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REMOVAL OF ARSENIC FROM WATER USING ADSORPTION ON ALUMINA/MEMBRANE SEPARATION

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ABSTRACT

Arsenic contamination of water is a serious problem facing many communities in Canada and around the world. The high toxicity of arsenic makes the development of efficient and cost effective technologies for the treatment of arsenic contaminated water and soil a high priority task particularly if increasingly stringent effluent discharge and water quality criteria are to be met.

A novel process has been developed to remove arsenic from wastewater and contaminated water effectively. The process consists of three major steps: adsorption of arsenic on finely dispersed activated alumina, separation of adsorbent particles from the liquid phase via membrane separation, and regeneration of the adsorbent. The effect of process parameters such as pH, residence time, adsorbent characteristics, presence of competing ions, and initial arsenic concentration were studied. A number of commercially available alumina samples were characterized and tested. Spent activated alumina was successfully regenerated at pH 12, using sodium hydroxide, and reused. Up to 70% of the adsorbed arsenic was desorbed during the regeneration of spent alumina.

Arsenic concentrations of less than 50 μg/L were obtained within 10 minutes from initial arsenic levels of greater than 40 mg/L. Both specialty and commercially available gamma type aluminas were used in all experiments. It was found that the best samples of alumina with respect to arsenic removal were those with the smallest particle size (4 μm in diameter) and the largest surface area (880 m^2/g). The optimum pH for the arsenic removal was found to be in the range of 2 to 5. The effect of sulphate as a competing species on the overall rate of the adsorption process was not significant for sulphate concentrations of up to 100 mg/L.

Two different membrane systems were tested for the separation of the alumina particles from treated water: 1) a hollow fibre membrane module with a pore size of 200,000 molecular cut-off and a surface area of 0.5 m^2 and 2) an ENKA polypropylene Tubular membrane with a nominal pore size of 0.2 μm and a surface area of 0.036 m^2. Adsorbent concentrations of up to 60 g/L were easily handled by the membrane systems tested and a stable flux over a period of one day was observed.

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I would also like to thank my wife and my family for their encouragement, support and patience.

NOMENCLATURE

A	Empirical constant in Equation (3.7)	dimensionless
a	Elovich equation constant, related to initial reaction velocity	dimensionless
b	Langmuir constant in Equation (3.1)	mg^{-1}
b	Elovich equation constant, related to the activation energy; in Equation (3.6)	dimensionless
C_e	Liquid phase arsenic concentration at equilibrium	mg/L
C_o	Initial liquid phase arsenic concentration	mg/L
C_t	Liquid phase arsenic concentration at time t	mg/L
k	Freundlich model constant	dimensionless
K'	Empirical constant in Equation (3.7)	dimensionless
K	Elovich equation constant	dimensionless
n	Freundlich model constant	dimensionless
P	Partial Pressure	Pa
P_o	Saturation pressure of nitrogen	Pa
q	Adsorbent loading	mg As/ g alumina
q_e	Adsorbent loading at equilibrium	mg As/ g alumina
q_t	Adsorbent loading at time t	mg As/ g alumina
Q	Langmuir constant, maximum adsorption capacity of the adsorbent	mg/g
R	Universal gas constant	J/mol.°K
r_k	Kelvin radius of cylindrical capillary pore	Å
t	Time	min, s, hr
t	Thickness of adsorbed layer; in Equation (3.10)	Å
T	Temperature	°K
V_L	Molar volume of nitrogen in liquid form	m^3

GREEK LETTERS

γ	Surface tension of liquid nitrogen	N/m
θ	Contact angle between liquid nitrogen and pore walls	degree

LIST OF ABBREVIATIONS

BET	Brunauer, Emmett, and Teller
BJH	Barret, Joyner, and Halenda
BV	Bed volume
CCME	Canadian Council of Ministers of the Environment
gfd	Unit for flux through membrane (gal/ft^2/day)
MF	Microfiltration
MOEE	Ministry of Environment and Energy of Ontario
NF	Nanofiltration
RO	Reverse Osmosis
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency

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CHAPTER 1

1. INTRODUCTION

Arsenic (As) has a long history of beneficial applications. Many of its derivatives have desirable biological properties enabling them to be used as medicines, wood preservatives, insecticides, and herbicides. However, extensive use and misuse of arsenical compounds has resulted in elevated levels of arsenic in the environment which have had adverse effects on plants, animals, and human health.

Contamination of water by arsenic is a serious problem facing many communities in Canada and around the world. The seriousness of the problem, due to the high toxicity of arsenic and its health hazards makes the development of efficient and cost effective technologies for the treatment of arsenic contaminated water and soil a high priority task, particularly if increasingly stringent effluent discharge and water quality criteria are to be met.

The present technologies applied for the removal of arsenic from contaminated water are not efficient enough to reduce arsenic concentration of contaminated water to discharge levels set by the federal and provincial governments in both Canada and United States.

This Chapter introduces a brief overview of arsenic sources, hazards, the environmental criteria imposed on the industry by different governments, and the objectives of this work.

1.1. SOURCES OF ARSENIC

Small quantities of arsenical compounds occur naturally in the environment. The natural occurrence of arsenic in ground waters is directly related to the rock composition and geothermal activities in a contaminated area. Arsenic contamination can result from the leaching of anthropogenic toxic compounds into ground water, or from the natural dissociation of minerals from the subterranean strata such as the case in Nova Scotia and California [Hathaway and Rubel, 1987]. The major anthropogenic sources of arsenic contamination are industries such as mining, agriculture, wood, iron and steel, and smelting. The arsenic loading due to the Metal Mining Sector in Ontario between February 1, 1990 and January 31, 1991 was 12,458 kg of arsenic. Table 1.1 shows the annual arsenic loading due to different sub-sectors of the Metal Mining Sector in the province of Ontario, Canada. At least three active mine sites and one abandoned mine site in Ontario had high arsenic discharge levels exceeding the Recommended Maximum Discharge Limit (RMDL) of 0.05 mg/L [Ontario Ministry of Environment and Energy, 1992]. The arsenic discharge from various mine sites varied from 0.001 to 2.24 mg/L.

Arsenic concentrations of as high as 0.010 mg/L have been reported in fresh waters. Arsenic concentrations of 4.0 mg/L have been reported in some springs and mineral wells. Sea water usually contains 0.006 mg/L arsenic [Fletcher et al., 1994]. In the case of anthropogenic arsenic contamination, concentrations of up to several hundred mg/L have been encountered in under ground and surface waters [Hathaway and Rubel, 1987]. Canadian emissions of arsenic in 1990 were 471 tonnes, the majority of which were attributed to the copper, nickel, iron and steel industries [Canadian Minerals Yearbook, 1992].

Table 1.1. Total annual arsenic loading in Ontario due to a specific metal mining sector [Ontario Ministry of Environment and Energy, 1992].

Copper, Nickel, Lead, Zinc Sub-Sector (kg/year)	**Gold Sub-Sector (kg/year)**	**Uranium Sub-Sector (kg/year)**	**Total (kg/year)**
697	11,500	261	12,458

1.2. ENVIRONMENTAL CRITERIA FOR ARSENIC

In order to protect the environment from the adverse toxic effects of arsenic, environmental quality criteria has been set by different levels of government in both Canada and United States. Table 1.2 summarises some of the water quality criteria. In Canada, arsenic and its compounds have been listed in Group 1 of the Federal Priority Substances List. The Ontario Ministry of the Environment and Energy had previously established a 0.1 mg/L limit for arsenic in an unfiltered sample to protect aquatic life. Also the provincial mining effluent discharge limits for arsenic should not exceed a monthly average of 0.5 mg/L, or a daily average of 1 mg/L in the province of Ontario. Ontario Ministry of the Environment and

Table 1.2. Water quality criteria for arsenic (the values are point of use criteria unless specified). [Fletcher et al., 1994; CCME, 1991; USEPA 1985, Canadian Water Quality Guidelines, 1995]

Water Type	**Criteria Source (mg/L)***					
	CCME	**USEPA**	**Manitoba**	**New York**	**Ohio**	**Ontario**
Drinking	0.025	0.05	0.050	0.05	0.05	**0.025**
Fresh Water/ Aquatic Life	0.05	0.19[1] 0.36[2]	0.050	0.19[3] 0.36[4]	0.19[3] 0.36[4]	**0.1**
Irrigation	0.1	-	0.100	-	-	-
Livestock Watering	0.500-5.00	-	-	-	-	-
Mining Effluent Discharge	-	-	-	-	-	**0.50[3]-1[4]**

*(-) indicates that the data was either not available or the criteria does not exist for that certain category.

[1] Four-day average

[2] One hour average

[3] Monthly average

[4] Daily average

Energy has placed arsenic on its secondary list of candidate substances for bans or phase-outs because of its toxicity, persistence and bioaccumulation potential. Environment Canada has established a guideline of 0.05 mg/L of total arsenic to protect aquatic life which was also adopted by the province of Manitoba. Arsenic and its compounds are also on the Canadian Environmental Protection Act's Priority Toxic Substance List [Fletcher et al., 1994]. The United States Environmental Protection Agency (USEPA) established an As(III) criteria for the protection of fresh water aquatic life. Discharge limits of 0.190 mg/L and 0.360 mg/L were set for a four-day and one-hour average respectively. These concentrations were also adopted by the state of New York to protect fish life and fish survival. The drinking water criteria in the United States is 0.05 mg/L which is under review [USEPA, 1985]. Present arsenic criteria are very stringent; for example a limit of 0.190 mg/L has been set by the state of Ohio for total recoverable arsenic as the 30 day average ambient water concentration to protect aquatic life. Ohio EPA has also established an arsenic criteria of 0.05 mg/L for Lake Erie. Other states also have very similar criteria for arsenic.

1.3. HAZARDOUS EFFECTS OF ARSENIC

Arsenic affects all physiological systems. The toxicity of arsenic to humans is principally due to inhibition and deactivation of sulfhydryl enzymes as a result of the reaction of arsenoxide and arsenite that is the first step in cell damage. Arsenic also uncouples phosphorylation through the formation of arsenate esters, which in turn disrupts cellular respiration [Rosenblum and Clifford, 1983].

Small doses of inorganic arsenic can cause vasodilation, nausea, diarrhoea, vomiting, abnormal skin pigmentation, headache and anorexia. Long term exposure to arsenic can cause hyper pigmentation, skin cancer, liver cancer, circulatory disorders, jaundice, peripheral arteriosclerosis such as black foot disease in Taiwan, and many other life threatening health problems [Hisa and Shang-Lien Lo, 1990; Shen, 1973; Gosh and Teoh, 1985]. In plants high concentrations of arsenic destroy chlorophyll in the foliage and thus reduce crop yield [McNeely et al., 1979; Goodman and Gilman, 1975].

1.4. HISTORICAL APPLICATION OF ALUMINAS AS ADSORBENTS

Aluminas have been used as adsorbents for many years. Aluminas were introduced in 1932 by the Aluminum Company of America (ALCOA) for water adsorption. The earliest known application of activated alumina as adsorbent was in the chromatographic separation of liver extracts in 1901 [Goodboy and Fleming, 1984]. In the 1930's activated alumina was the chromatographic column packing material of choice when laboratory scale chromatography became a common analytical technique. Prior to 1940 the only large scale application of adsorbent aluminas was as a desiccant for the dehydration of air and natural gas. In later years dehydration with aluminas was extended to cracked gas and heavier hydrocarbon streams, as well as streams containing carbon dioxide and ammonia. In the 1950's and 60's aluminas were applied to the separation of isotopes of many actinide series as well as to other applications such as separation of impurities from aqueous streams and degenerative organic acids from hydrocarbons [Goodboy and Fleming, 1984]. In the 1960's liquid dehydration of aromatic and paraffinic hydrocarbons, halogenated hydrocarbons, and gasoline became common practices. In recent years, aluminas have been extensively and widely used as adsorbents for a variety of applications such as treatment of municipal wastes and purification of polymers and pharmaceuticals.

In the past three decades the variety and complexity of the applications for activated aluminas have increased. With the advent of more stringent environmental regulations the applications of alumina has become more versatile and new applications have been developed. Activated aluminas have also been extensively used for the removal of metals and metalloids such as arsenic, chromium, lead and other heavy metals from liquid streams.

1.5. RESEARCH OBJECTIVES

The objectives of the present work were to:

- Complete the design of a water treatment process for arsenic removal from contaminated water that employs adsorption on activated alumina.
- Determine the effect of different operating conditions on process performance.
- Determine the optimum range of values for different parameters.

- Study the adsorption characteristics of alumina such as pore diameter, particle size and surface area on the adsorption process using commercial and specialty samples of alumina.
- Determine the overall process rate as well as to select an activated alumina candidate sample for a future pilot study.
- Investigate the effect of sulphate as a competing ion that would compete with arsenic for adsorption sites.
- Study the effect of initial arsenic concentration on arsenic removal efficiency and removal rate.
- Evaluate different membranes for the separation of the adsorbent particles from the slurry.
- Study the feasibility of adsorbent regeneration and determine a suitable reagent as well as operating conditions.

The parameters that were looked at were pH of the feed solution to the process, arsenic speciation, contact time, adsorbent surface area, adsorbent particle size, adsorbent pore diameter and area, initial arsenic concentration, competing ion concentration, and adsorbent type. This study concentrated on the removal of As(V). The synthetic water samples prepared for the experiments contained only As(V), the reason being that As(III) at pH levels of below pH 6 is in the form of H_3AsO_3 which is neutral and would not be adsorbed by activated alumina [Vaishya and Agarwal, 1993].

CHAPTER 2

2. BACKGROUND AND LITERATURE REVIEW

This chapter presents a summary of the literature relevant to the work performed in this project. Based on the information extracted from the literature, the available methods for arsenic removal from contaminated water and different industrial discharge effluents are: chemical precipitation, coagulation, adsorption on solid adsorbents and metal oxides and hydroxides, ion exchange, filtration, distillation, evaporation, adsorbing colloid floatation, and membrane separation. These methods have been tested at both pilot and lab scale and some of them such as filtration, chemical precipitation, coagulation, and membrane separation are available on a commercial scale. Chemical precipitation, ion exchange, adsorption and reverse osmosis showed the best performance and potential for arsenic removal. The majority of the pilot and laboratory scale tests reviewed, were carried out using waters with arsenic concentrations less than a few mg/L.

2.1. SIGNIFICANCE OF ARSENIC PROBLEM

Globally human activities do not affect the arsenic cycle greatly; however, smelting of ores or application of arsenical pesticides and herbicides and release of arsenic into the environment through a variety of human activities may alter and disrupt the cycle locally [Gosh and Teoh, 1985].

The problem of arsenic contamination faces many communities in North America and around the world, such as Deloro, Ontario, Canada (result of mining operation) and parts of the province of Nova Scotia, Canada (a result of natural conditions and bedrock composition) [Mortazavi et al., 1993]. Taiwan is another example of a country facing serious arsenic problem where exposure to high arsenic concentrations in drinking well water has resulted in a great deal of health problems such as Blackfoot disease [Hisa and Shang-Lien Lo, 1990; Shen, 1973].

The storage and disposal of waste residues containing arsenic, the disposal of arsenic-containing waste solutions and the disposal of acid mine waters containing arsenic, are common industrial problems. The sources of arsenic, industrial hydrometallurgical process problems and potential stability of arsenical waste residues were extensively discussed by Robins in an EPA Workshop on Arsenic and Mercury [USEPA Arsenic and Mercury Workshop, 1992].

The assessment of the potential release of arsenic from energy technologies has estimated that in the United States, over 4,900 tons of arsenic may be released every year by coal conversion processes alone. Large volumes of arsenic bearing bodies of water such as that contained in the Berkeley open mine pit in Butte, Montana, United States, which holds over 20 billion Gallons of contaminated water at a pH of about 2 have caused serious concerns. The volume of contaminated water in the pit is rising at a rate of 5 million gallons per day and contains 300-400 mg/L of arsenic along with a wide range of other heavy metals [Twidwell et al., 1994]. This is another example of environmental problems and challenges that have to be addressed. The challenge is the development of technologies that are efficient and economically self-sufficient.

2.2. APPLICATIONS OF ARSENIC

Arsenic has a wide variety of commercial applications and is a commodity which is traded on a large scale worldwide. Various industrial activities such as smelting, petroleum refining, pesticide and herbicide manufacturing, and glass and ceramic production utilize arsenic [Gosh and Teoh, 1985].

Arsenic has been widely used in agricultural applications as insecticides and herbicides, feed additives and fertilizers [Richardson et al., 1978; Gosh and Teoh, 1985]. Calcium arsenate has been extensively used for boll weevil control in cotton. Boll weevil is a small American weevil, *Anthonomus grandis*, whose larvae destroy cotton bolls. It has also been used as an insecticide in blueberry fields. Lead arsenate has been used in tobacco fields and orchards for insect control. Since 1950, methane arsonates have been used for post mergence weed control in cotton fields. In 1991, The USEPA announced its preliminary decision to cancel the registration of products containing arsenic acid used as a desiccant on cotton fields [Richardson et al., 1978].

Arsenic acid has been of economic importance in cotton growing areas, such as in Texas, in which the area used for cotton growing is in the range of million hectares. Arsenic acid was extensively used as a desiccant to facilitate mechanical harvesting [Richardson et al., 1978]. Continuous application of arsenic compounds results in dangerously elevated arsenic levels in both soil and runoffs which in turn results in elevated arsenic levels in surface and ground waters, jeopardizing natural water resources. The problem has resulted in action by the governments to limit the application of arsenic by passing laws and implementing regulations as well as encouraging the use of substitute compounds for arsenic [Richardson et al. 1978].

Metallic arsenic is used in nonferrous alloys and in the electronics industry for semiconductor materials. The glass industry uses arsenic trioxide as a decolorizing and refining agent. The glass industry, due to environmental problems, has substituted arsenic acid by arsenic trioxide to avoid dust problems. Arsenic has extensive use in the wood industry as wood preservative in the form of chromated copper arsenate, ammonical copper arsenate, and fluorochrome arsenate phenol [Canadian Minerals Yearbook, 1992]. Arsenic trioxide is converted to arsenic acid for use in the production of wood preservative chemicals [Loebenstein, 1991].

The outlook for the demand for arsenic is somewhat uncertain despite the fact that supplies are abundant and demand has remained relatively flat over the years. There are substitutes for most applications of arsenic, but still arsenical compounds are either preferred for cost and effectiveness, or in some cases are the only product for specific applications. Future environmental criteria and regulations will be the major deciding factor affecting the supply and demand for arsenic [Loebenstein, 1991].

2.3. AQUEOUS CHEMISTRY OF ARSENIC

Arsenic has an atomic weight of 74.9216, atomic number of 23 and valences of +5, +3, 0, and -3. Elemental arsenic occurs in two solid forms: yellow and grey or metallic, having specific gravities of 1.97 and 5.73 respectively [Newland, 1985; Holtzclaw and Robinson, 1988].

The aquatic chemistry of arsenic is quite complicated because of the element's oxidation states (+5, +3, 0, -3) under various redox conditions. In solution, arsenic undergoes a number of transformations, which include precipitation/adsorption reactions, oxidation/reduction reactions, and biologically mediated transformations. In fresh waters arsenic is normally present in anionic form of arsenate (+5) and arsenite (+3) states and it can exist in both organic and inorganic forms. Elemental arsenic, although found in some ores, does not occur in the water table. Under high redox potentials (> +0.5 V) pentavalent arsenic species predominate, at mid redox potentials (-0.25 to +0.25 V) trivalent species start to form, and at low redox potentials (< -0.25 V) elemental arsenic and arsenic hydride are formed [Fletcher et al., 1994]. In surface waters the predominant arsenic species are: $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}; valance +5. Under moderately reducing conditions such as in underground water tables, the predominant arsenic species are: H_3AsO_3 , $H_2AsO_3^-$, and $HAsO_3^{2-}$; valance +3 [Yadava et al.,1988; Gosh, 1987]. Table 2.1 lists the free energy of formation for different arsenic species [Ferguson and Gavis, 1972].

Since arsenic forms oxyanions, it does not form complexes with chlorine and sulphate as do cationic metals. Arsenic forms bonds with organic sulphur, nitrogen and carbon which causes its toxic and carcinogenic characteristics. The complexation of As(III) and As(V) by dissolved organic matter in natural environments prevents adsorption and co-precipitation of arsenic with solid phase organics and inorganics. This results in increased mobility of arsenic in aquatic systems and soils.

The most abundant species of arsenic in ground and surface waters are arsenate and arsenite. The equilibria and equilibrium constants (pK) for arsenous acid (As(III)) and arsenic acid (As(V)) in aqueous solutions are as follows [Gulledge and O'Connor, 1973]:

Arsenic acid

$$H_3AsO_4 + H_2O \rightleftharpoons H_2AsO_4^- + H_3O^+ \qquad pK_{a1} = 2.20 \qquad (2.1)$$

$$H_2AsO_4^- + H_2O \rightleftharpoons HAsO_4^{2-} + H_3O^+ \qquad pK_{a2} = 6.97 \qquad (2.2)$$

$$HAsO_4^{2-} + H_2O \rightleftharpoons AsO_4^{3-} + H_3O^+ \qquad pK_{a3} = 11.53 \qquad (2.3)$$

Table 2.1. Free energy of formation for arsenic species at 25°C, and one atmosphere (ΔG_f° Kcal/mole).

Species	**State**	**ΔG_f°**
H_3AsO_4	aqueous	-184.0
$H_2AsO_4^-$	aqueous	-181.0
$HAsO_4^{2-}$	aqueous	-171.5
AsO_4^{3-}	aqueous	-155.8
H_3AsO_3	aqueous	-154.4
$H_2AsO_3^-$	aqueous	-141.8
$HAsO_3^{2-}$	aqueous	-125.3
$HAsS_2$	aqueous	-11.61
AsS_2^-	aqueous	-6.56
AsS	solid	-16.81
As_2S_3	solid	-40.25
As	solid	0
AsH_3	aqueous	23.8
AsH_3	gas	16.5
As_2O_3	solid	-140.8
As_2O_5	solid	-186.9

Arsenous acid

$$H_3AsO_3 + H_2O \rightleftharpoons H_2AsO_3^- + H_3O^+ \qquad pK_{a1} = 9.22 \qquad (2.4)$$

$$H_2AsO_3^- + H_2O \rightleftharpoons HAsO_3^{2-} + H_3O^+ \qquad pK_{a2} = 12.13 \qquad (2.5)$$

$$HAsO_3^{2-} + H_2O \rightleftharpoons AsO_3^{3-} + H_3O^+ \qquad pK_{a3} = 13.40 \qquad (2.6)$$

Figure 2.1 illustrates the speciation of arsenic at different pH's. This plot can be constructed by calculating the distribution of different species of arsenic at various pH values, using equations 2.1 to 2.6.

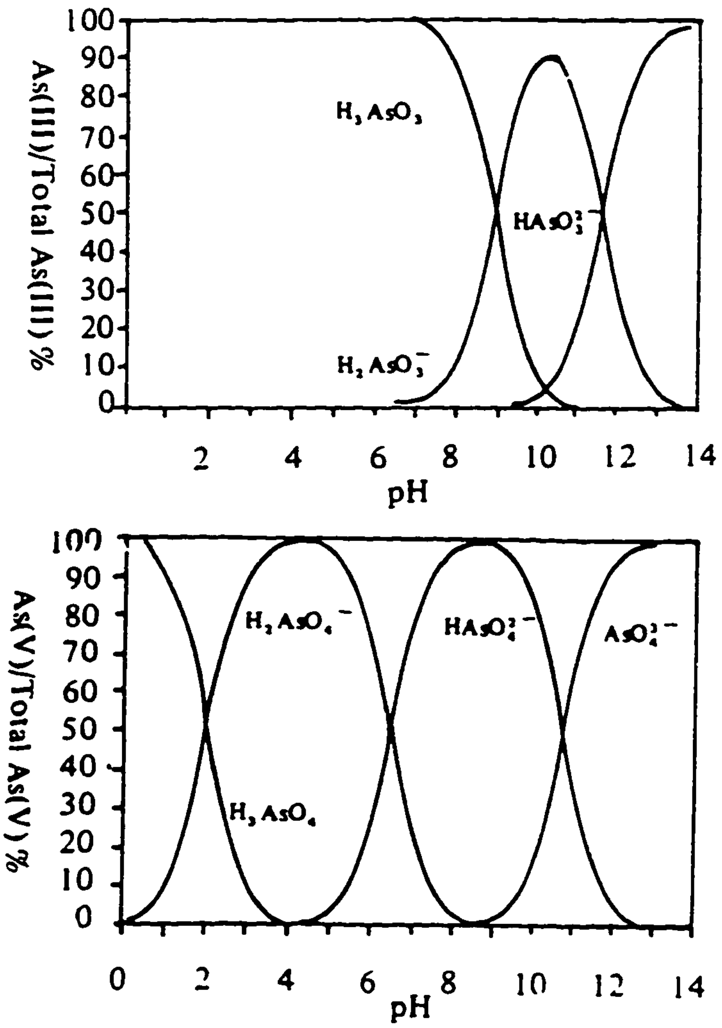


Figure 2.1. Predominance diagram for As (III) and As (V) as a function of pH.[Hisa and Shang-Lien Lo, 1990].

2.3.1. Analytical Methods for Determination of Arsenic

There are a number of methods for the determination of arsenic. Some of the more important methods for arsenic determination are: atomic absorption spectrophotometry, molecular absorption spectrophotometry, atomic emission spectroscopy, gas chromatography, gravimetric determination by co-precipitation, colorimetric determination, and polarographic techniques [Newland et al., 1985; Ferguson and Gavis, 1972].

For the determination of arsenic speciation, different species of arsenic can be determined by a sequential volatilization technique, where different arsenic species are volatilized as arsines. The arsines are separated by fractional volatilization or gas chromatography, and determined by atomic absorption, electron capture or flame ionization. The detection limit for arsenic hydride using atomic absorption equipped with a graphite furnace is about 0.05 ng arsenic per sample analyzed [Newland et al., 1985].

2.4. METHODS OF ARSENIC REMOVAL

A thorough search of the literature indicated that the techniques for the removal of aqueous arsenic fall into three major categories: ion exchange, activated alumina adsorption, and adsorption/co-precipitation by metal hydroxides. There are other methods for arsenic removal besideds the ones already named which have not been studied as extensively.

The conventional water treatment methods are able to remove trace amounts of arsenic from water up to several mg/L. Some examples of the known arsenic removal methods include coagulation and precipitation, adsorption onto solid media, ion exchange, and reverse osmosis [Rosenblum and Clifford, 1983; Harper and Kingham, 1992], evaporation, and adsorbing colloid floatation [Schlicher and Gosh, 1985; Nenon et. al., 1994]. When arsenic levels in contaminated waters exceed a few mg/L, conventional methods will no longer be effective to remove arsenic down to the set environmental criteria. Table 2.2 provides a list of available treatment methods, arsenic removals obtained, and costs involved [Patterson, 1975]. Table 2.3 shows a cost comparison between different technologies that were applied for the treatment of a certain wastewater under similar conditions. Tables 2.2 and 2.3 indicate that activated alumina adsorption is among the least expensive options for arsenic removal from wastewaters.

Table 2.2. Available water treatment technologies for arsenic removal.

Technology	Cost $/1000 gal	1994 Cost $/1000 gal	Initial [As] mg/L	Final [As] mg/L	% Removal	Reference
Coagulation, Sedimentation and Filtration	0.15-0.40	0.33-0.89	0.2-362	0.03-26.4	70-100	Patterson 1975
Coagulation/ Flocculation	1.9-2.39*	2.31-2.91	10.8	<0.5	>95	Halverson et al., 1987
Adsorption on Activated Alumina and Fe(OH)$_3$	0.21	0.60	0.56-0.94	Trace-0.47	38-100	Shen, 1973
Activated Alumina Adsorption (Column)	0.221-0.381	0.27-0.46	0.11	Trace	>99	Hathaway, 1987

* The process involved removal of Cu, Zn, Pb, Ni, and CN destruction.

Table 2.3. Estimated total treatment cost for 90% removal of arsenate from a wastewater with initial arsenic concentration of 7.5 - 37.5 mg/L.[Leckie et al., 1985].

Process	Total Cost $/1000 gal
Iron Adsorption	0.38
Activated Alumina	0.50
Lime-Soda Ash	0.56
Ion Exchange	1.12
Reverse Osmosis	2.60
Electrodialysis	2.60

2.4.1. Coagulation Using Iron and Alum

In treatment plants and experimental studies, trace levels of arsenic have been removed with varying degrees of success by precipitation on aluminum or iron hydroxides, and lime softening, followed by settling or filtration. Moderate success has been obtained in removing arsenic from water using coagulation and precipitation. Arsenic levels as high as 132 mg/L in gold mine effluents have been reduced to 13.2 mg/L with the addition of alum using a 4:1 alum:As ratio at pH 7 to 8 [Rosenblum and Clifford, 1983]. Shen (1973) removed only 32% of a 1 mg/L solution of arsenic with 20 mg/L alum at pH 6.8. Trelles and Amato (1950) reported that coagulation by iron or alum followed by filtration and pH adjustment has been successfully used in Argentina. They also reported that this method removed water hardness as well, which reduced its selectivity and increased the amount of sludge generated. Harper and Kingham (1992) treated contaminated water with arsenic levels of 48 mg/L using different types and combinations of coagulants such as hydrated lime, sodium sulfide, hydrated lime/sodium sulfide, hydrated lime/alum, and hydrated lime/ferric chloride at different concentrations and a pH range of 8 to 12.

Among the available coagulants, ferric chloride has been the most successful agent. The problem with coagulation and precipitation is generation of large amounts of sludge, lack of selectivity, and high residual arsenic concentrations with respect to water discharge criteria. Precipitations with some form of iron have been performed principally with ferric or ferrous sulphate, or ferric chloride [Harper and Kingham, 1992]. Water hardness can reduce the arsenic removal efficiency of this method.

There has been moderate success in removing arsenic with alum. Operating in a pH range of 6-8 and alum concentrations of 25 to 586.7 mg/L have yielded 32-95% arsenic removals with varying initial arsenic concentrations. A limiting factor is the increased solubility of aluminum hydroxide at pH levels greater than pH 7. This method is very sensitive to arsenic speciation and the efficiency decreases drastically in the presence of As(III) [Rosenblum and Clifford, 1983].

Lime softening has been demonstrated to effectively remove arsenic from contaminated water through co-precipitation of arsenic on the hydrous magnesium oxide floc [Rosenblum and Clifford, 1983]. Nillson (1971) used aluminum sulphate and Lime to remove As(III) and As(V) and achieved removals of up to 94% under different experimental conditions. Rosenhart and Lee (1972) applied chemical precipitation using aluminum sulphate, ferric sulphate, ferric chloride, lime, and sodium hydroxide to obtain arsenic removals of 80 to 95 percent at a pH range of 7 to 12. Other studies such as Gulledge and O'Connor (1973), Cherkinskii et al. (1973), Nillson (1971), Patterson (1975), Shen (1973), and Sorg and Logsdon (1978) have reported relative success in arsenic removal using precipitation and coagulation.

Some of the reagents that have been studied and tested are: lime and ferric sulphate which showed variable removals of arsenic ranging from 4.5 to 99.99%; lime and ferrous sulphate which showed arsenic removals of better than 99%; dolomite and ferric sulphate which showed removals of better than 99%; lime magnesium hydroxide and ferric sulphate which yielded arsenic removals of generally in excess of 98%. These studies also showed that the finer the lime particle size enhanced arsenic removal [Jones et al., 1977/78].

Earlier research has demonstrated that the commonly used industrial process for removing arsenic from aqueous solution as calcium arsenate (lime contacting), produces a solid product that is not stable in conventional chemical ponds, due to conversion of calcium arsenite and arsenate to calcium carbonate with concurrent release of arsenic into solution. At present the major means of arsenic removal from process effluents and waste solutions and the method of choice by industry is precipitation of arsenic as ferric arsenate. The stability of the ferric arsenate solid precipitated material has also been questioned since it has been demonstrated that arsenic removal by ferric precipitation is via adsorption and not by chemical formation of ferric arsenate. The long term stability of the ferric-arsenate product is presently unknown [Twidwell et al., 1994].

2.4.2. Reverse Osmosis

Reverse osmosis (RO) is a very effective method for the removal of ions from water. Application of reverse osmosis in a pilot study in San Ysidor, New Mexico, to contaminated water containing 88 μg/L total arsenic, resulted in >97% arsenic removal and the removal of >94% of water hardness [Clifford and Lin, 1991]. Other studies have shown similar removals for As(V) and lower rejections for As(III). The membranes used were manufactured by Dupont and Osmonics and for both membranes the permeate concentrations of arsenic were dependent on the initial arsenic concentrations. Arsenic concentrations below detection limit were observed when the initial concentrations were below 0.75 mg/L. Both membranes showed 80% rejection for As(III) [Rosenblum and Clifford, 1983]. Although reverse osmosis has been proven to be a very effective method, it is non-selective requiring the removal of all ions present in the wastewater.

2.4.3. Ion Exchange

A wide range of anion and cation exchangers have been tested for arsenic removal. Anion exchangers in chloride form have showed removals of 55-82% [Rosenblum and Clifford, 1983]. A study by Gosh and Teoh (1985) indicated that strong base anion exchange resins are capable of complete arsenic removal; however, the low exchange capacity of resins makes the application of these resins less economical and attractive and at high arsenate concentrations the maximum contaminant levels may be exceeded.

In a pilot study by Hathaway and Rubel (1987) strong-base anion exchange resin was used in the removal of arsenic from contaminated water with no pH control. The ion exchange resin was regenerated successfully using a 10 percent sodium chloride solution. Feed water to the process contained a 100 mg/L sulphate and 0.1 mg/L of arsenic. Sulphate and the alkalinity in the water lowered the capacity of the ion exchange resin to retain arsenic and sulphate replaced arsenic on the resin after the arsenic breakthrough point. In comparison to parallel activated alumina adsorption column runs, Hathaway and Rubel (1987) reported preference for activated alumina over ion exchange due to a significantly better performance.

In summary strong-base anion exchange (SBA) at neutral pH is a poor choice for As(V) removal because of the relatively low preference SBA resins have for the predominant forms of arsenic in the neutral pH range. Weak base anion exchange at low pH is an even poorer choice simply for the same reasons. Removal of As(III) by ion exchange is much more difficult than As(V) [Rosenhart and Lee, 1972; Lee and Rosenhart, 1972]. Presence of high salt concentrations interferes with this technique.

Pilot scale studies on point-of-use arsenic treatment systems, have demonstrated effective removal of arsenic to 0.050 mg/L from a raw water with initial arsenic concentration of 1.16 mg/L. Studies showed strong competition of other anionic species in groundwater that resulted in diminished performance of ion exchange resins [United States Army Report, 1990].

Rajaković and Mitrović (1992) investigated the concept of multiple separation by chemisorptive filters for the removal of arsenic from contaminated water. Chemisorption filters were made by paper manufacturing method which consisted of a blend of cellulose, cationic and anionic exchangers, activated carbon and a corresponding chemical agent. Chemisorption filters were activated with Ag^+, Mg^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+} ions. The results demonstrated that the arsenic removal is valence dependent and the removal of As(V) can be achieved easier and with higher efficiency. Initial arsenic concentration, pH, and presence of other anionic species were found to be of great importance for the process. In this study chemisorptive filters exhibited high efficiency in the removal of arsenic from water. It was found that the affinity of the ion exchange resin decreased according to the series: $SO_4^{2-} > NO_3^- > AsO_3^{3-} > Cl^- > OH^-$. It is important to emphasize that chemisorptive filters could not be regenerated and can only be used on a throw-away basis which would make the process an expensive choice in a large scale operation.

2.4.4. Polymer Binding

Polymer binding has been used for metals removal from contaminated water. This method becomes especially effective when it is combined with ultrafiltration. Studies by Legault et al. (1993) and Legault and Tremblay (1994) showed arsenic removals of up to 99%. Two polymers of poly-ethyleneimine and poly-diallyl-dimethyl-ammonium-chloride were used. The same study also showed that at salt concentrations of about 100 mg/L, arsenic rejection drops to as low as 60% and the rejection drops to almost zero at salt concentrations of >1000 mg/L. This problem may be overcome by developing more arsenic selective polymers.

2.4.5. Electrodialysis

Clifford and Lin (1991), studied the application of electrodialysis for the removal of arsenic in a pilot scale test. Electrodialysis removed 73% of total arsenic but it failed to effectively remove As(III) and the overall performance of this technique was not satisfactory enough for it to be seriously considered as a potential treatment technology. No record of the application of electrodialysis for the removal of As(V) from contaminated water was found.

2.4.6. Adsorptive Filtration

In adsorptive filtration, grains of sand are coated with iron hydroxide which adsorbs the metals in solution. Problems can occur with stability of the hydroxide film and regeneration. In a study where this technique was tested, claims were made that the film was stable but the range of conditions under which stability was maintained has not been mentioned. The available adsorption surface area to metal ions was less than that of activated alumina [Lewis, 1993].

2.4.7. Adsorbing Colloid Flotation

The use of adsorbing colloid flotation has been extensively studied. This process involves the addition of a floc-forming substance, usually ferric chloride or alum, in order to collect the dissolved heavy metals via adsorption and/or co-precipitation on metal hydroxides by adding a base. The flocs formed are subsequently removed by flotation in a column using a surfactant. Despite the availability of limited data on arsenic removal, the feasibility of the method has been demonstrated with several other heavy metals [Schlicher and Gosh, 1985].

In a flotation study by Schlicher and Gosh (1985), for synthetic arsenic contaminated water solutions, a surfactant, sodium lauryl sulphate and a collector (alum or ferric chloride) were used and compressed humidified air was applied to the column. The results of the study indicated that adsorption and colloid flotation can be used effectively for the purpose of the removal of aqueous arsenate. The process requires short retention times, small space, low energy, and produces a small volume of sludge. The method offers a great deal of promise for industrial wastewater treatment. The process is however only applied to the treatment of potable water since the allowable residuals of arsenic and alum may not be met.

2.4.8. Adsorption by Inorganic Adsorbents

Since activated alumina was used in this work, this section is mostly devoted to the discusion of the characteristics of activated alumina and the review of the studies involving it.

2.4.8.1. Alumina structure and surface chemistry

Alumina is a general term for aluminum oxides and hydroxides. Several forms of activated alumina have been classified according to the temperatures at which they are obtained from aluminum hydroxide. The form of alumina most frequently used and commercially available is the gamma (γ) type. This class of alumina is further characterized by a crystalline structure called "defective spinel", a cubic close-packed lattice with two and two-thirds vacancies on the octahedral positions of the unit cell. The alumina has both macro- and micropores of 30 to 1,000,000 Å. When contacted with water, the aluminum atoms at the surface of the crystal act as a Lewis acid (electron acceptor) and become hydroxylated by coordination and dissociative adsorption of water. The hydroxyl groups can then be replaced by an arsenic anion [Rosenblum and Clifford, 1983].

The molecular structure of alumina essentially determines its adsorptive characteristics. They exist as at least five thermodynamically stable phases and many more metastable transition forms. All aluminas with the exception of some alpha (α) aluminas, have surface hydroxyls which can have a certain degree of activity in adsorption. The crystallographically stable aluminas are not very useful since they have very little porosity and surface area. Transition forms of alumina constitute the largest group used as adsorbents. These aluminas are usually formed via thermal decomposition of hydroxides. This process results in the loss of hydroxyls which causes a defect in the aluminum and oxygen lattice structures. Depending on the particular transition form, the Al^{3+} and O^{2-} ions can be tetrahedrally or octahedrally coordinated in cubic or hexagonal close packed systems. For instance γ alumina, the best known form and most widely applied as adsorbent, has a defective spinel structure in which the oxygens are in cubic close packing. In this type of alumina the oxygen sublattice is fairly well ordered while there is a significant degree of disorder in the aluminum sublattice. The lattice structure of alumina and degree of defect in the structure dictates the nature of the surface characteristics. For example eta (η) alumina, a transition form of alumina with a spinel structure similar to γ alumina has a strong one dimensional disorder of the cubic close packed lattice. This disorder in the lattice results in a greater concentration of surface acid sites in η alumina than γ. This is an important consideration in adsorption systems [Kirk Othmer, 1991].

