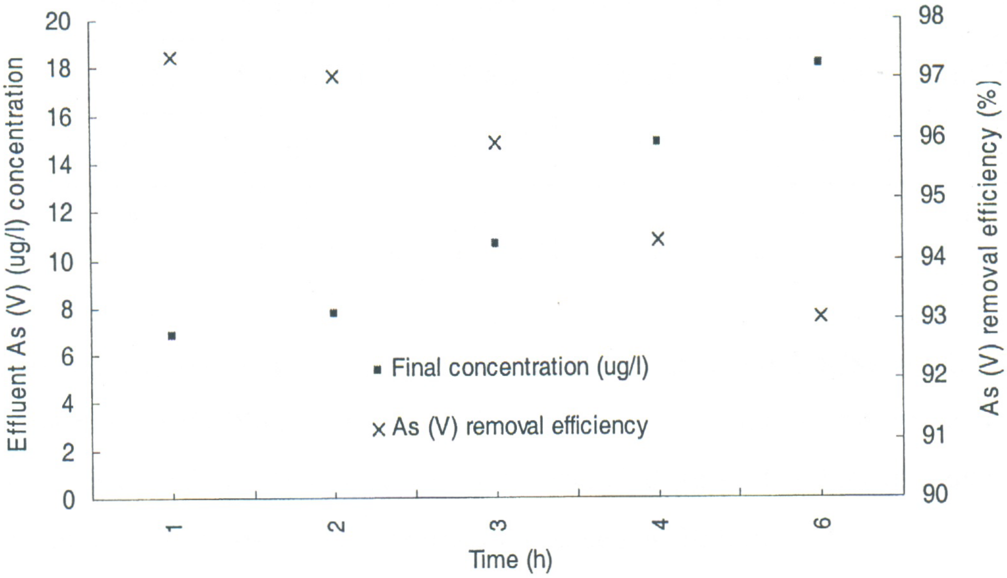


Figure 4.23. Removal of As(V) by IOCSp tray, cycle 2
(Initial As(V) concentration = 265 µg/L; IOCSp's weight = 13.4 g)

In comparision with IOCSp filter system, the arsenic removal efficiency of IOCSp tray system was much lower. The first reason of the low removal efficiency of IOCSp tray is the short contact time between water and IOCSp (2 – 3 minutes). In addition, water was not distributed equally in the tray as the water distribution system was not good. As a result, some parts of IOCSp on the tray were not really involved in the treatment process.

4.10 Comparison of IOCSp with other adsorbent materials

Arsenic removal was also studied with the column packed with surfactant modified zeolite/zero-valent iron (SMZ/ZVI). The efficiency was much better with IOCSp both in terms of the throughput volume and bed volume (as shown in section 5.3.4 of Chapter 5). Table 4.13 shows the throughput volume and bed volume of IOCSp and SMZ/ZVI columns in removing arsenic of concentration of 1,000 μg/L down to a value of 50 μg/L.

Table 4.13. Comparison of the efficiencies of IOCSp and SMZ/ZVI columns for removing arsenic up to value 50 μg/L

	Weight of media (g)		Throughput volume (L)		Bed volume	
	IOCSp	SMZ/ZVI	IOCSp	SMZ/ZVI	IOCSp	SMZ/ZVI
As(III)	25	68	153	1.7	123	22
As(V)	25	68	178	5.1	144	67

Another comparative study was made with columns packed with IOCSp and IOCS-2. The flow rates in IOCSp and IOCS-2 columns were 3 m/h and 4.6 m/h respectively. Arsenic concentration in the synthetic water was 260 μg/L. The breakthrough (the maximum allowable effluent) concentration was kept at 50 μg/L.

Table 4.14. Comparison of arsenic removal efficiencies by IOCSp and IOCS-2

Weight of media (g)		Throughput volume (mL)		Effluent As concentration		Bed volume	
IOCS	IOCSp	IOCS	IOCSp	IOCS-2	IOCSp	IOCS-2	IOCSp
90	10	1872	1920	3	2	33	9
90	10	24336	24960	11	6	427	122
90	10	46800	46080	67	37	821	226
90	10	54288	53760	68	40	952	263

The removal efficiency of arsenic by IOCSp columns was better than that of IOCS-2 column even though the weight of IOCSp was only 11% in comparison with the one with IOCS-2.

4.11 Conclusions

Sponge could be coated in an optimum manner by iron oxide under the following conditions: pH value of 4, time of contact between iron oxide and the sponge during coating of 10 hours; coating temperature of 110°C; and time of drying of sponge after the coating of 20 hours.

Iron oxide coated sponge exhibited a high arsenic removal capacity in both batch and column experiments. The high removal capacity of IOCSp was due to its characteristics (high internal porosity and specific surface) as well as high iron oxide content (12%). The IOCSp adsorption equilibrium with synthetic water was reasonable fitted with Freundlich, Langmuir, and Sips models. The adsorption capacity of IOCSp (up to 4.18 and 4.6 mg of As(III) and As(V) per gram of IOCSp respectively) was much higher than that with a number of adsorbents such as ferruginous manganese ore (0.680 mg/g), iron oxide coated sand (0.029 mg/g), activated alumina (0.180 mg/g), red mud (0.66 mg/g), iron oxide impregnated activated alumina (0.734 mg/g), and activated red mud (0.87 mg/g).

The IOCSp filter performed consistent arsenic removal efficiency for a long term of operation. A column (4.5 cm diameter and 78 cm IOCSp bed depth) packed with 25 g of IOCSp could maintain about 95% arsenic removal from high contaminated water containing arsenic of 1,000 µg/L for more than 153 L and 178 L of As(III) and As(V) respectively. IOCSp could be regenerated with NaOH and it did not have any significant decrease in removal as compared to the fresh IOCSp. IOCSp filter was also tested successfully with groundwater. The dynamic adsorption kinetics of arsenic on IOCSp can successfully be described and predicted by the Thomas and Nikolaidis modified model.

The removal efficiency of the IOCSp tray system was lower than the IOCSp filter system because of short contact time between water and IOCSp (2 – 3 minutes) and unequal distribution of water in the tray.

Simple designs for removing arsenic from water are presented in Appendix A.

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CHAPTER 5

ARSENIC REMOVAL BY IRON OXIDE COATED SAND 2 AND SURFACTANT MODIFIED ZEOLITE/ ZERO VALENT IRON

Chapter 5 Arsenic removal by iron oxide coated sand 2 and surfactant modified zeolite/zero valent iron

5.1 Introduction

The unit operation of adsorption is now being widely and successfully used to remove arsenic from water due to its simplicity, ease of operation and handling, and relatively simple regeneration procedure. A number of adsorbent materials such as activated alumina, fly ash, activated carbon, and manganese dioxide coated sand have been tested and applied to adsorb arsenic and other pollutants from water (Sorg and Logsdon, 1978, Diamadopoulos et al., 1993, Ghurye et al., 1999, Bajpai and Chaudhuri, 1999).

Among the adsorbent materials, iron-based sorbent materials have attracted attention in removing arsenic from drinking water because iron oxides have a strong affinity for dissolved arsenic and adsorb it from the water. Arsenic is strongly attracted to sorption sites on the surfaces of these materials, and is effectively removed from water.

Iron oxide coated sand was found to able to remove heavy metals in water such as arsenic, cadmium, copper, nickel, and chromium (Sang et al., 1997; Khaodhiar et al., 2000, Thirunavukkarasu et al., 2001). Thirunavukkarasu et al. (2001) showed that 90% of the arsenic was removed from water containing 325 μg/L arsenic by iron oxide coated sand and ferrihydrite. A simple fixed bed unit packed with 75 g of IOCS was able to treat 163 - 184 and 149 - 165 bed volumes of groundwater spiked with 1,000 μg/L arsenite and arsenate respectively before arsenic reached 10 μg/L in the effluent (Joshi and Chaudhuri, 1996).

Zero valent iron (ZVI) could be used to eliminate a wide range of contaminants in water. To improve the adsorption capacities, ZVI has been modified in various ways such as coating iron with Pd, Pt, Ni, and Cu (Muftikian et al. 1995; Liang et al., 1997; Li and Farrell, 2000; Gui et al., 2000). A material that combines ZVI with surfactant-modified zeolite (SMZ) in a pelletized form showed encouraging results in removing contaminants from water. This material has a high hydraulic conductivity (9.7 cm/s), surface area (28.2 m^2/g) and has 16% zeolite, 49% ZVI, 0.7% HDTMA-Cl, and 34% glass foam (by weight). With its characteristics, SMZ/ZVI can be used in removing arsenic from water. There is a need to study the effectiveness of SMZ/ZVI for arsenic removal to achieve the permissible concentration in drinking water.

The main objectives of this chapter are as follows:

(1) Evaluating capabilities of iron oxide coated sand 2 (IOCS-2) in removing arsenic

(2) Evaluating capabilities of surfactant modified zeolite/zero valent iron (SMZ/ZVI) in removing arsenic.

Both batch studies (adsorption equilibrium and kinetics) and filter column experiments were conducted.

5.2 Arsenic removal by iron oxide coated sand 2 (IOCS-2)

5.2.1 Properties of the adsorbent

The sand was weighed (as dry weight) before and after coating. Both coated and uncoated sand were dried in an oven at 100°C for 24 hours and desiccated prior to weighting.

The results showed that the iron content of iron oxide coated sand 2 (IOCS-2) was approximately 4.5%. A previous study (Thirunavukkarasu et al., 2003b) showed that the surface area of IOCS-2 was 10.6 m^2/g, was nearly double that of IOCS.

5.2.2 Batch kinetic studies

IOCS-2 was used in the batch kinetic studies to study the removal of both As(III) and As(V) from synthetic water. The effect of pH was also studied. The pH of the synthetic water was adjusted to predesigned values of 6, 7, and 8.1 respectively, with 1M HNO_3 and 1 M NaOH. In the kinetic studies using IOCS-2, the initial concentrations of As(III) and As(V) in the synthetic water were kept at 260 μg/L. In these studies, 1g of IOCS-2 was placed in a flask containing 100 mL of As solution.

The batch adsorption results showed that less than 26.1 μg/L of arsenic (more than 90% removal) was remaining in the solution at all pH values studied. In the initial phase of contact (first hour), only 29 - 37.6% of arsenic was removed. However, the removal efficiency increased rapidly and reached more than 80% after 5 hours of contact.

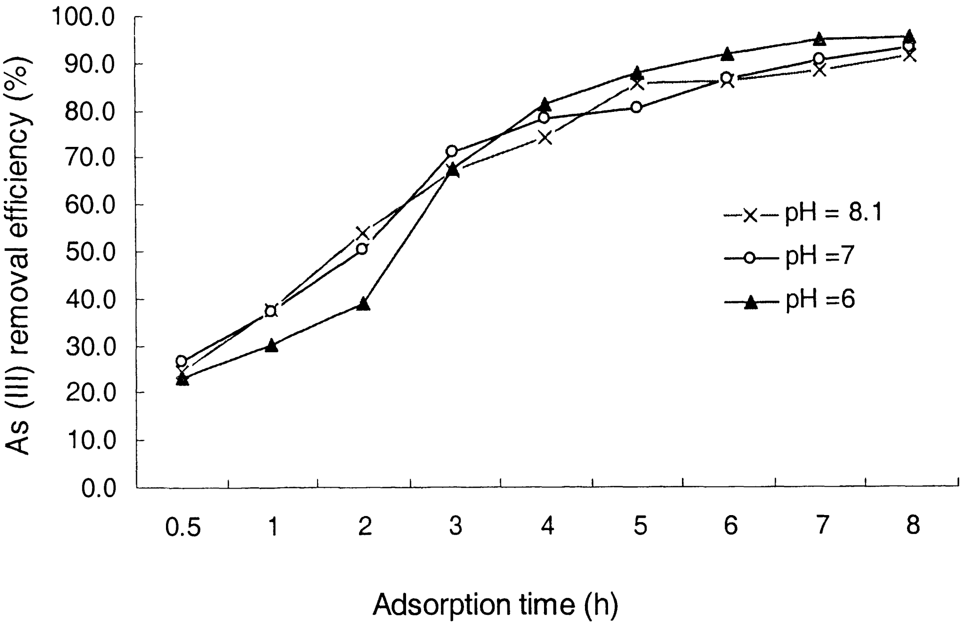


Figure 5.1. Removal efficiency of As(III) as a function of adsorption time (Initial As(III) concentration = 260 μg/L; IOCS-2 weight = 1 g, Temperature = 22^0C, volume of As solution = 100 mL)

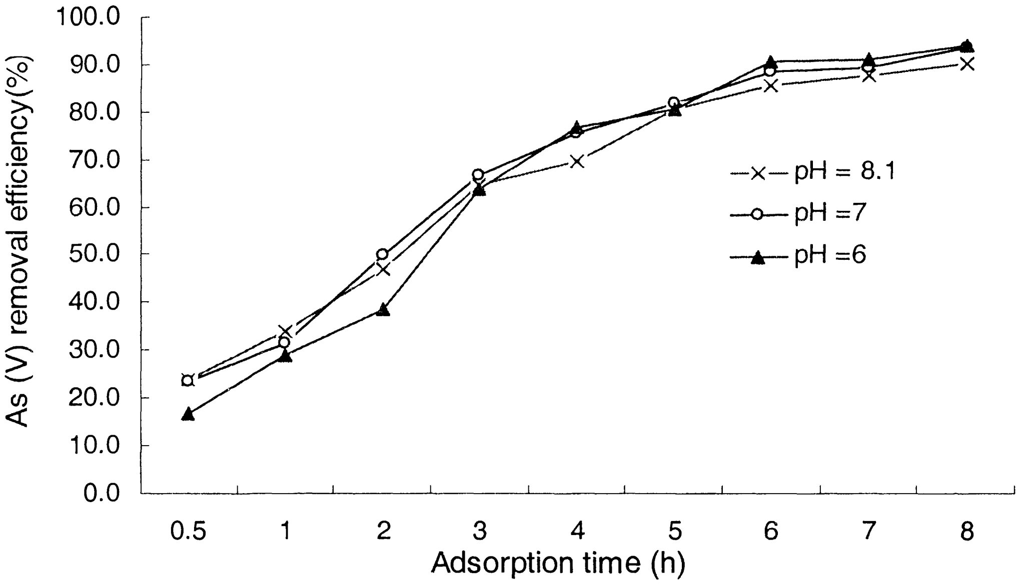


Figure 5.2. Removal efficiency of As(V) as a function of adsorption time (Initial As(V) concentration = 260 μg/L; IOCS-2 weight = 1 g, Temperature = 22^0C, volume of As solution = 100 mL)

Kinetic adsorption of IOCS-2 with arsenic was also found to be described well by the Ho model (Figures 5.3 and 5.4). The values of parameters (q and K_H) are given in Table 5.1.

Table 5.1. Kinetics adsorption parameters of Ho model for IOCS-2 adsorption

Arsenic species	pH	q	K_H	Equation	Correlation coefficient (r)
As(III)	6	0.036	5.6	$q_t = 0.0145\,t / (1+0.40t)$	0.954
	7	0.034	5.5	$q_t = 0.0116\,t / (1+0.34t)$	0.989
	8.1	0.034	5.3	$q_t = 0.0123\,t / (1+0.36t)$	0.994
As(V)	6	0.036	4.2	$q_t = 0.0109\,t / (1+0.30t)$	0.996
	7	0.036	4.1	$q_t = 0.0106\,t / (1+0.30t)$	0.994
	8.1	0.035	4	$q_t = 0.0098\,t / (1+0.28t)$	0.992

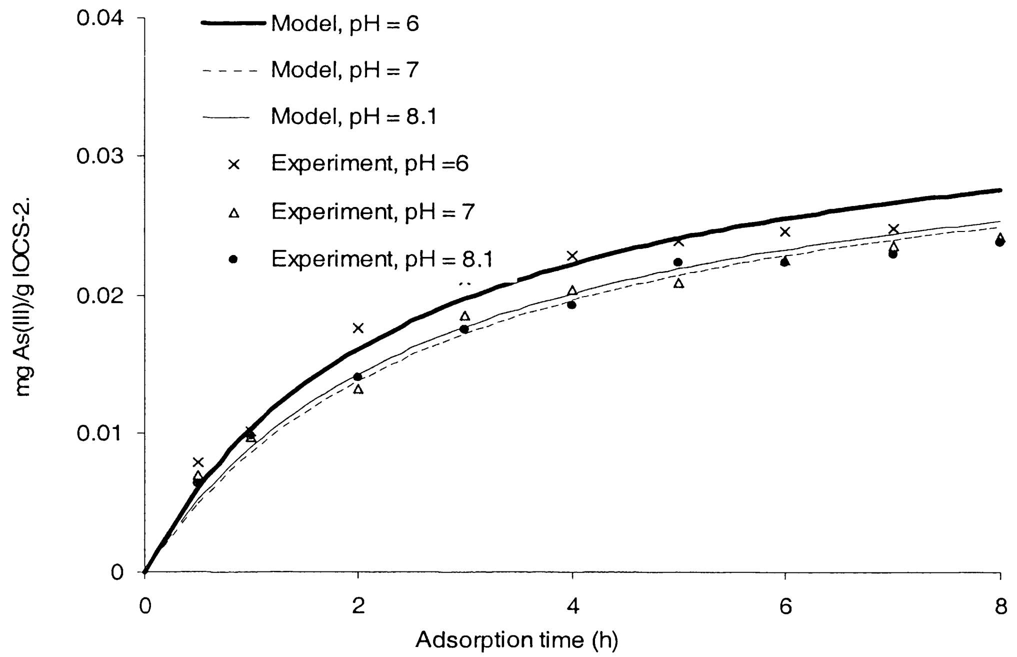


Figure 5.3. Prediction of adsorption kinetics of IOCS-2 with As(III) by Ho model (Initial As(III) concentration = 260 μg/L; weight of IOCS-2 = 1 g, temperature = 22 ^{0}C, volume of As solution = 100 mL, mixing rate = 175 rpm)

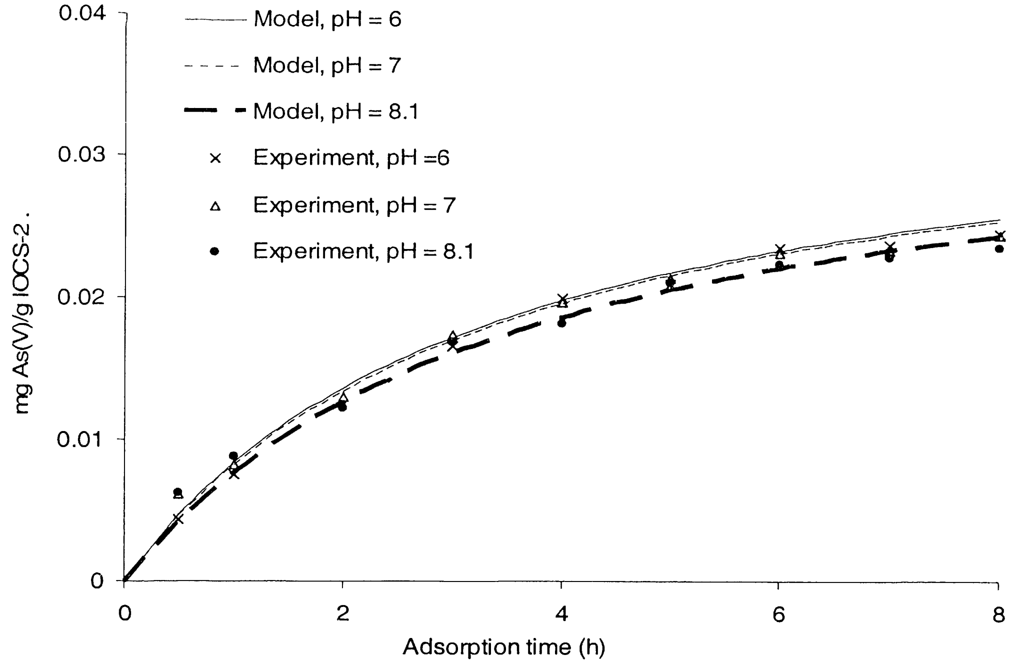


Figure 5.4. Prediction of adsorption kinetics of IOCS-2 with As(V) by Ho model (Initial As(V) concentration = 260 μg/L; weight of IOCS-2 = 1 g, temperature = 22 ^{0}C, volume of As solution = 100 mL, mixing rate = 175 rpm)

The results of the kinetic studies for the removal of both As(III) and As(V) using IOCS-2 are presented in Appendix B (Tables B17 to B18).

