INVESTIGATION OF A NOVEL APPROACH FOR ARSENIC REMOVAL FROM WATER USING MODIFIED RHYOLITE

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INVESTIGATION OF A NOVEL APPROACH FOR ARSENIC REMOVAL FROM WATER USING MODIFIED RHYOLITE

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CHAPTER I

INTRODUCTION

Overview

In the process of human evolution, some of the issues confronting today's society are safe guarding the natural environment and maintaining a good quality of life. However, a slight imbalance in any equilibrium in the environment is bound to manifest itself in the form of what can be called an environmental hazard. The occurrence of arsenic in groundwater is one such imbalance of equilibrium.

Arsenic contamination of groundwater is a concern in many parts of the world (Thirunavukarasu et al., 2001). Some of the south east Asian countries, like Bangladesh and India, have highly unsafe arsenic concentrations which need immediate attention. In the United States, it has recently become a serious issue. Recognized as a toxic element for centuries, arsenic today is a human health concern. Arsenic contamination in drinking water supplies is a large-scale problem that will require extensive adaptation to meet the standards set by the Environmental Protection Agency (EPA) and the World Health Organization (WHO). An ideal solution for this problem would be to find an inexpensive, reliable removal technology that works over a broad range of relevant conditions and has limited disposal issues.

Project Objective

The federal drinking water standard for arsenic of 50 parts per billion (ppb) was set by the U.S. Public Health Service in 1942 (Selecky et al., 2003). The Safe Drinking Water Act, as amended in the year 1996, requires the US Environmental Protection Agency (USEPA) to (1) review the drinking water standards for arsenic, (2) propose a maximum contaminant level for arsenic by January1, 2000, and (3) issue a final regulation by January 2001 (Focazio et al., 1999). In the final rule, published on January 22, 2001 (66 FR 6976), EPA lowered the arsenic maximum contaminant level (MCL) from 50 ppb to 10 ppb and required the existing sources to be in compliance with the new MCL by January 2006. This new standard is expected to require modification for over 3000 community water systems across the nation (Severn Trent Technologies, 2004). The WHO recommended guideline for arsenic in drinking water has been revised from 50 ppb to 10 ppb (Tiemann, 2001).

The objective of the project is to find a potential solution for the problem. The ideal solution would require minimal improvement in terms of process changes and financial investment to the existing water systems. Primary factors include high removal efficiency, process reliability, safe and easy application, affordability and compatibility with other treatment processes (Saha et al., 2001).

CHAPTER II

ARSENIC BACKGROUND

Arsenic in Drinking Water

Arsenic is one of the commonly occurring natural contaminants in drinking water. It ranks twentieth among the elements in abundance in the earth's crust (Saask, 2002). Arsenic is present in the environment in both organic and inorganic forms. Inorganic arsenic compounds mostly occur as the sulfide form in complex minerals containing copper, lead, iron, nickel and cobalt (Report on Carcinogens, 1980). Inorganic arsenic, the more toxic among the two, is in groundwater, surface water and in many food items. The primary routes of arsenic exposure are inhalation and ingestion. Most human exposure to inorganic arsenic is through drinking water (The National Academy of Science, 1997).

Arsenic contamination in groundwater is a major public health issue in many parts of the world where groundwater is the major source of drinking water, especially the south east Asian countries. Countries like Bangladesh, India, Vietnam, Taiwan and China have arsenic contamination in their groundwater sources (Saask, 2002). It has been estimated that globally, tens of millions of people are at risk due to exposure to excessive levels of arsenic.

Western states of the United States have water systems with arsenic levels exceeding 10 ppb, and levels exceed 50 ppb in some areas. EPA projects that 5.5% of the water systems serving 11 million people are likely to exceed the 10 ppb level (Tiemann, 2001). The map (Figure 1) that follows shows the arsenic concentration at different locations throughout the United States.

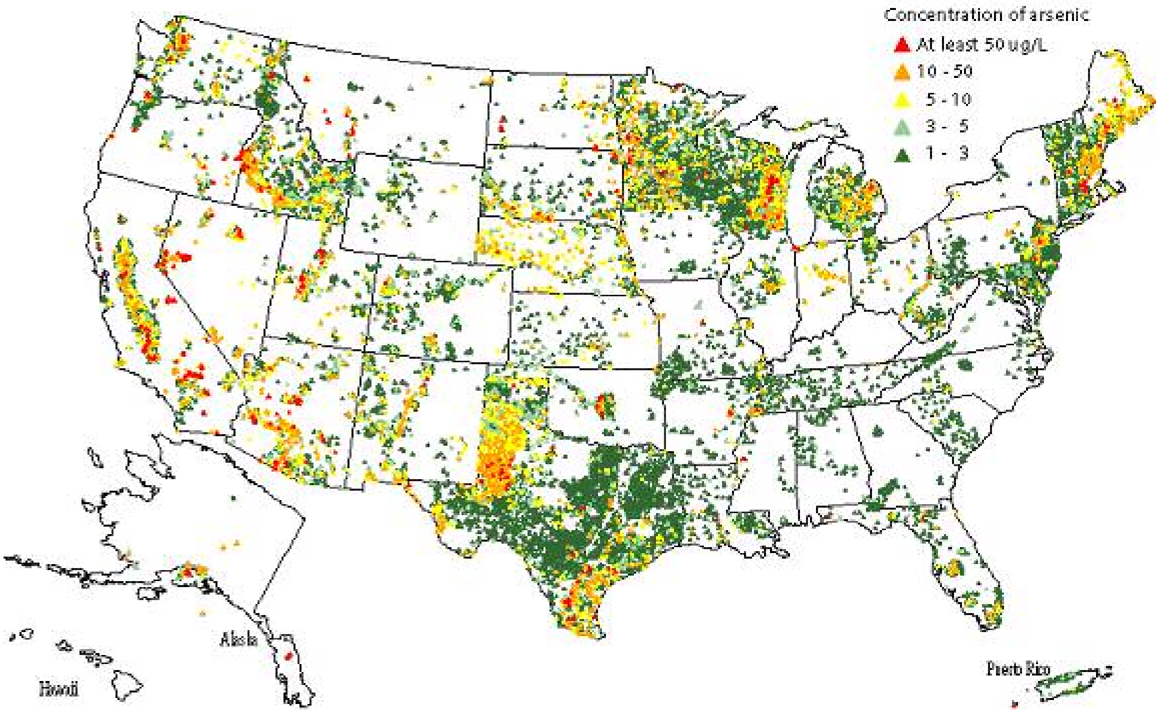


Figure 1: Groundwater arsenic concentration map of the United States
(Source: http://co.water.usgs.gov/trace/pubs/geo_v46n11/fig1.html)

Speciation

Removal of arsenic is dependent on the arsenic speciation in water. Arsenic exists mainly in three different valances i.e., -3, +3 and + 5. In an aqueous environment arsenic is present in two oxidation states: trivalent (III) arsenite and pentavalent (V) arsenate form. Arsenate is more efficiently removed than arsenite and hence oxidation of arsenite might be required to enhance arsenic removal. Ionic forms of arsenate dominate at pH greater than 2.3 and arsenite exists as non-ionic H_3AsO_3 up to pH 9 (Aragon et al., 2002). As(III) species consist primarily of arsenous acid (H_3AsO_3) and As(V) species consist primarily of $H_2AsO_4^-$ and $HAsO_4^{2-}$ (EPA, 2000). Arsenite when present in aerobic waters becomes oxidized to arsenate at pH values above 7.0 and arsenate is reduced at low pH. Figure 2 shows the speciation of As(III) and As(V) at various pH.

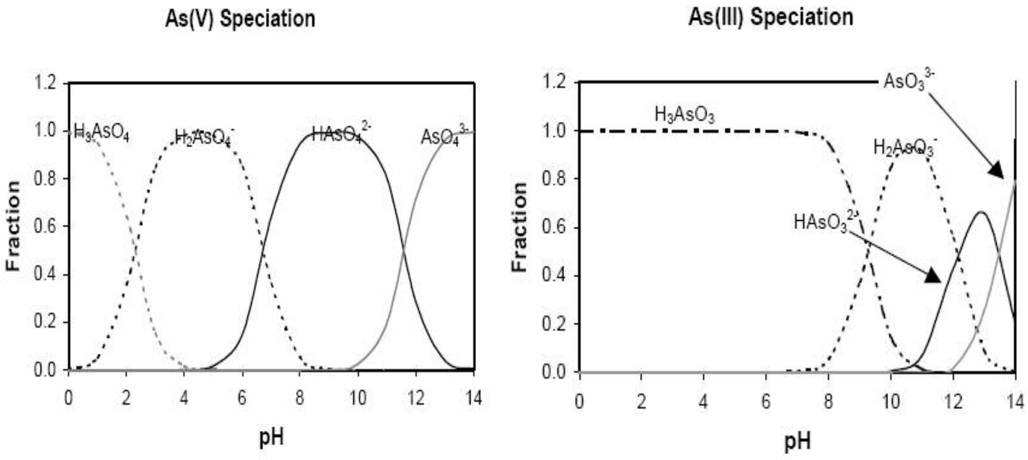


Figure 2: Aqueous arsenic speciation (Aragon et al., 2002)

Toxicity and Health Effects

Arsenic has been used as a poison throughout the history of mankind. One of the earliest documented cases of arsenic poisoning was Nero's poisoning of Brittannicus to secure the Roman throne in 55 A.D (Adedge Technologies, 2003). French scientists believe that French and British conspirators poisoned Napoleon with arsenic. Many scientists believe the death of 90 percent of the population of Jamestown colony was the result of arsenic poisoning at the hands of the Spanish government intent on getting rid of the English colony (Adedge Technologies, 2003). Today, arsenic continues to poison millions of Americans (Adedge Technologies, 2003). The element occurs naturally and enters the water supplies throughout the United States, especially in the west, mid-west and New England. The potential short-term and long-term health effects associated with arsenic exposure are as listed in Table 1 and Table 2, respectively.

Table 1: Potential short-term health effects (Adedge Technologies, 2003)

Stomach pain	Difficulty in swallowing
Vomiting	Low blood pressure
Skin lesion	Convulsions
Pigmentataion	Gastrointestinal problems

Table 2: Potential long-term health effects (Adedge Technologies, 2003)

Bladder cancer	Gangrene	Immunological disorder
Skin cancer	Endocrine disorder	Pulmonary disease
Kidney cancer	Keratosis	Hematological disorder
Liver cancer	Neurological effects	Reproductive problems
Prostate cancer	Cardiovascular disease	Lung cancer

According to a 1999 study of the National Academy of Sciences (The National Academy of Science, 1999), arsenic in drinking water could harm the central and peripheral nervous systems, as well as heart and blood vessels. In a study done by Adedge Technonologies (Adedge Technologies, 2003), it was predicted that even at the new level of 10 ppb, three in 1,000 people exposed will die from cancer.

CHAPTER III

LITREATURE REVIEW

ARSENIC REMOVAL TECHNOLOGIES

The United States Environmental Protection Agency (USEPA) had identified oxidation/filtration, ion exchange, activated alumina adsorption, enhanced coagulation/filtration, reverse osmosis and electrodialysis as “Best Achievable Technologies” (BATs) for arsenic removal (Selecky et al., 2003). Each of these individual technologies are briefly discussed in the following chapter.

Oxidation/Filtration

Arsenic in groundwater exists in varying proportions as As(III) and As(V). Most of the treatment methods are effective in removing arsenic in the pentavalent arsenate form and therefore require a pretreatment (oxidation) step for the conversion of arsenite to arsenate (Ahmed, 2001). Oxygen, free chlorine, hypochlorite, permanganate, hydrogen peroxide are some of the commonly used oxidants for this purpose.

In the oxidation/filtration process, arsenic binds to the iron oxides during oxidation and is then removed by filtration. The process is most effective when the pH is less than 7.5 and the concentration of iron to arsenic is 20:1 or greater (Selecky et al., 2003).

Developed in Bangladesh, solar oxidation and removal of arsenic (SORAS) is one of the simplest method of arsenic removal. This method uses irradiation of water with sunlight in polyethylene terephthalate (PET) or UV-A transparent bottles to remove arsenic from contaminated water. As(III) in water is photochemically oxidized to the more adsorbing As(V). Fe(III)-oxides formed from the iron naturally present in the water is allowed to settle to the bottom of the bottle along with the As(V) adsorbed to it (Wegelin et al., 2000).

The arsenic removal efficiency is limited to approximately 50-70% and raw water up to only 100-150 μg/L can be treated using SORAS (Wegelin et al., 2000). In-situ oxidation could reduce arsenic concentration to about 50% and passive sedimentation could reduce the concentration of arsenic up to 25% of the initial concentration (Ahmed, 2001).

Co-precipitation

Coagulation/filtration (C/F) is a treatment method for arsenic removal using either metal salts or lime softening. C/F uses the conventional chemical and physical treatment processes of chemical addition, rapid mix, coagulation, flocculation, and filtration.

Pentavalent arsenic can be more effectively removed than the trivalent form and hence would require a preoxidation step prior to chemical treatment (Ahmed, 2001).

Iron Coagulation

Arsenic in the arsenate form can be readily removed by adding ferric iron salts if the optimum conditions are maintained to effect that removal. Coagulation using iron salts such as ferric chloride and ferrous sulfate can remove up to 90% of As(V) at pH 7 and about 50% of As(III) (PUREFLOW Filtration Systems, 2005). Arsenite is generally less efficiently removed by ferric chloride than As(V) (EPA, 2000). Removal efficiency of 80% can be achieved over the pH range of 4-8 with ferric chloride (Hering et al., 1997). With ferric sulfate, removal efficiency of over 95% As(V) was obtained within pH range of 5-7.5 for dosages between 10 and 50 mg/L (EPA, 2000).