Transition aluminas, depending on their method of synthesis, can be amorphous. A number of commercial products available as γ alumina are amorphous. Amorphous aluminas (as distinguished from amorphous hydroxide) have larger concentration of defect structures, i.e. chemical activity, than the more structured transition aluminas. The higher the concentration of defect structures, the higher would be the surface concentration of Lewis acid sites which results in a surface that is chemically more active. A considerable rearrangement of the anion and cation sublattice takes place in the transition from crystalline to amorphous forms. During the process of transition of structural form, a large number of defect structures can be envisioned which results in active sites for adsorption. Most commercial transition aluminas are mostly between amorphous state and a state less structured than crystalline [Goodboy and Fleming, 1984].

Gelatinous aluminas are another group of aluminas that are important as adsorbents. Some exhibit good adsorptive properties for phosphates and arsenates in aqueous solutions. Gelatinous aluminas possess extremely high surface areas and chemical activity. Beta (β) aluminas are another group of aluminas which exhibit good adsorptive properties. Beta (β) alumina consist of alkali-substituted aluminates and their related compounds. These compounds are mostly used for desulphurising flue gas. Alpha (α) alumina is another type of alumina that despite its reactivity is not normally considered for adsorption applications. Alpha (α) alumina exhibits greater acidity per surface area than transition aluminas and can have strong adsorptive characteristics. Halides, water, and inorganic acids adsorb well on α alumina [Goodboy and Fleming, 1984].

The chemical nature of the active sites on the alumina surface that are responsible for the adsorption phenomena are well understood. Defect structures formed as a result of surface dehydroxylation result in localized regions of adsorptive and catalytic activity. The surface activity cannot be attributed to anion vacancies. For adsorption, activated alumina can be considered as possessing both Lewis and Bronsted acidic and basic sites of different strength and concentrations. Acidity of the surface is contributed by coordinatively unsaturated Al^{3+} ions, protonated by hydroxyls, and some acidic hydroxyls.

At least five different distinct forms of surface hydroxyl groups have been identified. These groups can possess different degrees of both acidic and basic character in adsorption depending on their synthesis, geometric orientation, and concentration.

In the recent years efforts to create aluminas of highly-specific nature and better characterized has resulted in a number of transition alumina forms for particular adsorption applications at a commercial scale. These aluminas include γ, Chi (χ), and η as well as amorphous. ALCOA's CP and CPN grades of alumina are examples of amorphous and transition forms respectively. The chemical purity of alumina is an important factor in its adsorption characteristics. Other important factors are surface area, and porosity. Representative pore distribution of various commercial and experimental aluminas are in the range of 3-10,000 Å [Goodboy and Fleming, 1984].

Modification of alumina surface chemistry is another way of improving the alumina adsorption characteristics. Activated aluminas are multi-functional materials with broad capability for different ratios of surface sites. By controlling the surface hydroxyl concentration, the total surface Lewis and Bronsted acidity and basicity are altered to the desired levels. Relative concentrations of surface anion vacancies, hydroxyl functionalities, and unsaturated Al^{3+} cations are altered over a broad spectrum of acidity and basicity. Another way of modifying the surface functionalities of activated aluminas is the application of chemical modifiers that increase the concentration of the existing desired functionalities. This technique has existed in over 20 years and has been applied in catalysis. Work at ALCOA has shown that virtually any metal ion can be adsorbed to some degree by alumina with efficient regeneration [Goodboy and Fleming, 1984].

A number of alumina forms are capable of both anion and cation exchange. With chemical modification these properties can be enhanced. A number of these same materials are amphoteric, i.e. they exhibit positive surface functionalities below and negative charges above their isoelectric point. Adsorption of metals using alumina is one of the recent applications which is in use as adsorption towers and columns by different industries. Because of the unique versatility of aluminas and increasing understanding of their properties, these materials have found applications in industries which were formerly not considered as a market for these materials [Goodboy and Fleming, 1984].

2.4.8.2. Oxidation of arsenic (III) to arsenic (V)

Many researchers have found that the affinity of activated alumina to As(V) is much higher than that for As(III) [Frank and Clifford, 1986; Rosenblum and Clifford, 1983; Gosh and Teoh, 1985]. Frank and Clifford (1986) concluded that pre-oxidation of As(III) to As(V) is essential to achieve efficient removals of arsenic using activated alumina. Oxidation of As(III) to As(V) takes place by addition of free chlorine at a dosage of 1 mg/L to a water sample containing 100μg/L of arsenic, in a pH range of 6 to 10; however, the reaction rate is affected by the total organic carbon (TOC) content. Addition of chloramine (1 mg/L) oxidized 45 percent of As(III) to As(V) in the pH range of 6 to 10.The following reaction was suggested:

$$NH_2Cl + H_3AsO_3 + H_2O \rightleftharpoons NH_4^+ + HAsO_4^{2-} + Cl^- + 2H^+ . \qquad (2.14)$$

This reaction has a standard free energy of -82.4 Kcal/mol [Frank and Clifford, 1986].

2.4.8.3. Mechanism of anion adsorption on alumina

The mechanism of anion adsorption on activated alumina is similar to that for such minerals as gibbsite, serpentine, and clay minerals. The anion adsorption sites on these materials are aquo groups ($-M-OH_2^+$) and hydroxo groups ($-M-OH$). The surface chemistry of an oxide in contact with an aqueous solution to a large extent is determined by deprotonation or a hydroxyl association reaction; i.e. for a positively charged surface:

$$-M-OH_2^+ \rightleftharpoons -M-OH + H^+ \qquad (2.7)$$

For a neutral surface:

$$-M-OH_2^+ + OH^- \rightleftharpoons -M-OH + H_2O \qquad (2.8)$$

or

$$-M-OH \rightleftharpoons -M-O^- + H^+ . \qquad (2.9)$$

For a negatively charged surface:

$$-M-OH + OH^- \rightleftharpoons -M-O^- + H_2O \qquad (2.10)$$

Equation (2.7) is favoured at lower pH range while Equation (2.10) is favoured at the higher pH range [Choi and Chen, 1979]. No evidence has been found, in the study of fluoride adsorption, to indicate that an anion in the absence of its acid, to donate a proton, could be adsorbed on neutral or negative surface. For the anion to adsorb onto the alumina surface, a source of proton is required to protonate the surface to create a potential between the adsorbent surface and the adsorbate molecule, in order to facilitate the adsorption process. That is despite the high affinity of fluoride for the metal ions on the surface of adsorbents, they were only adsorbed on positively charged surfaces [Hingston et al., 1972]. The next two equations show the ligand exchange scheme proposed for the adsorption of an anion such as arsenate or fluoride on a metal oxide surface [Hingston et al., 1972].

$$\text{-M-OH} + \text{HX} \rightleftarrows \text{-MOH}_2^+ \cdots\cdots\cdots \text{X}^- \tag{2.11}$$

$$\text{-MOH}_2^+ \cdots\cdots\cdots \text{X} + A^- \rightleftarrows \text{-M-}A + \text{X} + \text{H}_2\text{O} \tag{2. 12}$$

Where *A* is the anion adsorbate. Some evidence also suggests that anions like fluoride and arsenate can be adsorbed by an ion exchange mechanism even though the surface is neutral [Choi and Chen, 1979]:

$$\text{-M-OH} + A^- \rightleftarrows \text{-M-}A + \text{OH}^-. \tag{2.13}$$

2.4.8.4. Adsorption onto activated alumina

Activated alumina has been applied with limitted success for the removal of arsenic from contaminated water in the past. Activated alumina has, both on laboratory scale and pilot scale tests, performed better than ion exchange and activated carbon adsorption [Rosenblum and Clifford, 1983; Clifford and Lin, 1991; United States Army Report, 1990]. Inorganic arsenic (As(V) and As(III)) and organoarsenical compounds such as mono-methyl arsenate, di-methyl arsenic acid, and trimethyl arsine oxide can be removed from water by activated alumina. The affinity of common ions for the adsorption sites at the surface of the alumina is: $OH^- > H_2PO_4^- > F^- > H_2AsO_4^- > HSeO_3^- > (SO_4^{2-}, SeO_4^-, -HCO_3^-, Cl^-) > NO_3^- > H_3AsO_3$ [United States Army Report, 1990]. The researchers at the Aluminum Company of America Ltd. (ALCOA) have reported a pH between 5.5 to 6 yields maximum uptake of arsenic. Control of pH allows for the control of arsenic speciation and valence of arsenic as well as the surface charge of the activated alumina [ALCOA, 1994(a)].

In almost all of the references sited in which activated alumina was applied and tested, the alumina used was ALCOA's F-1 activated alumina with an arsenic loading capacity of about 14 mg As(V)/g alumina at pH 6 and 25 °C [ALCOA, 1994(b)]. The particle size of choice for F-1 alumina used was 28 x 48 Tyler mesh size (297 to 595 micron). The particle size selected by the researchers and recommended by ALCOA is due to the fact that a larger particle size would minimize flow problems in an adsorption column configuration. The draw back to the use of larger particle size is reduced arsenic loading [ALCOA, 1994(a)].

Hathaway and Rubel (1987) carried out a pilot scale test that used activated alumina (γ- Al_2O_3), ALCOA F-1 alumina in a column configuration. The initial concentration of arsenic (mostly in the form of As(V)) ranged between 0.080-0.116 mg/L and the arsenic concentration in treated water, at pH 5.5, was below 0.005 mg/L after 8,542 bed volumes (BV) and 0.050 mg/L after 15,536 BV. The pH was adjusted using a dilute solution of sulphuric acid. It should be noted that some researchers have found that sulphate ions have adverse effect on the adsorption of arsenic on activated alumina [Rosenblum and Clifford, 1983]. The activated alumina continued to remove arsenic up to 24,545 BV when the arsenic concentration reached 0.085 mg/L. Each test lasted three months before the activated alumina was nearly exhausted. At this point the arsenic loading of the solid phase was 1507 g/m^3 of activated alumina. In the same pilot study, with the tests carried out without pH adjustment, the activated alumina in the columns was exhausted between one to three days and 101 BV were treated with discharge water having 0.090 mg/L of arsenic. Hathaway and Rubel (1987) regenerated the spent activated alumina using a 4-5% (1-1.25 N) NaOH solution; 80 % adsorption capacity recovery was reported.

Another pilot study [Clifford and Lin, 1991] was carried out in San Ysidor, New Mexico in which activated alumina was tested for the removal of arsenic. Approximately 9,000 BV were treated at pH 6, reducing the initial arsenic concentration of 0.088 mg/L to <0.050 mg/L. At natural pH of 7.2 only 1900 BV were treated. In a pilot study at the Sharpe Army Depot (United States Army), column adsorption using activated alumina was tested at an average pH of 5. 10,656 BV were treated, and the arsenic concentration was reduced from 0.145 to 0.320 mg/L to about 0.0025 mg/L [United States Army Report, 1990].

Gupta and Chen (1978) found that activated alumina performed far better than activated carbon or activated bauxite. Rosenblum and Clifford (1983), obtained residual concentrations of 0.004 mg/L from initial 5 mg/L arsenic solutions. In their tests Rosenblum and Clifford obtained 0.096 mg/L arsenic from starting solutions of 4.5 mg/L after half day of contact between the adsorbent and arsenic contaminated water.

In a study by Gosh and Teoh (1985) and a similar study by Gosh (1987) the rate of arsenic removal by F-1 alumina varied significantly with pH. Removal was rapid in the first 24 hours and then slowed considerably as the reaction approached equilibrium. At lower pH values over 90 % of the maximum adsorption took place within a few hours implying that adsorption may have been non-specific. Although specific adsorption could not be completely ruled out it was concluded that coulombic or physical processes played significant role in arsenate adsorption at low pH levels. The maximum removal occurred at pH 5. It was concluded that the $H_2AsO_4^-$ was the major adsorbing species and the major mechanism of adsorption were inferred to be coulombic attraction and specific chemical adsorption. The presence of sulphate had no effect on the adsorption process at pH levels below pH 7. At pH levels of above pH 7 slight decrease in adsorption of arsenic in the presence of sulphate was reported. Phosphate was reported to have no effect on the adsorption process at pH levels below pH 6 and noticeable hinderence of the adsorption process was noted at pH levels of above 7.

Gosh and Teoh (1985) regenerated spent alumina with sodium hydroxide at concentrations of 0.5 % or higher. At a sodium hydroxide concentration of 3 % large alumina losses of up to 5.6 % were observed. They reported adsorption capacity regenerations of greater than 79 %. In a similar study by Schlicher and Gosh (1985) results similar to the above were achieved and a maximum arsenate loading of 10 mg As(V) /g of alumina at pH 6 was reported. Gosh (1987) reported minimal effect of salt concentration on the removal of arsenic in the pH range of 4 to 9 (the concentration range of 0.001 M to 0.1 M $NaNO_3$ was studied).

Many other studies have demonstrated the effectiveness of activated alumina for the removal of arsenic [Fox and Sorg, 1987; Rosenblum and Clifford, 1983; Shen, 1973]. Bellack (1971) successfully removed arsenic from groundwater using activated alumina columns and successfully regenerated the spent alumina using a 1 % caustic solution. Factors that have been identified to affect the arsenic removal process are: initial arsenic concentration, pH, temperature, presence of other ions and arsenic speciation. The optimum pH range for activated alumina application to remove arsenic has been reported to be between 4-6. The majority of the studies sited used a column configuration and dealt with arsenic concentrations of less than few mg/L. A column adsorption process would probably not be as effective in presence of high arsenic concentrations, because large columns and very low flowrates would be required which can make the process throughput low and uneconomical. This problem can be solved by contacting arsenic contaminated water or wastewater with activated alumina in the form of a mixed suspension and separating the adsorbent from the treated water via a membrane system.

2.4.9. Other Organic and Inorganic Adsorbents

2.4.9.1. Zeolites

Zeolites have been used for the removal of metal ions from water. Zeolites are alumina silicates and because of their crystalline structure, their net surface charge is negative which renders them unsuitable for metals that form oxyanions, such as arsenic and chromium. Some work has been done on modification of the zeolite surface with cationic organic oligomers for the removal of chromium which has not been very successful. The major problems encountered were the very small pore diameter of zeolites that limited the available adsorption surface to the external surface, as well as finding a suitable non toxic surface agent. Problems with regeneration were also anticipated [Santiago et al., 1992].

2.4.9.2. Activated carbon adsorption

Rosenhart and Lee (1972) studied activated carbon for arsenic removal from water which demonstrated very poor arsenic removals. A pilot study at a U.S. military base also showed poor arsenic removals by activated carbon [United States Army Report, 1990]. Arsenic adsorption onto activated carbon was compared to adsorption on activated alumina and ion exchange. The results indicated that to achieve a certain arsenic residual concentration from an initial contaminated water sample, the required dosage of activated carbon was substantially higher than activated alumina or ion exchange resin dosage. Huang and Fu (1984) found that activated carbon could effectively reduce typical concentrations of aqueous arsenate to drinking water standard level with maximum removals at a pH between 4 to 5. Gupta and Chen (1978) investigated the adsorption of arsenic by activated alumina, activated bauxite and activated carbon. They reported that although adsorption rates were not significantly higher for alumina, the adsorption capacities for alumina were significantly higher than that of activated carbon. Using 5 mg/L of HD-3000 carbon, and initial As(V) and As(III) concentrations of 5 and 10 mg/L respectively, equilibrium was reached in about two days at pH 7.

2.4.9.3. Other adsorbents

Other adsorbents that have been used and tested for the removal of arsenic are flyash, china clay [Yadava et al, 1988], bauxite, and Ganga-sand [Vaishya and Agarwal, 1993]. There are also a variety of ion exchange resins and polymers available that have been applied and tested for arsenic removal. Some examples are IR-120 and IR-400 manufactured by Rohm and Haas.

CHAPTER 3

3. THEORY

3.1. GENERAL ADSORPTION MODELS

Several mathematical models have been developed in order to quantify adsorption such as the Langmuir and Freundlich adsorption models. The simplest theoretical model for monolayer adsorption is the Langmuir adsorption model. The Langmuir model was originally developed to describe and quantify chemisorption on a set of distinct localized adsorption sites and it has been used to describe both physical and chemical adsorption. The basic assumptions for the Langmuir model are [Ruthven, 1984]:

- each active site interacts with only one adsorbent molecule,
- adsorbate molecules are adsorbed on well defined localized sites,
- the adsorption sites are all energetically equivalent, and
- neighbouring adsorbed molecules do not interact with each other.

The Langmuir equation relates solid phase adsorbate concentration (q_e) to the equilibrium liquid adsorbate concentration (C_e) as follows.

$$q_e = \frac{Q\ b\ C_e}{1 + b\ C_e} \tag{3.1}$$

Where Q represents the maximum adsorption capacity for the solid phase loading and b is an energy constant related to the heat of adsorption [Rosenblum and Clifford, 1983; Weber, 1972]. The Langmuir constants are obtained from the experimental data by plotting the linearized Langmuir equation

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{b\ Q}\ \frac{1}{C_e} \tag{3.2}$$

A second mathematical model used to quantify adsorption reactions is the Freundlich model. Freundlich model has also been used to describe adsorption equilibria. Freundlich model describes adsorption in terms of the adsorbate concentration [Carberry, 1976],

$$q_e = k\,C_e^{\frac{1}{n}} \tag{3.3}$$

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \tag{3.4}$$

The values of Freundlich constants are derived from the experimental data by plotting the linearized form of Equation (3.3) by plotting *ln* q_e against *ln* C_e, the Y-intercept is equal to *ln k* and the slope gives the value of *1/n* [Rosenblum and Clifford, 1983]. Both Langmuir and Freundlich adsorption models were evaluated for describing the experimental data. obtained from experiments described in section 4.4.2.8. Details of the calculation of the constants are presented in section D-1 in Appendix D.

3.2. KINETICS OF SURFACE REACTIONS

Kinetic studies are of great value for interpreting the mechanism of homogenous reactions. The interpretation of heterogeneous reaction kinetics has been less successful because of the difficulty in the analysis of experimental data. In the study of chemisorption at gas-solid interfaces the Elovich equation has been used to address problems of data analysis and interpretation. The simplest form of this model is [Hingston, 1981],

$$\frac{dq_t}{dt} = a \exp(-bq) \tag{3.5}$$

where q_t is the amount of adsorbate adsorbed by the adsorbent in time t, a is a constant related to the initial reaction velocity, and b is a constant related to the activation energy of adsorption.

Integrating Equation 3.5 with the boundary condition q = 0 at t = 0 yields,

$$q_t = b^{-1} \left(\ln \frac{(t + K)}{K} \right) \tag{3.6}$$

where $K = (ab)^{-1}$. Theoretical studies of the Elovich model and its applicability have shown that accurate data are required, to fit results of adsorption and desorption in oxide-aqueous solution systems especially for short reaction times [Hingston, 1981].

Another kinetic model, which is an empirical model developed by Prakash et al. (1987) has been successfully applied for describing the kinetics of the adsorption of As(III) onto china clay [Yadava et al., 1988] and Haematite [Singh et al., 1988]. The equation of the model is,

$$\log_{10} (t+1) = K' (C_o - C_t)^A . \tag{3.7}$$

The values of the empirical constants depend upon the initial concentration, the density and porosity of the adsorbent and other influencing factors [Singh et al., 1988].

Another kinetic model that is used to describe the sorption kinetics is [Weber, 1972],

$$q = K' t^{1/2} . \tag{3.8}$$

The plot of q versus $t^{1/2}$ has been used by Yadava et al. (1988) and Singh et al. (1988) to calculate the rate constant for pore diffusion as well as to confirm whether intraparticular mass transfer was the rate limiting step in the systems studied.

3.3. CHARACTERIZATION OF ACTIVATED ALUMINA SAMPLES

3.3.1. Determination of Pore Area Distributions Using the BJH Method

A Micromeritics Accelerated Surface Area and Porosimetry system Model ASAP 2000 was used for characterization of activated alumina samples as explained in section 4.2 in Chapter 4. The ASAP 2000 uses a program executing a BJH (Barret, Joyner, and Halenda) calculation for determining the pore area distribution of a porous material [Micromeritics, 1990].

Determination of the pore size distribution was made from a detailed interpretation of nitrogen adsorption/desorption isotherms. In the method used in the ASAP 2000, a BET adsorption curve of nitrogen is constructed at the liquid nitrogen temperature (-195.8 °C) by plotting the volume of adsorbed nitrogen versus the relative pressure P/P_o, where P is the applied pressure of the nitrogen gas and P_o is the saturation pressure of nitrogen at the liquid nitrogen temperature. During the adsorption of nitrogen an adsorbed layer is formed which becomes thicker with increasing pressure until a pore is completely filled, resulting in the formation of a meniscus due to surface tension. During the desorption capillary evaporation takes place, whenever pressure drops and the desorption pressure is given by the Kelvin equation [Kelvin, 1871],

$$RT \ln \left(\frac{P}{P_o}\right) = \frac{2\,\gamma V_L}{r_k} \cos(\theta) \tag{3.9}$$

where r_k is the Kelvin capillary radius, γ is liquid nitrogen surface tension, V_L is the molar volume of nitrogen in liquid form, and θ is the contact angle between liquid nitrogen and the pore wall [Linsen, 1970].

The desorption part of the isotherm is utilized to calculate the amount of nitrogen lost, by comparing with the adsorption isotherm, to the pores that have been emptied. The thickness of the adsorbed layer remaining on the wall of capillaries is calculated by [Micromeritics, 1990; Barret et al., 1951],

$$t = \left[\frac{13.99}{0.034 - \log\left(\frac{P}{P_o}\right)} \right]^{0.5} \tag{3.10}$$

As the pressure is reduced successively the values of t decreases and the amount of nitrogen desorbed is determined at each desorption step and added to the previous volumes measured and the total surface of the walls exposed is determined and a new t is calculated. The sum of t and the r_k gives the pore radius. The detailed description of the algorithm is explained in Barret's paper (1951) and the Micromeritics ASAP 2000 manual [Micromeritics, 1990].

CHAPTER 4

4. EXPERIMENTAL

In this chapter the materials and equipment used for the experiments, the experimental procedures, description of the equipment used, analytical procedure and explanation of the methods used are presented.

4.1. MATERIALS AND EQUIPMENT

A complete list of the materials and equipments used in this study is presented in Appendix A.

4.1.1. Activated Alumina Samples

Samples of specialty and commercial grade activated aluminas were obtained from Scientific Adsorbents Ltd., Atlanta, Georgia, USA, and Aluminum Company of America Ltd. Vidalia, Louisiana, USA, respectively. A list of the samples is presented in Table A-1 in Appendix A.

4.2. CHARACTERIZATION OF ACTIVATED ALUMINA SAMPLES

Activated alumina samples were charachterized using nitrogen sorption porosimetry, by determination of their physical characteristics such as average pore diameter, specific surface area, pore volume and pore area distribution.

4.2.1. Equipment Description

Activated alumina samples were characterized for their adsorption properties and physical characteristics using a Micromeritics Accelerated Surface Area and Porosimetry System; ASAP 2000. The ASAP 2000 consists of one analyser and a multi function control module. ASAP 2000 is a tabletop model and is fully automated. The machine is equipped with two separate internal vacuum systems; one for sample analysis and the other for sample preparation. There is one sample analysis port and there are two ports for sample preparation. Between the vacuum pump and manifold in both analysis and degas systems in-line cold traps have been included. There is a port next to the sample analysis port from which the sample saturation pressure, P_o, is measured. The port's opening is located inside the liquid nitrogen container. The machine is also equipped with two heating mantels which are used for the heating of the samples during the degassing procedure (Figure 4.1).

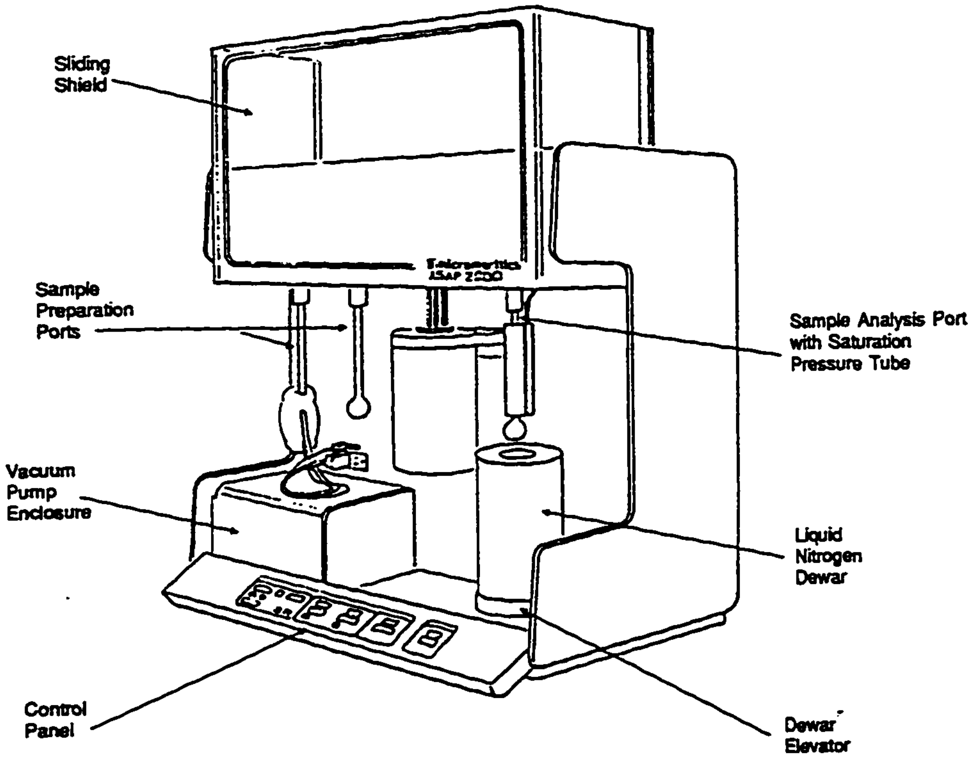


Figure 4.1. Schematic illustration of the Micromeritics Accelerated Surface Area and Porosimetry system (ASAP 2000).[Micromeritics, 1990].

4.2.2. Sample Preparation and Characterization

Prior to loading the alumina sample into the machine the sample tubes were washed with laboratory detergent and dried under vacuum. The weight of the empty and dry tube was recorded and a small sample of the desired activated alumina was weighed into the tube. The weight of the tube and alumina was recorded and the tube was connected to vacuum in the degassing section of the machine. A heating mantel was then placed on the lower section of the sample tube and the temperature was set to 350 °C. The valve to the vacuum pump was opened and the sample was degassed for at least four hours. The amount of alumina had to be kept below 0.5 g. Large alumina sample sizes exceeded the capacity of the machine during some runs which was probably due to activated alumina's high porosity and large surface area. After the completion of the degassing process, the analysis port liquid nitrogen container was filled and placed on the elevator below the analysis port. The sample tube was weighed and connected to the analysis port. The proper settings were then entered in the computer program controlling the porosimeter to initiate the analysis.

The analysis involved the generation of an isotherm at the liquid nitrogen temperature, by determination of the volume of nitrogen gas adsorbed and desorbed. The isotherms were then analysed using the BJH method [Micromeritics, 1990]. The BJH desorption pore surface area, pore area, average pore diameter and pore volume were reported.

4.3. ARSENIC DETERMINATION

A Perkin Elmer atomic absorption spectrophotometer model 3100 (Air-acetylene flame) equipped with a Perkin Elmer MHS-10 Mercury/Hydride system was used for the determination of arsenic concentration. The machine was connected to an IBM PC computer and remote controlled by the computer during the course of the analyses.

Figure 4.2 illustrates the schematic of the Perkin Elmer MHS-10 Mercury/Hydride system. The MHS-10 Mercury/Hydride system which operates together with an atomic absorption spectrophotometer, is a manually operated accessory for high sensitivity determination of mercury and other hydride generating elements such as, As, Se, Sb, Te, Bi, and Sn. The cell assembly consists of a quartz cell and a mounting bracket. The mount is installed on the spectrophotometer standard burner head allowing the quartz tube to be heated to high temperatures.

In the method of analysis utilized, sodium borohydride (Na_2BH_4, reagent grade, assay 98%, supplied by Caledon Laboratories Ltd.) was used as a reducing agent. Sodium borohydride releases hydrogen on contact with acids. The reaction mechanism involved is complicated and involves formation of radicals and intermediates. When sodium borohydride is used, As (V) is reduced to As(III) and arsenic hydride is formed. The violent reaction and release of gas results in the transport of arsenic hydride gas to the quartz cell. In the quartz cell the arsenic hydride molecule thermally breaks down and atomic arsenic absorbs the light energy emitted from the arsenic lamp and absorbence is measured by the detector. The following equations represent the simplified version of the reactions involved [Perkin Elmer, 1984] :

$$As^{3+} + 3\ BH_4^- \rightleftharpoons AsH_3\uparrow + 3/2\ B_2H_6 \qquad (4.1)$$

$$2\ AsH_3 \overset{\Delta T}{\rightleftharpoons} 2\ As + 3\ H_2 \qquad (4.2)$$

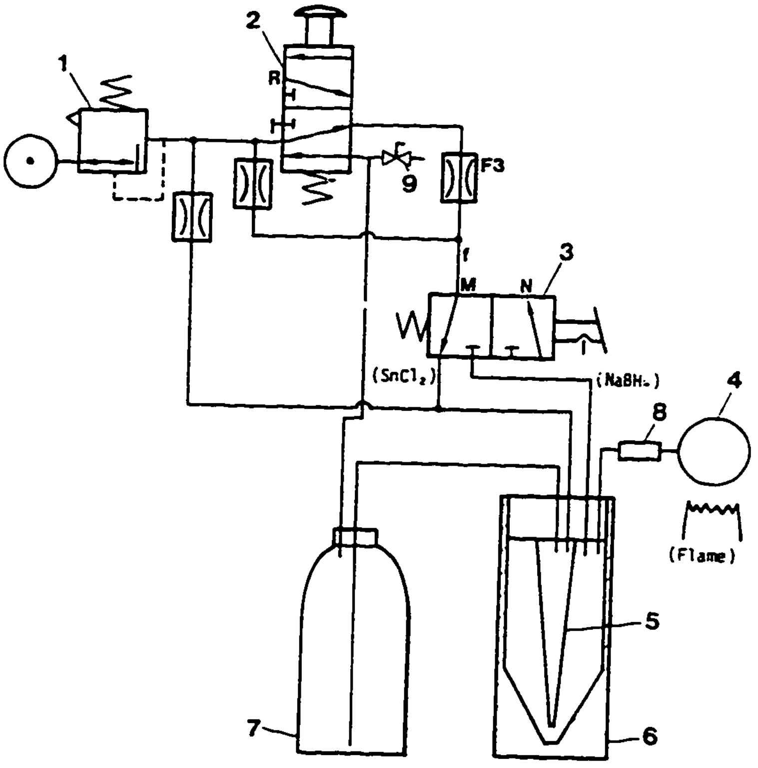
A Perkin Elmer EDL System 2; Electrodeless Discharge Lamp, was added to the atomic absorption to increase the accuracy of the arsenic measurements. Arsenic emits light having a wavelength of 193.7 nm which is in the visible range. An Electrodeless Discharge Lamp (EDL) consists of a quartz bulb containing the element or the salt of the element to be determined in an inert atmosphere. When a radio frequency field is applied to the bulb, the inert gas is ionized and the coupled energy excites the vaporized analyte atoms. The emission spectra produced is typically much more intense than that from the hollow cathode lamps. Use of the lamp also limited the interference of the visible light from the laboratory lamps [Perkin Elmer, 1991].

4.3.1. Arsenic Analysis

Before the analysis, a 5% hydrochloric acid (HCl, reagent grade, assay 36.5-38%, supplied by Caledon Laboratories Ltd., diluted by Milli-Q water-18MΩ water generated by Milli-Q plus water system by Millipore, with deionized water feed) and a 3% sodium borohydride solution in 10% sodium hydroxide (Sodium hydroxide pellets, assay 97%, supplied by Caledon Laboratories Ltd.), dissolved in Milli-Q water was prepared. A 1 mg/L (ppm) standard solution was also prepared from a 1000 mg/L arsenic standard solution (Atomic absorption standard solution for arsenic, assay 1002, with nitric acid as supporting acid, supplied by Caledon Laboratories). The reductant reservoir (Figure 4.2) was 3/4 filled with sodium borohydride, and the flame was lit for heating up the quartz cell. The reaction vessel was connected to nitrogen gas cylinder.

To carry out the arsenic determination 10 mL of 5% hydrochloric acid was added to the reaction vessel. A volume equal to the volume of arsenic containing sample to be analysed was removed and then the sample was added in order to maintain a total reaction volume of 10 mL. Samples were diluted by Milli-Q water as required in order to keep the absorbence values within the range of the standard curve.

To start the determination, sodium borohydride was forced into the reaction vessel by depressing a plunger located on top of the MHS-10 unit which is a valve allowing nitrogen gas to flow into the sodium borohydride bottle and create a pressure difference sufficient to force sodium borohydride into the reaction vessel. After completion of each determination the result of the determination appeared as an absorbence value as well as a peak on the screen of the computer monitor and the cycle was repeated. Faulty and erroneous readings were screened based on the shape of the peaks. These readings, corresponding to peaks with a distorted shape were discarded. A standard curve was constructed by running a blank and different volumes of a one mg/L arsenic standard solution (volumes of 10 μL, 25 μL, 50 μL, 75 μL, and 100 μL) from which the actual sample concentrations were determined.



1	Pressure Reducer
2	Multipath Valve with Plunger
3	Changeover Valve with Toggle Switch
4	Quartz Cell
5	Immersion Tube
6	Reaction Flask
7	Reductant Reservoir
8	Flashback Arrestor
9	Pressure Relief Valve

Figure 4.2. Schematic of the MHS-10 Mercury/Hydride System.

4.3.2. Data Analysis

The absorbances and dilution factors for the arsenic samples analysed were recorded and a polynomial equation was fitted to the standard curve data using the software Delta Graph Professional. Applying the resulting equation to the absorbances of the unknown samples and correcting for dilutions, the arsenic concentration of the samples analyzed were determined. The error of analysis was determined by performing multiple determinations of each sample and calculating the standard deviation of the measured concentrations. The error for the results presented in sections 5.1 to 5.3, was between 2 to 15 % for the determination of the initial arsenic concentration values, and between 1 to 11% for the other determinations. The analysis error was variable for different concentrations with a maximum error of less than 5% for the results in section 5.4 to 5.8 which were analysed by Seprotech Laboratories, Ottawa, Ontario. For the results of sections 5.1 to 5.3 it has been assumed that a 15 % error applies to initial arsenic concentration values and an 11% error applies to all other determinations. For the results in section 5.4 to 5.8 an error of 5% has been assumed for all determinations when studying the results of the experiments.

4.4. ADSORPTION / MICROFILTRATION

Figures 4.3 and 4.4 show schematic representations of the two parts of the process, adsorption and regeneration respectively, that were developed for the removal of arsenic from contaminated ground water during the present study. The process utilizes finely dispersed activated alumina for adsorption of arsenic. As illustrated in Figure 4.3, arsenic contaminated water enters the adsorption reactor where arsenic is picked up by the finely dispersed activated alumina. Fresh activated alumina is also introduced into the reactor when needed in order to compensate for the lost adsorption capacity during the course of the process. Nitric acid is added to the reactor content to keep the pH of the suspension constant. The arsenic loaded activated alumina particles are then separated from the liquid phase by a microfiltration membrane and the membrane permeate is discharged. The membrane used in this process is ZeeWeed™ which is a hollow fibre membrane manufactured by Zenon Environmental Ltd., Burlington, Ontario, Canada. The hollow fibre membrane is placed directly inside the reactor and the separation is facilitated by an aerator or bubble diffuser. There is only one permeate stream leaving the membrane unit and there are no concentrate streams. The concentrate basically remains inside the reactor and is mixed with the rest of the suspension.

The permeate arsenic concentration is continuously monitored. When the permeate arsenic concentration reaches the discharge limit, the feed flow into the reactor is stopped and the spent adsorbent is regenerated inside the reactor. The regeneration is carried out by increasing the pH of the reactor content using sodium hydroxide. As the arsenic is desorbed from the activated alumina particles, the arsenic rich liquid is separated from the alumina particles by the ZeeWeed™ membrane. The arsenic rich effluent is directed into a second reactor in which arsenic is precipitated by the addition of ferric chloride and sulphuric acid. Lime can be used to replace sulphuric acid. The precipitate is removed from the reactor and discarded.

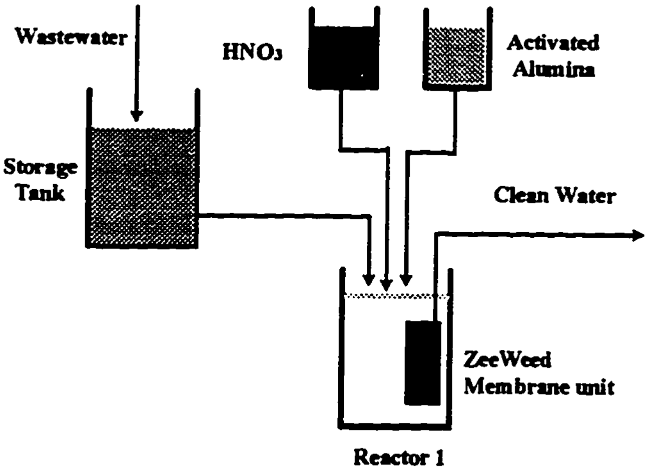


Figure 4.3. Schematic of the adsorption/microfiltration process for the removal of arsenic from water.

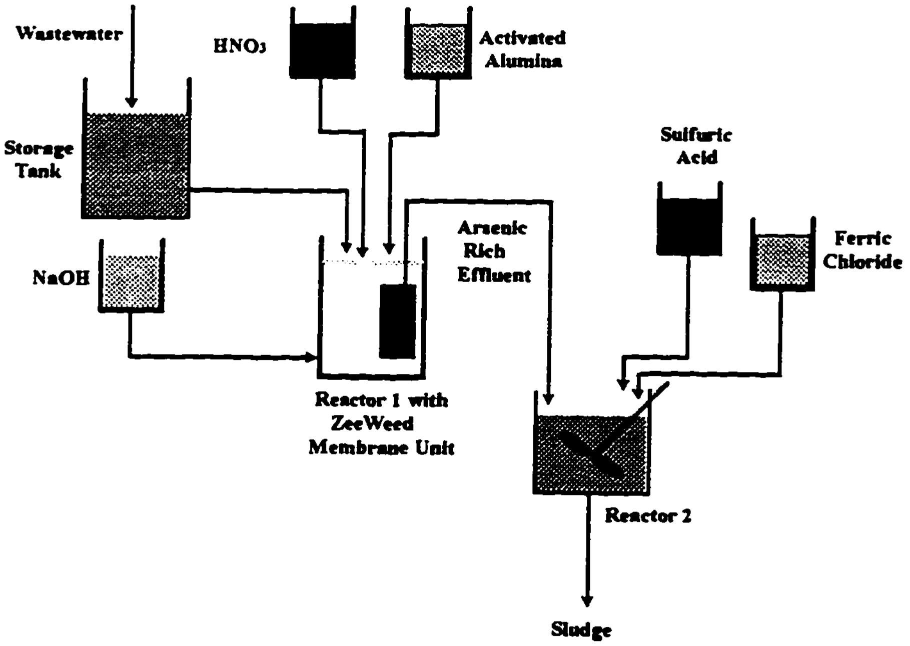


Figure 4.4. Schematic of the adsorbent regeneration stage of the adsorption/ microfiltration process for the removal of arsenic from water.

4.4.1. Technical Novelty

The process described above is a hybrid membrane process which incorporates a membrane separation stage in a conventional adsorption process. When activated alumina is exposed to the arsenic contaminated water, three mass transfer steps precede the adsorption of arsenic onto the alumina surface. An arsenate anion travels to the exterior surface of the particle via bulk diffusion. The second step is film diffusion through which arsenate passes the stagnant liquid adjacent to the particle surface. In a third step the arsenate anion diffuses into the pores of the activated alumina particle. The final stage is the adsorption of arsenate anion to the alumina surface. The binding of the arsenate anion happens as soon as the anion diffuses into close proximity of an active site . The pore diffusion step is the slowest of the process and the rate limiting step [Yadava et al., 1988]. Figure 4.5 shows a schematic illustration of the process described above.