5.2.3 Adsorption equilibrium experiments

Adsorption equilibrium studies were conducted at the room temperature of 22^{O}C. In the experiments, predetermined amounts of adsorbent (0.1 to 1 g) were transferred to 100 mL synthetic water containing 260 µg/L of As(III) and As(V). The samples were placed on the shaker and shaken at 175 rpm. The equilibrium time determined from the kinetic studies was kept as the contact time. After the equilibrium was reached (after 8 hours), samples from each flask were decanted and analysed for residual As.

The equilibrium results were then fitted with 3 isotherm models (Langmuir, Freundlich, and Sips). The model equations and the isotherm parameters are shown in Table 5.2. The results showed that the "r" values are all close (0.931 to 0.976) and high, representing a good correlation of the simulated data with observed data.

Table 5.2. Isotherm equations for arsenic removal using IOCS-2

Parameters		Arsenic species	
		As(III)	As(V)
Langmuir	q_m	0.051	0.055
	b	78	73
	r	0.960	0.976
	Equation	$q_e = 3.98\ C / (1 + 78\ C)$	$q_e = 4.02\ C / (1 + 73\ C)$
Freundlich	K_F	0.074	0.076
	n	4.4	4.7
	r	0.973	0.970
	Equation	$q_e = 0.074\ C^{0.23}$	$q_e = 0.076\ C^{0.21}$
Sips	q_m	0.048	0.052
	b	408	390
	n	0.676	0.676
	r	0.931	0.966
	Equation	$q_e = 0.048\ (408\ C)^{1.48} / (1 + (408\ C)^{1.48})$	$q_e = 0.052\ (390\ C)^{1.48} / (1 + (390\ C)^{1.48})$

The predicted and the experimental concentrations of As(III) and As(V) remaining in solution are shown in Figures 5.5 and 5.6.

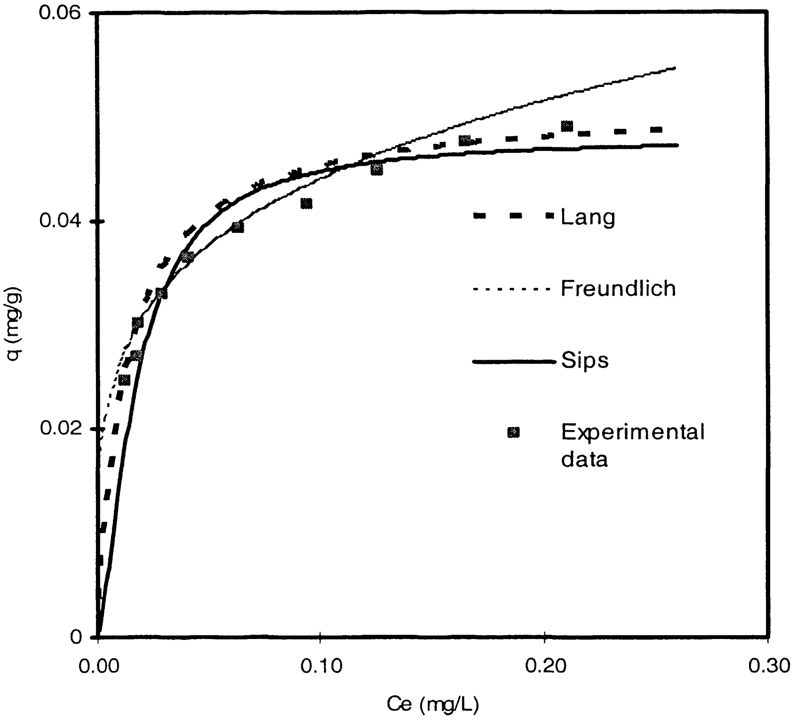


Figure 5.5. Prediction of equilibrium adsorption of As(III) by different adsorption models (contact time = 8 hours, mixing rate = 175 rpm, temperature = 22^0C)

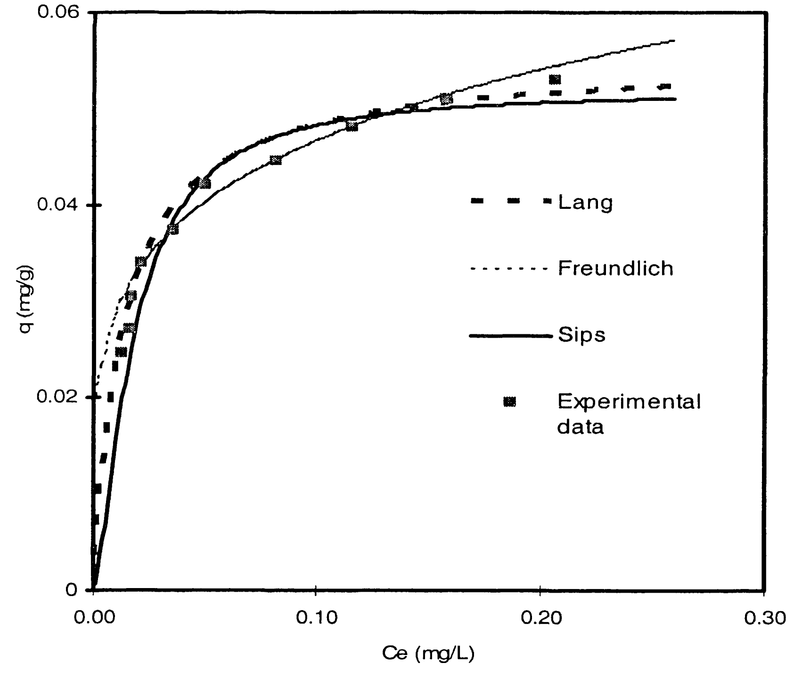


Figure 5.6. Prediction of equilibrium adsorption of As(V) by different adsorption models (contact time = 8 hours, mixing rate = 175 rpm, temperature = 22^0C)

The values of arsenic adsorption capacity q_m estimated by Langmuir and Sips models gave rise to same values (0.048 – 0.055 mg/g IOCSp). These values were much lower than that of IOCSp.

The low 1/n (<0.23) from Freundlich suggests that any large change in the equilibrium concentration of soluble arsenic would not result in a change in the amount of arsenic sorbed by the IOCS-2.

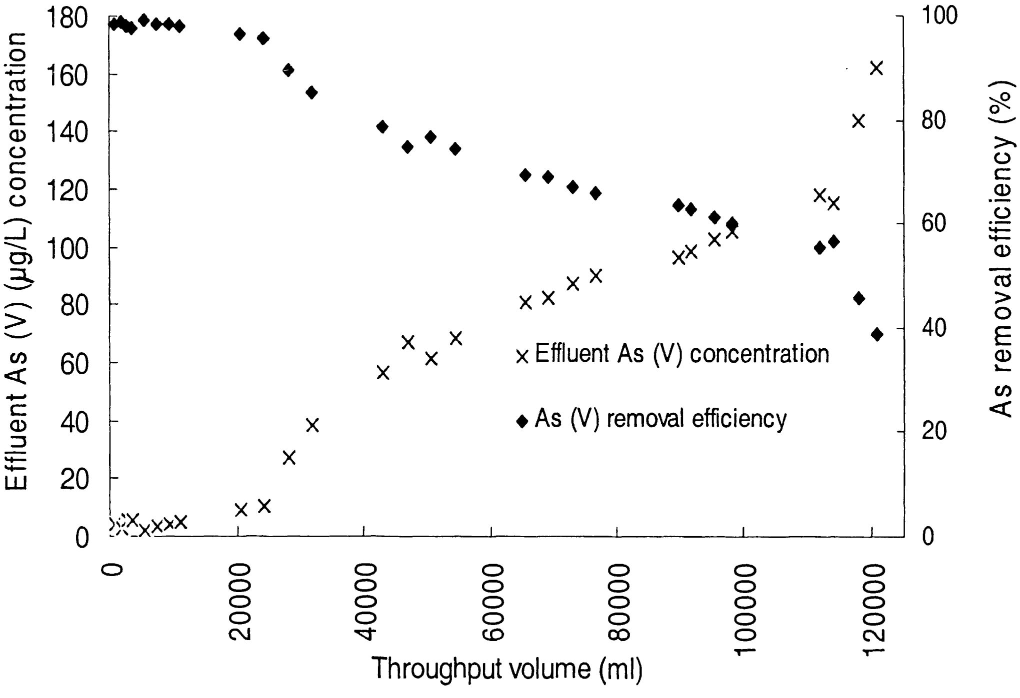
The low standard error (0.0014 – 0.0022) and squares of deviations (0.0009 – 0.0016) also showed the well fitness between experimental data and simulated values by the different models.

The detailed results of the equilibrium experiments for the removal of both As(III) and As(V) using IOCS-2 are presented in Appendix B (Tables B19 to B20).

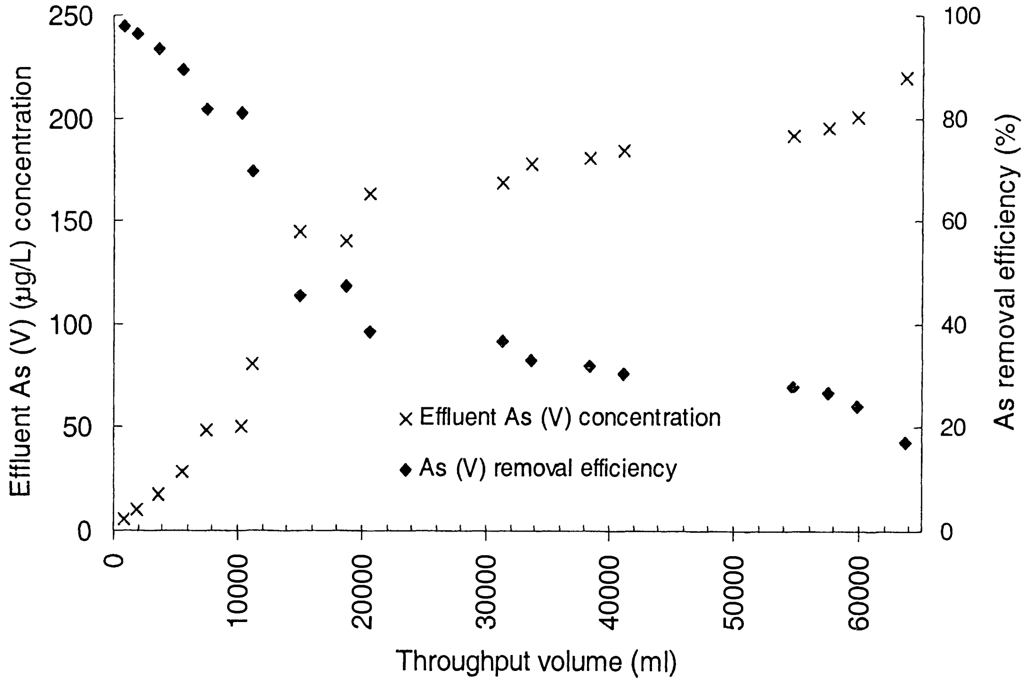
5.2.4 Column studies

An adsorption column study was also conducted using IOCS-2 as the adsorbent medium. Experiments were conducted to study the removal of As(V) from synthetic water, spiked with As(V). A glass column of 16 mm diameter and 450 mm height was used in the study. The synthetic water spiked with the required concentrations of As(V) was pumped through the packed column using a peristaltic pump at a flow rate 15.6 mL/minute (or at a throughput rate of 4.6 m/h). All of the column experiments were conducted in the down-flow mode and at a pH of 7.4 - 7.6. The column was packed with 90 g (57 mL) of the IOCS-2, ensuring enough headspace to allow for the expansion of the media in the column. At regular time intervals, the effluent was collected and analyzed for residual As using GF-AAS. In this study, the medium was regenerated with NaOH at the end of each cycle, and backwashed with deionized water.

The results showed that a volume of 31.8 L was collected during the first cycle, which corresponds to a bed volume of 559 before the effluent arsenic concentration exceeded a value of 50 μg/L. As one would expect, a decrease in the number of volumes was observed in subsequent cycles. The bed volumes during the second and third cycles were 180 and 99 respectively. The filter operation after the first and second backwash/regeneration is referred to as second and third cycles respectively

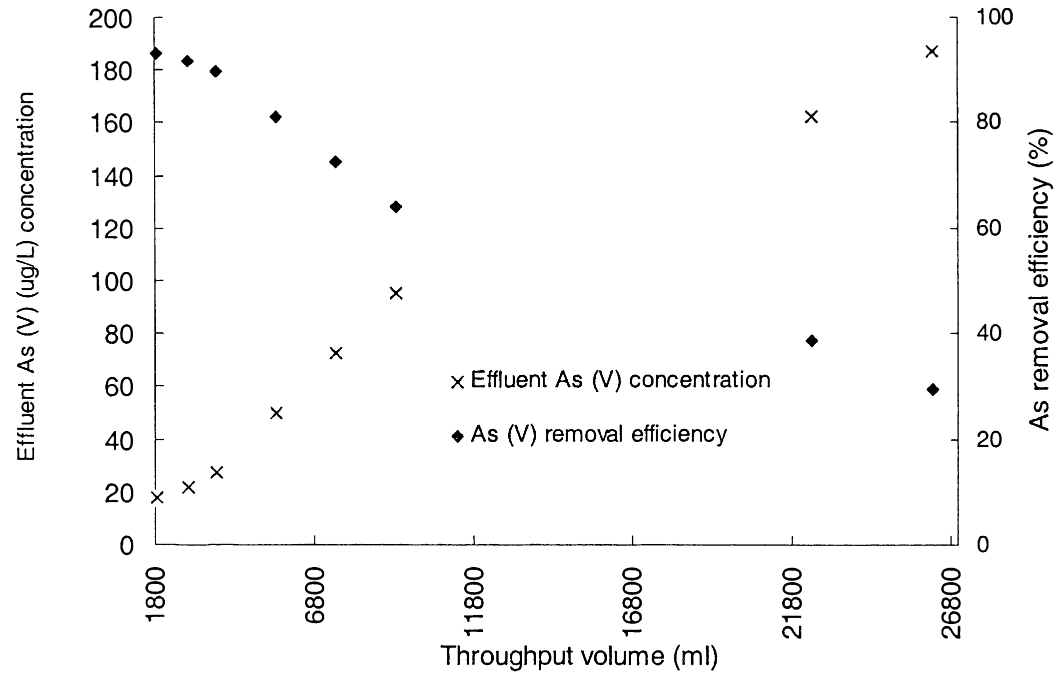


(a) First cycle



(b) Second cycle

Figure 5.7. Removal of As from synthetic water by IOCS-2 column (Initial As(V) concentration = 260 µg/L; Weight of IOCS-2 = 90 g)



(c) Third cycle

Figure 5.7. Removal of As from synthetic water by IOCS-2 column (Initial As(V) concentration = 260 μg/L; Weight of IOCS-2 = 90 g)

5.3 Arsenic removal by surfactant modified zeolite – zero valent iron medium

5.3.1 Adsorption kinetics

The arsenic removal efficiency of SMZ/ZVI with time was investigated in kinetics experiments. The kinetics of SMZ/ZVI was evaluated at an arsenic concentration of 1,000 μg/L. The results of SMZ/ZVI adsorption kinetics of As(III) and As(V) are presented in Figure 5.8. Arsenic in the synthetic water was quickly adsorbed within the first hours. The results show that SMZ- ZVI could remove 11% to 17% of As(III) and As(V) within a contact time of 5 minutes of contact. After one hour, 83.4% to 89.2% of As(III) and As(V) were adsorbed. Arsenic was nearly completely adsorbed after four hour adsorption (more than 99.6% or less than 4 μg/L of As remaining in the water). In these experiments, 2 g of SMZ/ZVI was placed in a flask containing 100 mL of As solution.

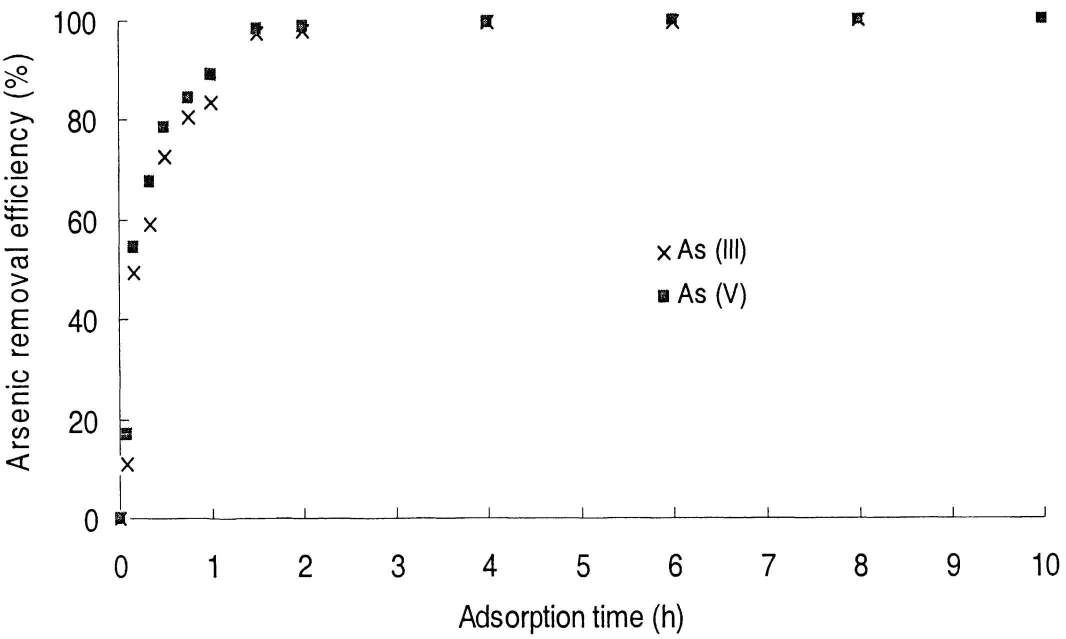


Figure 5.8. Removal efficiency of arsenic as a function of adsorption time (Initial As(III) concentration = 1,000 μg/L; weight of SMZ – ZVI = 2 g, temperature = 22 ^{0}C, volume of As solution = 100 mL, mixing rate = 130 rpm)

The detailed results of the kinetics of arsenic removal (for both As(III) and As(V)) are shown in Appendix B (Tables B24 and B25).

Kinetic adsorption of SMZ – ZVI with arsenic is also be described well by the Ho model (Figures 5.9 and 5.10). The parameters of the Ho model are given in Table 5.3.

Table 5.3. Kinetics adsorption parameters of Ho model for SMZ/ZVI adsorption

Arsenic species	q	K_H	Equation	Correlation coefficient (r)
As(III)	0.05	131	0.655 t / (1 + 13 t)	0.978
As(V)	0.051	132	0.714 t / (1 + 14 t)	0.990

The correlation coefficients (R) for the modeled plots were more than 0.978, representing a good correlation of the observed data.

