Biosorption of Arsenic by Anaerobic Biomass

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Abstract

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Arsenic is known around the globe in recent history due to the consequence of mass poisoning through the exposure of drinking water. Due its carcinogenic and many other adverse health effects, the regulatory authorities like the world health organization (WHO), United States environmental protection agency (USEPA) have reduced the maximum contamination level (MCL) of total arsenic in drinking water from 50 μg/L to 10 μg/L.

Biosorption, a process of passive sequestration of contaminant materials by some dead and inactive biomass, has been preferred in this study to remove arsenic from contaminated water due to its eco-friendly nature and cost-effectiveness in comparison to the conventional technologies.

An anaerobic digestion sludge obtained from a wastewater treatment plant was introduced to remove inorganic arsenic from contaminated water. The biomass was prepared in a granular form by drying, grinding and sieving. This granular biomass was investigated in equilibrium batch experiments and used in a continuous flow fixed-bed column operation. The biomass was also treated with KH_2PO_4 and KCl to improve the sorption capacity but treatment did not contribute to the improvement as anticipated. Removal of arsenate [As (V)] was found pH dependent with the maximum removal at a pH range of 5 to 6, whereas arsenite [As (III)] was almost

insensitive to pH over a range of 3 to 10. Initial arsenic concentration and contact time, in addition to pH, affected the biosorption capacity. The biosorption capacity of arsenate [As (V)] was 152 μg/g at a pH of 5 and that of arsenite [(As (III)] was 60 μg/g at a pH of 8 at an initial arsenic concentration of 2000 μg/L for both cases. Adsorption data fitted with Langmuir isotherm model. Kinetic data followed pseudo-second-order model. A 40-minute contact time was sufficient to complete almost 95% of the total biosorption. In column operation, at a pH value of 5, 90 and 220 bed volumes of contaminated water with the respective arsenate concentration of 500 μg/L and 200 μg/L were treated by bringing the concentrations down to the regulatory limit of 10 μg/L. Desorption of almost 40% arsenate was achieved using 0.5M NaCl solution. Protein/amino acid-arsenic interaction was proposed as the dominant mechanism in the biosorption process.

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Dedication

To my parents

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Nomenclature

AA	Activated alumina
BAT	Best available technology
BV	Bed volume
B	Adsorption equilibrium constant ($k_{adsorption}$ / $k_{desorption}$)
COD	Chemical oxygen demand
C_i	Initial sorbate concentration in the liquid phase (μg/L)
C_e	Equilibrium sorbate concentration in the liquid phase (μg/L)
C_t	Sorbate concentration in the liquid phase at any time t (μg/L)
EBCT	Empty bed contact time (min)
h	Initial sorption rate (μg/g.min)
IX	Ion exchange
K_F	Freundlich constant indicative of the adsorption capacity of the adsorbent (L/μg)
k_1	First-order rate constant (/min)
k_{s1}	Pseudo-first-order rate constant (/min)
k_2	Second-order rate constant (L/μg.min)
k	Pseudo-second-order rate constant (g/μg.min)
M	Mass of biomass (g)
n	Constant indicative of the adsorption intensity of the adsorbent.
q_e	Equilibrium sorption capacity of the sorbent (μg/g)
q_{max}	Maximum sorption capacity of the sorbent, (μg/g)

q_t	Sorption capacity of the sorbent at any time t (μg/g)
R	Hall's separation factor
R^2	Co-efficient of correlation of the linear regression
TCLP	Toxicity characteristics leaching procedure
TFS	Total fixed solids
TS	Total solids
TSS	Total suspended solids
TVS	Total volatile solids
TVSS	Total volatile suspended solids
V	Volume of solution (L)

Chapter 1

Introduction

1.1 Background

Arsenic, a metalloid, possesses both metallic and non-metallic properties, is ubiquitously present in air, soil, natural water, mineral deposits and rocks and biota (Matschullat, 2000; Miteva, et al., 2005) in varying concentrations. It can be released into the environment by both natural and anthropogenic processes. Natural processes are volcanic emissions, biological activities, burning of fossil fuels and weathering of arsenic bearing rocks and minerals such as realgar (AsS), orpiment (As_2S_3), arsenopyrite (FeAsS), and lollingite ($FeAs_2$) (USGS, 2001; Cullen and Reimer, 1989). Anthropogenic sources include applications of arsenical pesticides and insecticides (Korte and Fernando, 1991; Davis et al.,1992; Peryea and Creger, 1994), wood preservatives, paints, drugs, dyes, semiconductors, incineration of arsenic containing substances, industrial wastewater discharge, mine tailing/landfill leaching, and manufacturing of arsenic compounds (Azcue and Nriagu, 1994;USEPA 1998a and 2000a; Welch et al., 1998). Arsenic can be present both in inorganic and organic forms depending on the ambient environment (i.e. pH, Eh) and microbial activity (Yong and Mulligan, 2004) but the inorganic form is more toxic than the organic one (Smedley and Kinniburgh, 2002). In spite of its wide spread presence in the atmosphere, the great concern is the toxic effects to human health mainly through drinking water in many parts of the world such as Argentina, Bangladesh, India,

Pakistan, Mexico, Mongolia, Germany, Thailand, China, Chile, USA, Canada, Hungary, Romania, Vietnam, Nepal, Myanmar, and Cambodia . Ingestion of elevated concentration of arsenic through drinking water causes many types of acute poisoning such as stomach pain, nausea, vomiting or diarrhea, which may lead to shock, coma and even death as well as chronic poisoning like cancer to many different human organs and skin lesions. Due to this increasing awareness of the toxicity of arsenic, the regulatory authorities, including the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA), had to reduce the maximum contamination level (MCL) of total arsenic from 50 to 10 μg/L. However, some developing countries still use the higher standard of 50 μg/L, primarily because of economic factors. The new guideline by WHO and USEPA regulates the development of emerging technologies or the modification of the conventional ones which would be technologically sound and efficient as well as cost effective.

Since arsenic is a metallic element, it is indestructible. It can only change from one form to another, and be transported from one medium to another. Arsenic in air will settle to the ground or be washed out by rain. Arsenic in water may precipitate out of the solution, or adsorb onto rocks and soils. Arsenic-containing rocks and soils may release arsenic into the water by dissolution or desorption.

My research introduces an anaerobic biomass to remove arsenic from water through a sorption phenomenon. Biosorption is a property of certain types of inactive, dead, microbial biomass to bind and concentrate metals from aqueous solutions through a complex phenomenon that involves different sorption processes like ion exchange, complexation, chelation, and micro-precipitation. Most studies have

focused on removal of cationic metal contaminants whereas only a very few have dealt with anionic species. The novelty of this work is that biosorption has been introduced to remove anionic contaminants like arsenic.

1.2 Objectives of the study

The objective of this study is to develop a system to remove arsenic from contaminated water. To achieve the objectives, the following tasks were performed.

- Comparative study of untreated and treated anaerobic granulated biomass.
- Performance study of chemically treated biomass.
- Sorption behavior of arsenate (As V) and arsenite (As III)
- Studies on the factors controlling arsenic removal efficiency
- Batch adsorption isotherm and kinetic studies
- Dynamic column studies
- Desorption to check the reusability of the biomass.

1.3 Scope of the study involved the following tasks

- This study focused on the sorption behavior of anaerobic biomass in removing inorganic, soluble pentavalent arsenate [As (V)] and trivalent arsenite [As (III)].
- Experimental studies were limited to lab-prepared water.

1.4 Organization of the thesis

This thesis is comprised of eight chapters. The first one is the introductory chapter. Chapter Two contains the literature review on sources, occurrence and distribution of arsenic in the environment. Chapter Three describes the health exposure, toxicity and health effects of arsenic. In Chapter Four, different arsenic removal technologies with their advantages and disadvantages have been presented. Chapter Five deals with materials used and the methods adopted in the study. Chapter Six presents the results of the experiments and the possible explanation of the results. In Chapter Seven, conclusions of the research are summarized and some recommendations are made for future research. Finally references are listed in chapter Eight.

Chapter 2

Sources, Occurrence and Distribution of Arsenic in the Environment

2.1 Natural Sources

Natural weathering processes contribute approximately 40,000 tonnes of arsenic to the global environment annually, while twice this amount is being released by human activities (Paige et al., 1996). Arsenic ranks twentieth in abundance of elements in the earth's crust, fourteenth in seawater and is the twelfth most abundant element in the human body (Mandal and Suzuki, 2002) with an average level of 1.8 mg/kg in the earth's crust (Greenwood and Earnshaw, 1984). Normal background concentrations are 0.2-15 mg/kg in the lithosphere, less than 15 mg/kg in soils, 0.02-2.8 ng/m^3 in the atmosphere, and less than 1 μg/L in aquatic environment (Technische Universitat Bergakademie Freiberg, 2001).

It is the main constituent of some 245 mineral species (Valberg et al., 1997; Thronton and Fargo, 1997; NRC, 1977) of which approximately 60% are arsenates, 20% sulfides and sulfosalts; the remaining 20% includes arsenides, arsenites, oxides, silicates and elemental arsenic (As) (Onishi, 1969). As^0 and As^{3-} are rare in aquatic environments (Mandal and Suzuki, 2002; Goldberg and Johnstony, 2001). Only a few of these hundreds of arsenic minerals are common in hydrogeochemical environments (Hering and Kneebone, 2002; Kanivetsky, 2000). For example, in reducing environments, arsenic is present in iron sulfide minerals such as arsenopyrite

(FeAsS), realgar (AsS) and orpiment (As_2S_3); it is also present in pyrite (FeS) as a contaminant. In oxidizing environments, arsenic is found in arsenolite (As_2O_3) and claudetite (As_2O_3). Under a wide range of geochemical conditions, arsenic has also been associated with minerals such as iron oxides (Fe_2O_3), iron hydroxides (FeOOH), other metal oxides and hydroxides (e.g. Al), and magnetite (Fe, Mg) Fe_2O_4 (Hem, 1985; Holm and Curtiss, 1988; Hounslow, 1980; Kinniburgh and Smedley, 2001b; Korte, 1991; Ryker, 2003; Sullivan and Aller, 1996; Yan *et al.*, 2000). Arsenopyrite is the most common and is relatively insoluble in water. The sulfides in arsenopyrite, however, can be oxidized to more soluble forms allowing arsenic to leach into groundwater. The arsenic content of minerals is usually between 0.02-0.50%, but arsenopyrite can sometimes contain as much as 5% (Hindmarsh, 2000).

2.2 Anthropogenic Sources

There are several anthropogenic sources of arsenic. The total arsenic added to the soil from anthropogenic activities, about 23% comes from coal fly ash and bottom ash, 14% from atmospheric fallout, 10% from mine tailings, 7% from smelters, 3% from agriculture and 2% from manufacturing, urban and forestry wastes (Bhumbla and Keefer, 1994). Some anthropogenic sources are mentioned below:

(i) From processing a variety of ores like Cu, Au, Ni, Pb, and Zn (Leist et al., 2000)

(ii) From ingredients of many insecticides and herbicides (Korte and Fernando, 1991)

(iii) From cotton and wool processing (Chen et al., 1995)

(iv) From arsenic-based wood preservatives (Bureau of Reclamation, Denver, 2001)

(v) From feed additives in various metal alloys and in mining (Mandal and Suzuki, 2002; Bureau of Reclamation, Denver, 2001)

(vi) From seepages from hazardous waste sites (Bureau of Reclamation, Denver, 2001)

(vii) From areas near cemeteries where burials were conducted from about 1880 to 1910 when arsenic was used as an embalming fluid (Bureau of Reclamation, Denver, 2001)

(viii) From power generation by the burning of arsenic contaminated coal (McNeill and Edwards, 1997)

(ix) From semiconductor and glass manufacturing units (Leist et al., 2000).

2.3 Behavior of Arsenic in the Environment

Due to the toxic nature of arsenic, it is important to know its sources and fate in the environment, and hence mechanisms involved in its transport and transformation from one form to another. Arsenic in the environment can undergo a variety of reactions including oxidation and reduction, ligand exchange, precipitation, adsorption, and microbially mediated reactions (Ferguson, 1972; Korte, 1991; Lackovic, 2000; Banerjee, 1999). When arsenic enters the environment, it may be diluted, concentrated, or transformed by a variety of chemical, physical, and biological processes. These processes include oxidation and reduction, complexation, precipitation, adsorption, and microbially mediated reactions. As a result of these processes, arsenic can relocate within the environment. Soil and organic matter can

adsorb and release ions depending upon the physical, chemical, and biological nature of the surrounding environment. The species and form of arsenic present in the soil depends on many variables. Soil can adsorb and release ions depending upon the types of mineral particles present, the proportion of organic matter, pH, redox potential, biological activity, iron content, and moisture content (Oliver, 1997). Arsenic can be removed from the soil by the leaching of arsenic minerals. This in turn poses a problem to ground and surface waters as this arsenic becomes mobile in the aqueous phase. Colloidal and aqueous phase transport of arsenic may also occur (Korte, 1991). Most inorganic arsenic compounds are soluble, and therefore are mobile in subsurface environments. At the prevalent near neutral groundwater pH of 6 to 8, arsenite becomes more mobile (due to its neutrality) than arsenate, although both will increase in mobility. Therefore, weathering of arsenic minerals tends to release the more toxic arsenite into the groundwater (Hindmarsh, 2000). Arsenite is also more soluble in soils than the oxidized arsenate (Korte, 1991). Therefore in a reduced environment, there is a greater amount of water-soluble arsenic that can be transported by groundwater.

In surface water, there are interactions with atmospheric oxygen and carbon dioxide, which tends to lower the pH. Therefore, the less toxic arsenate dominates in surface waters (Hindmarsh, 2000). Surface waters can also transport industrial wastes. Fluctuations in the quality of surface water are influenced by the discharge of industrial effluents that can vary considerably in both amount and composition. The quality of surface water is generally dependent on flow rate, which determines the degree to which incoming discharges are diluted. Transport through surface and

ground water is a critical pathway in human exposure to arsenic, since we rely on these sources for our drinking water supplies.

2.4 Biogeochemical Cycling of Arsenic

Global cycling of arsenic in the environment is quite complex and not well understood. A simplified diagram for this cycle is presented in Figure 2.1. The largest arsenic fluxes occur from land and atmosphere to water, followed by water to sediments (Nriagu, 1994).

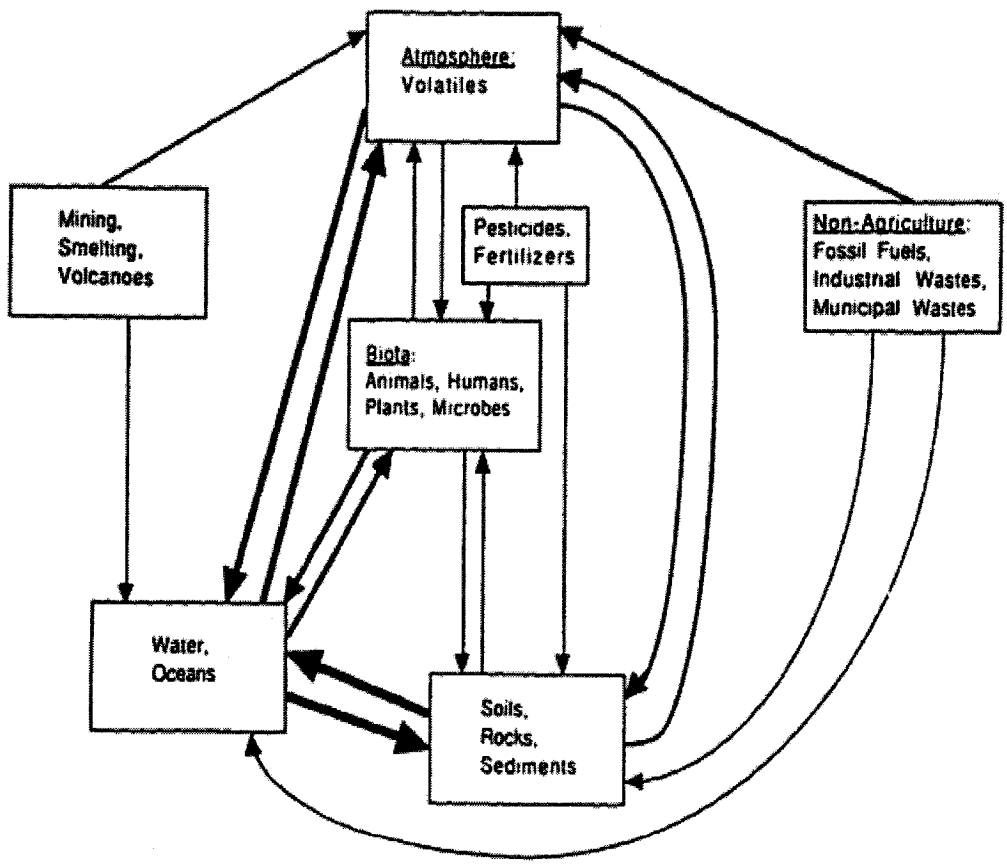

Figure 2.1.Cycling of arsenic in the environment (Bhumbla and Keefer, 1994)

Reaction kinetics, complexation, solid phase precipitation and re-dissolution, adsorption and desorption, as well as biologically mediated reactions are all processes which influence arsenic concentrations and speciation in the environment.

In soil and groundwater, aqueous phase arsenic can adsorb to clay particles and organic matter or precipitate out of solution, thus transporting itself from the aqueous to the solid phase. On the other hand, the opposite may occur. Adsorbed or precipitated arsenic can desorb or dissolve into solution or leach from arsenic-containing minerals, thus transporting from the solid phase to the aqueous phase.

The interactions between the solid and liquid phases include electrostatic interactions such as coulombic attraction or simply ion exchange and adsorption processes such as specific chemical adsorption, adsorption due to induced polarization, covalent bonding, and Van der Waals forces (Korte, 1991).

Oxidation and reduction of arsenicals can occur by chemical or biological reactions or a combination of both depending on pH and redox potential (Hindmarsh, 2000). Microorganisms such as bacteria and phytoplankton can reduce arsenate to arsenite; while the oxidation of arsenite to arsenate is catalyzed by a number of bacteria (Korte, 1991; Hindmarsh, 2000).

A number of different organisms throughout the environment can methylate arsenic under aerobic or anaerobic conditions (Hindmarsh, 2000). Methylation of arsenic to organoarsenicals occurs in vertebrates and invertebrates including humans. Fungi, yeast and bacteria can also methylate arsenic.

Although arsenic is widely distributed in the environment, the consumption of drinking water is the most significant, and often the primary route for ingestion of

inorganic arsenic. Therefore, with regard to human health and exposure, the most important arsenic cycling occurs between the water and solid phases (sediments and soils), which include interactions with biota. A cycle for arsenic in a stratified lake is illustrated in Figure 2.2. The main reactions include adsorption to and desorption from metal oxides in the sediments, biologically-mediated and abiotic redox transformations, solid phase precipitation and re-dissolution, and acid-base chemistry.

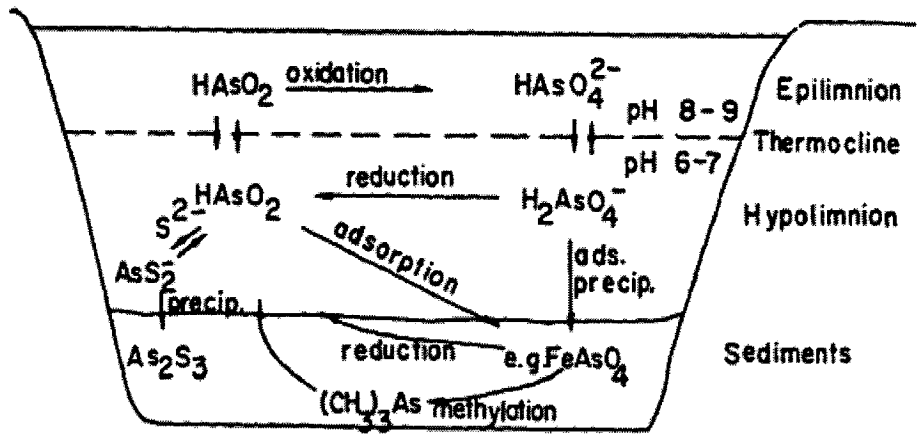

Figure 2.2 Local cycle of arsenic in a stratified lake (Ferguson and Gavis, 1972)

Although it is possible to estimate which reactions could be occurring for a particular body of water, but it is very difficult to predict reaction rates, the fate of arsenic entering a natural system, or the potential release of arsenic under changing environmental conditions. More studies are needed to gain insight into the complex geochemical and biological processes controlling arsenic concentration and mobility in natural waters.

2.5 Arsenic in Groundwater

Background concentrations of arsenic in groundwater are less than 10 μg/L in most countries, but a number of large aquifers in various parts of the world have been identified with concentrations above 50 μg/L. High concentrations of arsenic are found in both oxidizing and reducing aquifers and areas affected by geothermal, mining and industrial activity. In most cases high-arsenic groundwater is the result of natural occurrences. The anthropogenic causes may be severe locally but occurrences are relatively rare.

Smedley and Kinniburgh (2002) wrote an excellent review of high arsenic concentration in ground water. Bangladesh, India, Taiwan, Vietnam, Hungary and Romania are affected by groundwater arsenic problems because of its reducing environment. High level of arsenic presents due to oxidizing environments in groundwater in the arid region of Mexico, Chile, and Argentina. Because of mixed oxidizing and reducing environments, the groundwater arsenic problem exists in Southwestern USA.

In some places affected ground waters are found close to obvious geological or industrial sources rich in arsenic. In this case high arsenic concentrations in the source region are responsible. The concentration of arsenic in major drinking water sources such as rivers, lakes, reservoirs, ponds and aquifers are presented in Table 2.1.