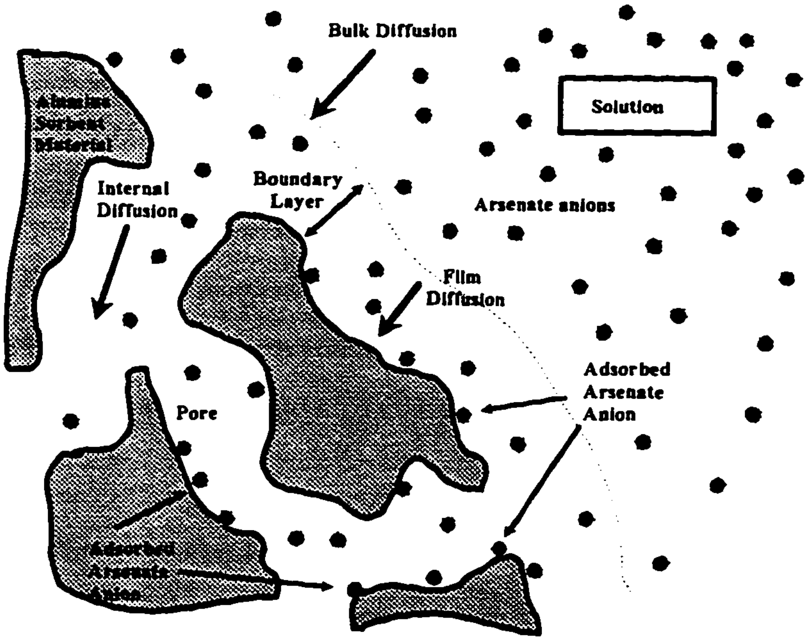


Figure 4.5. Schematic illustration of the adsorption process onto alumina.

The conventional applications of activated alumina which utilized alumina in a column setup is not fast enough for the process to be commercially viable on a large scale. In order to overcome this problem the size of the alumina particles were reduced. The particle size of the alumina used for adsorption columns is 28 x 48 Tyler mesh size (297 to 595 micron). Since the rate of arsenate diffusion into the pore is constant for a given system, a large particle size will limit the internal surface area of the alumina accessible to the arsenate anion per unit of time. This means that only a certain amount of surface area will be accessed by the adsorbate molecules in a given time period.

By reducing the particle size, for instance by crushing the adsorbent particles, increased accessibility of internal surface area to the adsorbate molecules results, allowing more to adsorb in a given time period under similar conditions; therefore, increasing the overall process rate. By introducing the adsorbent particles into an agitated reactor (agitation and mixing is achieved by vigorous aeration) problems such as pressure drop in a column, and boundary layer problem can be minimized or avoided.

4.5. EXPERIMENTAL PROCEDURE

4.5.1. Preparation of Water Samples

A stock arsenic solution was made by dissolving sodium arsenate (Sodium arsenate heptahydrate - $Na_2HAsO_4.7\ H_2O$- reagent grade, assay 98%-102%, supplied by Caledon Laboratories) in Milli-Q water (18MΩ water generated by Milli-Q plus water system by Millipore, with deionized water feed). The sodium arsenate crystals were placed in a standard laboratory drying oven at 30 °C for about 24 h until constant weight readings of a control crystal sample was achieved at room temperature prior to preparation of solutions, and stored in a desiccator. A 54.6 g/L solution of sodium arsenate was made from which appropriate dilutions were made to prepare the required solutions for subsequent adsorption experiments.

A stock sodium sulphate solution (Sodium sulphate anhydrous - Na_2SO_4- reagent grade (assay 98%), supplied by Caledon Laboratories Inc.) was prepared for the experiments to study the effect of a competing ion on the arsenic adsorption process by activated alumina. To prepare the sodium sulphate stock solution, anhydrous sodium sulphate was dried in a laboratory drying oven at 30 °C until constant weights were obtained for a control sample at room temperature. In a one litre volumetric flask a 100 g/L solution of sodium sulphate was prepared. The concentration of the stock solution was verified by determining the sodium concentration in the solution by atomic absorption.

For adsorption experiments, a 1250 μL aliquot of the arsenic stock solution (using Eppendorf pipettes, 10-100 μL and 100-1000μL) was added to 398.75 mL of Milli-Q water. The amount of the stock solution used was varied for few experiments where different arsenic concentrations were required. For the experiments related to the study of the effect of a competing ion, from the initial 400 mL Milli-Q water (pH was adjusted in advance using a Cole Parmer Digi-Sense pH meter model 05985-80) a volume equal to the combined volumes of the arsenic and sodium sulphate stock solutions was removed prior to their addition. A final pH adjustment was carried out for all solutions prior to commencing the experiments. All solutions were at laboratory temperature (23 °C to 24 °C). For the experiments where a different initial arsenic concentration was required the amount of the stock solution used was varied.

A sample of an actual contaminated water was obtained from the Deloro Water Treatment Facility, Deloro, Ontario. The water sample had an approximate 50 mg/L of arsenic which was the feed to the Deloro water treatment facility. The pH of the groundwater was adjusted to the required pH for the experiment by addition of nitric acid (HNO_3, reagent grade, assay 69.0-71%, supplied by Caledon Laboratories Ltd.). Table 4.1 shows that analysis of Deloro water sample used in the experiments determined by a commercial Laboratory.

Table 4.1. Composition of Deloro arsenic contaminated water sample.

Compound	Untreated Ground water (mg/L)
Chloride	73.4
CO_3^{2-}	4.8
HCO_3^-	222
NO_3^-	less than 0.1
SO_4^{2-}	114
Arsenic	~50

4.5.2. Adsorption Experiments

4.5.2.1. Preparation of activated alumina samples

The activated alumina samples received, each consisted of alumina particles with a certain size distribution. It was important that the samples of alumina used in the adsorption experiments to be identical as much as possible. To ensure this, the alumina containers were placed on a ball-Mill roller and mixed for at least one day prior to collecting alumina for the adsorption experiments. The samples were taken by spreading the alumina on a small tray and random grab samples were taken in order to ensure similarity of samples with respect to particle size distribution. The samples were placed in ceramic crucibles and activated in a muffle furnace at 250 °C overnight. Alumina samples were cooled in a desiccator for at least an hour and appropriate amounts of alumina were weighed (± 0.001g accuracy) for the adsorption experiments.

4.5.2.2. General test procedure

Arsenic contaminated water was prepared by making dilutions of stock arsenic solution and the pH was adjusted to the required pH for each specific experiment with a fresh concentrated nitric acid solution. The pH was adjusted to ± 0.01 unit of the desired pH. The choice of nitric acid was selected based on the information in the literature [United States Army Report, 1990] indicating that the affinity of nitrates for activated alumina's surface sites is significantly less than that of arsenate anion and the effect of nitrate competition for the surface sites would be negligible. All experiments were carried out at ambient temperature (23°C) and an adsorbent concentration of 3 g/L was used. The beakers were placed under a multiple stirrer with Teflon paddles and the stirring speed was set to the maximum (varied between 320 to 328 rpm).

Activated alumina samples were added to the beakers at time zero while the solution was being stirred. Upon the addition of the alumina to the beakers the pH of the solutions started to climb rapidly. The pH of the contents of each of the beakers was adjusted to the starting pH using a 0.1 Molar nitric acid solution. The adsorption mixtures were sampled at 5, 10, 20, 30, 40 minutes, 1 hour, 1.5 hour, and 2 hours. The volume of each sample was 3 mL. The samples were stored in poly ethylene vials with 5 μL of concentrated nitric acid added to ensure the stability of the samples. The samples were collected using 3 mL plastic syringes and filtered by polysulphone syringe filters (Acrodisc polysulphone nanofiltration syringe filters, 4.5 μm pore size, supplied by Gelman Sciences Inc.).

The pH of the reaction mixtures was adjusted by addition of 0.142 M nitric acid one minute prior to taking each sample. The pH of the solution as well as the amount of nitric acid added were recorded. The collected samples were then analysed for arsenic content, following the procedure described earlier.

4.5.2.3. Study of the pH effect on arsenic adsorption

These experiments were performed in order to determine the effect of solution pH on the arsenic uptake by activated alumina. Two activated alumina samples were used for this part of the study. The activated alumina samples used were a basic specialty alumina supplied by Scientific Adsorbents Ltd. (50-212 µm, basic alumina), and CPN-325 commercial grade alumina supplied by ALCOA Ltd.

In the first set of pH experiments 50-212 µm basic alumina was used. The pHs of 1, 3 and 7 were tested by following similar procedure described in the Section 4.5.2.2 except that the pH of the reaction mixture was not controlled during the experiment. Initial concentrations of the arsenic solutions were about 33 mg/L. During the initial sets of experiments samples were taken for up to 48 h, but it was noticed that a 2 hour sampling time frame was sufficient since the initial one hour of the experiment was of major interest; therefore the consecutive experiments were terminated after 2 hours. In the section where the experimental results are reported and discussed, only the experimental results of up to 2 hours have been reported.

In a different set or experiments pHs of 1, 3, 4, 6, 7, and 8 were tested while keeping the pH controlled and constant during the course of the test. Initial concentrations of the arsenic solution were about 26 mg/L. The optimum pH for maximum uptake of arsenic was determined during this set of experiments. In another set of experiments the pHs studied were narrowed down to the vicinity of the optimum pH with pH steps of half a pH unit (pHs of 2, 2.5, 3, 3.5, and 4). In a different set of experiments ALCOA's CPN-325 was tested at pHs of 2, 3, 4, and 5 with initial arsenic concentration of 43 mg/L. The choice of alumina was based on the results of a different set of experiments in which commercial grade activated aluminas supplied by ALCOA Ltd were tested and screened for best performance. The pH experiments with CPN-325 were carried out in order to ensure the applicability of the initial pH experiments to the commercial grade aluminas.

4.5.2.4. Study of particle and pore size effects on the arsenic uptake

Following the experimental procedure in section 4.5.2.2 and setting the initial pH of the experiment at pH 3 and an initial arsenic concentration of 25 mg/L, a set of experiments were carried out in order to study the effect of the characteristics of aluminas such as pore and particle size on the uptake of arsenic. Activated alumina samples were Manufactured by Scientific Adsorbents Ltd. Atlanta, Georgia, USA, to have specific characteristics with respect to average pore diameter and particle size in order to make this study feasible.

4.5.2.5. Arsenic removal using commercial activated aluminas

Eight samples of commercial grade activated aluminas were tested in order to select and recommend the best alumina sample with respect to the rate of arsenic removal, as a candidate for a continuous process as well as for a pilot study. The hierarchy of the alumina performances was also determined. The ALCOA's samples were tested at pH 3, with initial arsenic concentration of about 43 mg/L. The experimental procedure outlined in section 4.5.2.2 was followed.

4.5.2.6. Effect of initial arsenic concentration on the arsenic uptake

Following the procedure outlined in section 4.5.2.2, arsenic removal experiments were conducted at pH 3, using ALCOA's CPN-325 and initial arsenic concentrations of 2, 22, 43, 89, 132, and 177 mg/L. These experiments were conducted in order to observe the effect of increasing initial arsenic concentration on the removal of arsenic.

4.5.2.7. Effect of competition of other ions on arsenic uptake

Sulphate ion being one of the fiercest competitor of arsenic for active sites on the surface of the activated alumina [Rosenblum and Clifford, 1983; United States Army, 1990], was selected for this experiment. Sulphate concentrations of 0, 10, 30, 50, 300, and 600 mg/L with initial arsenic concentration of 46 mg/L and ALCOA's CPN-325 were used. The experimental procedure in outlined in section 4.5.2.2 was followed.

4.5.2.8. Determination of the adsorption isotherms

Adsorption isotherm for the adsorption of arsenic on the ALCOA's activated alumina was determined. In 10 different 120 mL polyethylene vials, 100 ml of arsenic solutions with initial arsenic concentrations ranging from 15 mg/L to 1050 mg/L were placed and 0.3 g CPN-325 alumina was added. The pH of the solutions were adjusted to pH 3 at ambient temperature (23 °C). Initial Samples were taken from the arsenic solutions prior to the addition of alumina. The vials were placed on a variable speed shaker (Variable speed shaker, 115 Volts, 50/60 Hz, Eberbach Corporation). The pH was kept constant by addition of concentrated nitric acid (maximum required addition of acid during the course of the test was 5 µL of nitric acid at each pH adjustment). Volumes of acid added were recorded for determination of concentration correction factors due to dilution. Samples were taken after one, three and seven days. Sampling procedure was as outlined in section 4.5.2.2.

4.5.3. Regeneration of Spent Alumina

In this part of the study the feasibility and conditions of adsorbent regeneration were investigated. In the first set of experiments following the procedure outlined in section 4.5.2.2, adsorption experiments were carried out using ALCOA's HTC-100 at pH 3 and initial arsenic concentration of 42 mg/L. Three parallel experiments were performed. The alumina-arsenic solution suspensions were filtered. The filter cakes were placed in individual beakers and 100 mL of sodium hydroxide solution at pHs of 10, 12, and 13 were added to each beaker. The suspensions were mixed for one hour and filtered. The filter cakes were rinsed with Milli-Q water, dried and activated in a muffle furnace at 250 °C overnight. The arsenic adsorption tests were carried out the next day under similar conditions, but the volume of the solutions were adjusted to the remaining amounts of the activated alumina samples, so that the desired 3 g/L concentration of activated alumina was achieved. The regeneration was repeated for a second time and a third set of arsenic adsorption tests was performed under similar conditions.

In another experiment, feasibility of the application of sodium sulphate as a suitable reagent for regeneration was investigated. A sample of activated alumina was exposed to a 100 g/L of a sodium sulphate solution for three days. The alumina was then filtered, dried and activated in a muffle furnace at 250°C overnight. Arsenic adsorption experiments were carried out at pH 3 and initial arsenic concentration of 24 mg/L using the sulphate loaded alumina sample and a similar fresh alumina sample. The experimental procedure followed was as outlined in Section 4.5.2.2.

In a different set of experiments to each of three different 2 L beakers, one litre of a 1000 mg/L arsenic at pH 3 was added. 20 g of ALCOA's CPN-325 was added to each of the beakers. The reason for the selection of such a high alumina concentration in this test was that the membrane separation experiments indicated that alumina concentrations of as high as 60 to 70 g/L could be handled by the process. In an initial attempt of this experiment a 60 g/L alumina concentration was selected; however due to sampling problems such as very slow filtration rate of the collected samples and fouling of the syringe filters, the test failed and a lower alumina concentration had to be selected. The contents of the beakers were mixed using a magnetic stirrer for 24 h while keeping the pH constant by periodic pH measurement and addition addition of concentrated nitric acid. After 24 h the pH of the reaction mixtures in each beaker was adjusted to a different pH value of 11, 12, and 13. Keeping the pHs constant samples of the beaker contents were taken every 10 to 15 minutes for a period of abut 4 hrs, following the sampling procedure outlined in section 4.5.2.2. An extra sample was also taken every hour for determination of the extent of alumina loss.

4.5.4. Settling of Activated Alumina

Settling experiments were carried out in order to determine feasibility of the use of this method for the separation of finely dispersed activated alumina particles from the treated water, as well as to justify application of a membrane system for this purpose. Two alumina samples: ALCOA's CP-1.5 and HTC-100 were used for this test.

In a large 250 mL graduated cylinder a suspension of activated alumina in Milli-Q water was prepared. At time t=0 the bed volume was recorded. Bed volume readings were taken at different times up to 1,623 minutes (27.05 h). The settling test for the two aluminas were performed in parallel.

4.5.5. Membrane Filtration Tests

Two different microfiltration membranes were tested in order to investigate different options of membrane separation using two different types of microfiltration membranes:

- ENKA polypropylene tubular membrane, and
- ZeeWeed ™ hollow fibre membrane.

For both membrane tests, a model suspension was prepared by suspending and mixing different amounts of a commercial grade activated alumina sample CP-1.5, with an average particle size of 1.5 μm, in Milli-Q water, in the absence of arsenic. Selection of ALCOA's CP-1.5 activated alumina was because of its small average particle size. When handling suspensions with membranes the problems of pore plugging and membrane fouling occurs with finer particle sizes. The objective of the membrane separation experiments in this part of the work was to study the stability of flux and the membrane's susceptibility to fouling at different alumina concentrations.

4.5.5.1. Tubular ENKA microfiltration system experiments

The schematic of a tubular microfiltration bench-scale installation is presented in Figure 4.6. The tubular ENKA microfiltration system consisted of a membrane module, a low-pressure circulation pump, feed/concentrate tank (10L suspension volume), pressure control valve, pressure gauge, flowmeter on the concentrate and permeate line, heat exchanger, and a thermometer. Both permeate and concentrate lines were returned to the feed/concentrate tank. The membrane module manufactured by ENKA consisted of three polypropylene tubular membranes. Each membrane had an inner tube diameter of 5 mm and an nominal pore diameter of 0.2 μm. The total surface area of the membrane was 0.036 m^2.

The activated alumina slurry was pumped into the membrane module where the feed stream was separated into the permeate stream (free of activated alumina particles) and the concentrate stream (enriched with activated alumina particles). Both streams were redirected to the feed/concentrate tank in order to keep the total system circulation volume constant allowing for continuous operation without the need for additional feed to the system. Keeping the total volume of the system constant, an increase in alumina concentration was achieved by weighing and dispersing additional amounts of alumina into the feed/concentrate tank.

The quality of the permeate was monitored by periodic sampling and determination of the turbidity of the collected sample. The concentrate and permeate flowrates were determined using two online flowmeters. A heat exchanger was utilized to maintain a constant temperature. The membrane was cleaned sequentially by back flushing the system with water.

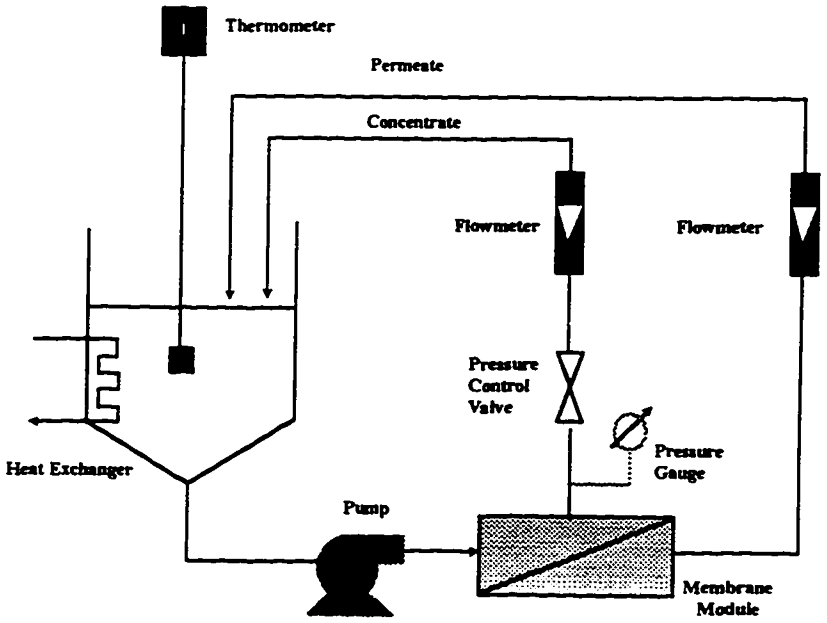


Figure 4.6. Schematic of the membrane system for the ENKA tubular membrane system.

4.5.5.2. ZeeWeed™ hollow fibre microfiltration system experiments

Figure 4.7 illustrates the schematic of the hollow fibre microfiltration bench-scale installation used in the tests for this part of the work. The membrane system setup consisted of the ZeeWeed™ membrane module, a vacuum pump (10 inHg (254 mmHg)), feed/concentrate tank (150 L alumina suspension volume), pressure control valves, pressure gauge, air blower and aerator, thermometer, and flowmeter. The membrane module manufactured by Zenon Environmental Inc., consisted of bundle of hollow fibre membranes with an average molecular weight cut-off of 200,000 and a total membrane surface area of 0.5 m^2.

The activated alumina slurry was prepared in the feed/concentrate tank. The alumina particles were kept suspended by introducing mixing via injection of air through an aerator at a rate of 1.5 scfm. A vacuum pump was used to created sufficient pressure difference for water to permeate through the membrane. The permeate stream was redirected to the tank in order to maintain a constant volume allowing the system to run continuously without addition of any further water to the tank. Keeping the volume of the activated alumina suspension in the tank constant, an increase in the alumina concentration was achieved by weighing and dispersing additional amounts of alumina to the slurry.

Permeate quality was monitored by periodic sampling and monitoring the permeate turbidity. Permeate flowrate was measured volumetrically, using a graduated cylinder. Vacuum and air pressure were controlled by two control valves and pressure gauges. The membrane was periodically cleaned to recover lost flux by shutting off the vacuum pump and letting the fibres shake as a result of aeration; a process called relaxation cleaning.

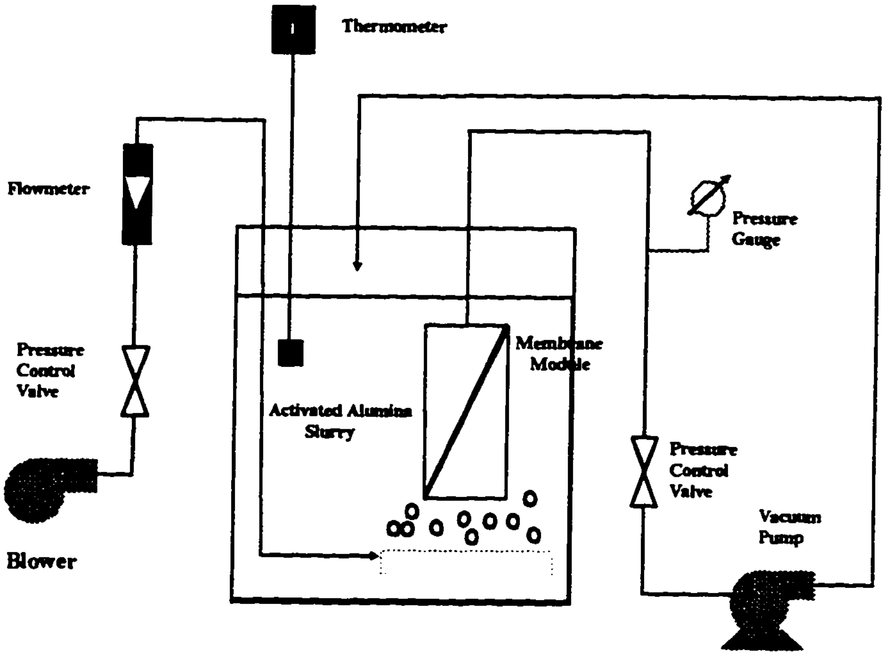


Figure 4.7. Schematic of the membrane system for the ZeeWeed™ membrane experiments.

CHAPTER 5

5. RESULTS AND DISCUSSION

5.1. EFFECT OF pH ON THE ARSENIC UPTAKE

The importance of the effect of pH on arsenic uptake by activated alumina and other adsorbents such as china clay, and flyash has been emphasised by many researchers [Gosh and Teoh, 1985; Rosenblum and Cliford, 1983; Yadava et al., 1988]. The pH of the solution dictates the speciation of the adsorbate ions as well as the charge and acidity/basicity of the surface.

Just as the charge on the surface of the adsorbent varies with pH, the adsorbate becomes more or less ionic by going through protonation or deprotonation. The pH dependence of anionic adsorbates such as arsenate (oxyanions) can be described in two steps: In the first step a rise in pH results in an increase in the proportion of the oxyanion adsorbate and increased potential between the adsorbent surface (alumina) and the adsorbate (arsenate), resulting in increase in adsorption. Second, pH increases past the pK_a of the adsorbate results in its deprotonation until it is entirely in anionic form, which ultimately converts to AsO_3^{3-} species. This means pH increase past pH 2.2 increases deprotonation of H_3AsO_4 to $H_2AsO_4^-$ (Equation (2.1)), and pH increase past pH 6.97 increases deprotonation of $H_2AsO_4^-$ to $HAsO_4^{2-}$ (Equation (2.2)). Any pH increase beyond this point, which is pH greater than 11.53, results in the inhibition of adsorption. This is due to the fact that an increase in pH results in the greater proportion of hydroxyl ions in the liquid which compete with the adsorbate for the available sites on the surface of the alumina, reducing the potential between the adsorbate and adsorbent and reducing the adsorption [Rosenblum and Clifford, 1983].

In order to study the effect of the pH on the adsorption of arsenate and determine the optimum pH for the best arsenic removal for the process being studied, several experiments using two different types of alumina (Scientific Adsorbent's 50-212 μm alumina, and ALCOA's CPN-325) were performed following the experimental procedure outlined in sections 4.5.2.2 and 4.5.2.3. The results of the experiments have been presented in Tables B-1 to B-17 in Appendix B. Two different sets of experiments were performed in order to observe the extent of arsenic removal under variable and constant pH.

5.1.1. Variable pH Experiments

In the first set of experiments, pH 1, 3, and 7 were studied using the Scientific Adsorbent's 50-212 µm alumina. The pH of arsenic solutions were adjusted to the desired value at the beginning of the experiment and there were no further pH adjustments during the course of the experiment. The final pH of the reaction solutions were measured after 48 hrs. Table 5.1 lists the initial and final pH values measured.

Table 5.1. Initial and final pH values for arsenic removal experiments at different initial pH values and dominant arsenic species, with no pH control, using the Scientific Adsorbents's 50-212 µm alumina.

Initial pH	**Dominant Arsenic Species**	**Final pH**	**Dominant Arsenic Species**
1.00	H_3AsO_4	1.01	H_3AsO_4
2.98	H_3AsO_4	3.53	$H_2AsO_4^-$
6.90	$H_2AsO_4^-$	7.69	$H_2AsO_4^{2-}$

The results of these experiments are shown in Figure 5.1. The residual arsenic concentrations achieved after 10 minutes of contact, were 19.9 mg/L at pH 1, starting from 33.5 mg/L (a 41% drop), 7.9 mg/L at pH 3 starting from 31.9 mg/L (a 75% drop), and 25.8 mg/L at pH 7, starting from 33.8 mg/L (a 24% drop) (Table B-1 in Appendix B).

Table 5.1 shows that at pH 1 the dominant arsenic species is H_3AsO_4 which is an electrically neutral species. The dominant species at pH 3 was calculated to be H_3AsO_4 as well; however, at pH 3 a lower residual arsenic concentration was achieved. This can be explained by looking at the distribution of different arsenic species at pH 1 and pH 3. Table 5.2 lists the distribution of the 4 different species that arise from deprotonation of arsenic acid.

At pH 3, as $H_2AsO_4^-$ is adsorbed, the equilibrium in Equation (2.1), shifts to the right which results in further adsorption of the singly charged arsenate species until equilibrium is reached. Since the pH is not controlled, it rises as the result of arsenic adsorption (when hydroxyl groups are released) [Rosenblum and Clifford, 1983; Gosh and Teoh, 1987]. This in turn results in $H_2AsO_4^-$ becoming the dominant species. It seems that the affinity of $H_2AsO_4^-$ for the activated alumina surface is greater than that of $HAsO_4^{2-}$.

At pH 7 the arsenic removal is the slowest and the least efficient of the other two pH values. To explain this the other important factor which is the alumina's surface charge has to be considered. As the pH changes the charge on the surface changes as a result of surface protonation and deprotonation reactions.

The pH_{zpc} (the pH at which the alumina surface is electrically neutral) for commercial alumina has been reported to be between 7.4 to 9 for γ-alumina [Gosh and Teoh, 1987]. The acidity of each surface site is affected by one of the neighbouring sites. As the pH increases from acidic to basic the surface charge moves towards neutral to negative, as shown in Equations (2.7) to (2.10). As a result of the change in the surface charge, the potential between the adsorbate and adsorbent diminished which results in a decrease in adsorption.

Table 5.2. Distribution of different arsenic species arising from arsenic acid deprotonation. (Calculation of Species is presented in Appendix C).

pH	**As(V)/Total As(V) (%)**			
	H_3AsO_4	**$H_2AsO_4^-$**	**$HAsO_4^{2-}$**	**AsO_4^{3-}**
1	99.73	0.27	-	-
3	79.97	19.97	0.001	-
4	28.51	71.26	0.03	-
6	0.37	94.29	5.28	0.05
7	0.025	64.01	35.86	0.097
8	0.006	15.13	84.84	0.024

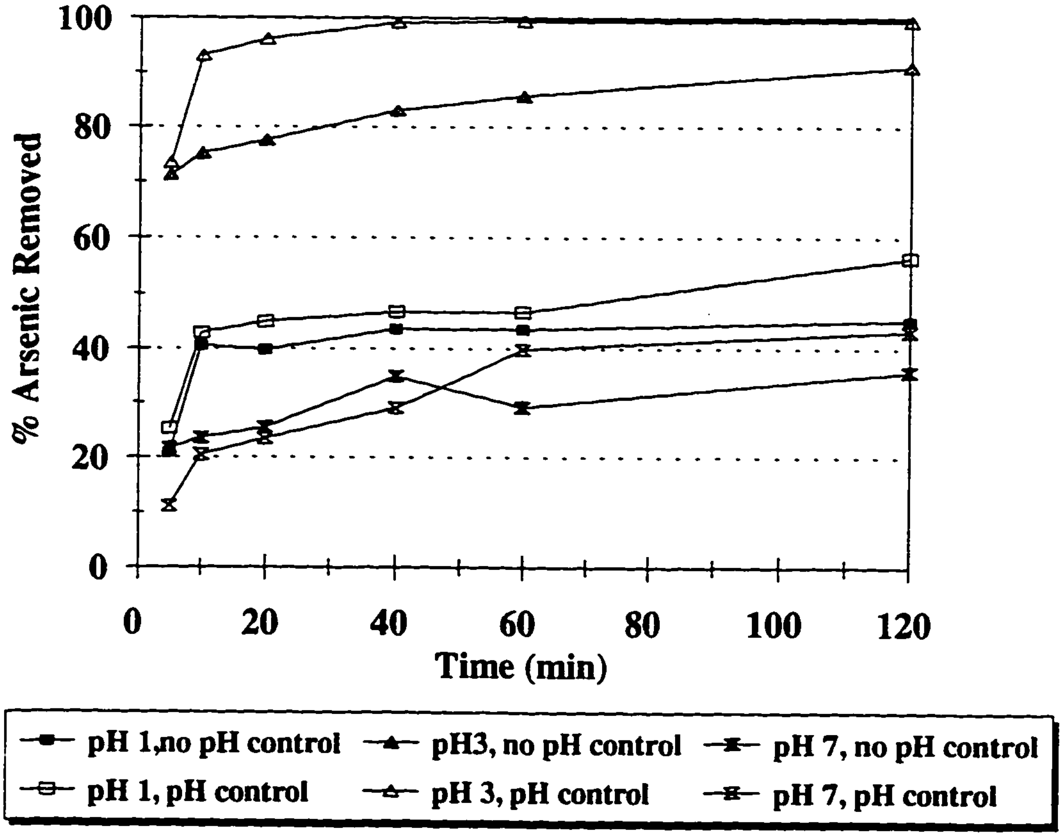


Figure 5.1. Comparison of arsenic removal with Scientific Adsorbent's 50-212 μm alumina, with and without pH control, at 3 g/L alumina concentration, 23 °C and initial arsenic concentration of 23 to 33 mg/L.

5.1.2. Constant pH Experiments

Experiments were carried out, covering the pH range of 1 to 8 (pH 1, 3, 4, 6, 7, and 8), while maintaining a constant pH throughout the experiment. The pH of the mixture was maintained constant by titrating the mixture by 0.142 molar nitric acid. Figure 5.1 shows a comparison between arsenic removals with Scientific Adsorbent 50-212 μm alumina under constant and variable pH conditions. As can be seen from this figure, conditions with controlled pH are much better for arsenic removal. Figure 5.2 shows a plot of arsenic concentration versus time for the pH range 1 to 8 under constant pH. The results of these experiments are also presented in Table B-3 to B-8 in Appendix B.

Figure 5.1 shows that pH 1, 3, and 7, maintaining a constant pH resulted in better arsenic removal. This is because the dominance of the favourable arsenate species for adsorption is maintained when the pH is kept constant during the adsorption process and the alumina surface charge is also kept constant when pH is controlled. The results in Figure 5.2 can be explained using the same argument as above. The adsorption mixture's pH was controlled by addition of 0.142 M nitric acid. The amount of acid that was necessary to maintain a constant pH indicated that an excess amount of acid was required in comparison to the amount of arsenic uptake. This indicates that both $H_2AsO_4^-$ and $HAsO_4^{2-}$ species adsorb onto the surface, and also surface complexation reactions such as shown in Equation (5.1) and Equation (5.2) also contribute to the arsenic uptake quite significantly [Gosh and Teoh, 1987]. Surface protonation/deprotonation reactions are another reason for the requirement for excess acid.

$$\text{-AlOH} + H_2AsO_4^- \rightleftharpoons \text{-AlH}_2\text{As}_4 + OH^- \qquad (5.1)$$

$$2\ \text{-AlOH} + HAsO_4^{2-} \rightleftharpoons \text{-Al}_2\text{HAsO}_4 + 2\ OH^- \qquad (5.2)$$

Anderson and Malotky (1979) have also reported that singly and doubly charged adsorbing arsenate species have identical chemical adsorption energies and have similar affinity towards alumina.

In another set of experiments the range of pH was narrowed down to between 2 to 4 in order to study the pH range in the vicinity of pH 3. The pH values of 2, 2.5, 3, 3.5, and 4 were selected and studied while pH was maintained constant at its initial value for each corresponding solution. Figure 5.3 shows the arsenic concentration in solution with time. Arsenic removal after 10 minutes of contact at pH's ranging from 1 to 8 are shown in Figure 5.4 for the pH range of 2 to 3.5, significantly better arsenic removals were achieved, with pH 3 showing slightly better performance.

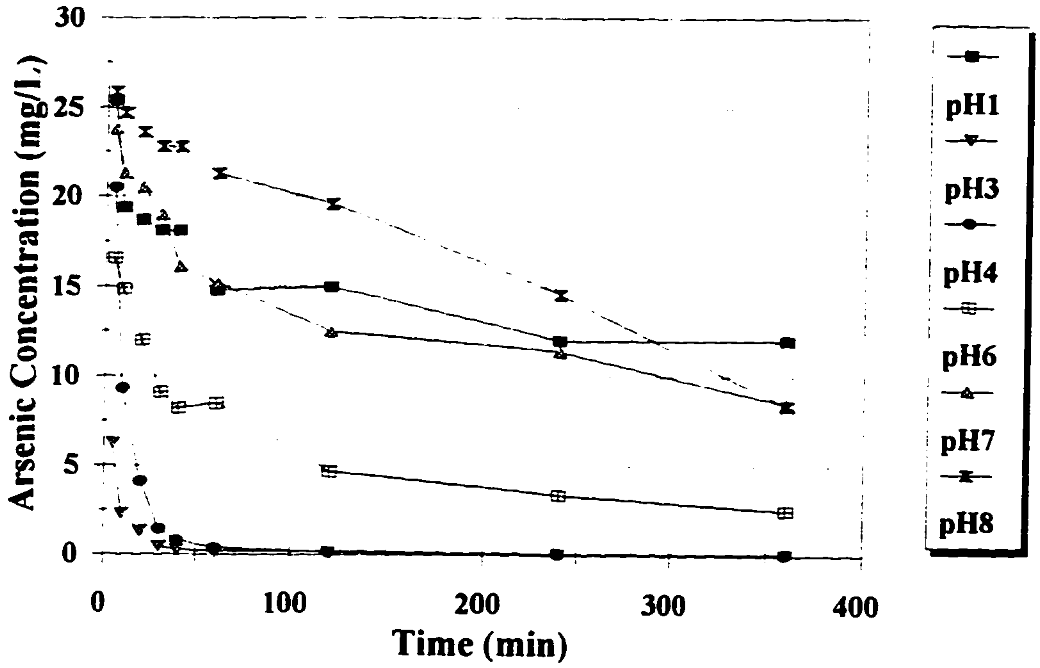


Figure 5.2. Plot of arsenic concentration versus time for pH range of 1 to 8, under constant pH, using 3 g/L of Scientific Adsorbent's 50-212 μm alumina at 23 °C and initial arsenic concentration of 26 mg/L.

The Scientific Adsorbent's 50-212 μm alumina is a specialty alumina and is not commercially available on a large scale. In order to verify that the results obtained are valid for commercially available aluminas as well, ALCOA's CPN-325, a readily available commercial activated alumina, was selected and tested for a pH range of 2 to 5 (pH's 2, 3, 4, and 5). The results are presented in Figure 5.5. Figure 5.6 shows a plot of % arsenic removed at different pH values after a contact time of 10 minutes.

The residual arsenic concentrations achieved from an initial arsenic level of 43 mg/L, after 10 minutes of contact were 0.37 mg/L for pH 2, 0.01 mg/L for pH 3, 0.11 for pH 4, and 0.14 for pH 5. It can be observed that if the objective of the process were to meet environmental criteria such as drinking water limit (25 μg/L) or the effluent discharge for the mining effluents (1 mg/L), the operating pH of 3 would be the preferred pH for the process.

It should also be noted that except for mining and industrial effluents and water contaminations resulting from mining activities and acid mine drainage, one cannot find arsenic levels as high as the levels used in these experiments. Gosh and Teoh (1987) achieved an arsenate concentration drop from 5 mg/L to 0.1mg/L in a few hours at a pH of 6 to 7, and Rosenblum and Clifford (1983) achieved an arsenate drop from 5 mg/L to 0.75 mg/L in 12 hours and to 0.5 mg/L in 6 days at a pH of 8. ALCOA's activated alumina F1 was used in both studies. The experiments in this study showed that a very short contact time was required in order to achieve below environmental standard levels of arsenic which is significant for the process economics. Neither Gosh and Teoh (1987) or Rosenblum and Clifford (1983) studied pHs below pH 5.

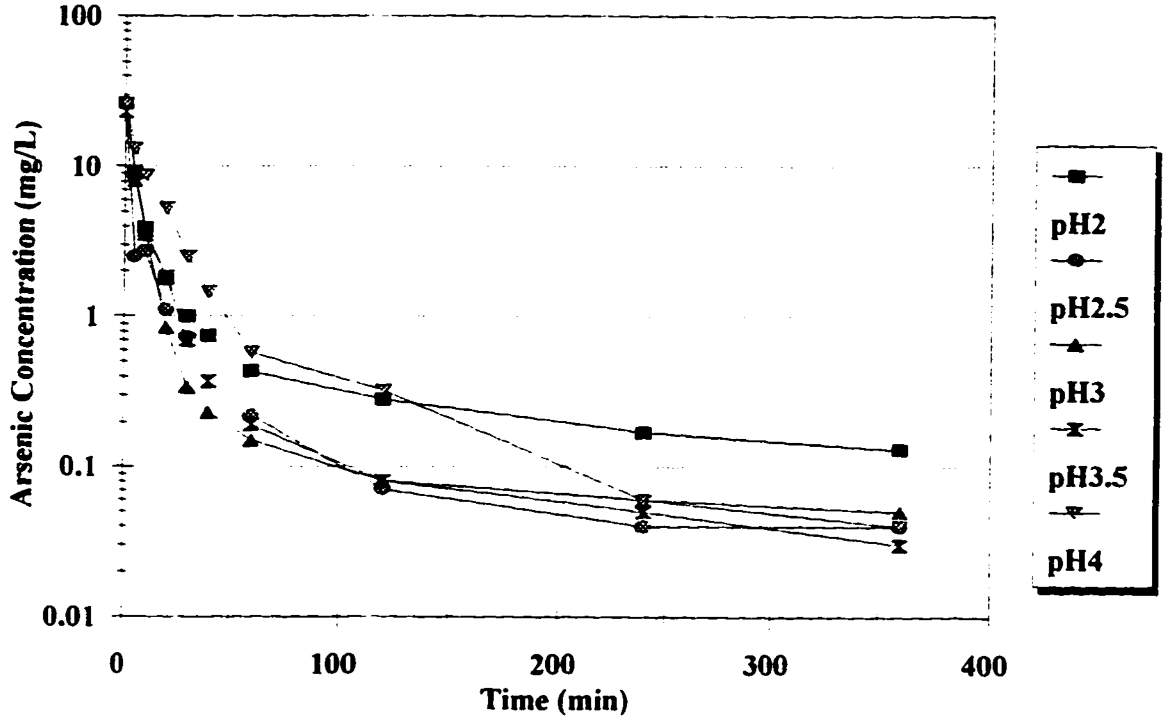


Figure 5.3. Plot of As concentration versus time for Scientific Adsorbent's 50-212 μm alumina, at initial arsenic concentration of 23-27 mg/L, 3 g/L alumina, and 23 °C.