Alum Coagulation

Alum can be used to remove arsenate, but is less effective than other processes over a narrower pH range for arsenate removal. Alum coagulation is not that efficient for removal of arsenite (Ali et al., 2001). Over 90% of As(V) was removed with alum coagulation, but only at dosages greater than 30 mg/L and within the pH range 5-7 (EPA, 2000).

Lime softening

Lime softening, excess lime treatment, split lime treatment and lime-soda softening are all effective in reducing arsenic. Lime softening uses addition of $Ca(OH)_2$ and Na_2CO_3 for removal of carbonate and non-carbonate hardness and is also capable of removal of arsenic present in water. Removal of both the forms of arsenic by lime softening is pH dependent (EPA, 2000). Addition of lime increases the pH and creates a shift in the carbonate equilibrium. Bicarbonate gets converted to carbonate as the pH increases and calcium is precipitated as calcium carbonate. The formation of calcium carbonate, magnesium hydroxide and ferric hydroxide enhances the removal of arsenic (Veenstra et al., 2004). Sludge disposal is a problem in this treatment method (EPA, 2000) and is recommended to have this type of treatment only if hardness must also be removed.

Membrane Techniques

Membrane techniques like Reverse Osmosis (RO), Nanofiltration (NF) and Electrodialysis (ED) can be used to remove dissolved solids in water including arsenic. The techniques could be used for point of use and point of entry applications at low flowrates, especially if arsenic is one of the several contaminants to be removed. Reverse osmosis and nanofiltration membranes have pore sizes appropriate for removal of dissolved arsenic. Reverse osmosis and electrodialysis, can be effective processes, but may be applied only if partial or total desalting is necessary in addition to arsenic separation (Das, 1998). Reverse osmosis and electrodialysis are capable of removing all kinds of dissolved solids from the water, thus resulting in demineralized water (Das, 1998). High pressure processes like RO and NF have relatively small pores and remove broader range of contaminants by chemical diffusion.

Reverse Osmosis (RO)

RO seems to be one of the most effective methods for removing arsenic from a domestic water supply. RO can provide removal efficiencies of greater than 97 % (Vance, 2001). Pentavalent arsenic removal rate is higher than the rate of trivalent arsenic removal (EPA, 2001). Hence preoxidation of arsenite to arsenate is required. RO requires very little regular maintenance, no chemical addition, is very reliable, and installation is fairly straightforward. However the capital and operational costs would be high (EPA, 2000).

Reverse osmosis is extensively used for removing inorganic contaminants from groundwater and drinking water. Reverse osmosis when used for arsenic removal would remove all the inorganic materials that impart taste to the drinking water. Excessive amounts of iron or manganese should be removed prior to RO treatment which would require additional treatment.

Nanofiltration (NF)

NF can remove both forms of arsenic and hence is a reliable process for groundwater with 90% dissolved arsenic. NF membrane can remove over 95% of As(V), under relatively low-applied pressure of less than 1.1 MPa, and more than 75% of As(III) could be removed using this membrane without any chemical additives (Sato et al., 2002) . Both the arsenate and arsenite removals by NF membranes were not affected by source water composition, and hence it is suggested that NF membranes can be used in any types of waters. The smaller pores of the NF membrane are prone to fouling which may deteriorate the membrane performance

Electrodialysis (ED)

ED is an electrochemical membrane process initially developed for the treatment of saline or brackish waters. Instead of hydrostatic pressure, the process uses an applied direct current (DC) voltage to move dissolved anions and cations from alternate cells through semi-permeable membranes. This purifies a portion of the feed water, while concentrating another. Electrodialysis is capable of removing arsenic up to 80% of the initial concentration. Electrodialysis reversal (EDR) is an ED process which reverses the polarity of the electrodes on a controlled time cycle, which reverses the direction of ion movement in a membrane stack. EDR typically requires little or no pretreatment to minimize fouling of the membrane.

While capable of removing arsenic to low levels, the process is equipment, energy and labor intensive. It also creates a concentrate which must be disposed of, and is quite wasteful of water. ED/EDR systems are not considered to be economically viable for any but very small installations. When compared to RO and NF, EDR is not considered to be competitive with respect to costs and process efficiency.

Sorption Techniques

Many researchers have focused on surface adsorption as the most effective means of removing arsenic. Saha et al. (2001) evaluated the adsorbents like kimberlite tailing, wood charcoal, banana pith, coal fly ash, spent tea leaf, mushroom, saw dust, rice husk, sand, water hyacinth, activated carbon, bauxite, hematite, laterite, iron-oxide coated sand, activated alumina, CalSiCo and hydrous granular ferric oxide for selecting an appropriate adsorbent to remove arsenic from ground water. Saha et al. conducted batch adsorption studies with an arsenic solution of concentration 1 mg/L for a 6 hour contact time. The results they obtained from their experiments are shown in Table 3.

Table 3: Removal Efficiency of Different Media (Saha et al., 2001)

Adsorbent	Dose (g/l)	% Removal	
		As (III)	As(V)
Kimberlite tailing	10	25	40
Water hyacinth	10	45	70
Wood charcoal	10	19	37
Banana pith	10	12	18
Coal fly ash	10	20	28
Spent tea leaf	10	25	42
Mushroom	10	22	35
Saw dust	10	28	36
Rice husk ash	10	5	12
Sand	10	15	22
Activated carbon	10	50	65
Bauxite	10	58	80
Hematite	10	40	60
Laterite	10	45	70
Iron-oxide coated sand	10	72	90
Activated alumina	10	90	96
CalSiCo	5	90	98
Hydrous granular ferric oxide	2	92	99

Most of the adsorbents studied showed relatively poor adsorption of arsenic except for iron-oxide coated sand, activated alumina, CalSiCo and hydrous granular ferric oxide. These four adsorbents had removal efficiencies of 72, 90, 90 and 92 % for As(III) and 90, 96, 98 and 99 % for As(V), respectively (Saha et al., 2001). Adsorption processes such as activated alumina and granular ferric hydroxide have been proved to be the most promising arsenic removal technologies.

Activated Alumina (AA)

Studies by the American Water Works Research Foundation indicate that low cost and disposability of AA makes it an attractive choice for smaller municipal systems and point-of-use treatment devices (French, 2005). Activated alumina is one of the adsorbents that has great affinity for various organic and inorganic pollutants and can be easily regenerated and reused (Sing et al., 2004). The arsenic removal efficiency by activated alumina is typically > 95% (Johnston et al., 2001 and Singh et al., 2001), but has more preference towards As(V) than As(III). Activated alumina column experiments showed that breakthrough was attained faster in the case of arsenite than arsenate (EPA, 2000). Hence it is recommended to oxidize As(III) to As(V) before treatment.

Adsorption of arsenic by activated alumina is highly pH dependent. The optimum pH for arsenic adsorption onto activated alumina is from 5.5 – 6 (Vance, 2002). Maximum adsorption of As(V) occurs at pH 4-7 and the maximum adsorption of As(III) occurs at pH above 9 (Twidwell,1999).

If the phosphate concentration in the water is more than 10 mg/L, the removal efficiency of arsenic decreases. It also decreases when the fluoride concentration is more than 2 mg/L and EDTA more than 0.01 moles/L (Saha et al., 2001). Some researchers have determined that arsenic removal declined by 50% in the presence of sulfate and sometimes chloride (Aragon et al., 2002 and EPA, 2000). In a pilot plant study for arsenic removal using activated alumina at pH 7.5, it was reported that the arsenic removal capacity varied very slightly with increasing EBCT (Thirunavukkarasu et al., 2003). Activated alumina is highly selective towards As(V); and this strong attraction resulted in regeneration problems, leading to 5-10% loss of adsorptive capacity for each run (Bhaumik et al., 2004). The capability of activated alumina to remove arsenite has not been explained much by researchers. Disposal of the spent regenerant and media would be a problem in using this treatment method.

Ion Exchange Resins

This process of arsenic removal is very similar to the AA technique except for the medium which is a synthetic resin of ion exchange capability. Exchange of ions take place between the resin and the feed water. A chloride form strong base anion-exchange resin is used for this process. Typically 300 to 60,000 bed volumes can be treated before the bed reaches exhaustion (EPA, 2000). The resin is regenerated after it gets exhausted with a brine solution. Strong base resins permit the use of ordinary sodium chloride brine for regeneration, and eliminate the need for the use of strong acids. This method of arsenic removal is independent of pH.

Ion exchange can remove As(V) efficiently, but hardly removes As(III). Hence it would require pre-oxidation of arsenite to arsenate. High levels of TDS, selenium, sulfate, fluoride and nitrate in water can affect the life span of resin. Suspended solids and precipitates can cause clogging of the ion exchange bed, hence appropriate pretreatments should be done. Disposal of the highly concentrated spent regenerant could be a serious problem. Regeneration is a slow and water-intensive process.

Granular Ferric Hydroxide (GFH)

This treatment option is capable of removing both forms of arsenic. Kinetics studies showed that less than 5µg/l of As could be achieved at the pH levels of 6 and 7.6 with a maximum of 96% of As(V) removal at a pH of 7.6 at an equilibrium time of 6 h (Thirunavukkarasu et al., 2003). Research has show that GFH is less sensitive to pH and has higher capacity than AA. Preoxidation of raw water is not required and both arsenic valence states are removed to the same extent. GFH is classified as a non-regenerative media that must be removed from the filter vessel when exhausted, and replaced with new media. Periodic backwashing of the media is required depending on raw water quality. Research is being conducted to determine the feasibility of regenerating GFH. This type of treatment requires iron removal as pretreatment to prevent the filter bed from clogging up.

Iron Oxide Coated Sand (IOCS)

Iron oxide coated sand is prepared by treating river sand with acid solution, then mixed with Iron (III) nitrate nanohydrate at a weight ratio of 10:1 and heating to 110°C for at least 20 hours (Yuan et al., 2002). Batch studies with IOCS showed that effluent arsenic level could be achieved below 5 to 10 µg/L with an adsorption capacity of 136µg/g (Thirunavukkarasu et al., 2005). IOCS had a removal efficiency of 68.85% and 83.65% for As(III) and As(V), respectively and very strong hardness of water affected the removal efficiency of arsenite alone (Yuan et al., 2002). Between 350 to 400 bed volumes were treated before attaining breakthrough using a bed of depth 40 cm, flow rate of 10 to 15 ml/min and a contact time of 3 to 3.5 minutes (Poole, 2001).

The performance of this treatment option is highly variable. This technology for arsenic removal can be effective with arsenic concentrations up to at least 300 ppb. It does not seem to be viable with very high concentrations (Ashraf et al., 2001).

Auminum Loaded Shirasu Zeolite

Aluminum-loaded Shirasu Zeolite P1 (Al-SZP1) was prepared and employed for removal of arsenic from drinking water at Kagoshima University, Japan. The adsorption process followed first-order kinetics and the mechanism of adsorption was reported to be a ligand-exchange process between As(V) ions and the hydroxide groups present on the surface of Al-SZP1. The pH of water had a slight impact on adsorption of arsenic over a range of 3-10 (Xu, 2002). The presence of coexisting ions like chloride, nitrate, sulfate, chromate and acetate had no effect on arsenic adsorption. The presence of phosphate ions greatly interfered with adsorption. This adsorbent was found to be suitable for drinking water with low arsenic concentration. Desorption of the medium was done effectively with sodium hydroxide and hydrochloric acid solutions. The desorbed Al-SZP1 was loaded again with aluminum sulfate solution and the adsorption capacity was restored to 94% (Xu et al., 2002).

Xu et al. (2002) proposed that the adsorption of As(V) ion onto the Al-SZP1 is due to the formation of aluminum hydroxide on the adsorbent surface, followed by the exchange of As(V) ion for the hydroxide ion. This proposed mechanism has been described as

$[Al(OH)_3] – SZP + 3H_2AsO_4^- \longrightarrow [Al(H_2AsO_4)_3] – SZP + 3OH^-$ ------------- (1)

and/or

$[2Al(OH)_3] – SZP + 3HAsO_4^{2-} \longrightarrow [Al_2(HAsO_4)_3] – SZP + 6OH^-$ ------------ (2)

Evaluation of Arsenic Removal Technologies

A treatment technique could be considered as BAT (Best Available Technology) if it has

- High removal efficiency
- Affordability
- General geographic applicability
- Compatibility with other waste water treatment technologies
- Process reliability
- Ability to bring all of a system's water into compliance

Coagulation with metal salts, lime softening and iron/manganese removal have been the most commonly used arsenic removal technologies in the past. Coagulation processes are sometimes unable to remove arsenic to levels below 10µg/L (Johnston et al., 2001). These treatment techniques are not appropriate for small systems and disposal of sludge may be a problem. Though conventional iron and manganese removal could significantly remove arsenic, the process has several complications and hence it is not that simple.

Membrane processes are more expensive than other treatment methods. Usually the water rejection in membrane processes is about 20-25 % of the influent and this could be an issue in water-scarce regions.

The disposal of the highly concentrated regenerant stream will be a drawback of the AA treatment process. The ion exchange process has a drawback in frequent regeneration of the resin beds and hence its inability to treat relatively more bed volumes of water before reaching breakthrough. Disposal of the highly concentrated regenerant stream could be a problem (EPA, 2001).