Table 2.1 Typical arsenic concentration in natural waters (Smedley and Kinniburgh, 2002)

Water body and location	Arsenic concentration average or range (µg/L)	References
River water		
Norway	0.25	Lenvik et al., 1978
USA	2.1	Sonderegger and Ohguchi, 1988
Sierra Nevada, USA	0.20-264	Benson and Spencer, 1983
Dordogne, France	0.7	Seyler and Martin, 1990
Po River, Italy	1.3	Pettine et al., 1992
Northern Chile	190-21800	Caceres et al., 1992
Cordoba, Argentina	7-114	Lerda and Prosperi, 1996
Lake water		
Ontario	0.7	Azcue and Nriagu, 1995
France	0.73-9.2	Seyler and Martin, 1990
Western USA	0.38-1000	Benson and Spencer, 1983
Northwest Territories, Canada	270	Bright et al., 1996
Ontario, Canada	35-100	Azcue and Nriagu, 1995
Seawater		
Deep Pacific and Atlantic	1-1.8	Seyler and Martin, 1990
Groundwater		
Baseline UK	<0.5-10	Edmunds et al., 1989
As-rich provinces (e.g. Bengal basin, Argentina, Mexico, northern China, Taiwan, Hungary)	10-50,000	Das, 1995; BGS and DPHE, 2001; Nicolli et al., 1989; Smedley, 2001a; Del Razo, 1990; Luo, 1997; Hsu, 1997; Varsanyi et al., 1991;
Sediment pore water		
Baseline, clays, Saskatchewan, Canada	3.2-99	Van et al., 2000
Mining contaminated, British Columbia, Canada	50-360	Azcue et al., 1994
Tailing impoundment, Ontario, Canada	300-100,000	McCreadie et al., 2000
Oilfield and related brine		
Ellis Pool, Alberta, Canada	230	White et al., 1963
Searles Lake brine, California	up to 243,000	White et al., 1963

2.6 Speciation of Arsenic

Arsenic forms a number of inorganic and organic compounds. Naturally occurring inorganic arsenic is stable in oxidation states of -3 as in arsine gas (AsH_3), 0 as in crystalline/elemental arsenic, +3 as in arsenite, and +5 as in arsenate. The elemental state is extremely rare whereas -3 oxidation state is found only at extremely reducing conditions. Arsenate species are stable in oxygenated waters. Under mildly reducing conditions, arsenites predominate (Andreae, 1978; Moore et. al., 1984).

Organic arsenic species include monomethylarsonic acid (MMA), and dimethylarsonic acid (DMA). They may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Organic forms may, however, occur where waters are significantly impacted by industrial pollution (Irgolic, 1982).

Generally, inorganic arsenic accounted for 85-99% of the total arsenic (Irgolic, 1982). The order of expected occurrence of arsenic in drinking water is arsenate (AsV), arsenite (AsIII), monomethylarsonic acid (MMA) and dimethyl arsonic acid (DMA). At the high redox potential values characteristic of oxygenated surface and ground waters, inorganic arsenate (As V) is the expected form of arsenic (Ferguson and Gavis, 1972). Irgolic (1982) developed analytical methods for inorganic arsenic speciation for highly contaminated waters and his method revealed a highly variable arsenite to arsenate ratio of 0.007 to 3.4. Table 2.2 summarizes some of the published literature on the distribution of the arsenic species found in the ground and surface waters.

Table 2.2 Arsenic concentration and speciation in natural waters.

Source	As (T) (μg/L)	As III (%)	AsV (%)	MMA (%)	DMA (%)	Reference
Nova Scotia I	8000	56.3	43.8	<MDL	<MDL	Irgolic, 1982
Barefoot, Alaska	3100	77.4	22.6	<MDL	<MDL	Irgolic, 1982
Yenshei II, Taiwan	1100	2.2	98.2	<MDL	<MDL	Irgolic, 1982
Yenshei I, Taiwan	850	2.7	98.8	<MDL	<MDL	Irgolic,1982
Antofagasta, Chile (Untreated)	750	2.1	98.7	<MDL	<MDL	Irgolic, 1982
Nova Scotia II	630	49.2	50.8	<MDL	<MDL	Irgolic, 1982
Antofagasta, Chile (Treated)	410	0.7	99.3	<MDL	<MDL	Irgolic, 1982
Hinkley, Utah	180	5.6	94.6	<MDL	<MDL	Irgolic, 1982
Delta, Utah	20	50	50	<MDL	<MDL	Irgolic, 1982
Hanford, CA (Well # 19)	90	100	0	ND	ND	Clifford, 1986
San Ysidro, NM (Well # 4)	250	100	0	ND	ND	Clifford, 1991
San Ysidro, NM (Well # 1)	88	35.2	64.8	ND	ND	Clifford,1991
Hanford, CA (Various wells)	9-75	89	11	ND	ND	Hering, 2000
Hanford, CA (Storage tank)	25	4-14	86-96	ND	ND	Hering, 2000
Beaver Area, UT Well (M002)	30	77	23	<MDL	<MDL	Ficklin, 1983
Beaver Area, UT Well (M021)	3	0	100	<MDL	<MDL	Ficklin, 1983
Beaver Area, UT Well (M022)	7	29	71	<MDL	<MDL	Ficklin, 1983
New R. Braley, CA	11.3	0.1	99.5	0.1	0.1	Andreae, 1977
Squaw Lake, CA (Surface)	3.7	23.5	74.5	0.6	1.4	Andreae, 1977
Colorado R. Laguna Dam, CA	3.3	3.6	93.3	2.7	0.3	Andreae, 1977
Colorado R., Topcock, CA	2.8	3.1	81.1	4.7	11.2	Andreae, 1977
Kaweah R., Fish Camp, CA	2.8	3.8	88.7	0.3	7.2	Andreae, 1977
Coot Bay Pond, Everglades, FL	2.4	33.5	52.8	0.4	13.3	Andreae, 1977
Colorado R, Parker, AZ	2.2	5.2	89.5	2.9	2.3	Andreae, 1977

< MDL = Less than minimum detection level; ND = Not Determined

2.7 Arsenic Chemistry

2.7.1 Acid-Base Chemistry

Depending on the pH, different forms of arsenite [As(III)] are H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} whereas different forms of arsenate [As(V)] are H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}. Figures 2.3 and 2.4 show the protonation forms of arsenite and arsenate at various pHs. These diagrams are generated by the following equilibrium relationships.

For arsenite (As III),

$$H_3AsO_3 \leftrightarrow H_2AsO_3^- + H^+ \qquad pK_{a1} = 9.22$$

$$H_2AsO_3^- \leftrightarrow HAsO_3^{2-} + H^+ \qquad pK_{a2} = 12.13$$

$$HAsO_3^{2-} \leftrightarrow AsO_3^{3-} + H^+ \qquad pK_{a3} = 13.40$$

For arsenate (As V),

$$H_3AsO_4 \leftrightarrow H_2AsO_4^- + H^+ \qquad pK_{a1} = 2.20$$

$$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+ \qquad pK_{a2} = 6.97$$

$$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+ \qquad pK_{a3} = 11.53$$

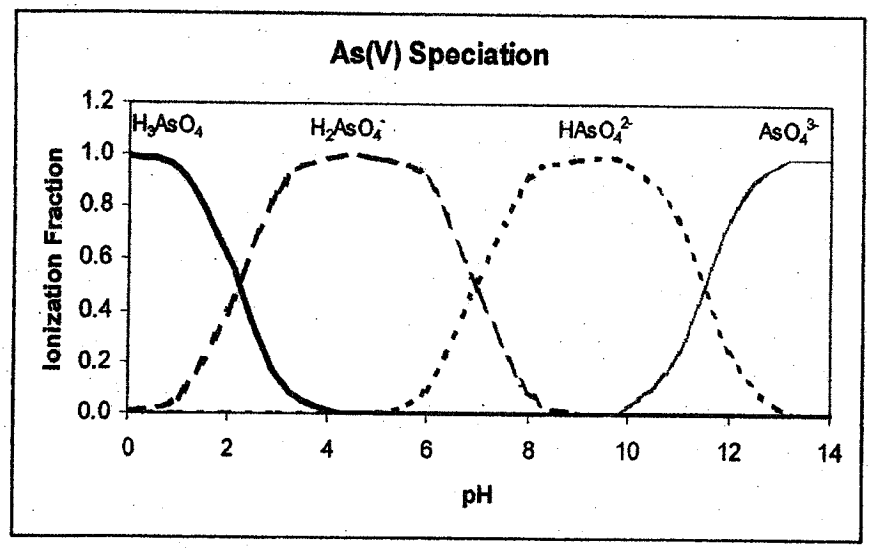

Figure 2.3 Speciation diagram for arsenate, As(V) (David and Allison, 1999)

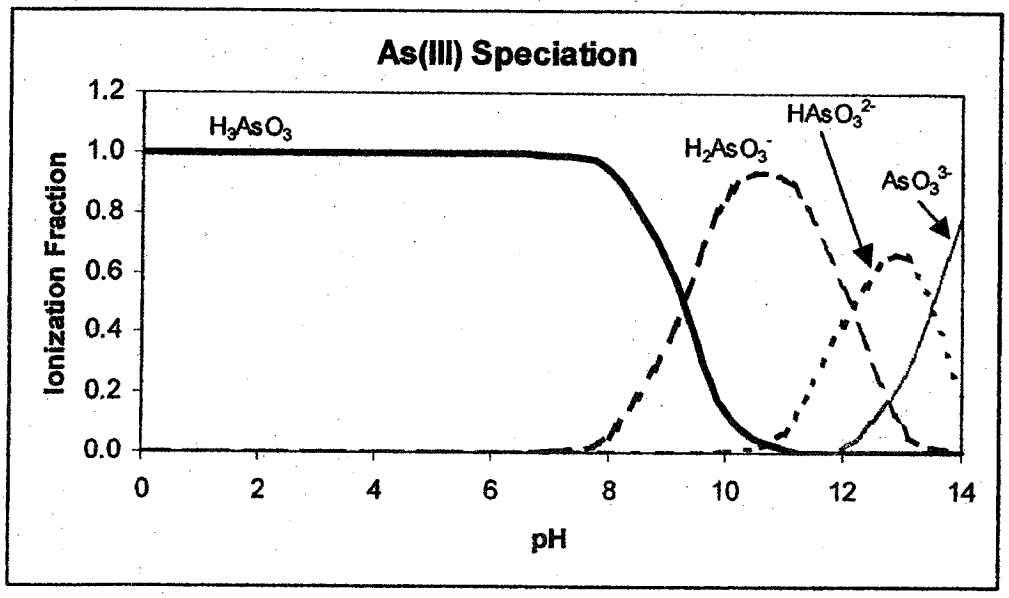

Figure 2.4 Speciation diagram for arsenite, As(III) (David and Allison, 1999)

The amount of protonation of both arsenite and arsenate is an important factor governing the mobility of these chemical species. For example, the pH of groundwater is often between 6 and 8. Within this range, arsenite is uncharged while arsenate is negatively charged. As a result, arsenite is more mobile than arsenate. The movement of arsenate is retarded by electrostatic attraction to positively charged particles, such as iron hydroxides (Domenico et al., 1998). This information is also useful in designing effective arsenic removal technologies and in determining the arsenic speciation by ion exchange separation technique.

2.7.2 Reduction-Oxidation (Redox) Chemistry

Given the acid-base chemistry, combined with Gibb's free energy change of the oxidation/reduction reactions between arsenite and arsenate, an Eh-pH diagram (Pourbaix diagram) can be constructed (AWWA, 1990; Morel and Hering, 1993). Figure 2.5 shows an Eh-pH diagram of arsenic.

The Eh-pH diagram shows the arsenic speciation and oxidation states at a particular pH and redox potential (Gonzales, 1997). The diagram also shows the expected change in arsenic state when environmental conditions differ. For example, anoxic groundwater usually has a low redox potential. When the water is pumped to the ground surface and exposed to the atmosphere, the presence of dissolved oxygen increases the redox potential. As a result, arsenite will naturally oxidize to arsenate. This information is very useful because different oxidation states of arsenic have different toxicities. Studies show arsenite can be a degree of magnitude more toxic than arsenate (Coddington, 1986; Saranko et al., 1998).

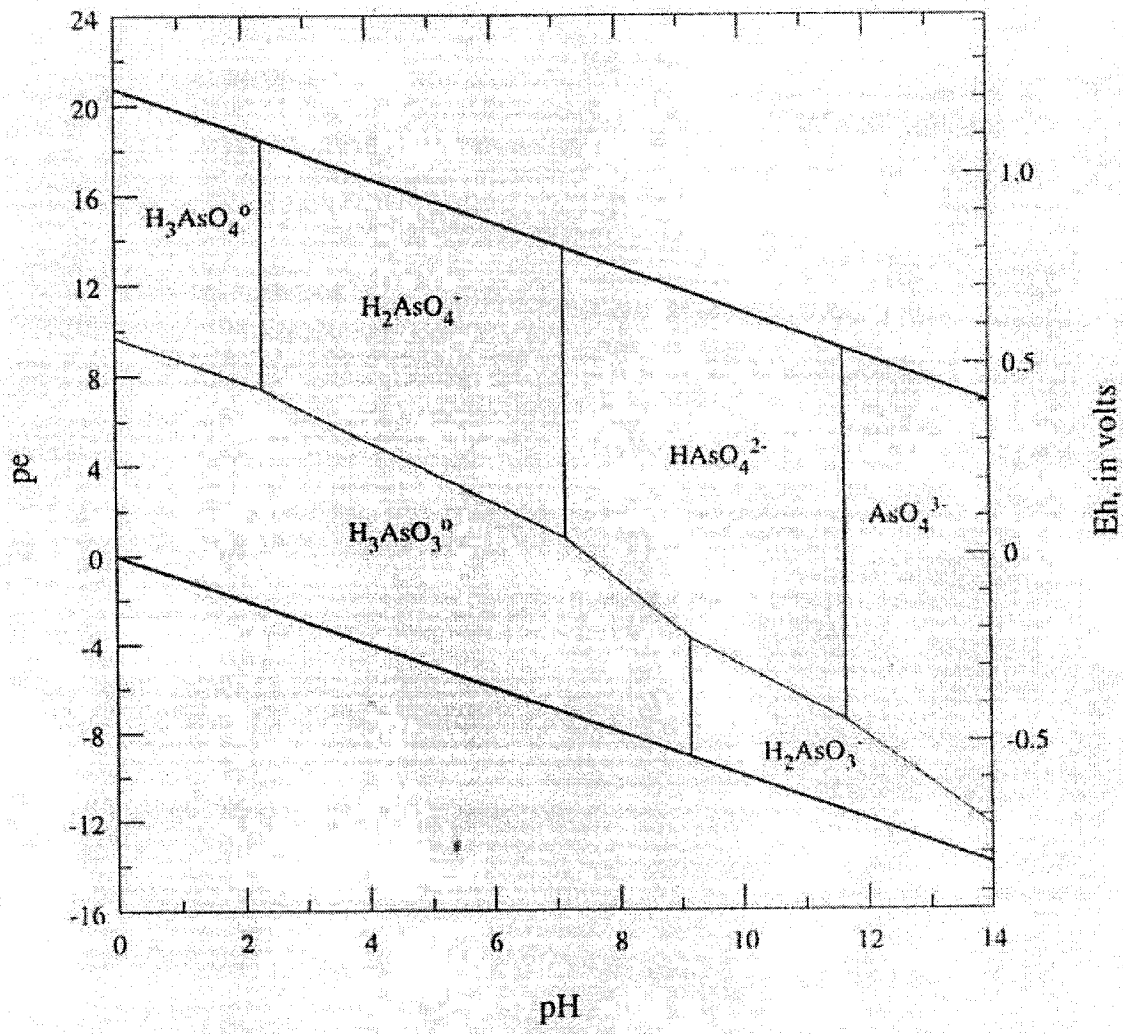

Figure 2.5 Eh-pH diagram of aqueous arsenic species in the system As-O_2-H_2O at 25^0C and 101.3 kPa total pressure (Nordstrom and Archer, 2003)

Chapter 3

Health Exposure, Toxicity and Effect of Arsenic

3.1 Maximum Contamination Level (MCL)

Arsenic is classified as a Group A carcinogen by the United States Environmental Protection Agency (USEPA) (Lien and Wilkin, 2005), World Health Organization (WHO, 1993) and International Agency for Research on Cancer (Welch et al., 1988). The increasing awareness of the toxicity of arsenic, the regulatory authorities have reduced the maximum contamination level (MCL) of total arsenic in drinking water. Table 3.1 shows the MCL of some regulatory authorities.

Table 3.1 Maximum Contamination Level (MCL) of different regulatory authorities

Authority/Country	**Maximum Contaminant Level (MCL)** (μg/L)	**References**
WHO	10	WHO, 1996
Australia	7	NHMRC, 1996
US EPA	10	USEPA, 2001
European Community (EC)	10	European commission directive, 1998
Canada	10	Health Canada, 2006
Bangladesh, China, India, Taiwan, Vietnam, etc.	50	Nordstrom, 2002

3.2 Route of Exposure

The possible routes of entry of arsenic from different environmental media include inhalation of arsenic contaminated air, ingestion of arsenic containing food and water, and skin contact (WHO, 2002). Airborne arsenic concentrations are

usually between 0.02 and 4 ng/m^3. This concentration is too low to induce any noticeable health effects by inhalation (WHO, 2002). As for skin contact, arsenic does not readily absorb into skin upon contact. Therefore, inhalation and skin contact are negligible sources of entry for arsenic. The drinking of arsenic contaminated water is the most important route of entry (Gebel, 2000).

3.3 Toxicity of Different Species

Arsenic is considered as the king of poisons and the poison of kings. The severity of toxicity depend on the chemical form, oxidation state, and water solubility of the arsenical involved (Fowler, 1977); the route, dose, and duration of exposure; and individual and local tissue susceptibilities (Morton, 1994). The toxicity scale of arsenic decreases in the following order: arsines > inorganic As(III) > organic As (III) > inorganic As(V) > organic As(V) > metallic/elemental arsenic (Morton, 1994; Hindmarsh, 2000).

3.4 Health Effect

3.4.1 Acute Effect

Acute poisoning results from ingestion of high doses of arsenic with lower exposure times. Due to ingestion of high doses of arsenic, symptoms may appear within 30 to 60 minutes, though they may be delayed when taken with food. Acute arsenic poisoning may start with a metallic or garlic-like taste, burning lips and dysphagia following violent vomiting and hematemesis (WHO, 2002) as a result of

intestinal injury caused by dilatation of splanchnic vessels leading to mucosal vesiculation. After these initial gastrointestinal problems, multi-organ failures may occur, followed by death. Survivors of acute arsenic poisoning commonly incur damage to their peripheral nervous system (WHO, 2002). Acute poisoning has a mortality rate of 50-75% and death usually occurs within 48 hours. A lethal dose varies with arsenic speciation but 0.2-0.3 g of arsenic trioxide is usually fatal for adult humans (University of Western Australia, 2002). Reported arsenate (As V) LD_{50} values in rats are 110 mg/kg, while the LD_{50} values in rats for arsenite (As III) varies from 15 mg/kg to 110 mg/kg. Therefore, arsenite (As III) is a magnitude more acutely toxic than arsenate (As V) (Saranko et al., 1998).

Table 3.2 Acute toxicity of different species (Pontius et al. 1994)

Species	**LD_{50} (mg/kg)**
Rats	15 -293
Mice	26 – 43
Guinea pigs	9
Humans	1 – 4 (approx.)

3.4.2 Chronic Effect

Chronic poisoning occurs due to low doses of consumption for a long period of time. The chronic arsenic poisoning has effects on many parts of the bodily systems, including the gastrointestinal system, respiratory system (Morton, 1994), cardiovascular system (Franzblau, 1989; Morton, 1994), peripheral nervous system

(Morton, 1994; Hindmarsh, 2000), skin (Hindmarsh, 2000; Morton, 1994; Mass, 1992), and mucous membranes (Franzblau, 1989). Arsenic has also teratogenic, reproductive, mutagenic (Morton, 1994; Vahter, 2000; Domingo, 1994; Fowler 1977), and carcinogenic effects (Morton, 1994; Hindmarsh, 2000; Mass, 1992). In the context of drinking water supply, acute poisoning is less common than chronic exposure.

3.5 Arsenic Metabolism

The process of arsenic uptake and distribution in organisms adapts the pathway of the element phosphorus, which is an important element for living organisms. Phosphorus forms nerve tissue, bones and teeth. It also makes up a part of the membrane tissue that surrounds living cells and transports the energy that fuels muscle contraction (Button and Davis, 1997). Phosphorus and arsenic have similar oxidation states and ability to form covalent bonds with sulfur. These characteristics contribute to arsenic's toxicity. Arsenate (H_3AsO_4) is an analogue of phosphate and is taken up via the phosphate transport system by most organisms. Arsenate has been postulated to replace phosphate in energy transfer phosphorylation reactions (Smedley and Kinniburgh 2002). The comparison of arsenic and phosphorus is partly illustrated by comparing dissociation constants for arsenic and phosphoric acid from equation 3.1 to 3.3 (Linge, 2002).

Acid dissociation constants for phosphoric acid (arsenic acid in brackets) (Linge, 2002)

$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$	$pK_{a1} = 2.15$ (2.20)	(3.1)
$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$	$pK_{a2} = 7.20$ (6.97)	(3.2)
$HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+$	$pK_{a3} = 12.38$ (11.53)	(3.3)

Arsenite (As III) has a high affinity for thiol groups of proteins, inactivating many enzymes and tissue proteins such as keratin in skin, nails, and hair, and has a longer half-life than other arsenic species in mammalian systems. Due to the bioaccumulation of arsenic in the body, the effects are irreversible.

Chapter 4

Arsenic Removal Technologies

4.1 Arsenic Treatment Options: an Overview

Arsenic is present in groundwater as trivalent arsenites (As III) and pentavalent arsenates (As V), in different proportions. Arsenite is generally more difficult to remove than arsenate by conventional treatment methods (Kartinen and Martin, 1995; Lackovic, et, al., 2000). Hence, most methods require an oxidation step as pre-treatment that converts arsenites to arsenates for effective arsenic removal. Oxygen is the preferred oxidant because it avoids the formation of residuals and oxidation by-products, but the process is extremely slow (Jekel, 1994). For the selection of oxidants, in the case of drinking water treatment, some important factors like residuals of oxidants, oxidation by-products, and the oxidation of other inorganic and organic water constituents are considered. Some effective oxidants are free chlorine, hypochlorite, ozone, permanganate, and hydrogen peroxide (Jekel, 1994). In addition to these chemical oxidants, MnO_2-based solid oxidizing media (SOM), Filox-R^{TM}, was also successfully used by Ghurye and Clifford (2001).