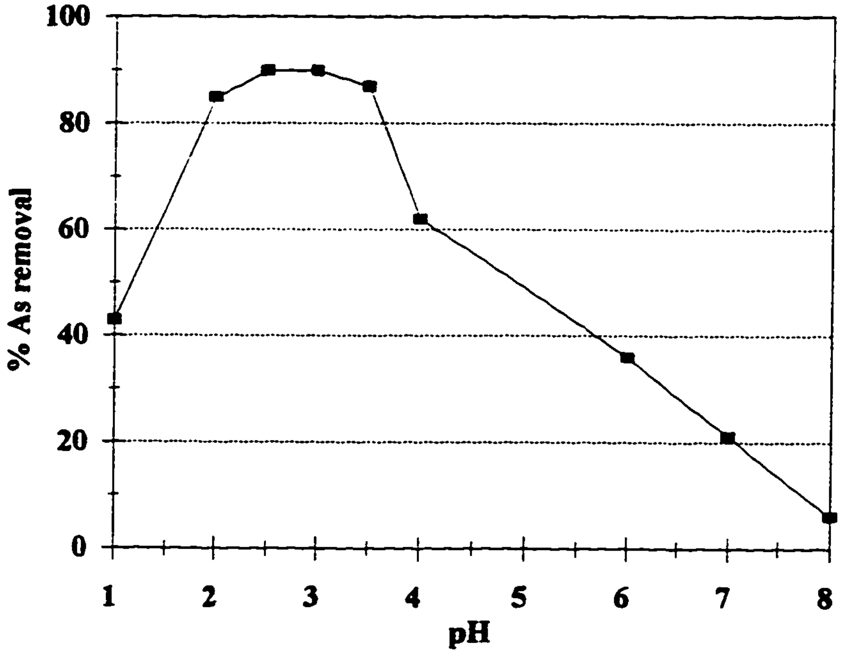


Figure 5.4. Plot of % arsenic removed versus pH after 10 minutes of contact with activated alumina at initial arsenic concentration of 23-27 mg/L, for the pH range of 1 to 8, 3 g/L Scientific Adsorbent's 50-212 μm alumina, and 23 °C.

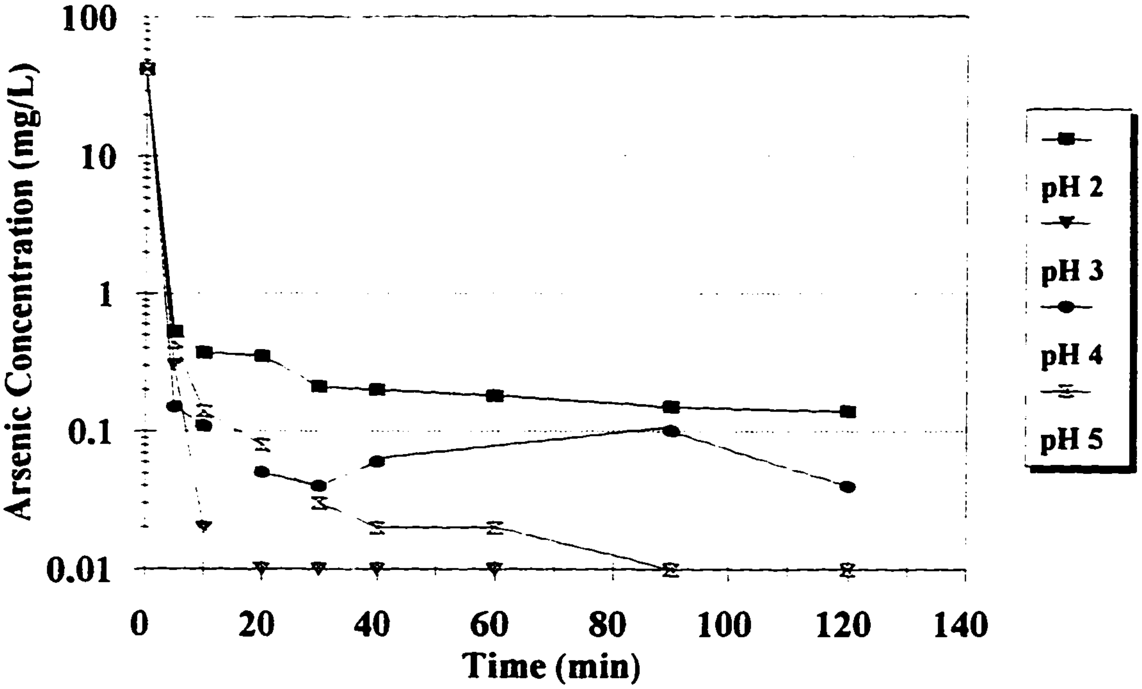


Figure 5.5. Plot of arsenic concentration versus time for ALCOA's CPN-325 activated alumina, at initial arsenic concentration of 43 mg/L, pH 2-5, 3 g/L alumina, and 23 °C.

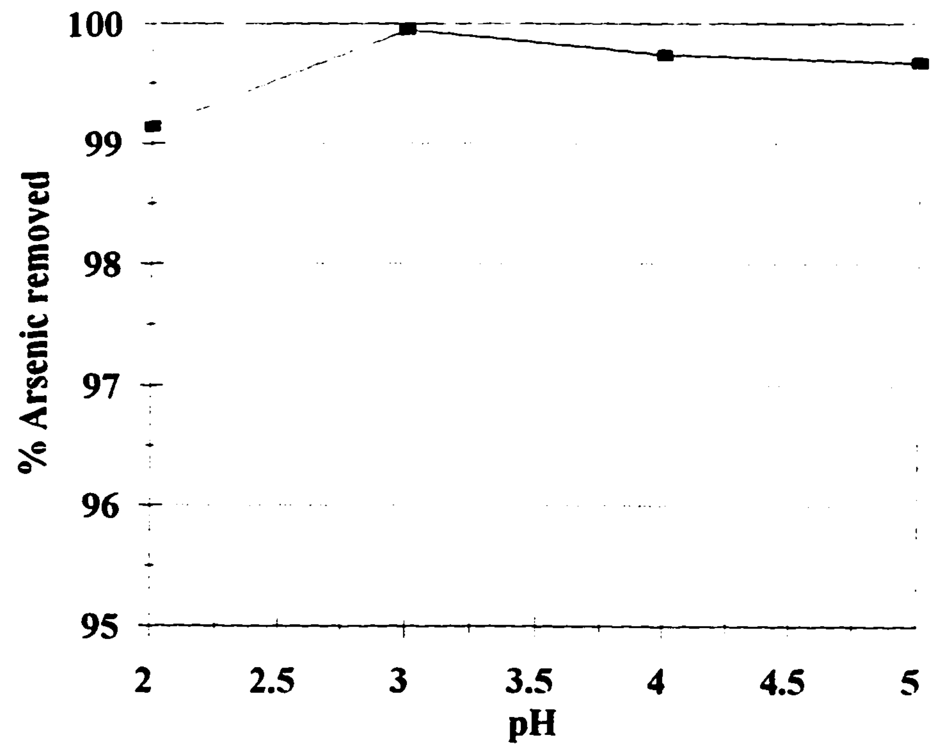


Figure 5.6. Plot of % arsenic removed versus pH after 10 minutes of contact with ALCOA's CPN-325 activated alumina at an initial arsenic concentration of 43 mg/L, for the pH range of 2 to 5, alumina concentration of 3 g/L, and 23 °C.

The high levels of removal at lower pH levels such as pH 3 and 4 imply that the adsorption of arsenic might be non-specific at lower PH values. Chemisorption is usually slower than coulombic or physical processes under similar conditions, due to the fact that it is site specific and proper ligand orientation might be required for steric reasons [Gosh and Teoh, 1987, Kirk Othmer, 1991]. Although the results of acid titration has indicated that some degree of specific chemisorption happens at lower pH it is apparent that coulombic or physical processes play a significant role in the process of arsenate adsorption onto the activated alumina surface.

5.2. KINETICS OF ADSORPTION

As discussed in section 3.2, by plotting q versus $t^{1/2}$, it can be determined whether the intraparticular mass transfer is the rate limiting step [Yadava et al., 1988; Singh et al., 1988]. Figures 5.7 and 5.8 show plots of q versus $t^{1/2}$ for Scientific Adsorbent's 50-212 µm basic alumina and ALCOA's CPN-325 respectively. In Figure 5.7 it can be seen that the curves are almost linear for pH 7 and 8. As the pH moves towards pH 1, the curves become more nonlinear. This implies faster adsorption at lower pHs. The non-linearity of the curves in Figure 5.7 indicate that the rate limiting step is not the intraparticular diffusion for the system studied and that the mechanism of the reaction could be different at lower pH values (most obvious at pH 3 and 4) from that at higher pHs of 7 and 8. Figure 5.8, for CPN-325 shows very little difference between the curves for pH 2 to 5. The plots do not go through the origin and imply a very fast adsorption rate since the first data points of the graph corresponds to time of 5 minutes.

Figure 5.9 shows a comparison of the plots of q versus $t^{1/2}$ for Scientific Adsorbent's 50-212 µm alumina and ALCOA's CPN-325 at pH 3. The figure indicates that (as can be seen in Tables B-12 and B-15) the rate of arsenic uptake is much faster for CPN-325 than that of the 50-212 µm alumina. The differences between the two aluminas are in the particle size (4.5 µm for CPN-325 as opposed to 50-212 µm for Scientific Adsorbent's), and the crystalline structure. ALCOA's CPN-325 is a transition γ-alumina while the other sample was a more crystalline and structured sample. The exact effect of the structural differences was not an objective in this study; however, it is important to note that a transition alumina such as ALCOA's CPN-325 which is less structured than the Scientific Adsorbent's 50-212 µm alumina, has higher concentrations of defect structures i.e. higher surface chemical activity [Goodboy and Fleming, 1984]. The higher concentration of defect structures results in higher surface concentrations of active sites which would result in higher arsenic uptake rates. The smaller particle size of CPN-325 was another important factor in its better performance compared to that of 50-212µm basic alumina.

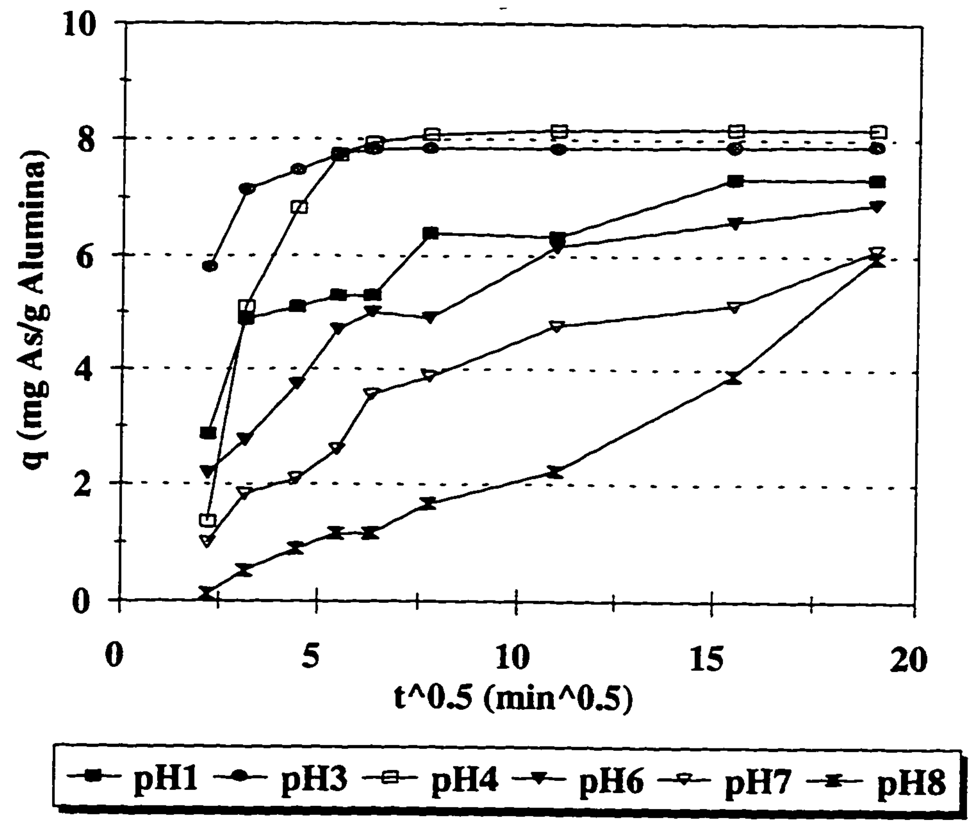


Figure 5.7. Plot of alumina arsenic loading, q, versus $t^{1/2}$ for Scientific Adsorbent's 50-212 µm alumina at different pH values, initial arsenic concentration of 23-27 mg/L, 3 g/L alumina concentration, and 23 ° C.

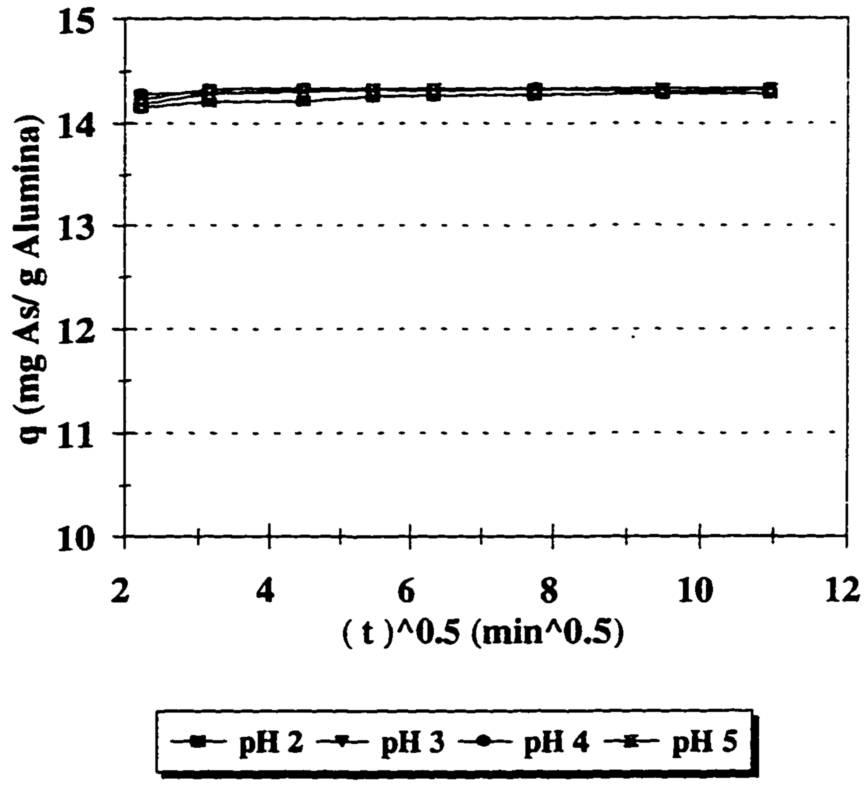


Figure 5.8. Plot of alumina arsenic loading, q, versus $t^{1/2}$ for ALCOA's CPN-325 alumina at different pH values, 43 mg/L initial arsenic concentration, 3 g/L alumina concentration, and 23 °C.

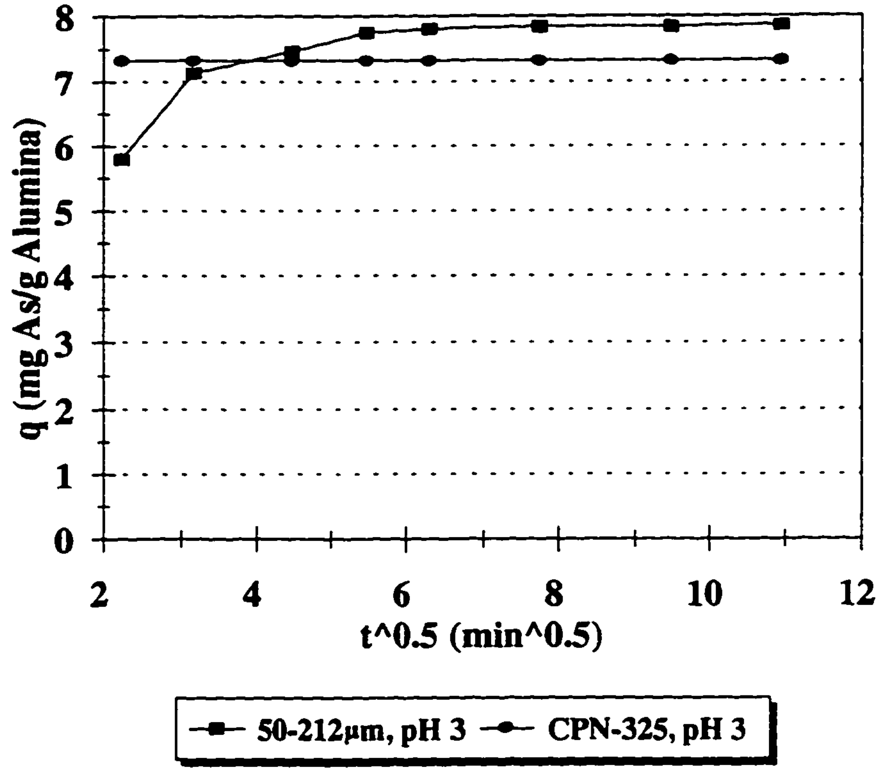


Figure 5.9. Comparison of the plots of alumina arsenic loading, q, versus $t^{1/2}$ for ALCOA's CPN-325 and Scientific Adsorbent's 50-212 µm aluminas at pH 3, 3 g/L alumina concentration.

In the attempt to obtain an equation that could be used for the prediction of arsenic removal or activated alumina arsenic loading, the applicability of two empirical models was investigated.

One of the models has previously been used to describe adsorption of arsenic on china clay and haematite (III) [Singh et al., 1988; Yadava et al., 1988] as well as the uptake of calcium from water by coconut shell [Prakash et al., 1987]. The model equation is given by Equation (3.7). In order to determine the values of K and A in Equation (3.7), $\log_{10}$ [log(t+1)] was plotted against log(C_o-C), with slope being A and Y-intercept being $log\, K$. This model failed to describe the system for adsorption of arsenate on activated alumina.

One reason for that might be the mathematical nature of the model i.e. the log-log nature of the plotted equation. The other reason for the failure could be that the uptake of arsenate by alumina is much more complicated than that of arsenite uptake which is mainly via physical process since arsenite exists in the uncharged form of H_3AsO_3 up to pH 9 [Yadava et al., 1988].

The other model is the Elovich equation which was more successful in describing the data. This model has been applied for describing the kinetics of chemisorption on heterogenous surfaces [Carberry, 1976]. The Elovich equation, Equation (3.6) was fitted to the results of the pH experiments with the Levenberg-Marquardt method (Delta Graph Professional software). The equation was fit using a user defined curve fit option and inputting initial guesses for the Elovich equations constants until the best r^2 value was achieved. Looking at the r^2 values in Table 5.3, it can be seen that a better fit was obtained for the data at pH 6, 7, and 8. Figures 5.10 and 5.11 show the experimental data and Elovich model predictions. The poor fit for lower pH's could be due to high adsorption rates at pH 3 and 4. For high adsorption rates, accurate data are required for the Elovich model to fit to the experimental data. The fastest change in the residual arsenic concentration took place in the first 5 minutes of the experiment and it was technically not feasible to collect more samples within the first 5 minutes of the experiment. Table 5.3 lists the values of the constants obtained for the Elovich model. The constants were calculated by fitting the Elovich Equation to the experimental data using a Levenberg-Marquardt procedure (Delta Graph Professional software). Description of the model and the significance of the constants have been explained in section 3.2.

Table 5.3. Calculated constants for the Elovich equation at 3 g/L of Scientific Adsorbent's 50-212 μm alumina and initial arsenic concentration of 24-34 mg/L.

pH	b	K	a	r^2
1	1.0654	0.1099	8.5403	0.85
3	1.2785	0.0018	432.621	0.85
4	0.3447	2.8361	1.0229	0.861
6	0.8569	0.7769	1.5021	0.971
7	0.754	3.9219	0.3382	0.978
8	0.1951	180.17	0.02845	0.972

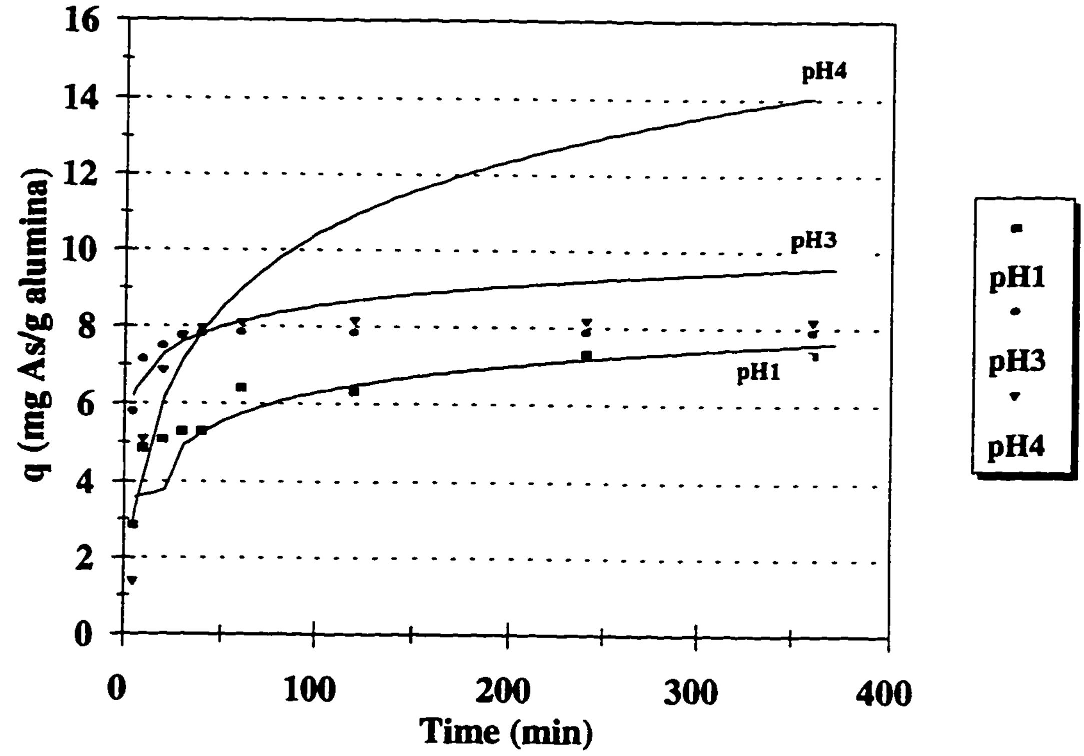


Figure 5.10 Plot of q vs t for pH 1, 3, and 4, for experimental data and the Elovich model predictions for the data obtained with Scientific Adsorbent's 50-212 μm alumina.

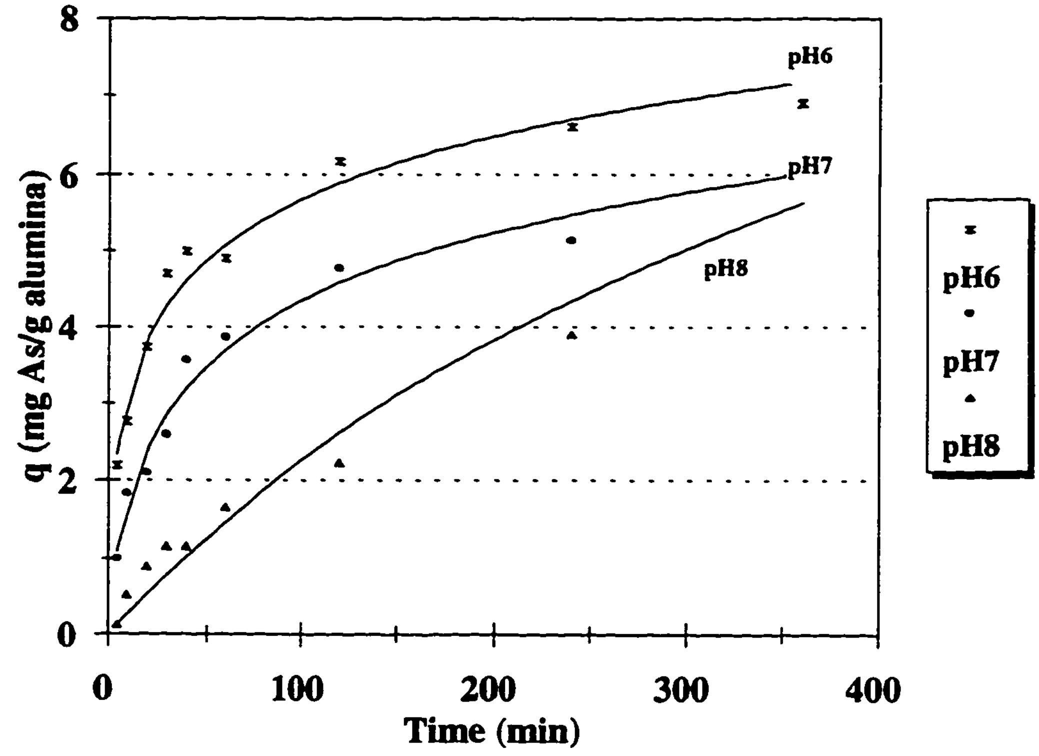


Figure 5.11. Plot of q vs t for pH 6, 7, and 8, for experimental data and the Elovich model predictions for the data obtained with Scientific Adsorbent's 50-212 μm alumina.

5.3. STUDY OF PARTICLE AND PORE SIZE EFFECTS ON ARSENIC UPTAKE

A series of experiments were conducted in order to study the effect of particle size, pore diameter and surface area, of the activated alumina samples, on the degree of arsenic uptake following the procedures outlined in section 4.5.2.4. Samples of activated alumina were characterized as outlined in section 4.2. Physical characteristics of the activated alumina samples were determined using nitrogen sorption porosimetry. Table 5.4 summarizes the results of the adsorbent characterizations.

Table 5.4. Summary of the physical characteristics and performance of activated alumina samples from Scientific Adsorbents Ltd at an average initial arsenic concentration of 25 mg/L.

Alumina Sample(1)	Residual [As] mg/L After 10 min	Surface Area m^2/g (2)	Pore Volume cc/g	BJH Pore Diameter Å
20-30 µm, 300Å	0.04	392.50	1.089	78.80
100 µm, 300Å	0.13	373.08	0.748	82.78
100 µm, 200Å	0.3	218.38	0.510	90.65
100 µm, 50-100Å	0.74	215.57	0.477	43.79
10 µm, 50-100Å	0.83	200.46	0.212	37.70
50-212 µm	N/A	151.28	0.456	55.02

(1) Average particle diameter, average pore size as specified by the manufacturer
(2) BJH desorption surface area

Arsenic removal tests were carried out using five samples provided by Scientific Adsorbents Inc. at pH 3, 23 °C and 3 g/L of alumina. Figure 5.12 shows the plot of arsenic concentration versus time. Using initial arsenic concentrations of 23-28 mg/L, removals of 92 to 99% were achieved after 10 minutes of contact between alumina and arsenate. Other numerical detailed results of the experiments are presented in Table B-18 to B-22 in Appendix B.

Figure 5.12 shows that the order of samples with respect to degree of removal achieved was:

20-30µm-300Å > 100µm-300Å > 100µm-200Å > (100µm-50-100Å, 10µm-50-100Å).

Looking at Table 5.4, it seems like the surface area is of primary importance followed by pore diameter. When the surface areas are similar, the effect of pore diameter would be more significant.

Unfortunately the characterizations of these samples did not agree with those provided by the manufacturer. However, the results of the arsenic removal test were compared with the results of the alumina characterization. As seen in Table 5.4 the residual arsenic concentration is related to the amount of surface area available on the alumina. Figure 5.13 shows that the first 3 samples in the above order had the highest pore area frequency within the pore size range of about 40 to 150 Å. The same figure shows that the pore area frequency for the pore diameter range of 17 to 40 Å was higher for 10μm-50-100Å and 100μm-50-100Å, and lowest for 100μm-200Å yet the latter provided a better degree of removal than the first two since it had a higher pore area frequency within the pore size range of 50 to 150 Å.

A comparison of the arsenic removal for the best two adsorbents, 100 μm-300Å and 20-30 μm-300Å, can be seen in Figure 5.12. Comparing their pore area frequency plots in Figure 5.14, and surface areas in Table 5.4 the two samples have very similar pore area and pore size distribution. This implies that for the sample 100 μm-300Å, its large particle size was compensated for by its pore size distribution in the range of 40 to 150 Å. A similar situation can be observed for the 10μm-50-100Å and 100μm-50-100Å. Although the 10μm-50-100Å has a smaller particle size than the 100μm-50-100Å, it did not perform better. The pore size and pore area frequency of 100μm-50-100Å compensated for its larger particle size. It can be concluded that provided the alumina sample has a certain pore size distribution, the effect of the particle size above 20 μm becomes secondary; however, the physical characteristics of the alumina samples available were not controlled enough to allow for determination of any sort of cutoff point for the magnitude of particle size and pore diameter.

The residual arsenic concentration for the 100 μm aluminas can be seen in Figure 5.12. The figure shows better performance of 100 μm-300Å over 100μm-200Å and 100μm-50-100Å. The residual arsenic concentration for 100 μm-300Å, 100μm-200Å and 100μm-50-100Å after 10 minute contact were 0.13 mg/L, 0.6 mg/L, and 3.4 mg/L respectively (Tables B-18, B-19, and B-20). This can be explained from the plot of pore area frequency versus pore diameter in Figure 5.15. The 100μm-50-100Å alumina has a significantly lower pore area frequency for any given pore size within the 40 to 150 Å range and has more pores in the size range of <40 Å. Comparing the 100 μm-300Å and 100 μm-200Å, the first sample has a higher pore area frequency in the range for pores of up to 70 Å and for pores of about 110 to 150 Å. The area frequency for the range of 70 to 110 Å was slightly higher for 100 μm-200Å alumina. Overall the 100 μm-300Å sample had a higher cumulative pore area in the range of 50 to 150 Å (253 m^2 versus 195 m^2 - Table C-11 and C-12 in Appendix C), which explains its better performance.

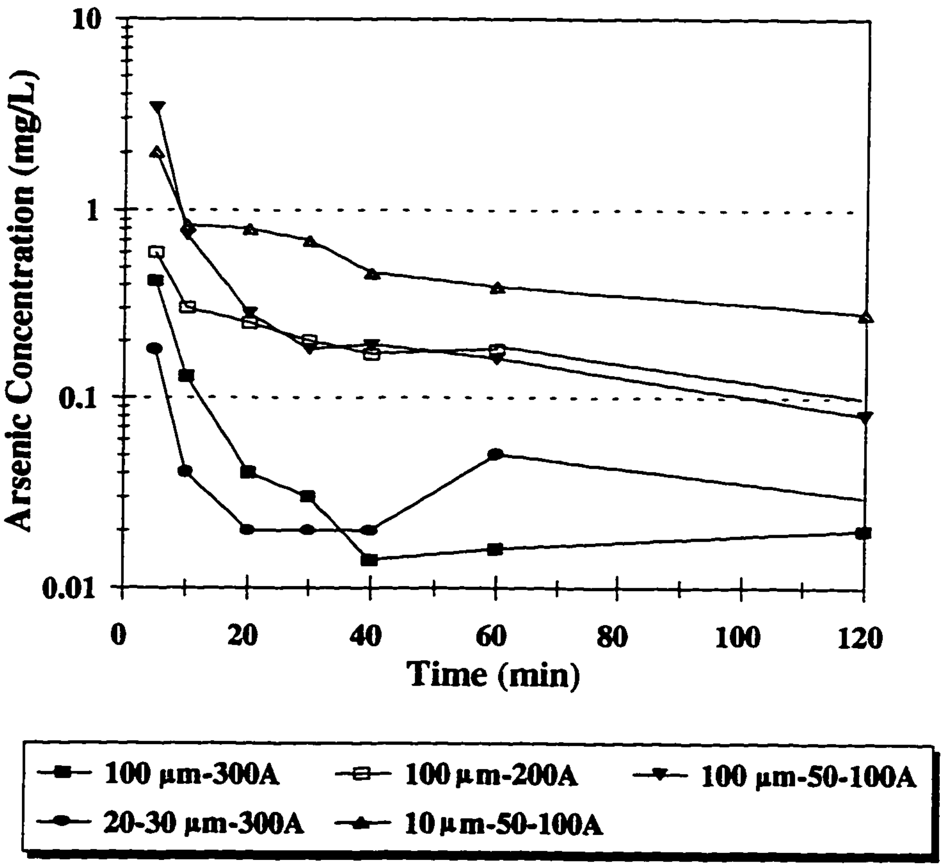


Figure 5.12. Plot of arsenic concentration versus time for Scientific Adsorbent Inc. Alumina samples at 3 g/L alumina, pH 3 and initial arsenic concentration of 23-28 mg/L. Labels for the aluminas are particle size - pore size.

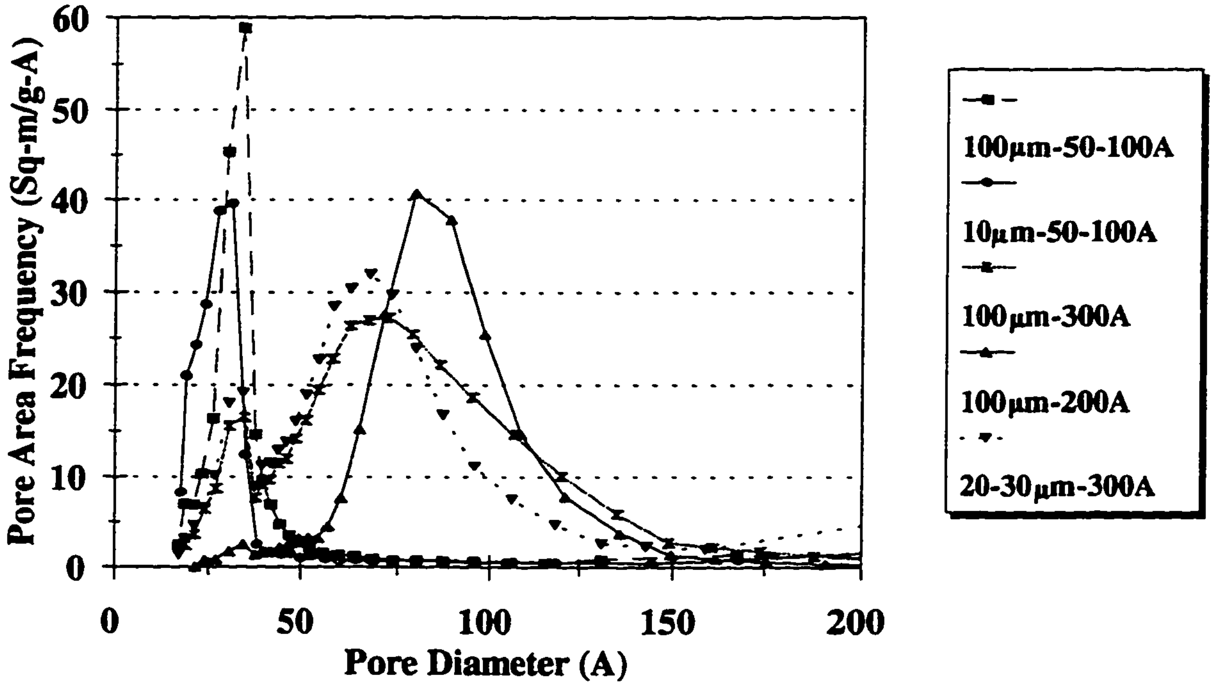


Figure 5.13. Pore area frequency versus pore diameter for specialty activated alumina samples supplied by Scientific Adsorbents Ltd.

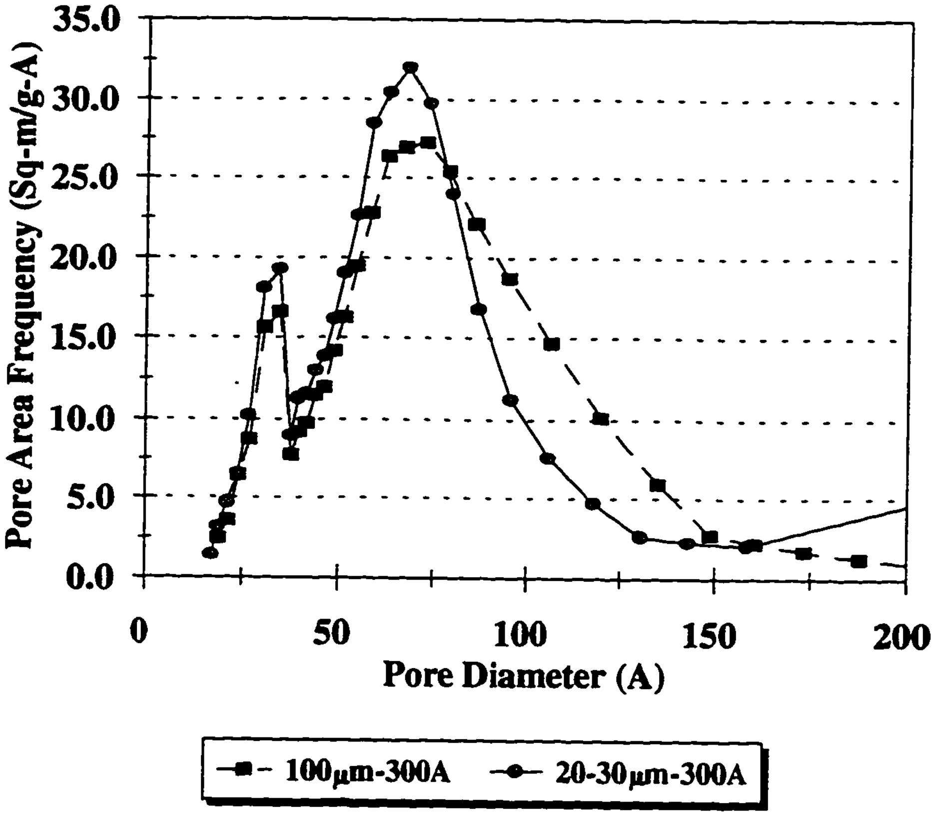


Figure 5.14. Plot of pore area frequency against pore diameter for Scientific Adsorbent Inc. Alumina samples 100 µm-300Å and 20-30 µm-300Å.

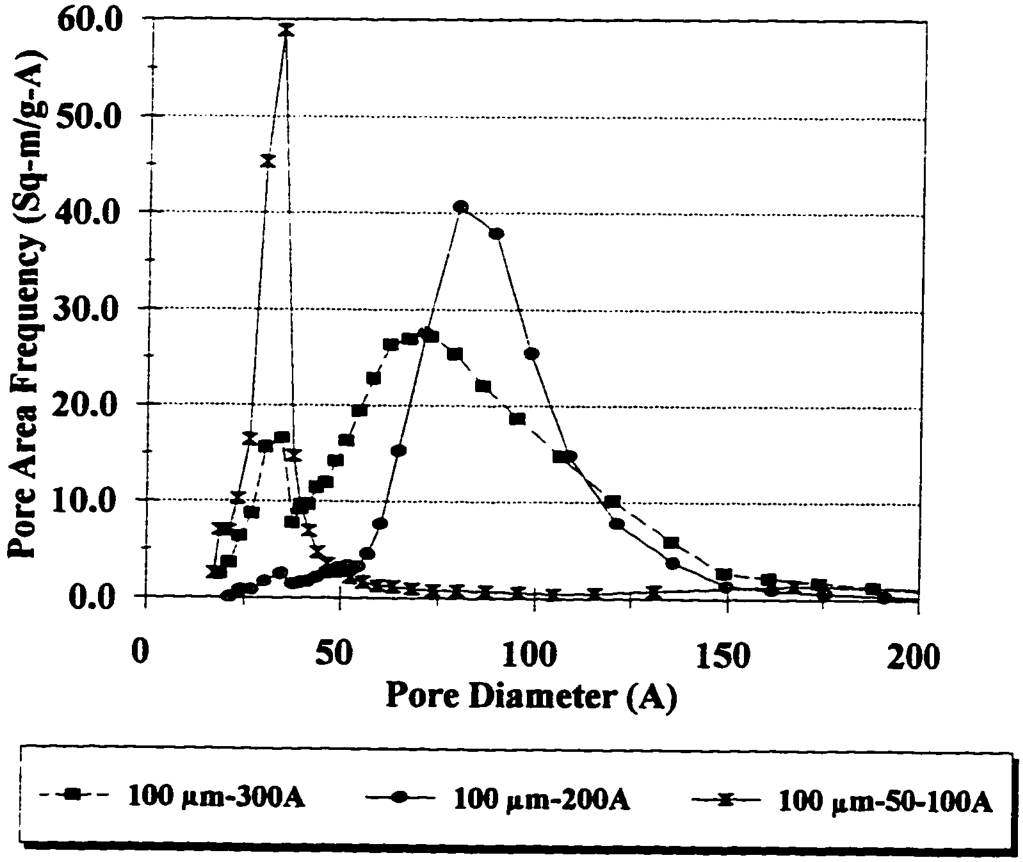


Figure 5.15. Plot of pore area frequency against pore diameter for Scientific Adsorbent Inc. Alumina samples 100µm-300Å and 100µm-200Å and 100µm-50-100Å.