Table 4 gives an idea of the effectiveness of the different treatment options considered for discussion.

Table 4: Treatment Options & Maximum Achievable Percent Removal (EPA, 2000)

Treatment Technology	**Maximum Achievable % Removal**
Coagulation/Filtration	95
Coagulation Assisted Microfiltration	90
Lime Softening (pH > 10.5)	90
Ion Exchange (sulfate < 50 mg/L)	95
Activated Alumina	95
Reverse Osmosis	>95
POU Activated Alumina	90
POU Ion Exchange	90

Overview of Emerging Technologies

The development and implementation of new adsorption technologies continue to accelerate, providing new adsorbent materials as options. This section reviews some of the emerging technologies that have applications in removal of arsenic and discuss the fundamental principles of the given technologies.

Inorganic adsorbents, calcined synthetic hydrotalcite and calcined boehmite had been tested in with water having neutral pH. Results showed removal efficiencies of 70% for As(V) compounds (Dousova et al., 2003). Hydrotalcite is a magnesium aluminum hydroxide hydrate mineral and boehmite is a major constituent of most bauxite ores and has a chemical formula of AlO(OH). A synthetic exchanger Mg-Al-hydrotalcite was synthesized using a mixture of $MgCl_26H_2O$, $AlCl_36H_2O$ and NaOH. The anions in the media get exchanged with $HAsO_4^{2-}$ and $HAsO_4^-$ to give arsenic-free of water. Removal efficiencies up to 91% were be obtained using this new hydrotalcite adsorbent (Bhaumik et al., 2004).

An investigation is being done on removing arsenic from drinking water with akageneite at the University of New Mexico. The team has found that cotton treated with akagenite removed up to 90% of arsenic (EWRI Currents, 2004). Colorado-based ADA Technologies has developed an adsorbent media with the primary ingredient as akagenite which is iron oxide. The ADA formulation has been shown to reduce arsenic contamination as high as 1,000 μg/L to10 μg/L in as little as 30 minutes and effective in the pH range of 6.5 to 8.5 (Frazer, 2005).

Researchers at DeMontfort University, England have found that fine powder prepared from dried roots of the water hyacinth, *Eichhornia crassipes,* could reduce arsenic concentration below the 10 ppb limit. It has been reported that it could remove 93% of arsenite and 95% of arsenate from a solution with an arsenic concentration of 200 ppb (C& EN, 2005). Ashok Gadgil, a scientist of the Lawrence Berkeley Lab, California has discovered that coal ash could be used for arsenic removal.

Synthetic Zeolites

Synthetic zeolites are hydrated aluminosilicates with symmetrically stacked alternating silicon-oxygen and aluminum-oxygen tetrahedrons which result in an open and stable three dimensional honey comb structure with a negative charge (Zeo Agronomics Technology, 2004). The negative charge within the pores is neutralized by positively charged ions such as sodium which are not rigidly fixed to the skeleton of zeolite so that they are capable of interchanging (Scott, 1980).

Zeolites of Type A and Faujasite are the most important types of synthetic zeolites (Zeo Agronomics Technology, 2004). The simplest synthetic zeolite is the zeolite A with a molecular ratio of one silica to one alumina to one sodium cation. The zeolite A synthesis produces sodalite units which have 47% open space, ion exchangeable sodium, water(s) of hydration and electronically charged pores (Zeo Agronomics Technology, 2004). Zeolite A exhibits the Linde Type A structure i.e., a 3-dimensional pore structure with pores running perpendicular to each other in the x, y and z planes (Breck, 1974). The cavity is surrounded by eight sodalite cages connected by their square faces in a cubic structure. Figure 3 shows the framework of a simple zeolite in which each aluminate tetrahedra are linked to four silicate tetrahedrals in all the three dimensions.

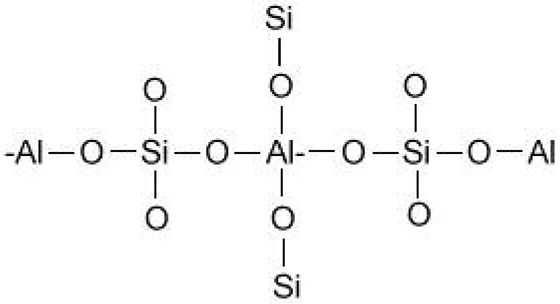


Figure 3: Basic Zeolite Framework
(Source: http://www.cheresources.com/zeolitezz.shtml)

Some of the most important differences between natural and synthetic zeolites are: (Zeo Agronomics Technology, 2004)

- The synthetic zeolites are manufactured from energy consuming chemicals and the natural zeolites are obtained from natural ores.
- Synthetic zeolites have silica to alumina ratio of 1:1 and the natural zeolites have the ratio as 5:1.
- Synthetic zeolites breakdown in a mildly acidic condition, whereas natural zeolites do not breakdown under this condition.

Zeolite Synthesis

Zeolite synthesis occurs by a hydrothermal process with reagents being a silica source, an alumina source, a mineralizing agent such as OH^- or F^-, and for higher Si/Al ratio zeolites, organic molecules which serve as structure-directing agents (Breck, 1974).

Zeolite A can be synthesized using sources of alumina (usually sodium aluminate) and silica (usually sodium silicate) mixed in a basic aqueous solution to give a gel. The alkali agent can be NaOH or solutions of quaternary ammonium salts, amines or other polar organics. Zeolite A is crystallized at temperatures ranging from 25 to 150ºC (optimum in the vicinity of 100°C) with the crystallization time varying from 2.5 hours to 14 days (Breck, 1974). The Zeolite thus synthesized is normally in the Na^+ form.

Common analytical methods used in the water and wastewater industry have been published by the EPA, the American Society for Testing and Materials (ASTM), and the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF) (EPA, 1999).

The analytical method appropriate for measuring arsenic in drinking water should reflect what is needed to demonstrate compliance with the Maximum Contaminant Level (MCL). The current MCL of 10μg/L is based on the total arsenic present in an unfiltered water sample. This had been taken into consideration in reviewing the published analytical methods.

Analytical Methods for Analysis of Arsenic in Drinking Water

There are eight methods currently approved for the analysis of arsenic in drinking water, of which three are multi-element or multi-analyte and the remaining five are element-specific or single-analyte techniques (EPA, 1999). Table 5 (EPA, 1999) lists the approved methods and the Method Detection Limits (MDLs) that are typical of the approved methods. MDL is the minimum concentration of a substance that can be reported with 99% confidence that the analyte concentration is greater than zero.

Table 5: Approved Analytical Methods for Analysis of Arsenic in Drinking Water (EPA, 1999)

Method		Technique	MDL (μg/L)
Multi-Analyte Methods	EPA 200.8	Inductively coupled plasma/ Mass spectrometry	1.4
	EPA 200.7	Inductively coupled plasma/Atomic emission spectrometry	8
	SM 3120B	Inductively coupled plasma/Atomic emission spectrometry	50
Single-Analyte Methods	EPA 200.9	Graphite furnace atomic absorption spectrometry	0.5
	SM 3113 B	Graphite furnace atomic absorption spectrometry	1
	ASTM 2972-93, Test Method C	Graphite furnace atomic absorption spectrometry	5
	SM 3114 B	Gaseous hydride atomic absorption	0.5
	ASTM D 2972-93, Test Method B	Gaseous hydride atomic absorption	1

SM = Standard Methods
ASTM = American Society for Testing Materials

Overview of Research Gaps

Most of the research works on arsenic removal using adsorption focus on determination of adsorption kinetics, adsorption capacity and comparisons with other adsorbents. Few researchers have focused on the feasibility of regenerating the media and further potential of the regenerated adsorbent media for arsenic removal. Little attention has been given to the generation and disposal of spent regenerant and media. Disposal of the spent regenerant and media could potentially cause problems and hence extensive studies need to be done in that area. The leaching potential of the adsorbent media has not been checked by researchers. The use of adsorbents to produce drinking water with low levels of arsenic on a long term basis and varying operational conditions has not been studied (EPA, 2001).

CHAPTER IV

MATERIALS AND METHODS

Xu et al. (2002) obtained high removal efficiencies of As(V) from water using Al-loaded shirasu zeolite. The authors proposed that the As(V) ions get exchanged with the OH^- ions of the aluminum hydroxide that is formed on the adsorbent surface. Shirasu is a volcanic rock found in Japan with 13 % aluminum as alumina. As this technology appeared to be a viable method to remove arsenic from water, investigation was done to identify a rock that is available in the United States, with a composition similar to that of shirasu. Rhyolite is a volcanic rock available in the US which has a composition similar to that of shirasu. As a result Rhyolite was used as the adsorbent media in an attempt to find a potential solution for removing arsenic from water in the United States. The preparatory steps involved in converting shirasu material into zeolite and then loading with aluminum were followed in creating the rhyolite media.

The word rhyolite comes from the Greek word for stream (rhyax) + the suffix lite. Rhyolite is a volcanic rock (extrusive igneous rock) formed from eruptions of lava. Rhyolite was named streaming rock because of its beautiful flow bands. It is a light-colored rock with silica (SiO_2) content greater than 68 percent by mass, sodium and potassium oxides both can reach approximately 5 percent by mass (USGS, 2005).

Some of the United States' largest and most active calderas were formed during eruption of rhyolitic magmas (for example, Yellowstone in Wyoming, Long Valley in California and Valleys in New Mexico). Rhyolite often erupts explosively because its high silica content contributes to an extremely high viscosity, which hinders degassing (USGS, 2005). Table 6 gives the typical mineral composition of rhyolite and shirasu.

Table 6: Composition of Rhyolite and Shirasu

(http://www.clas.ufl.edu/users/dfoster/courses/09_igneous2010.htm)

Component	**Shirasu** (% Mass)	**Rhyolite** (% Mass)
SiO_2	69.41-70	72.08
Al_2O_3	13.24-13.44	13.86
K_2O	3.67-5.26	5.46
Na_2O	3.57-5.36	3.08
FeO	-	1.67
CaO	1.32-1.44	1.33
Fe_2O_3	1.58-1.82	0.86
MgO	0.65-0.72	0.52
TiO_2	-	0.37
MnO	-	0.06

Sorption Media

The media required for the research, rhyolite, was obtained from Hansen Aggregates WRP, Inc. quarry in Davis, Oklahoma. The raw rhyolite was synthetically made into a zeolite (type A) to improve the adsorption properties of the starting media.

The preparation of the material used for the investigation, modified rhyolite, consisted of the following series of steps

- The rhyolite material obtained from Hansen Aggregates WRP, Inc. was sieved using sieves of the required sizes. Standard US Sieve sizes of 50 (300 µm) and 200 (75 µm) were used.
- Ten grams of rhyolite of the required size was mixed with 250 ml of a 1 M sodium hydroxide (NaOH) solution and heated in a water bath at 95 °C for 3 hrs in a 500 ml round bottomed flask.
- The NaOH treated rhyolite was cooled in air to room temperature and then washed in 500 ml of distilled water for two hours.
- The washed rhyolite, free of impurities, was contacted with 1 litre of a 0.1 M sodium nitrate solution for 12 hrs.
- Rhyolite treated with $NaNO_3$ was then contacted with 1 litre of a 7mM aluminum sulfate solution for 12 hrs.
- The chemically treated rhyolite was then washed with distilled water and air dried.
- A speed of 300 rpm was maintained on the mechanical shaker for contacting the adsorbent with the various solutions.
- Erlenmeyer flasks of sizes 250 ml and 1 L were used for contacting the rhyolite with the reagents and arsenic contaminated water.

A type A zeolite is formed when the rhyolite material is heated in a 1 M NaOH solution at 95°C for 3 hours. In the strong NaOH solution, the zeolite A gets converted to a hydroxysodalite phase. Sodalite is formed from the zeolite-A by substitution of NaCl or other sodium species, such as NaOH, into the zeolite-A lattice structure.

The product thus crystallized is treated with a sodium nitrate solution to ensure the formation of sodalite. Nitrite, phosphate or chloride salts inhibit the transformation of type A zeolite to other minerals while nitrate positively affects the formation of sodalite (Deng et.al., 2005). The formed sodalite is rich in exchangable sodium ions.

The granules obtained are next treated with an aluminum sulfate solution with concentration of 7 mM. As a result of ion exchange (Al^{+3} for Na^{+}), the sodium content of the gel granules is lowered. The granules are washed then with distilled water to remove the SO_4^{2-} ions. The resulting adsorbent material formed by ion exchange is a Linde Type A (LTA) zeolite. Figure 4 shows the exchange of ions during the aluminum sulfate treatment step.