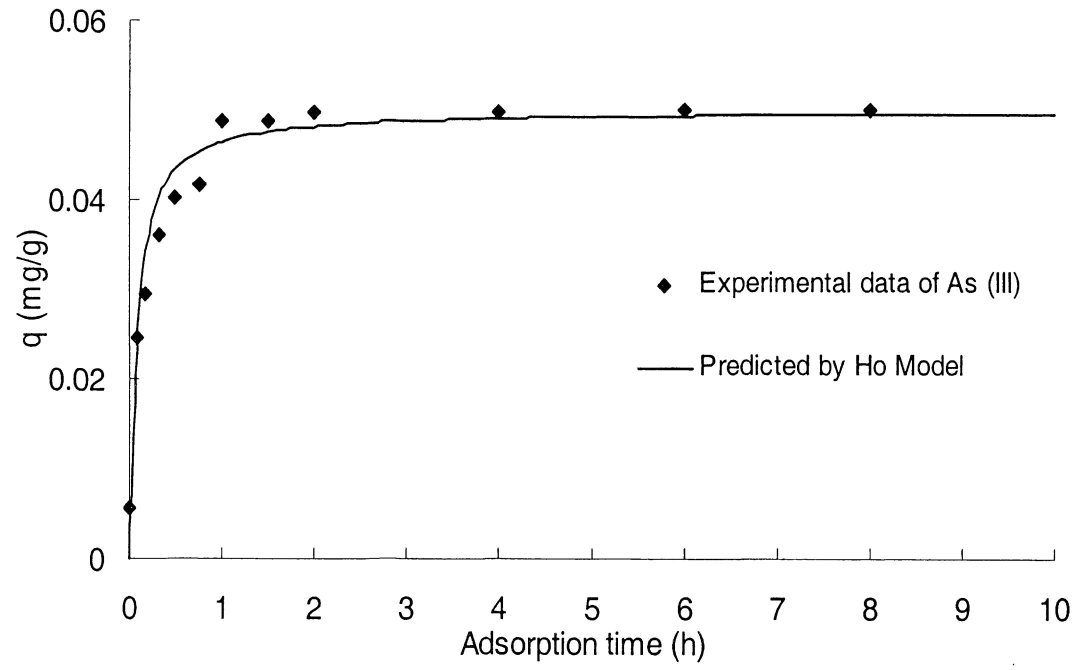


Figure 5.9. Prediction of adsorption kinetics of SMZ/ZVI with As(III) by the Ho model (Initial As(III) concentration = 1,000 μg/L; weight of SMZ/ZVI = 2 g temperature = 22 ^{0}C, volume of As solution = 100 mL, mixing rate = 130 rpm)

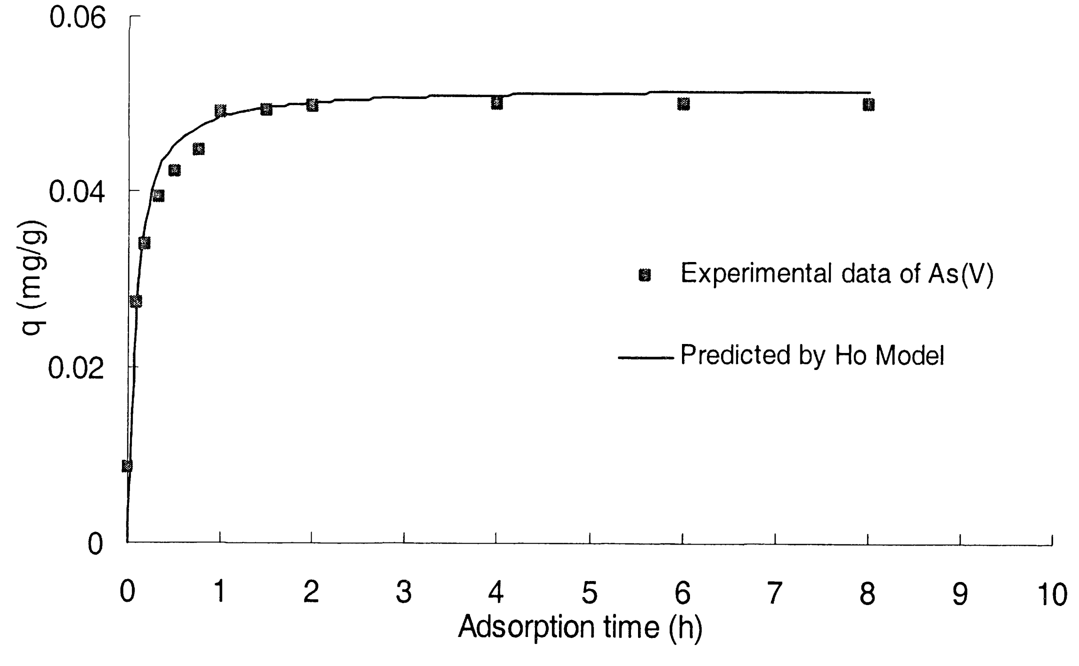


Figure 5.10. Prediction of adsorption kinetics of SMZ/ZVI with As(V) by the Ho model (Initial As(V) concentration = 1,000 μg/L; weight of SMZ/ZVI = 2 g, temperature = 22 ^{0}C, volume of As solution = 100 mL, mixing rate = 130 rpm)

5.3.2 Adsorption equilibrium experiments

In this study, 2 g of SMZ/ZVI was placed in 100 mL of As(III) and As(V) solutions and mixed at 130 rpm for 4 days. All experiments were performed at 22^{0}C. Then the suspensions were allowed to settle for 1 hour, and the supernatant solution was filtered through 0.45 μm membrane filters before measuring arsenic concentration by hydride generation atomic absorption spectrometry (HGAAS). Experiments were conducted at a pH of 6.7. The initial concentrations of As(III) and As(V) in the synthetic water were kept between 1,000 μg/L and 30,000 μg/L. The effect of phosphate on arsenic removal by the SMZ/ZVI was also studied by adding 2 mg/L phosphorus-phosphate to the As(III) solution. The equilibrium results were then fitted with the Langmuir, Freundlich, and Sips isotherm equations. The model equations and the isotherm parameters are shown in Table 5.4.

Table 5.4. Isotherm equations for arsenic removal using SMZ/ZVI

Parameters		Arsenic species	
		As(III)	As(V)
Langmuir	q_m	1.87	2.05
	b	0.041	0.039
	r	0.986	0.984
	Equation	$q_e = 0.0767\ C$ $/ (1 + 0.041\ C)$	$q_e = 0.08\ C$ $/ (1 + 0.039\ C)$
Freudlich	K_F	0.095	0.097
	n	1.36	1.37
	r	0.991	0.994
	Equation	$q_e = 0.095\ C^{0.74}$	$q_e = 0.097\ C^{0.73}$
Sips	q_m	1.79	1.99
	b	0.022	0.018
	n	0.79	0.775
	r	0.995	0.996
	Equation	$q_e = 1.79\ (0.022\ C)^{1.26}$ $/ (1 + (0.022\ C)^{1.26})$	$q_e = 1.99\ (0.018\ C)^{1.29}$ $/ (1 + (0.018\ C)^{1.29})$

The predicted and the experimental concentrations of As(III) and As(V) remaining in solution are shown in Figures 5.11 and 5.12.

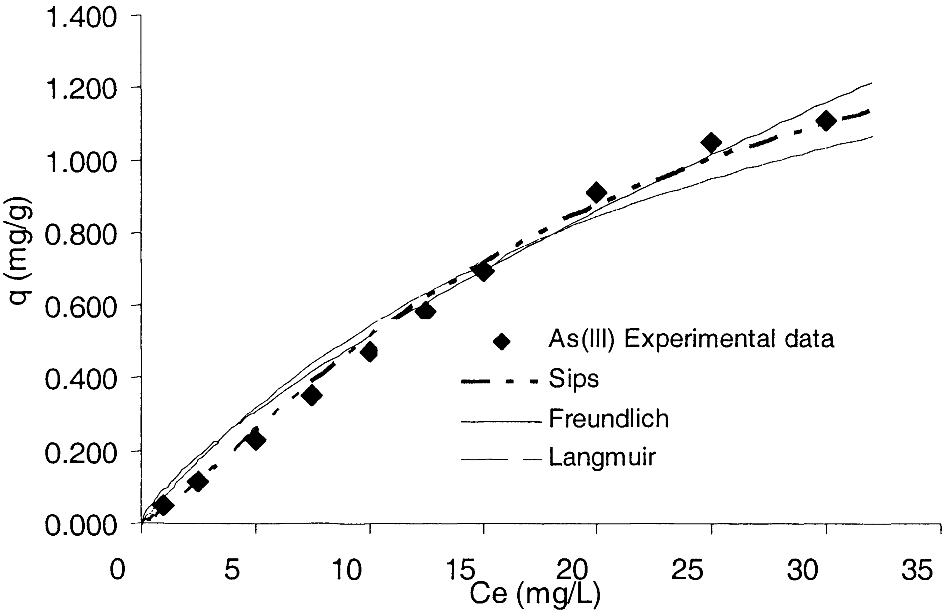


Figure 5.11. Prediction of equilibrium adsorption of As(III) by different adsorption models (contact time = 96 hours, mixing rate = 130 rpm, temperature = 22^{0}C)

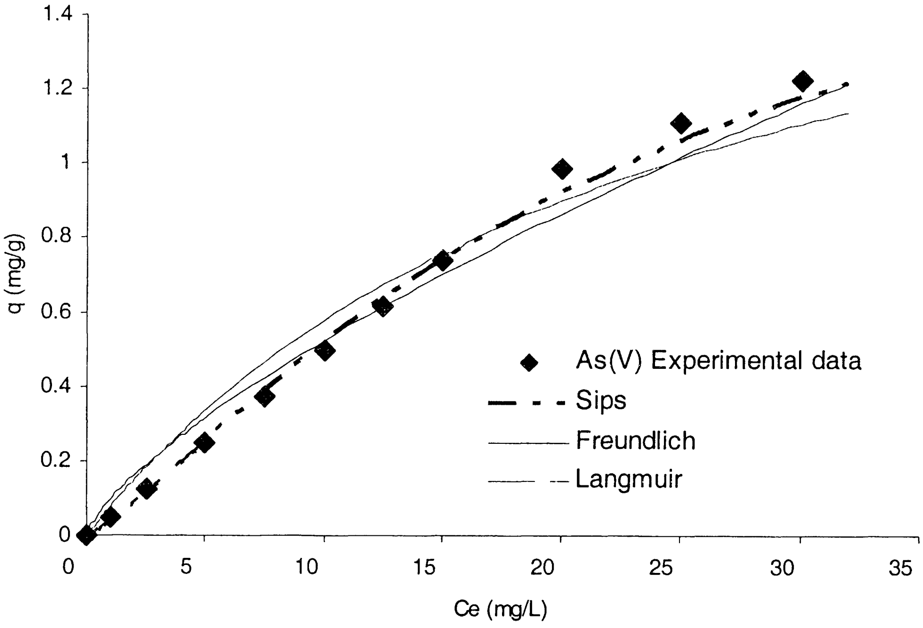


Figure 5.12. Prediction of equilibrium adsorption of As(V) by different adsorption models (contact time = 96 hours, mixing rate = 130 rpm, temperature = 22^{0}C)

The values of arsenic adsorption capacity q_m estimated by Langmuir and Sips models gave the same (1.79 – 1.87 mg As(III) / g SMZ/ZVI and 1.99 – 2.05 mg As(V)/ g SMZ/ZVI). These values were higher than that of IOCS-2 but still lower than that of IOCSp.

The results also showed that the presence of phosphate in water reduced only slightly the removal efficiency of arsenic by SMZ/ZVI pellets (0.4 – 4.3% for As(III) and 0.8 – 5.2% for As(V)). This reduction can be explained by the strong affinity of phosphate with metal oxides, and its similarity to the arsenate ion. The anions compete with arsenic for adsorption sites. Meng et al. (2000), and Chunming and Robert (2001) indicated that PO_4^{3-} is a potential interference to the adsorption of arsenic during ZVI adsorption.

5.3.3 Column experiments

Column experiments were conducted separately with As(III) and As(V) solutions to examine the effect of SMZ/ZVI pellets on arsenic removal. A glass column 16 mm in diameter and 450 mm in height was used in this study. Zeolite/ZVI cubes (2.5 cm in each dimension) were manually crushed to smaller size pellets (with a longest dimension of 0.5 cm) and 68 g of SMZ/ZVI were packed into the column. As(III) and As(V) solutions with concentration 1,000 μg/L were continuously injected into the column in an upward - flow mode and the effluent concentration of As(III) and As(V) at different time intervals were monitored. The filtration rate of 1.32 m/h was kept constant during the experiments.

The results on the removal of As(III) and As(V) by SMZ/ZVI column system are presented in Figure 5.13. The results show that during the first 22 bed volumes, the removal efficiencies were very high (more than 95%) for both of As(III) and As(V). The arsenic concentrations in the effluent water were below 50 μg/L. During the flow of next 250 bed volumes, the removal efficiency of As(III) decreased sharply to a value of 70% whereas the removal efficiency of As(V) decreased to a lesser extent, to a value of 80%. However, during the next 500 bed volumes, there was not much difference between the removal efficiencies of As(III) and As(V). The removal efficiencies were around 60% corresponding to an effluent arsenic concentration of 400 μg/L. The removal efficiency of As(V) then decreased dramatically after that.

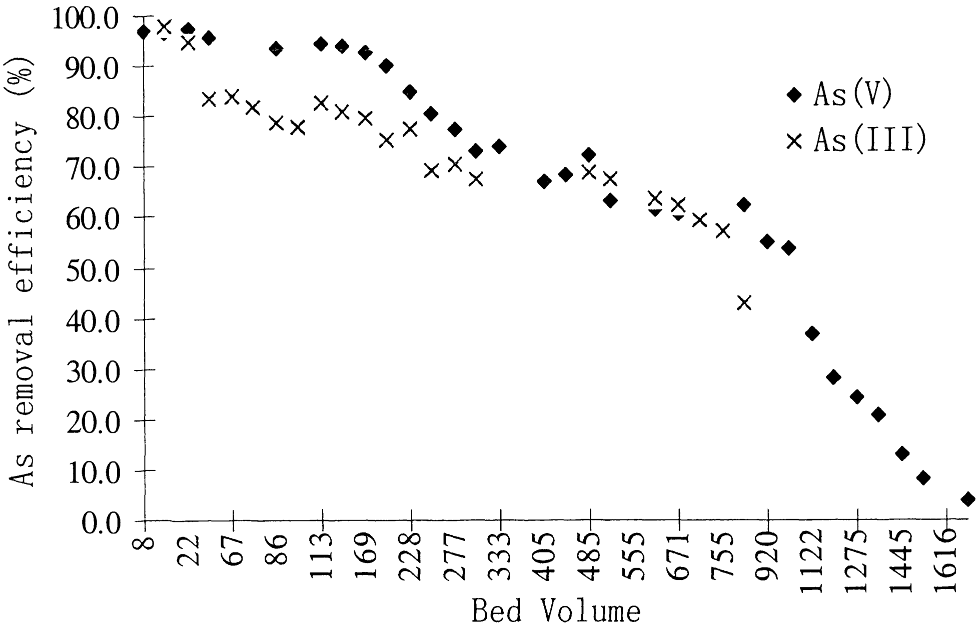


Figure 5.13. Removal efficiency of As(III) and As(V) from synthetic water by SMZ/ZVI column (Initial As(III) and As(V) concentration = 1,000 µg/L; weight of SMZ/ZVI = 68 g, filtration rate = 1.32 m/h)

5.3.4 Mathematical modelling of SMZ/ZVI column

5.3.4.1 Thomas Model

Figures 5.14 and 5.15 present the experimental data and model simulation curves. The maximum solid phase concentrations (q_m) estimated from the Thomas model for As(III) and As(V) were 0.941 and 0.985 mg/g SMZ/ZVI respectively. The Thomas rates (k_T) was 1.06x10^{-7} and 1.28x10^{-7} L/min.mg with As(III) and As(V) respectively. The correlation coefficient ‘r’ with As(III) of the Thomas model was low (0.83) but this value with As(V) was better (0.95). The prediction by Thomas model deviates significantly at very low throughput volume. The reason for this was maybe the iron in SMZ – ZVI pellets were washed out at different rates from the column as iron in SMZ – ZVI pellets has a quite weak linkage with SMZ.

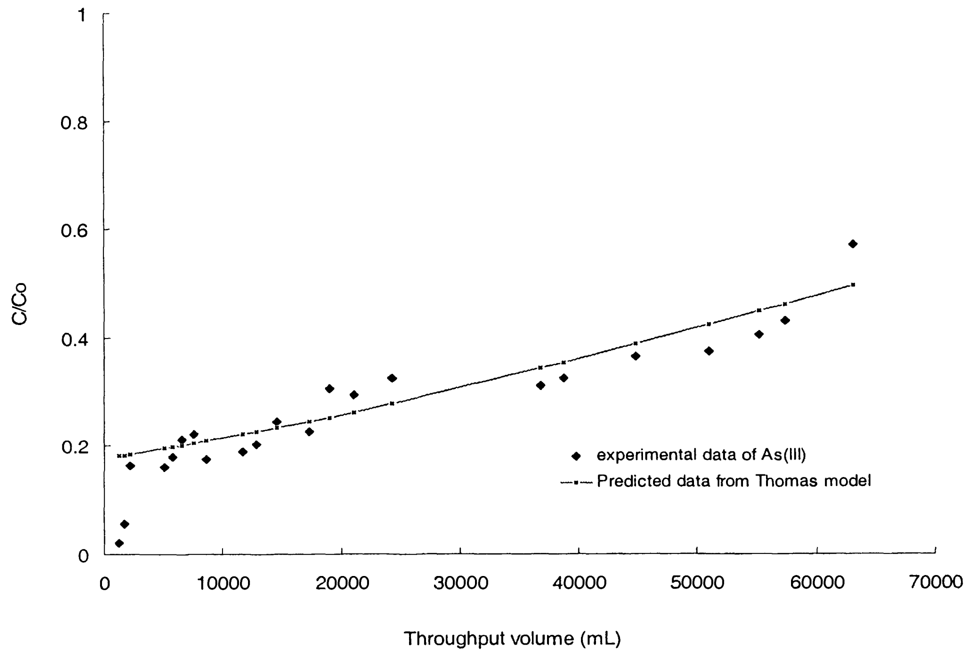


Figure 5.14. Experimental and simulated As(III) profiles by the Thomas model in the SMZ/ZVI column studies

(Initial As concentration = 1,000 μg/L; weight of SMZ/ZVI = 68 g)

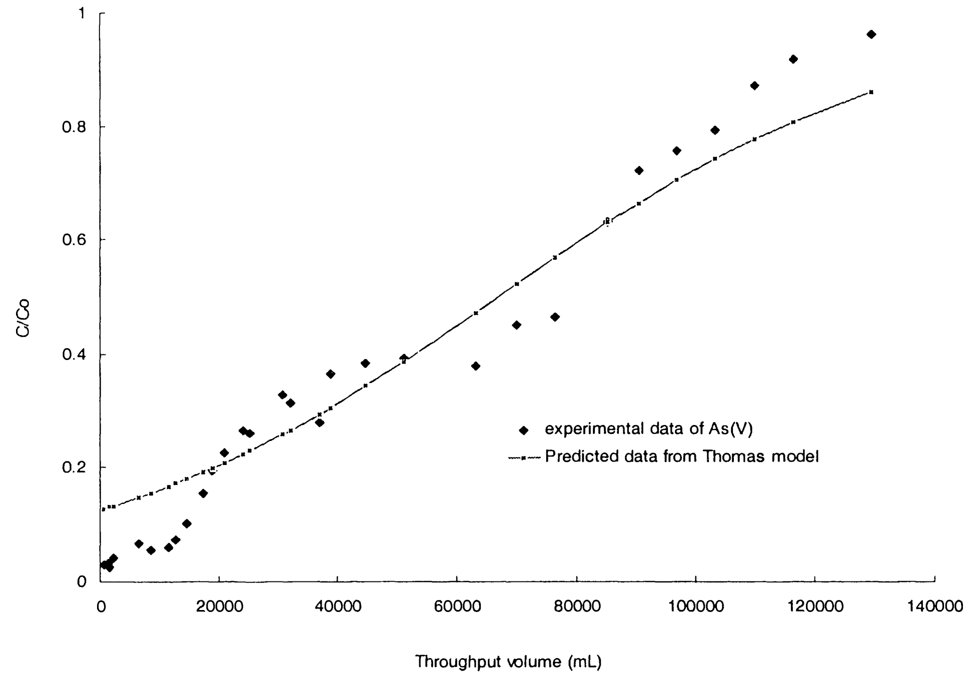


Figure 5.15. Experimental and simulated As(V) profiles by the Thomas model in the SMZ/ZVI column studies

(Initial As concentration = 1,000 μg/L; weight of SMZ/ZVI = 68 g)

5.3.4.2 Nikolaidis modified Model

The experimental data and model simulation curves for As(III) and As(V) are presented in Figures 5.16 and 5.17. The parameters of the model are presented in Table 5.5.