Oxidation alone does not remove arsenic from solution but must be combined with an arsenic removal process. If oxidation is considered as a separate subject, all of the arsenic removal technologies can be put in two categories, membrane separations and adsorbents. Membrane separations include reverse osmosis, nanofiltration and electrodialysis (Viraraghavan, 1999; Su and Puls, 2001; Prasad, 1994). Adsorbents

include fixed bed adsorbent media, metal hydroxides precipitated from solution and ion exchange resins. Fixed bed adsorbent media can be both engineered and bio materials.

Some engineered adsorbents are activated alumina, metal oxy-hydroxides, iron-based media, activated carbon, activated bauxite; manganese greensand and iron oxide coated sand (Chen, et. al., 1999; Frey, 1998; Chwirka, et.al., 2000; Clifford, 1999; Edwards, 1994; Jekel, 1994; Kartinen and Martin, 1995). Examples of biosorbents include modified fungal biomass, coconut coir pith, sea nodule, *Lessonia nigrescens* and orange waste (Viraraghavan et al., 2006; Matis et al., 2003; Anirudhan et al., 2006; Bhattacharjee et al., 2005; Hansen et al., 2006; Inoue et al., 2003). Arsenic is also removed from solution by adsorption-coprecipitation using coagulants e.g. alum or iron salts, lime softening; oxidation followed by filtration or precipitation (Banerjee, et.al., 1999; Kartinen and Martin, 1995; McNeill and Edwards, 1997; Mortazavi, et.al).

4.2 Best Available Technologies (BATs)

Among the conventional techniques USEPA (Federal Register, Vol. 66, No. 14, US EPA, 2001) has identified those presented in Table 4.1 as best available technologies (BATs) for effective arsenic removal from drinking water. Technologies are judged by the USEPA to be a BAT when they possess high removal efficiency, a history of full-scale operation, general geographic applicability, reasonable cost based on large and metropolitan water systems, reasonable service life, compatibility with other water treatment processes, and the ability to bring all of the water in a system

into compliance. In the following sections the best available technologies (BATs) are briefly described.

Table 4.1 Removal efficiency of arsenate by EPA-designated best available technologies, BATs, (US EPA, 2001)

Treatment Technology	**Max. % Removal (As V)**
Ion Exchange (sulfate ~ 50 mg /L)	95
Activated Alumina	95
Oxidation/Filtration (20: 1 Iron: Arsenic)	80
Modified Lime Softening (pH > 10.5)	90
Modified Coagulation/Filtration	95
Reverse Osmosis	>95
Electrodialysis	85

4.2.1 Ion Exchange (IX)

Ion exchange is the reversible interchange of ions between the solid and the liquid phase where there is no permanent change in the structure of the solid. Synthetic ion exchange resins are based on a cross-linked polymer matrix typically composed of polystyrene cross-linked with vinyl benzene. Charged functional groups are attached to the matrix through covalent bonding and fall into four groups (Clifford, 1999); strongly acidic, weakly acidic, strongly basic and weakly basic. These groups are exchanged for ions of similar charge in solution that have a stronger exchange affinity (i.e., selectivity) for the resin. Selectivity depends on the types of resin used.

Figure 4.1 shows a typical process flow diagram for ion exchange. Arsenate can be removed through the use of strong-base anion exchange resin (SBA) in either chloride or hydroxide form. These resins are insensitive to pH in the range 6.5 to 9.0 (USEPA, 2000 b; refer to Clifford et al., 1998).

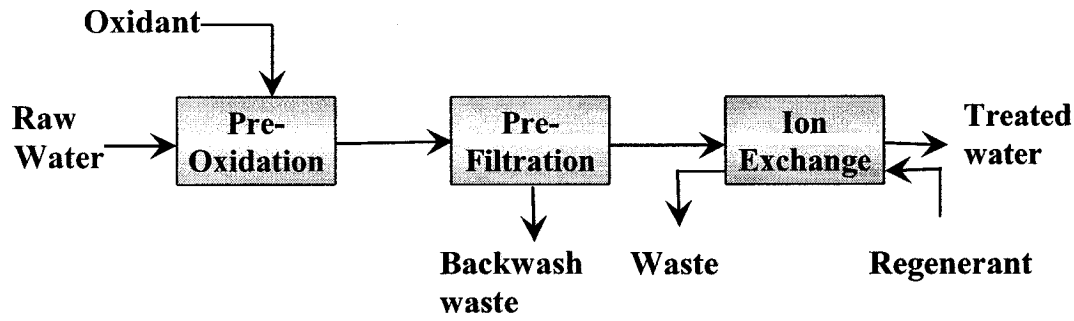

Figure 4.1 Ion exchange process flow diagram (USEPA, 2003).

If arsenic-contaminated source water contains less than 500 mg/L total dissolved solids (TDS) and less than 120 mg/L sulfate, then ion exchange may be the arsenic-removal process of choice (Clifford and Lin, 1986). As the resin becomes exhausted, it needs to be regenerated. The arsenic exchange and regeneration equation with common salt solutions at near-neutral pH are as follows:

Arsenic exchange:

$$2\ R\text{-}Cl + HAsO_4^{2-} \leftrightarrow R_2HAsO_4^{2-} + 2Cl^-$$

Regeneration:

$$R_2HAsO_4^{2-} + 2NaCl \leftrightarrow 2\ R\text{-}Cl + Na_2HAsO_4$$

Where R denotes the resin matrix

4.2.2 Activated Alumina

Activated alumina (AA) is a porous, granular material with a typical diameter of 0.6 to 0.3 mm having high surface area of 50-300 m^2/g. The media, aluminum trioxide (Al_2O_3), is prepared through the dehydration of precipitated aluminum hydroxide, $Al(OH)_3$, at a temperature range 300-600^{0}C. It is able to remove a wide range of anions using an ion exchange mechanism with the hydroxylated surface (Azizian, 1998). The mechanism of arsenate adsorption in acid solution can be written as:

$$\overline{\equiv Al-OH} + H^+ + H_2AsO_4^- \rightarrow \overline{\equiv Al-H_2AsO_4} + HOH$$

The arsenate desorption by hydroxide (alumina regeneration) is presented as:

$$\overline{\equiv Al-H_2AsO_4} + OH^- \rightarrow \overline{\equiv Al-OH} + H_2AsO_4^-$$

Where, $\equiv Al$ represents the alumina surface and an overbar denotes the solid phase. Figure 4.2 shows a typical process flow diagram for activated alumina. Dashed lines and boxes indicate optional streams and processes.

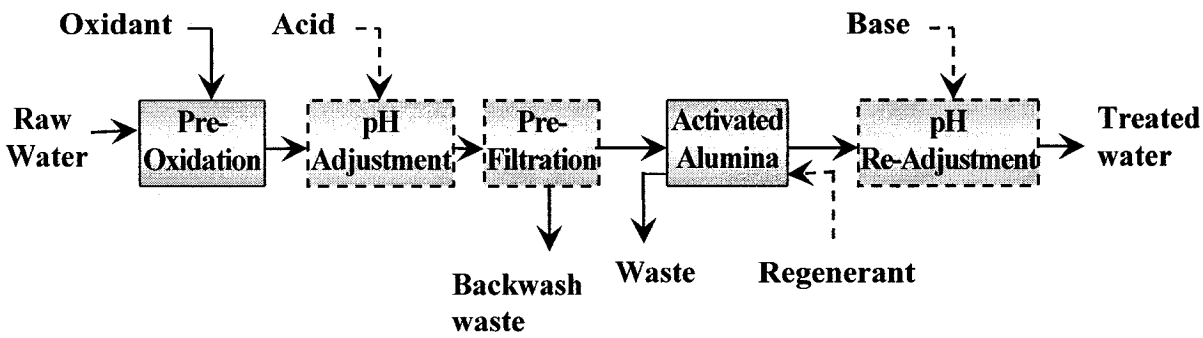

Figure 4.2 Activated alumina process flow diagram (USEPA, 2003).

Major factors affecting adsorption by activated alumina are pH, competing ions, EBCT (empty bed contact time) and arsenic oxidation state. Several different studies have established the optimum pH range as 5.0-6.0, and demonstrated greater than 98% arsenic removal under these conditions. AA column runs operated under acidic pH conditions are 5 to 20 times longer than under natural pH conditions (6.0-9.0). Ions compete to varying degrees with arsenate for adsorption sites (Clifford, 2000; Azizian, 1998). The following selectivity sequence has been established for AA adsorption (USEPA, 2000):

$OH^- > H_2AsO_4^- > Si(OH)_3O^- > F^- > HSeO_3^- > TOC > SO_4^{2-} > H_3AsO_3^-$

The poor selectivity, due to neutral molecular charge below the pK_{a1}= 9.2, of AA towards arsenite, requires a pre-oxidation of arsenite to arsenate.

4.2.3 Lime Softening

Lime softening is a chemical-physical treatment process used to remove calcium and magnesium cations from solution. To remove arsenate, additional lime is added to increase the pH above 10.5. In this range magnesium hydroxide precipitates and arsenate is removed by co-precipitation with it. Arsenate removal by co-precipitation with calcium carbonate (i.e., below a pH of 10.5) is poor (less than 10%) (USEPA, 2003). These precipitates are then amenable to removal by clarification and filtration.

4.2.4 Oxidation/Filtration

Oxidation/filtration refers to processes that are designed to remove naturally

occurring iron and manganese from water. The processes involve the oxidation of the soluble forms of iron and manganese to their insoluble forms and then removal by filtration. If arsenic is present in the water, it can be removed via two primary mechanisms: adsorption and co-precipitation. First, soluble iron and arsenite are oxidized. The arsenates then adsorb onto the iron hydroxide precipitates that are ultimately filtered out of solution.

Although some arsenic may be removed by adsorption/co-precipitation with manganese, iron is much more efficient for arsenic removal. The arsenic removal efficiency is strongly dependent on the initial iron concentration and the ratio of iron to arsenic. In general, the Fe : As mass ratio should be at least 20 : 1, which may yield an arsenic removal efficiency of 80-95% (Selecky et al., 2003).

The effectiveness of arsenic co-precipitation with iron is relatively independent of source water pH in the range 5.5 to 8.5. However, high levels of natural organic matter (NOM), orthophosphates, and silicates weaken arsenic removal efficiency by competing for sorption sites on iron hydroxide precipitates (Fields et al., 2000b).

4.2.5 Coagulation/Filtration

Coagulation is the process of destabilizing the surface charges of colloidal and suspended matter to allow for the agglomeration of particles. This process results in the formation of large, dense floc, which is amenable to removal by clarification or filtration through a granular media. The most widely used coagulants for water treatment are aluminum and ferric salts, which hydrolyze to form aluminum and iron hydroxide particulates, respectively.

The mechanism involves the adsorption of arsenate to an aluminum or ferric hydroxide precipitate. The arsenate becomes entrapped as the particle continues to agglomerate. Arsenite is not effectively removed because of its overall neutral charge under natural pH conditions. Therefore, pre-oxidation is recommended. A generic oxidation/coagulation/filtration process flow diagram is shown in Figure 4.3 for better understanding.

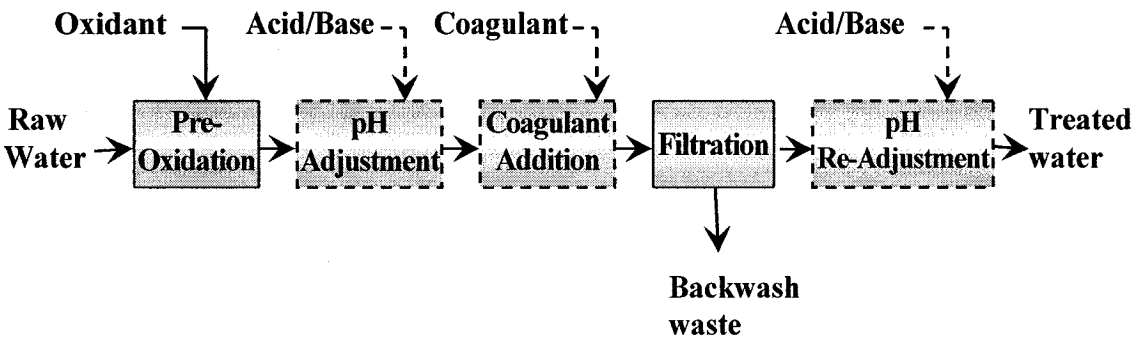

Figure 4.3 Generic oxidation/coagulation/filtration process flow diagram (USEPA, 2003)

The efficiency and economics of the system depend on several factors, including the type and dosage of coagulant, mixing intensity, and pH. In general, optimized coagulation-filtration systems are capable of achieving over 90% removal of arsenate.

4.2.6 Coagulation-Assisted Micro-filtration (CMF)

Coagulation-assisted micro-filtration uses the same coagulation process described above except that the water is forced through a semi-permeable membrane by a pressure differential instead of passing through the granular media. The

membrane retains the As(V) laden flocs formed in the coagulation step. The membrane must be periodically backwashed to dislodge solids and restore hydraulic capacity. Backwash water is typically a high-volume, low solids (less than 1.0%) waste stream. The specific amount of solids will depend on several factors, including coagulant type, dosage, filter run length, and ambient solids concentration (AWWARF 2000).

4.2.7 Membrane Techniques

Membrane techniques like reverse osmosis, nano-filtration and electrolysis are capable of removing almost all kinds of dissolved solids including arsenic from water. In this technique arsenic is separated from water by passing it through a semi permeable barrier or membrane. Pressure difference is the driving force for the separation. The removal efficiency depends on the pore size in the membrane and the particle size of arsenic species. For better removal efficiency water should be free from suspended solids and the arsenic should be in pentavalent form. Various types of membrane filtration techniques are mentioned in Table 4.2.

Table 4.2 Various types of membrane filtration (Majumder et al., 2006)

Membrane	**Operating structure (pore size)**	**Operating range (μm)**
Microfiltration	Macropores (>50 nm)	0.08-2.0
Ultrafiltration	Mesopores (2-50nm)	0.005-0.02
Nanofiltration	Micropores (<2 nm)	0.0001-0.001
Reverse osmosis	Dense (<2 nm)	0.0001-0.001

4.2.7.1 Reverse Osmosis (RO)

Figure 4.4 provides a process flow diagram for a typical RO membrane process. Dashed lines indicate optional streams and processes.

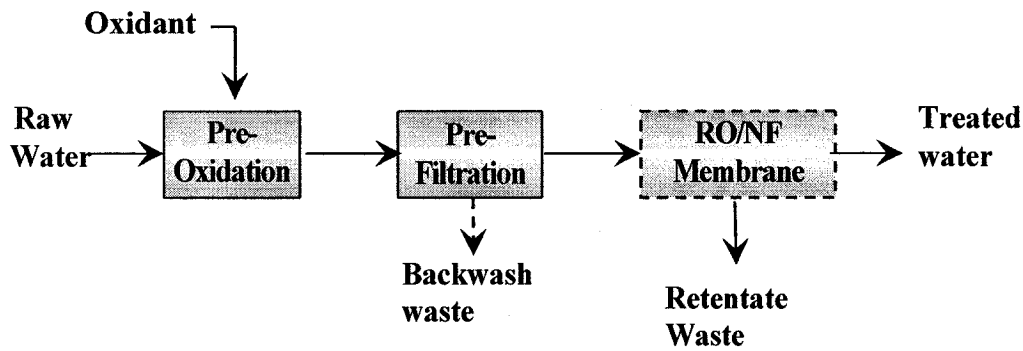

Figure 4.3 Reverse osmosis (RO) process flow diagram (USEPA, 2003)

RO is a pressure-driven membrane separation process capable of removing dissolved solutes from water by means of particle size, dielectric characteristics, and hydrophilicity/hydrophobicity. In addition to arsenic, RO can effectively remove several other constituents from water including organic carbon, salts, and dissolved minerals. The treatment process is relatively insensitive to pH. In order to drive water across the membrane surface against natural osmotic pressure, feed water must be sufficiently pressurized with a booster pump. Reverse osmosis is capable of achieving over 97% removal of arsenate and 92% removal of arsenite in a single pass (NSF, 2001a; NSF 2001b).

4.2.7.2 Electrodialysis

It is similar to reverse osmosis except that the driving force; an electric current is applied to draw the ions (dissolved solids) through the semi permeable membrane. Since, dissolved solids exist as cations (such as calcium and magnesium) and anions (such as sulfate and arsenic), the cations are attracted to a negatively charged electrode and the anions are attracted to a positively charged electrode. Electrodialysis is more effective in removing arsenate than arsenite (Ernest and Christopher, 1995).

4.3 Advantages and Disadvantages of the Different Technologies

The most efficient and cost effective arsenic treatment technology for a given utility will depend on the arsenic species and influent concentration, water quality parameters, existing treatment facilities, design flow and residual handling and disposal. The most efficient treatment still might not be cost-effective, because secondary treatment benefits and residuals handling should also be considered (Chen et.al., 1999). A comparative study of different technologies has been presented in Table 4.3 for better selection during application.

Table 4.3 Advantages and disadvantages of various treatment processes (USEPA, 2003)

Process	Advantages	Disadvantages
Ion exchange	Can produce treated water with As concentration less than 2μg/L	Efficiency affected by sulfate, nitrates, fluoride ions, total dissolved solids, selenium, etc.
Adsorption on activated alumina	Well established; suitable for home use; typically inexpensive with simple replacement requirements; improves test and odors	Need careful monitoring; effectiveness is based on contaminant type, concentration and rate of water usage; bacteria may grow on alumina surface
Adsorption on activated carbon	Typically inexpensive with simple replacement requirements; improves test and odors	Efficiency depends on the ash content in the carbon and on the metal concentration; not Proven
Precipitation with alum	Well established; suitable for home use	Use of chemicals; high arsenic contaminated sludge; dose of oxidizing chemicals highly influence the removal efficiency
Precipitation with iron	Proven and reliable	Use of chemicals; high arsenic contaminated sludge; dose of oxidizing chemicals highly influences the removal efficiency
Precipitation with Fe/Mn	Proven and reliable	Higher and lower pH reduces efficiency; use of chemicals; high arsenic contaminated sludge; dose of oxidizing chemicals highly influences The removal efficiency
Lime softening	Proven and reliable; reduces corrosion	Sulfate ions influence efficiency; secondary treatment is required; use of chemicals
Reverse Osmosis (RO)	Highest water quality; treats wide range of dissolved salts, minerals; turbidity	Expensive to install and operate; frequent membrane monitoring; pH, temperature and pressure control to meet membrane tolerance
Electro dialysis	Pure quality water	Less proven; costly; needs oxidizing agents

4.4 Biosorption Technology

Biosorption, sometimes referred to as passive uptake, is a property of certain types of inactive, dead, microbial biomass to bind and concentrate metals from aqueous solutions. Binding of metal species by biomass that acts like a chemical substance, is a complex phenomenon which involves different sorption processes like ion exchange, complexation, chelation and micro-precipitation. The sorption may occur due to only one or any combination or all of these processes at a time. It is particularly the cell wall structures of certain algae, fungi and bacteria which are found responsible for this phenomenon. The mechanisms by which microorganisms remove metals from solutions are: (i) extra-cellular accumulation/precipitation; (ii) cell-surface sorption or complexation; (iii) intra-cellular accumulation (Muraleedharan et al., 1991). Among these mechanisms, process (i) may be facilitated by using viable microorganisms, process (ii) can occur with alive or dead microorganisms, while the process (iii) requires microbial activity.

Although living and dead cells are capable of metal accumulation, there are differences in the mechanisms involved, depending on the extent of metabolic dependence (Gadd, 1990). The physiological state of the organism, the age of the cells, the availability of micronutrients during their growth and the environmental conditions during the biosorption process (such as pH, temperature, and presence of certain co-ions), are important parameters that affect the performance of a living biosorbent. The efficiency of metal concentration on the biosorbent is also influenced by metal solution chemical features (Volesky, 1990).

Whereas biosorption is a passive phenomenon, bioaccumulation is an active

phenomenon where metal uptake occurs by active metabolic activities (Shumate and Strandberg, 1985; Andres et al., 1992; Fourest and Roux, 1992; Hussein et al., 2001; Hussein et al., 2003). Feasibility studies for large-scale applications demonstrated that, biosorptive processes, involved in using non-viable biomass, are more applicable than the bioaccumulative processes, involved in using viable biomass. Because the living systems (active uptake) often require the addition of nutrients and hence increase biological oxygen demand (BOD) or chemical oxygen demand (COD) in the effluent. Active uptake by the cell membrane can be highly selective and often irreversible unless the living system is destroyed. Also maintenance of healthy microbial population is difficult due to metal toxicity. Active biomass can contribute pathogens in the effluent that need further treatment. In the case of passive uptake, process control is much simpler and biosorption is faster and the biomass storage is easier. Therefore, to overcome the disadvantages of viable biomass, non-viable one is considered for this study.

4.4.1 Biomass Types

The conventional technologies are either costly to implement or lack of reliability and efficiency in removing metals from aqueous solution that led to search for new eco-friendly and low cost treatment technology like biosorption that rely on industrial by-product or wastes, specially in the case of reusing biomass from food, pharmaceutical or waste water treatment (Zouboulis et al., 1997).

Recently, biological materials such as algae, bacteria, fungi, yeast (Matuschka and Straub a, 1993; Pagnanelli et al., 2000), aquatic moss *Fontinalis antipyretica*

(Martins et al., 2004) and agricultural waste products like sunflower stalk (Sun and Shi, 1998), sargassum seaweed biomass (Kratochvil et al., 1998), pinus cone biomass (Ucun et al., 2002), rice husk (Khalid et al., 1998), olive pomace (Pagnanelli et al., 2003), cocoa shells (Tyagi et al., 2003), and grape stalk waste (Isabel et al., 2004) have been recognized as cheap natural sorbents for the removal of toxic metals. Biomass like sugarcane bagasse (Simkovic and Laszlo, 1997) and Chinese Reed (Namasivayam and Holl, 2005) have been used as anion exchangers for nitrate and anionic dye respectively.