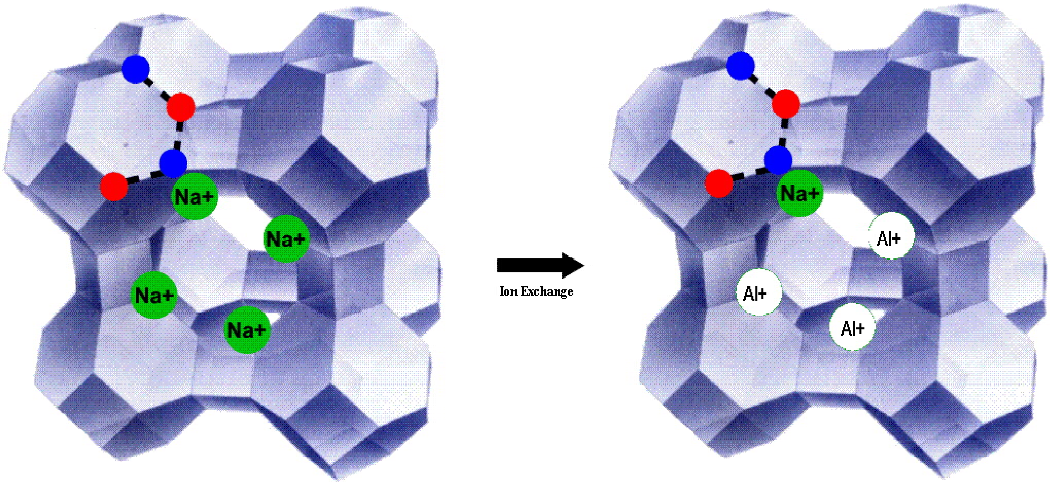
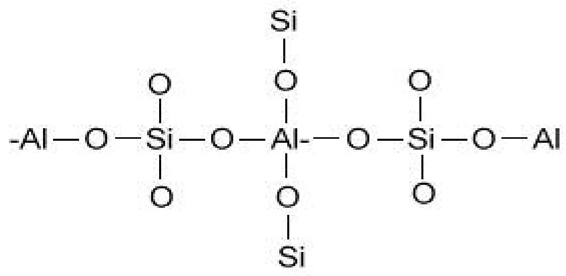


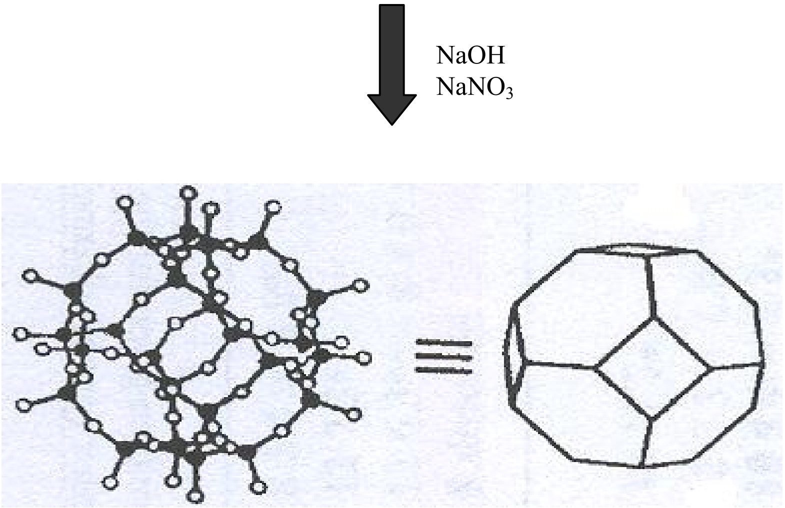
Figure 4: Exchange of Aluminum Ions (Modified from: http://www.gracedavison.com/eusilica/Adsorbents/product/zeolite_molecular_sieve.htm)

This process implemented for the preparation of the zeolite material is similar to the clay conversion process for the manufacture of zeolite from kaolin, which is hydrated silica of alumina with a composition similar to rhyolite. The reactants required for this process of zeolite manufacturing are caustic, calcined kaolin clay and water. The zeolite obtained from this process is also a type A zeolite. The raw kaolin is calcined to form metakaolin, which is then crystallized to zeolite A which is then converted by ion exchange to other forms such as molecular sieve type 4A or 5A.

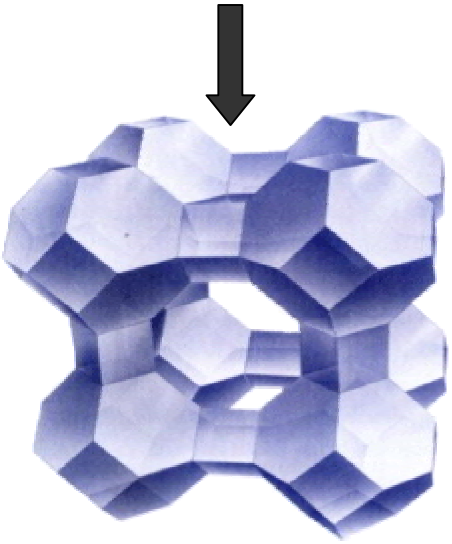
The chemically treated zeolite/non-zeolite made from rhyolite was then contacted with arsenic contaminated water (usually ≈ 300 μg/L). One hundred milliliters of As(V) and As(III) solutions were treated with varying amounts of the chemically treated zeolite/non-zeolite rock. Figure 5 illustrates the formation of Linde type A (LTA) zeolite.



Zeolite Frame Work [a]



Sodalite Cage [b]



Linde Type A Zeolite [c]

Figure 5: Formation of LTA Zeolite

[a] http://www.cheresources.com/zeolitezz.shtml
[b] http://481nts01.phys.metro-u.ac.jp/nmr-hp2.htm
[c] http://www.gracedavison.com/eusilica/Adsorbents/product.htm

Glassware

All the glassware used for the experiments was washed with glass cleaning liquid (Great Value), then washed with tap water, then rinsed with 1:1 nitric acid and finally rinsed with distilled water. The nitric acid used for preparing the 1:1 solution had a purity of 60-70% and was purchased from Pharmco.

Reagents

All the reagents used in the experiments were prepared using ACS reagent grade chemicals unless otherwise indicated. Distilled water was used for preparing the reagent solutions and making all dilutions.

Arsenic Solution

Sodium arsenate heptahydrate dibasic salt of 98 % purity purchased from Sigma was used for the preparation of arsenic contaminated water. Theoretically, 1.25 mg of the salt should be dissolved in 1litre of distilled water to get a concentration of 300 ppb. Due to the difficulty of measuring 1.25 mg, 4.16 g of the salt was dissolved in 1 L of water to get a solution of concentration 1 mg/L. A 300 ppb arsenic solution was obtained by making up 0.3 ml of the 1 mg/L solution to one liter.

Sodium arsenite manufactured by Fisher Scientific was used for preparing the arsenite solution. Arsenic (III) solution was prepared by dissolving 0.52 g of sodium arsenite, with a molecular weight of 129.91, in 1 liter of distilled water to give an As(III) solution with a concentration of 300 ppb. Sodium arsenite of weight 52 mg was dissolved in 1 L of distilled water to get a 30 ppm concentrated solution. A 300 ppb solution is obtained by diluting 10 ml of the 30 ppm solution to 1 liter.

Sodium Hydroxide Solution

A 1 M sodium hydroxide solution was used to convert the rhyolite into a zeolite. Sodium hydroxide purchased from Fisher Scientific with a purity of 98.1% was used to prepare the 1 M solution. Forty grams (40 gm) of NaOH pellets were dissolved in 1 liter of distilled water to prepare the solution.

Sodium Nitrate Solution

The 0.1 M sodium nitrate solution required for chemical treatment of the rhyolite was prepared by dissolving 8.499 g of sodium nitrate, with molecular weight of 84.99, in one liter of distilled water. A 99 % pure sodium nitrate stock purchased from EM Science was used.

Aluminum Sulfate Solution

Aluminum sulfate purchased from Fisher Scientific was used for preparation of the solution. The aluminum sulfate octadecahydrate, with a molecular weight of 666.44, was used for the preparation of this solution. A 7 mM solution of alum was obtained by dissolving 4.7 g of alum was dissolved in 1 liter of distilled water.

Hydrochloric Acid Solution

Hydrochloric acid with a 0.04 M concentration was used for regeneration of the adsorbent. The solution was prepared from a 0.1 N solution of 35% – 38% hydrochloric acid.

TCLP Extraction Fluid # 1

To make-up the TCLP extraction fluid 5.7 ml of glacial acetic acid was mixed with 500 ml of distilled water along with 64.3 ml of 1 N sodium hydroxide. This solution was then diluted to 1 liter. The 1 N sodium hydroxide solution was prepared by dissolving 40 g of 98.1 % pure NaOH pellets purchased from Fisher Scientific in 1 liter of distilled water. The glacial acetic was purchased from Fisher Scientific.

Instruments

Graphite Furnace Atomic Absorption Spectroscopy (GFAA)

The graphite furnace atomic absorption technique has been traditionally used to quantify arsenic in drinking water (EPA, 1999). The GFFA methods, EPA 200.9 and SM 3113 B, employ stabilized temperature platform graphite furnace atomic absorption (STP-GFFA) that greatly reduces interferences and improves analytical sensitivity.

A Perkin Elmer AAnalyst 300 atomic absorption spectrometer with a HGA 850 graphite furnace, a stabilized temperature platform graphite furnace with an auto sampler assembly, was used to analyze the arsenic concentration of the water samples. A 20 µL (typically 5-50 μL) aliquot of the sample was injected into the graphite tube placed along the optical path in between the light source and the detector of the atomic absorption spectrometer. An electrical furnace assembly heated the graphite tube through different steps to atomize the analyte. The light source was a hollow cathode lamp containing the element of interest. The amount of light absorbed by the free ground state atoms is directly proportional to the concentration of the analyte in solution within the linear calibration range of the instrument (EPA, 1999). Because of the greater percentage of analyte atoms vaporized and dissociated within the light beam passing through the graphite tube, greater analytical sensitivity is obtained and lower detection limits are possible as compared with flame atomic absorption (EPA, 1999).

Atomic adsorption is based on the principle that atoms will absorb light at some characteristic wavelength. These wavelengths are related to the atomic structure of an element and the energy required for the promotion of its electrons from one quantum level to another. Therefore, each element has its own characteristic wavelength. A wavelength of 193.7 nm is recommended for arsenic. The amount of light absorbed by an element at a certain wavelength can be correlated to the concentration of the element within the linear calibration range. The reliable calibration range is as low as 1-5 μg/L and as high as 200 μg/L. Dilution of samples with higher arsenic concentrations (greater than 200μg/L) may be required for accurate analysis.

Mechanical Shaker

A Thermolyne, Bigger Bill shaker was used for all the experiments to contact the arsenic adsorbent with the arsenic solution and for the chemical modification steps. A speed of 300 rpm was set for all the experiments.

Liquid – Solid Seperation

The separation was done with a vacuum filtration unit. Millipore AP40 glass fiber filters were used for separation of liquid and solid phases. The filters of diameter 47 mm were purchased from Millipore Corporation.

Fraction Collector

A Gilson FC – 80K Micro Fractionator was used for the column study. The fraction collector was operated in drop counting mode with 160 drops as the set point.

Methodology

The experiments conducted to investigate the performance and mechanism of arsenic removal with the novel media, modified rhyolite, involved different specifications of the adsorbent medium as appropriate for the investigatory part. The two different sizes of the rhyolite material used in the experiments along with quarry screenings were

i. Passing a No. 50 sieve or minus No. 50 material (300 µm)
ii. Passing a No. 200 sieve or minus No. 200 material (75 µm)

The quarry screenings would have rhyolite material of size 3/8th of an inch and lesser.

The adsorbent media used in the experiments and the treatment steps involved in the preparation of the adsorbents are given in Table 7.

Table 7: Media and Treatment Steps Involved

Medium	Treatment Undergone
Zeolite made from rhyolite, with chemical treatment	▪ Heated with 1M NaOH for 3 hrs at 95°C ▪ Washed with distilled water for 2 hrs ▪ Contacted with 0.1 M of $NaNO_3$ for 12 hrs ▪ Contacted with 7 mM of alum for 12 hrs ▪ Washed with distilled water for 2 hrs
Rhyolite, with chemical treatment	▪ Washed with distilled water for 2 hrs ▪ Contacted with 0.1 M of $NaNO_3$ for 12 hrs ▪ Contacted with 7 mM of alum for 12 hrs ▪ Washed with distilled water for 2 hrs
Zeolite made from rhyolite, without chemical treatment	▪ Heated with 1M NaOH for 3 hrs at 95°C ▪ Washed with distilled water for 2 hrs
Unmodified rhyolite	▪ Washed with distilled water for 2 hrs

Figure 6 provides a visual relationship of the different adsorbents media used in the experiments and the treatment steps involved in their preparation.