Table 5.5. Parameters of Nikolaidis modified model

No	Parameters	Unit	As(III)	As(V)
1	q_m	mg/g	3.49	3.49
2	k_N	1/s	$7\text{x}10^{-5}$	$7\text{x}10^{-5}$
3	K_d	m^3/mg	$6\text{x}10^{-3}$	$4.5\text{x}10^{-3}$
4	D_x	m^2/s	$10.5\text{x}10^{-5}$	$7\text{x}10^{-5}$
5	r		0.798	0.926

The model could not simulate well the column experimental data. The correlation coefficient 'r' for As(III) description curve was only 0.798. The standard error and squares of deviations were quite high, 0.058 and 0.58 respectivelly. The reason for this was the weak linkage between iron and SMZ in SMZ/ZVI pellets as described above. In the initial stage, as a result, the fraction C/C_o increased quickly, up to 0.22 and then the increased rate was slowed down.

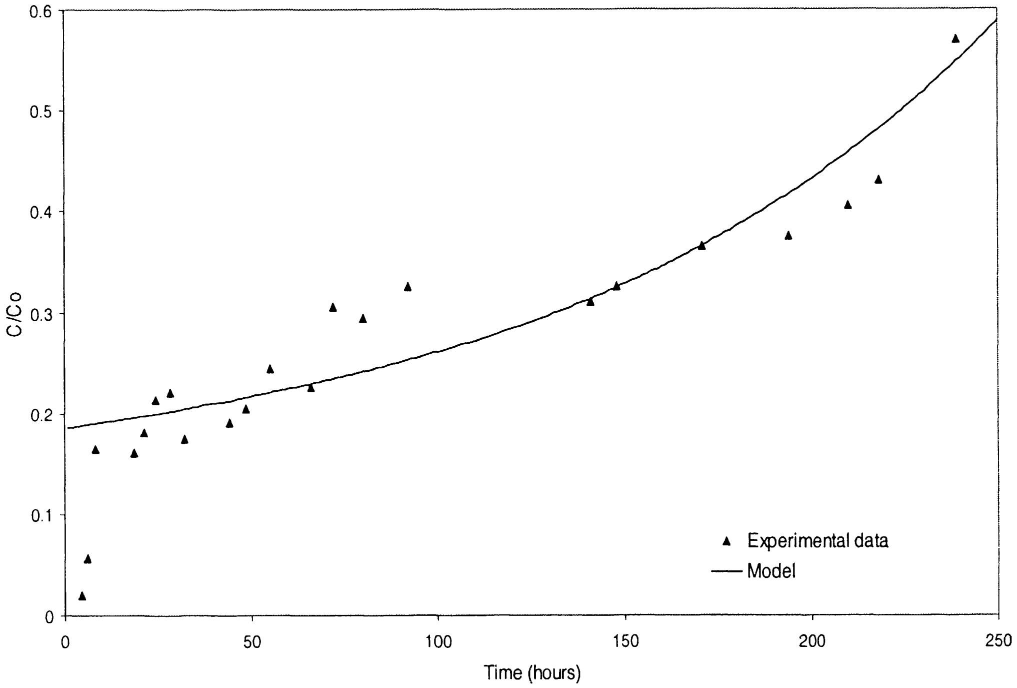


Figure 5.16. Experimental and simulated As(III) values by the Nikolaidis modified model in the SMZ/ZVI column studies

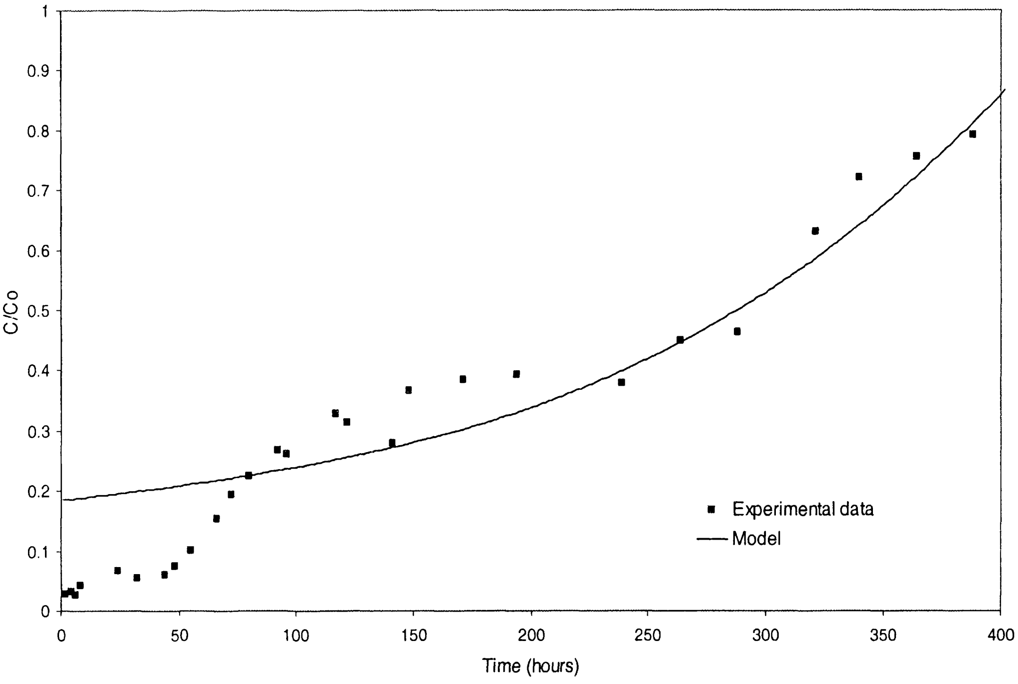


Figure 5.17. Experimental and simulated As(V) values by the Nikolaidis modified model in the SMZ/ZVI column studies

5.4 Conclusions

The results of the study showed that both iron oxide coated sand 2 (IOCS-2) and surfactant modified zeolite/zero valent iron (SMZ/ZVI) could effectively remove arsenic from water (more than 90% for both As(III) and As(V)). The Ho model was found to provide a good description of adsorption kinetics of arsenic on these adsorbents.

Arsenic adsorption by IOCS-2 and SMZ/ZVI is well-described by the Freundlich, Sips and Langmuir isotherms. The removal capacities of IOCS-2 and SMZ/ZVI were 0.051 - 0.062 mg/g and 1.79 - 2.05 mg/g respectively. The results also showed that phosphate present in water is a potential interference in the adsorption reaction of arsenic by SMZ/ZVI.

A filter column system packed with IOCS-2 and SMZ/ZVI led to high arsenic removal efficiency. A column of 68 g of SMZ/ZVI could remove more than 70% of As(III) and 80% of As(V) from the 1,000 μg/L arsenic solution up to a bed volume of 250. A column packed with 90 g of IOCS-2 could treat water containing 260 μg/L with a bed volume of 559 before the effluent arsenic concentration exceeded a value of 50 μg/L. IOCS-2 also can be regenerated by base solutions.

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CHAPTER 6

ARSENIC REMOVAL BY HYBRID PHOTOCATALYSIS AND MEMBRANE FILTRATION SYSTEMS

Chapter 6 Arsenic removal by hybrid photocatalysis and membrane filtration system

6.1 Arsenic removal by photocatalysis

6.1.1 Introduction

Arsenite is more difficult to be removed from water than arsenate because arsenite is present in uncharged form at pH values typical of drinking water. As(III) is typically removed by first oxidizing it to As(V) and then arsenate is removed using adsorption, precipitation, or ion exchange processes. Some of the processes being developed for arsenite oxidation include chemical and solid phase oxidations (Amy, 2000; Ghurye and Clifford, 2001).

Researchers from the Australian Nuclear Science and Technology Organisation (ANSTO, 1999), 1999) found that in the presence of light and naturally occurring light-absorbing materials, the oxidation rate of As(III) by oxygen can be increased ten-thousandfold. Tests showed that almost complete oxidation of As(III) is possible using photochemical processes, preferably in the presence of excess dissolved Fe(II) (iron to arsenic mole ratio: 22:1). Emett et al. (2001) also showed that ultraviolet radiation could catalyse the oxidization of arsenite in the presence of ferric iron by several orders of magnitude. Hug et al. (2001) found that dissolved oxygen and micromolar hydrogen peroxide did not oxidize As(III) on a time scale of hours. The rate of photochemical oxidation of As(III) in irradiated ferrioxalate solutions was found to decrease with increasing pH (Kocar et al., 2003).

Titanium dioxide (TiO_2) was used as a catalyst in the photooxidation of As(III) to As(V). Bissen et al. (2001) found that nanoparticulate suspensions of TiO_2 illuminated with UV light could oxidize As(III) to As(V) in less than three minutes. Lee and Choi (2002) shown that photo-oxidation by suspensions of TiO_2 effectively oxidizes As(III) to As(V). One of the drawbacks of this method is that it can be difficult to separate the treated solution and the particulate TiO_2 photocatalyst. An alternative approach is to immobilize the TiO_2 by coating it on a substrate. However, only limited work has been done to verify the feasibility of this technology.

The main objectives of the first part of chapter 6 are as follows:

(1) evaluating the effect of TiO_2 concentration (photocatalyst) on oxidation of As(III) into As(V);

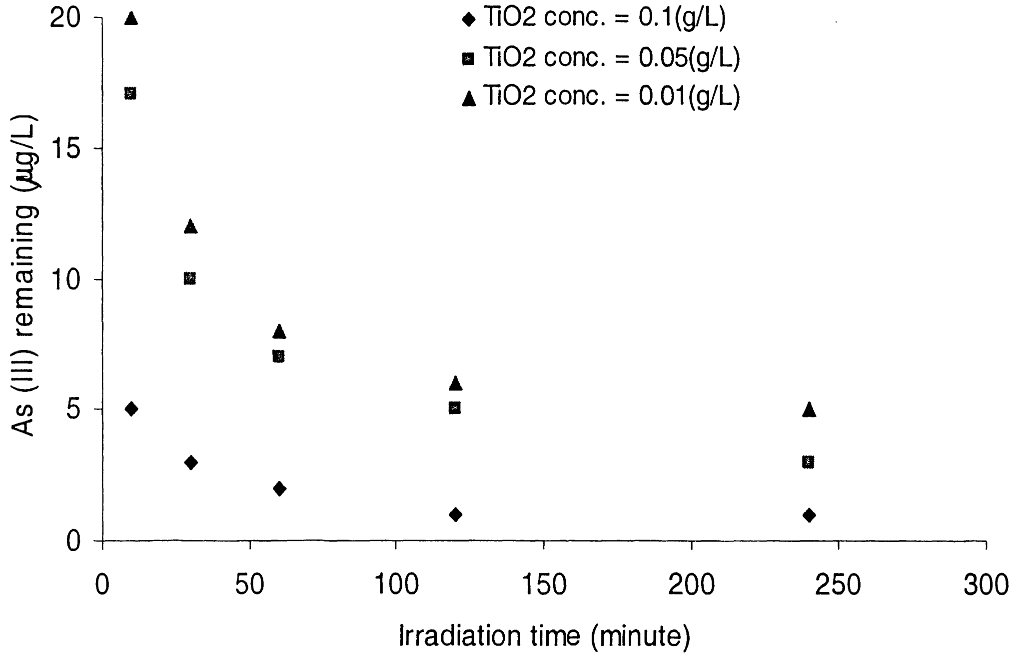
(2) determining the effect of addition of nanoscale zero valent iron on the effectiveness of photo-oxidation reaction of As(III).

6.1.2 Effect of TiO_2 concentration on oxidation of As(III) into As(V)

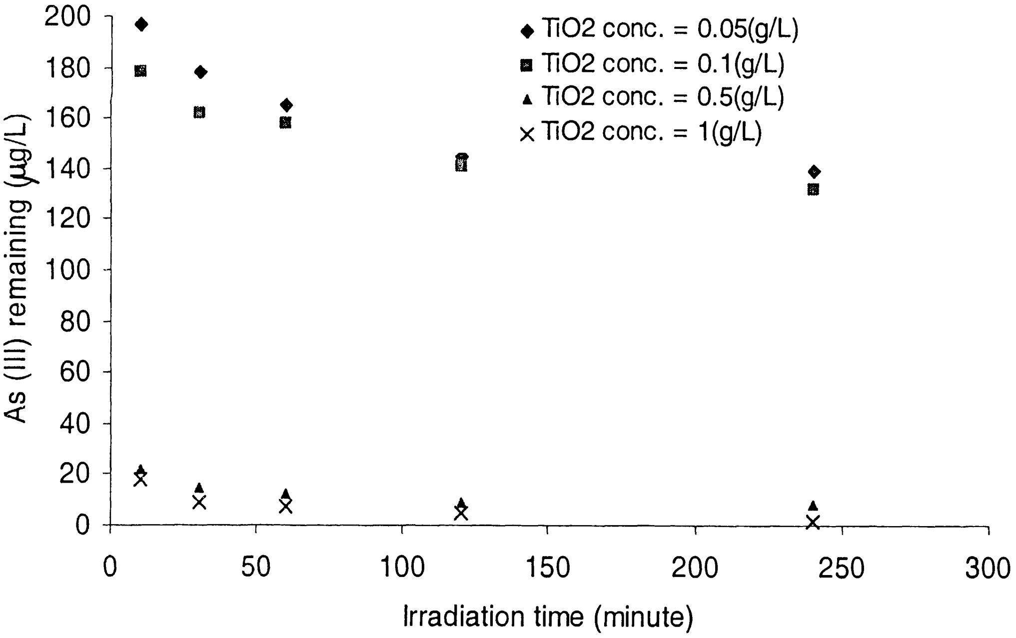
The arsenic removal efficiency of the TiO_2 photocatalysis reaction with As(III) solutions was investigated for different initial As(III) concentrations (100 μg/L to 1,000 μg/L) and different concentrations of photocatalyst of TiO_2 (0.01 to 1 g/L).

Figure 6.1 shows that the concentration of As(III) decreased with the increase in the concentration of TiO_2 and the time of irradiation. For the As(III) solution of low concentration (As(III) = 100 μg/L), 80% (or 80 μg) of arsenic was oxidized during the first 10 minutes of irradiation and adsorbed by 0.01g of TiO_2. The removal efficiency increased further to 95% after 240 minutes of reaction (Figure 6.1(a)).

The amount of 0.05 g of TiO_2 could remove up to 97% arsenic from 1 L As(III) solution containing 100 μg/L after 4 hours reaction whereas the same amount of TiO_2 under the same operating conditions could only remove 72% and 68% arsenic from the influent containing higher concentrations of As(III) of 500 and 1,000 μg/L respectively. When the concentration of TiO_2 was increased to 10 times (0.5 g/L), more than 98% of arsenic was able to be removed from the water containing As(III) at a concentration of 500 and 1,000 μg/L.

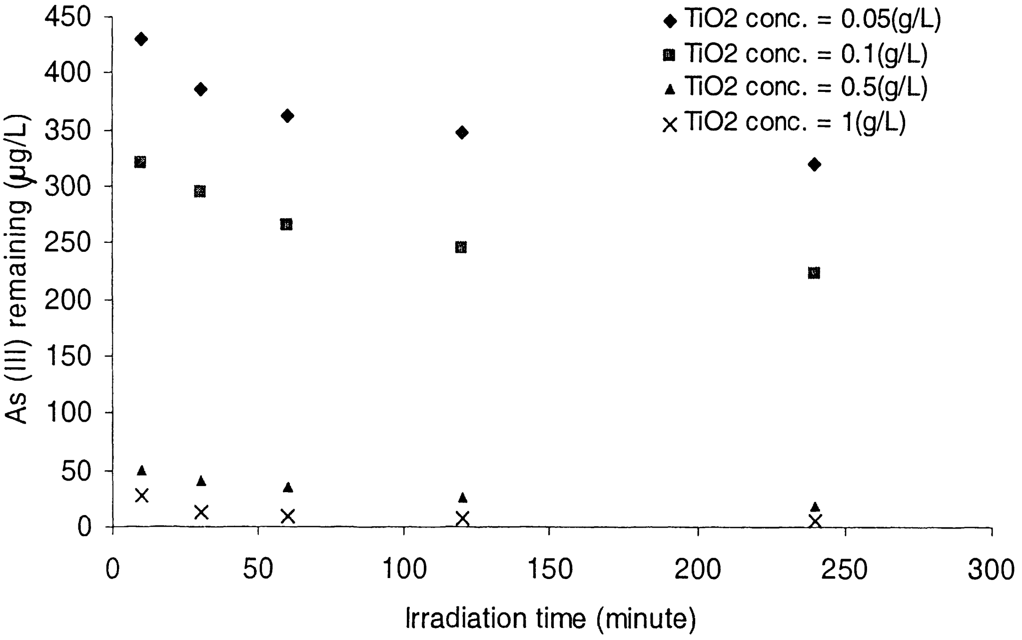


(a) Initial As(III) concentration: 100 μg/L



(b) Initial As(III) concentration: 500 μg/L

Figure 6.1. Arsenic removal efficiency by photocatalysis with TiO_2
(Weight of TiO_2: 0.01 – 1 g/L)



(c) Initial As(III) concentration: 1,000 μg/L

Figure 6.1. Arsenic removal efficiency by photocatalysis with TiO_2 (Weight of TiO_2: 0.01 – 1 g/L)

In these continuous flow photocatalysis experiments, the test solution, containing 1,000 μg/L of As(III), was passed through the photocatalytic column at a flow rate of 70 mL/min (Please refer to section 3.3.5 of Chapter 3 for details of the experiment). After only 10 minutes of reaction, the concentrations of total arsenic in the outflow were measured and their concentrations were around 50 μg/L, with the TiO_2 dose of 0.5 g/L, indicating that about 95% of As(III) had been removed (Figure 6.1(c)). Although the As(III) was assumed to be oxidized to As(V) and then adsorbed on the photocatalyst, some of the As(III) may have been adsorbed directly onto the photocatalyst.

Figure 6.2 shows the evolution of the concentrations of As(III) and As(V) in the arsenic solution. In the presence of the photocatalyst of TiO_2, even at a low TiO_2 concentration of 0.05 g/L, the oxidation of As(III) to As(V) was very fast with more than 95% of arsenite (As(III)) oxidized to arsenate (As(V)) within 10 minutes.