4.4.2 Mechanism of Biosorption

The binding of metals depends on certain factors like quantity of sites in the biosorbent materials, accessibility of the sites, chemical state of the sites (e.g. availability) and the affinity between site and metal (Volesky, 2003a). It is also necessary to have a clear view of these bio-molecules and their binding sites to understand the mechanisms in binding metals. The components of the cell wall of biomass take part in the binding mechanism. The main components of the cell are water, inorganic salts and mineral elements, proteins, nucleic acids, polysaccharides and lipids. Single most abundant component of cell is water that occupies almost 70% of the total cell weight whereas inorganic salts and mineral elements comprise only a very small fraction of the total dry weight, approximately 1% (Lehniger et al., 1993). Nearly all of the solid matter is organic and can be present in different forms such as proteins, nucleic acids, polysaccharides and lipids. These organic compounds contain different surface functional groups such as carboxyl, carbonyl, hydroxyl, amine,

phosphoryl and sulfhydryl groups (Green et al., 1987). The functional groups can complex with different metal ions according to their affinities (Delgado et al., 1998). For example, the main functional groups on polysaccharides in bacteria, other than OH groups, are the carboxyl and amino groups (Buffle, 1988). One study demonstrated that the chelating ability of polysaccharides was related to their content of carboxyl and hydroxyl groups (Kaplan et al., 1987). According to Tobin et al. (1984) and Figueira et al. (1997) carboxyl, sulfur and phosphate groups are actively involved in metal ions uptake along with hydroxyl groups. Amine groups, which can provide positive charges, were found active in sorption process of molybdate (Kratochvil and Volesky, 1998) and hexavalent chromium (Sudha Bai et al., 2001). Figure 4.4 represents a bio-molecule with different surface functional groups.

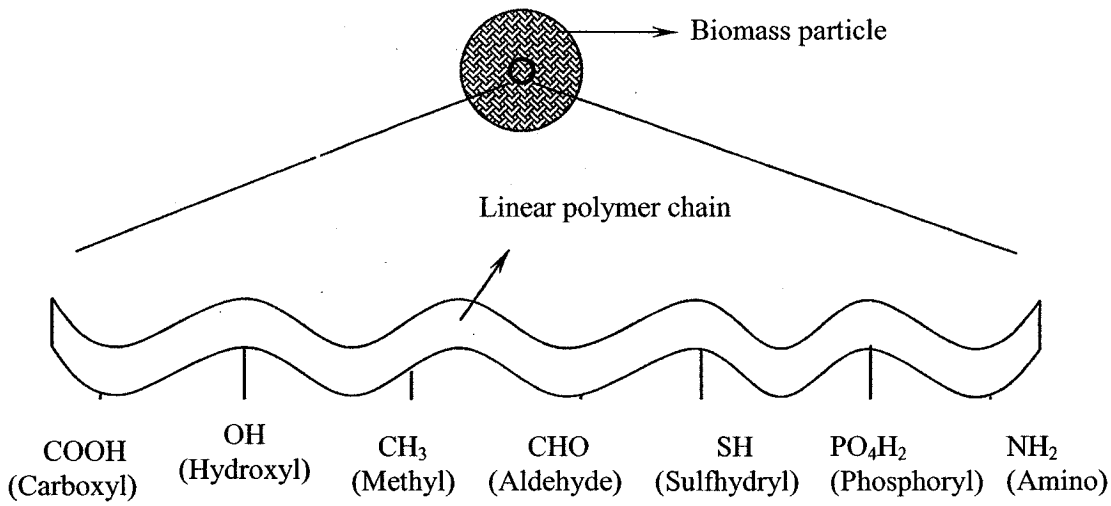

Figure 4.4 A bio-molecule with different surface functional groups (Reynolds and Richards, 1990)

Arsenic adsorption mechanisms may include molecule-surface interaction, electrostatic interaction (i.e., ion exchange, coulombic attraction) (Gupta and Chen, 1978), ligand exchange, surface complexation (Prasad, 1994), covalent bonding, and Van der Waals forces (Korte, 1991). It is very likely that all of these processes of binding may take place at the same time due to the complexity of the most cell walls (Volesky, 1990). Some technical terms mentioned above pertaining to the adsorption mechanism are defined below.

Micro-precipitation is the deposition of electrically neutral material at the surface of the biomass and does not necessarily involve a bond between the biomass and the deposited layer. Micro-precipitation may, however, be facilitated by initial binding of metal ions to reactive sites of the biomass, which serve as nucleation sites for further precipitation (Mayers and Everidge, 1989). This process is not limited to a mono-layer (or saturation of sites).

A complex (also referred to as a coordination compound) is a poly-atomic molecule that consists of one or more (then: poly-nuclear complex) central atoms (usually metal cations) surrounded by ligands that are attached to it. Complexes can be neutral or positively or negatively charged. The number of coordinating atoms (in the ligand) which are directly attached to the central atom is called coordination number and can be larger than the valence of the central atom (most common coordination numbers: 4 and 6). If one ligand is attached to the central atom through two or more coordination atoms, then the complex is called a chelate. Complexation plays an important role in metal-ligand interaction (Westall, 1987).

4.4.2.1 Adsorption by Mass Transport Mechanism

Adsorption of contaminants in solution onto a porous media (here biomass) is considered as a sequential process consisting of the following four sequential steps (Prasad, 1994; Snoeyink and Summers, 1999; Mortazavi, et.al., 1999). These transport steps are shown in Figure 4.5.

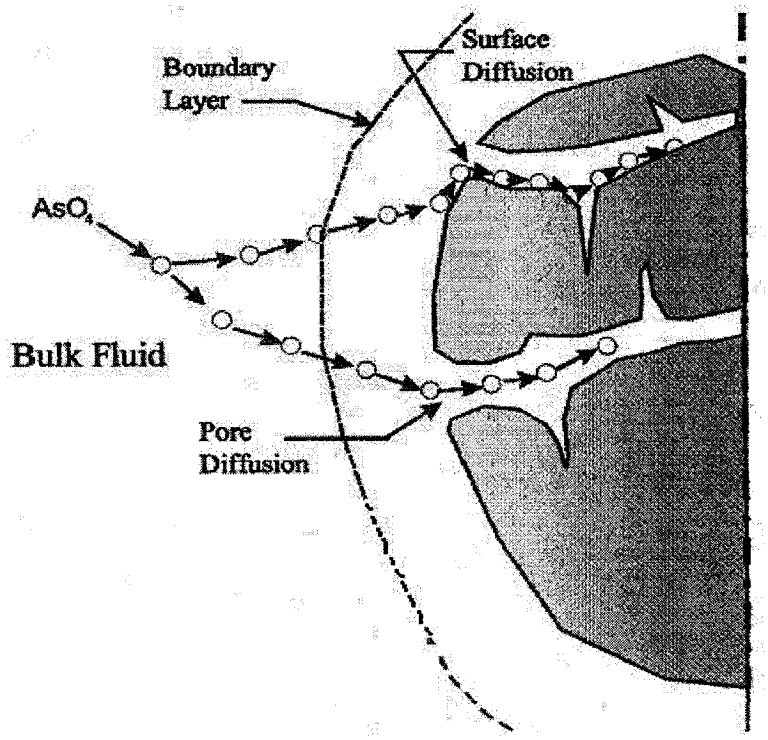

Figure 4.5 Mass transport mechanisms from bulk solution to adsorbent pores (Crittenden et al., 1981).

I. *Bulk solution transport* - Transport from the bulk solution to the hydrodynamic boundary layer surrounding the adsorbent. Depending on the velocity of the bulk solution, this transport will occur either by diffusion or turbulent mixing.

II. *External (film) resistance to transport*-Diffusion through the hydrodynamic boundary layer to the surface of the adsorbent. Transport through the boundary layer is due to molecular diffusion. The thickness of the boundary layer will depend on the velocity of the bulk solution. The size of the boundary layer will affect the rate of transport.

III. *Internal (pore) transport* - Intraparticle transport may occur by molecular diffusion through the solution in the pores (pore diffusion) or by diffusion along walls of the adsorbent pores (surface diffusion).

IV. *Adsorption* - Bonding of the adsorbate onto the adsorbent surface at available sites. This step is usually very rapid; therefore one of the preceding diffusion steps will control the rate of mass transfer.

Factors that affect the efficiency of an adsorption process include media characteristics, solution characteristics, and design parameters. Media characteristics of concern are the particle size, surface area, surface chemistry, and pore size distribution. Solution characteristics include adsorbate concentration, pH, redox conditions, temperature, dissolved organic and inorganic constituents, and microbial activity. Design parameters that affect adsorption efficiency include contact time, surface loading, and design flow (Aragon, 2004).

4.4.2.2 Binding Forces Causing Adsorption

Adsorption is the accumulation of materials at an interface, the liquid/solid boundary layer. The description in the above section clearly shows that this accumulation of materials, in other words adsorption, is a mass transfer process where the accumulated material is transferred from the liquid phase to the surface of the solid and becomes bound by chemical or physical forces. Binding by chemical force termed as chemical adsorption, or chemisorption, is based on electrostatic forces. The difference between physical adsorption and chemisorption is not distinct; the former is less specific for which compounds sorbed to which surface sites, has weaker forces and energies of bonding, operates over longer distances, and is more reversible. In chemical adsorption, the attraction between adsorbent (solid media) and adsorbate (contaminant to be removed) approaches that of covalent or electrostatic chemical bond between atoms, with shorter bond lengths and higher bond energies (Smith, 1981; Stumm and Morgan, 1970).

Physical forces can be subdivided into electrostatic and London-van der Waals forces (Myers, 1991). In the resulting bonds, the electrons stay in their original systems. Electrostatic (or coulombic) forces between ions or between ions and dipoles extend over a long range and are the strongest among the physical bonds (Myers, 1991). The interaction is repulsive for ion charges of the same sign and attractive for unlike charges. The magnitude of the force is proportional to the charge of each ion and inversely proportional to the square of the distance between the ions.

Other physical interactions among molecules, based on electrostatic force, include dipole-dipole interactions, dispersion interactions, and hydrogen bonding.

When two polar compounds are near each other, they tend to orient their charges to lower their combined free energy; negative charges of one tend to approach positive charges of the other. When electrostatic forces among the charges of the two molecules are summed, the net dipole-dipole interaction is an attraction between the two. Hydrogen bonding is a special case of dipole-dipole interaction in which the hydrogen atom in a molecule has a partial positive charge and attracts an atom on another molecule that has a partial negative charge. When two neutral molecules that lack permanent dipoles approach each other, a weak polarization is induced in each because of quantum mechanical interactions between their distributions of charge. The net effect is a weak attraction between the molecules, known as the dispersion interaction or the London-van der Waals force (Russell, 1980).

Chapter 5

Materials and Methods

5.1 Biomass

Anaerobic sludge was collected from an anaerobic wastewater treatment plant treating effluents from the cheese production located at Agropur, Notre Dame de Bon Conseil, Quebec, Canada (Figure 5.1).

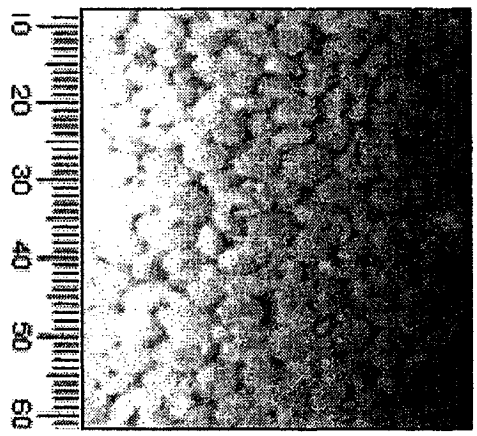

Figure 5.1 Anaerobic sludge obtained from an anaerobic wastewater treatment plant for cheese production.

The sludge was first centrifuged for 20 minutes at 3000 rpm. The pellets that were left by centrifugation at the bottom of the centrifuging tubes were dried in an oven at 50°C for 6 days. Thereafter, the dried biomass was ground and sieved into different size fractions. The fraction collected between mesh sizes 16 and 20, corresponding to a particle size ranging from 0.84 mm to 1.18 mm, was used in the experiments. This biomass was termed as 'untreated biomass' and shown in Figure 5.2.

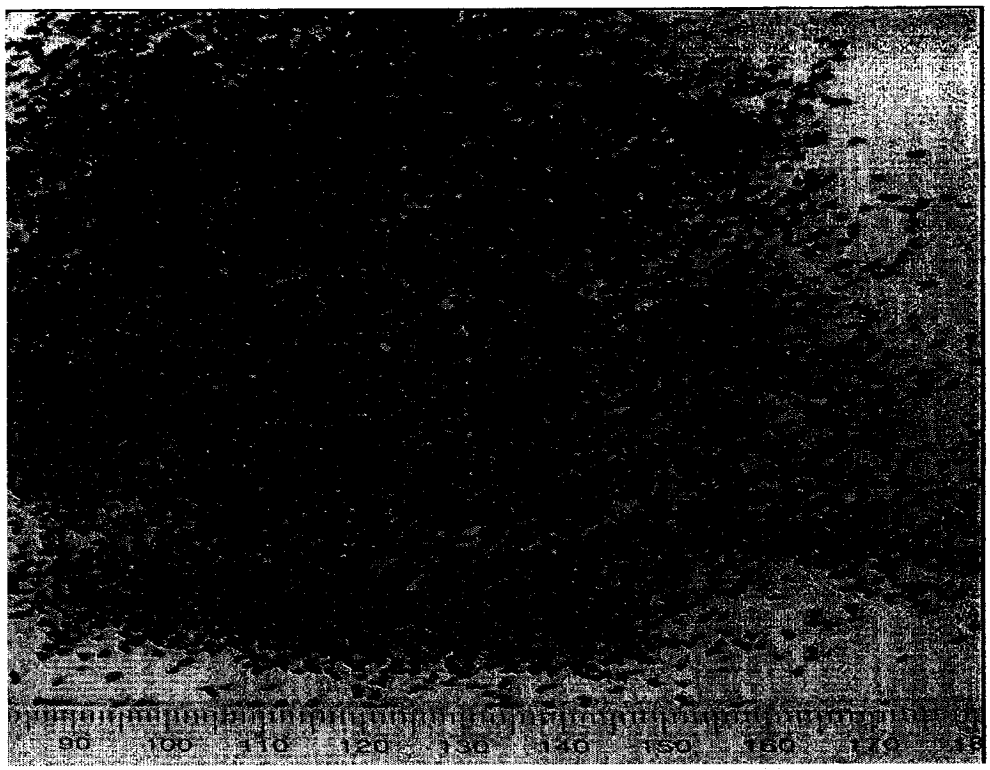

Figure 5.2 Dried and sieved biomass (particle size, 0.84 mm - 1.18 mm)

The biomass was then impregnated with PO_4 and Cl separately to check whether the impregnation would increase the biosorption capacity of arsenic. PO_4-impregnated biomass was prepared by combining sieved and dried biomass separately with 0.01 M and 0.02 M KH_2PO4 in a 2 L beaker for 3 hours at a biomass concentration of 20 g/L and a pH value of 7 and 12, adjusted by 0.1M NaOH. Subsequently the KH_2PO_4 solution was drained and the biomass was washed with distilled water 4 or 5 times. Finally, the wet biomass loaded with PO_4 was dried in the oven at 50°C for about 48 hours.

Biomass impregnation with Cl was prepared by the same method as PO_4-

biomass except mixing the dried and sieved biomass with 0.02 M KCl at a pH value of 4 and 7. The KCl solution was drained and the biomass was washed with distilled water 4 or 5 times. Finally, the wet biomass loaded with Cl was dried in the oven at 50°C for about 48 hours.

Phosphate competes with arsenate for sorption sites (Woolson et al., 1973). Phosphoric acid produces three anionic species at the pHs above their pKa values of 2.15, 7.20 and 12.38 respectively as shown in section 3.5. Biomass was loaded with Cl considering its analogy with the Cl-form synthetic resin. The protein/amino acids present on the biomass surface provide cationic sites between pH 4 and 8 as explained in section 6.10. It was speculated that these cationic sites would hold the anionic species of KH_2PO_4 and KCl that would be subsequently exchanged by the anionic species of arsenic.

5.2 Biomass Characteristics

5.2.1 Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand (COD) test measures the chemical oxidant required to break down organics. COD is an indicator of the concentration of organics in the solution. The Closed Reflux, Colorimetric Method from American Public Health Association (1995) was used.

The biomass was diluted 50, 100 and 200 times, 2.5 mL of the diluted samples were added to the standard tube which contains 7.5 mL of the digestion solution (commercially available pre-measured solution containing a 7.5 mL mixture of sulfuric acid, potassium dichromate, silver sulfate, mercuric sulfate, and sulfuric acid

in twist cap digestion vials, and potassium hydrogen phthalate (KHP) standard (425 mg KHP/L distilled water; having a theoretical COD of 500 mg O_2/L). The final dilution of the biomass was 200, 400 and 800 times. The samples were digested for two hours at 150°C. The tubes are then cooled and the test color was measured using a Perkin-Elmer Lambda 40 Spectrophotometer with cell adapters for COD vials. The standard vials cover a COD range of 0 - 125 mg O_2/L (in the final 10 mL digestion mixture). Since this 2.5 represents a 4X dilution (2.5 mL to 10.0 mL) for digestion, this corresponds to a maximum working range of 0 - 500 mg O_2/L. The average COD was found to be 66,700 mg O_2/L.

5.2.2 Settled Sludge Volume and Solids

According to the American Public Health Association (1995), an Imhoff cone was filled to the 1-L mark with a well-mixed sample of the sludge. The sample was left to settle for one hour. The settleable solids were found to be 860 mL/L.

The total solids of the sludge were determined. A well-mixed sample of 10 mL of the sludge was evaporated in a weighed dish and dried to constant weight in an oven at 105°C. The increase in weight over that of the empty dish represents the total solids (TS), the test was done in triplicate, and gave TS = 39,700 mg/L. To determine the total volatile solids (TVS) the residue from the previous procedure was ignited to a constant weight at 550°C. The weight lost on ignition is the volatile solids, the test was done in triplicate, and determined to be TVS = 27,800 mg/L. TVS offers a rough approximation of the amount of organic matter present in the solid fraction of the sludge. The other part of the sludge is the inorganic part which is represented by the

total fixed solids (TFS), and determined as TFS = 39,700 mg/L – 27,800 mg/L = 11,900 mg/L. From these results it can be seen that almost 70% of the solid fraction of the sludge is organic matter. The remaining 30% is inorganic matter which consists of inorganic salts and mineral elements.

To determine the total suspended solids (TSS), a 5 ml sample of the unsettled part in the Imhoff cone was filtered through a weighed standard glass filter and the residue retained on the filter was dried to a constant weight at 105°C. The increase in weight of the filter represents the total suspended solids, the test was done in triplicate and TSS = 1240 mg/L. To determine the total volatile suspended solids (TVSS) the residue from the previous procedure was ignited to a constant weight at 550°C. The weight lost on ignition is the volatile solids, the test was done in triplicate, TVSS was found to be 1140 mg/L, which indicated that almost 92% of the TSS was volatile (organic matter) and the rest of the 8% is inorganic salts and minerals. The characterization of the solids of the biomass is summarized in Table 5.1.

Table 5.1 Characterization of anaerobic biomass solids

Sludge Solid Characteristics	**Concentration (mg/L)**
Total Solids (TS)	39,700
Total Volatile Solids (TVS)	27,800
Total Fixed Solids (TFS)	11,900
Total Suspended Solids (TSS)	1,240
Total Volatile Suspended Solids (TVSS)	1,140

5.2.3 Specific Gravity

The specific gravity of the biomass is the ratio of the masses of equal volumes of biomass and distilled water. The specific gravity of the biomass was determined according to the American Public Health Association (1995) by comparing the mass of known volume of biomass sample at a specific temperature to the mass of the same volume of distilled water at 4°C. Three samples were taken and the average of the three samples was used to calculate the specific gravity of the biomass:

Specific Gravity (SG) = 0.78

5.2.4 Biomass Bulk Density

Bulk density is a measure of the weight of the biomass per unit volume (g/mL), usually given on a dry basis. Variation in bulk density is attributable to the relative proportion and specific gravity of solid organic and inorganic particles and to the porosity of the biomass. Since the biomass will not be dry during its use, it is required to measure the wet bulk density of the biomass.

The wet bulk density of the biomass was measured by saturating 1.56 g (dry weight) of the biomass (2.0 mL) with distilled water and measuring the increase of volume with time. The volume was measured until constant volume was achieved almost after 24 hours (3.40 mL). Three samples were taken and the average of the three samples was used to calculate the bulk density:

Wet bulk density = 0.46 g (dry weight)/mL (wet volume)

5.2.5 Specific Surface Area

The specific surface area of the samples was determined by the BET (Brunauer-Emmett-Teller) method using nitrogen physisorption at 77K. The measurements were carried out using the Micromeretics ASAP 2000 apparatus. Samples were outgassed in a vacuum for 4 hour at 373 K before N_2 physisorption.

Specific surface area found = 3.5 m^2/g

Table 5.2 Physical properties of the anaerobic biomass

Parameter	Value
Organic matter (%)	70
Specific surface area (m^2/g)	3.5
Specific gravity (SG)	0.78
Wet bulk density (g/mL)	0.46

5.3 Chemical Reagents

This study deals with the inorganic species of arsenic such as penta-valent arsenate and trivalent arsenite. Stock solutions of arsenate and arsenite were prepared in distilled water using dibasic sodium arsenate ($Na_2HAsO_4.7H_2O$) and arsenic trioxide (As_2O_3) respectively. The concentrations of both stock solutions were made to 1000 ppm (mg/L) and stored in high density polyethylene (HDPE) bottles at room temperature. The stock solutions were subsequently diluted to different concentrations according to the requirements of the test.

5.4 Batch Experiments

Varying amounts of dried biomass were suspended in 50 mL of arsenic solution in 50 mL centrifuge tubes. The tubes were placed on a shaker at 100 rpm and left to equilibrate for 24 hours (Figure 5.3). The supernatant solution was then filtered with the Whatman # 42 (0.45 μm pore size) filter paper and the concentration of arsenic in the filtrate was determined. Arsenic sorption capacity of the biomass was calculated from the difference between the initial and final supernatant concentrations. Since there was potential for arsenic adsorption onto the surface of the glassware or plastic ware, biosorbent-free known concentration of arsenic considered as blanks were used as controls with every set of experiments.