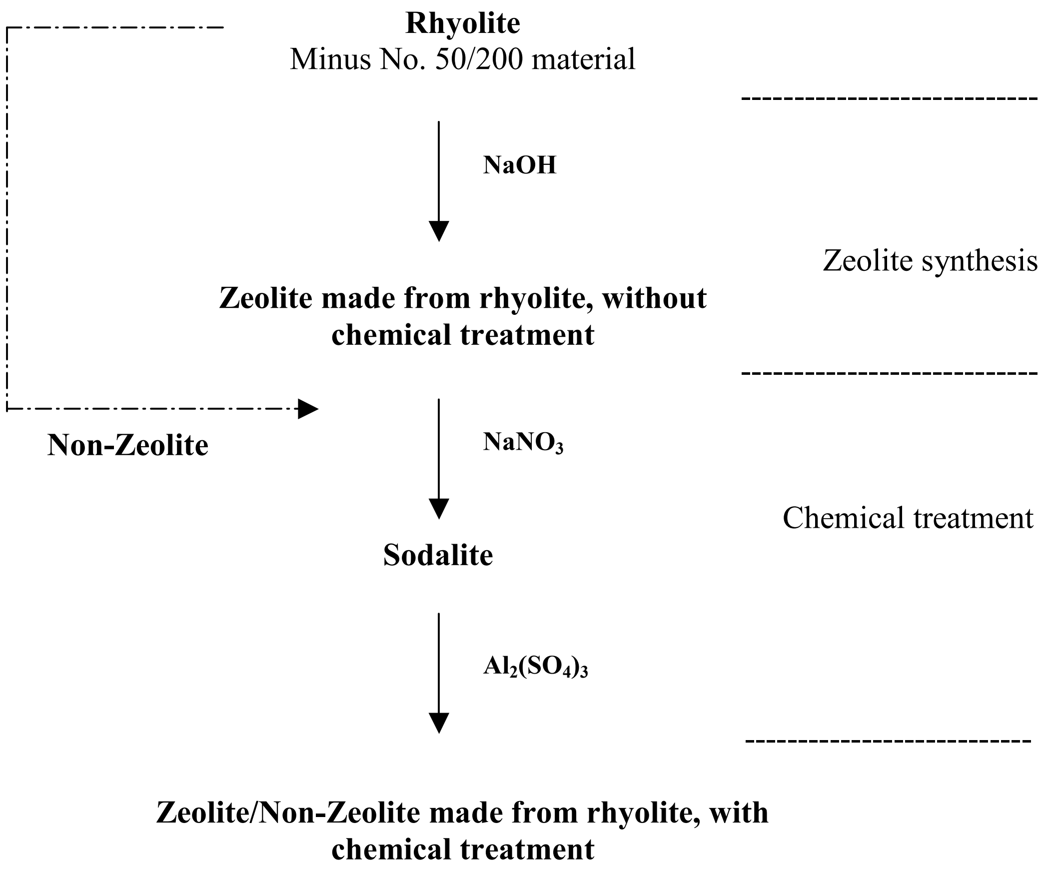


Figure 6: Making of Media

The investigation of arsenic removal using modified rhyolite involved the following experiments:

1. An adsorbent sample weighing 0.5 g was treated with 100 ml of an arsenic solution with an initial concentration of 526.5 ppb for 24 hours. The adsorbent used was non-zeolite made from minus No. 50 material, with chemical treatment.
2. The adsorption kinetics of quarry screenings, with chemical treatment was determined by using 0.5 g of the adsorbent contacted with 100 ml of an arsenic solution of concentration 360 ppb. Samples were collected and analyzed over a period of 48 hours.

3. Adsorption kinetics of non-zeolite made from minus No. 50 material, with chemical treatment were done by contacting 0.5 g of the adsorbent with 100 ml of the arsenic solution of concentration 335 ppb for 48 hours, where samples were periodically collected and analyzed.
4. A kinetic study for zeolite made from minus No 50 material, with chemical treatment using 0.5 g of samples contacted with 100 ml of the arsenic solution of concentration 298 ppb. Samples were analyzed for every 2 minutes for a total contact time of 10 minutes.
5. As a part of the investigation kinetics experiments were done with unmodified raw rhyolite of minus No. 200 material, zeolite made from minus No. 200 material, without chemical treatment, and zeolite made from minus No. 200 size material, with chemical treatment. In these experiments 0.5 g of the adsorption media was contacted with 100 ml of arsenic solutions of concentrations 420 and 493 ppb for a time of 10 minutes.
6. To get an understanding of the mechanism of the removal process an isotherm study was conducted with zeolite made from minus No. 50 material, with chemical treatment; minus No. 50 unmodified rhyolite material; minus No. 50 unmodified feldspar material and minus No. 50 unmodified sandstone material. In order to construct a Freundlich isotherm from the data 0.05, 0.25, 0.1 and 0.5 g of the adsorbent media was contacted with 100 ml of arsenic solutions of concentrations 317 ppb and 261 ppb for 5 hours.
7. An isotherm was prepared for both non-zeolite and zeolite made from minus No. 200 material, with chemical treatment where 0.05, 0.1, 0.25 and 0.5 g of the

adsorbent was contacted with 100 ml of an arsenic solution of concentration 516 ppb for 10 minutes.

8. An isotherm was prepared for zeolite made from minus No. 200 material, with chemical treatment in order to collect data that could be compared to data of other adsorbents that had been taken from other research works. Masses of media, 0.05, 0.1, 0.25, and 0.35 g, were contacted with 100 ml of an arsenic solution of concentration 1.6 mM (≈ 120 mg/L) for 10 minutes to obtain the data needed for plotting the isotherm.
9. Non-zeolite and zeolite made from minus No. 200 material, with chemical treatment, were tested for desorption/readsorption using a 0.04 M HCl solution. The samples were than checked for readsorption. The experimental sequence was as follows. Adsorbents samples of 0.05, 0.1, 0.25 and 0.5 g were treated with 100 ml of an arsenic solution of concentration 279 ppb for 10 minutes, the liquid was decanted and the media was desorbed with 100 ml of 0.04 M HCl solution for 10 minutes, again the liquid phase was decanted and finally the media was contacted with 100 ml of an arsenic solution of concentration 291 ppb to check the capability of the adsorbent to readsorb.
10. Zeolite made from minus No. 200 material, with chemical treatment was subjected to two cycles of desorption and readsorption. An arsenic solution of concentration 298 ppb was used for the study. Here 0.04 M HCl and 0.04 M NaOH solutions were used as the desorbent solutions. The experimental procedure utilized 0.1, 0.25 and 0.5 g of the adsorbent material contacted with 100 ml of the arsenic solution for 10 minutes, desorbed with 100 ml of the

selected desorbent for 10 minutes, and again treated with 100 ml of an arsenic solution of concentration 298 ppb for 10 minutes.

11. An experimental study to determine the effect of pH was conducted with zeolite made from minus No. 200 material, with chemical treatment. Half a gram (0.5 g) of the adsorbent samples was contacted with 100 ml of the arsenic solution of concentration 488 ppb for 10 minutes in the pH range of 5-10. Sodium hydroxide and nitric acid solutions were used to alter the pH of water.
12. The impact of competing ions in water on adsorption of arsenic was studied. Zeolite made from minus No. 200 material, with chemical treatment was contacted with 100 ml of arsenic solution which contained competing. Arsenic solution with phosphate, sulfate and nitrate ions at Initial Molar Ratios (IMRs) of 0, 1, 3, 5, 10, 20 and 30 were used for the study. Sodium phosphate, sodium sulfate and sodium nitrate were used for preparing the arsenic solution (500 ppb) with the competing ions.
13. An experiment was conducted to check the ability of the adsorbent to adsorb As(III). For this 0.05, 0.1, 0.25 and 0.5 g of the zeolite made from minus No. 200 material, with chemical treatment was treated with either 100 ml of As(V) solution with a concentration 516 ppb or an As(III) solution with a concentration 264 ppb. The duration of the experiment was 10 minutes.
14. A TCLP (Toxicity Characteristic Leaching Procedure) extract test was conducted to check the leaching ability of the arsenic adsorbed on to the adsorbent material. Zeolite made from minus No. 200 material, with chemical treatment, of weight 0.5 g was vigorously stirred for 5 minutes and the pH of the solution was checked.

Since the pH of the solution was found to be 4.5 (less than 5) TCLP extraction fluid # 1 was used. The pH of the extraction fluid was found to be 6. Two samples each weighing 0.75 g of the adsorbent media was contacted with 100 ml of arsenic concentration ppb. The adsorbent samples contacted with arsenic solutions of initial concentrations 342 ppb and 525 ppb were than shaken with 60 ml of the extraction fluid for 20 hours in a Zero Headspace Extractor (ZHE). The extraction fluid was analyzed for arsenic after 20 hours.

15. A column study was done to determine the operating capacity of the medium. A 50 ml burette stuffed with glass wool was used to hold the adsorbent. Half a gram (0.5 g) of the adsorbent, zeolite made from minus No. 200 material, with chemical treatment, was used to form the column for the experiment. An arsenic solution with an initial concentration of 516 ppb and a flow at a rate of 0.5 ml/minute were utilized in the experiment. The effluent from the bottom of the burette was collected in glass tubes using a fraction collector and analyzed for arsenic.

CHAPTER V

RESULTS AND DISCUSSION

EXPERIMENTAL QUALITY CONTROL

The very first experiment was done to check if rhyolite could remove arsenic from water and to check on the accuracy of the analytical test procedures utilized. Non-zeolite made from minus No 50 material, with chemical treatment was used. Adsorbent of weight 0.5 g was contacted with 100 ml of an arsenic solution of concentration 527 ppb for 24 hours. The water sample analyzed after contacting with the adsorbent had a concentration of 6.1 ppb. An aliquot of the water sample (identified as sample 1) was also sent to a private contract lab (Accurate Labs, Stillwater, OK). The result of the analysis showed a concentration of 8.2 ppb.

The accuracy of the analytical procedure was checked again with another sample (identified as sample 2, from a separate experiment) which was determined to have a concentration below the minimum detection limit of the Perkin Elmer AAnalyst 300 used was sent to the same contract lab for verification. The analysis done in the contract lab showed a concentration below their practical quantitation limit or minimum detection limit which was 2 ppb. The minimum detection limit of the Perkin Elmer AAnalyst 300 was determined to be 3 ppb. Table 8 shows the results of analysis for the two samples.

Table 8: External Quality Control

Sample ID	Method	Lab results	Contract lab results
Sample 1	EPA 200.9	6.1 ppb	8.2 ppb
Sample 2	EPA 200.9	BPQL*	BPQL

* Below Practical Quantitation Limit

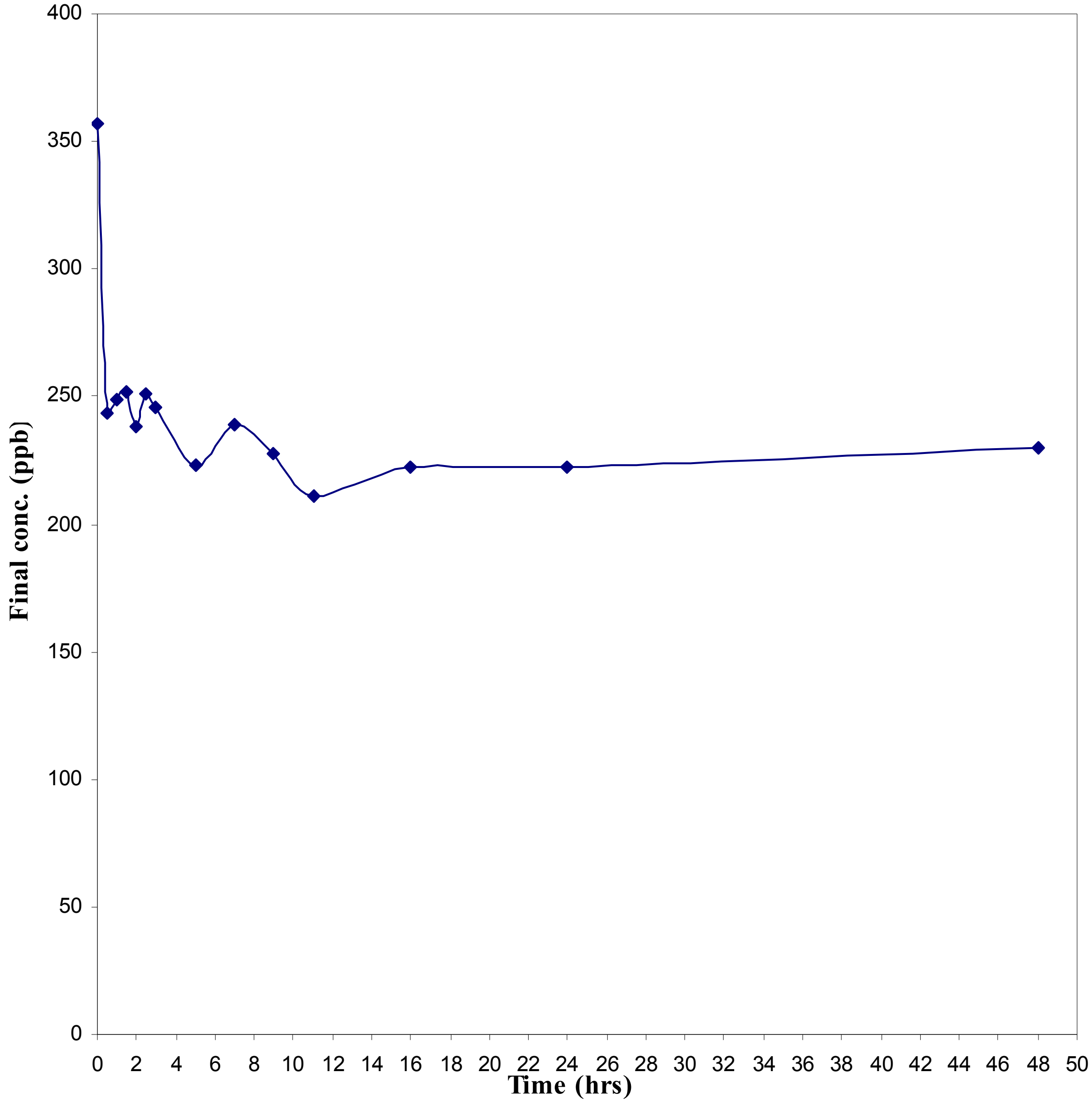
An experiment was done to check if the solid-liquid separation medium, filter removes any arsenic from the water while separation. Arsenic solution of concentration 267.5 ppb was used passed through the filter. The arsenic concentration before and after filtration were analyzed. The concentration of the filtered sample was found to be 265.9 ppb. The filtered solution had a 0.6 % variation in arsenic concentration with the influent solution, which says that the filter does not adsorb arsenic while separation.

RESULTS AND DISCUSSION

Quarry screenings, with chemical treatment was checked for its ability to remove arsenic over a period of 48 hours. Half gram of quarry screenings were contacted with 100 ml of water with an arsenic concentration of 360 ppb. Figure 7 is the graph which shows the kinetics of the adsorbent. The data used for the plot (Figure 7) is given in Appendix A. The results obtained showed that the quarry screenings had an arsenic removal efficiency of 36 % after a period of 48 hrs.