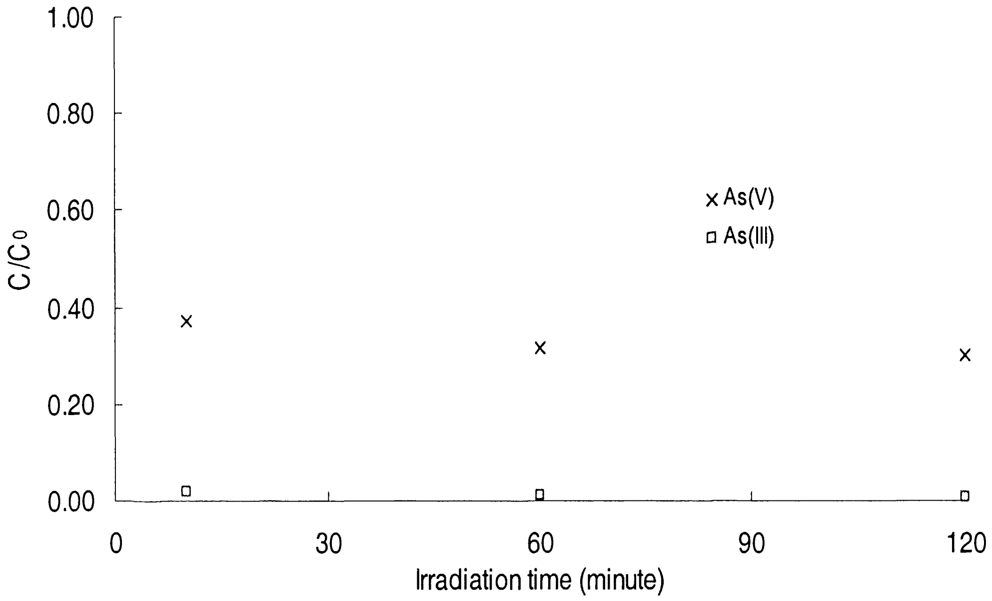
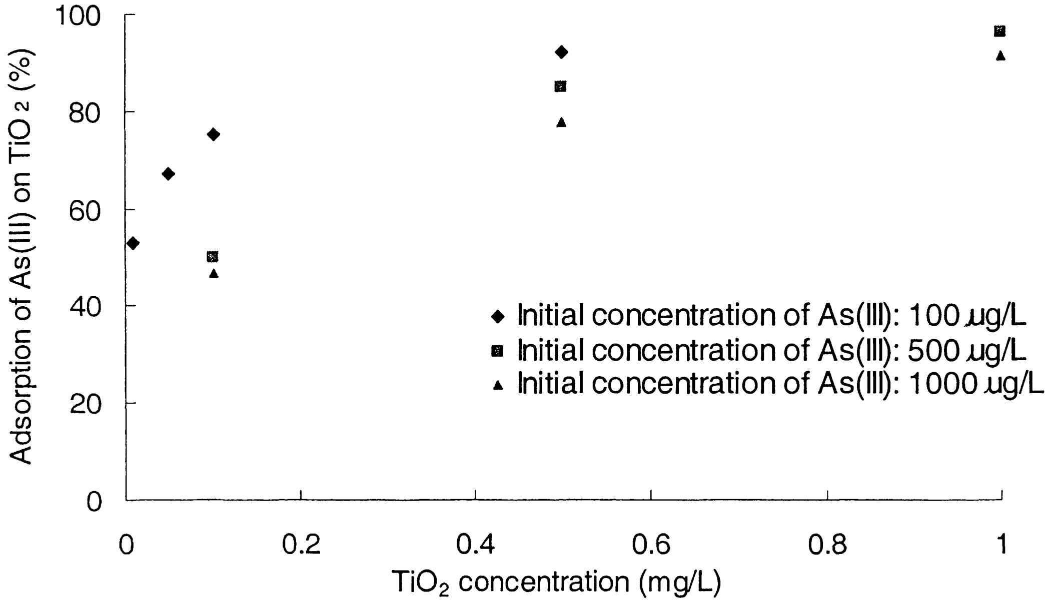


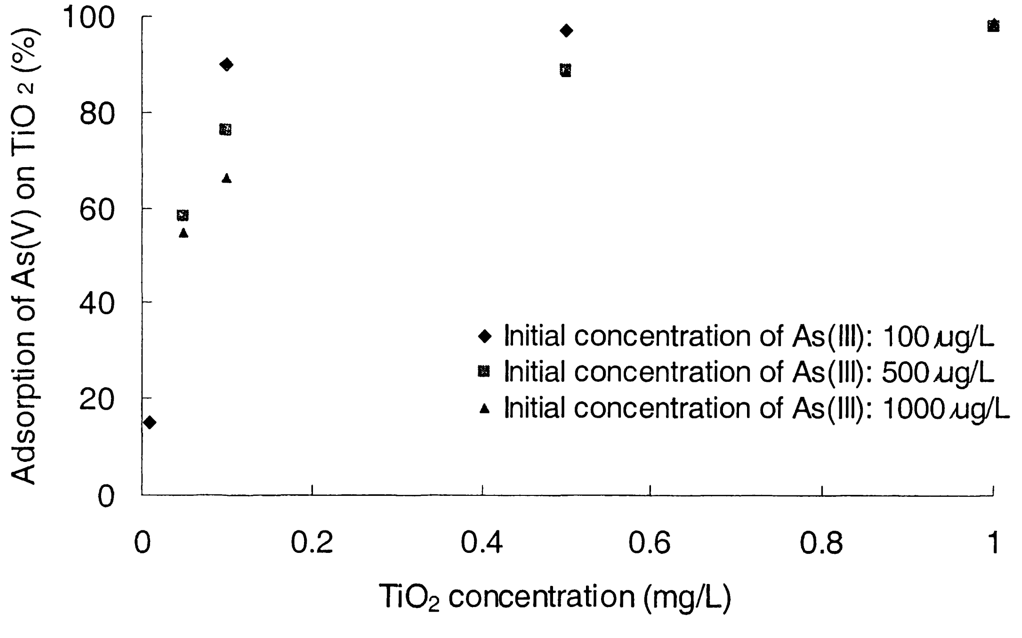
Figure 6.2. Relative concentrations of As(V) and As(III) in the arsenic solution as a function of UV irradiation time
(Initial arsenic (As(III)) concentration (Co): 500 µg/L; TiO_2 concentration: 0.05 g/L)

6.1.3 Adsorption of As(III) and As(V) onto TiO_2

Adsorption experiments were also performed without the use of UV irradiation in order to determine the amount of As(III) and As(V) adsorbed onto the TiO_2 surface. In the tests, arsenite and arsenate were observed to adsorb on the photocatalyst TiO_2. Figure 6.3 shows the amount of As(III) and As(V) adsorbed onto TiO_2 from the solutions of 100 – 1,000 µg/L of arsenic. The TiO_2 concentrations were varied between 0.01 and 1 g/L. The results shows that both As(III) and As(V) were adsorbed on TiO_2 (Figures 6.3(a) and 6.3(b)). The amount of adsorbed arsenic increased with the increase in the amount of TiO_2. Only 47 – 75% of As(III) and As(V) was adsorbed on TiO_2 (with a TiO_2 dose of 0.1 g/L), whereas 91 - 99% of As(III) and As(V) was adsorbed when the dose of TiO_2 was increased to 1 g/L.



(a) Adsorption of As(III) on TiO_2 in the absence of UV irradiation



(b) Adsorption of As(V) on TiO_2 in the absence of UV irradiation

Figure 6.3. Percentage of arsenic adsorbed on the TiO_2 surface (Samples were stirred for 2 hours in the dark).

In general, the percentage of As adsorbed onto the TiO_2 surface decreased with the increase in initial arsenic concentration in the solution. For example, 92% of As(III) and 97% of As(V) were adsorbed onto TiO_2 of 0.5 mg/L from the solution containing 100 μg/L arsenic whereas only 78% of As(III) and 88% of As(V) were adsorbed from the solution containing 1,000 μg/L arsenic. However, the amount of As adsorbed was higher with the increase in As concentration in the solution.

The percentage of arsenate As(V) adsorbed by TiO_2 was higher than that of arsenite As(III) (Figure 6.4). 50% of As(III) was adsorbed onto TiO_2 from 500 μg/L arsenic solution (TiO_2 concentration was 0.1mg/L), whereas in the case of As(V) up to 76% of adsorption was noticed. The reason for a better adsorption of As(V) onto TiO_2 is that it is present in anionic form as $H_2AsO_4^-$, $HAsO_4^{2-}$ whereas As(III) is present as H_3AsO_3.

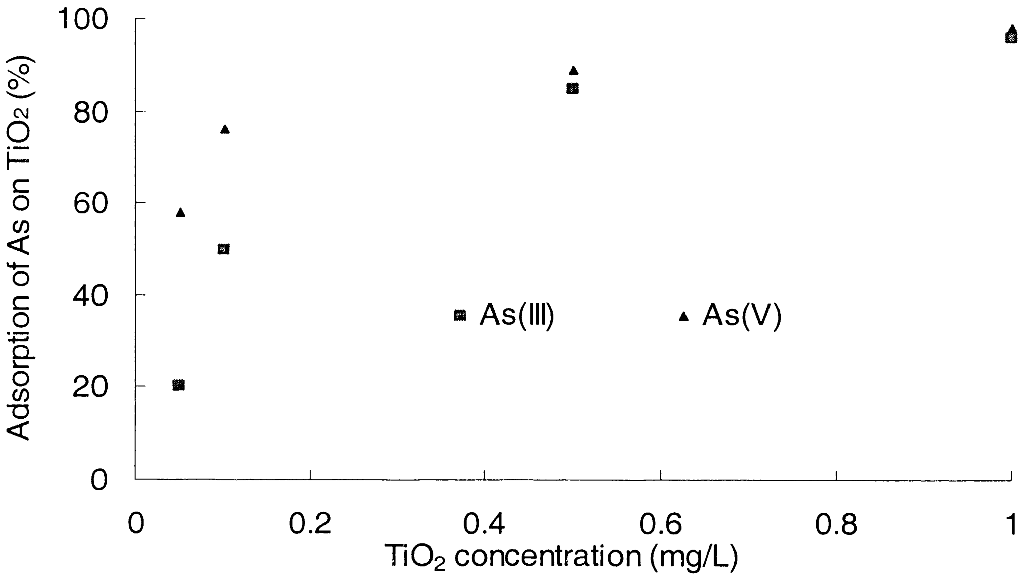


Figure 6.4. Comparison of percentage of As(III) and As(V) adsorbed on TiO_2 surface (Initial arsenic (As) concentration: 500 μg/L, samples were stirred for 2 hours in the dark)

6.1.4 Effect of nanoscale zero valent iron on arsenite removal by photocatalysis

The effect of nZVI on TiO_2 photocatalytic reaction was also studied in the following manner. Solutions containing 500 μg/L arsenite at an initial pH of 7.0 and three different nZVI concentrations (0.05, 0.1, and 0.2 g/L) were recirculated through the continuous flow photocatalytic reactor at the same flow rate of 70 mL/min. The TiO_2 concentration was kept at 0.1 g/L. The results are shown in Figure 6.5.

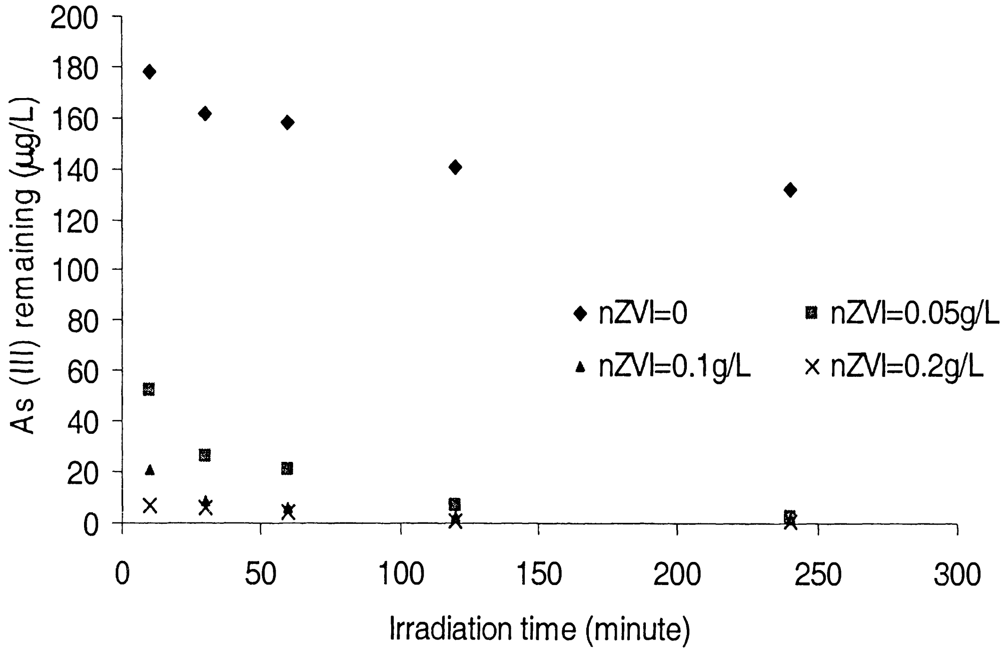


Figure 6.5. Arsenic removal efficiency by photocatalysis with TiO_2 with addition of nZVI (Initial arsenic concentration = 500 µg/L, TiO_2 = 0.1 g/L)

As can be seen from Figure 6.5, the arsenic removal efficiency increased dramatically when nZVI was added into the photocatalytic reactor. This positive effect was noticed even though the addition of nZVI partially prevented the light from reaching and activating the photocatalyst. With the influent arsenic solution of 500 µg/L, even a small amount of 0.05 and 0.2 g/L of nZVI addition could increase the removal efficiency of arsenic from only 64% to 90% and 99% respectively (even within a short irradiation time of 10 minutes). During the first period of reaction (10 minutes), the dose of nZVI had a significant effect on the efficiency of arsenic removal. However, this effect was insignificant with the increase in reaction time. After 2 hours of reaction, the difference of improvement between doses of 0.05 and 0.2 g/L of nZVI was less than 1%.

With the addition of nZVI at a concentration of 0.05 g/L in a photo reactor with a TiO_2 concentration of 0.1 g/L, the observed rate of arsenic photooxidation was similar for the one with a TiO_2 concentration of 0.5 g/L.

6.2 Arsenic removal by membrane

6.2.1 Introduction

A limited number of studies have been performed to examine the removal of arsenic by nanofiltration (NF) (Waypa et al., 1997; Urase et al., 1998, Seidel et al., 2001). A high removal of 96% or more for both As(V) and As(III) was obtained with the thin-film composite Film Tec NF-90 membrane (Waypa et al., 1997). They carried out experiments with an array of different operating conditions and test solution compositions. The high rejection of both arsenic species was attributed to the relatively large molecular weight of the arsenic species (126 g/g-mole for H_3AsO_3 and 140 g/g-mole for $HAsO_4^{2-}$), which controlled their separation by the membrane.

No studies have reported the efficacy of a hybrid system of micro/nanofiltration with in line addition of nZVI on arsenic removal. In this study, experiments were performed using a microfiltration (MF) and nanofiltration (NF) alone and in combination with in – line nanoscale zero valent iron addition.

The membrane experimental set up is described in section 3.3.6 of Chapter 3.

6.2.2 Effect of applied pressure on the membrane filtration

As a first step, arsenic removal by nanofiltration was studied.

Figure 6.6 presents the removal efficiency of arsenic by membrane filtration at different operating pressures. As can be seen from Figure 6.6, arsenic removal efficiency increased slightly with the increase in transmembrane pressure (TMP). The permeate flux increased as the pressure increased, which resulted in lower arsenic concentration in the permeate water. Removal efficiency of As(V) was significantly higher than that of As(III) within the investigated pressure range of 85 to 500 Kpa. For all the six pressure values studied, As(V) removal efficiency was above 80% while As(III) removal was less (which ranged from 54 – 59%). The reason for the difference may be that As(III) is present in a neutral molecular form while As(V) exists in a negatively monovalent form.

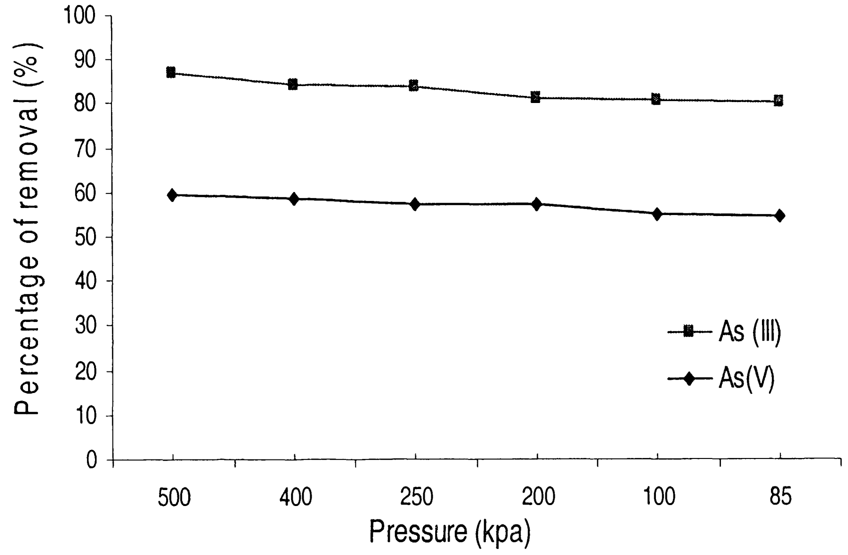


Figure 6.6. Effect of pressure on arsenic removal by NF

(Nanofilter used was NTR729HF, Initial arsenic concentration = 500 μg/L, Samples were collected after 2 hours of operation)

6.2.3 Effect of pH

The effect of pH on arsenic removal by NF is shown in Figure 6.7 as a function of pH. Solutions containing 500 μg/L of arsenic (either as As(V) or As(III)) were used as influent. At all pH levels studied, the removal of As(III) was lower than that of As(V).

The removal of As(III) by the NTR729HF nanofilter membrane is increased slightly with the increase of pH from 5 to 9. This may be due to the fact that the As(III) species remain uncharged at these pH values (i.e., as H_3AsO_3). The decrease in removal of As(V) species was more significant with the decrease in pH (Figure 6.7). Several factors contribute to the decline in removal of the As(V) species with decrease in pH. Firstly, as pH decreases, the speciation of As(V) changes from divalent ($HAsO_4^{2-}$) to monovalent ($H_2AsO_4^-$, $pK_a \sim 6.8$). Monovalent ions are rejected by the NTR729HF membrane at a much lower rate compared to the divalent ions due to the smaller hydrated radius of monovalent ions compared to divalent ions. Secondly, as pH value decreases, the zeta potential of the membrane becomes less negative, and therefore charge exclusion plays a less important role in removal.