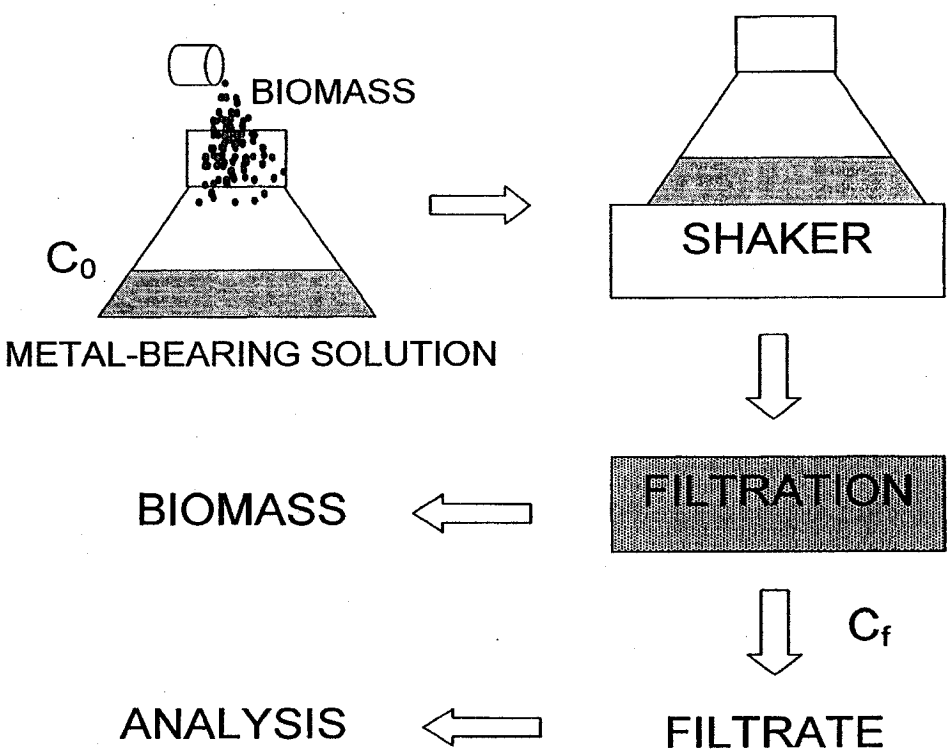

Figure 5.3 Schematic diagram of batch experiments

Three forms of biomasses were used for batch experiments; (i) untreated biomass (ii) PO_4-impregnated biomass and (iii) Cl-impregnated biomass.

In the first set of batch experiments, a fixed amount of treated and untreated biomass was separately suspended in arsenate solution to compare the sorption capacity between them. In the second set of batch experiment same amount of both types of biomass was again separately suspended in arsenite solution. From both sets of experiments, the sorption behavior of the treated and untreated biomass in arsenate and arsenite solution was established. Different initial arsenic concentrations were used to evaluate its effects on the sorption capacity of biomass. To analyze the influence of pH, a major controlling factor of this study, different pH values from 3 to 10 in a single interval were used for both sets of experiments. The pH of the solutions before and after the sorption experiment was monitored. Each set of tests was done in duplicate and the average was considered for producing the results.

5.5 Arsenic Concentration Analysis

5.5.1 Colorimetric (Hach) Method

The chemical analysis of the samples was done by a colorimetric method (Hach method) for the detection of arsenic (0-500 μg/L). The method was developed by Hach Company, Colorado, USA and the test kits were bought from Anachemia Science, Quebec, Canada.

Sulfamic acid and powdered zinc react to create strong reducing conditions in which inorganic arsenic is reduced to arsine gas (AsH_3). The arsine gas then reacts

with mercuric bromide impregnated test paper to form mixed arsenic/mercury halogenides (e.g. AsH_2HgBr). The mixed halogenides discolor the test strip depending upon the concentration of the arsenic in the sample. The color change is from white to yellow to tan to brown. According to the Hach method, inorganic arsenic whether it is in arsenite or arsenate form is converted to arsine gas as per the following reactions:

$$As_2O_3 + 6\ Zn + 12\ HCl \rightarrow 2\ AsH_3 + 6\ ZnCl_2 + 3\ H_2O$$

$$H_3AsO_4 + 4\ Zn + 8\ HCl \rightarrow AsH_3 + 4\ ZnCl_2 + 4\ H_2O$$

The liberated arsine gas is then reacted with a detector paper that has been impregnated with mercuric bromide. The reaction above indicates arsine gas is commonly generated by reduction with zinc metal and hydrochloric acid. As the Hach method is also often used in the field level arsenic detection, hydrochloric acid is substituted by a safer and more easily transported solid acid (sulfamic acid) packaged as a granular powder. The zinc powder and reagents in the Hach method are packaged in convenient unit doses to minimize handling. The mercuric bromide test paper is on the end of a long plastic strip to eliminate the need to come into contact with the mercuric bromide.

Another concern in arsenic testing is the generation of toxic arsine gas. The design of the cap for Hach's reaction vessel focuses the arsine gas on a very small surface. The test strip is held in position so the generated arsine is forced to react with the test strip. A 12.5 x 12.5 -mm mercuric bromide coated reaction pad is used as the indicator in the test, but the exposed hole is only 4.76 mm in diameter. This

arrangement allows all of the generated gas to come into contact with the mercuric bromide and be reacted. The excess paper around the hole provides sufficient reactant to absorb all of the generated arsine. This increases the sensitivity of the test pad and at the same time reduces the exposure of arsine gas to the operator.

Some representative samples were analyzed by Body Cote Testing Group, Pointe Claire, Quebec, Canada, using ICP-MS at the detection limit of 1 ppb to cross check the results.

5.6 Determination of Sorption Capacity and Removal Efficiency of Arsenic

Arsenic sorption capacity of biomass, q was evaluated from the following equation:

$$q = \frac{(C_i - C_e)V}{M} \qquad (5.1)$$

Arsenic removal efficiency was determined by the following equation:

$$\text{Removal efficiency} = \frac{C_i \quad C_e}{C_i} X100 \qquad (5.2)$$

Where,

q = Arsenic sorption capacity of biomass (μg/g)

C_i = Initial concentration of arsenic in the solution (μg/L)

C_e = Equilibrium concentration of arsenic in the solution (μg/L)

V = Volume of solution in the flask (L) and

M = Mass of biomass (g)

All the equilibrium biosorption experiments were performed at room temperature (23

- 25°C, maintained by a central air conditioning system).

5.7 Continuous Flow Column Tests

The main requirement of an industrial sorption system is that the sorbent can be used in a fixed or expanded bed column. The recovery of metal by biosorbent is performed by appropriate contact between the solution and the solid phase in a fixed packed-bed column. The column should not cause much pressure drop when the water is allowed to trickle across the bed. The biomass particles should have sufficient mechanical strength to resist the pressure (Mahan and Holcombe, 1992) otherwise they need to be immobilized in a synthetic polymer matrix (Jeffers and Corwin, 1993).

The biosorbent material used in this study is an anaerobic biomass. Unlike most of other biomass, immobilization or stiffening is not necessary prior to using the biomaterial. The particulate biomass was found to possess high mechanical strength. Even under aggressive chemical environments (acidic or basic conditions) the biomass demonstrated high stability with no visible structural damage. This implies that the biomass could be suitable for the continuous flow system.

The experimental setup for the fixed-bed column test is schematically shown in Figure 5.4. An amount of 4.6g of dried untreated biomass was packed into a plastic column of 7 cm high and 1.5 cm inner diameter. For homogeneous distribution of the influent at the inlet of the column a bed of glass spheres was placed at the bottom of the column before placing the biomass.

The arsenate bearing solution was stored in a 2L Erlenmeyer flask and the pH

value of 5 was adjusted using HCl and NaOH solution. A peristaltic pump connected with a flow meter was used to feed this solution into the column from the bottom at a flow rate of 1.5 BV/hr allowing a retention time of 40 min in the column. The effluent samples were collected from the top using a fraction collector at preset time intervals for subsequent analysis. The column operation was terminated after reaching the effluent concentration at its breakthrough point of 10 μg/L. The effluent pH was measured to ensure whether any change occurs after column operation. Finally to check the reusability of the biomass, regeneration was done by feeding a 0.5M NaCl solution preceded by distilled water from the bottom of the column.

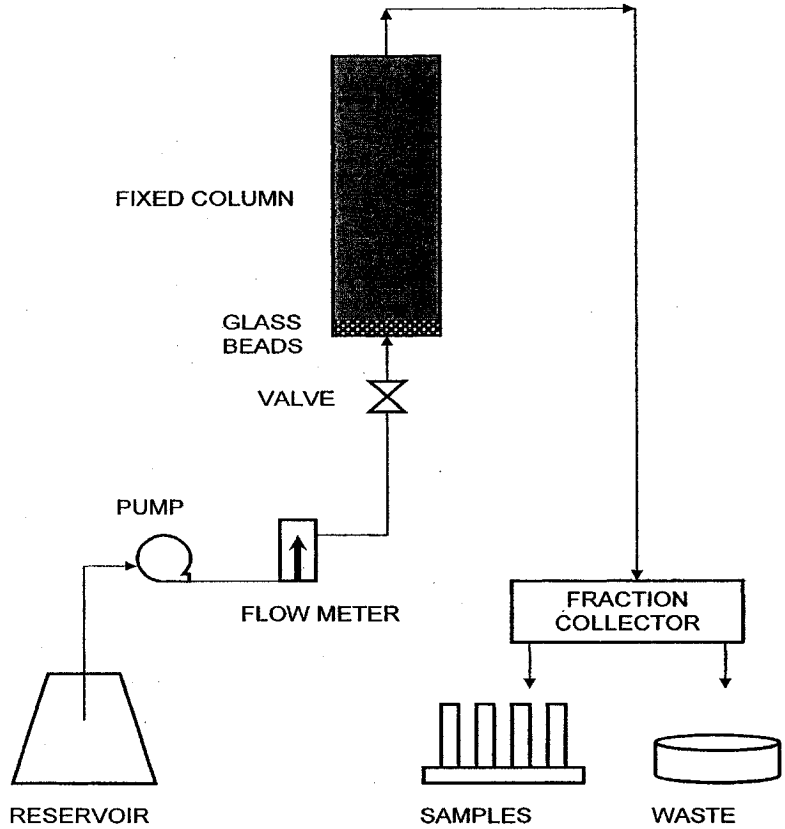

Figure 5.4 Schematic diagram of column experiments

5.8 Effect of pH

pH is considered as one of the most important factors that significantly affect the biosorption of metals (Lezcano et al., 2001). Adsorption is a process of interaction between the sorbent (biomass) and the sorbate (arsenic). The sorption capacity is a function of the degree of interaction which in turn depends on the properties of both the sorbent and the sorbate materials. This interaction is favored by the surface charge on the sorbent material and the speciation of arsenic. pH controls the ionization of the functional groups present on the biomass surface contributing the surface charge and the speciation of arsenic. As it is known that arsenic provides different anionic species

at different pHs depending on the pKa values (section 2.7.1), the interaction or the degree of interaction will depend on the properties of the sorbent material when all other controlling factors are considered constant. The interaction should occur when the sorbent material provides a positive or a partially positive surface charge for the anionic arsenic species to bind. The co-occurrence of the anionic arsenic species and the cationic biomass surface at a common pH range is required for the effective interaction to be taken place.

The difficulty of the removal of metal anions is that they do not precipitate out as hydroxides by simple pH adjustment (Matis et al., 2003). On the other hand, decreasing the pH value to extreme acidic conditions may damage the structure of the biosorbent material. Microscopic observations have shown distorted cells; significant weight loss and decrease in the sorption capacity. (Kuyucak and Volesky, 1989a).

Moreover, the pH of a solution can be changed as a result of biosorption. Previous experiments performed in closed batch systems without pH adjustment revealed that the sorption of metals onto acid washed biomass led to a decrease of the pH value in the solution (Crist et al., 1981). An increase of pH during sorption was reported by Kuyucak and Volesky (1989b), the release of carbonate ions from *Ascophyllum* biomass could be responsible for the observed increase in solution pH.

5.9 Effect of Initial Concentration

The effect of initial arsenate concentration on the biosorption capacity was examined. Different initial arsenate concentration with a fixed dose of biomass was investigated. In case of low metal concentration, a relatively slower transport due to

decreased diffusion coefficient and decreased mass transfer coefficient was previously observed (Aksu and Ferda, 2004). It was noticed that biosorption of arsenate with *Lessonia nigrescens* increased with the increase of initial concentration (Hansen et al., 2006). Similar results were found with arsenate adsorption on molybdate-impregnated chitosan beads (Guibal et al., 2000). The inverse relationship between initial arsenic concentration and throughput volume was also documented. Binding sites are quickly filled at higher initial concentration resulting in a decrease in breakthrough time (Pant and Singh, 2006).

5.10 Effect of Contact Time

A fixed dose of biomass was kept in contact with an arsenate solution of known concentration for different time periods to examine how the adsorption varies with time. All three forms of the biomass (untreated, PO_4-biomass and Cl-biomass) were investigated. This was done to determine the equilibrium time at which the biomass gets saturated and reaches its maximum sorption capacity. A 'good' sorbent material can be characterized by a fast sorption rate that means a lower equilibrium time indicating its potential for practical application.

A study on arsenic adsorption on poly-metallic sea nodule showed an equilibrium time of 30 minutes (Bhattacharjee et al., 2005). Investigations on arsenate removal by an anion exchanger derived from coconut coir pith revealed a rapid sorption up to 30 minutes and slowly reached saturation at about 4 hours. Almost 85% of the maximum sorption capacity was attained in the first 30 minutes (Anirudhan and Unnithan, 2006). A similar trend of rapid sorption up to 60 minutes followed by slower sorption

to reach equilibrium in 2 hours was observed when removing arsenic using plant biomass. The adsorption of arsenite and arsenate was 60.2% and 85.6% respectively in the first 60 minutes (Srivastava et al., 2005). The significance of the fast biosorption of a particular biosorbent material is that it can be used in a continuous flow column operation.

5.11 Desorption

Desorption of arsenic from the exhausted biomass inside the column was performed using 0.5M NaCl to investigate the reusability of the biomass. Effective desorption can help in reducing the volume of waste (biomass) by recycling it as well as the safe disposal of recovered contaminant. The efficiency of a desorbing agent or the eluant is often expressed by the *S/L* ratio, i.e. solid to liquid ratio. The solid represents the solid sorbent (mg dry weight) and the liquid represents the amount of eluant applied (in mL). High values of *S/L* are desirable for complete elution and to make the process more economical (Gupta et al., 2000). Desorption process should ensure three major issues: high elution efficiency, low biomass damage and low cost.

Acids like HCl, H_2SO_4, HNO_3 and salts like NaCl, $CaCl_2$ are used as eluant depending on the mechanism of desorption (Aldor et al., 1995; Kuyucak and Volesky, 1989c). Anirudhan and Unnithan (2007) recovered 96% to 93.8% of arsenic in four desorption cycle from coconut coir pith using 0.1M HCl. Srivastava et al. (2006) found 98% elution of arsenic from shelled *Moringa olifera* Lamarck seed (SMOS) using 0.05M HNO_3. Desorption of arsenic from molybdate-impregnated chitosan beads using H_3PO_4 was found 76% (Guibal et al., 2000).

Chapter 6

Results and Discussion

6.1 Batch Test

6.1.1 Effect of pH

pH is one of the most important controlling factors that affects the biosorption process (Lezcano et al., 2001). The optimum pH was determined for all the three forms of biosorbents as one form of biosorbent could differ from another in sorption capacities in different pH values. The biosorbents were experimented both in arsenate and arsenite solutions. The form of biosorbent that yielded the maximum sorption capacity was selected along with the corresponding pH value for subsequent analyses. To determine the effect of pH on sorption capacity with respect to each form of biosorbent, a biomass concentration of 10 g/L in both arsenate and arsenite solutions of 2000 μg/L was used with varying pH values.

The results are shown in Figures 6.1 and 6.2. It can be seen from the figures that the adsorption of arsenate was maximum at a pH range 5-6 whereas the adsorption of arsenite did not vary significantly over a pH range of 3-10. It was observed that the chemical treatment had an insignificant effect on the sorption capacity of the biomass. For example, the arsenate sorption capacity of untreated, PO_4-biomass and Cl-biomass at pH 5 are 152 μg/g (76%), 154 μg/g (77%) and 145 μg/g (72.5%) respectively. The corresponding values for arsenite are 60 μg/g (30%), 58 μg/g (29%) and 55 μg/g (27.5%) at a pH value near 8. The sorption capacity of arsenate found

was higher than that of arsenite. Arsenate exists mostly as monovalent ($H_2AsO_4^-$) anion in between pH 2.2 and 6.97 (section 2.7.1; pKa1 = 2.2, pKa2 = 6.97). The sorption of arsenate at pH 5 could be favorable due to the interaction between protein/amino acid in the biomass surface and the charged arsenate species. Arsenite (H_3AsO_3) exists as neutral below the pH of its first pKa value of 9.22. The reason behind poor adsorption of arsenite is the lack of interaction of the protein/amino acid with the arsenite due to its neutrality. More explanation is provided for the arsenic sorption mechanism later (section 6.10).

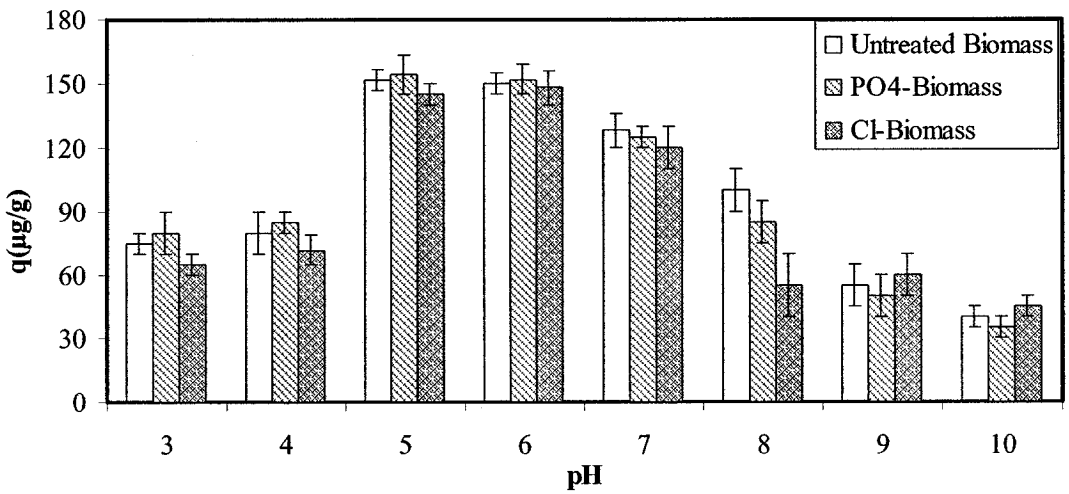

Figure 6.1 Effect of pH on arsenate sorption capacity of three forms of biomass

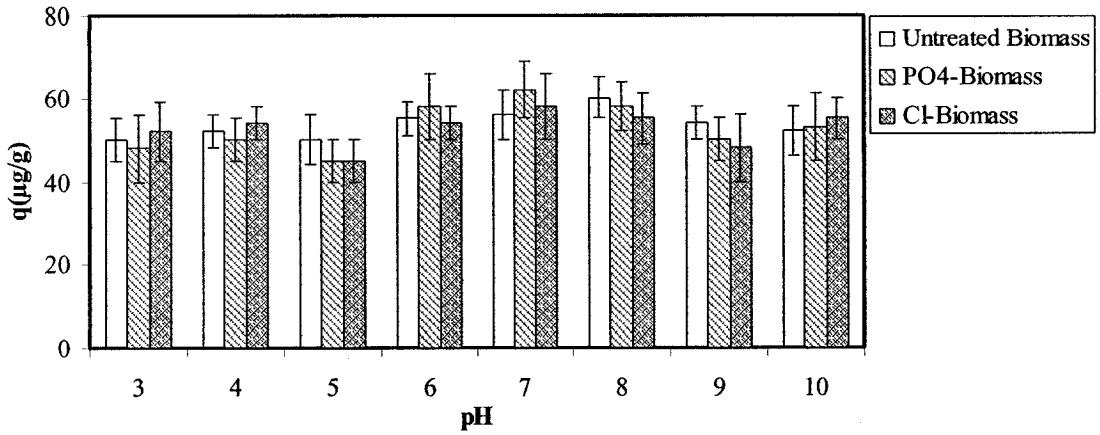

Figure 6.2 Effect of pH on arsenite sorption capacity of three forms of biomass

6.1.2 Effect of Initial Concentration

Different initial arsenate concentration with a biomass dose of 4 g/L was used at a pH value of 5. Figure 6.3 represents the sorption capacity per unit dry weight of the biomass and Figure 6.4 shows the percentage removal efficiency. It was found that the amount adsorbed increased from 106 μg/g to 155 μg/g with the increase of initial concentration from 500 μg/L to 4000 μg/L but the removal efficiency decreased from 85% to 16%. The removal efficiency depends on the number of active sites present on biomass surface. At higher initial concentration, the interaction of arsenic species with the available sites on the biomass surface could be higher than that with lower initial concentration; this may contribute to more sorption at higher initial concentration. On the other hand, for a fixed dose of biomass, the number of active sites is limited. When the initial concentrations are increased with the same biomass dose, the active sites become fewer for adsorption thereby decreasing the removal efficiency.