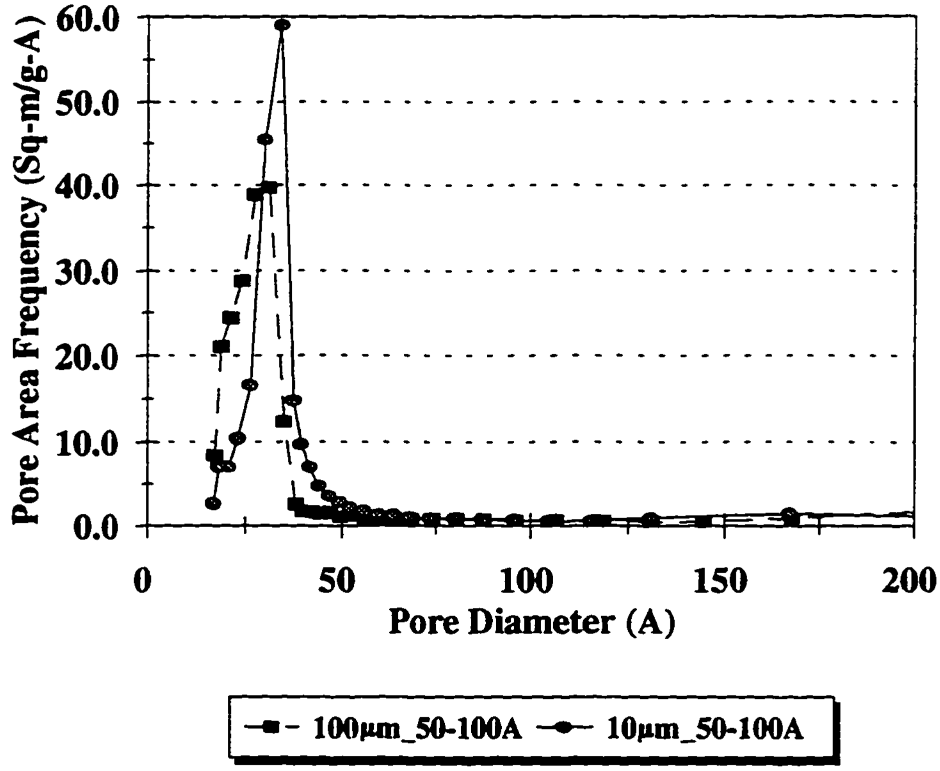


Figure 5.16. Plot of pore area frequency against pore diameter for Scientific Adsorbent Inc. alumina samples 100µm-50-100Å and 10µm-50-100Å.

5.4. ARSENIC REMOVAL USING COMMERCIAL GRADE ACTIVATED ALUMINA

Eight samples of commercial activated alumina were tested to select a candidate alumina for pilot scale testing. The samples of alumina included CP and CPN type aluminas which are examples of amorphous and transition γ-aluminas respectively. The experimental procedure outlined in section 4.5.2.5 was followed. The results of the experiments have been presented in Table B-23 to B-31 in Appendix B. The alumina samples were characterized using nitrogen sorption porosimetry. The results of the alumina characterization are presented in Table 5.5.

Table 5.5 . Summary of the physical characteristics and arsenic removal performance at 10 minute contact time for activated alumina samples from ALCOA Ltd at average initial arsenic concentration of 42 mg/L.

Alumina Sample	**Surface Area m^2/g**	**Pore Volume cc/g**	**BJH Pore Diameter Å**	**Residual [As] mg/L, after 10 minutes**
CPN-325	880.18	1.023	44.16	0.02
CP-5	305.81	0.370	41.49	0.1
CP-1.5	330.03	0.779	50.39	0.19
CPN-100	453.56	0.478	49.00	0.31
F1-100	786.12	.0.795	38.46	0.9
CP-100	118.52	0.315	42.19	1.6
HTC-100	450.98	0.539	54.51	3.9
CG-20	186.56	0.347	72.98	5.2

Figure 5.17 shows the plot of arsenic concentrations versus time for different commercial alumina at initial arsenic concentration of 38-44 mg/L, pH 3, and alumina concentration of 3 g/L. Table 5.5 shows that the order of performance of the alumina samples tested, After 10 minutes, were as follows:

CPN-325 > CP-5 > CP-1.5 > CPN-100 > F1-100 > CP-100 > HTC-100 > CG-20.

A residual arsenic concentration of 0.02 mg/L of alumina was achieved within 10 minutes using CPN-325, and residual arsenic concentration of 0.05 mg/L was achieved with CP-5 within 20 minutes and residual arsenic concentration of 0.08 mg/L was achieved within 30 minutes with CP-1.5 which are all significantly better than what was achieved by other workers who have achieved higher residual concentrations with lower starting arsenic levels, within several hours [Rosenblum and Clifford, 1983; Gosh, 1987].

In order to explain the difference in the performance of the alumina samples tested pore area frequencies of the samples were compared. Figure 5.17 shows a much more efficient arsenic removal capability for CPN-325 over CPN-100, both of which are transition aluminas with similar crystalline structure. Comparing their plots of pore area frequency versus pore diameter (Figure 5.18) it can be observed that CPN-325's curve lies above that of CPN-100 which implies larger pore size distribution. Also, CPN-325 has a much smaller average particle size (4.2 μm) than CPN-100 (61.8 μm).

Inspection of the pore area frequency versus pore diameter plots of CP-1.5, CP-5, and CP-100 and their comparison with CPN-325 in Figure 5.19 shows that CPN-325's curve clearly lies above all of the others. This shows that although CP-1.5 has a smaller particle size (1.2 μm) than CPN-325 (4.2 μm), the CPN-325's pore size compensated for its larger particle size. Within the pore size range of about 30 to 150Å the pore area frequency is the highest for CP-1.5 after CPN-325, followed by CP-5 and CP-100, but CP-5 showed better performance than CP-1.5 with respect to arsenic removal. The particle size of CP-1.5 is also slightly smaller than that of CP-5. Figure 5.19 shows that CP-5 had a higher pore area frequency than CP-1.5 in the pore size range of >150 Å which might be an explanation of the better performance of this sample. Structurally all CP aluminas are amorphous γ-aluminas and have similar concentrations of defect structures and hence similar surface chemistry [Goodboy and Fleming, 1984]; therefore the reason for their different arsenic removal behaviours lies in the difference in their physical characteristics.

Comparisons of pore area frequencies of CPN-325 with F1-100 HTC-100, CP-5, and CP-1.5 in Figure 5.20 clearly indicates higher porosity of CPN-325. It should also be noted that small particle size of CPN-325 (4.2 μm) has probably had a helping influence in CPN-325's better performance, as well.

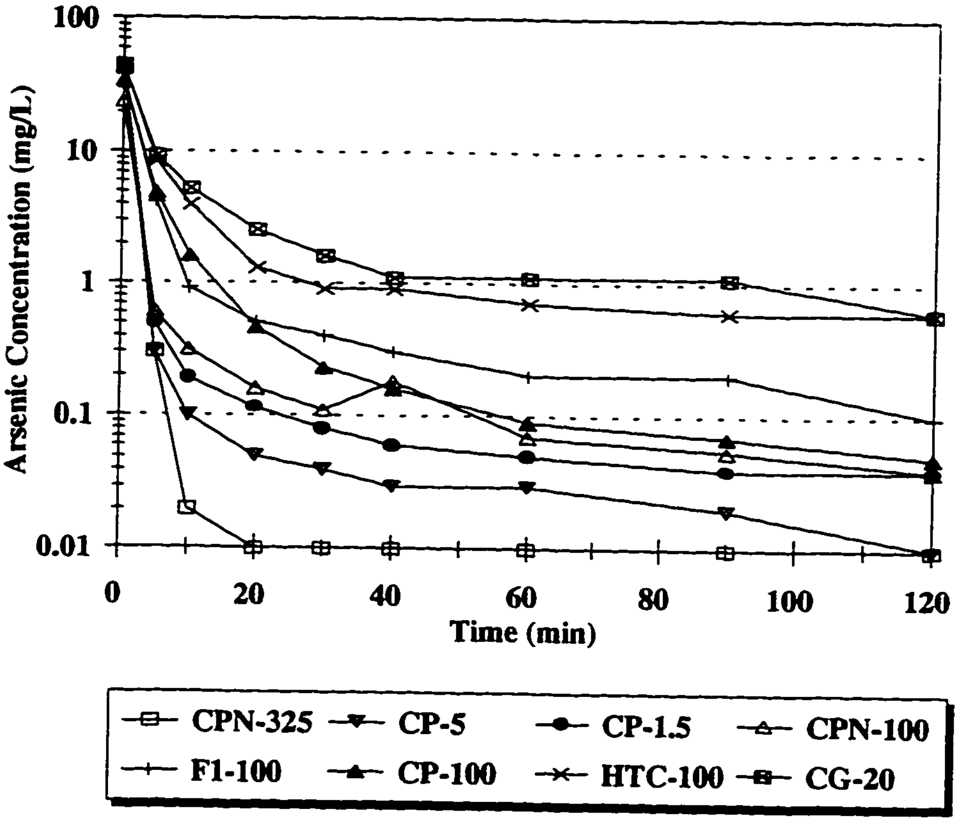


Figure 5.17. Plot of arsenic concentration versus time for different samples of commercial grade activated alumina at pH 3, initial arsenic concentration of 38 mg/L, and alumina concentration of 3 g/L.

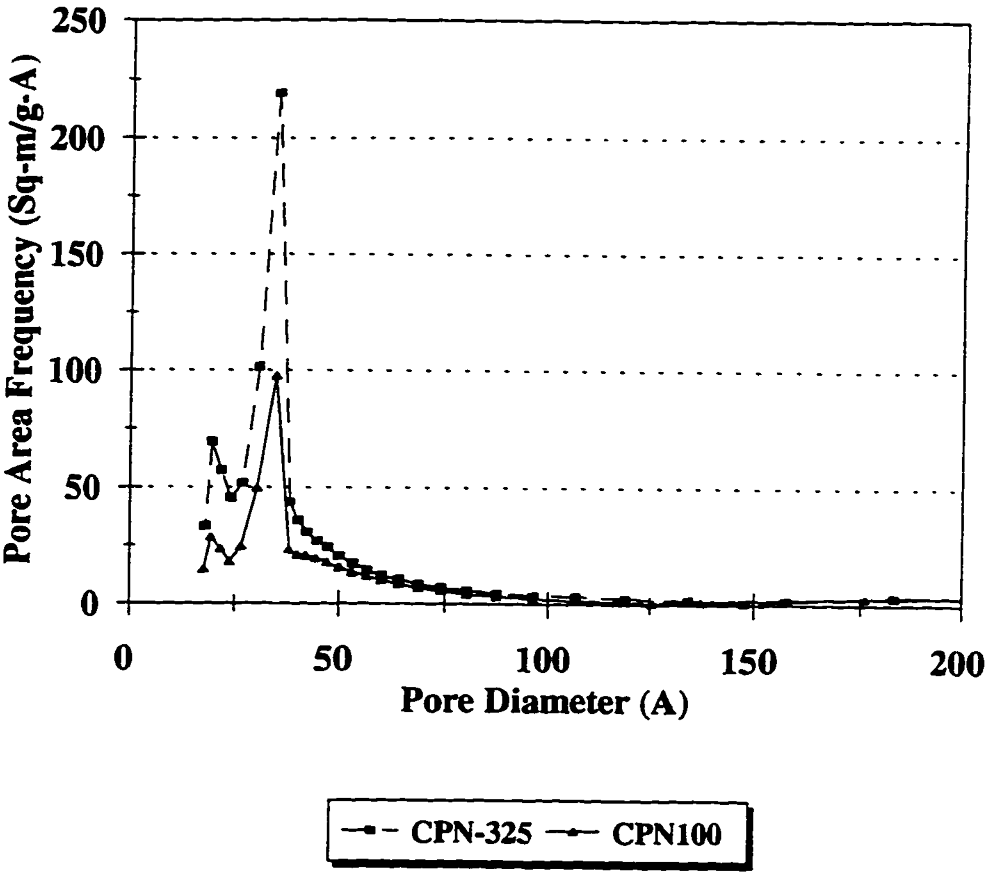


Figure 5.18. Plot of pore area frequency versus pore diameter for CPN-325 and CPN-100 activated alumina samples.

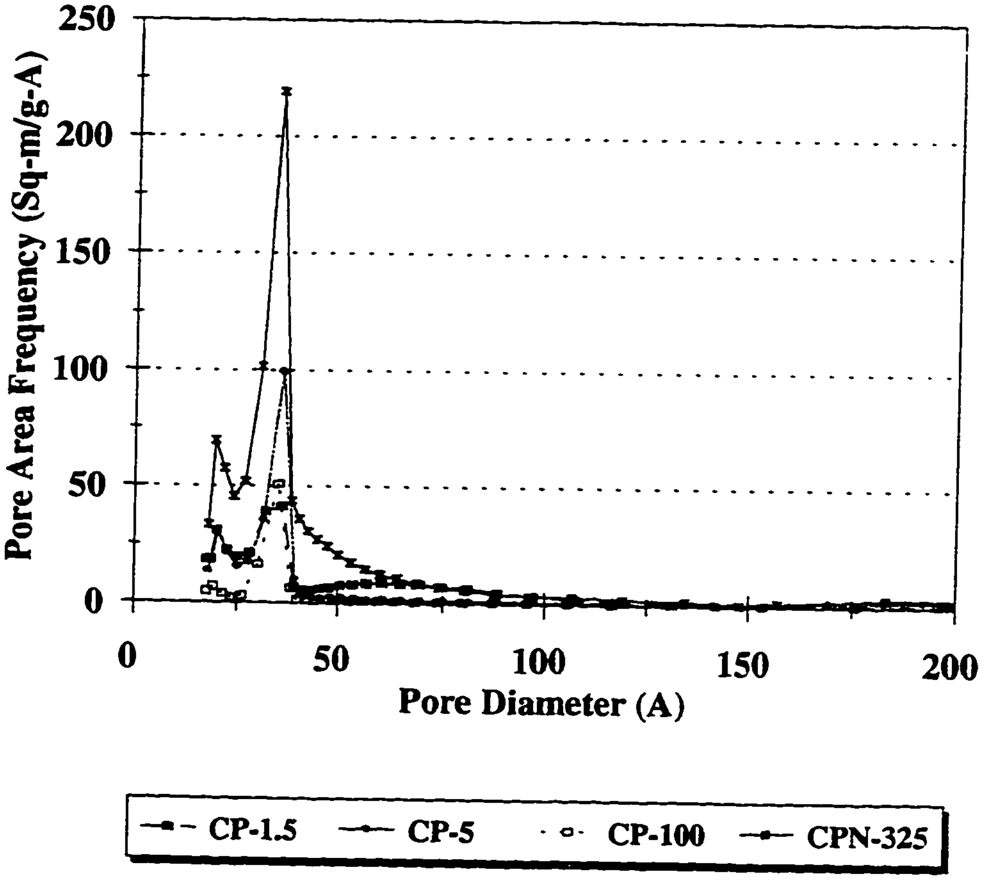


Figure 5.19. Plot of pore area frequency versus pore diameter for CP-1.5, CP-5, and CP-100 and CPN-325 activated alumina samples.

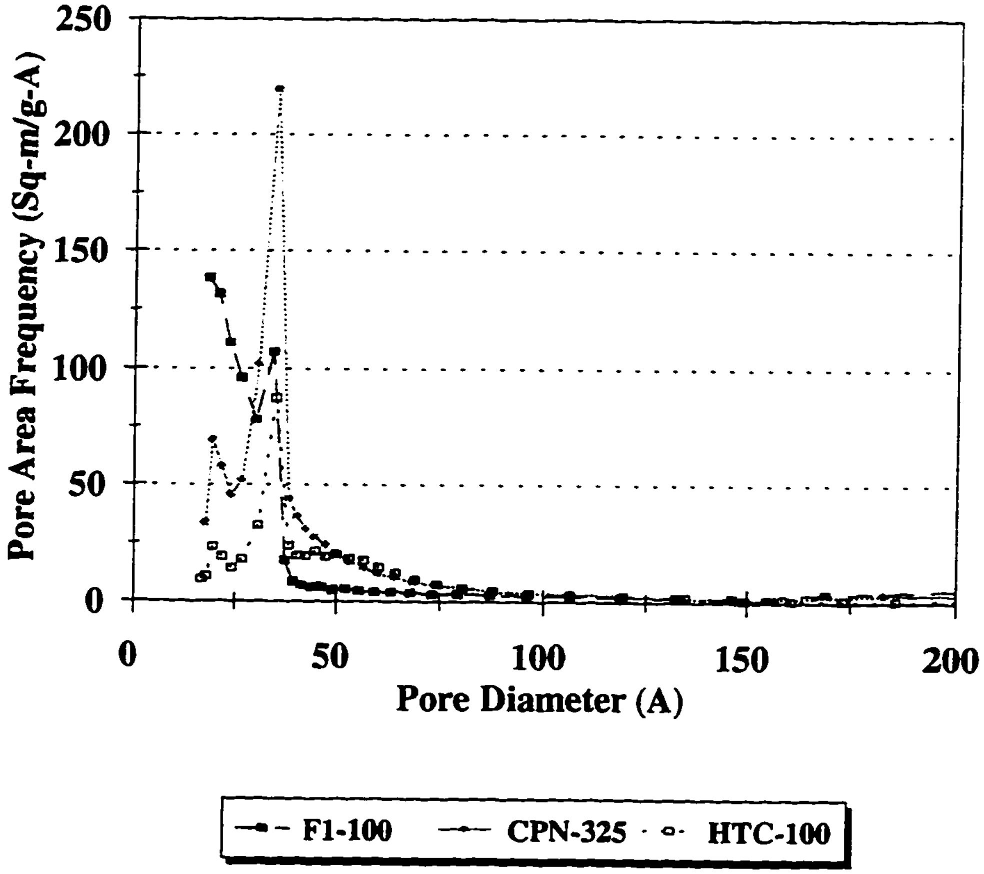


Figure 5.20. Plot of pore area frequency versus pore diameter for CPN-325 and F1-100 and HTC-100 activated alumina samples.

5.5. EFFECT OF COMPETITION OF OTHER IONS ON ARSENIC UPTAKE

The presence of competing ions can affect the efficiency of the adsorption process. The effect of the presence of sulphate ion on the adsorption process was studied since sulphate is found at very high levels in mining effluents and acid mine drainage. In order to determine the effect of sulphate competition on arsenic adsorption onto activated alumina, the procedure outlined in sections 4.5.1 and 4.5.2.7 were followed. Synthetic samples of arsenic contaminated water with six different sulphate concentrations (0, 10, 30, 50, 100, 300, 600 mg/L) were prepared and adsorption tests were performed at pH 3 , 46 mg/L initial arsenic concentration and 3 g/L on ALCOA's CPN-325. Another experiment using arsenic contaminated water from Deloro (Ontario) water treatment facility was performed. The results are presented in Tables B-32 to B-40 in Appendix B.

Figure 5.21 shows that in the absence of sulphate > 99% removal was achieved to residual arsenic concentrations of as low as 0.02mg/L, and the degree of removal was not significantly affected with sulphate concentrations of up to 50 mg/L. At sulphate concentration of 100 mg/L a significant drop in the removal was observed and at 300 and 600 mg/L the initial removal of arsenic dropped by as much as about 20%. Rosenblum and Clifford (1983) have also reported adverse effects of sulphate ions on the adsorption process, but Gosh (1985) and Gosh and Teoh (1987) reported a slight reduction in arsenic adsorption in the presence of sulphate ions at pH values greater than 7, but no effect if pH is less than 7 at sulphate levels of 60 to 300 mg/L. Distinct reduction in the degree of adsorption was observed in the presence of sulphate at pH 3 and similar sulphate levels as those studied by Gosh and Teoh.

Table 5.6 shows the initial rate of arsenic removal in terms of mg As/min, and mg As/min/gAlumina at different sulphate concentrations at pH 3 and initial arsenic concentration of 46 mg/L. The initial rates were determined based on the arsenic removal after 5 minutes. Figure 5.22 illustrates the plot of arsenic removal rate versus sulphate concentration. Similar to the previous observations it was observed that the initial rate was not affected significantly up to sulphate concentrations of 50 mg/L. The rate dropped by about 5% from 50 mg/L to 100 mg/L, by another 10% from 100 to 300 mg/L and by a further 6% from 300 mg/L to 600 mg/L. It seemed that the rate would drop sharply up to a certain level of sulphate and level off, however, sulphate levels of higher than 600 mg/L were not studied to justify this claim.

Table 5.6. Initial rates of arsenic uptake at different concentrations of sulphate for CPN-325, calculated for the first 5 minutes of the adsorption process at 3 g/L of activated alumina.

[Sulphate] mg/L	Initial rate mg As/min	Initial rate mg As/min/g AA
0	9.14	3.05
10	9.12	3.04
30	9.14	3.05
50	9.1	3.03
100	8.68	2.89
300	7.82	2.61
600	7.36	2.45

Figure 5.23 illustrates the % arsenic removal from an actual contaminated water sample in comparison to the degree of arsenic uptake from a synthetic contaminated water sample with initial arsenic concentration of 55 mg/L and a synthetic water with 600 mg/L of sulphate. The figure shows that degree of arsenic removal in the real water sample is less than that for the synthetic water by about 20%. The Deloro water sample contained other species that might compete with arsenate anion for adsorption (Table 4.1) and a fraction of its total arsenic content might have been in the As(III) form which explains the difference in the degree of arsenic removal.

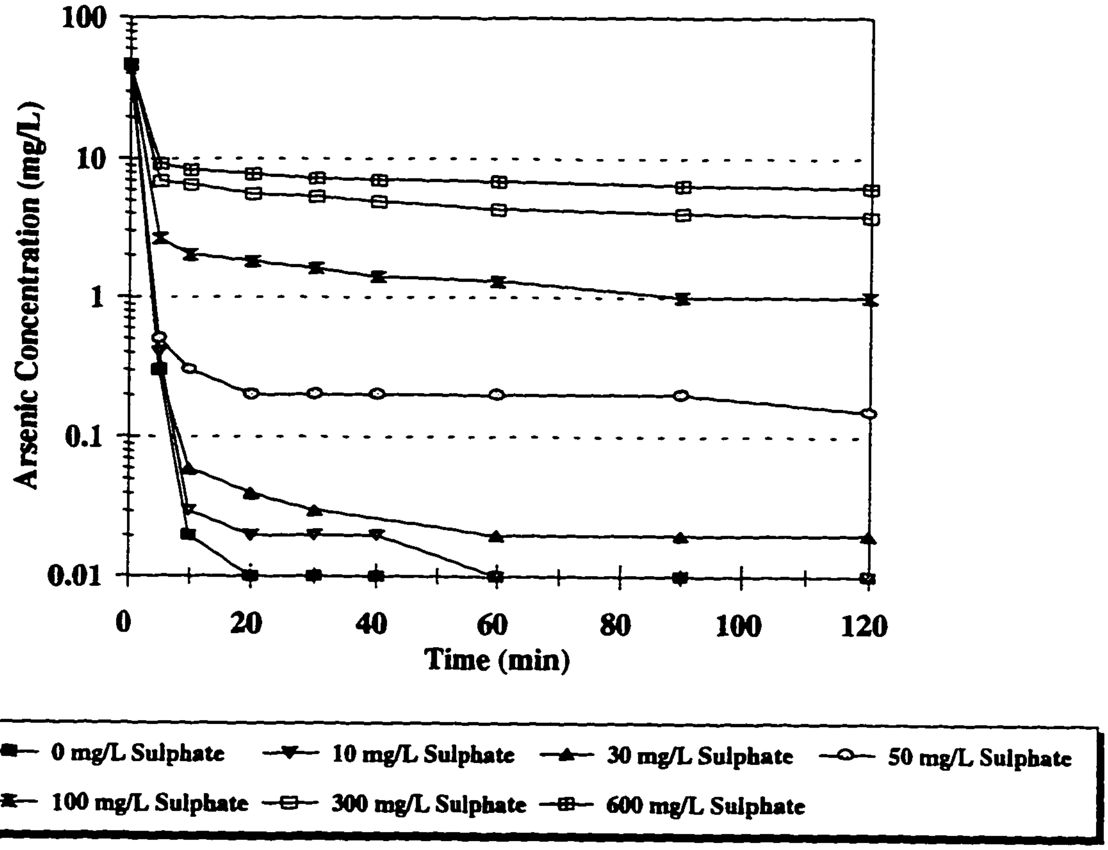


Figure 5.21. Plot of Arsenic concentration for different sulphate concentrations at pH 3, initial arsenic concentration of 46 mg/L, 3 g/L of ALCOA's CPN-325 activated alumina.

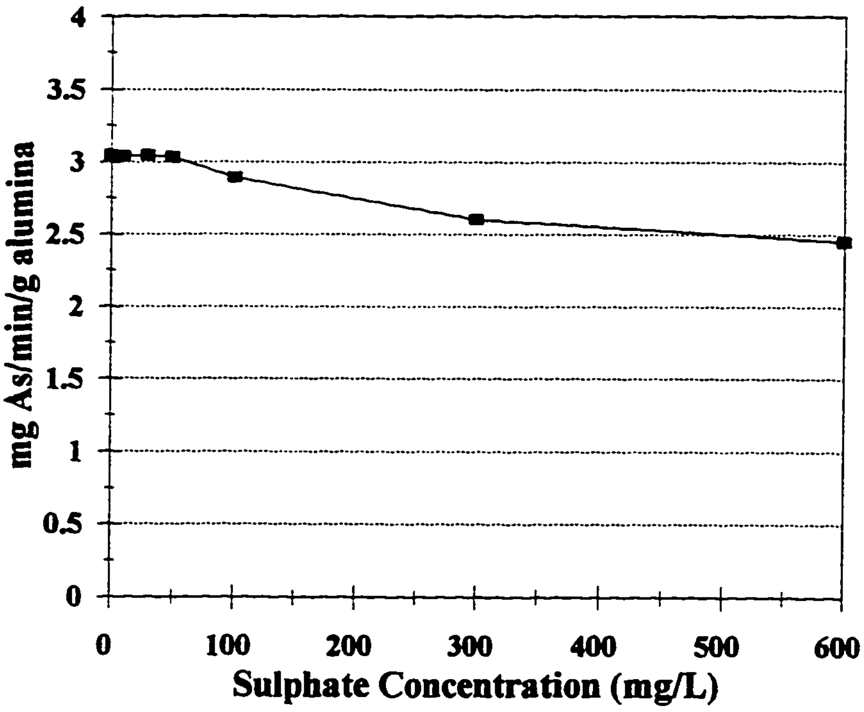


Figure 5.22. Plot of the initial rate of arsenic removal versus sulphate concentration at pH 3, initial arsenic concentration of 46 mg/L, 3 g/L of ALCOA's CPN-325 activated alumina.

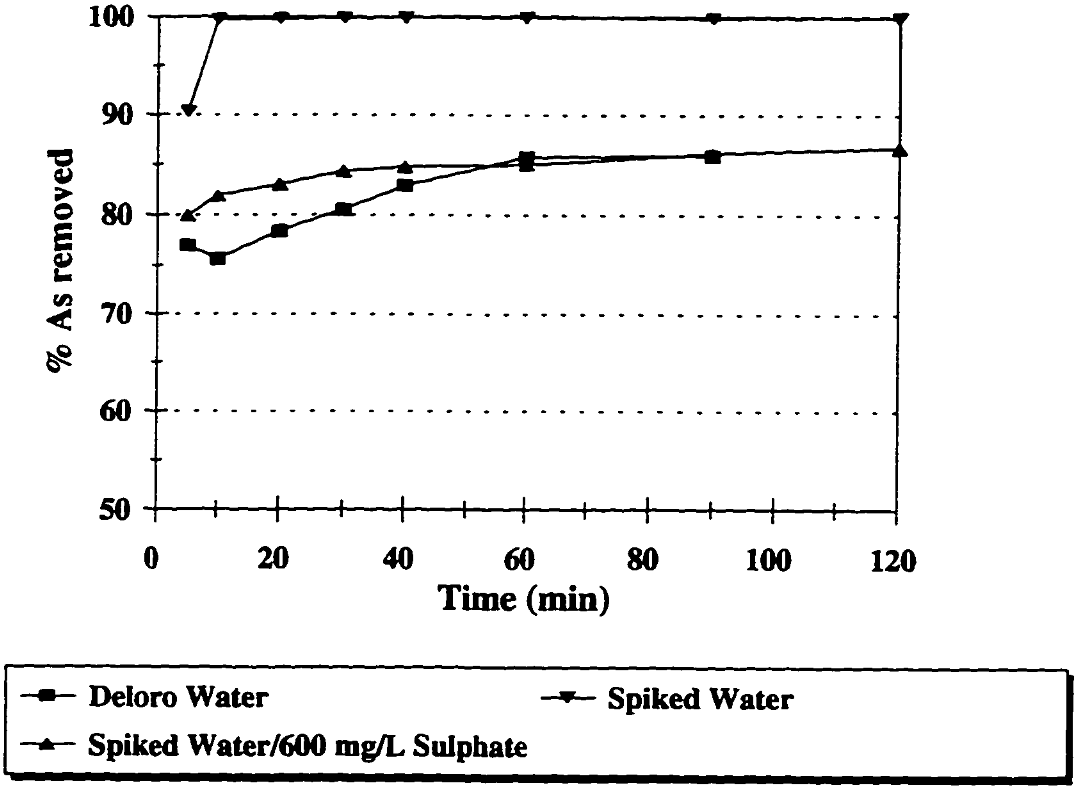


Figure 5.23. Plot of % arsenic removal versus time at pH 3 for real contaminated water and synthetic contaminated water at 3 g/L ALCOA's CPN-325 activated alumina.

5.6. EFFECT OF INITIAL ARSENIC CONCENTRATION ON ARSENIC UPTAKE

The effect of initial arsenic concentration on the degree of arsenic removal was studied following the procedure outlined in section 4.5.2.6. The results are presented in Table B-41 to B-46 in Appendix B. Figure 5.24 shows the plot of Arsenic concentration versus time for different initial arsenic concentrations. The results showed that residual arsenic concentrations of 20 µg/L and lower can be achieved within 10 minutes of contact between alumina surface and arsenate solution for initial arsenic concentrations of up to 43 mg/L. The data also showed that the most stringent environmental criteria for arsenic which has been set for the drinking water standard (25 μg/L) can be achieved within 10 minutes.

Figure 5.25 shows the change in initial rate of arsenic removal with initial arsenic concentration. As the initial arsenic concentration increases the initial rate of arsenic uptake increases, but the residual arsenic concentration in solution increases. This implies that there is either a saturation effect involved or some other limiting factor such as diffusion has a major influence.

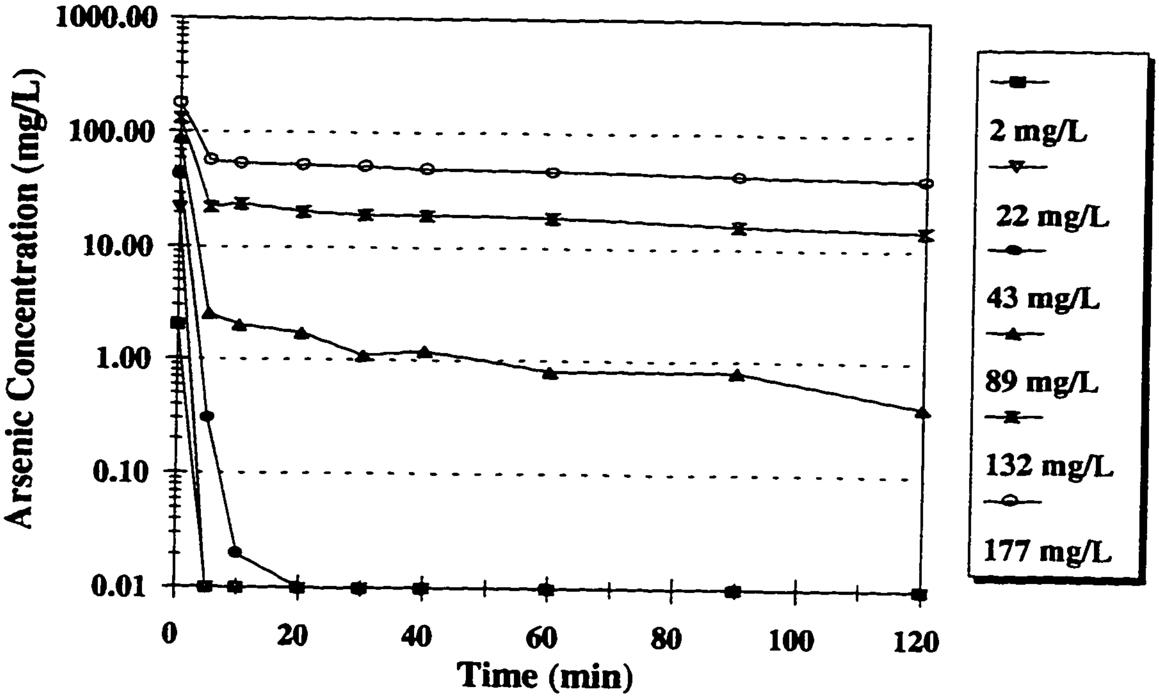


Figure 5.24. Plot of Arsenic concentration versus time for different initial arsenic concentrations at pH 3, and 3 g/L CPN-325 alumina, at 23 °C.

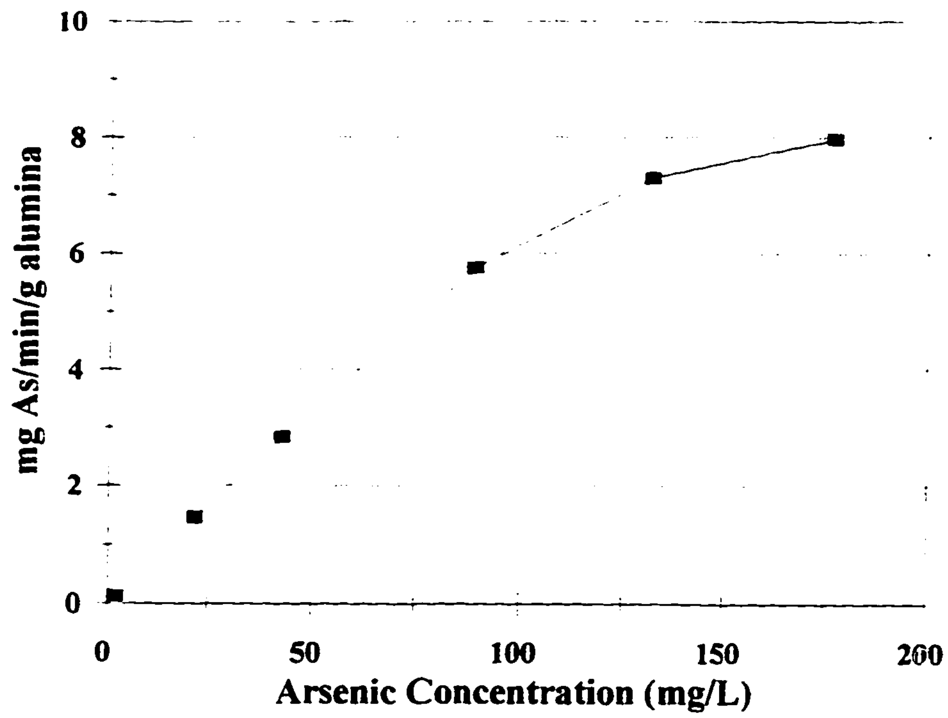


Figure 5.25. Plot of initial rate of arsenic removal against initial arsenic concentration at pH 3, and 3 g/L CPN-325 alumina.

5.7. THE DETERMINATION OF ADSORPTION ISOTHERMS

The adsorption isotherm for adsorption of arsenate at pH 3 onto ALCOA's CPN-325 at a concentration of 3 g/L was determined. The procedure outlined in section 4.5.2.8 was followed. Samples were taken after 1 day, 3 days, and 7 days. Figure 5.26 shows the plot of alumina loading (q_e) against solution arsenic concentration (C_e) for 1, 3, and 7 days.

The fact that the values are the same for days 1, 3, and 7, shows that equilibrium was reached within 1 day. Therefore, these values represent the actual equilibrium values which can be plotted as an isotherm. Adsorption of arsenic (III) and arsenic (V) have been described using both Langmuir and Freundlich adsorption models by different workers [ALCOA, 1994 (a); Rosenblum and Clifford, 1983; Singh et al., 1988; Yadava et al., 1988; Gosh, 1987; Gosh and Teoh, 1985; Choi and Chen, 1979; and Yuan et al., 1987] with varying degrees of success. Gosh and Teoh (1985) reported that Freundlich did not describe adsorption data for arsenate adsorption onto F1 alumina well. On the other hand Rosenblum and Clifford (1983) found that both Langmuir and Freundlich adsorption models described adsorption of arsenate on F1 alumina quite well.

The constants for the Langmuir and Freundlich model were determined using a least squares fit and are listed in Table 5.7 (Appendix D) for the isotherms obtained experimentally in this study. Figure 5.27 shows the arsenate/CPN 325 isotherm with prediction of the Langmuir model. Figure 5.28 shows arsenate/CPN 325 isotherm with Freundlich model's prediction. It can be seen that Freundlich model's prediction shows a closer fit to the experimental data than that of the Langmuir's model. The surface of activated alumina is a heterogeneous surface and the active sites and adsorbed molecules interact with each other. Langmuir model describes a monolayer adsorption onto surface sites of equal energy [Rosenblum and Clifford, 1983; Ruthven, 1984]. This could be why a good fit was not achieved with Langmuir model in Figure 5.27. On the other hand Freundlich model allows for adsorption onto sites of unequal energy. Figures 5.28 shows Freundlich model offers a better fit for the CPN-325/arsenate system.

Table 5.7. Linearized isotherm constants for CPN-325/arsenate system.

Langmuir Model		**Freundlich Model**	
Q (mg/g)	**b (mg^{-1})**	**K**	**n**
78.8947	0.3639	23.3277	3.4021

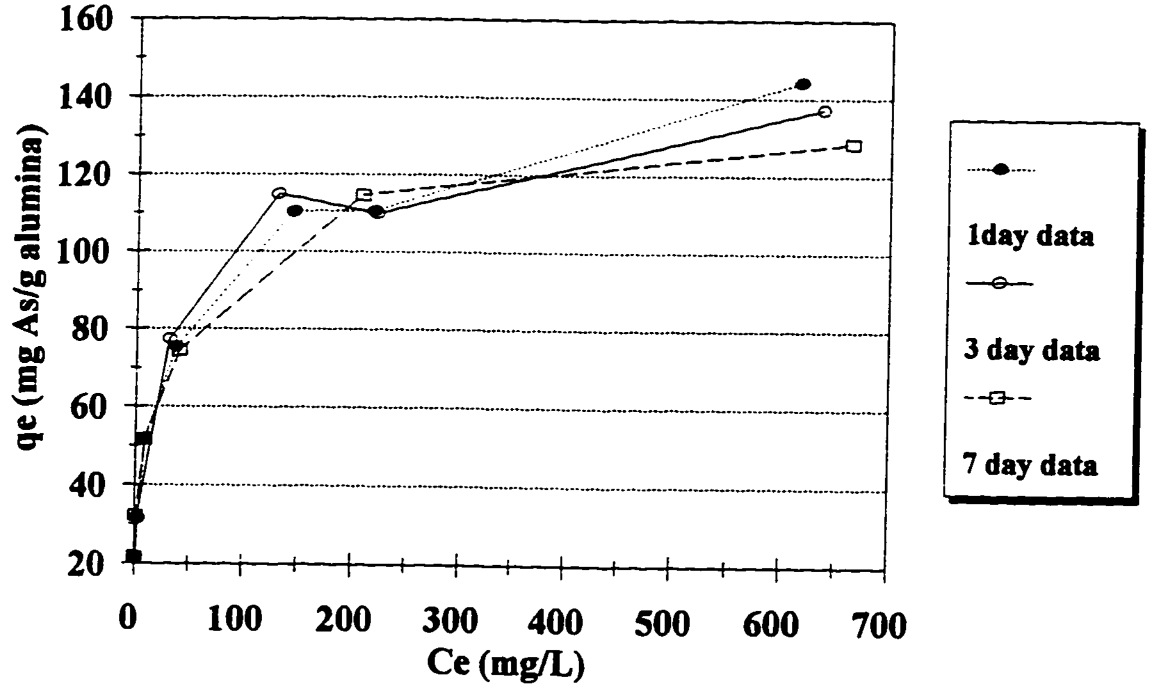


Figure 5.26. Adsorption isotherm for CPN-325/arsenate system at pH 3, 23 °C, and 3 g/L alumina.