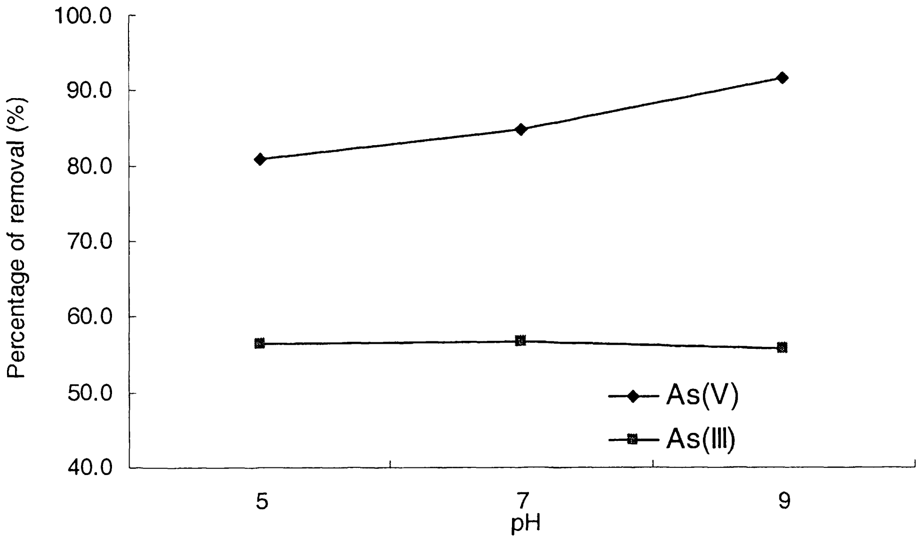


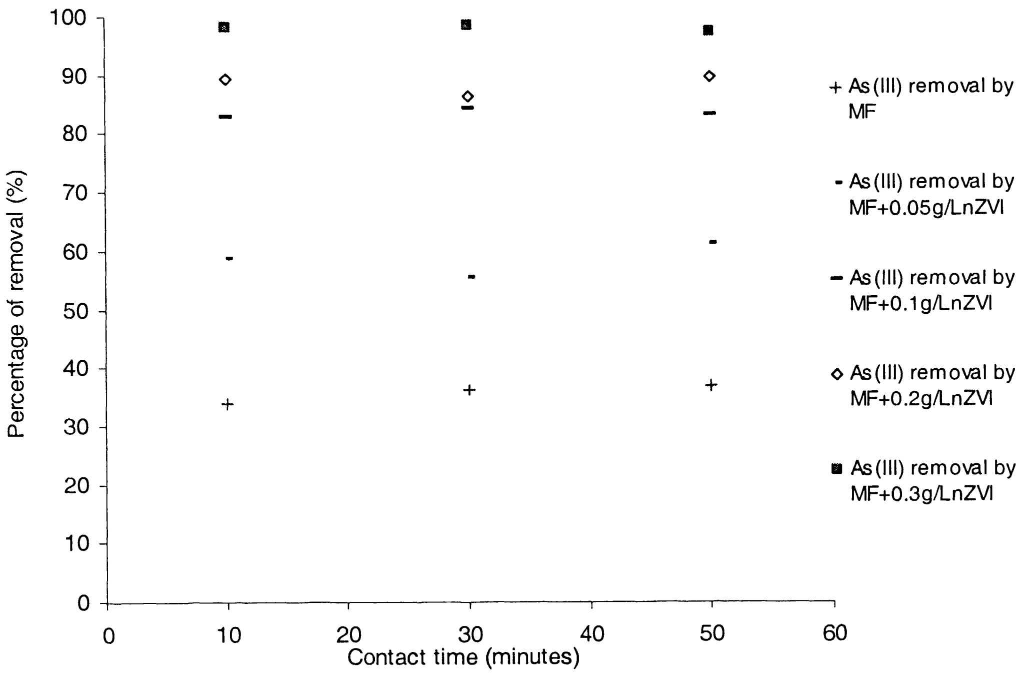
Figure 6.7. Effect of pH on arsenic removal by NF

(Nanofilter used was NTR729HF, Initial arsenic concentration = 500 μg/L, Pressure = 250 kpa, cross flow velocity = 0.72 m/d)

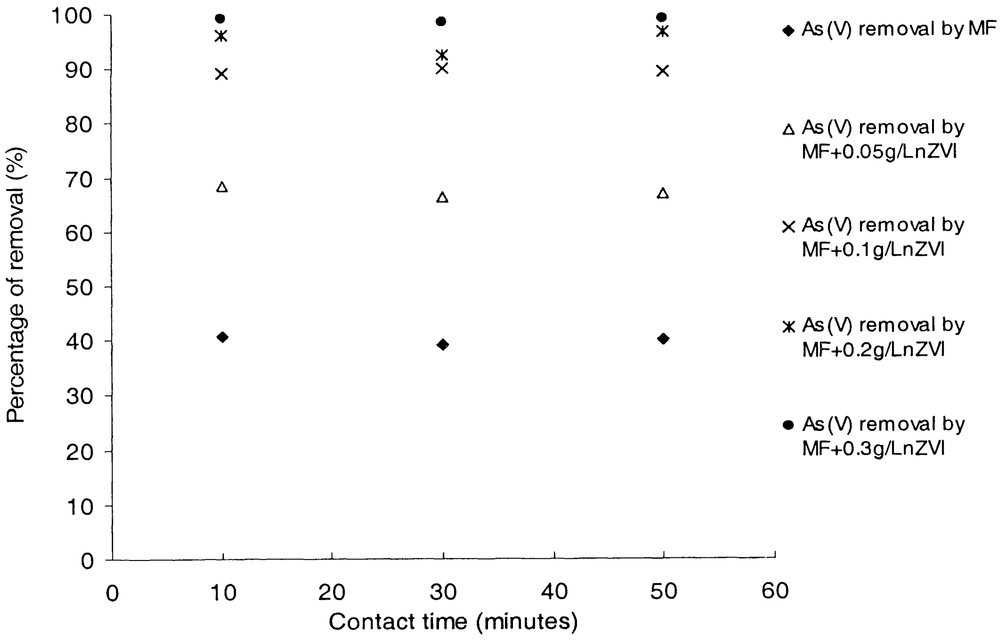
6.2.4 Effect of nanoscale zero valent iron

Figures 6.8 and 6.9 present the removal efficiency of As(III) and As(V) (initial concentration of 500 μg/L) by microfiltration (MF) and nanofiltration (NF) respectively.

As can be seen from Figure 6.8, the removal efficiency of MF alone was low (about 37% with As(III) and 40% with As(V)). The removal efficiency increased dramatically when nanoscale zero valent iron (nZVI) was added into the solution. The removal efficiency of As(V) was slightly higher than that of As(III). The efficiency reached to 90% with As(V) and 84% with As(III) when a small amount of nZVI of 0.1 g/L was added in arsenic solution.



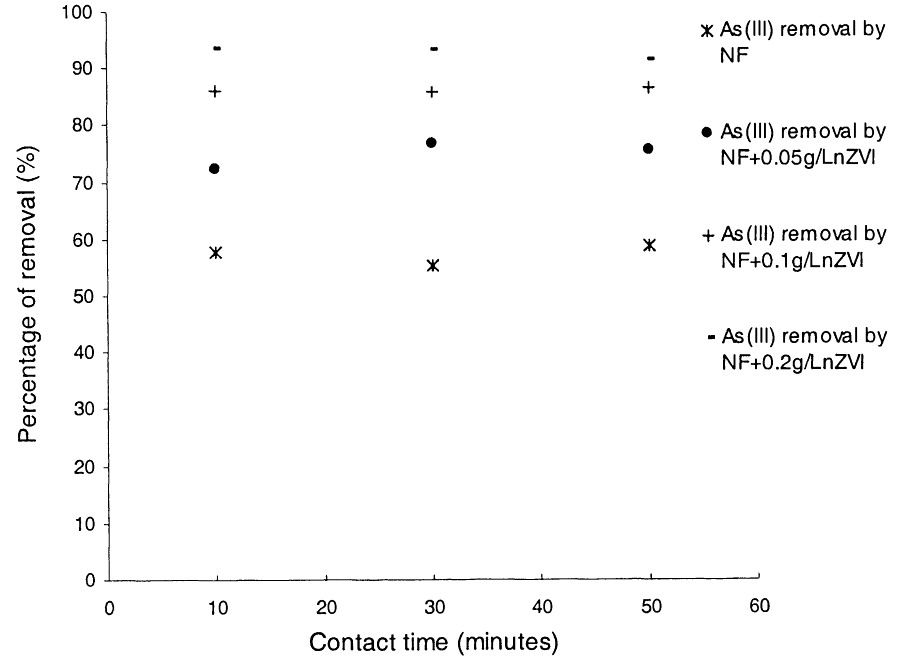
(a). As(III)



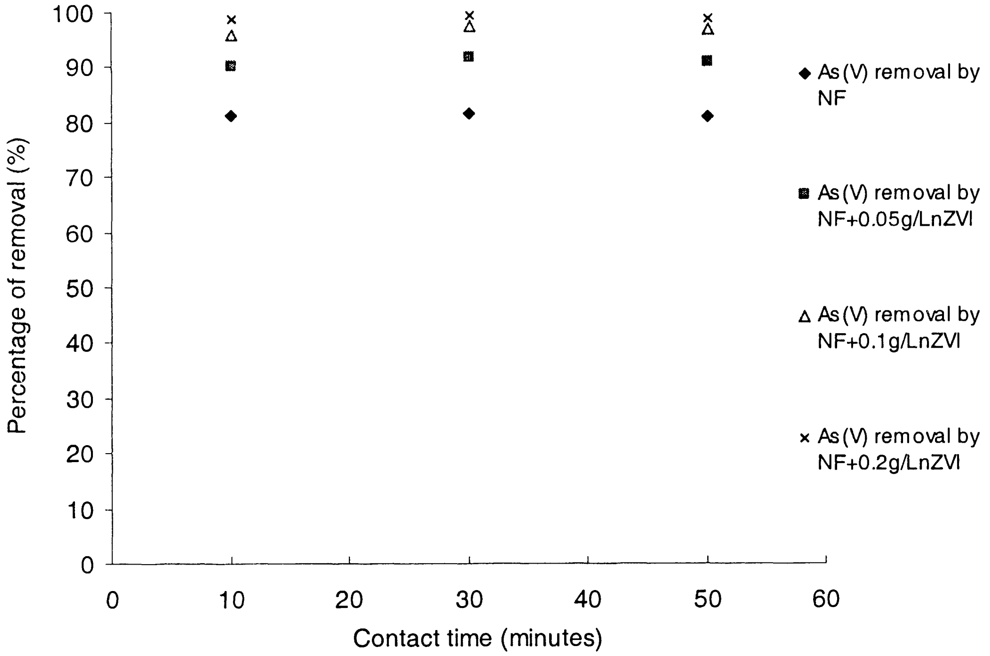
(b). As(V)

Figure 6.8. Arsenic removal efficiency by microfiltration (MF)

(Microfilter used was PVA, Initial As(III) and As(V) concentration = 500 μg/L, Pressure = 10 Kpa)



(a). As(III)



(b). As(V)

Figure 6.9. Arsenic removal efficiency by nanofiltration (NF)

(Reaction conditions: Initial As(III) and As(V) concentration = 500 μg/L, pressure = 200 Kpa, Nanofilter used was NTR729HF)

The use of NF improved the arsenic removal efficiency considerably compared to MF alone. NF alone could remove up to 81% of As(V) and 57% of As(III). The removal efficiency increased to 97% with As(V) and 86% with As(III) when 0.1 g/L of nZVI was added in the solution (Figure 6.9).

The removal efficiency of hybrid systems of NF – nZVI and MF – nZVI in comparison with MF and NF is presented in Tables 6.1 and 6.2 respectively.

Table 6.1. Comparison of removal efficiency of hybrid system MF-nZVI with MF (Microfilter used was PVA, nZVI concentration = 0.1 g/L, As concentration = 500 μg/L)

	Removal efficiency by MF (%)	Removal efficiency by MF-nZVI hybrid system (%)	Improvement of MF-NZVI in comparison with MF alone (%)
As(III)	37	84	47
As (V)	40	90	50

Table 6.2. Comparison of removal efficiency of hybrid system NF-nZVI with NF (Nanofilter used was NTR729HF, nZVI concentration = 0.1 g/L, As concentration = 500 μg/L)

	Removal efficiency by NF (%)	Removal efficiency by NF-nZVI hybrid system (%)	Improvement of NF-NZVI in comparison with NF alone (%)
As(III)	57	86	29
As(V)	81	97	16

The significant improvements in arsenic removal efficiency (16 – 50%) were observed by nZVI – NF and nZVI – MF hybrid systems in comparison with NF and MF systems.

The success of the combination of nZVI and membrane processes in the separation of arsenic in water can be described by the high arsenic adsorption onto nZVI prior to their separation by membranes. The increase in removal is also attributed to the distribution of nZVI on the membrane surface. Thus, it reduces the transport of arsenic through the membrane.

6.3 Conclusions

6.3.1 Photocatalysis

Photooxidation of As(III) to As(V) with TiO_2 as the photocatalyst is possible within a few minutes of irradiation time. TiO_2 can also adsorb both As(III) and As(V) on their surface so the photocatalysis reaction can reduce both arsenics in the water source. By adding the nZVI in the photocatalytic reaction, one can treat the water contaminated by arsenic to an acceptable drinking water standard value.

6.3.2 Membrane hybrid system

Removal of arsenic by membrane depends highly on the species of arsenic and the type of membrane (MF or NF). 81% of As(V) and 57% of As(III) were removed by NF whereas only 37% of As(III) and 40% of As(V) were removed by MF from a arsenic solution of 500 μg/L. Both microfiltration (MF) and nanofiltration (NF) could remove the majority of the arsenic (more than 90%) when a small amount of nZVI was added in the water. This hybrid process of nZVI – MF or nZVI – NF resulted in permeate arsenic concentrations of below 10 μg/L from water containing 500 μg/L. This meets the current standard of WHO and all countries. This method is feasible when high quality effluent is necessary.

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CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

Chapter 7 Conclusions and recommendations

7.1 Conclusions

Due to the problem of arsenic in drinking water, especially in developing countries and small communities, simple, reliable, and economical methods for arsenic removal are becoming more important. The adsorption method is the widely used process for arsenic removal in water treatment. However, the requirement for new adsorbents with high adsorption capacity and low costs is becoming very important. In this study, a new adsorbent material, iron oxide coated sponge, was developed and investigated in detail for its capacity to remove arsenic from water. In addition, other media, including iron oxide coated sand 2 (IOCS-2) and surfactant modified zeolite – zero valent iron (SMZ/ZVI), were also tested for their arsenic removal capability. The advantages of combining nanoscale zero valent iron with photocatalysis and membrane processes in removing arsenic were also investigated.

7.1.1 Iron oxide coated sponge (IOCSp) for arsenic removal in water treatment

General

- Sponge could be coated in an optimum manner by iron oxide under the following conditions: pH value of 4, time of contact between iron oxide and the sponge during coating of 10 hours; coating temperature of 110°C; and time of drying of sponge after the coating of 20 hours. Results showed that IOCSp had a high iron content (12% w/w) which facilitates the removal of arsenic. Based on the color of iron oxide, it was assumed that the iron oxide coating on the sponge might be a combination of goethite and haematite.
- IOCSp exhibited a high arsenic removal capacity during both the batch and dynamic (column) experiments.
- The IOCSp was found to be an excellent adsorbent for arsenic removal. The IOCSp filter can be a good practical solution for improving the arsenic

removal from water as IOCSp filter has high removal efficiency, long life cycle, and simplicity in operation and regeneration.

Batch experiments

- The maximum adsorption capacity of IOCSp (4.6mg arsenic/g IOCSp) was much higher than the other adsorbents such as nanoscale zero valent iron (3.5 mg/g), surfactant modified zeolite/zero valent iron (1.1 mg/g), activated red mud (0.87 mg/g), iron oxide impregnated activated alumina (0.734 mg/g), ferruginous manganese ore (0.680 mg/g), red mud (0.66 mg/g), activated alumina (0.180 mg/g), and granular ferric hydroxide (0.11 mg/g).

Column experiments

- The IOCSp filter yielded consistent arsenic removal efficiency for a long period of time. A 4.5 cm diameter column of 78 cm IOCSp bed depth packed with 25 g of IOCSp maintained about 95% arsenic removal from synthetic water at a filtration rate of 0.17 m/h. This filter produced more than 153 L and 178 L of clean water from synthetic water containing 1,000 μg/L of As(III) and As(V) respectively. An IOCSp filter (with a diameter of column of 2 cm, bed depth of 65 cm, IOCSp amount of 8 g, and a filtration rate of 1.5 m/h) could reduce arsenic from 156 μg/L to a concentration of less than 50 μg/L while treating 75 L of groundwater contaminated with arsenic.

- The rate and amount of arsenic adsorbed onto IOCSp were affected by the operating conditions such as filtration velocity and size of IOCSp etc. Smaller size of IOCSp led to better arsenic removal. Decrease in filtration velocity also resulted in higher arsenic removal.

- The removal efficiency of the IOCSp tray system was much lower than IOCSp filter system due to short contact time between water and IOCSp (2 – 3 minutes) and unequal distribution of water in the tray.

- IOCSp could be regenerated by washing it with 0.3M NaOH solution and the regenerated IOCSp did not have any significant decrease in arsenic removal efficiency as compared to the fresh IOCSp.

Mathematical models

- Adsorption kinetics of arsenic on IOCSp could be described well by the Ho model. Equilibrium arsenic concentration on IOCSp was fitted successfully using Freundlich, Langmuir, and Sips isotherm equations. The dynamic (column) adsorption kinetics were successfully predicted by the Thomas and Nikolaidis modified models.

7.1.2 Performance of iron oxide coated sand (IOCS-2) and surfactant modified zeolite – zero valent iron (SMZ/ZVI) in arsenic removal

- As(III) and As(V) removal by IOCS-2 and SMZ/ZVI fitted well with the Sips and Langmuir isotherms. The arsenic removal capacity of IOCS-2 was only 0.051 - 0.062 mg/g while that of SMZ/ZVI was 1.79 - 2.05 mg/g.
- Iron oxide coated sand (IOCS-2) and surfactant modified zeolite/zero valent iron (SMZ/ZVI) provided an good removal (more than 90%) of both As(III) and As(V). The Ho model was found to provide a good description of adsorption kinetics of arsenic on IOCS-2.
- Column experimental results indicated that both IOCS-2 and SMZ/ZVI were able to remove As(III) and As(V) to a value less than 50 μg/L. However, IOCS-2 performed better than SMZ/ZVI in terms of bed volumes achieved. IOCS-2 also can be regenerated by base solutions.

7.1.3 Hybrid systems of photocatalysis and membrane filtration with nanoscale zero valent iron (nZVI)

- TiO_2 can also adsorb both As(III) and As(V) on their surfaces and photooxidation of As(III) to As(V) with titanium dioxide (TiO_2) as a photocatalyst is possible within minutes. The photocatalysis reaction with TiO_2 can reduce arsenite concentration to less than 10 μg/L from an arsenite solution of 500 μg/L. Nanoscale zero valent iron can be combined with photocatalysis to improve the effectiveness of this process. The combination of nZVI with photocatalysis can help in improving the quality of treated water. By adding nanoscale zero valent iron (nZVI) of 0.05 g/L in the photo reactor, the photocatalysis hybrid system can remove 97% of arsenite where the amount of TiO_2 was only 0.1 mg/L, 5 times less than a normal photocatalysis system.

- Properties of membranes and species of arsenic affect the arsenic removal efficiency by membrane filtration. Nanofilter (NTR729HF, 700 molecular weight cutoff) could remove 57% of As(III) and 81% of As(V) from 500 μg/L arsenic solution whereas the microfilter (PVA, pore size of 0.4 μm) removed only 37% of As(III) and 40% of As(V).
- Arsenic removal efficiency of a membrane hybrid system could reach more than 98% by an inline addition of 0.3 g/L of nZVI. However, these processes are still expensive and only suitable when high quality water is needed.

7.2 Recommendations

- The handling of waste after the adsorption process is very important to prevent the spreading of toxicants into the environment. Safe disposal of exhausted IOCSp containing arsenic is very necessary. Encapsulation of exhausted IOCSp through the solidification/stabilization technique can solve the waste disposal problem. An experiment on solidification/stabilization of IOCSp with cement is being carried out. If successful, this simple method can help in managing the disposal of waste in an inexpensive and safe way.
- Although iron oxide coated sponge can adsorb significant amount of arsenic in water, the procedure of coating is still quite complicated. To resolve this problem, supplies procedure of coating should be studied. The possibility of incorporation of a larger amount of iron oxide into the structure of the sponge should be investigated.
- Experiments with different initial arsenic concentrations, filtration rates and heights of filter with adsorbents and a pilot scale studies with IOCSp should be carried out to study the effect of these parameters on the adsorption behavior of adsorbents.

- In addition, the influence of other components in water such as phosphate, silicate, hardness, and ionic strength on arsenic removal should be investigated to estimate the effect of other components on arsenic removal capacity.
- Detailed pilot scale experiments on the hybrid systems of nZVI-photocatalysis and nZVI-membrane are necessary to modify the hybrid systems and optimize the design and operational conditions.
- An industrial coating process for producing iron oxide coated sponge should be established.
- The calculation for the cost (including cost of disposal and social context) should be conducted in the future studies so that a truly sustainable (engineering, economic, social and environmental) method could have been chosen

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Appendix A

SIMPLE DESIGNS FOR REMOVING ARSENIC FROM GROUNDWATER

Appendix A

Simple designs for removing arsenic from water

Many households still lack safe drinking water. Some of them have groundwater containing arsenic. To remove arsenic from water, following are some simple treatment configurations, which use iron coated sponge (IOCSp) as absorbent.