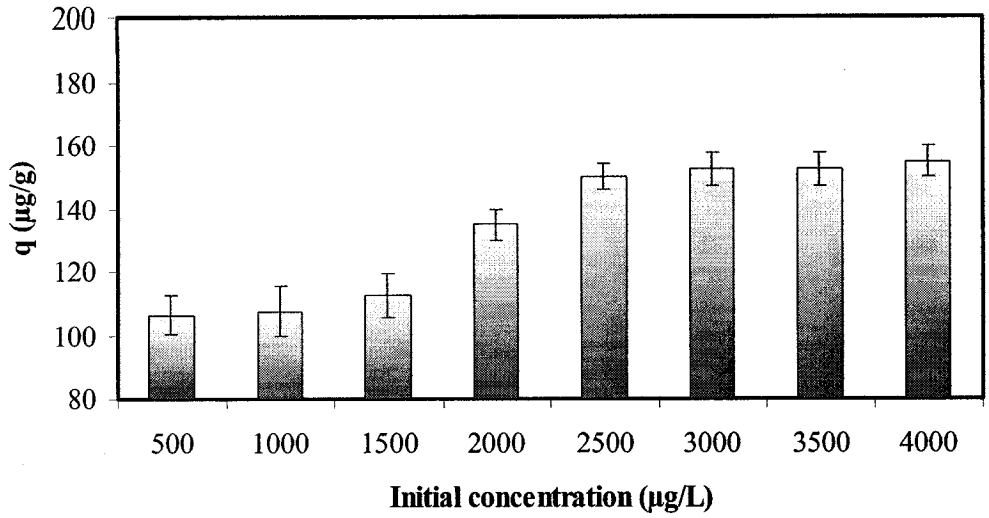

Figure 6.3 Effect of initial concentration on arsenate sorption

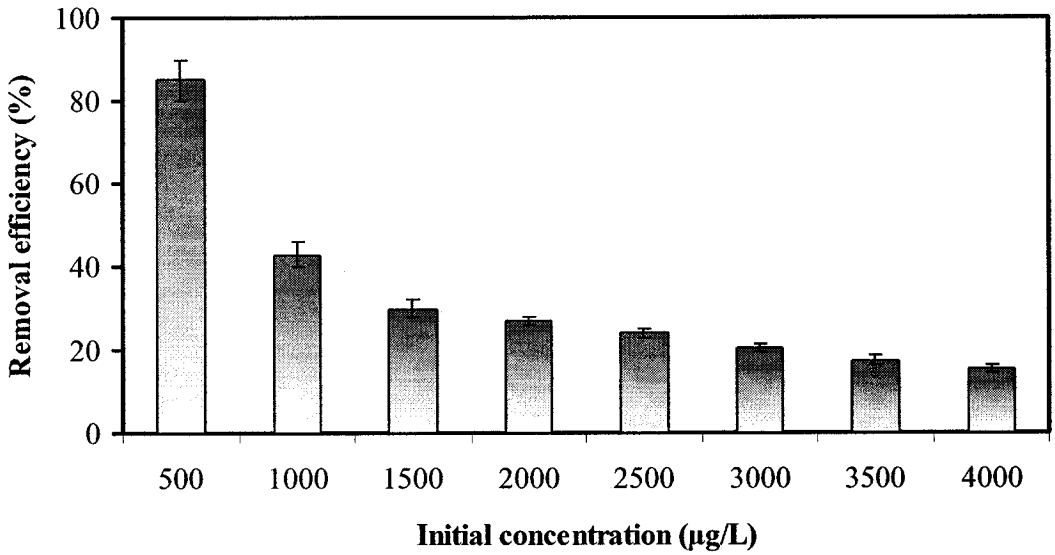

Figure 6.4 Effect of initial concentration on arsenate removal efficiency

6.1.3 Effect of Contact Time

The biomass with a concentration of 4 g/L was kept in contact with 500 µg/L arsenate solution over different time periods (Figure 6.5) at a pH value of 5. Three

forms of biomass were used to compare their sorption rate. The rate of sorption for all three forms increases very rapidly up to about 40 min and slowly reaches saturation at about 90 minutes. The adsorption of arsenate remained constant after 90 minutes implying that equilibrium had been reached.

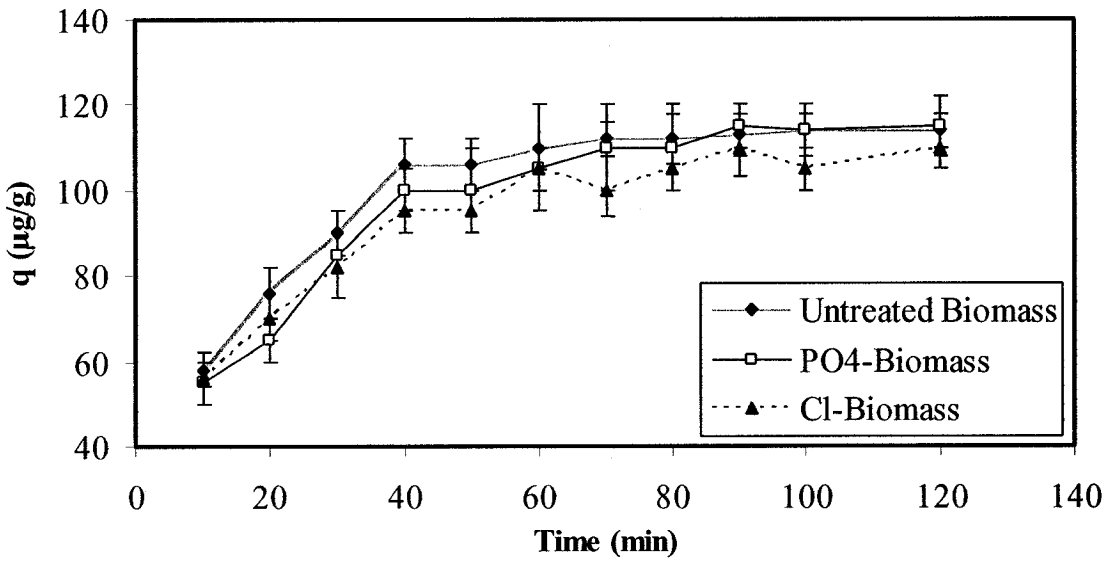

Figure 6.5 Effect of contact time on arsenate sorption

Again different initial arsenate concentrations with an untreated biomass dose of 4 g/L were used at a pH value of 5 (Figure 6.6). The plots also show that the time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption for all the concentrations is independent of initial concentration.

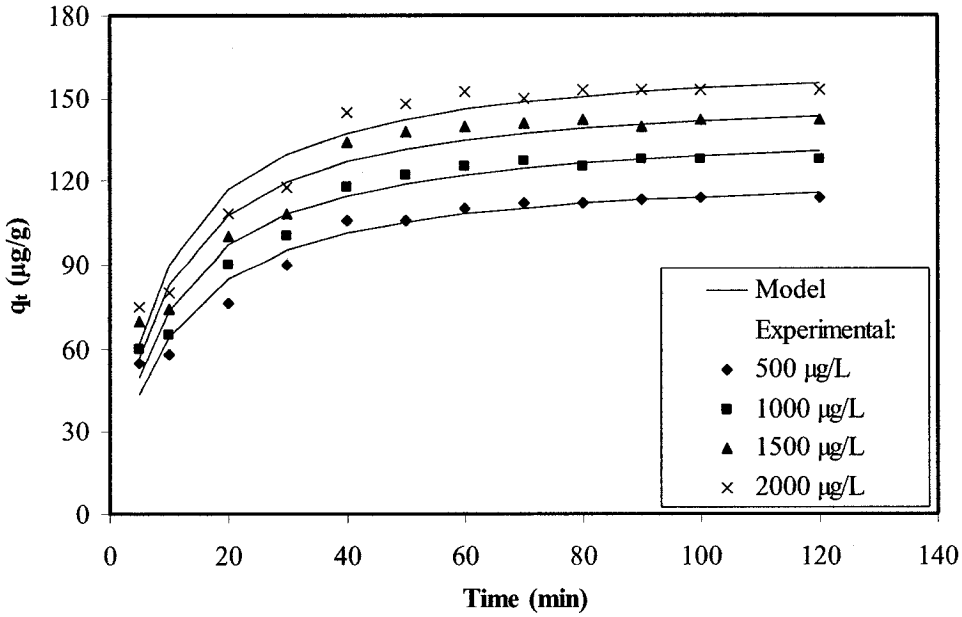

Figure 6.6 Time profile of arsenate sorption of untreated biomass at different initial concentrations.

6.2 Biosorption Isotherm

The graphical representation of materials (sorbate) adsorbed to the solid phase as a function of the sorbate present in the aqueous phase at equilibrium condition and constant temperature is termed as the adsorption isotherm. Biosorption isotherms were experimentally determined for untreated biomass at room temperature and a pH value of 5. A fixed biomass dose of 4 g/L with varying initial arsenate concentrations of 500, 1000, 1500, 2000, 2500, 3000, 3500 and 4000 µg/L were used. A 200 mg of biomass was placed in 50 mL plastic tubes filled with arsenate solutions of above concentrations. The tubes were then placed on a rotary shaker at 100 rpm until an equilibrium state was reached. After 24 hours of shaking, the supernatant was filtered with Whatman #42 filter paper (pore size 0.45µm) and the filtrate was analyzed to find the effluent concentration. The biomass sorption capacity was determined from

the difference between the influent and effluent concentration. The experimental data were graphically represented by plotting the effluent concentration (C_e) in the X-axis and the biomass sorption capacity (q) in the Y-axis. The data were also fitted with Langmuir isotherm models to obtain several parameters.

From Figures 6.7, it can be seen that at an initial stage the sorption capacity increases in a linear way with rising equilibrium concentration and finally reaches its saturation limit where a plateau can be observed. This is due to the fixed number of active sites on the biomass which take part in the sorption yielding a maximum sorption capacity. The maximum sorption capacity (q_{max}) for arsenate was 155 µg/g in comparison to 164 µg/g found from the Langmuir isotherm model.

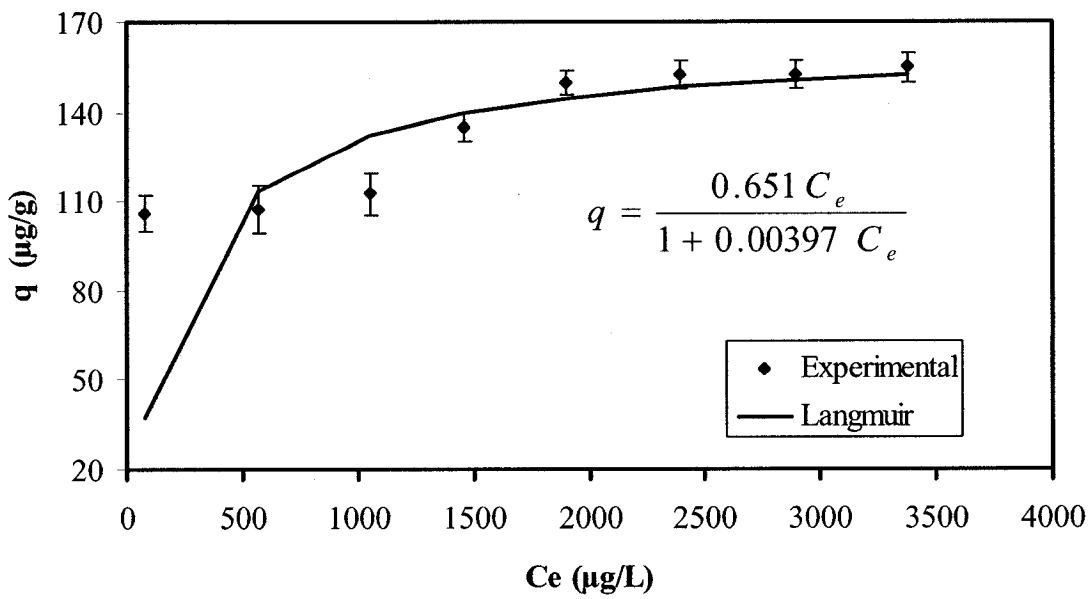

Figure 6.7 Biosorption isotherm for untreated biomass

6.3 Adsorption Isotherm Models

Several mathematical models have been developed to describe the relationship between the concentrations of the sorbate in the solid and aqueous phases. Depending on the sorbent and sorbate, one of the sorption models used may describe the system better than others, however, characteristics of more than one model are usually found for any system. This study among others focuses on the mostly used Langmuir and Freundlich adsorption isotherm models to describe the sorption behavior of arsenic on anaerobic biomass.

6.3.1 Freundlich Adsorption Isotherm Model

The Freundlich adsorption 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 Langmuir isotherm. The equation is expressed as:

$$q = K_F C_e^{\frac{1}{n}} \qquad (6.1)$$

The linearized form of equation 6.1 can be written as:

$$\ln q = 1/n \ln C_e + \ln K_F \qquad (6.2)$$

Where, q denotes the sorption of sorbate per unit mass of the sorbent (μg/g), C_e is the equilibrium sorbate concentration in the liquid (μg/L), K_F is an experimental constant indicative of the adsorption capacity of the adsorbent (L/μg), and n is an experimental constant indicative of the adsorption intensity of the adsorbent.

Equation 6.2 yields a straight line with a slope of 1/n and an intercept of $\ln K_F$

when lnC_e and lnq are plotted in the X and Y-axis respectively and it is shown in Figure 6.8.

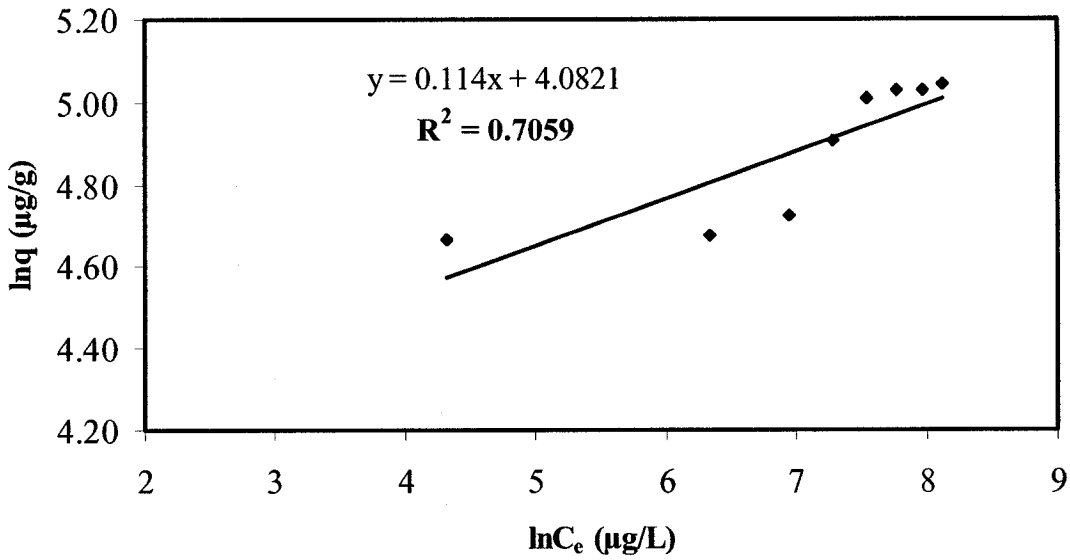

Figure 6.8 Freundlich isotherm model for untreated biomass

From Figure 6.8 it is found that the Freundlich isotherm model does not represent the experimental results very well at least on the basis of R^2 value. The Freundlich model does not indicate a finite sorption capacity of the sorbent, the sorbate concentration at the surface does not approach a saturating value with the increase of initial concentration, and hence it often represents the adsorption equilibrium over a limited range in solute concentration. The Freundlich isotherm model parameters are presented in Table 6.1.

Table 6.1 Freundlich isotherm model parameters

K_F (L/μg)	n	Freundlich Equation	R^2
59.27	8.771	$q = 59.27C_e^{1/8.771}$	0.7059

6.3.2 Langmuir Adsorption Isotherm Model

The Langmuir model assumes that the rate of adsorption is proportional to the concentration of the solute in the fluid phase and to the solid surface. The Langmuir model is developed based on the following assumptions (Weber 1972; Faust and Aly 1987; Cooney 1999):

- Fixed number of adsorption sites.
- Each site can bind only one molecule of the adsorbing species (i.e. monolayer)
- All sorption sites are uniform (i.e. constant heat of energy)
- No interaction between sorbed species.

The Langmuir isotherm can be derived as follows:

If the fraction of the sorbent surface θ_i is occupied by a sorbate molecule i then the unoccupied fraction will be $(1 - \theta_i)$. The concentration of i in the liquid phase is C and the rate of adsorption, r_{ads} is given by:

$$r_{ads} = K_a C (1 - \theta_i) \qquad (6.3)$$

The rate of desorption depends only on the occupied fraction, θ_i of the sorbent surface by the sorbate molecule i and can be expressed as:

$$r_{des} = k_d \theta_i \qquad (6.4)$$

At equilibrium, the rate of adsorption and desorption are equal,

$$k_a C_e (1 - \theta_i) = k_d \theta_i \quad (6.5)$$

The occupied fraction, θ_i is thus expressed as:

$$\theta_i = k_a C_e / (k_d + k_a C_e) \quad (6.6)$$

$$\text{or} \quad \theta_i = (k_a / k_d) C_e / [1 + (k_a / k_d) C_e] \quad (6.7)$$

$$\text{or} \quad \theta_i = bC_e / (1 + bC_e) \quad (6.8)$$

Where, b is the adsorption equilibrium constant. The fraction of the surface occupied, θ_i is equal to the ratio of the amount of sorbate actually adsorbed to the maximum which could be adsorbed:

$$\theta_i = q / q_{max} \quad (6.9)$$

Equations 6.8 and 6.9 can be combined that yield:

$$q = \frac{q_{max} bC_e}{1 + bC_e} \quad (6.10)$$

Where,

q = Amount of sorbate adsorbed per unit mass of sorbent, (μg/g)

q_{max} = Maximum sorption capacity of the sorbent, (μg/g)

C_e = Equilibrium sorbate concentration in the liquid phase (μg/L)

b = Adsorption equilibrium constant ($k_{adsorption} / k_{desorption}$)

To facilitate the fitting of the model to the experimental data and its parameter evaluation, equation 6.10 can be linearized as follows:

$$\frac{C_e}{q} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \quad (6.11)$$

The graphical representation (as per equation 6.11) of C_e versus C_e/q in the X- and Y-directions respectively makes a straight line (Figure 6.9) with a slope of $1/q_{max}$ and an

intercept of $1/bq_{max}$ from where the values of q_{max} and b are determined.

Hall et al. (1966) showed that the Langmuir constant, b can be expressed in terms of an equilibrium parameter known as a separation factor (R) defined as follows:

$$R = \frac{1}{1 + bC_i} \tag{6.12}$$

When,

R > 1: Unfavorable adsorption

R = 1: Linear adsorption

0 < R <1: Favorable adsorption

R = 0 : Irreversible adsorption

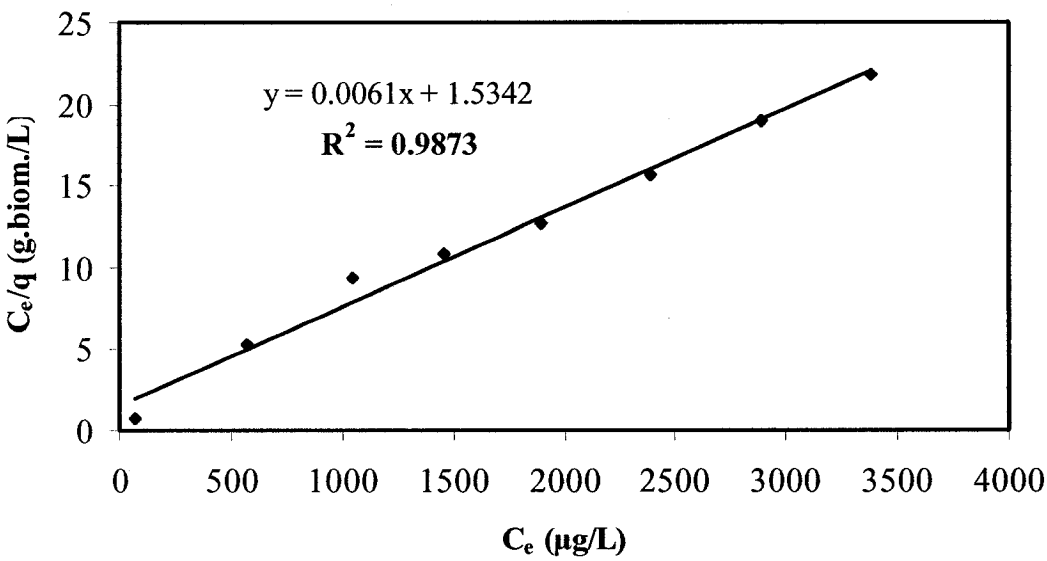

Figure 6.9 Langmuir isotherm model for untreated biomass

It can be seen from Figure 6.9 that the data fits well to the Langmuir isotherm model. Uptake is eventually limited by the fixed number of active sites and the resulting

plateau satisfied the phenomenon of Langmuir isotherm. The maximum uptake is well described by the Langmuir parameter, q_{max}, as shown in Table 6.2. The Langmuir model provides information on sorption capabilities and the values obtained from it (q_{max} and b) can provide information on the screening of the sorbents. The more favorable sorbent is indicated by the higher value of the slope of an adsorption isotherm. It means that potentially "good" sorbent can be comparatively evaluated from values of q_{max} and b. However, the Langmuir model does not focus on the mechanistic aspects of sorption.

Table 6.2 Langmuir isotherm model parameters and experimental q_{max} for untreated biomass.

q_{max} (µg/g) Langmuir model	**q_{max} (µg/g) Experimental**	**b (L/µg)**	**Langmuir Equation**	**R^2**
164	155	0.00397	$q = \frac{0.651C_e}{1+0.00397C_e}$	0.9873

The value of the Hall dimensionless separation factor R was between 0 and 1 for all the initial concentrations tested, which indicates the favorable adsorption of arsenate on anaerobic biomass. Moreover, the considerably lower cost of the anaerobic biomass and its physical characteristics make it an attractive biosorbent.

6.4 Adsorption Kinetics Modeling

The rates of reaction of three types of biomass such as untreated biomass, PO_4-

biomass, and Cl-biomass were determined separately by equilibrium batch tests. The data obtained from section 6.1.3 were used to apply the proposed model. All three types of biomass with a concentration of 4 g/L were suspended in arsenate solution of 500 μg/L for varying time periods (10, 20, 30, up to 120 min). The experimental data were analyzed by four reaction kinetic models. The first order rate equation based on the solute concentration in the aqueous phase can be expressed as (Benefield et al., 1982):

$$-\frac{dC_t}{dt} = k_1 C_t \qquad (6.13)$$

Rearranging equation 6.13 and integrating within the boundary conditions t = 0 to t and $C_t = C_0$ to C_t, gives the linearized form as:

$$\ln C_t = \ln C_0 - k_1 t \qquad (6.14)$$

Where,

C_0 = Initial sorbate (As) concentration in the liquid phase (μg/L)

C_t = Sorbate (As) concentration in the liquid phase at any time t (μg/L)

k_1 = First-order rate constant (/min)

First order reaction kinetic model for three forms of biomass is presented in Figure 6.10.