The 36 % removal efficiency of the medium, quarry screenings, with chemical treatment, seemed to be much smaller than the other conventional methods of arsenic removal and in addition EPA's MCL of 10 ppb was not obtained. Rhyolite of smaller size and larger surface area, which was believed would enhance the removal efficiency, was then utilized in the remaining experiments.

Half gram quantities of the minus No. 50 material, with chemical treatment were immersed in 100 ml of arsenic contaminated water of a concentration of 335 ppb for several intervals of time up to 48 hrs. Figure 8 shows that equilibrium was attained at 3 hours. The pH was monitored all through the experiment and was found to increase very slightly in the range 7.0 to 8.0. The data used for the generation of the curve in Figure 8 is given Appendix B.



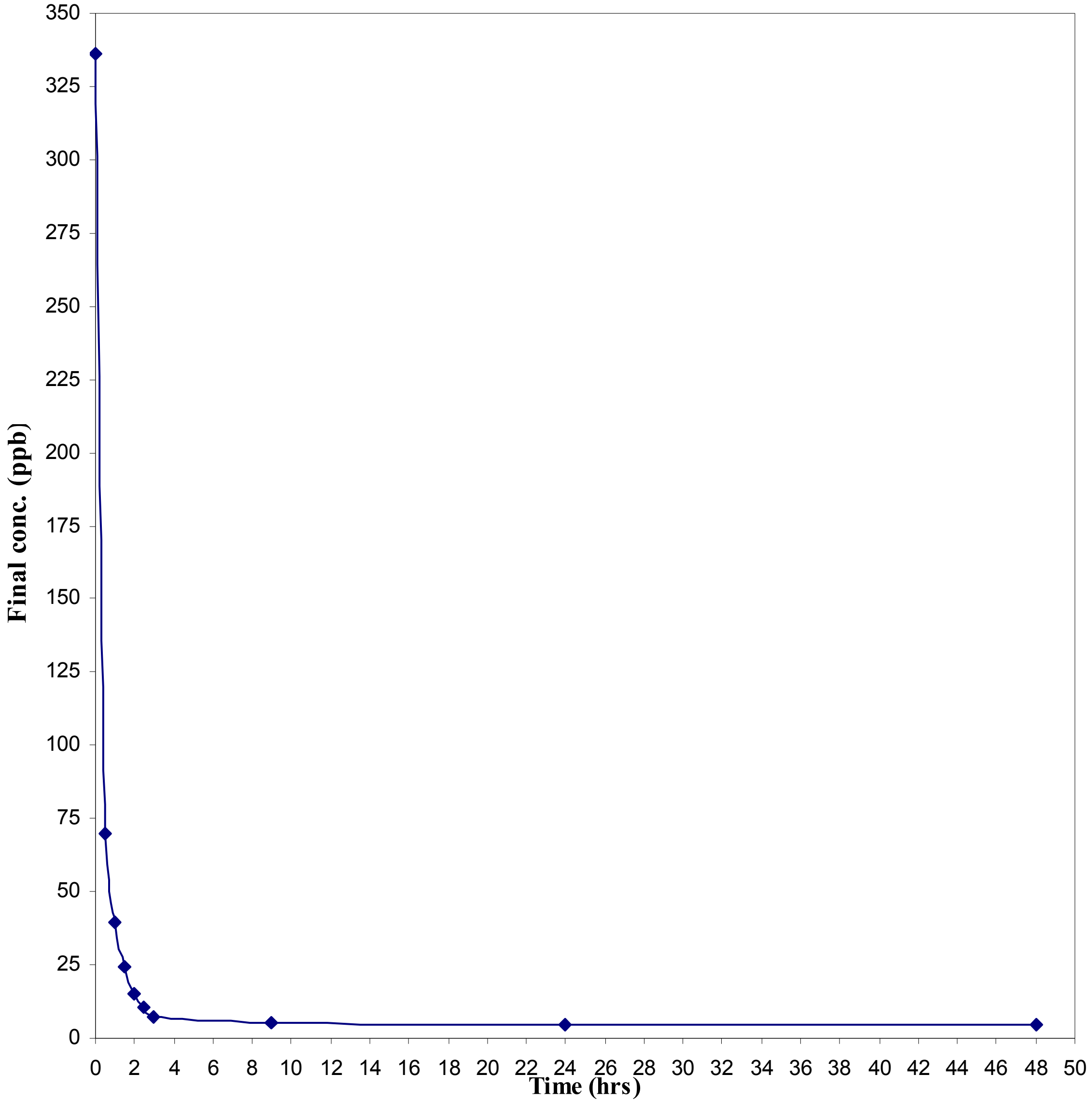
Medium: Quarry screenings with chemical treatment

Amount of medium used = 0.5 g

Influent concentration = 360 ppb

Volume of arsenic solution used = 100 ml

Figure 7: Kinetics – Quarry Screenings, with Chemical Treatment



Medium: Non-zeolite made from minus No. 50 material, with chemical treatment

Amount of medium used = 0.5 g

Influent concentration = 335 ppb

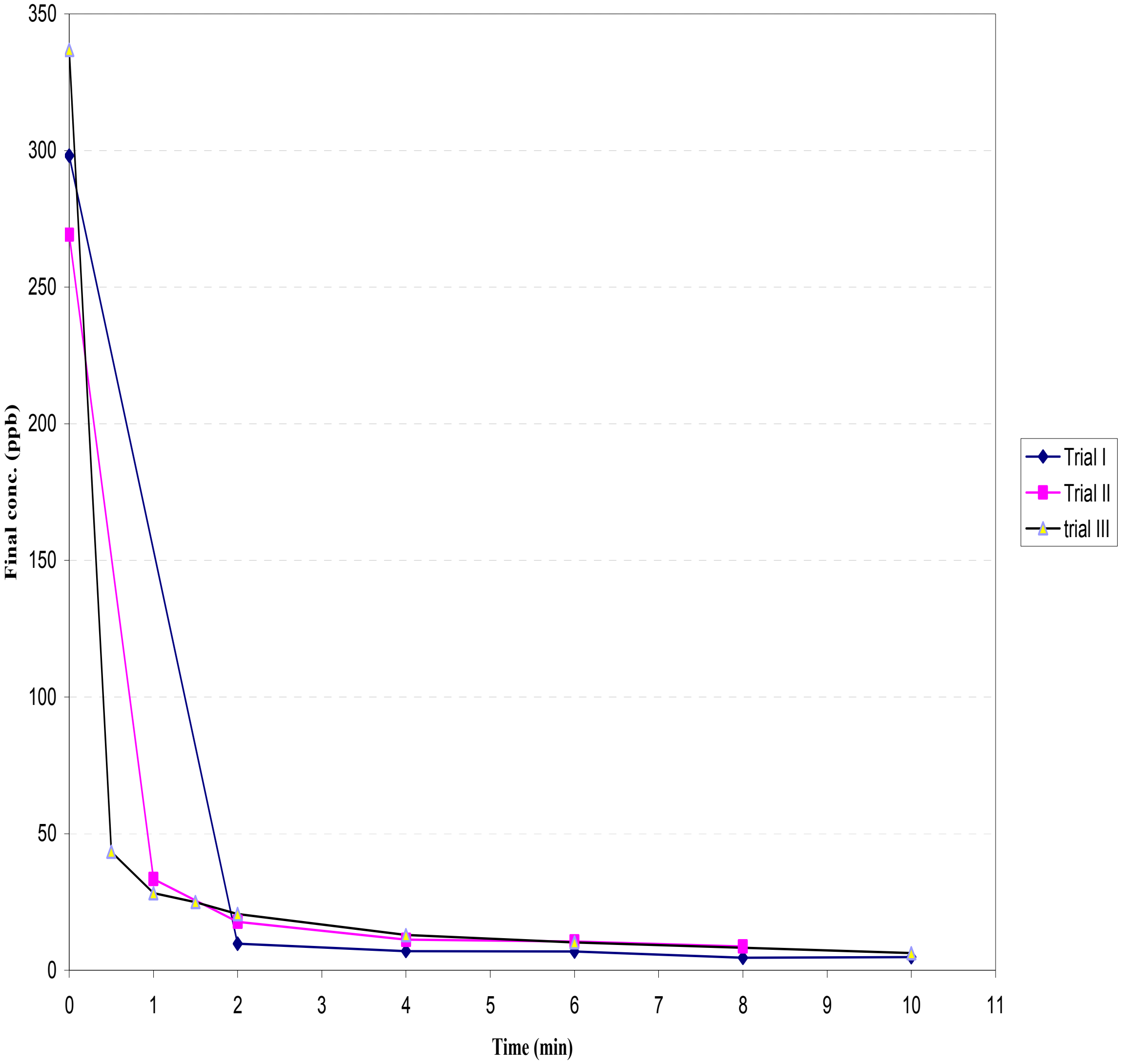
Volume of arsenic solution used = 100 ml

Figure 8: Kinetics – Non-zeolite Made from Minus No. 50 Material, with Chemical Treatment

For the minus No. 50 material, the effluent concentration obtained for the 48 hour sample was 4.6 ppb which yielded a removal efficiency of 98.6%. An effluent concentration below the 10 ppb standard was obtained at 3 hours. The larger surface area for adsorption of this smaller size material, approximately 7.5 ft^2/lb (Roberts, 1996), was believed to have made the difference. From Figure 8 it could be seen that the medium reaches equilibrium at 3 hours and hence a contact time of 5 hours was used for the experiments that utilizes the minus No. 50 material.

The hypothesis that the smaller size of the adsorbent, which provided more surface area for adsorption, would give better performance in a shorter time was put to test. A kinetic experiment was conducted with zeolite made from minus No. 200 material, with chemical treatment. The minus No. 200 material has a surface area approximately equal to16 ft^2/lb (Roberts, 1996). The graph showing the kinetics of the medium is shown in Figure 9 and the data for the kinetics experiment is given in Appendix C.

The data collected for the three trials showed than an arsenic concentration of less than 10 ppb was obtained at a maximum of 6 minutes with zeolite made from minus No. 200 material, with chemical treatment. A maximum removal efficiency of 98.4% was achieved in 10 minutes. The 6 minutes time, taken to reach a concentration below the MCL of 10 ppb, is much faster than the 3 hours taken by the minus No. 50 material.



Medium: Zeolite made from minus No. 200 material, with chemical treatment

Amount of medium used = 0.5 g

Inf. concentrations used = 298 ppb (Trial I), 269.2 ppb (Trial II) & 336.8 ppb (Trial III)

Volume of arsenic solution used = 100 ml

Figure 9: Kinetics - Zeolite made from minus No. 200 material, with chemical treatment

The 6 minutes time taken by the modified rhyolite appears to be quicker than many other adsorbents used for arsenic removal. For an influent concentration of 1 ppm (1 mg/L) and a contact time of 6 hours activated alumina had a removal efficiency of 96%, iron oxide coated sand had 90%, and granular ferric hydroxide had 99% efficiency for an initial concentration of 1 mg/L (Saha et al., 2001). It is also reported that activated alumina yielded a removal efficiency of 87% in 4 hours for an influent concentration of 1.5 ppm (Singh et al., 2004), while granular ferric hydroxide was capable of giving 80% efficiency in 3 hours for an influent concentration of 100 ppb (Thirunavukkarasu et al., 2003) and iron oxide coated sand gave a removal efficiency of 72.2% in 40-50 minutes time for an initial concentration of 1 ppm (Yuan et al., 2002).

The pH readings were noted down while conducting the kinetics experiments with modified rhyolite medium. The pH readings are given in Appendix C. A suppression of pH was observed with time. This indicates that H^+ ions are released in to water when the medium is contacted with arsenic contaminated water.

The kinetic data obtained were plotted to determine the order of the reaction. Table 9 has the reaction orders, the equations obtained for each of them and the R^2 values obtained for the plots. Looking at the equation and the R^2 values given in the table and the graphs plotted, it could be said that the reaction follows second order. Figure 10 shows the second order reaction graph for Trial II.