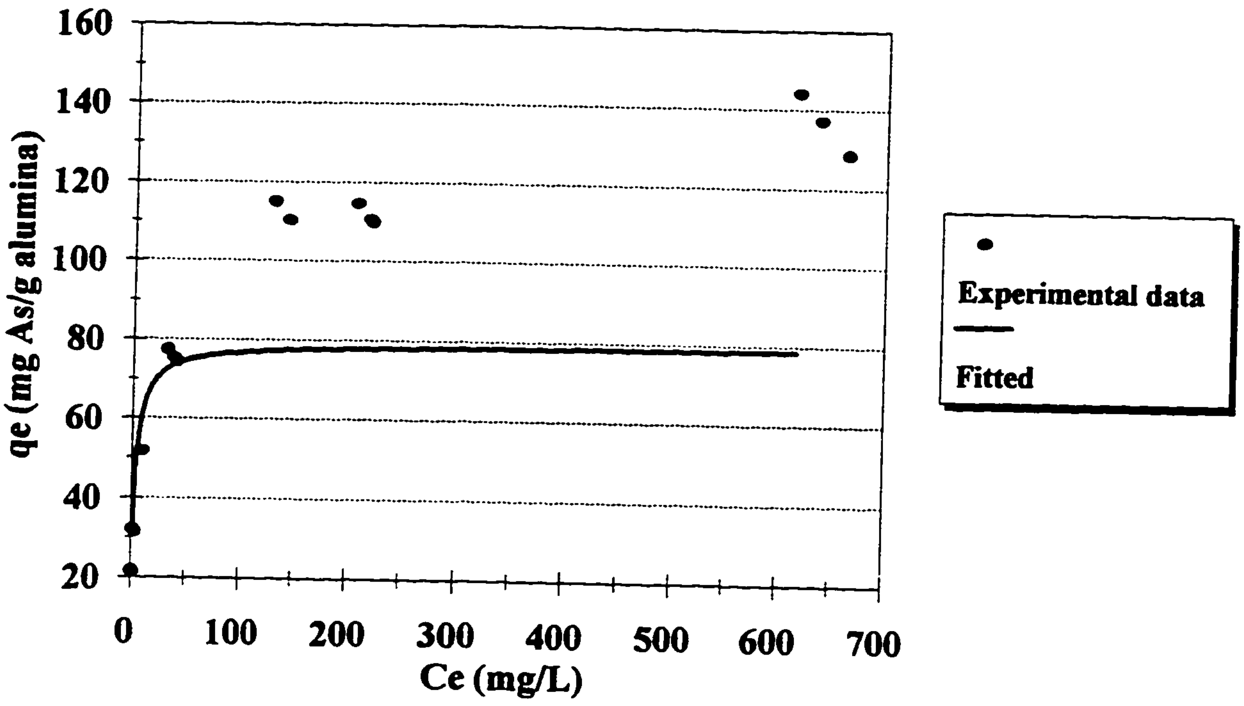


Figure 5.27. Adsorption isotherm for CPN-325/arsenate system at pH 3, 23 °C, and 3 g/L alumina compared with Langmuir model prediction.

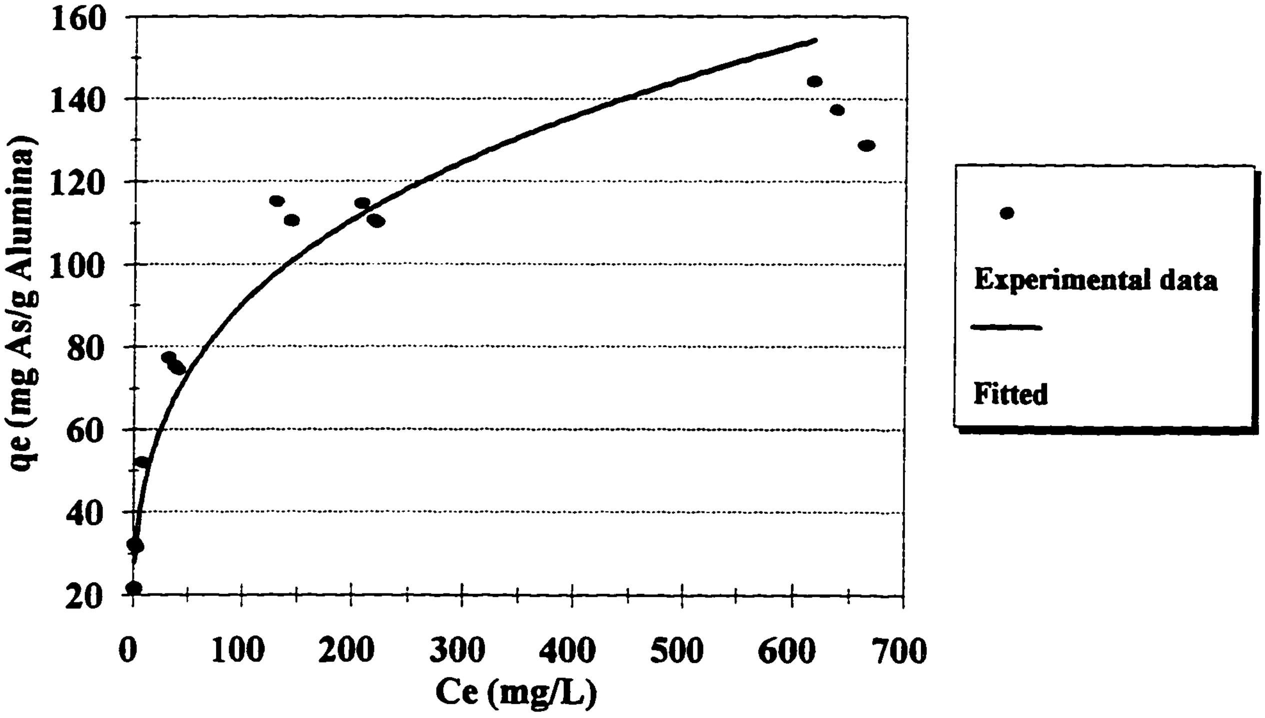


Figure 5.28. Adsorption isotherm for CPN-325/arsenate system at pH 3, 23 °C, and 3 g/L alumina compared with Freundlich model prediction.

5.8. ADSORBENT REGENERATION STUDY

Feasibility of the regeneration and reuse of spent activated alumina was investigated. The objective of this part of the study was to determine the extent of the recovery of the adsorption capacity of the spent activated alumina. The regeneration experiments were carried out according to the procedure outlined in section 4.5.3. The results of this section are presented in Tables B-50 To B-64 in Appendix B.

In order to regenerate spent alumina, it should be exposed to conditions that would cause the desorption of arsenic from the active surface sites. This can be achieved by changing the pH to a value that would change the speciation of the adsorbed arsenate as well as the surface charge of the alumina, reducing the affinity of the adsorbent surface to arsenate and releasing it from the alumina surface.

A possibility would be to introduce a competing ion that would have higher affinity towards the surface active sites of the alumina, to replace the arsenate. The choices considered for regeneration were; pH increase using sodium hydroxide, application of a concentrated phosphate solution, and the use of a sulphate solution. The use of phosphate was ruled out because of the strict water discharge criteria for phosphate.

The feasibility of using sulphate was investigated by performing adsorption experiments with an alumina sample that was exposed to a 100 g/L sodium sulphate solution for three days and comparing its performance with a fresh alumina sample following the procedure outlined in section 4.5.2.2. Figure 5.29 shows the plot of arsenic concentration versus time for experiments using fresh and sulphate loaded alumina. The figure shows that when sulphate was already adsorbed onto surface of activated alumina, arsenate could not effectively replace it and at the five minute contact time there was a 40% loss in the degree of arsenic removal. This means that if the alumina is regenerated by sulphate solution, 40% of alumina capacity would be lost.

The option to increase pH with sodium hydroxide was investigated to determine the suitable regeneration conditions as well as the feasibility of reusing the regenerated alumina. The regeneration of alumina was performed after it was filtered and separated from the reaction solution. The spent alumina was added to 100 mL of sodium hydroxide solution at three different pH values; pH 10, pH 12, and pH 13; and mixed for an hour. After one hour the alumina was filtered again and reused. This process was repeated twice. The results were compared to those of the initial run. Figures 5.30, 5.31, and 5.32 show the results of the adsorption experiments before and after first and second regenerations at 3 different pH values. It was observed that the initial loss in the degree of arsenic removal was approximately 10% at pH 13 and 20% for pH 10 and 12 after two regenerations. It is important to note that the activated alumina consisted of particles with a size distribution. Some of the finer alumina particles were lost at each filtration and regeneration stage. This alumina loss contributed to the observed drop in the degree of arsenic removal. The experiments were terminated after two regenerations because the particle size distribution of the alumina had significantly changed due to loss of the finer alumina particles. In a continuous process where filtration is carried out by membrane, the loss of alumina would be minimized and better results would be expected.

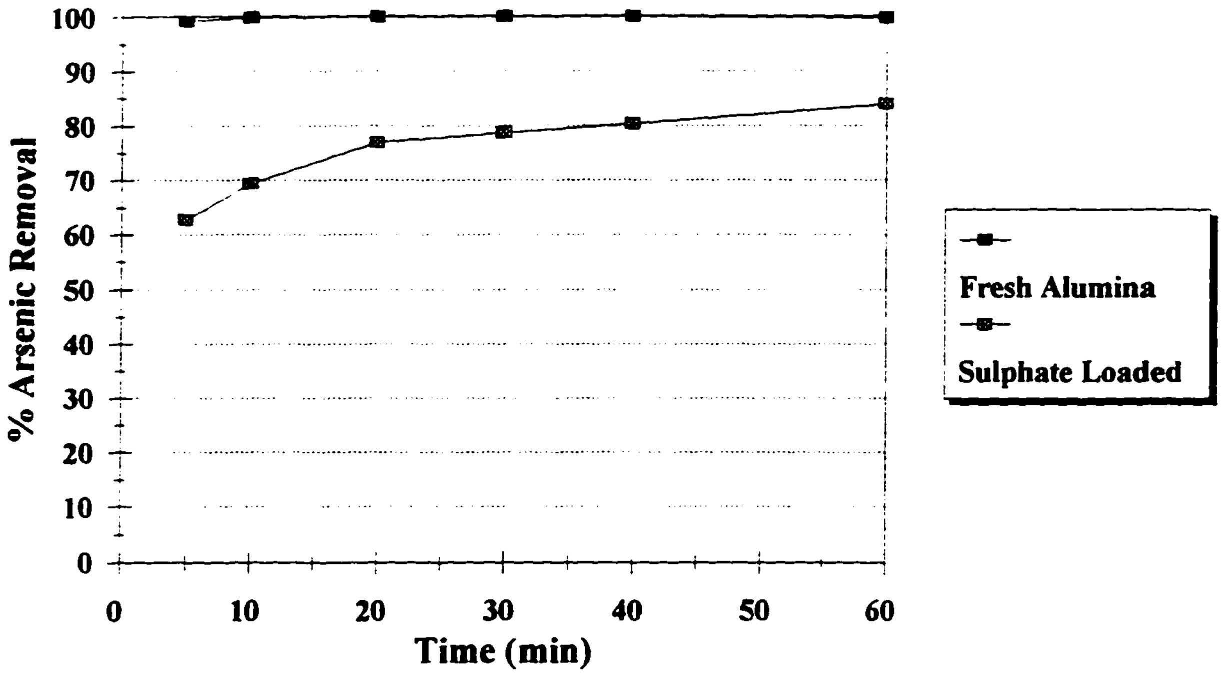


Figure 5.29. Comparison of arsenic removal by a fresh and sulphate loaded activated alumina 24 mg/L initial arsenic concentration, pH 3, 3 g/L activated alumina (20-30 µm, 300 Å).

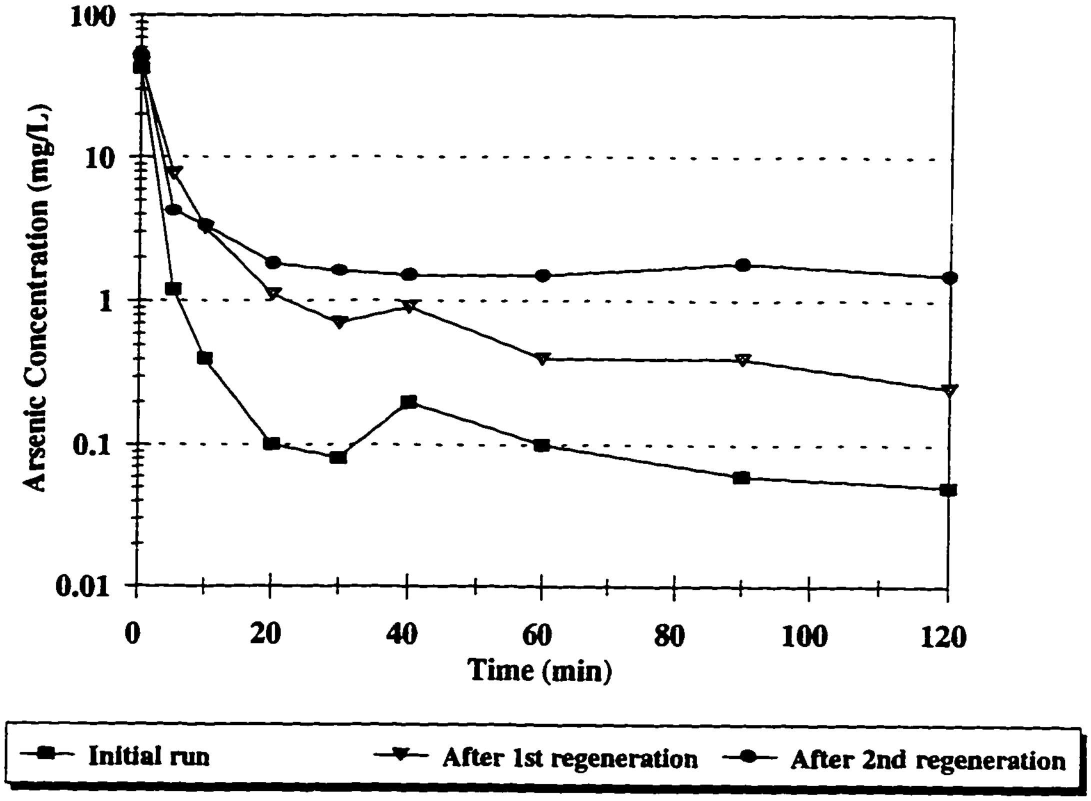


Figure 5.30. Plot of arsenic concentration versus time after alumina regeneration at pH 10. The runs were performed at pH 3, 43-50 mg/L initial arsenic concentration, 3 g/L activated HTC-100 alumina.

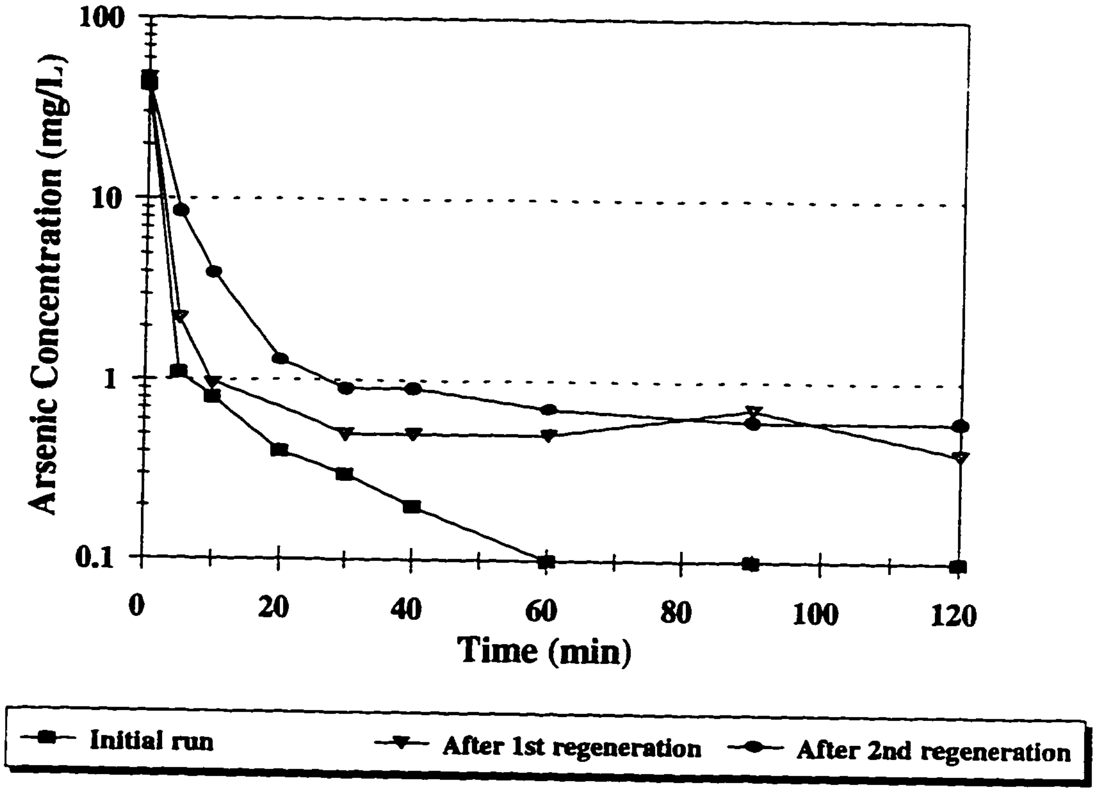


Figure 5.31. Plot of arsenic concentration versus time after alumina regeneration at pH 12. The runs were performed at pH 3, 43-50 mg/L initial arsenic concentration, 3 g/L activated HTC-100 alumina.

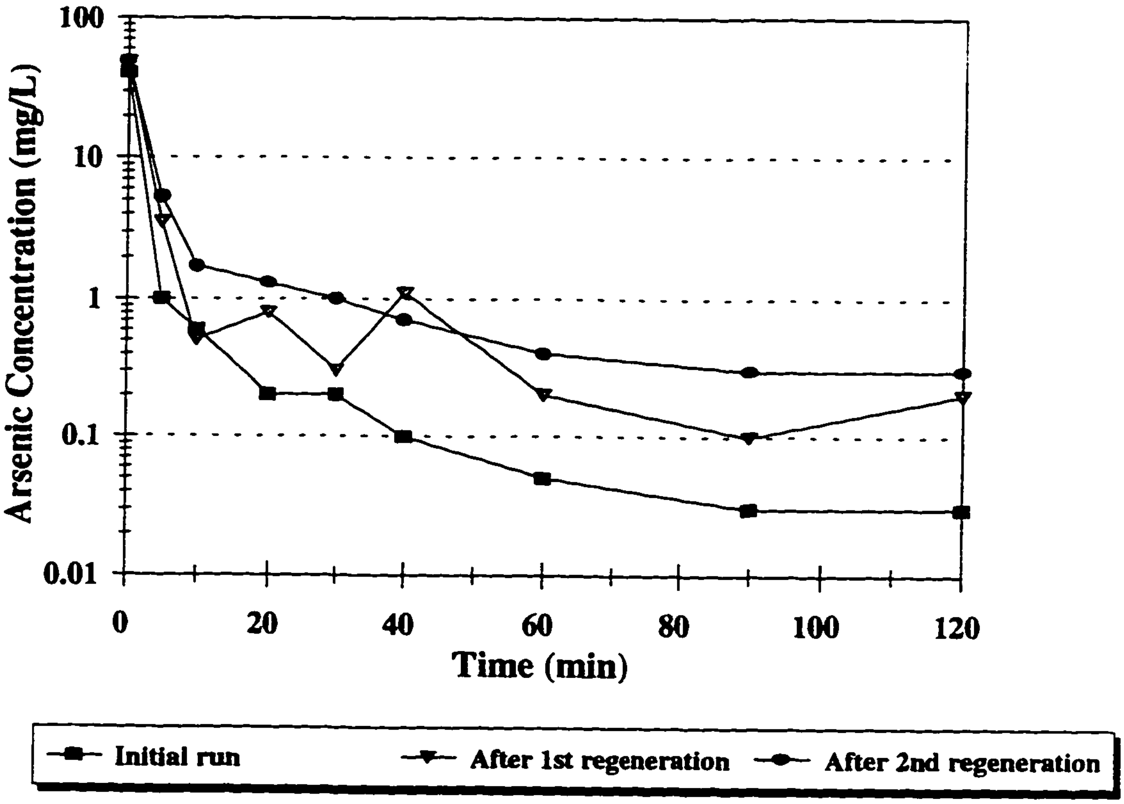


Figure 5.32. Plot of arsenic concentration versus time after alumina regeneration at pH 13. The runs were performed at pH 3, 43-50 mg/L initial arsenic concentration, 3 g/L activated HTC-100 alumina.

In a third experiment the regeneration was performed in the same reactor without removing any liquid or changing the volume of the reactor contents. The procedure followed was as outlined in section 4.5.3. After 24 hours of adsorption at pH 3, pH was adjusted to pH 11, 12, and 13 in three parallel experiments which were sampled every 10 to 20 minutes. Samples were also taken in order to determine alumina loss due to hydrolysis. Figure 5.33 shows a plot of % arsenic desorbed with time and Figure 5.34 shows a plot of % alumina loss with time. The degree of arsenic desorption was determined by calculating the amount of arsenic released into solution and comparing it to the initial arsenic loading of the alumina prior to initiation of regeneration. It can be seen that the degree of arsenic desorption was very close at pH 12 and 13, while the loss of alumina at pH 12 was approximately half as much at pH 13. Therefore the best choice of pH for the regeneration of the spent alumina is pH 12.

Figure 5.33 shows that the system approached equilibrium during the desorption stage. As the arsenate anions desorb and enter into solution, the concentration gradient inside the pore depletes and the desorption process slows down. At a very high pH the surface of alumina becomes hydroxylated and the desorbed arsenate anions become further deprotonated to AsO_4^{3-} which is the dominant arsenate species at that pH and the surface of alumina becomes negative which repels AsO_4^{3-} anion. By flushing the pores of the alumina and removing the desorbed arsenate anions (mostly AsO_4^{3-}) from the vicinity of the alumina surface and hence maintaining a sufficient driving force increases the levels of desorption and make it more feasible.

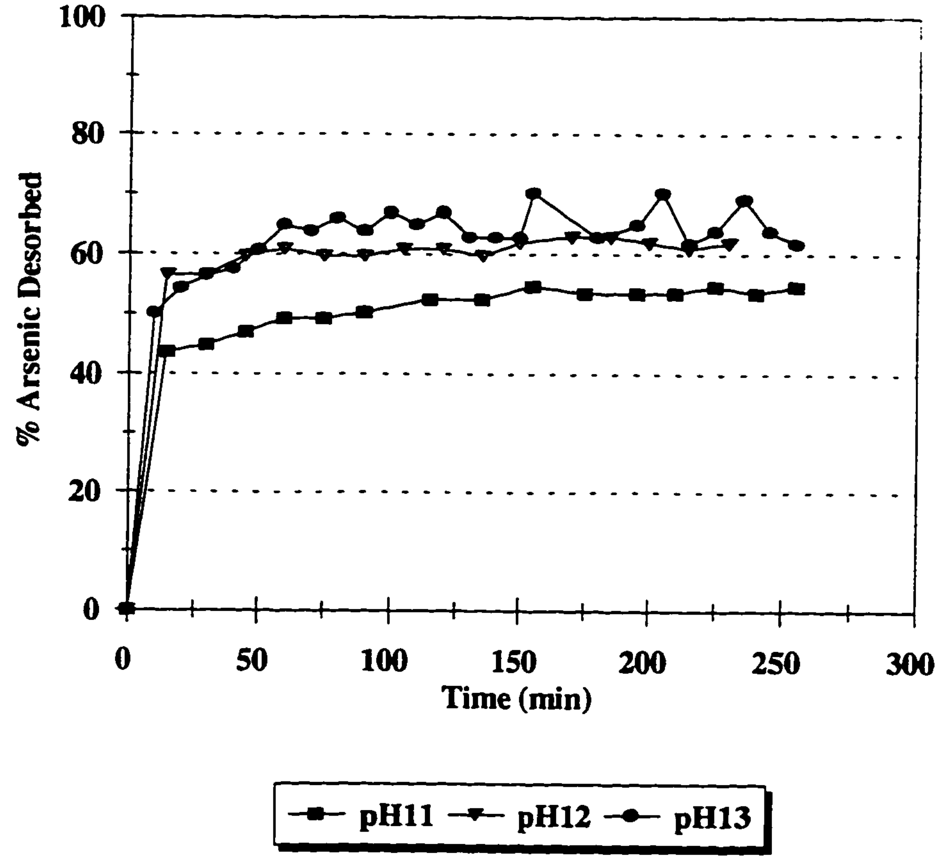


Figure 5.33. Plot of % arsenic desorbed versus time at pH 11, 12, and 13 for CPN-325.

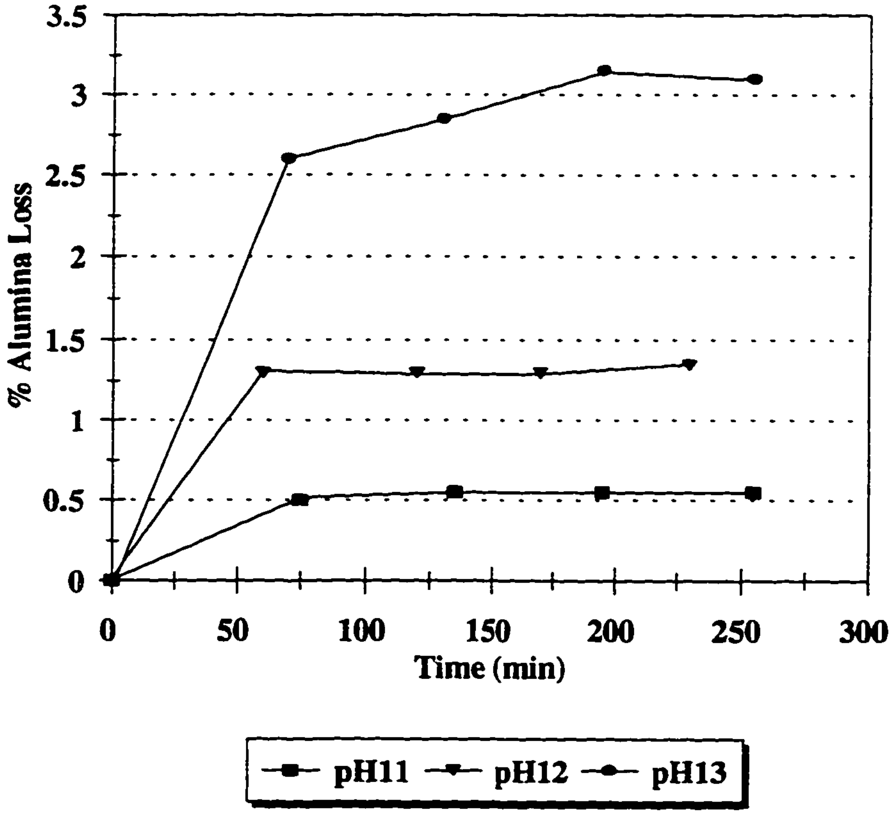


Figure 5.34. Plot of % alumina loss versus time at pH 11, 12, and 13 for ALCOA's CPN-325 alumina.

5.9. ACTIVATED ALUMINA SETTLING TESTS

A set of settling experiments were carried out following the procedure outlined in section 4.5.4. The objective of these tests were to determine the settling rate of activated alumina particles. ALCOA's CP-1.5, with an average particle size of 1.5 μm, and HTC-100, with a particle size range of 105-177μm, were used to observe the settling of very small and large sized alumina particles. Table 5.8 shows the results of these experiments. Figure 5.35 shows the plot of bed height versus time and Figure 5.36 shows the plot of settling rate versus time.

Table 5.8. Activated alumina settling test results for ALCOA's CP-1.5 and HTC-100.

Time (min)	Bed Height (mm)		Settling Rate (mm/min)	
	CP-1.5	**HTC-100**	**CP-1.5**	**HTC-100**
0	205	205		
1.5	204	202	0.67	2
4	201	195	1	2.5
7	193	185	1.71	2.86
10	186	176	1.9	2.9
21	148	141	2.71	3.05
29	125	114	2.76	3.14
35	119	94	2.46	3.17
58	107	49	1.69	2.69
74	104	41	1.36	2.22
102	103	35	1	1.67
110	103	35	0.93	1.55
120	103	34	0.85	1.43
1085	103	34	0.09	0.16
1623	103	34	0.06	0.11

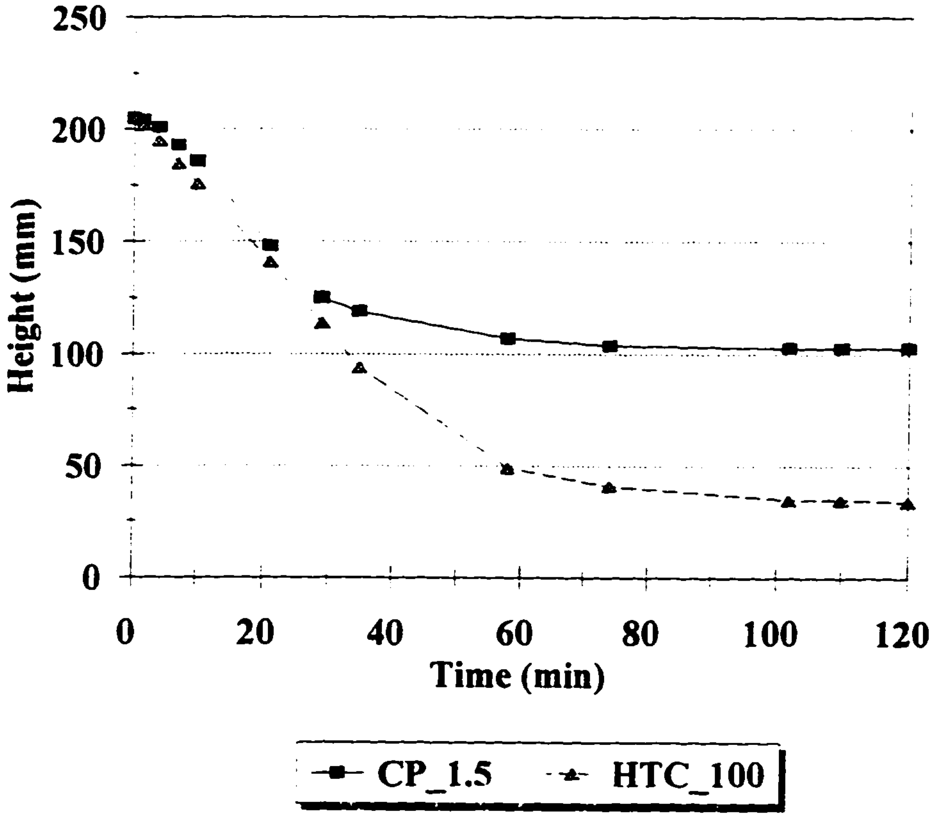


Figure 5.35. Plot of bed height versus time for activated alumina samples CP-1.5 and HTC-100.

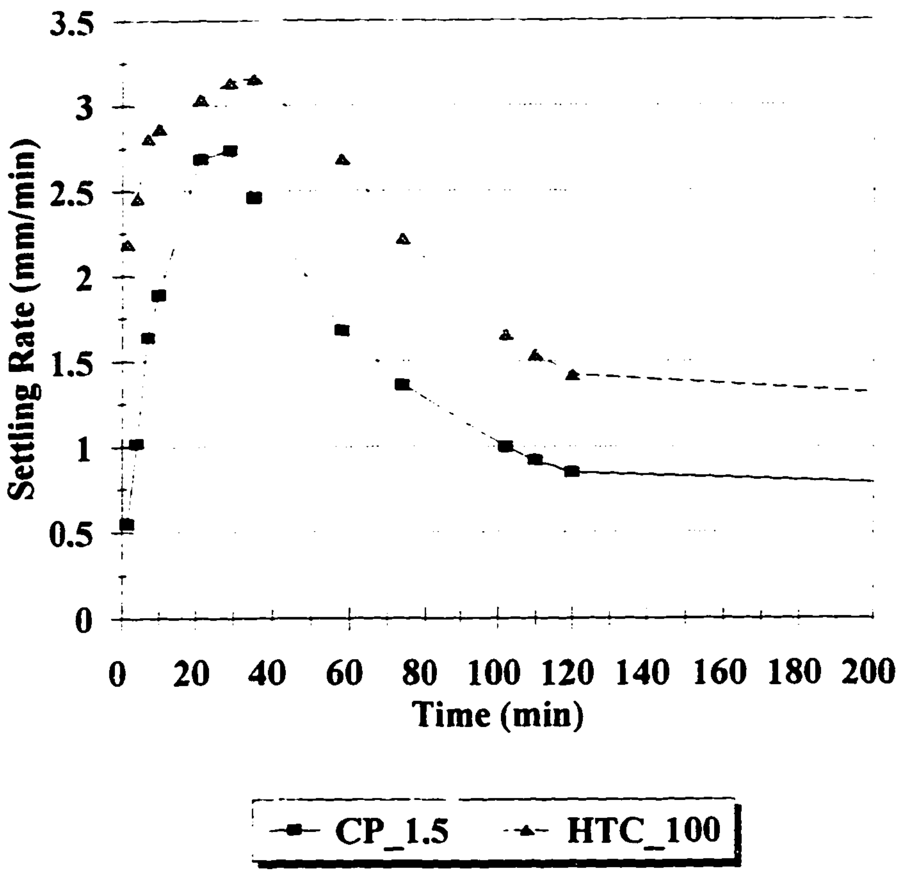


Figure 5.36. Plot of settling rate versus time for activated alumina samples CP-1.5 and HTC-100.

Figure 5.35 shows that the bed height remained constant after about 100 minutes. Although the volume of the bed remained constant the clear solution above the alumina bed remained cloudy and did not change for the duration of the experiment. It should be noted that both specialty and commercial activated aluminas consist of particles having a range of sizes. Figure 5.36 simply implies that a particle size distribution exists in both CP-1.5 and HTC-100 alumina. The rate change shows that there might be some aggregation of particles.

The application of settling as a stand alone separation technique for the process is not a suitable option since all of the suspended alumina particles do not settle completely, even after 1,623 minutes (27.05 hrs). Considering the time requirement for the bed volume to stabilize and the fact that the actual contact time required for arsenic contaminated water and the alumina particles is basically less than 20 minutes, the application of a membrane separation process is justified.

5.10. MEMBRANE FILTRATION EXPERIMENTS

Two types of membrane configurations were tested: a conventional tubular ENKA membrane module and a hollow fibre ZeeWeed™ membrane manufactured by Zenon Environmental Inc., Burlington, Ontario. The description and experimental procedure is explained in section 4.5.5. Tubular membranes have been used in industry for the filtration of suspensions; therefore, they were an obvious choice to consider. On the other hand hollow fibre membranes have had very limited or almost no application for solids removal due to their high susceptibility to fouling. The ZeeWeed™ module however is quite different from conventional hollow fibre membrane modules.

The ZeeWeed™ module, was placed within the suspension and vacuum was applied to create the required pressure difference for permeation (in this case water permeation). There is no concentrate stream leaving the module and a single permeate stream leaves the membrane module.

5.10.1. Tubular ENKA Flux Data

The setup for the ENKA module test installation is shown in Figure 4.6. The ENKA tubular polypropylene module had a nominal pore size of 0.2 μm and a total surface area of 0.036 m^2. The flux data are presented in Table B-66 in Appendix B. RO water was used in the experiments. The water flux was initially measured at different feed flowrates varying from 1 to 6 gpm (3.84 to 23.04 L/min) which corresponds to cross-flow velocities of 65.19 m/min to 391.17 m/min. The water flux through the membrane was 3700 gfd (6290 L/m^2 h) at 1 gpm (3.785 L/min) and 2500 gfd (4250 L/m^2 h) at 5 gpm (18.925 L/min) at 25 °C. The drop in flux was due to the hydraulic resistance of the system. The experiments and data reported are for a feed rate of 5 gpm (18.925 L/min).

Figure 5.37 shows a plot of flux versus time for the ENKA membrane at an alumina concentration of 10 g/L. When activated alumina was added to water to make a 10g/L alumina suspension, the flux suddenly started to decline and within about 8 minutes the flux dropped from 2520 gfd (4284 L/m^2 h) to 384 gfd (652.8 L/m^2 h). 118 minutes later the flux was 132 gfd (224.4 L/m^2 h). This indicated fouling of the membrane by the alumina particles. In order to recover the membrane water flux, the system was back washed with water and for a period of 40 minutes. After 20 minutes the measured water flux at 25 °C was at 2094 gfd (3559.8 L/m^2 h) (Table B-66). The flux immediately dropped to 1644 gfd (2794.8 L/m^2 h) when the test was resumed and when alumina was added to the tank (10 g/L), the flux eventually dropped to 307 gfd (521.9 L/m^2 h). After back flushing the system for the second time, only 40% of the initial flux was recovered and the membrane was fouled.

As it is seen in Figure 5.37 the flux during the second run was relatively more stable than that in the initial run. The membrane was not back washed after the initial water flux measurement prior to the initial run; however, it was backwashed prior to the second run. With backwash of the membrane after the initial run, the porosity might have increased which would explain the higher flux during the second run.

It should be noted that the ENKA membrane had a flux of 307 gfd (521.9 L/m^2 h). The alumina used for this test was CP-1.5 with an average particle size of 1.5 μm with a particle size distribution including particles smaller than 1.5 μm which can get into the pores of the membrane and plug them. The other factor that should be considered is that in a system which would allow very high linear speed of the feed along the membrane surface the pore plugging and fouling might be significantly reduced. The linear speed of the feed in the test system varied between 1 to about 6 m/s; therefore, higher linear speeds than that obtained in the test might be required. The choice of alumina, the alumina concentration required and economic considerations such as module and pumping costs, would determine the applicability of the ENKA membrane.