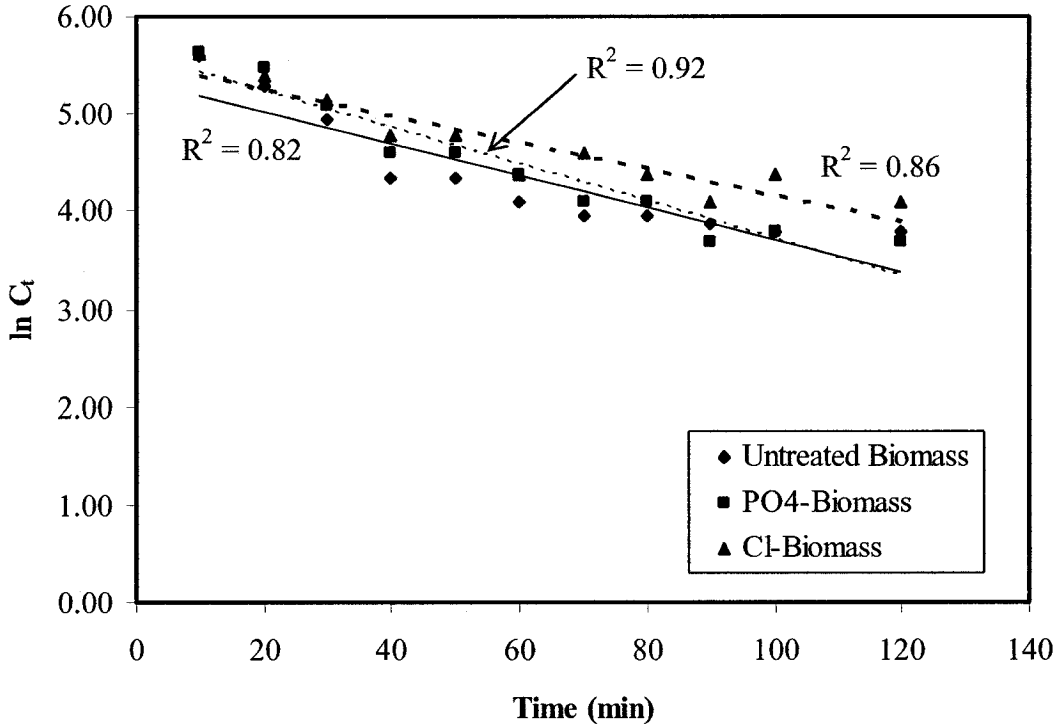

Figure 6.10 First-order reaction kinetic models of the three forms of biomass

The pseudo-first order kinetic model based on the sorption capacity of the solid phase can be represented as (Zhang et al., 2003):

$$\frac{dq_t}{dt} = k_{s1}(q_e - q_t) \qquad (6.15)$$

Integrating within the boundary conditions t = 0 to t and $q_t = 0$ to q_t equation 6.15 gives the linearized form as:

$$\ln (q_e - q_t) = \ln q_e - k_{s1}t \qquad (6.16)$$

Where,

q_e = Equilibrium sorption capacity of the sorbent (μg/g)

q_t = Sorption capacity of the sorbent at any time t (μg/g)

k_{s1} = Pseudo-first-order rate constant (/min)

According to equation 6.16, pseudo-first order kinetic model is shown in Figure 6.11.

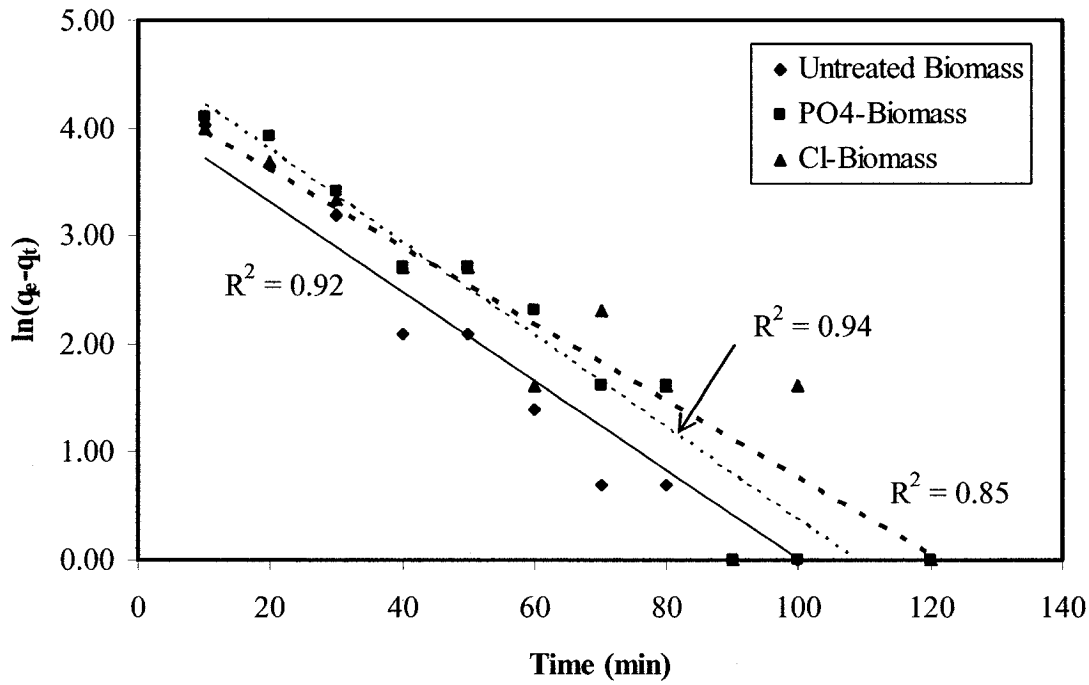

Figure 6.11 Pseudo-first-order reaction kinetic models of the three forms of biomass

According to Ho and Mckay (2000) the second order kinetic model can be expressed as:

$$-\frac{dC_t}{dt} = k_2 C_t^2 \qquad (6.17)$$

Rearranging and integrating equation 6.17 within the boundary conditions t = 0 to t and $C_t = C_0$ to C_t, gives the linearized form as:

$$\frac{1}{C_t} - \frac{1}{C_0} = k_2 t \qquad (6.18)$$

Where,

k_2 = Second-order rate constant (L/μg.min)

The data for the second order reaction kinetic model are plotted in Figure 6.12.

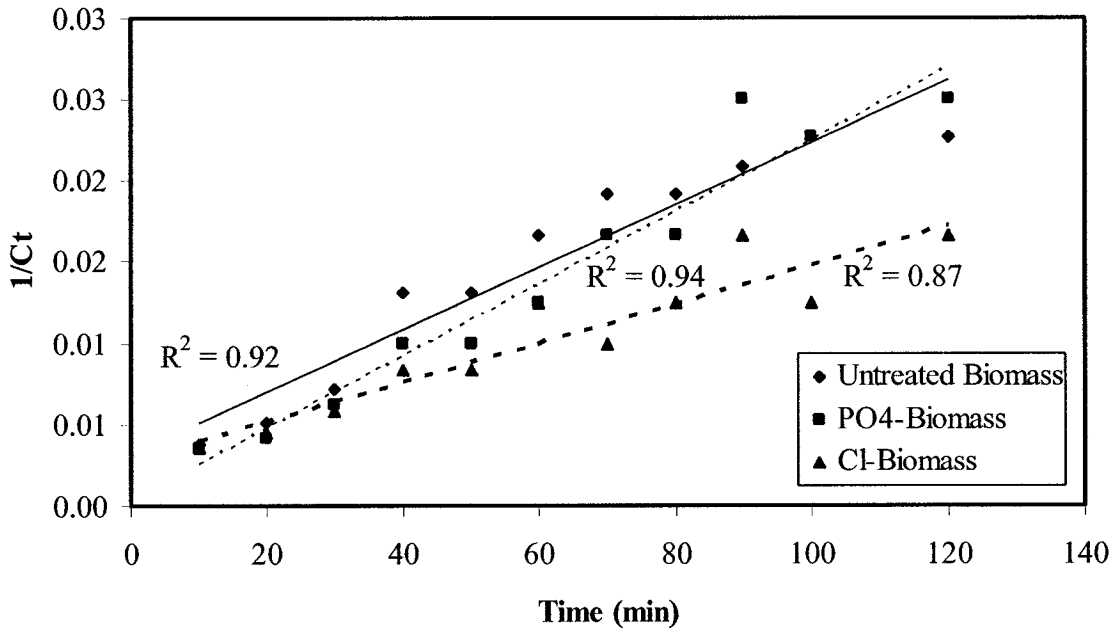

Figure 6.12 Second-order reaction kinetic models of the three forms of biomass

The pseudo-second order reaction kinetic model based on the equilibrium sorption capacity can be expressed as (Ho and Mckay, 2000):

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad (6.19)$$

Rearranging and integrating equation 6.19 within the boundary conditions t = 0 to t and $q_t = q_0$ to q_t, gives the linearized form as:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \qquad (6.20)$$

This is the integrated rate law for a pseudo-second order reaction. Rearranging

equation 6.20 and putting $h = kq_e^2$, we get,

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad (6.21)$$

Where,

h = Initial sorption rate (μg/g.min)

k = Pseudo-second-order rate constant (g/μg.min)

Pseudo-second order reaction kinetic model is plotted in accordance with equation 6.21 and shown in Figure 6.13.

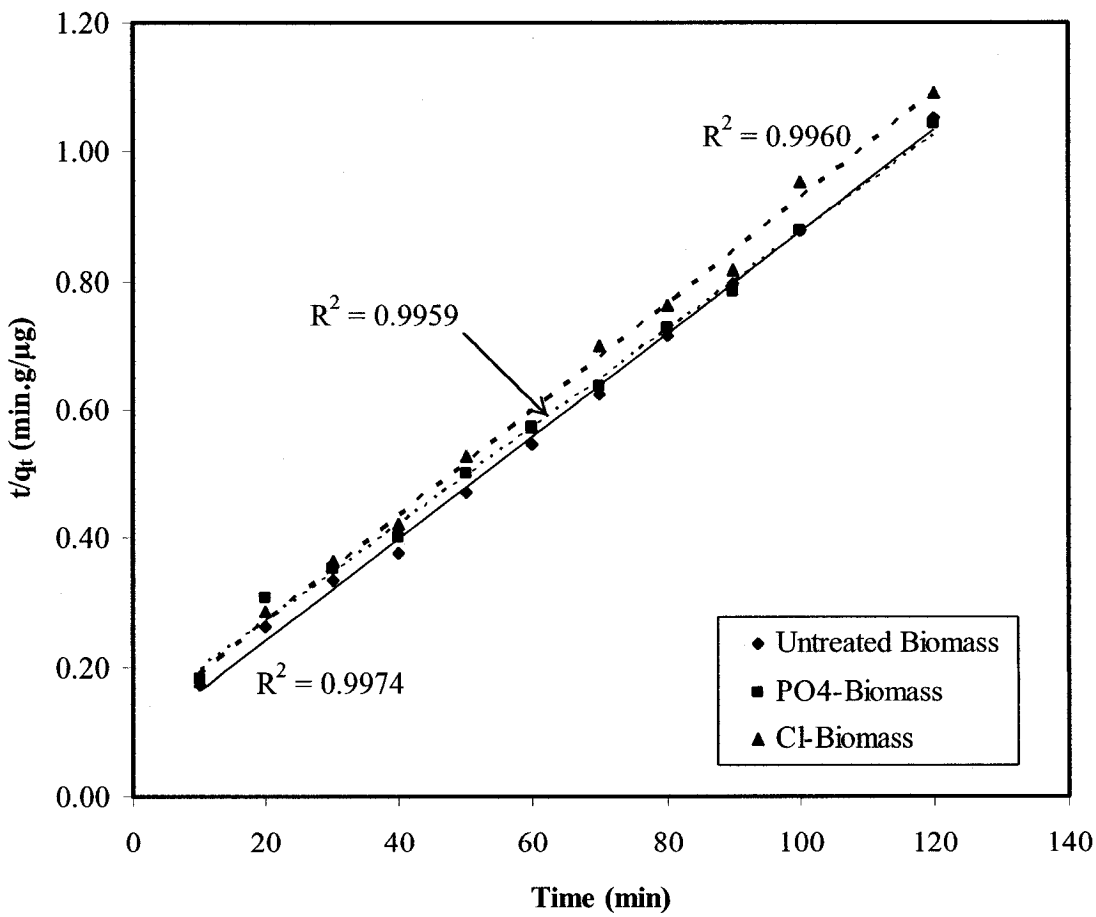

Figure 6.13 Pseudo-second-order reaction kinetic models of the three forms of biomass

Table 6.3 R^2-values of four reaction kinetic models for the three forms of biomass

Biomass Type	Correlation co-efficient, R^2				h μg/g.min
	First-order	Pseudo-first-order	Second-order	Pseudo-second-order	
Untreated Biomass	0.82	0.92	0.92	0.9974	11.806
PO_4-Biomass	0.92	0.94	0.94	0.9959	8.319
Cl-Biomass	0.86	0.85	0.87	0.9960	9.380

The values of correlation co-efficient of four reaction kinetic models of the three types of biomass are summarized in Table 6.3. It is seen from the table that the co-efficient of pseudo-second-order reaction kinetic model of each type of biomass is greater than the other kinetic models. Hence, the adsorption kinetics can be best described by the pseudo-second-order model for each type of biomass. It is also clear that the co-efficient of the pseudo-second-order reaction kinetic model of untreated biomass is greater than those of the other two types of biomass; As a result, the value of initial sorption rate (h) for untreated biomass is higher than those of the other two. Based on the h-value, the suitability of the biomass as a biosorbent material can be expressed in descending order as: Untreated Biomass > Cl-Biomass > PO_4-Biomass. For untreated biomass with the initial arsenate concentration of 500 μg/L the experimental value of equilibrium sorption capacity (q_e), 114 μg/g is commensurate with the value of 126 μg/g determined from the pseudo-second-order kinetic model. This again supports that the rate of adsorption of untreated biomass is followed by pseudo-second-order kinetic model. The significance of an adsorption process in following the pseudo-second-order reaction kinetics is that the mechanism of removal

is mainly by chemical bonding or chemi-sorption (Ho and Mckay, 1999). Bio-materials can act as a synthetic mixed resin having the properties of both anion and cation exchange capacity. It was anticipated that the Cl-loaded biomass would act like a Cl-form synthetic anion exchange resin. The PO_4-loaded biomass was prepared because of the competing behavior of phosphate with arsenate. It was presumed that both Cl and PO_4-loaded biomass would provide higher arsenic sorption capacity than the native biomass by ion-exchange mechanism. But the experimental results are not in agreement with the assumptions made regarding the chemical treatment of the biomass. Therefore, untreated biomass was used for the column operation.

6.5 Fixed Bed Column Test

In a water treatment unit operation based on sorption phenomenon, usually large cylindrical reactors, filled with sorbent materials, are used through which the contaminated influent is allowed to percolate and the contaminant is retained by the sorbent. Fixed bed column operation where dynamic sorption of the solute occurs (Faust and Aly, 1987) is much more efficient than the batch process. The column can be single or multiple in series or parallel in the case of regeneration in either downflow or upflow mode. In the laboratory a small plastic cylinder generally termed a column, a prototype of the field scale reactor, filled with sorbent materials, is tested to check the sorption behavior of the materials inside the column under predefined operational conditions. Based on the parameters found from the column test, scale up factors are determined for reactor design. In a column test sorbent materials becomes gradually saturated starting from the inlet to outlet zone. The column operation was

terminated when the sorbate concentration in the effluent has reached a pre-set level. At this stage either regeneration or replacement of the sorbent materials is needed to run the next cycle of operation.

The breakthrough curve is an important tool for better understanding of the sorption behavior inside the column (Kogej and Pavko, 2001; Mahan and Holcombe, 1992; Matheickal and Yu, 1999; Yan and Viraraghavan, 2001). It is described as the history of the effluent concentration as a function of time. This time can be of two types-breakthrough or service time and saturation time. Breakthrough time is defined as the time when the effluent concentration reaches a pre-defined threshold level, whereas saturation time is referred to as the time when the sorbent materials reach its full saturation e.g. when the influent and effluent concentration becomes equal. The breakthrough curve tells us the number of bed volumes that can be treated in a specified time; the more the treated bed volume occurs before the breakthrough, the more efficient the sorbent is.

6.6 Arsenate Breakthrough Curve

To establish the breakthrough curve two column tests were performed separately with an arsenate influent concentration of 500 μg/L and 200 μg/L at a pH value of 5. The upward flow rate was 1.5 BV/h (bed volume, BV = dry weight of biomass used in the column / wet bulk density of the biomass) with an average empty bed contact time (EBCT) of 40 minutes based on batch experiment. The bed volume was 10 mL and was loaded with 4.6 g of dried untreated biomass. Figure 6.15 represents the resulting breakthrough curve for an influent concentration 500 μg/L. Arsenate

concentration in the effluent is plotted as a function of cumulative bed volume (e.g. V/V_0). As it is seen from Figure 6.15, at up to 90 BV, the effluent concentration remained close to zero or below the detection limit and after that it gradually increased. This happened due to the formation of a mass transfer zone in the column (Volesky, 2003b). When the arsenate bearing solution comes in to contact with a layer of fresh biomass in the column, arsenate is adsorbed onto the biomass until it reaches equilibrium with the influent concentration. At this point, the portion of the biomass reaches its capacity and became exhausted. As the mass transfer zone moves upward towards the direction of flow, as shown in Figure 6.14, sorption continues to next layer of fresh biomass making it again exhausted. This way the mass transfer zone moves up through the column until it reaches at the outlet. In the column system, arsenate bearing solution percolates through the active bed of biomass which acts like a series of batch reactors.

From Figure 6.15 it was observed that the breakthrough occurred after 90 bed volumes when the effluent concentration reached 10 μg/L which is the maximum allowable concentration according to most regulatory authorities like the WHO and the USEPA. An approximate amount of 900 mL of 500 μg/L influent was treated before the breakthrough occurred. It took around 3600 minutes to reach the breakthrough assuming an empty bed contact time of 40 minutes. The arsenate removed by 4.6 g of dry biomass was approximately 444 μg, yielding an average arsenate sorption capacity of 96 μg/g. This sorption capacity is considered as the operating capacity of the biomass in the column system. This capacity is 16% less than the maximum sorption capacity (q_{max}) found in the experimental batch test. One

of the reasons behind this is due to the formation of channels that lead to develop zones of unexposed biomass. Another reason is that there was still some unused portion of the biomass at the exiting end of the column (as shown in Figure 6.14) after the breakthrough occurred. This happened as the column was not run until the full saturation of biomass, at which the sorption should have reached its maximum level (i.e. q_{max}).

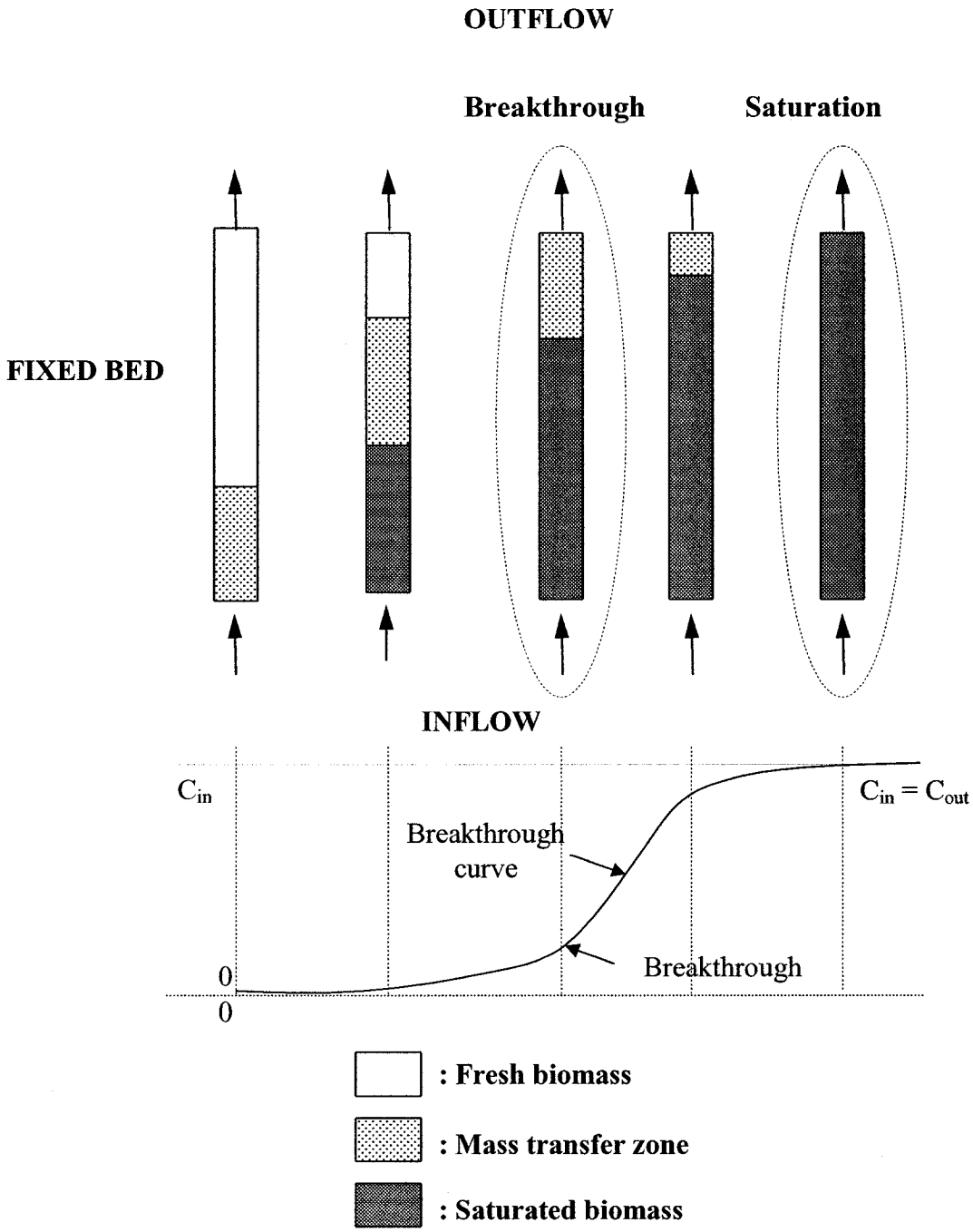

Figure 6.14 Movement of the mass transfer zone through a fixed bed adsorption column and development of the breakthrough curve.