1. Aeration - IOCSp filter hybrid system

This system can be used for groundwater containing both arsenic and high concentrations of iron and/or manganese. This design provides aeration, helps to oxidize ferrous iron and manganese to higher oxidation states and immobilizes these elements as precipitates. This method not only removes iron and manganese (which cause taste and smell problems if present in excess quantity in water) but also improves arsenic removal by iron or manganese oxide formed during the aeration/oxidation. A network of lateral piping is laid above the tank surface. The small diameter orifices made in the pipe at uniform intervals distribute the effluent uniformly over the bed packed with IOCSp. The sand layer underneath the IOCSp layer prevents the passage of IOCSp with effluent and retains (filters out) the iron and manganese precipitation. The gravel layer prevents the sand escaping into effluent and helps to achieve uniform flow of effluent throughout the cross-section of the filter.

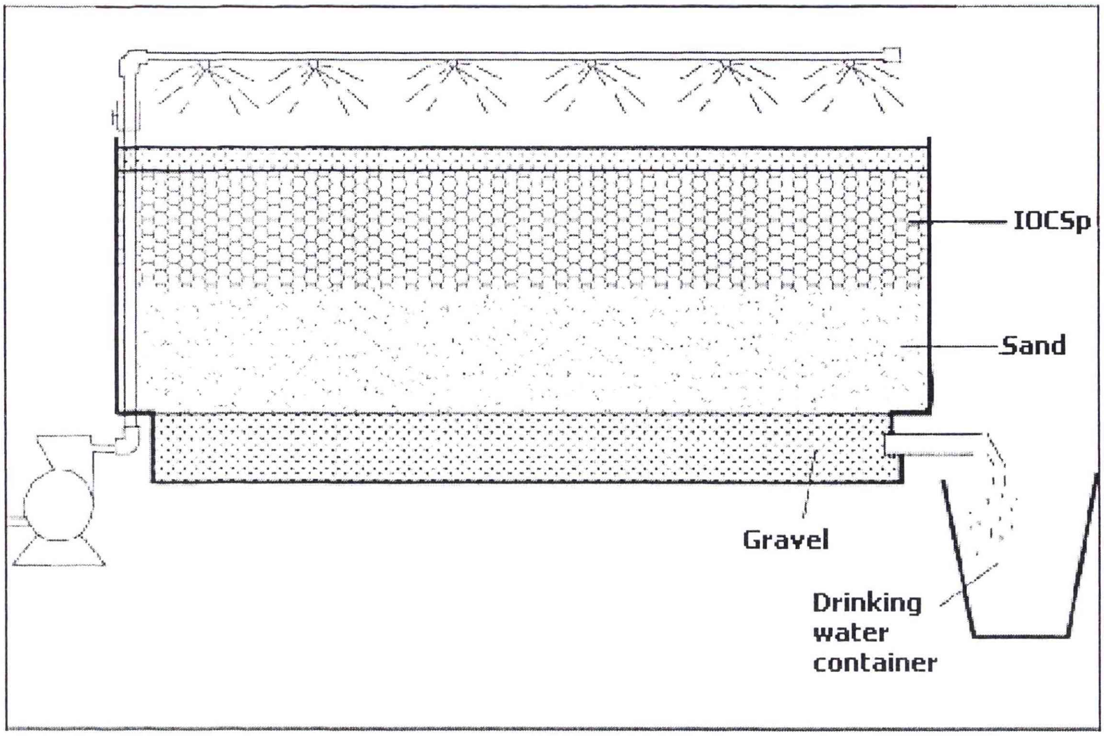

Figure A1. Schematic of a hybrid system of aeration - IOCSp filter

The filter needs to be backwashed regularly, depending on the turbidity and oxidised iron precipitate concentration in the water and the amount of spare water available for flushing.

Based on the experimental results of IOCSp with natural water, a tank with a dimension L x W x H = 1.4 x 0.8 x 1.3 m (the depths of IOCSp and sand are 0.8 and 0.2 m respectively) packed with 18 kg IOCSp can remove arsenic from 170 m^3 water (initial arsenic concentration of 160 μg/L) to an acceptable level of 50 μg/L (standard level for drinking water in most of developing countries). Assuming a drinking water demand per head of 30 liters/day, the above tank can supply the drinking water source for a small community of 25 households for about 2 months (an average of 4 people per household is assumed).

2. Low rate IOCSp filter system for high concentration of arsenic

In the low rate IOCSp filtration system, the water flows slowly through a bed packed with IOCSp (depth of 0.8 m), fine sand and gravel (depths of 0.2 m) at a slow constant rate (0.15 m/h) (Figure A2). This system is suitable for water, which is relatively low in turbidity and has low concentrations of iron and/or manganese.

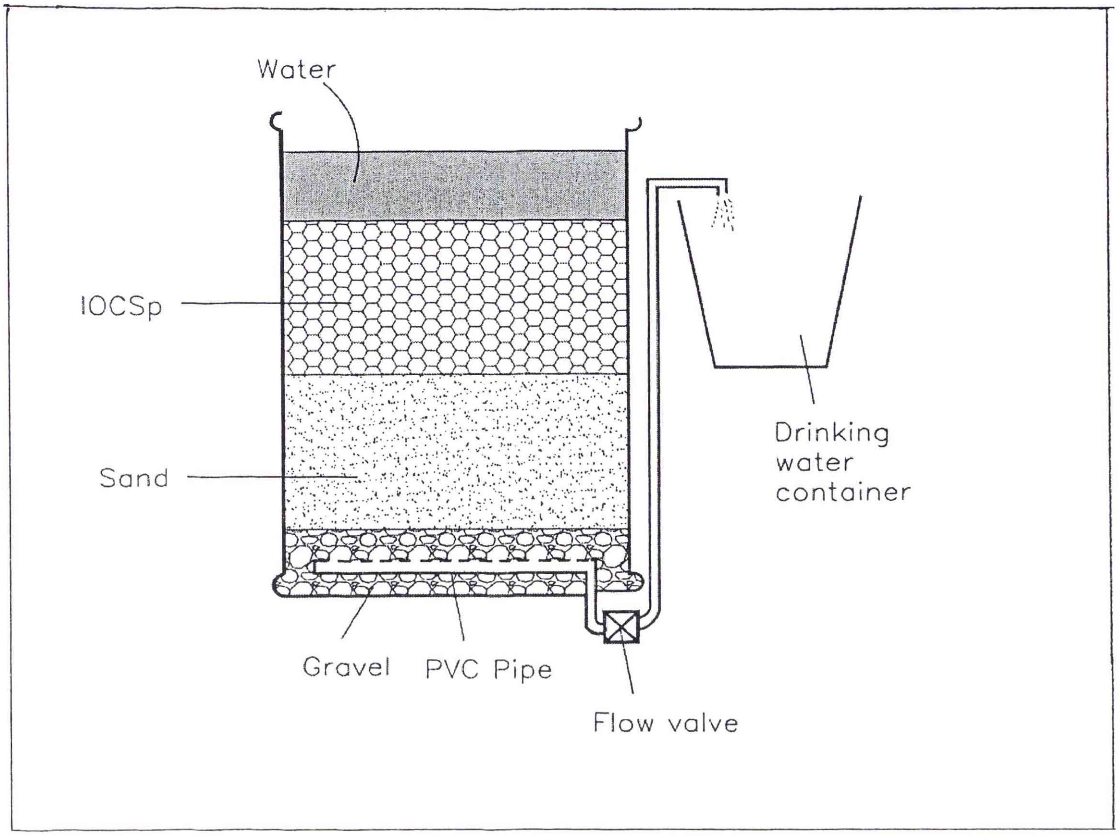

Figure A2. Schematic of low rate IOCSp filter

A tank with the same dimension L x W x H = 1.4 x 0.8 x 1.3 m can be used to treat an amount of 110m^3 water contaminated as high as 1,000 µg/L arsenic to a value below 50 µg/L. This system is suitable for a small community water supply for 20 families and can operate for one and a half months before IOCSp need to be changed.

Figure A3 presents a schematic of an IOCSp filter in series. The system uses at least two IOCSp filters. The first container is the feed tank. After one day of detention, when sediments have already settled down, the supernatant water is led into the second container (IOCSp filter) where arsenic is removed. The clean water which is relatively free from arsenic from the first filter, flows under gravity into the third tank. Since the arsenic concentration in the water may vary, sometimes being thousands ppb, the treatment system is equipped with additional IOCSp filters (2 or more, depending on the initial arsenic concentration and effluent quality standard).

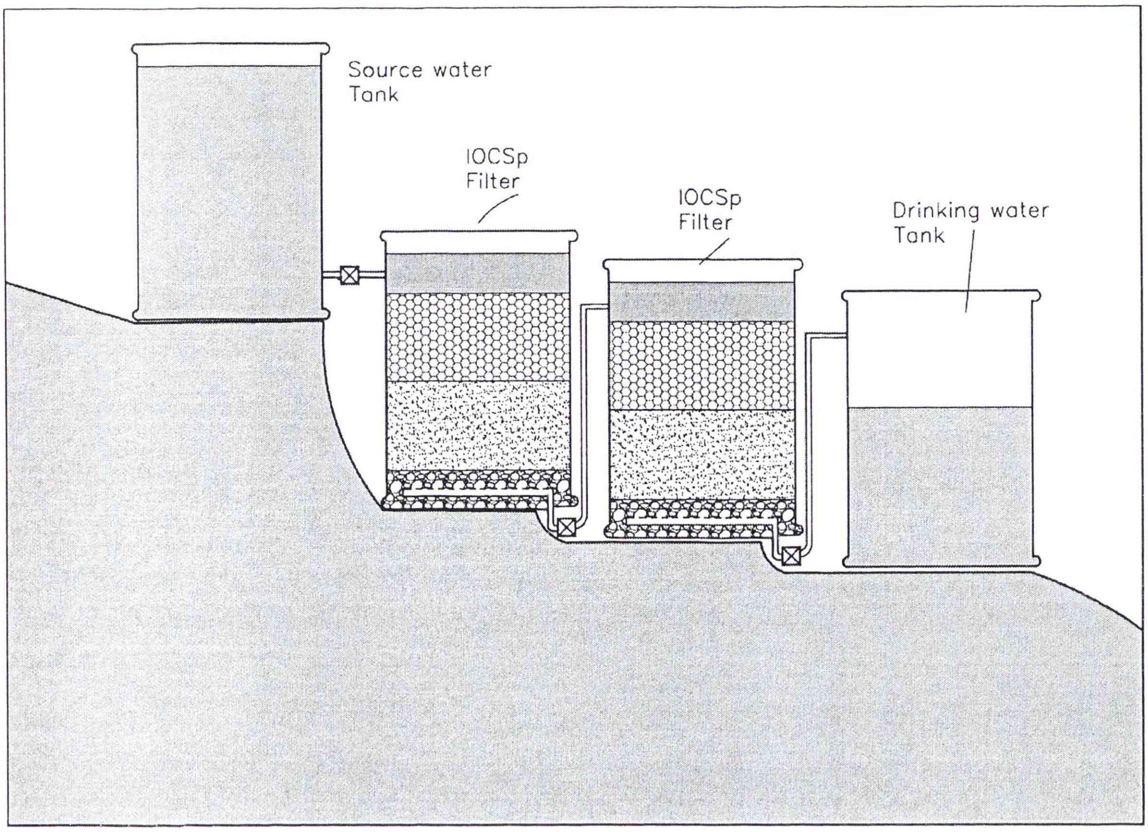

Figure A3. Scheme of slow IOCSp filter

PVC pipes or brick tanks can be used to construct the filter system. The filter is also equipped with PVC underdrain pipes.

This system is suitable for a small community water supply scheme rather than for a single household use.

3. Portable IOCSp filter system

The proposed portable IOCSp filter below (Figure A4) is simply a container of IOCSp packed in perforated metal cage. A sand layer is provided below the IOCSp medium to ensure uniform flow of filtered water through the filter. The filtration rate can be as high as 0.5 m/h.

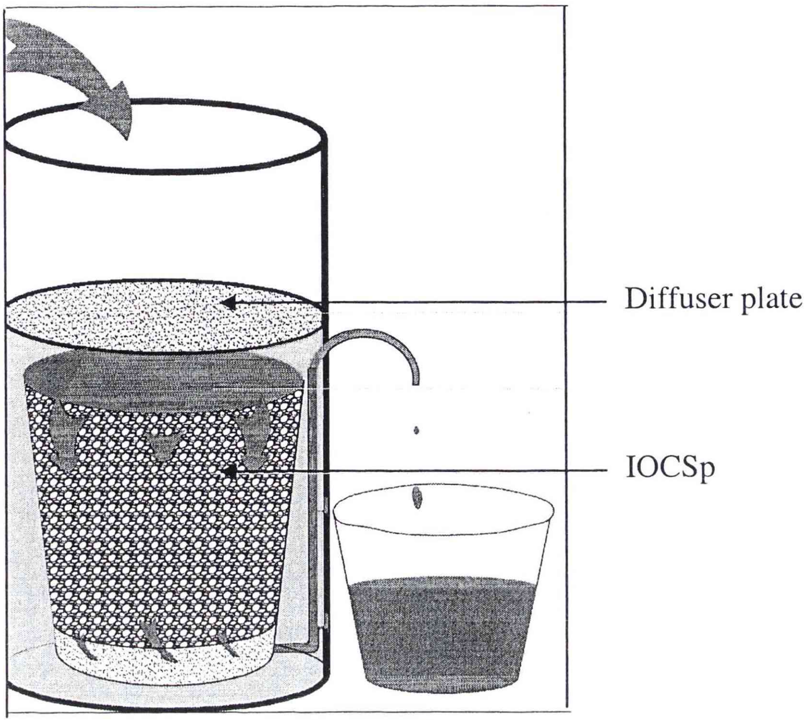

Figure A4: Schematic of portable IOCSp filter

A small container with a diameter of 9 cm and height of 30 cm (the depths of IOCSp and sand are 20 and 5 cm respectively) containing 25 g IOCSp can treat more than 250 L water containing arsenic of 260 μg/L to below 50 μg/L. This small container can provide enough water for a household (4 people) in two days.

Advantages of the system:

- Is within control of the users - the family
- Reduces suspended solids
- Provides consistent final water quality
- Low operating cost
- Does not require complex infrastructure
- Is suitable for rural households
- Is easy to use and to maintain
- Is affordable

- Is a good solution in terms of efficacy, cost effectiveness, returns and sustainability

Limitations:

- Possible bacterial contamination.
- Uncertainty on the frequency of IOCSp replacement as the household cannot measure the arsenic concentration.

Appendix B

EXPERIMENTAL DATA

Table B.1. Treat As(III) by IOCSp - kinetics experiment

Influent As(III): 260 μg/L, Volume of arsenic solution: 100 mL, IOCSp: 0.15g

No	T (h)	pH = 8		pH = 7		pH = 6	
		As concentration (μg/L)	Removal efficiency E (%)	As concentration (μg/L)	Removal efficiency E (%)	As concentration (μg/L)	Removal efficiency E (%)
1	0.5	-	-	116.8	55.1	-	-
2	1	93.2	64.2	86.2	66.8	91.1	65
3	2	65.6	74.8	72.4	72.2	60.2	76.8
4	3	50.5	80.6	58.2	77.6	44.8	82.8
5	4	39.8	84.7	43.6	83.2	29.3	88.7
6	5	34.4	86.8	39.8	84.7	25.5	90.2
7	6	31.7	87.8	32.5	87.5	19.4	92.5
8	7	22.8	91.2	28.7	89	17.8	93.2
9	8	18.8	92.8	23	91.1	15.4	94.1
10	9	11.9	95.4	19.7	92.4	13.7	94.7

Table B.2. Treat As(V) by IOCSp - kinetics experiment

Influent As(V): 260 μg/L, Volume of arsenic solution: 100 mL, IOCSp: 0.15g

No	T (h)	pH = 8		pH = 7		pH = 6	
		As concentration (μg/L)	Removal efficiency E (%)	As concentration (μg/L)	Removal efficiency E (%)	As concentration (μg/L)	Removal efficiency E (%)
1	0.5	-	-	136.4	47.5	-	-
2	1	101.5	61	95.4	63.3	137	47.3
3	2	81.2	68.8	84.2	67.6	56.5	78.3
4	3	53.5	79.4	62.4	76	44.5	82.9
5	4	45.2	82.6	48.5	81.4	31.4	87.9
6	5	33.8	87	36.4	86	27.3	89.5
7	6	29.6	88.6	31.6	87.8	18.1	93
8	7	22.9	91.2	25.1	90.4	17.8	93.2
9	8	22	91.5	20.3	92.2	13.6	94.8
10	9	17.9	93.1	18.2	93	10.5	96

Table B.3. Treat As(III) by IOCSp - isotherm experiment

Contact time = 20 hours, mixing rate = 130 rpm, temperature = 22^0C, Volume of arsenic solution = 100 mL

No	IOCSp weight (g)	As final concentration
1	0	5559
2	0.180	4969
3	0.327	4503
4	0.760	3439
5	0.109	2683
6	0.183	1775
7	0.441	429
8	0.650	81
9	0.813	69
10	1.296	32

Table B.4. Treat As(V) by IOCSp - isotherm experiment

Contact time = 20 hours, mixing rate = 130 rpm, temperature = 22^{0}C, Volume of arsenic solution = 100 mL

No	IOCSp weight (g)	As final concentration
1	0	5316
2	0.185	4672
3	0.334	4200
4	0.756	3152
5	0.109	2550
6	0.182	1488
7	0.441	305
8	0.651	66
9	0.813	48
10	1.295	19

Table B.5. Column study data for arsenic removal using IOCSp

Short term, filtration rate: 1.5 m/h

Initial arsenic concentration: 260 μg/L, weight of IOCSp: 10 g

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	1	480	1
2	2	960	1
3	4	1920	1
4	12	5760	1
5	20	9600	2
6	24	11520	2
7	30	14400	3
8	36	17280	1
9	49	23520	1
10	58	27840	3
11	66	31680	5
12	78	37440	12
13	86	41280	21
14	99	47280	32
15	104	49920	39
16	111	53280	54
17	123	59040	57

Table B.6. Column study data for arsenic removal using IOCSp

Short term, filtration rate: 3 m/h

Initial arsenic concentration: 260 μg/L, weight of IOCSp: 10 g

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	0.5	480	1
2	2	1920	2
3	4	3840	2
4	8	7680	2
5	12	11520	3
6	16	15360	5
7	20	19200	6
8	26	24960	6
9	32	30720	24
10	36	34560	30
11	40	38400	32
12	48	46080	37
13	56	53760	40
14	60	57600	78
15	66	63360	95

Table B.7. Column study data for As(III) removal using fresh IOCSp

Long term, filtration rate: 0.17 m/h

Initial arsenic concentration: 1,000 μg/L, weight of IOCSp: 25 g

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	24	6480	1
2	32	8640	1
3	48	12960	1
4	56	15120	2
5	72	19440	3
6	96	25920	3
7	120	32400	4
8	144	38880	4
9	168	45216	2
10	192	51552	3
11	216	57888	4
12	240	64224	2
13	264	70560	4
14	315	84024	7
15	336	89568	6
16	367	97752	9
17	384	102240	10
18	413	109896	10
19	437	116232	18
20	480	127584	16
21	504	133920	26

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
22	528	140256	34
23	552	146592	38
24	576	152928	48
25	600	159264	68
26	624	165600	78
27	648	171936	86
28	672	178272	116
29	696	184608	128
30	720	190944	134
31	744	197280	158
32	768	203616	167
33	795	210744	185
34	840	222624	222
35	864	228960	264
36	888	235296	280
37	912	241632	298
38	942	249552	309
39	984	260904	356
40	1009	267234	384
41	1032	273312	390