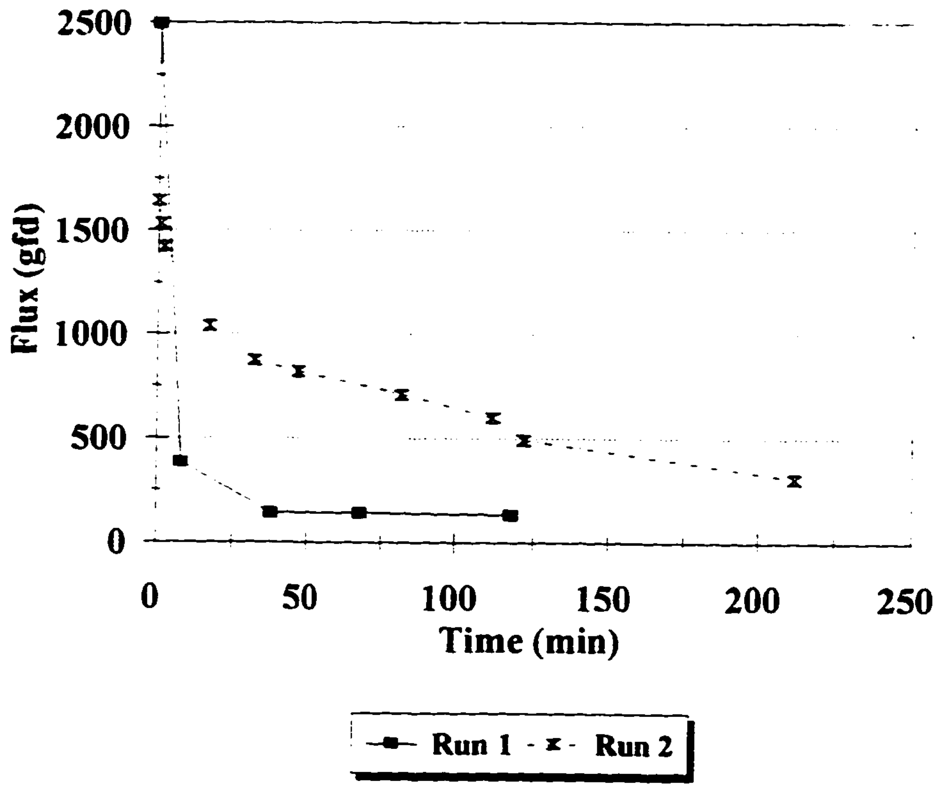


Figure 5.37. Plot of flux versus time for ENKA tubular membrane at 10 g/L of activated alumina.

5.10.2. ZeeWeed™ Flux Data

The experimental procedure for this part of the tests is outlined in section 4.5.5.2 and a diagram of the experimental setup has been presented in Figure 4.7. The ZeeWeed™ membrane was initially placed in a tank containing 150 L of RO water and the pure water flux was determined to be 56 gfd (95.2 L/m^2 h) at 25 °C. The results of the ZeeWeed™ tests are presented in Table B-63 In Appendix B. The ZeeWeed™ had a membrane area of 0.5 m^2 and pore size of 200,000 molecular weight cut off. The pressure difference required for water permeation was generated by a vacuum pump generating a 10 inHg vacuum. The activated alumina particles were kept in suspension by mixing, produced by an aerator injected with air at flowrate of 100 cfh.

Activated alumina was added to the tank to generate a 3 g/L suspension. The permeate flux had an initial drop to 48.58 gfd (82.59 L/m^2 h) from the initial 56.12 gfd (95.40 L/m^2 h), upon the addition of alumina and a further drop to 41.06 gfd (69.80 L/m^2 h) in the water flux was observed in the next 15.4 hrs.

Activated alumina additions were made to increase the alumina concentration to 6, 12, 14, 25, 35, 50, and 60 g/L. Before any alumina addition the membrane was cleaned through a procedure called "relaxation cleaning" which is aerating the membrane without applying the vacuum. The permeate flux change with alumina concentration change are presented in Figure 5.38. At concentrations of higher than 60 g/L significant drops in flux were observed in very short periods of time, but the water flux could be recovered by relaxation cleaning of the membrane.

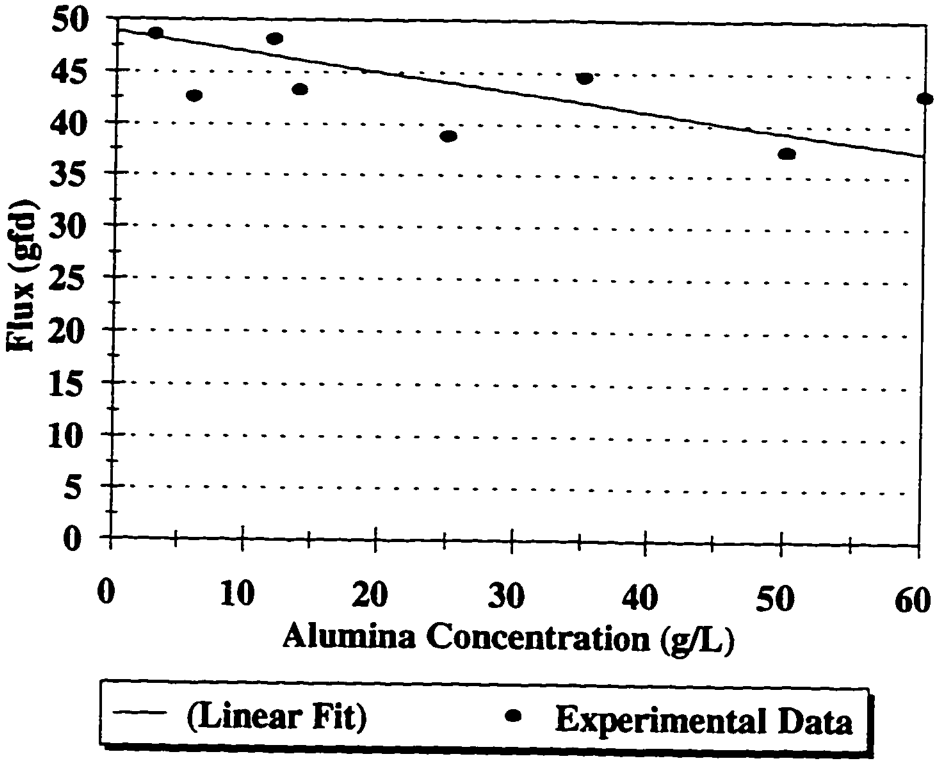


Figure 5.38. Plot of flux versus time for ZeeWeed™ membrane at different concentrations of activated alumina.

5.11.3. Summary of Membrane Separation Experiments

Two different membrane systems were tested and evaluated for the separation of the finely dispersed activated alumina particles from the adsorption mixture. The conventional tubular ENKA membrane showed a significant drop in its initial pure water flux due to the plugging of its pores, but maintained a flux of 307 gfd (521.9 L/m^2 h).

Without any costing information and actual operating data for both systems with actual wastewater, it is impossible to positively recommend one system over the other based on the available data. However, the ENKA modula should be operated below 10 g/L alumina. Since tubular membrane systems require pumping of the slurry through the membrane and as a result these modules are susceptible to pump failure.

The ZeeWeed ™ membrane did not foul severely and its smaller pores are less susceptible to plugging. The system does not require direct pumping of the slurry through the membrane which offers considerable operating advantage.

CHAPTER 6

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. CONCLUSIONS

The following conclusions were made based on the results of the present work:

- The process studied demonstrated significant potential for treatment of arsenic contaminated water with adsorption on activated alumina. Residual arsenic concentrations below drinking water criteria were achieved within 10 minutes, from initial arsenic levels of >40 mg/L.

- The pH significantly affects the arsenic uptake in the adsorption process. The pH range of 2 to 5 was found to be the optimum pH range for the adsorption process with pH 3 resulting in slightly better arsenic removal. Maintaining a constant pH resulted in higher arsenic removal. During the adsorption process, the overall rate of arsenic uptake was higher at lower pH's. The results indicated that arsenic adsorption onto activated alumina takes place via both physical adsorption and chemisorption. The degree of contribution of each of these mechanisms to arsenic uptake is affected by the pH, which dictates the surface charge of alumina as well as the speciation of the arsenate anion.

- Study of the adsorption kinetics indicated that the Elovich model can describe the adsorption process at pH values of greater than pH 6. At lower pH values the rate of adsorption was very fast for any of the kinetic models considered to describe the process. More data in the first 5 minutes of the process would be required.

- A study of the effect of particle and pore size on the arsenic removal indicated that a smaller particle size and higher pore area is a desirable combination. The results also showed that the particle size effect can become less significant if the alumina sample has a large pore area.

- Screening commercially available alumina samples from ALCOA Ltd. showed that they can be applied for arsenic removal from contaminated water. ALCOA's CPN-325 was found to be the best sample among the ones tested. The more amorphous alumina samples performed better. The order of the samples tested with respect to performance was:
  CPN-325 > CP-5 > CP-1.5 > CPN-100 > F1-100 > CP-100 >HTC-100 > CG-20

- Study of the effect sulphate showed that the degree of arsenic removal is significantly affected at sulphate levels of greater than 100 mg/L. Comparison of arsenic removal from an actual contaminated water with the removals achieved with synthetic water samples indicated that the process can be inhibited by the presence of other ions in the water. This means that arsenic adsorption by activated alumina is not a highly selective process.

- Study of the initial arsenic concentration on the degree of arsenic removal showed that the rate of arsenic uptake increases with increasing initial concentration; however, the residual arsenic concentration also increases which implies that either a saturation effect is present or another limiting factor such as diffusion is inhibiting the process at higher initial concentrations.

- Adsorbent regeneration studies showed that spent alumina can be regenerated and reused. Spent alumina was regenerated by sodium hydroxide solution at pH 12 with less than 1.5% alumina loss. Up to 70% of the adsorbed arsenic was desorbed during the regeneration process.

- Settling tests on alumina samples indicated that settling is not a suitable option for the separation of the alumina particles from the adsorption mixture as a stand-alone separation method; however, there is potential for a hybrid process in which settling is the primary method of separation and membrane separation is used as a polishing step. This would reduce the cost of membrane replacement and prolong the life of membranes.

- Tubular ENKA membrane and ZeeWeed™ hollow fibre membranes were tested for alumina separation from water at different alumina concentrations. ENKA membrane had a higher flux than the ZeeWeed™; however, it was more susceptible to flux decline while ZeeWeed™ was less susceptible and more stable. Alumina concentrations of up to 60 g/L were handled.

6.2. RECOMMENDATIONS

The following considerations for future can be useful:

- A revised experimental setup in which automatic sampling and condition control are possible would allow for more accurate and frequent sampling, especially in the first few minutes of the process, allowing for a more accurate study of the process kinetics.

- Effect of the presence of As(III) on the process should be studied and options for pre-treatment such as pre-oxidation of As(III) be investigated, since it is almost always present in real remediation operation.

- Better characterization of alumina samples and use of samples with more controlled physical characteristics would allow for better understanding of the particle and pore size effect on the arsenic removal process. Development of an alumina sample with larger particle size is always more desirable since it makes the materials handling and separation processes simpler.

- The effect of other ions that naturally occur in surface and ground waters and industrial effluents should be studied in more detail.

- A pilot scale test of the adsorption/microfiltration process is recommended for testing it on a large scale during a field trial. This would allow for an accurate economic feasibility study of the process to be carried out.

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APPENDIX A:
LIST OF CHEMICALS AND EQUIPMENT

A-1. Materials and Reagents

Materials and reagents used in this work were as follows:

- Arsenic contaminated water, supplied by Deloro water treatment plant, Deloro, Ontario,
- Activated alumina samples supplied by Aluminum Company of America Ltd., and Scientific Adsorbents Ltd. (Table 4.1),
- Sodium arsenate heptahydrate ($Na_2HAsO_4.7H_2O$), reagent grade (assay: 98-102%), supplied by Caledon Inc. for preparation of synthetic arsenic contaminated water,
- Atomic adsorption standard solution for arsenic determination (assay 1002 ppm); supplied by Caledon Laboratories Ltd.,
- Sodium hydroxide 0.1 N standard solution for acid/base titration, supplied by Caledon Laboratories Ltd.,
- Sodium hydroxide pellets (assay 97%), supplied by Caledon laboratories Ltd.,
- Nitric acid (assay 70 %), reagent grade, supplied by Caledon Laboratories Ltd.,
- Hydrochloric acid (assay 37 %), reagent grade, supplied by Caledon Laboratories Ltd.,
- Sodium borohydride, reagent grade (assay min 95%), supplied by caledon Laboratories Ltd.,
- Pressurized air,
- Nitrogen gas, supplied by Matheson gas,
- Acetylene gas, supplied by Matheson gas,
- Anhydrous sodium sulphate, reagent grade (assay 98%), supplied by Caledon Laboratories Ltd.,
- Milli-Q water (18 MΩ), generated by Milli-Q plus system by Millipore, with deionized water feed, and
- Buffer solutions of pH 4, 7, and 10, supplied by Caledon Laboratories Ltd.

Table A.1. List of activated alumina samples used in the adsorption experiments.

Alumina	Manufacturer
100um, 300A, basic	Scientific Adsorbents
100um, 200A, basic	Scientific Adsorbents
100um, 50-100A, basic	Scientific Adsorbents
10um, 50-100A, basic	Scientific Adsorbents
20-30um, 300A, basic	Scientific Adsorbents
F1-100	ALCOA
CG-20	ALCOA
CPN-100	ALCOA
CPN-325	ALCOA
CP-1.5	ALCOA
CP-5	ALCOA
CP-100	ALCOA

A-2. Equipment

- Six paddle stirrer Model 7790-400 by Phipps & Bird with Teflon coated paddles,
- Type 47900 muffle furnace, supplied by Thermolyne Inc.,
- Variable speed shaker, 115 Volts, 50/60 Hz, supplied by Eberbach Corporation,
- Cole Parmer pH metre (resolution 0.01),
- Acrodisc polysulphone microfiltration syringe filters (0.45 μ), Product No. 4473, supplied by Gelman Scientific Inc.,
- 3 mL plastic syringe,
- Eppendorf pipettes, 10-100 μL, 100-1000 μL, and 5 mL,
- 120 ml plastic bottles with caps,
- 20 ml polyethylene vials,
- Zenon's ZeeWeed^{TM} microfiltration membrane system (including hosing, container, piping, and pumps)
- Microfiltration membrane (tubular microfiltration ENKA module equipped with 0.2 μm polypropylene membrane),
- Other microfiltration equipment (pumps, pressure gauges, regulating valves; piping, etc.),
- Micromeritics nitrogen sorption porosimeter (Micromeritics, Model ASAP 2000),
- liquid nitrogen,

- Perkin Elmer, model 3100 Atomic absorption spectrometer (Air-Acetylene flame),
- Perkin Elmer MHS-10 Mercury/Hydride system,
- Perkin Elmer EDL System 2 (Electrodeless discharge arsenic lamp with power supply),
- drying oven,
- laboratory scales (0.0001 g resolution),
- glassware (100 mL, 250 mL, 500 mL and 1000 mL volumetric flasks, glass funnels, 600 mL beakers, porcelain crucibles, burettes, 250 mL Erlenmeyer flasks.),
- Desiccator,
- Flowmeter,
- Vacuum pump,
- Aearator,
- ZeeWeed™ and ENKA membrane modules,
- Thermometer, and
- Air blower.

APPENDIX B:
EXPERIMENTAL DATA

B-1. EFFECT OF pH ON THE ARSENIC UPTAKE

B-1.1. Results of pH Experiments With no pH Control

Table B-1. Residual arsenic concentration (mg/L) with time at pH 1, 3, and 7, 3 g/L of 50-212 µm alumina, 23 °C with no pH control.

Time (min)	pH		
	1	3	7
	Arsenic Concentration (mg/L)		
0	33468.75	31875	33787.5
5	26460	9180	26456.25
10	19890	7905	25818.75
20	20145	7140	25181.25
40	18870	5406	21993.75
60	18870	4539	23906.25
120	18360	2847.5	21675
360	17850	1551	21196.88
1440	13843	497.25	24225
2880	7686.4	520	22695

Table B-2. Initial and final pH of reaction mixture during pH experiments in the absence of pH control.

pH		
Initial	**Final**	**Change**
1	1.01	0.01
2.98	4.08	1.1
6.9	7.69	0.79

B-1.2. Results of pH Experiments With pH Control for pH 1, 3, 4, 6, and 8.

Table B-3. Residual arsenic concentration (mg/L) with time at pH 1, 3 g/L of 50-212 µm alumina, 23 °C with pH control with addition of 70% nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	34		
5	25.4	25.29	0
10	19.4	42.94	0
20	18.7	45.00	0
30	18.1	46.76	0
40	18.1	46.76	0
60	14.8	56.47	0
120	15	55.88	0
240	12	64.71	0
360	12	64.71	0

Table B-4. Residual arsenic concentration (mg/L) with time at pH 3, 3 g/L of 50-212 µm alumina, 23 °C with pH control with addition of 70% nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	23.7		
5	6.3	73.42	0
10	2.3	90.30	0
20	1.3	94.51	20
30	0.45	98.10	0
40	0.27	98.86	0
60	0.17	99.28	0
120	0.17	99.28	10
240	0.09	99.62	5
360	0.05	99.79	10

Table B-5. Residual arsenic concentration (mg/L) with time at pH 4, 3 g/L of 50-212 µm alumina, 23 °C with pH control with addition of 70% nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	24.6		
5	20.5	16.67	0
10	9.3	62.20	10
20	4.1	83.33	0
30	1.4	94.31	0
40	0.78	96.83	<<5
60	0.35	98.58	0
120	0.14	99.43	5
240	0.08	99.67	35
360	0.08	99.67	120

Table B-6. Residual arsenic concentration (mg/L) with time at pH 6, 3 g/L of 50-212 µm alumina, 23 °C with pH control with addition of 70% nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	23.2		
5	16.6	28.45	5
10	14.9	35.78	0
20	12	48.28	<<5
30	9.1	60.78	0
40	8.2	64.66	<<5
60	8.5	63.36	5
120	4.7	79.74	0
240	3.4	85.34	0
360	2.5	89.22	10

Table B-7. Residual arsenic concentration (mg/L) with time at pH 7, 3 g/L of 50-212 µm alumina, 23 °C with pH control with addition of 70% nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	26.8		
5	23.8	11.19	5
10	21.3	20.52	0
20	20.5	23.51	0
30	19	29.10	0
40	16.1	39.93	0
60	15.2	43.28	<<5
120	12.5	53.36	0
240	11.4	57.46	0
360	8.5	68.28	<<5

Table B-8. Residual arsenic concentration (mg/L) with time at pH 8, 3 g/L of 50-212 µm alumina, 23 °C with pH control with addition of 70% nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	26.3		
5	25.9	1.52	0
10	24.7	6.08	0
20	23.6	10.27	<5
30	22.8	13.31	<5
40	22.8	13.31	0
60	21.3	19.01	0
120	19.6	25.48	<<5
240	14.6	44.49	0
360	8.4	68.06	0

B-1.3. Results of pH Experiments With pH Control for pH 2, 2.5, 3, 3.5, and 4.

Table B-9. Residual arsenic concentration (mg/L) with time at pH 2, 3 g/L of 50-212 µm alumina, 23 °C with pH control with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	26		
5	9.1	65	0
10	3.9	85	0
20	1.76	93.23	0
30	1	96.15	0
40	0.74	97.15	30
60	0.43	98.35	1000
120	0.28	98.92	1300
240	0.17	99.35	700
360	0.13	99.5	0

Table B-10. Residual arsenic concentration (mg/L) with time at pH 2.5, 3 g/L of 50-212 µm alumina, 23 °C with pH control with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	26		
5	2.5	90.38	710
10	2.7	89.62	550
20	1.1	95.77	900
30	0.73	97.19	200
60	0.22	99.15	400
120	0.07	99.73	600
240	0.04	99.85	1300
360	0.04	99.85	200

Table B-11. Residual arsenic concentration (mg/L) with time at pH 3, 3 g/L of 50-212 µm alumina, 23 °C with pH control by addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	27		
5	8	70.37	700
10	3.7	86.3	300
20	0.84	96.89	400
30	0.34	98.74	0
40	0.23	99.15	500
60	0.15	99.44	200
120	0.08	99.7	600
240	0.06	99.78	750
360	0.05	99.81	600

Table B-12. Residual arsenic concentration (mg/L) with time at pH 3.5, 3 g/L of 50-212 µm alumina, 23 °C with pH control by addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	23		
5	8.9	67.04	1300
10	3.5	87.04	400
20	1.83	93.22	200
30	0.69	97.44	200
40	0.37	98.63	100
60	0.19	99.3	100
120	0.08	99.7	200
240	0.05	99.81	650
360	0.03	99.89	300

Table B-13. Residual arsenic concentration (mg/L) with time at pH 4, 3 g/L of 50-212 µm alumina, 23 °C with pH control by addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	26		
5	13	51.85	900
10	8.65	67.96	300
20	5.2	80.74	450
30	2.5	90.74	100
40	1.45	94.63	100
60	0.57	97.89	100
120	0.32	98.81	200
240	0.06	99.78	150
360	0.04	99.85	50

B-1.4. Results of pH Experiments With pH Control for pH values 2, 3, 4 and 5 Using a Commercial alumina.

Table B-14. Residual arsenic concentration (mg/L) with time at pH 2, 3 g/L of CPN-325 alumina, 23 °C with pH control by addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Vol.Acid Added µL
0	43		
5	0.53	98.77	8900
10	0.37	99.14	5000
20	0.35	99.19	0
30	0.21	99.51	0
40	0.2	99.53	0
60	0.18	99.58	0
90	0.15	99.65	0
120	0.14	99.67	0

Table B-15. Residual arsenic concentration (mg/L) with time at pH 3, 3 g/L of CPN-325 alumina, 23 °C with pH control by addition of 0.142 N nitric acid.

Time min	[As] (mg/L)	%As removal	Volume Acid Added µL
0	43		
5	0.3	99.30	300
10	0.02	99.95	0
20	0.01	99.98	800
30	0.01	99.98	500
40	0.01	99.98	400
60	0.01	99.98	0
90	0.01	99.98	0
120	0.01	99.98	0

Table B-16. Residual arsenic concentration (mg/L) with time at pH 4, 3 g/L of CPN-325 alumina, 23 °C with pH control by addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	43		
5	0.15	99.65	5200
10	0.11	99.74	0
20	0.05	99.88	200
30	0.04	99.91	200
40	0.06	99.86	100
90	0.1	99.77	100
120	0.04	99.91	300

Table B-17. Residual arsenic concentration (mg/L) with time at pH 5, 3 g/L of CPN-325 alumina, 23 °C with pH control by addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	43		
5	0.44	98.98	2400
10	0.14	99.67	200
20	0.08	99.81	0
30	0.03	99.93	100
40	0.02	99.95	0
60	0.02	99.95	0
90	0.01	99.98	0
120	0.01	99.98	0

B-2. STUDY OF PARTICLE AND PORE SIZE EFFECTS ON ARSENIC UPTAKE

Table B-18. Residual arsenic concentration with time at pH 3, 3 g/L of 100µm-300Å alumina and 23 °C, at controlled pH by addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	24		
5	0.42	98.25	1850
10	0.13	99.46	500
20	0.04	99.83	700
30	0.03	99.88	600
40	0.014	99.42	600
60	0.016	99.33	700
120	0.02	99.92	1700
240	0.07	99.71	2200
360	0.04	99.83	1400

Table B-19. Residual arsenic concentration with time at pH 3, 3 g/L of 100µm-200Å alumina and 23 °C, at controlled pH by addition of 0.142 N nitric acid.

Time min	**[As] mg/L**	**%As removal**	**Volume Acid Added µL**
0	28		
10	0.6	97.86	1900
20	0.3	98.93	800
30	0.25	99.11	300
40	0.2	99.29	500
60	0.17	99.39	200
120	0.18	99.36	600
240	0.17	99.39	1700
360	0.15	99.46	700

Table B-20. Residual arsenic concentration with time at pH 3, 3 g/L of 100µm-50-100Å alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	**[As] mg/L**	**%As removal**	**Volume Acid Added µL**
0	26		
5	3.4	86.92	1500
10	0.74	97.15	500
20	0.28	98.92	400
30	0.18	99.31	300
40	0.19	99.27	400
60	0.16	99.38	300
120	0.08	99.69	700
360	0.07	99.73	2000

Table B-21. Residual arsenic concentration with time at pH 3, 3 g/L of 20-30µm-300Å alumina and 23 °C at controlled pH by addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	24		
5	0.18	99.31	2100
10	0.04	99.85	600
20	0.02	99.92	800
30	0.02	99.92	600
40	0.02	99.92	500
60	0.05	99.81	1000
240	0.01	99.96	3000
360	0.02	99.92	1400

Table B-22. Residual arsenic concentration with time at pH 3, 3 g/L of 10µm-5.300Å alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	23		
5	2	92.31	6400
10	0.83	96.81	0
20	0.8	96.92	1800
30	0.69	97.35	0
40	0.46	98.23	700
60	0.39	98.50	300
120	0.28	98.92	500
240	0.22	99.15	600
360	0.18	99.31	400

B-3. Arsenic Removal Using Commercial Grade Activated Alumina

Table B-23. Residual arsenic concentration with time at pH 3, 3 g/L of CG-20 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	**[As] mg/L**	**%As removal**	**Volume Acid Added µL**
0	44		
5	9.3	78.86	1400
10	5.2	88.18	500
20	2.5	94.32	400
30	1.6	96.36	200
40	1.1	97.50	400
60	1.1	97.50	0
90	1.1	97.50	300
120	0.6	98.64	500

Table B-24. Residual arsenic concentration with time at pH 3, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	**[As] mg/L**	**%As removal**	**Volume Acid Added µL**
0	43		
5	0.3	99.3	3800
10	0.02	99.95	700
20	0.01	99.98	500
30	0.01	99.98	600
40	0.01	99.98	700
60	0.01	99.98	400
90	0.01	99.98	1400
120	0.01	99.98	800

Table B-25. Residual arsenic concentration with time at pH 3, 3 g/L of CPN-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	23.9		
5	0.6	97.49	1900
10	0.31	98.7	600
20	0.16	99.33	0
30	0.11	99.54	1000
40	0.18	99.25	400
60	0.07	99.71	400
90	0.055	99.77	500
120	0.04	99.83	300

Table B-26. Residual arsenic concentration with time at pH 3, 3 g/L of CP-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	34		
5	4.8	85.88	2900
10	1.6	95.29	0
20	0.46	98.65	1200
30	0.23	99.32	0
40	0.16	99.53	0
60	0.09	99.74	0
90	0.07	99.79	900
120	0.05	99.85	300

Table B-27. Residual arsenic concentration with time at pH 3, 3 g/L of CP-5 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	44		
5	0.3	99.32	2500
10	0.1	99.77	600
20	0.05	99.89	600
30	0.04	99.91	600
40	0.03	99.93	0
60	0.03	99.93	600
90	0.02	99.95	300
120	0.01	99.98	100

Table B-28. Residual arsenic concentration with time at pH 3, 3 g/L of HTC-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	45		
5	8.4	81.33	5800
10	3.9	91.33	3300
20	1.3	97.11	4000
30	0.9	98	4500
40	0.9	98	6000
60	0.7	98.44	4800
90	0.6	98.67	3000
120	0.6	98.67	2000

Table B-29. Residual arsenic concentration with time at pH 3, 3 g/L of CP-1.5 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	44		
5	0.488	98.89	1600
10	0.19	99.57	300
20	0.115	99.74	800
30	0.08	99.82	300
40	0.06	99.86	400
60	0.05	99.89	400
90	0.04	99.91	700
120	0.04	99.91	300

Table B-30. Residual arsenic concentration with time at pH 3, 3 g/L of F1-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	38		
5	4.1	89.21	2500
10	0.9	97.63	800
20	0.5	98.68	400
30	0.4	98.95	400
40	0.3	99.21	400
60	0.2	99.47	500
90	0.2	99.47	400
120	0.1	99.74	500

Table B-31. Residual arsenic concentration with time at pH 3, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	22		
5	0.05	99.77	4100
10	0.05	99.77	800
20	0.04	99.82	1000
30	0.03	99.86	400
40	0.02	99.91	600
60	0.02	99.91	1100
90	0.015	99.93	200
120	0.009	99.96	400

B-4. EFFECT OF COMPETITION OF OTHER IONS ON ARSENIC UPTAKE

Table B-32. Residual arsenic concentration with time at pH 3, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid in the absence of sulphate.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	46		
5	0.3	99.35	3800
10	0.02	99.96	700
20	0.01	99.98	500
30	0.01	99.98	600
40	0.01	99.98	700
60	0.01	99.98	400
90	0.01	99.98	1400
120	0.01	99.98	800

Table B-33. Residual arsenic concentration with time at pH 3, 10 mg/L of sulphate, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	**[As] mg/L**	**%As removal**	**Volume Acid Added µL**
0	46		
5	0.4	99.13	3800
10	0.03	99.93	1100
20	0.02	99.96	900
30	0.02	99.96	600
40	0.02	99.96	800
60	0.01	99.98	900
90	0.01	99.98	900
120	0.01	99.98	500

Table B-34. Residual arsenic concentration with time at pH 3, 30 mg/L of sulphate, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	**[As] mg/L**	**%As removal**	**Volume Acid Added µL**
0	46		
5	0.3	99.35	5500
10	0.06	99.87	700
20	0.04	99.91	900
30	0.03	99.93	1000
60	0.02	99.96	1200
90	0.02	99.96	600
120	0.02	99.96	700

Table B-35. Residual arsenic concentration with time at pH 3, 50 mg/L of sulphate, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added μL
0	46		
5	0.5	98.91	3500
10	0.3	99.35	1300
20	0.2	99.57	1400
30	0.2	99.57	900
40	0.2	99.57	0
60	0.2	99.57	1500
90	0.2	99.57	1200
120	0.15	99.67	0

Table B-36. Residual arsenic concentration with time at pH 3, 100 mg/L of sulphate, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added μL
0	46		
5	2.6	94.35	6500
10	2	95.65	1800
20	1.8	96.09	1400
30	1.6	96.52	700
40	1.4	96.96	600
60	1.3	97.17	800
90	1	97.83	300
120	1	97.83	900

Table B-37. Residual arsenic concentration with time at pH 3, 300 mg/L of sulphate, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	46		
5	6.9	85.00	8400
10	6.5	85.87	1300
20	5.6	87.83	1000
30	5.3	88.48	400
40	4.9	89.35	200
60	4.3	90.65	300
90	4	91.30	900
120	3.8	91.74	800

Table B-38. Residual arsenic concentration with time at pH 3, 600 mg/L of sulphate, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	46		
5	9.2	80.00	8300
10	8.3	81.96	1300
20	7.8	83.04	1300
30	7.2	84.35	1300
40	7	84.78	600
60	6.9	85.00	700
90	6.4	86.09	800
120	6.1	86.74	600

B-4.1. Comparison of Arsenic Removal with Actual and Synthetic Arsenic Contaminated Water.

Table B-39. Residual arsenic concentration with time for actual contaminated water from Deloro, Ontario, at pH 3, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	54		
5	16.3	69.81	8800
10	17.3	67.96	1500
30	15.3	71.67	1800
40	13.8	74.44	700
60	12.1	77.59	800
90	10.1	81.30	0
120	10	81.48	1000

Table B-40. Residual arsenic concentration with time for synthetic contaminated water, at pH 3, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	55		
5	5.3	90.36	5500
10	0.1	99.82	1100
20	0.07	99.87	0
30	0.05	99.91	500
40	0.02	99.96	500
60	0.03	99.95	1000
90	0.04	99.93	1000
120	0.03	99.95	400

B-5. EFFECT OF INITIAL ARSENIC CONCENTRATION ON ARSENIC UPTAKE

Table B-41. Residual arsenic concentration with time at pH 3, 2 mg/L initial arsenic concentration, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	2		
5	0.01	99.50	2700
10	0.01	99.90	1100
20	0.01	99.80	1700
30	0.01	99.80	1000
40	0.01	99.55	1000
60	0.01	99.50	1700
90	0.01	99.50	0
120	0.01	99.60	400

Table B-42. Residual arsenic concentration with time at pH 3, 22 mg/L initial arsenic concentration, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	22		
5	0.01	99.95	5900
10	0.008	99.96	1100
20	0.008	99.96	1400
30	0.005	99.98	0
40	0.009	99.96	0
60	0.003	99.99	0
90	0.003	99.99	1000
120	0.01	99.95	700

Table B-43. Residual arsenic concentration with time at pH 3, 43 mg/L initial arsenic concentration, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	43		
5	0.3	99.30	3800
10	0.02	99.95	700
20	0.01	99.98	500
30	0.01	99.98	600
40	0.01	99.98	700
60	0.01	99.98	400
90	0.01	99.98	1400
120	0.01	99.98	800

Table B-44. Residual arsenic concentration with time at pH 3, 89 mg/L initial arsenic concentration, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	89		
5	2.5	97.19	7300
10	2	97.75	800
20	1.7	98.09	1100
30	1.1	98.76	0
40	1.2	98.65	600
60	0.8	99.10	700
90	0.8	99.10	900
120	0.4	99.55	800

Table B-45. Residual arsenic concentration with time at pH 3, 132 mg/L initial arsenic concentration, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	132		
5	22.4	83.03	5700
10	24	81.82	1400
20	20.6	84.39	1500
30	19.5	85.23	1200
40	19.3	85.38	0
60	18.7	85.83	100
90	16	87.88	0
120	14.6	88.94	0

Table B-46. Residual arsenic concentration with time at pH 3, 177 mg/L initial arsenic concentration, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	%As removal	Volume Acid Added µL
0	177		
5	57.4	67.57	7100
10	54	69.49	1400
20	52.8	70.17	1800
30	51	71.19	0
40	49	72.32	0
60	47.2	73.33	0
90	43.8	75.25	0
120	41.4	76.61	0

B-6. DETERMINATION OF ADSORPTION ISOTHERM

Table B-47. Residual arsenic concentration and alumina arsenic loading after 1 day at pH 3, at different initial arsenic concentrations, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of concentrated nitric acid.

[As] initial mg/L	C_e mg/L	qe mg As/g Alumina
15	1.86	4.37
70	1.8	21.47
100	3.84	31.52
170	9.3	51.83
260	37.6	75.47
480	145	110.33
550	220	110.67
1050	617	144.33

Table B-48. Residual arsenic concentration and alumina arsenic loading after 3 day s at pH 3, at different initial arsenic concentration, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of concentrated nitric acid.

[As] initial mg/L	C_e mg/L	qe mg As/g Alumina
15	3.26	3.90
70	1.9	21.43
100	3.16	31.75
170	0.67	54.71
260	31.6	77.47
480	131	115.00
550	222	110.00
1050	638	137.33

Table B-49. Residual arsenic concentration and alumina arsenic loading after 7 day s at pH 3, at different initial arsenic concentration, 3 g/L of CPN-325 alumina and 23 °C at controlled pH with addition of concentrated nitric acid.

[As] initial mg/L	C_e mg/L	qe mg As/g Alumina
15	0.74	4.74
70	0.72	21.83
100	1.78	32.21
170	9.3	51.83
260	40.4	74.53
550	208	114.67
1050	664	128.67

B-7. ADSORBENT REGENERATION STUDY

B-7.1. Comparison of Fresh versus Sulphate Loaded Alumina

Table B-50. Residual arsenic concentration with time at pH 3, 3 g/L of 20-30µm-300Å alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	% As removal	Volume Acid Added µL
0	24.1		
5	0.182	99.2448	2100
10	0.04	99.8340	600
20	0.02	99.9170	800
30	0.02	99.9170	600
40	0.02	99.9170	500
60	0.05	99.7925	1000

Table B-51. Residual arsenic concentration with time at pH 3, 3 g/L of sulphate loaded 20-30μm-300Å alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid.

Time min	[As] mg/L	% As removed	Volume Acid Added μL
0	24.09		
5	8.965	62.79	6200
10	7.37	69.41	1000
20	5.555	76.94	1000
30	5.115	78.77	600
40	4.73	80.37	200
60	3.85	84.02	500

B-7.2. RESULTS OF ARSENIC REMOVAL AFTER ALUMINA REGENERATION AT DIFFERENT pH

Table B-52. Residual arsenic concentration with time at pH 3, 3 g/L of HTC-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid - initial run for the regeneration test at pH 10.

Time min	[As] mg/L	% As removed	Volume Acid Added μL
0	42.5		
5	1.2	97.18	6800
10	0.4	99.06	3300
20	0.1	99.76	4000
30	0.08	99.81	4500
40	0.2	99.53	6000
60	0.1	99.76	4800
90	0.06	99.86	3000
120	0.05	99.88	2000

Table B-53. Residual arsenic concentration with time at pH 3, 3 g/L of HTC-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid - second run after regeneration at pH 10.

Time min	[As] mg/L	% As removed	Volume Acid Added µL
0	46		
5	7.7	81.88	2100
10	3.2	92.47	900
20	1.1	97.41	600
30	0.7	98.35	500
40	0.9	97.88	300
60	0.4	99.06	500
90	0.4	99.06	300
120	0.25	99.41	400

Table B-54. Residual arsenic concentration with time at pH 3, 3 g/L of HTC-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid -third run after regeneration at pH 10.

Time min	[As] mg/L	% As removed	Volume Acid Added µL
0	52		
5	4.2	90.12	2400
10	3.3	92.24	800
20	1.8	95.76	800
30	1.6	96.24	600
40	1.5	96.47	600
60	1.5	96.47	600
90	1.8	95.76	900
120	1.5	96.47	600

Table B-55. Residual arsenic concentration with time at pH 3, 3 g/L of HTC-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid - initial run for the regeneration test at pH 12.

Time min	[As] mg/L	% As removed	Volume Acid Added µL
0	42		
5	1.1	97.41	12700
10	0.8	98.12	5500
20	0.4	99.06	6200
30	0.3	99.29	3000
40	0.2	99.53	4000
60	0.1	99.76	3000
90	0.1	99.76	2500
120	0.1	99.76	2000

Table B-56. Residual arsenic concentration with time at pH 3, 3 g/L of HTC-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid - second run after regeneration at pH 12.

Time min	[As] mg/L	% As removed	Volume Acid Added µL
0	46		
5	2.2	94.82	4100
10	0.95	97.76	900
30	0.5	98.82	1700
40	0.5	98.82	500
60	0.5	98.82	800
90	0.7	98.35	1000
120	0.4	99.06	800

Table B-57. Residual arsenic concentration with time at pH 3, 3 g/L of HTC-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid - third run after regeneration at pH 12.

Time min	[As] mg/L	% As removed	Volume Acid Added µL
0	45		
5	8.4	80.24	3000
10	3.9	90.82	500
20	1.3	96.94	600
30	0.9	97.88	300
40	0.9	97.88	300
60	0.7	98.35	700
90	0.6	98.59	600
120	0.6	98.59	500

Table B-58. Residual arsenic concentration with time at pH 3, 3 g/L of HTC-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid - initial run for the regeneration test at pH 13.

Time min	[As] mg/L	% As removed	Volume Acid Added µL
0	41		
5	1	97.65	9300
10	0.6	98.59	5000
20	0.2	99.53	5900
30	0.2	99.53	2000
40	0.1	99.76	2000
60	0.05	99.88	2000
90	0.03	99.93	2000
120	0.03	99.93	4000

Table B-59. Residual arsenic concentration with time at pH 3, 3 g/L of HTC-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid - second run after regeneration at pH 13.

Time min	[As] mg/L	% As removed	Volume Acid Added µL
0	48		
5	3.5	91.76	4500
10	0.5	98.82	1200
20	0.8	98.12	900
30	0.3	99.29	800
40	1.1	97.41	700
60	0.2	99.53	800
90	0.1	99.76	1100
120	0.2	99.53	1100

Table B-60. Residual arsenic concentration with time at pH 3, 3 g/L of HTC-100 alumina and 23 °C at controlled pH with addition of 0.142 N nitric acid - third run after regeneration at pH 13.

Time min	[As] mg/L	% As removed	Volume Acid Added µL
0	49		
5	5.2	87.76	4800
10	1.7	96.00	900
20	1.3	96.94	600
30	1	97.65	700
40	0.7	98.35	400
60	0.4	99.06	700
90	0.3	99.29	700
120	0.3	99.29	700

Table B-61. % arsenic desorption after regeneration of spent alumina with sodium hydroxide at pH 10, 12, and 13, after 1 hour contact.

Regeneration #	[As] mg/L at end of regeneration	pH	Initial q mg As/g alumina	final q mg As/g alumina	% As Desorbed
1	86	10	14.15	5.97	57.8
2	91	10	15.33	5.04	67
1	82	12	13.97	6.00	57.05
2	91	12	15.2	3.89	74.40
1	102	13	13.66	4.36	68.08
2	138	13	15.93	0.141	99.11

B-7.3. RESULTS OF ARSENIC DESORPTION AND ALUMINA LOSS AT pH 11, 12, AND 13

Table B-62. Residual arsenic concentration and alumina loss with time for spent alumina regeneration at pH 11.

Time min	[As] mg/L in solution	q mg As/g AA	% As desorbed	[Al] mg/L	% Al loss
0	35	46.2	0		0
15	440	25.97	43.78		
30	450	25.47	44.86		
45	470	24.48	47.02		
60	490	23.48	49.19		
75	490	23.48	49.19	100	0.5
90	500	22.98	50.27		
115	520	21.98	52.43		
135	520	21.98	52.43	110	0.55
155	540	20.98	54.59		
175	530	21.48	53.51		
195	530	21.48	53.51	110	0.55
210	530	21.48	53.51		
225	540	20.98	54.59		
240	530	21.48	53.51		
255	540	20.98	54.59	110	0.55

Table B-63. Residual arsenic concentration and alumina loss with time for spent alumina regeneration at pH 12.