Table 9: Reaction Order

Order		Equation	R^2
Zero	Trial II	Y = -53.325 X + 176.21	0.5346
	Trial III	Y = -51.997 X + 155.8	0.3338
First	Trial II	Y = -0.7173 X + 4.854	0.7603
	Trial III	Y = 0.6253 X + 4.5598	0.5945
Second	Trial II	Y = 0.0213 X + 0.0075	0.9846
	Trial III	Y = 0.0172 X + 0.0121	0.952

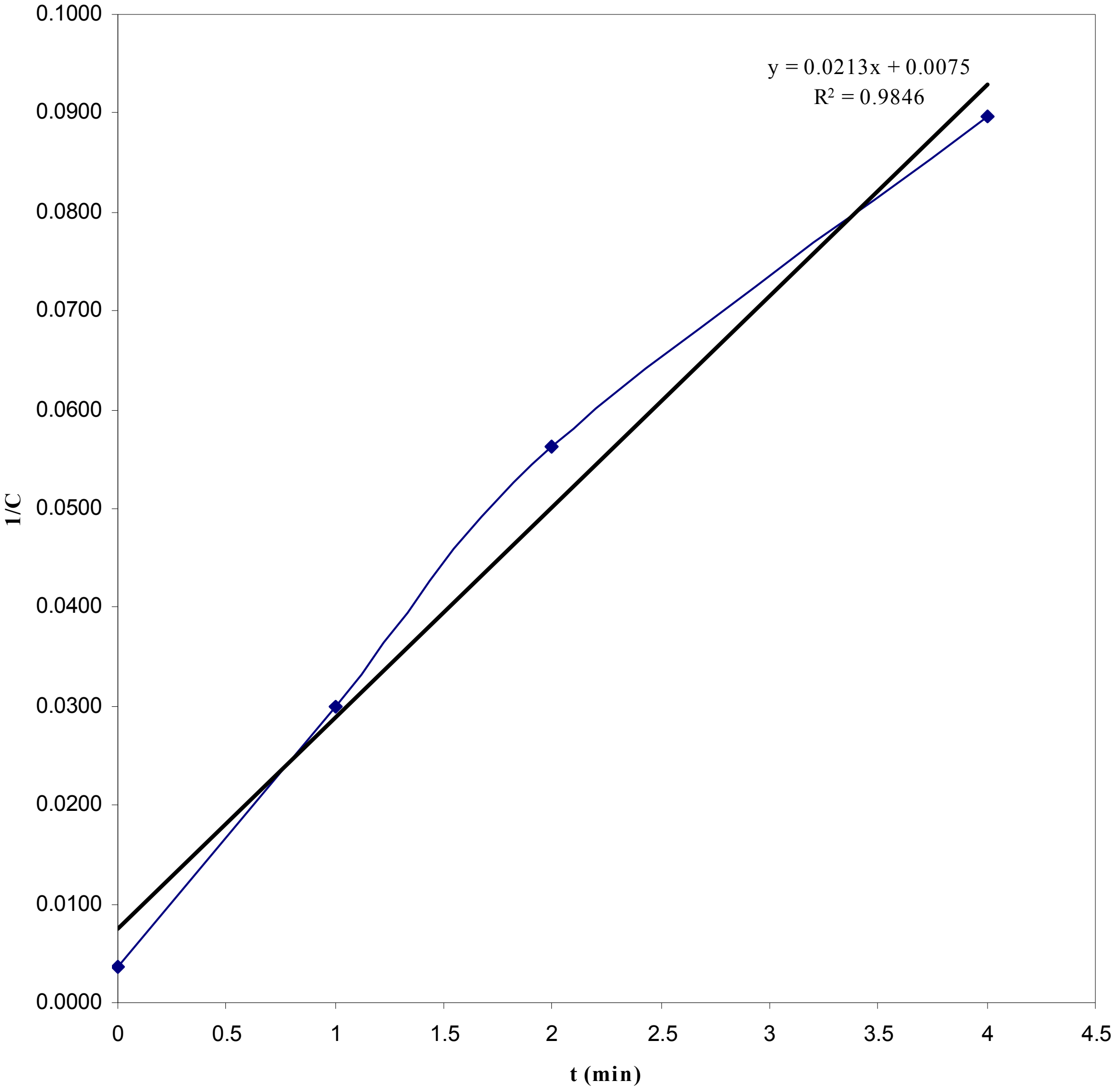


Figure 10: Reaction Order

As a part of the investigation, a kinetic experiment was done to determine the reason behind the very high arsenic removal efficiency on to modified rhyolite. The three different rock samples used for this experiment were:

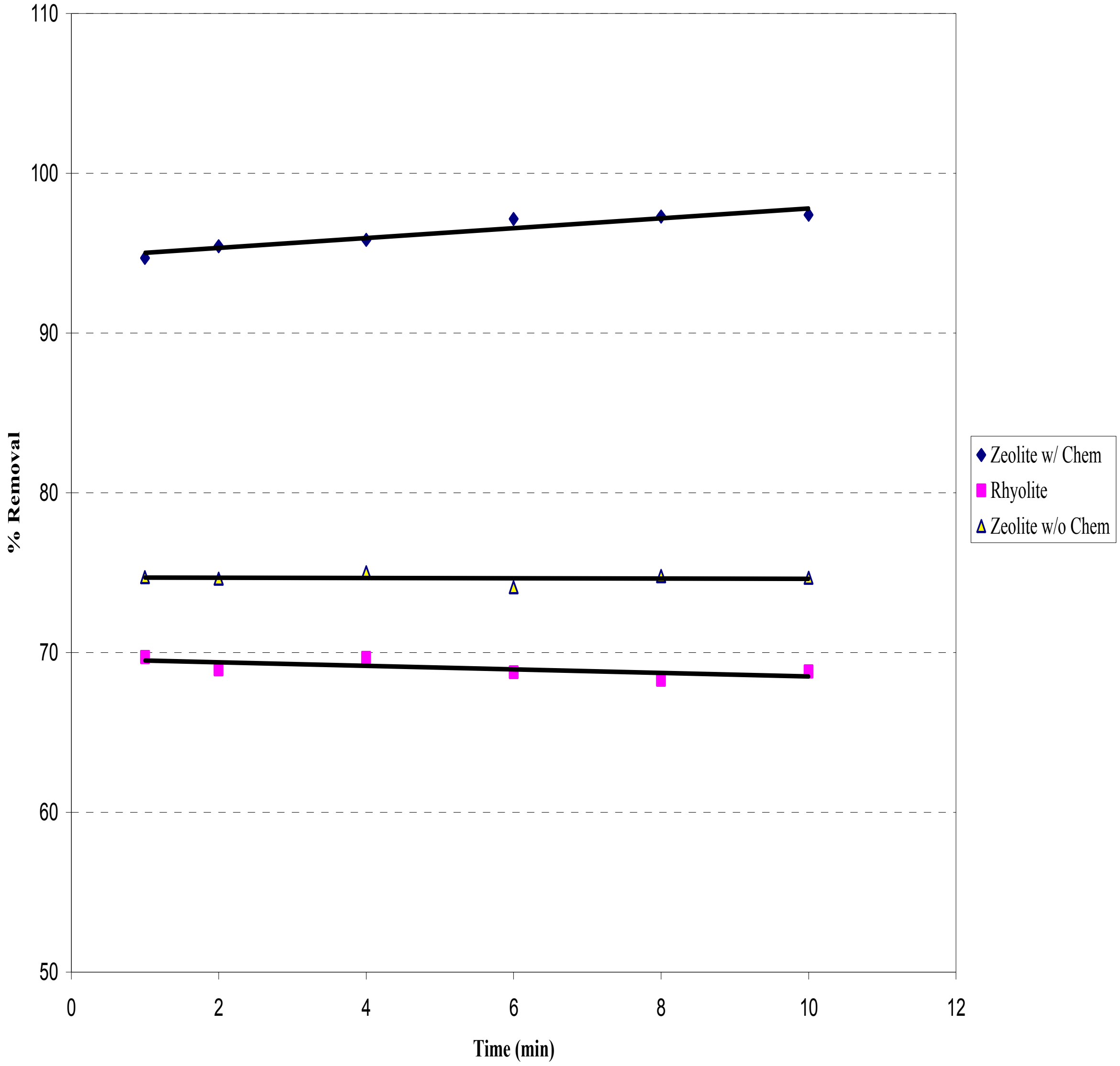
Rock Sample 1: Unmodified raw rhyolite of minus No 200 material
Rock Sample 2: Zeolite made from minus No 200 material, without chemical treatment
Rock Sample 3: Zeolite made from minus No 200 material, with chemical treatment

For this series of experiments 0.5 g of the rock samples were treated with an arsenic solution with a concentration of 420 ppb for the rock samples 1 and 3 and 493 ppb for the 2nd rock sample. The effluent concentrations were analyzed on samples taken every 2 minutes over the total contact time of 10 minutes. A higher concentration was used, instead of 300 ppb, to get good readable values of the final arsenic concentration so that the difference caused by adsorption could be clearly defined.

A plot of time vs % removal was plotted for all the three rock samples (Figure 11). The data set used for preparing the plot is given in Appendix D. The removal efficiencies obtained were:

Rock Sample 1: 68.3 to 69.7 %
Rock Sample 2: 74 to 75 %
Rock Sample 3: 94.7 to 97.4 %

The results suggest that the high removal efficiency obtained with the Rock Sample 3: zeolite made from minus No 200 material, with chemical treatment, is likely because of the larger number of aluminum ions present in this particular sample. The results also suggest a mechanism that likely in the result of preparation of the adsorbent material. The sodium ions become attached on the rhyolite material when it is treated with sodium hydroxide in the zeolite conversion step. These sodium ions present in the rhyolite material are exchanged for the aluminum ions during its treatment with aluminum sulfate solution. Aluminum ions are exchanged with the arsenate ions in the arsenic contaminated water to give higher removal efficiencies than the other two rock samples used. Rock Samples 1 and 2 have relatively equal number of aluminum ions which is essentially the aluminum present in the rhyolite rock. Typically, rhyolite rock has 13.83% of aluminum as Al_2O_3 as given in Table 5.



Adsorbents: Zeolite made from minus No. 200 material, with chemical treatment (♦), *non-zeolite made from minus No. 200 material, without chemical treatment* (▲) *and unmodified raw rhyolite* (■).

Amount of adsorbent used = 0.5 g

Influent concentrations = 420 ppb (▲) and 493 ppb (♦ & ■)

Volume of arsenic solution used = 100 ml

Figure 11: Investigation of Mechanism of Removal

An experiment aimed at getting a basic understanding of the mechanism of arsenic removal with the modified rhyolite was conducted. The different media employed for the study were:

1. Zeolite made from minus No. 50 material, with chemical treatment
2. Unmodified minus No. 50 material
3. Unmodified minus No. 50 feldspar
4. Unmodified minus No. 50 sandstone

Samples weighing 0.05, 0.1, 0.25 and 0.5 g of media were treated with 100 ml of influent arsenic concentrations of 317 ppb for medium 2 and 261 ppb for media 1, 3 and 4. A contact time of 5 hours was used for all the media. The obtained results were plotted as a Freundlich isotherm shown in Figure 12. The data used for generation of the isotherm are given in Appendix E.

The Freundlich isotherm was used in the linearized form,

$$\log (x/m) = \log K + (1/n) \log Ce$$

Where, *C* is equilibrium concentration (ppb)

x is mass of As(V) ions adsorbed (μg)

m is mass of adsorbent (g)

K is a constants which indicates the capacity of the medium

1/n is a constant which indicates the adsorption intensity of the medium

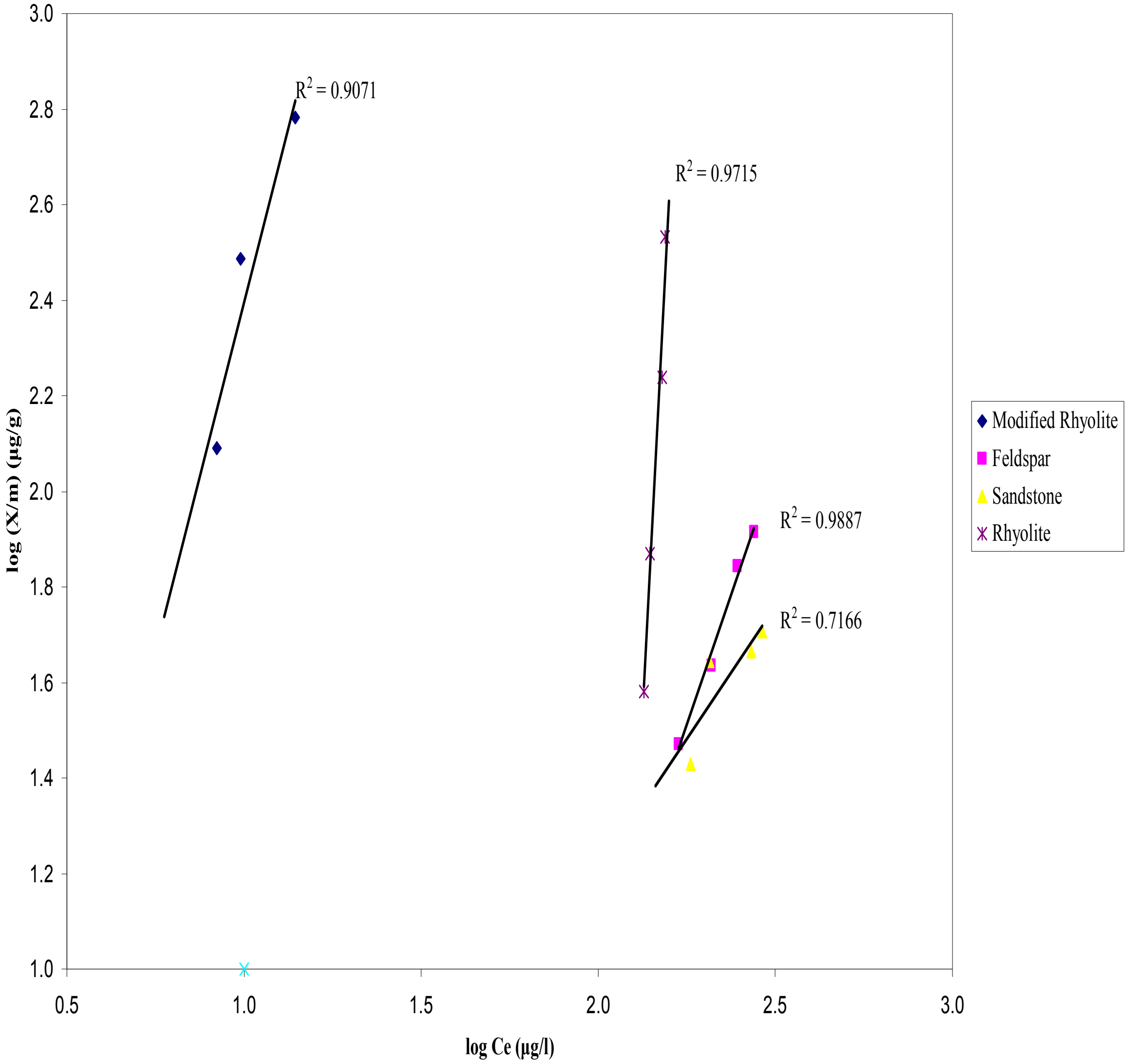
Quartz is a felsic mineral which is pure silicon dioxide and contains no aluminum (Igneous Rocks, 2005). Another important felsic mineral is feldspar in which a quarter or a half of the silicon has been replaced by aluminum (Igneous Rocks, 2005). Feldspar could be chemically defined as silicate of aluminum, containing sodium, potassium, iron, calcium or barium or combination of these elements. Potassium Feldspar, used for the experiment, has the formula $KAlSiO_3O_8$ (Foster et al., 1976). From the formula, the percent aluminum in the feldspar mineral was calculated to be ≈ 10 %. Sandstone has a chemical composition similar to that of sand. It is composed of 93 to 94 % of silicon dioxide and 1.4 to 1.5 % alumina (Sandstone Chemical Properties, 2005).