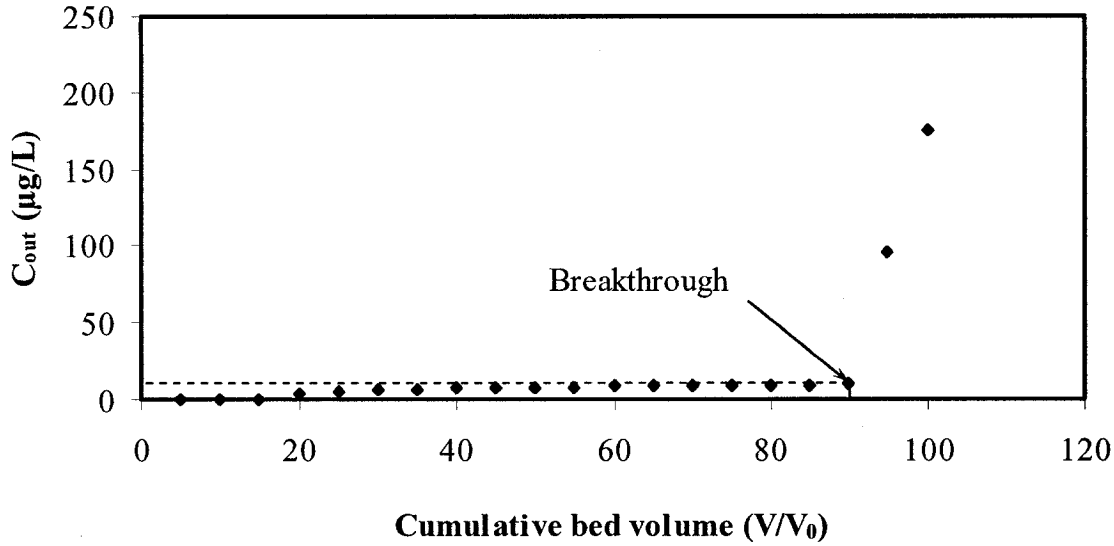

Figure 6.15 Arsenate breakthrough curve (influent concentration 500 µg/L)

Figure 6.16 shows the breakthrough curve for influent concentration of 200 µg/L. In this case the breakthrough occurred at a bed volume of 220. Before the breakthrough occurred an amount of 2200 mL of water was treated in 8800 minutes assuming an empty bed contact time of 40 minutes. The total amount of arsenate adsorbed by 4.6g of biomass was approximately 429 µg resulted an average sorption capacity of 93 µg/g. For lower initial concentration less arsenate is available to be adsorbed in comparison to the same amount of water with higher initial concentration. As a result the number of treated bed volumes increased from 90 to 220 when the initial arsenate concentration decreased from 500 µg/L to 200 µg/L.

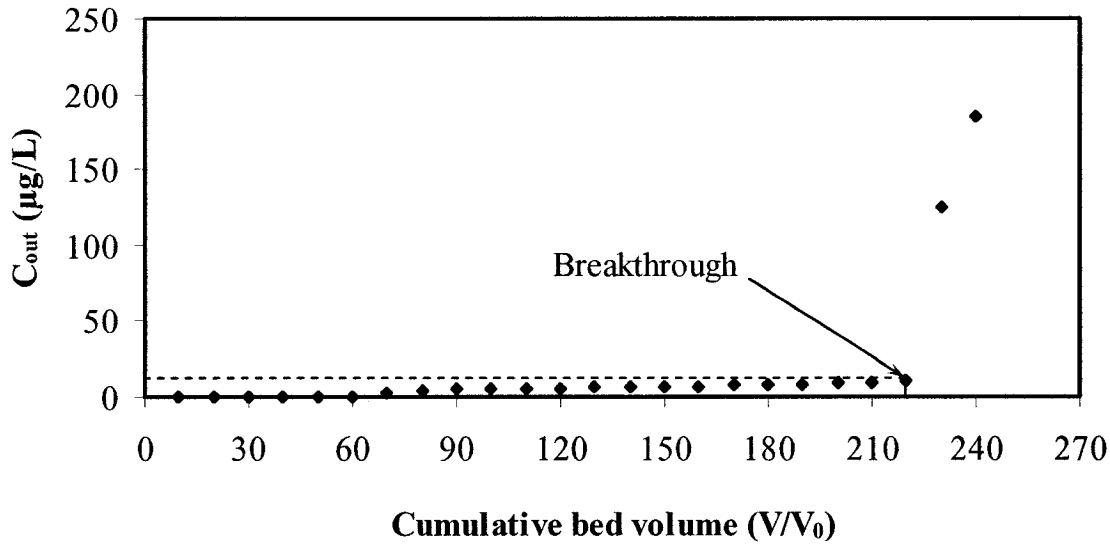

Figure 6.16 Arsenate breakthrough curve (influent concentration 200 µg/L)

6.7 pH in the Column Bed

One of the major factors in column operation is to maintain the expected pH in the column. As it is very difficult to control the pH inside the column, such adsorbent materials should carefully be chosen those have minimum influence on pH change during column operation. We used the untreated biomass in our column that was run until 100 bed volumes and the breakthrough occurred at 90 bed volumes. The change of pH after column operation was measured along with the effluent concentration analysis. The pH of the feed solution was 5 and it can be seen from Figure 6.17 that the pH change in the column is insignificant. This once again justifies the anaerobic biomass as a good potential candidate for biosorption.

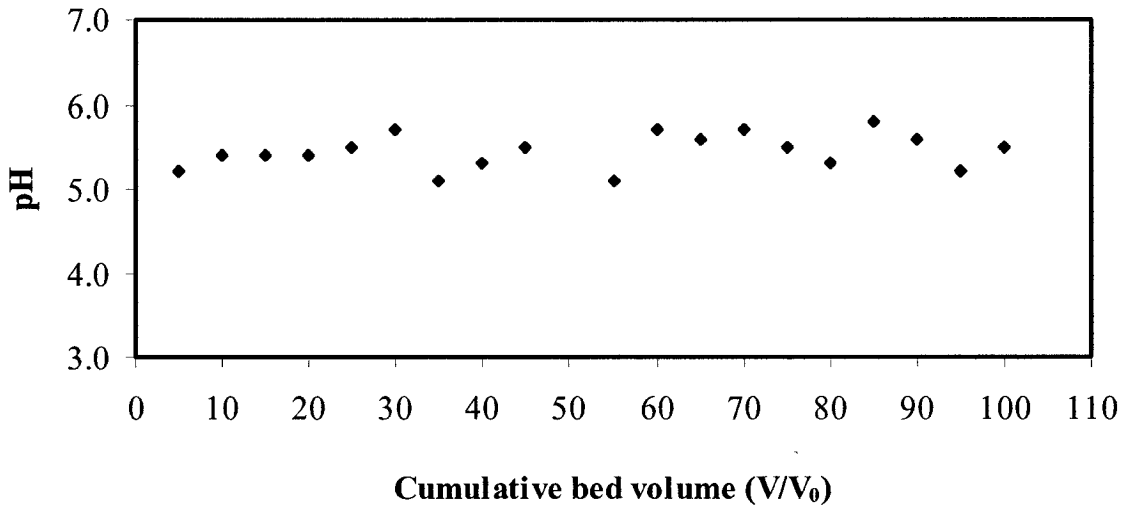

Figure 6.17 pH change in the effluent with initial arsenate concentration 500 μg/L

6.8 Desorption

Desorption is done when the biomass in the column is exhausted after breakthrough occurs. It is performed to recover the sorbate materials from the sorbent for safe disposal of both sorbate and sorbent. It also renews the sorbent materials for further cycles of operation that help to reduce the amount of waste materials. The overall efficiency of the regeneration process depends on the cost of the sorbent materials and the chemicals for regeneration and also on the post-renewal number of cycles of operation. For example, in the case of a costly sorbent material to be effective, it will need not only longer time to reach the breakthrough but also will require several cycles of operation after regeneration. On the other hand, cheaper sorbent materials can compete with their costly counterparts even having their lower breakthrough times and they can be discarded without regeneration.

In this case the biomass was partially saturated as the column operation was terminated after a few bed volumes of the breakthrough occurred. The desorption process was carried out by passing 0.5M NaCl for the first column (initial concentration 500 μg/L) with an upward flow rate of 1.5BV/hr allowing a residence time of 40 minutes. Figure 6.18 shows the concentration history of arsenate during desorption in the column. It is observed from Figure 6.18 that up to 15 bed volumes, an average elution of arsenate reached a concentration of 1.56 mg/L. The mechanism of arsenate desorption could be due to the exchange of arsenate ion with the chloride ion. The comparison between the amount of arsenate retained by the biomass and that of the amount eluted by NaCl shows that only 40% was recovered. On the basis of this result it is recommended that the biomass be disposed of without desorption.

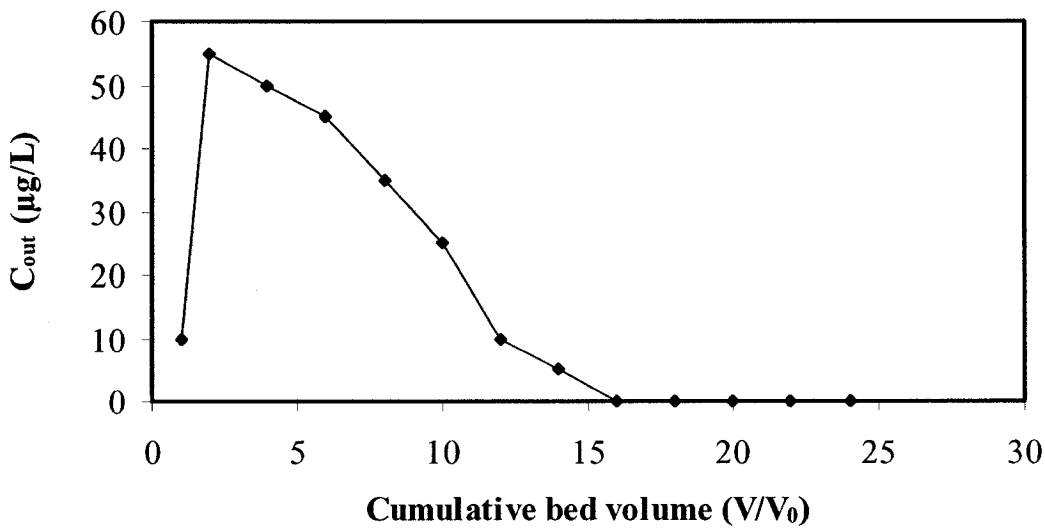

Figure 6.18 Desorption of arsenate from the exhausted biomass

6.9 Disposal of Spent Biomass

In the previous section it was suggested that the disposal of spent biomass without desorption is more effective than the regeneration. As seen in Figure 6.15, it is found that 90 bed volumes (900 mL) of arsenate-rich water were treated by 4.6 g of dry biomass yielding an average sorption capacity of 96 μg/g. To treat 100,000 L of water with an initial arsenate concentration of 500 μg/L, 512 kg of dry biomass would be required; the amount of arsenate removed by this amount of biomass would be approximately 49g. The arsenate content of the biomass is 0.0096% by weight and the required space for disposal of that amount of biomass is approximately 1.12 m^3.

For sanitary landfill disposal, the solid waste/sludge requires to meet specific criteria that determine if it is hazardous. According to the Resource Conservation and Recovery Act (RCRA) (USEPA, 1999), a waste is hazardous when it appears on one of the four hazardous wastes lists (F-list, K-list, P-list, or U-list), or exhibits at least one of four characteristics—ignitability, corrosivity, reactivity, or toxicity. With treatment residuals containing arsenic, toxicity is the primary characteristic of concern. The EPA (USEPA, 1992) has established an analytical method (method 1311), the Toxicity Characteristic Leaching Procedure (TCLP), to measure the toxicity of a waste. The current TCLP limit for arsenic is 5 mg/L.

In the TCLP, the solid waste is mixed with an acidic extraction liquid (dilute acetic acid) that is supposed to simulate the acid fluid at the bottom of a landfill. The solid sample should weigh at least 100 grams and the extraction liquid equal to 20 times the weight of the solid sample. This sample and the extraction fluid are then placed into a tumbler and mixed for at least 18 hours. This tumbling simulates the

leaching action of water seeping through waste in a landfill. After tumbling, the mixture is filtered and the filtrate/extract is analyzed. If it contains arsenic at or greater than 5 mg/L, the waste is hazardous (USEPA, 1992).

As per the conditions of TCLP if we would mix 100g of spent sludge (containing 96 μg/g of arsenate) to 2L of extraction liquid and in that case even all arsenate leached out of the sludge, the concentration of arsenate in the extraction fluid would be 4.8 mg/L which is still less than the TCLP limit of 5 mg/L. This clearly shows that it is not required to perform the TCLP test but the sludge can be disposed in the sanitary landfill as a non-hazardous material.

6.10 Arsenic Sorption Mechanism

Heavy metal removal by sludge is a consequence of the interaction between metals in the aqueous phase and the microorganism cell surface (Nelson, 1976). The cell wall consists of covalently linked polysaccharide and polypeptide chains, which form a bag-like structure that completely encases the cell (Voet and Voet, 1990). The amine groups in amino acids may be ionized in solution and may contribute to the metal binding capacity (Hunt, 1986).

Many functional groups such as hydroxyl, carboxyl, sulfhydryl, sulfonate and phosphonate are neutral when protonated and negatively charged when deprotonated. When the pH of the solution exceeds their pKa, these groups become mostly available for the attraction of cations. Amine, imine, amide and imidozole groups on the other hand, are neutral when deprotonated and positively charged when protonated. Therefore, they attract anions if the pH is lowered such that the groups are protonated

(Volesky, 2003).

The solid matter present in the anaerobic sludge is mostly organic (70%, section 5.2.2) in nature and protein constitutes the major part of the solid matter. It was found that the major part of the amino acids present in the biomass has isoelectric points in the pH range of 4.0-8.0 (Kefala et al., 2000, Delvin, 2002, Costa et al., 1997). In this pH range the majority of the amino acid molecules contain cationic sites. If pH is increased, the carboxylic group of the amino acid would progressively be deprotonated as the carboxylate ligands, simultaneously protonating the amino groups. This positively charged NH_3^+ ions could facilitate the biomass-arsenic binding. Protein/amino acid-arsenic interaction was also supported by arsenic induced loss in protein content in several plant biomasses (Basu et al., 2003). Such arsenic induced decrease in protein content might be due to an increase in the breakdown of amino acid (Cooley and Martin, 1979) at higher arsenic concentrations.

The arsenate ion occurs mainly in the monovalent form of $H_2AsO_4^-$ in the pH range between 2.2 and 6.9 while a divalent anion $HAsO_4^{2-}$ dominates at a higher pH range between 6.9 and 11.5. So, it can be said that the negatively-charged species will interact with the positively charged amino acids. A decrease in the pH below 5 shows a decrease in the adsorption even though the adsorption surface is positively charged and the sorbate species are negatively charged. In this case, more protonated arsenate species are less adsorbable than the less protonated one. This could be attributed to lack of electrostatic attraction between the surface and the protonated arsenate species. The decrease in the adsorption at a pH above 8 may be attributed to the increasing electrostatic repulsion between the negative surface sites and the negative

arsenic species.

In the case of arsenite the nonionic form H_3AsO_3 exists at a pH below its first pKa value of 9.22. Monovalent arsenite, $H_2AsO_3^-$ and divalent arsenite, $HAsO_3^{2-}$ exist above the pHs of their pKa values of 9.22 and 12.13 respectively. But at these high pHs the amino acid molecules present in the biomass surface do not provide any cationic sites to interact with the anionic arsenic species. The arsenite remains undissociated below pH 9.22 on the other hand, amino acid molecules remain dissociated between pHs 4 and 8, when the cationic sites may be available (Costa et al., 1997). The dissociation of arsenite and amino acid molecules at different pH values contributes to the least or no interaction between them resulting in lower arsenic removal efficiency. The adsorption of arsenite does not vary significantly over the pH range of 3 to 10. The poor removal of arsenite could be due to the non-specific adsorption on the biomass surface.

The results of our experiments are compared with those found in the literature. It is crucial in comparing different test results due to varying experimental conditions employed in different studies; high removal/technical efficiency alone can misinterpret the viability of particular technology if it does not meet the economical feasibility. Many researchers have focused on surface adsorption as the most effective means of removing arsenic. Saha et al. (2001) evaluated the adsorbents like kimberlite tailing, wood charcoal, banana pith, coal fly ash, spent tea leaf, mushroom, saw dust, rice husk, sand, water hyacinth, activated carbon, bauxite, hematite, laterite, iron-oxide coated sand, activated alumina, CalSiCo and hydrous granular ferric oxide for selecting an appropriate adsorbent to remove arsenic from ground water. They

conducted batch adsorption studies with an arsenic solution of concentration 1 mg/L for a 6 hour contact time. The results obtained from their experiments are shown in Table 6.4.

Table 6.4 Arsenic removal efficiency of different media (Saha et al., 2001)

Adsorbent	Biosorbent dose (g/L)	Adsorption capacity (μg/g)	
		As (III)	As(V)
Kimberlite tailing	10	25	40
Water hyacinthe	10	45	70
Wood charcoal	10	19	37
Banana pith	10	12	18
Coal fly ash	10	20	28
Spent tea leaf	10	25	42
Mushroom	10	22	35
Saw dust	10	28	36
Rice husk ash	10	5	12
Sand	10	15	22
Activated carbon	10	50	65
Bauxite	10	58	80
Hematite	10	40	60
Laterite	10	45	70
Iron-oxide coated sand	10	72	90
Activated alumina	10	90	96
CalSiCo	5	180	196
Hydrous granular ferric oxide	2	460	495
Anaerobic biomass	4	-	106

The removal efficiency of the examined biomass depends on the initial concentration and the dose of the biomass. As shown in section 6.1.2, an initial arsenate concentration of 500 μg/L together with the biomass dose of 4 g/L yielded the biosorption capacity of 106 μg/g and the removal efficiency of 85%. Depending on the dose of biomass and the initial arsenic concentration, the removal efficiency can be increased or decreased. The dose-response removal efficiency of the anaerobic biomass establishes its superiority over other adsorbent materials.

Chapter 7

Conclusions and Recommendations for Future Research

7.1 Conclusions

The following conclusions can be drawn based on the experimental results:

- A dose-response phenomenon was observed in determining removal efficiency. That means the efficiency will increase with increasing biomass doses if all other controlling factors like pH, initial concentration and contact time are kept constant.

- The removal of arsenate is pH dependent. Maximum removal occurred for arsenate at a pH range 5-6. Adsorption of arsenite is not so effective and did not vary significantly over a pH range 3-10. If arsenite is dominant in the influent a pretreatment oxidation step is required. Because the lack of interaction occurs between arsenite and the protein/amino acids due to their non-concurrent dissociation (i.e. different pKa values).

- The initial concentration of arsenate affected the removal efficiency. A higher initial concentration decreased the removal efficiency but did not have any effect on equilibrium time. In column operation when the initial concentration of arsenate was dropped from 500 μg/L to 200 μg/L the treated bed volume

increased from 90 to 220.

- The effect of contact time was found to be significant. It was observed that in the first five minutes of contact period almost 50% and in forty minutes almost 95% of total sorption was completed. Adsorption equilibrium reached after 90 minutes of biomass addition. This result shows that the sorption of arsenic by anaerobic biomass is a fast phenomenon; this has an advantageous effect in designing water treatment systems, the implication is that the materials would be suitable for the continuous flow system.

- The experimental data fitted the Langmuir isotherm model. The value of Hall's separation factor, R for all different initial concentrations was between 0 and 1, justified the anaerobic biomass as a favorable adsorbent material.

- Removal of arsenate [As (V)] was found more effective in the study. The maximum sorption capacity for arsenate was determined as 155 μg/g as compared to Langmuir equilibrium constant (q_{max}) of 164 μg/g.

- Chemical treatment of biomass was neither able to increase the sorption capacity nor the kinetics of reaction.

- A possible binding mechanism was proposed as protein/amino acid-arsenic interaction.

- The pH in the column remained unchanged. As it is difficult to maintain the

pH inside the column, this behavior justifies the suitability of the biomass for continuous flow column operation.

- Direct disposal of the biomass in the landfills as a non-hazardous material is possible.

- The biomass is available as a by-product of the commonly used anaerobic wastewater treatment plants around the world. The USEPA (2006) estimates that the publicly owned wastewater treatment works (POTWs) generate over 8 million tons (dry weight) of anaerobic sludge annually. This huge amount of sludge can easily be recycled to treat arsenic-rich water.

- Finally, it could be concluded that the anaerobic biomass is a cost-effective and eco-friendly biosorbent that may gain the status of commercial synthetic materials due to its availability, particulate shape, porous structure, sufficient mechanical strength, fast sorption rate, and easiness of disposal.

7.2 Recommendations

The following recommendations are made for future research:

- Arsenic speciation needs to be studied as the natural water generally contains both arsenate and arsenite in different proportions. An additional oxidation step is to be considered if arsenite is present.

- Natural water contains many impurities; the effect of these impurities on removal efficiency needs more examination for practical application.

- Further investigation into desorption improvement using other chemicals.

- Biosorption of arsenic by viable biomass should be considered for comparative studies.

- Pilot scale investigation with contaminated water is recommended to compare the validity of the experimental results.

Chapter 8

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