Time min	[As] mg/L in solution	q mg As/g AA	% As desorbed	[Al] mg/L	% Al loss
0	12	45.85	0		0
15	530	19.98	56.42		
30	530	19.98	56.42		
45	560	18.48	59.69		
60	570	17.98	60.78	260	1.3
75	560	18.48	59.69		
90	560	18.48	59.69		
105	570	17.98	60.78		
120	570	17.98	60.78	260	1.3
135	560	18.48	59.69		
150	580	17.48	61.87		
170	590	16.98	62.96	260	1.3
185	590	16.98	62.96		
200	580	17.48	61.87		
215	570	17.98	60.78		
230	580	17.48	61.87	270	1.35

Table B-64. Residual arsenic concentration and alumina loss with time for spent alumina regeneration at pH 12.

Time min	[As] mg/L in solution	q mg As/g AA	% As desorbed	[Al] mg/L	% Al loss
0	30	46.95	0	0	0
10	500	23.48	50.00		
20	540	21.48	54.25		
30	560	20.48	56.38		
40	570	19.98	57.44		
50	600	18.48	60.64		
60	640	16.48	64.89		
70	630	16.98	63.83	520	2.6
80	650	15.98	65.96		
90	630	16.98	63.83		
100	660	15.48	67.02		
110	640	16.48	64.89		
120	660	15.48	67.02		
130	620	17.48	62.76	570	2.85
140	620	17.48	62.76		
150	620	17.48	62.76		
155	690	13.99	70.21		
180	620	17.48	62.76		
195	640	16.48	64.89	630	3.15
205	690	13.99	70.21		
215	610	17.98	61.70		
225	630	16.98	63.83		
235	680	14.49	69.15		
245	630	16.98	63.83		
255	610	17.98	61.70	620	3.1

Table B-65. Arsenic residual concentration at pH 3 for arsenic adsorption prior to regeneration of the spent alumina at pH 11, 12, and 13.

Test	Initial [As] mg/L	Final [As] mg/L	% As Removed
pH 11 test	960	35	96.35
pH 12 test	930	12	98.70
pH 13 test	970	30	96.90

B-8. ACTIVATED ALUMINA SETTLING TEST

Table B-66. Activated alumina settling test for CP-1.5 and HTC-100.

Time (min)	Bed Volume (mL)		Bed Height (mm)		Clear Volume (mL)		Settling Rate (mm/min)	
	CP-1.5	HTC-100	CP-1.5	HTC-100	CP-1.5	HTC-100	CP-1.5	HTC-100
0	250	350	205	205	0	0		
1.5	249	246	204	202	0	2	0.67	2
4	245	238	201	195	2	5	1	2.5
7	236	226	193	185	6	10	1.71	2.86
10	227	215	186	176	9	14	1.9	2.9
21	181	172	148	141	28	31	2.71	3.05
29	153	139	125	114	39	44	2.76	3.14
35	145	115	119	94	42	54	2.46	3.17
58	131	60	107	49	48	76	1.69	2.69
74	127	50	104	41	49	80	1.36	2.22
102	126	43	103	35	50	83	1	1.67
110	126	43	103	35	50	83	0.93	1.55
120	126	42	103	34	50	83	0.85	1.43
1085	126	41	103	34	50	84	0.09	0.16
1623	126	41	103	34	50	84	0.06	0.11

B-9. MEMBRANE FILTRATION EXPERIMENTS

B-9.1. Tubular ENKA Flux Data

Table B-67. Results of the membrane filtration experiments for the ENKA tubular membrane.

Date and Time	Pressure (psi)	Temperature (°C)	Feed Flow (gpm)	Permeate Flow (Lpm)	Permeate Flux at T (gfd)	Permeate Flux at 25°C (gfd)
	RO water flux					
1/17/95 12:50	43	21	1	3.4	3,338	3,726
1/17/95 13:10	43	21	2	3	2,946	3,288
1/17/95 13:30	43	21	3	3	2,946	3,288
1/17/95 13:50	43	21	4	2.7	2,651	2,959
1/17/95 14:10	43	21	5	2.3	2,258	2,520
1/17/95 14:30	43	21	6	2.1	2,062	2,301
1/17/95 16:02	**Alumina added to make slurry concentration = 10 g/L**					
1/17/95 16:10	43	21	5.1	0.35	344	384
1/17/95 16:20	43	21	6	0.28	275	307
1/17/95 16:30	43	21	3	0.28	275	307
1/17/95 16:35	43	21	1	0.2	196	219
1/17/95 16:40	43	21	5	0.13	128	142
1/17/95 17:10	43	21	5	0.13	128	142
1/17/95 18:00	43	21	5	0.12	118	132
1/17/95 18:10	**MF stopped; the system washed with RO water; RO water flux data:**					
1/17/95 18:20	43	16	6.5	1.5	1,473	1,923
1/17/95 18:30	43	19	5.1	1.8	1,767	2,094
1/17/95 18:35	43	21	3	2.2	2,160	2,411
1/17/95 18:40	43	21	1	2.3	2,258	2,520
1/17/95 18:50	**Test stopped**					
1/18/95 9:30	**Test resumed; RO water flux data:**					
1/18/95 9.35	43	16	6.5	0.8	786	1,025
1/18/95 10:15	43	21	5	0.8	786	877
1/18/95 10:30	43	21	5	0.75	736	822
1/18/95 11:05	43	21	5	0.65	638	712
1/18/95 11:35	43	21	5	0.55	540	603
1/18/95 11:45	43	21	5	0.45	442	493
1/18/95 13:15	43	21	5	0.28	275	307
	MF stopped; The system washed with RO water; RO water flux data:					
1/18/95 13:30	43	21	5	0.28	270	301

B-9.2. ZeeWeed^{TM} Flux Data

Table B-63. Results of the membrane filtration experiments for the ENKA tubular membrane.

Date and Time	Temperature (°C)	Permeate Flow (Lpm)	Permeate Flux at T (gfd)	Permeate Flux at 25°C (gfd)
11/01/94, 14:50	**RO Water Flux**			
11/01/94, 14:50	19	0.67	47.4	56.12
11/01/94, 14:50	**Aeration rate increased to 100 ft^3/hr**			
11/01/94, 15:20	19	0.69	48.8	57.8
11/01/94, 15:45	**Alumina added to make slurry with alumina concentration of 3 g/L**			
11/01/94, 15:46	19	0.58	41	48.58
11/01/94, 15:51	19	0.58	40.7	48.16
11/01/94, 16:02	19	0.79	55.8	66.17
11/01/94, 16:40	18.5	0.56	39.6	47.64
11/01/94, 17:15	18.5	0.57	40.3	48.49
11/01/94, 18:00	18.5	0.57	40.3	48.49
11/01/94, 19:00	18.5	0.56	39.6	47.64
11/02/94, 08:55	17	0.46	32.5	41.06
11/02/94, 09:10	17	0.46	32.5	41.06
11/02/94, 09:15	**Relaxation cleaning**			
11/02/94, 09:20	17	0.54	38.2	48.2
11/02/94, 09:30	**Concentrating initiated**			
11/02/94, 09:45	17	0.59	41.7	52.66
11/02/94, 09:50	**Concentrating halted**			
11/02/94, 10:05	**Alumina added. Concentration increase to 6 g/L**			
11/02/94, 10:30	17	0.48	33.9	42.85
11/02/94, 11:00	17	0.48	33.6	42.4
11/02/94, 11:05	**Relaxation cleaning**			
11/02/94, 11:10	17	0.53	37.5	47.31
11/02/94, 12:05	17	0.51	36.1	45.52
11/02/94, 12:05	**Further alumina addition to increase concentration to 12 g/L**			
11/02/94, 12:20	Relaxation cleaning			
11/02/94, 12:35	17	0.54	38.2	48.2
11/02/94, 12:50	**Further alumina addition to increase concentration to14 g/L**			
11/02/94, 14:20	17	0.49	34.3	43.29
11/02/94, 14:35	**Relaxation cleaning**			

11/02/94, 14:40	**Zeeweed™ removed from tank and scale removed**			
Date and Time	**Temperature (°C)**	**Permeate Flow (Lpm)**	**Permeate Flux at T (gfd)**	**Permeate Flux at 25°C (gfd)**
11/02/94, 14:48	17	0.57	40.3	50.88
11/02/94, 14:55	17	0.57	40.3	50.88
11/02/94, 15:20	17	0.55	38.9	49.09
11/02/94, 17:10	17	0.53	37.5	47.31
11/02/94, 17:10	**Further alumina addition to increase concentration to 25 g/L**			
11/02/94, 17:35	**Relaxation cleaning**			
11/02/94, 17:45	17	0.43	30.4	38.38
11/02/94, 18:25	17	0.44	31.1	39.28
11/02/94, 18:30	**Relaxation cleaning**			
11/02/94, 18:43	17	0.41	29	36.6
11/03/94, 08:50	17	0.46	32.5	41.06
11/03/94, 09:00	**Mechanical cleaning**			
11/03/94, 09:05	**Relaxation cleaning**			
11/03/94, 09:20	17	0.54	38.2	48.2
11/03/94, 09:25	17	0.54	38.2	48.2
11/03/9409:40	17	0.52	36.8	46.42
11/03/94, 10:00	17	0.5	35.3	44.63
11/03/94, 11:40	17	0.48	33.9	42.85
11/03/94, 11:45	**Relaxation cleaning**			
11/03/94, 11:55	17	0.57	40.3	50.88
11/03/94, 12:15	**Further alumina addition to increase concentration to 35 g/L**			
11/03/94, 12:20	17	0.5	35.3	44.63
11/03/94, 12:30	**Relaxation cleaning**			
11/03/94, 13:15	17	0.54	38.2	48.2
11/03/94, 15:25	17	0.45	31.8	40.17
11/03/94, 15:30	**Relaxation cleaning**			
11/03/94, 15:38	17	0.52	36.8	46.42
11/03/94, 16:10	**Further alumina added to increase concentration to 50 g/L**			
11/03/94, 16:20	17	0.44	31.1	39.28
11/03/94, 18:00	17	0.4	28.3	35.7
11/03/94, 18:01	**Relaxation cleaning**			
11/03/94, 18:13	17	0.52	36.8	46.42
11/04/94, 09:00	18	0.44	31.1	38.03
11/04/94, 09:05	**Mechanical cleaning**			
11/04/94, 09:20	18	0.5	35.3	43.21
11/04/94, 10:40	15	0.46	32.5	43.95
11/04/94, 12:00	**Relaxation cleaning**			

Date and Time	Temperature (°C)	Permeate Flow (Lpm)	Permeate Flux at T (gfd)	Permeate Flux at 25°C (gfd)
11/04/94, 12:08	14.5	0.47	33.2	45.7
12/07/94, 12:38	**RO water flux**			
12/07/94, 13:38	16	0.71	50.2	65.53
12/07/94, 13:38	**Further alumina addition to increase concentration to 60 g/L**			
12/07/94, 13:45	17.5	0.49	34.6	43.03
12/07/94, 14:30	29	0.23	16.3	14.73

APPENDIX C:
RESULTS OF ACTIVATED ALUMINA CHARACTERIZATION BY NITROGEN SORPTION POROSIMETRY

Table C-1. Pore area and pore volume distributions for F1-100 alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	**Pore Vol. cc/g**	**Cumulative Pore Vol. cc/g**	**Pore Area (m^2/g)**	**Cumulative Pore Area (m^2/g)**
376.9	0.189425	0.189425	20.106	20.106
232.0	0.040852	0.230277	7.043	27.149
169.4	0.015086	0.245362	3.563	30.711
146.4	0.006851	0.252214	1.872	32.584
132.6	0.005506	0.257720	1.661	34.245
118.8	0.005847	0.263567	1.968	36.213
106.6	0.006809	0.270376	2.555	38.768
96.2	0.006081	0.276457	2.528	41.296
87.2	0.006598	0.283055	3.026	44.322
79.7	0.006541	0.289596	3.283	47.605
73.5	0.005905	0.295501	3.214	50.819
68.2	0.006458	0.301960	3.790	54.609
63.4	0.006564	0.308524	4.139	58.747
59.3	0.005976	0.314501	4.034	62.782
55.5	0.006340	0.320841	4.566	67.348
52.2	0.007295	0.328136	5.590	72.938
49.1	0.006129	0.334265	4.989	77.927
46.4	0.007607	0.341872	6.560	84.487
43.9	0.006899	0.348771	6.292	90.778
41.5	0.007536	0.356307	7.257	98.035
39.4	0.008486	0.364793	8.614	106.649
37.4	0.016449	0.381242	17.573	124.222
34.4	0.091973	0.473215	107.020	231.242
30.2	0.058989	0.532204	78.086	309.328
26.6	0.063913	0.596117	96.024	405.352
23.7	0.065788	0.661906	110.980	516.332
21.0	0.069069	0.730974	131.266	647.598
18.5	0.064105	0.795079	138.521	786.119

Table C-2. Pore area and pore volume distributions for CPN-325 alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	Pore Vol. cc/g	Cumulative Pore Vol. cc/g	Pore Area (m^2/g)	Cumulative Pore Area (m^2/g)
442.1	0.208899	0.208899	18.902	18.902
264.5	0.024588	0.233486	3.719	22.621
183.3	0.014287	0.247773	3.117	25.738
157.4	0.005832	0.253606	1.482	27.221
148.0	0.002955	0.256560	0.798	28.019
134.4	0.006067	0.262628	1.805	29.825
119.2	0.007078	0.269705	2.376	32.200
106.7	0.008366	0.278071	3.138	35.338
96.4	0.008622	0.286693	3.577	38.915
87.9	0.009675	0.296368	4.404	43.319
80.7	0.011443	0.307811	5.672	48.991
74.5	0.012954	0.320765	6.953	55.944
69.1	0.014496	0.335261	8.389	64.333
64.4	0.016810	0.352071	10.444	74.777
60.2	0.018097	0.370168	12.024	86.801
56.5	0.020403	0.390571	14.453	101.254
53.1	0.023062	0.413633	17.371	118.625
50.1	0.025621	0.439254	20.461	139.086
47.3	0.028857	0.468111	24.386	163.472
44.8	0.030440	0.498551	27.186	190.658
42.5	0.032727	0.531279	30.835	221.493
40.3	0.036285	0.567564	35.985	257.477
38.4	0.042138	0.609702	43.931	301.409
35.1	0.192518	0.802220	219.413	520.822
30.7	0.077800	0.880019	101.472	622.293
26.9	0.035023	0.915042	52.068	674.361
24.2	0.027530	0.942573	45.488	719.849
21.9	0.031447	0.974020	57.508	777.357
19.5	0.033856	1.007876	69.516	846.873
17.9	0.014897	1.022773	33.309	880.182

Table C-3. Pore area and pore volume distributions for CP-1.5 alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	**Pore Vol. cc/g**	**Cumulative Pore Vol. cc/g**	**Pore Area (m^2/g)**	**Cumulative Pore Area (m^2/g)**
1816.5	0.456783	0.456783	10.058	10.058
311.9	0.013099	0.469882	1.680	11.738
175.7	0.002696	0.472578	0.614	12.352
141.8	0.002088	0.474666	0.589	12.941
131.0	0.002146	0.476812	0.655	13.596
119.6	0.003505	0.480316	1.172	14.768
107.6	0.006019	0.486335	2.237	17.005
97.3	0.008113	0.494448	3.334	20.339
88.7	0.010481	0.504929	4.725	25.064
81.4	0.013108	0.518038	6.440	31.504
75.1	0.013649	0.531687	7.268	38.772
69.7	0.014199	0.545885	8.148	46.919
65.0	0.013765	0.559650	8.473	55.392
60.8	0.013160	0.572810	8.662	64.054
57.0	0.011942	0.584752	8.376	72.430
53.7	0.010447	0.595200	7.786	80.216
50.6	0.009252	0.604452	7.309	87.525
47.9	0.007675	0.612127	6.408	93.933
45.4	0.006896	0.619023	6.072	100.005
43.2	0.005994	0.625017	5.556	105.560
41.0	0.005552	0.630569	5.411	110.971
39.1	0.006988	0.637557	7.148	118.119
36.1	0.037329	0.674886	41.339	159.458
32.0	0.031347	0.706233	39.208	198.667
28.2	0.014894	0.721127	21.095	219.762
25.2	0.012441	0.733568	19.746	239.508
22.6	0.012712	0.746280	22.471	261.979
20.2	0.015657	0.761937	30.952	292.931
18.6	0.008734	0.770671	18.741	311.671
17.6	0.008094	0.778765	18.361	330.033

Table C-4. Pore area and pore volume distributions for CP-5 alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	**Pore Vol. cc/g**	**Cumulative Pore Vol. cc/g**	**Pore Area (m^2/g)**	**Cumulative Pore Area (m^2/g)**
366.7	0.108894	0.108894	11.877	11.877
229.3	0.018464	0.127358	3.221	15.098
169.5	0.007441	0.134799	1.756	16.854
147.4	0.002454	0.137253	0.666	17.520
133.7	0.002792	0.140045	0.835	18.355
120.0	0.001905	0.141951	0.635	18.990
107.8	0.002344	0.144295	0.870	19.860
97.5	0.001933	0.146228	0.793	20.653
88.9	0.002308	0.148536	1.039	21.692
81.6	0.001921	0.150457	0.942	22.634
75.4	0.002168	0.152626	1.151	23.785
70.0	0.001857	0.154483	1.061	24.846
65.3	0.002061	0.156544	1.263	26.109
61.1	0.002321	0.158864	1.518	27.627
57.4	0.002000	0.160865	1.394	29.022
54.0	0.002799	0.163663	2.072	31.093
51.0	0.002595	0.166258	2.035	33.128
48.2	0.002989	0.169247	2.478	35.606
45.7	0.002370	0.171617	2.074	37.679
43.4	0.003135	0.174752	2.890	40.570
41.3	0.003374	0.178126	3.271	43.841
39.3	0.009723	0.187849	9.893	53.733
36.0	0.089354	0.277203	99.203	152.937
31.7	0.028100	0.305303	35.462	188.398
28.0	0.012228	0.317531	17.442	205.840
25.3	0.009916	0.327447	15.673	221.513
22.9	0.012171	0.339618	21.294	242.807
20.4	0.015983	0.355601	31.308	274.114
18.8	0.008689	0.364290	18.453	292.567
17.9	0.005913	0.370203	13.249	305.816

Table C-5. Pore area and pore volume distributions for CP-100 alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	**Pore Vol. cc/g**	**Cumulative Pore Vol. cc/g**	**Pore Area (m^2/g)**	**Cumulative Pore Area (m^2/g)**
1080.5	0.204168	0.204168	7.558	7.558
362.6	0.007437	0.211605	0.820	8.378
197.4	0.005974	0.217579	1.211	9.589
153.7	0.002025	0.219605	0.527	10.116
131.3	0.001894	0.221499	0.577	10.694
116.7	0.001210	0.222709	0.415	11.108
105.8	0.001334	0.224043	0.504	11.612
95.9	0.001157	0.225199	0.482	12.095
87.5	0.001300	0.226499	0.594	12.689
80.3	0.001135	0.227635	0.566	13.255
74.1	0.001092	0.228726	0.589	13.844
68.7	0.001160	0.229886	0.675	14.520
64.0	0.001215	0.231102	0.760	15.279
59.8	0.001150	0.232252	0.769	16.048
56.1	0.001182	0.233434	0.843	16.891
52.8	0.001233	0.234667	0.934	17.825
49.8	0.001262	0.235929	1.015	18.840
47.0	0.001297	0.237226	1.104	19.944
44.5	0.001351	0.238577	1.215	21.159
42.2	0.001304	0.239881	1.236	22.395
40.0	0.001568	0.241449	1.566	23.962
38.2	0.005931	0.247380	6.217	30.179
35.1	0.044860	0.292240	51.077	81.256
30.2	0.012402	0.304642	16.409	97.664
26.2	0.002003	0.306645	3.063	100.727
23.7	0.001325	0.307971	2.239	102.966
21.5	0.002032	0.310003	3.774	106.740
19.2	0.003295	0.313297	6.870	113.610
17.6	0.002163	0.315460	4.914	118.524

Table C-6. Pore area and pore volume distributions for CPN-100 alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	**Pore Vol. cc/g**	**Cumulative Pore Vol. cc/g**	**Pore Area (m^2/g)**	**Cumulative Pore Area (m^2/g)**
299.8	0.033482	0.033482	4.467	4.467
176.3	0.011923	0.045405	2.706	7.173
137.5	0.004525	0.049929	1.317	8.490
125.7	0.002144	0.052073	0.682	9.172
117.1	0.003047	0.055120	1.041	10.213
106.5	0.004294	0.059414	1.612	11.825
96.5	0.005525	0.064939	2.290	14.115
87.9	0.006789	0.071728	3.088	17.203
80.6	0.008208	0.079936	4.071	21.275
74.4	0.010689	0.090626	5.744	27.018
69.0	0.011973	0.102599	6.938	33.957
64.3	0.013920	0.116519	8.663	42.619
60.1	0.015419	0.131937	10.261	52.880
56.4	0.016448	0.148386	11.671	64.551
53.0	0.018044	0.166429	13.612	78.163
50.0	0.019653	0.186082	15.727	93.890
47.2	0.021136	0.207218	17.902	111.792
44.7	0.022082	0.229300	19.762	131.554
42.4	0.021750	0.251050	20.542	152.096
40.2	0.021191	0.272241	21.087	173.182
38.2	0.022211	0.294453	23.239	196.421
35.0	0.085497	0.379950	97.635	294.056
30.5	0.038014	0.417964	49.856	343.912
26.6	0.016343	0.434307	24.557	368.469
23.9	0.010770	0.445077	17.988	386.458
21.7	0.012874	0.457950	23.707	410.165
19.4	0.013951	0.471901	28.706	438.871
17.8	0.006554	0.478455	14.694	453.565

Table C-7. Pore area and pore volume distributions for HTC-100 alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	Pore Vol. cc/g	Cumulative Pore Vol. cc/g	Pore Area (m^2/g)	Cumulative Pore Area (m^2/g)
509.2	0.031912	0.031912	2.507	2.507
324.5	0.016411	0.048323	2.023	4.530
243.5	0.008646	0.056970	1.420	5.950
205.6	0.006416	0.063386	1.249	7.199
186.2	0.004154	0.067540	0.892	8.091
173.4	0.003798	0.071338	0.876	8.967
161.0	0.003714	0.075052	0.923	9.890
149.6	0.003141	0.078192	0.839	10.729
135.0	0.005849	0.084041	1.733	12.462
119.4	0.007103	0.091144	2.380	14.842
106.6	0.007594	0.098738	2.849	17.691
96.5	0.008487	0.107225	3.520	21.211
88.0	0.010127	0.117352	4.602	25.813
80.8	0.011453	0.128805	5.670	31.482
74.6	0.013875	0.142680	7.436	38.919
69.3	0.015935	0.158615	9.204	48.122
64.5	0.019880	0.178495	12.320	60.443
60.3	0.022333	0.200827	14.806	75.248
56.6	0.025019	0.225846	17.691	92.940
53.2	0.024460	0.250306	18.405	111.345
50.1	0.025217	0.275523	20.134	131.479
47.3	0.022902	0.298425	19.354	150.834
44.8	0.024086	0.322511	21.505	172.339
42.5	0.020840	0.343351	19.622	191.961
40.3	0.019854	0.363205	19.690	211.651
38.4	0.022944	0.386150	23.885	235.536
35.1	0.076787	0.462937	87.522	323.057
30.7	0.024787	0.487724	32.301	355.358
27.0	0.012178	0.499903	18.035	373.393
24.4	0.008837	0.508739	14.498	387.891
22.1	0.010604	0.519343	19.225	407.116
19.7	0.011504	0.530847	23.412	430.528
18.1	0.004971	0.535818	11.014	441.543
17.0	0.004022	0.539840	9.438	450.981

Table C-8. Pore area and pore volume distributions for CG-20 alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	Pore Vol. cc/g	Cumulative Pore Vol. cc/g	Pore Area (m^2/g)	Cumulative Pore Area (m^2/g)
2407.9	0.044752	0.044752	0.743	0.743
560.6	0.017300	0.062052	1.234	1.978
332.1	0.014200	0.076252	1.710	3.688
249.9	0.007083	0.083335	1.134	4.822
217.4	0.004560	0.087895	0.839	5.661
201.6	0.002829	0.090724	0.561	6.222
188.3	0.003022	0.093746	0.642	6.864
174.6	0.003240	0.096986	0.742	7.606
161.6	0.003678	0.100663	0.910	8.517
149.6	0.003960	0.104623	1.059	9.575
135.0	0.006517	0.111140	1.931	11.507
119.4	0.008571	0.119711	2.872	14.378
106.4	0.009467	0.129178	3.559	17.937
96.0	0.009590	0.138768	3.997	21.933
87.5	0.010241	0.149009	4.683	26.616
80.4	0.012130	0.161139	6.033	32.649
74.3	0.014250	0.175390	7.675	40.324
68.9	0.016722	0.192111	9.712	50.036
64.2	0.019137	0.211248	11.928	61.964
59.9	0.020475	0.231723	13.662	75.626
56.1	0.019835	0.251558	14.142	89.768
52.6	0.018272	0.269830	13.885	103.653
49.6	0.014998	0.284828	12.107	115.759
46.8	0.010938	0.295766	9.358	125.118
44.2	0.007725	0.303492	6.985	132.103
42.0	0.005753	0.309244	5.475	137.578
40.0	0.004436	0.313680	4.433	142.011
38.1	0.003405	0.317086	3.571	145.581
35.1	0.013957	0.331042	15.893	161.475
31.0	0.006901	0.337943	8.890	170.365
27.4	0.002927	0.340870	4.269	174.634
24.5	0.002189	0.343059	3.578	178.212
21.9	0.001652	0.344711	3.024	181.235
19.4	0.001698	0.346409	3.502	184.737
17.8	0.000811	0.347220	1.820	186.557

Table C-9. Pore area and pore volume distributions for 100μm,50-100Å alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	Pore Vol. cc/g	Cumulative Pore Vol. cc/g	Pore Area (m^2/g)	Cumulative Pore Area (m^2/g)
1013.1	0.292654	0.292654	11.555	11.555
286.6	0.002185	0.294839	0.305	11.860
167.4	0.006104	0.300943	1.459	13.318
130.9	0.002768	0.303711	0.846	14.164
115.7	0.001674	0.305385	0.579	14.743
105.1	0.001275	0.306660	0.485	15.228
95.9	0.001626	0.308286	0.679	15.906
87.5	0.001663	0.309949	0.760	16.667
80.2	0.001612	0.311561	0.803	17.470
73.9	0.001547	0.313107	0.837	18.307
68.5	0.001693	0.314800	0.989	19.296
63.7	0.001955	0.316755	1.227	20.523
59.6	0.002012	0.318768	1.351	21.874
55.9	0.002335	0.321103	1.672	23.546
52.5	0.002802	0.323905	2.134	25.680
49.5	0.003404	0.327309	2.751	28.431
46.8	0.004136	0.331445	3.538	31.969
44.2	0.005227	0.336672	4.727	36.697
41.9	0.007281	0.343953	6.949	43.646
39.7	0.009571	0.353524	9.632	53.278
37.8	0.013881	0.367405	14.695	67.973
34.4	0.050675	0.418080	58.972	126.945
30.1	0.034165	0.452245	45.341	172.286
26.4	0.010840	0.463085	16.443	188.729
23.4	0.006036	0.469121	10.300	199.029
21.1	0.003676	0.472797	6.969	205.999
18.8	0.003299	0.476095	7.015	213.014
17.3	0.001103	0.477198	2.554	215.567

Table C-10. Pore area and pore volume distributions for 10μm,50-100Å alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	**Pore Vol. cc/g**	**Cumulative Pore Vol. cc/g**	**Pore Area (m^2/g)**	**Cumulative Pore Area (m^2/g)**
434.4	0.052964	0.052964	4.877	4.877
226.5	0.012033	0.064997	2.125	7.002
167.8	0.003697	0.068694	0.881	7.883
144.8	0.001728	0.070423	0.477	8.361
131.4	0.001578	0.072001	0.481	8.841
118.8	0.001617	0.073618	0.545	9.386
106.8	0.001706	0.075324	0.639	10.025
96.5	0.001384	0.076708	0.573	10.598
88.0	0.001493	0.078201	0.679	11.277
80.7	0.001662	0.079863	0.824	12.101
74.4	0.001507	0.081371	0.811	12.912
69.0	0.001155	0.082526	0.670	13.582
64.3	0.001285	0.083811	0.800	14.382
60.2	0.001166	0.084977	0.775	15.157
56.4	0.001275	0.086252	0.903	16.060
53.1	0.001672	0.087924	1.260	17.320
50.0	0.001290	0.089214	1.031	18.351
47.3	0.001841	0.091054	1.557	19.908
44.8	0.001555	0.092610	1.389	21.297
42.5	0.001731	0.094341	1.630	22.927
40.3	0.001721	0.096061	1.706	24.633
38.4	0.002451	0.098512	2.556	27.189
35.2	0.010898	0.109411	12.391	39.580
31.4	0.031185	0.140595	39.679	79.259
27.7	0.026931	0.167526	38.836	118.096
24.4	0.017548	0.185074	28.711	146.806
21.7	0.013203	0.198277	24.344	171.150
19.3	0.010131	0.208408	21.022	192.173
17.8	0.003681	0.212089	8.292	200.464

Table C-11. Pore area and pore volume distributions for 100µm,300Å alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	Pore Vol. cc/g	Cumulative Pore Vol. cc/g	Pore Area (m^2/g)	Cumulative Pore Area (m^2/g)
1012.2	0.104424	0.104424	4.127	4.127
572.6	0.012602	0.117026	0.880	5.007
314.3	0.019120	0.136146	2.433	7.440
245.3	0.008018	0.144164	1.308	8.748
216.6	0.007360	0.151524	1.359	10.107
200.9	0.004832	0.156356	0.962	11.069
188.1	0.006107	0.162462	1.299	12.367
173.8	0.007588	0.170050	1.746	14.113
160.8	0.008926	0.178977	2.220	16.334
149.1	0.010177	0.189154	2.731	19.065
135.3	0.020167	0.209322	5.960	25.025
120.1	0.030501	0.239822	10.160	35.185
106.6	0.039200	0.279022	14.714	49.900
95.4	0.044580	0.323602	18.688	68.587
86.4	0.047833	0.371434	22.137	90.724
79.1	0.050272	0.421706	25.431	116.155
72.8	0.049634	0.471340	27.265	143.420
67.3	0.045359	0.516700	26.957	170.377
62.5	0.041177	0.557877	26.366	196.744
58.3	0.033272	0.591148	22.836	219.580
54.6	0.026570	0.617718	19.461	239.041
51.5	0.020953	0.638671	16.289	255.330
48.7	0.017313	0.655984	14.214	269.544
46.2	0.013828	0.669812	11.965	281.509
43.9	0.012606	0.682418	11.486	292.995
41.7	0.010138	0.692556	9.721	302.716
39.7	0.009115	0.701671	9.192	311.909
37.7	0.007308	0.708980	7.747	319.655
34.7	0.014390	0.723369	16.602	336.257
30.7	0.011998	0.735368	15.634	351.891
27.1	0.005906	0.741273	8.710	360.601
24.1	0.003867	0.745140	6.427	367.027
21.4	0.001924	0.747064	3.595	370.622
19.0	0.001167	0.748231	2.462	373.084

Table C-12. Pore area and pore volume distributions for 100μm,200Å alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	**Pore Vol. cc/g**	**Cumulative Pore Vol. cc/g**	**Pore Area (m^2/g)**	**Cumulative Pore Area (m^2/g)**
870.6	0.065615	0.065615	3.015	3.015
404.2	0.000803	0.066418	0.079	3.094
270.3	0.001626	0.068044	0.241	3.335
228.3	0.000852	0.068896	0.149	3.484
209.0	0.001344	0.070240	0.257	3.741
191.1	0.001859	0.072099	0.389	4.130
175.5	0.002830	0.074930	0.645	4.775
161.6	0.003919	0.078849	0.970	5.745
149.8	0.005224	0.084073	1.395	7.140
136.0	0.012936	0.097009	3.804	10.944
121.1	0.023751	0.120760	7.845	18.789
108.7	0.040239	0.161000	14.806	33.595
98.6	0.062863	0.223863	25.498	59.093
89.3	0.084635	0.308498	37.927	97.020
79.9	0.081415	0.389913	40.738	137.758
71.5	0.049320	0.439234	27.600	165.358
64.9	0.024848	0.464081	15.310	180.669
60.3	0.011595	0.475676	7.694	188.363
57.0	0.006551	0.482227	4.597	192.960
54.5	0.004438	0.486664	3.258	196.218
52.0	0.004352	0.491016	3.345	199.563
49.4	0.003894	0.494910	3.154	202.716
46.7	0.002997	0.497907	2.567	205.283
44.2	0.002389	0.500297	2.164	207.447
41.9	0.001831	0.502128	1.750	209.197
39.7	0.001639	0.503767	1.650	210.846
37.8	0.001372	0.505139	1.453	212.299
34.6	0.002188	0.507327	2.528	214.827
30.7	0.001352	0.508679	1.763	216.590
27.2	0.000610	0.509288	0.897	217.487
24.2	0.000488	0.509777	0.808	218.295
21.5	0.000047	0.509824	0.088	218.383

Table C-13. Pore area and pore volume distributions for 20µm,300Å alumina determined by Micromeritics ASAP 2000.

Pore Diameter (A)	**Pore Vol. cc/g**	**Cumulative Pore Vol. cc/g**	**Pore Area (m^2/g)**	**Cumulative Pore Area (m^2/g)**
1532.4	0.484479	0.484479	12.646	12.646
348.1	0.030025	0.514504	3.450	16.096
200.2	0.023214	0.537718	4.638	20.734
159.0	0.008272	0.545990	2.081	22.815
143.1	0.008182	0.554172	2.287	25.102
130.8	0.008618	0.562790	2.636	27.738
118.4	0.014016	0.576806	4.736	32.473
106.2	0.020174	0.596980	7.596	40.069
95.9	0.026937	0.623917	11.239	51.309
87.3	0.036721	0.660638	16.820	68.129
80.1	0.047991	0.708629	23.975	92.104
73.6	0.054697	0.763326	29.725	121.829
67.8	0.054216	0.817542	31.982	153.811
62.8	0.047767	0.865309	30.436	184.247
58.4	0.041519	0.906828	28.420	212.667
54.7	0.030996	0.937824	22.679	235.346
51.4	0.024436	0.962260	19.009	254.355
48.6	0.019646	0.981906	16.154	270.509
46.1	0.015996	0.997902	13.867	284.376
43.8	0.014231	1.012133	12.999	297.376
41.6	0.012026	1.024159	11.567	308.943
39.5	0.011137	1.035297	11.281	320.224
37.5	0.008387	1.043684	8.938	329.161
34.4	0.016525	1.060209	19.203	348.364
30.5	0.013762	1.073972	18.067	366.431
26.9	0.006887	1.080858	10.228	376.659
23.9	0.003938	1.084796	6.592	383.251
21.2	0.002490	1.087287	4.691	387.942
18.8	0.001474	1.088760	3.139	391.081
17.2	0.000611	1.089372	1.420	392.501

APPENDIX D:
SAMPLE CALCULATIONS

D-1. Determination of Langmuir and Freundlich Model Constants

D-1.1. Langmuir Model Constants

In order to determine the values of the Langmuir model constants, as described in section 3.1 of Chapter 3, the constants of the Langmuir adsorption model are obtained from the adsorption experimental data by plotting the linearized Langmuir equation

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{b\,Q}\,\frac{1}{C_e} \qquad \text{(D-1)}$$

where $1/Q$ is the intercept and $1/bQ$ is the slope of the line. The constants Q which is the maximum adsorption capacity of the adsorbent and b where determined for the 1 day adsorption isotherm. Table D-1 presents the values for $1/q_e$ and $1/C_e$ which were plotted. In order to determine the slope and Y-intercept a straight line was fitted to the data using the Least Squares method. Table D-2 shows the results of the linear fit.

Table D-1. Values of $1/q_e$ and $1/C_e$ potted for determination of the Langmuir equation constants for the 1 day arsenic adsorption isotherm.

C_e	q_e	$1/C_e$	$1/q_e$
1.8	21.47	0.5556	0.0466
3.84	31.52	0.2604	0.0317
9.3	51.83	0.1075	0.0193
37.6	75.47	0.0266	0.0133
145	110.33	0.0069	0.0091
220	110.67	0.0045	0.0090
617	144.33	0.0016	0.0069

Table D-2. Regression output for the Least Squares linear fit for the plot of $1/q_e$ versus $1/C_e$.

Regression Output:	
Constant	0.012675
Std Err of Y Est	0.007801
R Squared	0.721287
No. of Observations	19
X Coefficient(s)	0.034831
Std Err of Coef.	0.005251

From the values of the slope and intercept b and Q were calculated to be 0.3639 g^{-1} and 78.8947 mg/g respectively.

D-1.2. Freundlich Model Constants

To determine the values of the constants in the Freundlich adsorption isotherm as explained in section 3.1 of Chapter 3, the using the 1 day isotherm experimental data the linearized form of the model equation was plotted

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \qquad \text{(D-2)}$$

where *ln k* and *1/n* are the Y-intercept and slope of a straight line fitted to the plot of *ln* q_e versus *ln* C_e. Table D-3 shows the values of *ln* q_e and *ln* C_e that were plotted in the attempt to determine the Freundlich equation constant values. In order to determine the slope and Y-intercept a straight line was fitted to the data using the Least Squares method. Table D-4 shows the results of the linear fit.

Table D-3. Values of *ln* q_e and *ln* C_e potted for determination of the Freundlich equation constants for the 1 day arsenic adsorption isotherm.

Ce	qe	Ln Ce	Ln qe
1.8	21.47	0.5878	3.0665
3.84	31.52	1.3455	3.4506
9.3	51.83	2.2300	3.9480
37.6	75.47	3.6270	4.3237
145	110.33	4.9767	4.7035
220	110.67	5.3936	4.7065
617	144.33	6.4249	4.9721

Table D-4. Regression output for the Least Squares linear fit for the plot of *ln* q_e versus *ln* C_e.

Regression Output:	
Constant	3.149644
Std Err of Y Est	0.14657
R Squared	0.95699
No. of Observations	19
X Coefficient(s)	0.29393
Std Err of Coef.	0.015113

From the values of the slope and intercept *k* and *n* were calculated to be 23.3277 and 3.4021 respectively.

D-2. CALCULATION OF THE ARSENATE SPECIES DISTRIBUTION

Distribution of the arsenate species at different pH was determined by rearranging the equations 2.1 to 2.3 to obtain a system of equations that were solved simultaneously at different pH values. The system of equations solved were as follows:

$$[\ H_2AsO_4^-\ ] = \frac{K_1\ [\ H_3AsO_4\ ]}{[\ H^+\ ]} \tag{D-3}$$

$$[\ HAsO_4^{2-}\ ] = \frac{K_2\ [\ H_2AsO_4^-\ ]}{[\ H^+\ ]} \tag{D-4}$$

$$[\ AsO_4^{3-}\ ] = \frac{K_3\ [\ HAsO_4^{2-}\ ]}{[\ H^+\ ]} \tag{D-5}$$

$$[\ H_3AsO_4\ ] + [\ H_2AsO_4^-\ ] + [\ HAsO_4^{2-}\ ] + [\ AsO_4^{3-}\ ] = T_{[As]} \tag{D-6}$$

$$[\ H^+\ ] = 10^{-pH} \tag{D-7}$$

where K_1, K_2, and K_3 are acid dissociation constants for Arsenic acid and

$$K_i = 10^{pK_{a_i}} \quad i = 1,\ 2,\ 3 \tag{D-8}$$

APPENDIX E:
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July 24, 1995

Mr. Saviz Mortazavi
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Dear Mr. Mortazavi :

Following our recent telephone conversation, this is to confirm that we are permitting you to use the photographs of the following models in your thesis :

- EDL-2 Power Supply System
- MHS-10 Mercury/Hydride System
-

We wish thank you for the interest you are showing in our company and its products.

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Mr. Mortazavi:

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