Table B.8. Column study data for As(V) removal using fresh IOCSp

Long term, filtration rate: 0.17 m/h

Initial arsenic concentration: 1,000 μg/L, weight of IOCSp: 25 g

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	48	12936	1
2	74	19776	1
3	97	25920	1
4	122	32454	1
5	151	39786	3
6	175	45636	2
7	190	49686	2
8	214	56166	2
9	238	62646	4
10	263	69246	4
11	287	75726	2
12	319	84366	3
13	335	88686	2
14	359	95166	10
15	367	97326	4
16	390	103636	2
17	431	114606	5
18	439	116718	9
19	455	120942	8
20	479	127278	10
21	487	129390	14

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
22	503	133614	16
23	527	139950	16
24	599	158958	20
25	623	165294	27
26	647	171630	38
27	671	177966	49
28	695	184302	71
29	746	197766	116
30	767	203310	132
31	844	223638	194
32	868	229974	214
33	911	241326	250
34	935	247662	264
35	959	253998	268
36	1031	273006	304

Table B.9. Column study data for As(III) removal using regenerated IOCSp

Long term, filtration rate: 0.17 m/h

Initial arsenic concentration: 1,000 μg/L, weight of IOCSp: 25 g

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	11	2970	12
2	45	11742	3
3	57	14982	1
4	69	18222	2
5	81	21462	7
6	117	31182	2
7	129	34350	6
8	141	37518	7
9	153	40614	5
10	165	43710	4
11	177	46806	6
12	203	53514	4
13	215	56610	4
14	225	59310	6
15	237	62550	4
16	249	65862	4
17	261	68958	3
18	286	75408	5
19	297	78246	3
20	309	81342	6
21	321	84582	4
22	333	87750	4
23	370	97518	6
24	381	100488	8

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
25	393	103728	14
26	405	107040	20
27	417	110352	29
28	429	113592	34
29	445	118008	40
30	465	123528	49
31	477	126840	58
32	489	130080	64
33	509	135360	76
34	521	138600	86
35	553	147240	91
36	565	150480	101
37	577	153720	104
38	597	159120	132
39	621	165600	142
40	641	171000	145
41	665	177408	159
42	685	182808	178
43	729	194616	200
44	749	199896	218
45	761	203064	235
46	773	206232	272
47	793	211512	284
48	805	214680	290

Table B.10. Column study data for As(V) removal using regenerated IOCSp

Long term, filtration rate: 0.17 m/h

Initial arsenic concentration: 1,000 µg/L, weight of IOCSp: 25 g

No	Time (h)	Throughput volume (mL)	As final concentration (µg/L)
1	22	5940	2
2	94	24948	5
3	118	31428	5
4	142	37908	6
5	166	44532	5
6	238	63972	6
7	262	70164	8
8	286	76644	8
9	310	83124	9
10	334	89748	11
11	386	103788	14
12	410	110268	18
13	430	115548	19
15	478	128220	26
16	502	134556	38
17	526	140748	49
18	576	154248	51
19	598	160056	64
20	622	166536	83
21	646	173016	113
22	670	179352	124

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
23	744	198888	167
24	766	204960	194
25	790	211440	224
26	814	217776	237
27	838	224256	256
28	862	230736	278
29	894	239376	296

Table B.11. Column study data for Kelliher groundwater

Initial arsenic concentration: 56 μg/L, filtration rate = 3m/h,

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)	
			weight of IOCSp: 8g	weight of IOCSp: 6g
1	1	930	3	6
2	3.5	3255	3	5
3	5	4650	4	5
4	7	6510	5	7
5	9	8370	6	8
6	11	102307	6	9
7	20	18600	10	11
8	22	20460	12	12
9	24	22320	12	13
10	26	24180	12	14
11	29	26970	14	16
12	31	28830	14	16
13	35	32550	14	17
14	44	40920	14	17
15	48	44640	14	18
16	57	53010	14	17
17	68	63240	14	17

Table B.12. Column study data for Hanoi groundwater

IOCSp size: 3 mm

Initial arsenic concentration: 156 µg/L, weight of IOCSp: 8 g, filtration rate = 3m/h,

No	Time (h)	Throughput volume (mL)	As final concentration (µg/L)
1	0.5	468	5
2	8	7488	7
3	12.5	11700	6
4	19	17784	6
5	24	22464	10
6	33	30420	15
7	38	35100	18
8	43	40248	18
9	47	43992	35
10	71	66456	40
11	80	74880	50

Table B.13. Column study data for Hanoi groundwater

IOCSp size: 5 mm

Initial arsenic concentration: 156 μg/L, weight of IOCSp: 8 g, filtration rate = 3m/h,

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	0.5	468	8
2	8	7488	8
3	12.5	11700	8
4	19	17784	6
5	24	22464	8
6	33	30420	15
7	38	35100	50
8	43	40248	60
9	47	43992	66
10	71	66456	67
11	80	74880	79

Table B.14. Tray study data for As(III) removal using fresh IOCSp

Weight of IOCSp: 19.2 g, flow rate = 15.6mL/minute
Initial arsenic concentration: 145 μg/L

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	0.08	62.4	18
2	0.50	390	11
3	1.00	780	5
4	2.00	1560	6
5	2.50	1950	10
6	3.00	2340	5
7	3.50	2730	7
8	4.00	3120	7

Table B.15. Tray study data for As(III) removal using regenerated IOCSp

Weight of IOCSp: 19.2 g, flow rate = 15.6mL/minute

Initial arsenic concentration: 260 μg/L

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	0.5	468	21
2	1	936	22
3	2	1872	26
4	3	2808	31
5	4	3744	31
6	5	4680	30
7	6	5616	26
8	7	6552	33
9	8	7488	34
10	9	8424	40
11	10	9360	42
12	11	10296	54
13	12	11232	71
14	13	12168	76
15	14	13104	84
16	15	14040	92
17	16	14976	85
18	17	15912	94
19	18	16848	106
20	19	17784	113
21	20	18720	117
22	21	19656	116

No	Time (h)	Throughput volume (mL)	As final concentration (µg/L)
23	22	20592	118
24	24	22464	119
25	26	24336	119
26	28	26208	122
27	30	28080	124

Table B.16. Tray study data for As(V) removal using fresh IOCSp

Weight of IOCSp: 13.4 g, flow rate = 15.6mL/minute
Initial arsenic concentration: 265 μg/L

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	1	936	29
2	2	1872	32
3	3	2808	39
4	4	3744	42
5	5	4680	43
6	6	5616	49
7	7	6552	53
8	8	7488	58
9	9	8424	65
10	10	9360	72
11	11	10296	68
12	13	12168	77
13	15	14040	79
14	17	15912	85
15	19	17784	90
16	20	18720	91
17	23	21528	96
18	24	22464	104
19	26	24336	101
20	28	26208	110

Table B.17. Treat As(III) by IOCS-2 - kinetics experiment

Influent As(III): 260 µg/L, Volume of arsenic solution: 100 mL, IOCS-2: 1g

No	T (h)	pH = 8		pH = 7		pH = 6	
		As concentration (µg/L)	Removal efficiency E (%)	As concentration (µg/L)	Removal efficiency E (%)	As concentration (µg/L)	Removal efficiency E (%)
1	0.5	196	24.6	191	26.7	200	23.1
2	1	162	37.6	163	37.2	181	30.4
3	2	120	53.9	128	50.6	158	39.1
4	3	85	67.3	75	71.2	84	67.7
5	4	68	74.0	56	78.3	49	81.2
6	5	37	85.6	51	80.3	31	87.9
7	6	37	85.8	35	86.5	21	91.7
8	7	31	88.2	25	90.5	14	94.6
9	8	23	91.2	19	92.9	12	95.4

Table B.18. Treat As(V) by IOCS-2 - kinetics experiment

Influent As(V): 260µg/L, Volume of arsenic solution: 100 mL, IOCS-2: 1g

No	T (h)	pH = 8		pH = 7		pH = 6	
		As concentration (µg/L)	Removal efficiency E (%)	As concentration (µg/L)	Removal efficiency E (%)	As concentration (µg/L)	Removal efficiency E (%)
1	0.5	198	24.0	199	23.5	217	16.7
2	1	172	33.8	179	31.3	185	29.0
3	2	139	46.7	130	49.9	160	38.5
4	3	92	64.6	87	66.5	95	63.5
5	4	79	69.5	64	75.4	61	76.5
6	5	51	80.5	48	81.5	51	80.3
7	6	38	85.3	30	88.4	26	90.2
8	7	33	87.4	28	89.2	24	90.9
9	8	26	90.0	17	93.5	16	93.8

Table B.19. Treat As(III) by IOCS-2 - isotherm experiment

Influent As(III): 260μg/L
Volume of arsenic solution: 100 mL, IOCS-2: 0.1 - 1g

No	IOCSp weight (g)	As final concentration
1	0.1	211
2	0.2	165
3	0.3	126
4	0.4	94
5	0.5	64
6	0.6	41
7	0.7	30
8	0.8	19
9	0.9	18
10	1	13

Table B.20. Treat As(V) by IOCS-2 - isotherm experiment

Influent As(V): 260μg/L
Volume of arsenic solution: 100 mL, IOCS-2: 0.1 - 1g

No	IOCSp weight (g)	As final concentration
1	0.1	207
2	0.2	158
3	0.3	116
4	0.4	82
5	0.5	50
6	0.6	36
7	0.7	22
8	0.8	17
9	0.9	16
10	1	12

Table B.21. Column study data for As(V) removal using fresh IOCS-2

Initial arsenic concentration: 260 µg/L, weight of IOCS-2: 90 g,
filtration rate: 4.6 m/h

No	Time (h)	Throughput volume (mL)	As final concentration (µg/L)
1	1	936	4
2	2	1872	3
3	3	2808	5
4	4	3744	6
5	6	5616	2
6	8	7488	4
7	10	9360	5
8	12	11232	5
9	22	20592	9
10	26	24336	11
11	30	28080	28
12	34	31824	39
13	46	43056	56
14	50	46800	67
15	54	50544	61
16	58	54288	68
17	70	65520	81
18	74	69264	82
19	78	73008	87
20	82	76752	90
21	96	89856	96

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
22	98	91728	99
23	102	95472	103
24	105	98280	105
25	120	111852	118
26	122	114192	115
27	126	117936	144
28	129	120744	162

Table B.22. Column study data for As(V) removal using 1st regenerated IOCS-2

Initial arsenic concentration: 260 µg/L, weight of IOCS-2: 90 g,
filtration rate: 4.6 m/h

No	Time (h)	Throughput volume (mL)	As final concentration (µg/L)
1	1	936	6
2	2	1872	10
3	4	3744	17
4	6	5616	28
5	8	7488	48
6	11	10296	50
7	12	11232	81
8	16	14976	144
9	20	18720	140
10	22	20592	163
11	34	31356	168
12	36	33696	178
13	41	38376	180
14	44	41184	184
15	59	54756	192
16	62	57564	194
17	64	59904	201
18	68	63648	220

Table B.23. Column study data for As(V) removal using 2nd regenerated IOCS-2

Initial arsenic concentration: 260 μg/L, weight of IOCS-2: 90 g,
filtration rate: 4.6 m/h

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	2	1872	18
2	3	2808	22
3	4	3744	27
4	6	5616	50
5	8	7488	73
6	10	9360	95
7	24	22464	162
8	28	26208	187

Table B.24. Treat As(III) by SMZ/ZVI - kinetics experiment

Initial arsenic concentration: 260 μg/L, Weight of SMZ/ZVI = 2 g,
Mixing rate = 130 rpm, temperature = 22^0C, Volume of arsenic solution = 100 mL

No	Reaction time (minute)	Final As(III) Concentration (μg/L)	Final As(V) Concentration (μg/L)
1	5	890	830
2	10	505	454
3	20	410	324
4	30	276	214
5	45	196	158
6	60	166	108
7	90	26	18
8	120	22	14
9	240	4	3
10	360	3	1
11	480	2	1
12	600	1	1

Table B.25. Treat As(V) by SMZ/ZVI - isotherm experiment

Weight of SMZ/ZVI = 2 g, Mixing rate = 130 rpm,
Temperature = 22^0C, Volume of arsenic solution = 100 mL

No	Initial As(III) concentration (μg /L)	Final As(III) Concentration (μg /L)
1	1000	1
2	2500	40
3	5000	84
4	7500	114
5	10000	144
6	12500	178
7	15000	206
8	20000	324
9	25000	2780
10	30000	5588

Table B.26. Treat As(III) by SMZ/ZVI - isotherm experiment

Weight of SMZ/ZVI = 2 g, Mixing rate = 130 rpm,
Temperature = 22^{0}C, Volume of arsenic solution = 100 Ml

No	Initial As(V) concentration (μg /L)	Final As(V) Concentration (μg /L)
1	1000	1
2	2500	164
3	5000	346
4	7500	486
5	10000	574
6	12500	784
7	15000	1112
8	20000	1760
9	25000	4050
10	30000	7864

Table B.27. Column study data for As(III) removal using SMZ/ZVI

Initial arsenic concentration: 1,000 μg/L, weight of SMZ/ZVI: 68 g,
Filtration rate: 1.32 m/h

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
1	4	1281	20
2	6	1686	56
3	8	2226	164
4	19	5062	161
5	21	5736	181
6	24	6510	213
7	28	7542	221
8	32	8574	175
9	44	11670	190
10	49	12830	204
11	55	14508	245
12	66	17346	226
13	72	18966	306
14	80	21030	295
15	92	24270	325
16	141	36828	310
17	148	38676	325
18	171	44796	365
19	194	51006	375
20	210	55230	405
21	218	57342	430
22	239	63138	570

Table B.28. Column study data for As(V) removal using SMZ/ZVI

Initial arsenic concentration: 1,000 µg/L, weight of SMZ/ZVI: 68 g,
Filtration rate: 1.32 m/h

No	Time (h)	Throughput volume (mL)	As final concentration (µg/L)
1	2	576	29
2	4	1280	33
3	6	1686	26
4	8	2226	43
5	19	5124	50
6	24	6510	66
7	32	8574	55
8	44	11670	61
9	49	12830	75
10	55	14508	101
11	66	17368	154
12	72	18966	194
13	80	21030	226
14	92	24270	266
15	96	25302	262
16	117	30750	329
17	122	32040	314
18	141	36828	278
19	148	38676	366
20	171	44796	384
21	194	51006	393
22	239	63138	378

No	Time (h)	Throughput volume (mL)	As final concentration (μg/L)
23	264	69888	450
24	288	76368	463
25	321	85278	630
26	340	90408	720
27	364	96888	756
28	388	103368	792
29	412	109848	870
30	436	116328	918
31	484	129288	960

Table B.29. Arsenite removal efficiency by photocatalysis with TiO_2

Weight of TiO_2: 0.01 – 0.1 g/L, initial arsenite concentration: 100 μg/L

No	TiO_2 concentration (g/L)	Irradiation time (minute)	Final arsenic concentration (μg/L)
1.	0.01	10	20
2.		30	12
3.		60	8
4.		120	6
5.		240	5
6.	0.05	10	17
7.		30	10
8.		60	7
9.		120	5
10.		240	3
11.	0.1	10	5
12.		30	3
13.		60	2
14.		120	1
15.		240	1

Table B.30. Arsenite removal efficiency by photocatalysis with TiO_2

Weight of TiO_2: 0.05 – 1 g/L, initial arsenite concentration: 500 μg/L

No	TiO_2 concentration (g/L)	Irradiation time (minute)	Final arsenic concentration (μg/L)
1.	0.05	10	197
2.		30	178
3.		60	165
4.		120	145
5.		240	139
6.	0.1	10	178
7.		30	162
8.		60	158
9.		120	141
10.		240	132
11.	0.5	10	22
12.		30	15
13.		60	12
14.		120	9
15.		240	8
16.	1	10	18
17.		30	9
18.		60	7
19.		120	5
20.		240	2

Table B.31. Arsenite removal efficiency by photocatalysis with TiO_2

Weight of TiO_2: 0.05 – 1 g/L, initial arsenite concentration: 1,000 μg/L

No	TiO_2 concentration (g/L)	Irradiation time (minute)	Final arsenic concentration (μg/L)
1.	0.05	10	430
2.		30	386
3.		60	362
4.		120	348
5.		240	320
6.	0.1	10	320
7.		30	295
8.		60	266
9.		120	246
10.		240	223
11.	0.5	10	50
12.		30	41
13.		60	34
14.		120	26
15.		240	19
16.	1	10	28
17.		30	12
18.		60	9
19.		120	7
20.		240	5

Table B.32. Arsenite adsorbed on the TiO_2 surface

Sample was stirred for 2 hours in the dark

No	As(III) initial concentration (μg/L))	TiO_2 concentration (mg/L)	Final arsenic concentration (μg/L)
1.	100	0.01	47
2.		0.05	33
3.		0.1	25
4.		0.5	8
5.	500	0.1	251
6.		0.5	76
7.		1	21
8.	1.000	0.1	534
9.		0.5	225
10.		1	87

Table B.33. Arsenate adsorbed on the TiO_2 surface

Sample was stirred for 2 hours in the dark

No	As(V) initial concentration (μg/L))	TiO_2 concentration (mg/L)	Final arsenic concentration (μg/L)
1.	100	0.01	85
2.		0.05	64
3.		0.1	10
4.		0.5	3
5.	500	0.05	210
6.		0.1	120
7.		0.5	56
8.		1	11
9.	1.000	0.05	450
10.		0.1	340
11.		0.5	118
12.		1	11

Table B.34. Arsenite removal efficiency by photocatalysis with TiO_2 with addition of nZVI

Initial arsenic concentration = 500 μg/L, TiO_2 = 0.1 g/L

No	nZVI concentration (g/L)	Irradiation time (minute)	Final arsenic concentration (μg/L)
1.	0	10	178
2.		30	162
3.		60	158
4.		120	141
5.		240	132
6.	0.05	10	52
7.		30	26
8.		60	21
9.		120	7
10.		240	3
11.	0.1	10	21
12.		30	9
13.		60	6
14.		120	3
15.		240	2
16.	0.2	10	7
17.		30	6
18.		60	4
19.		120	1
20.		240	1

Table B.35. Effect of nZVI on As(III) removal by MF

Microfilter: PVA, Initial arsenic concentration: 500 μg/L

No	nZVI concentration (g/L)	Contact time (minute)	Final arsenic concentration (μg/L)
1.	0	10	331
2.		30	319
3.		50	316
4.	0.05	10	206
5.		30	222
6.		50	195
7.	0.1	10	86
8.		30	79
9.		50	84
10.	0.2	10	54
11.		30	68
12.		50	52
13.	0.3	10	9
14.		30	7
15.		50	13

Table B.36. Effect of nZVI on As(V) removal by MF

Microfilter: PVA, Initial arsenic concentration: 500 μg/L

No	nZVI concentration (g/L)	Contact time (minute)	Final arsenic concentration (μg/L)
1.	0	10	297
2.		30	304
3.		50	299
4.	0.05	10	158
5.		30	169
6.		50	166
7.	0.1	10	54
8.		30	49
9.		50	52
10.	0.2	10	20
11.		30	37
12.		50	16
13.	0.3	10	4
14.		30	7
15.		50	5

Table B.37. Effect of nZVI on As(III) removal by NF

Nanofilter: NTR729HF, Initial arsenic concentration: 500 μg/L

No	nZVI concentration (g/L)	Contact time (minute)	Final arsenic concentration (μg/L)
1.	0	10	211
2.		30	223
3.		50	206
4.	0.05	10	138
5.		30	116
6.		50	122
7.	0.1	10	70
8.		30	72
9.		50	68
10.	0.2	10	32
11.		30	34
12.		50	43

Table B.38. Effect of nZVI on As(V) removal by NF

Nanofilter: NTR729HF, Initial arsenic concentration: 500 μg/L

No	nZVI concentration (g/L)	Contact time (minute)	Final arsenic concentration (μg/L)
1.	0	10	94
2.		30	92
3.		50	96
4.	0.05	10	50
5.		30	42
6.		50	46
7.	0.1	10	21
8.		30	12
9.		50	16
10.	0.2	10	6
11.		30	3
12.		50	7