As in Figure 11, the zeolite made from minus No. 50 material, with chemical treatment showed very high adsorptive capacity compared to other adsorbents. The unmodified raw rhyolite had a lower adsorptive capacity, but had a relatively greater capacity than the unmodified feldspar and sandstone.

The difference in the capacities is again likely due to the difference in the aluminum content of each of the four adsorbents. The maximum alumina content of sandstone is around 1.5 %, whereas feldspar has a greater percentage of Al than sandstone and raw rhyolite at 13.86 % Al as alumina. Zeolite made from less than 50 mesh size rhyolite, with chemical treatment, had the greatest percentage of Al which was incorporated into the adsorbent during the modification steps. Sodium ions from the NaOH solution get adsorbed on to the rhyolite material while converting it into zeolite. The sodium ions along with the added sodium ions in the raw rhyolite gets exchanged with the aluminum ions when treated with aluminum sulfate solution.

This experiment supports the hypothesis that the removal of arsenic from groundwater using the proposed novel adsorbent is likely due to the exchange of arsenic ions with aluminum ions present in the media. The results of the experiment support the hypothesis, the greater the percentage of aluminum in the adsorbent material, greater the adsorption capacity.

An experiment was conducted to investigate the potential release of aluminum from the medium when treated with arsenic contaminated water. Analysis of water samples for Al was conducted at a contract lab, Soil Water and Forage Testing Lab at Oklahoma State University, Stillwater. An arsenic solution of initial concentration ppb was contacted with zeolite and non-zeolite made from minus No 200 material, with chemical treatment for 10 minutes and the final arsenic concentrations were found to be 11.3 ppb and 140 ppb for the zeolite and non-zeolite, respectively. The influent arsenic solution of concentration 439 ppb had an aluminum concentration of 190 ppb. This represents the background aluminum concentration in distilled water. The arsenic solution analyzed after contacting for 10 minutes had aluminum concentrations of 390 ppb and 2120 ppb for the zeolite and non-zeolite material respectively. This shows that exchange of aluminum ions for arsenate ions is most likely the reason for removal of As. But the exchange of cations with oxyanions makes the proposed mechanism questionable.



Adsorbents: Zeolite made from minus No. 50 material, with chemical treatment (♦) *and unmodified minus No 50 feldspar* (■)*, sandstone* (▲) *and rhyolite* (x)

Amount of adsorbent used = 0.05, 0.1, 0.25 and 0.5 g

Volume of arsenic solution used = 100 ml

Contact time = 5 hours

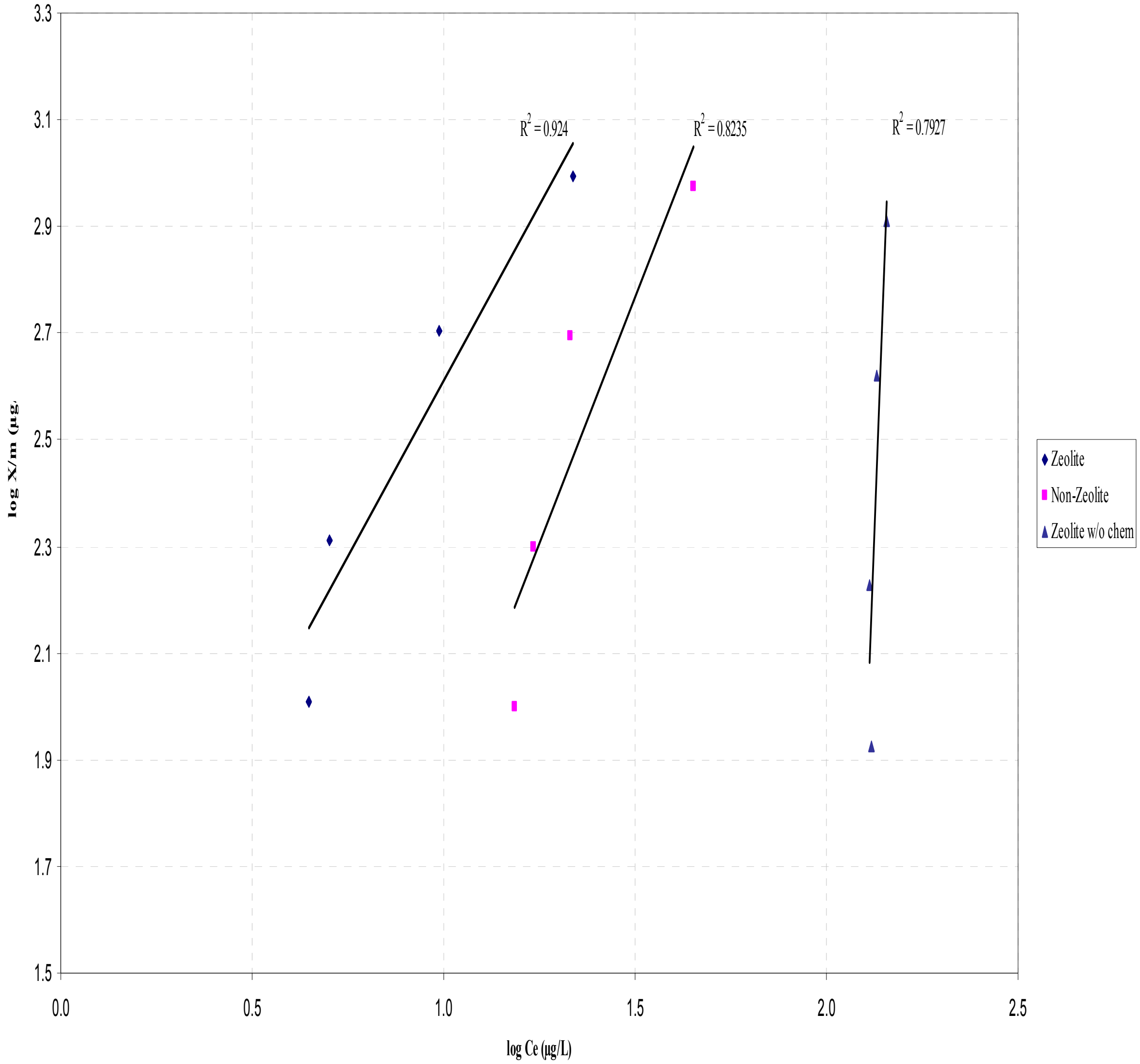
Figure 12: Investigation of Mechanism of Removal with Feldspar and Sandstone

The Al concentration in water, found to be a little excessive, could violate the drinking water standard for aluminum. The National Secondary Drinking Water Standard for Al is 0.05 to 0.2 mg/L (EPA, 2005).

Further investigation to understand the mechanism of arsenic removal was done with zeolite and non-zeolite made from minus No. 200 material, with chemical treatment and zeolite made from minus No. 200 material, without chemical treatment. Rock samples, 0.5 g, were treated with 100 ml of an arsenic solution of an initial concentration of 516 ppb for 10 minutes. The Freundlich isotherm prepared with the results obtained are shown in Figure 13. The data for the isotherm is given in Appendix F. The coefficients K and 1/n obtained were:

Table 10: Freundlich Isotherm Constants – Zeolite and Non-Zeolite

Adsorbent	**K (µg/g)**	**1/n**
Zeolite	398	1.3
Non-zeolite	70.79	0.008



Media used: Non - zeolite and zeolite made from minus No. 200 material, with chemical treatment (♦&■) *and zeolite made from minus No. 200 material, without chemical treatment* (▲)

Amount of medium used = 0.05, 0.1, 0.25 and 0.5 g

Influent concentrations = 516 ppb (♦&■) and 552 ppb (▲)

Volume of arsenic solution used = 100 ml

Contact time = 10 minutes

Figure 13: Isotherm – Zeolite vs Non-Zeolite

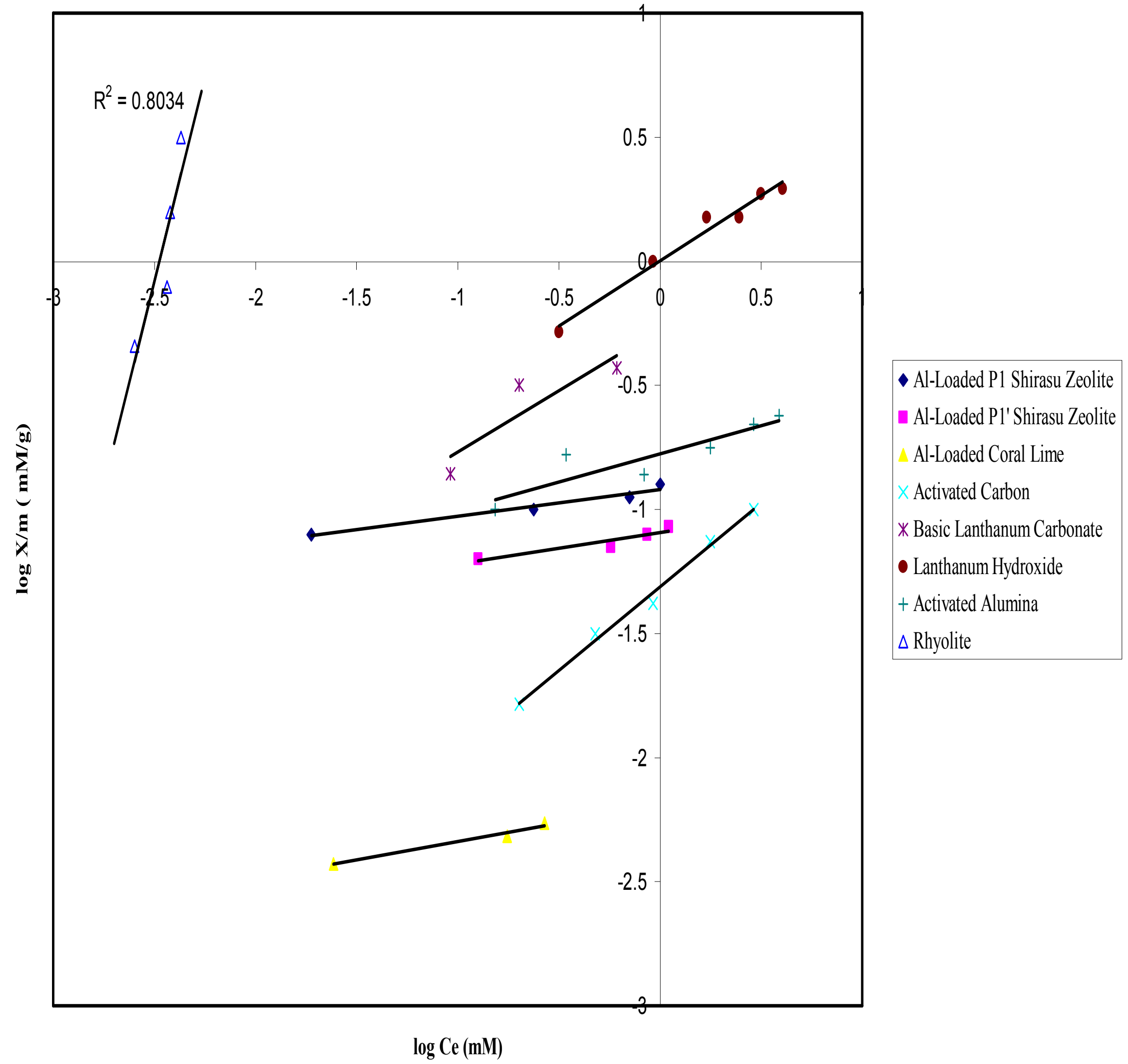
The Freundlich constant, K obtained show that the zeolite made material had a larger removal capability than the non-zeolite material. The zeolite made from minus 200 material, without chemical treatment, had a negative K value. The difference in removal should be because of the sodium ions that were attached to the rhyolite while converting it into zeolite. The added sodium ions along with the sodium ions in the rock itself are exchanged with the aluminum ions when the material is treated with aluminum sulfate solution. The non-zeolite adsorbent did not have any addition of sodium ions to it as there was no zeolite conversion step involved. The number of sodium ions that were present in this particular adsorbent was the same as that of raw rhyolite. The greater the number of sodium ions, the more exchange for aluminum ions and hence greater the removal capacity.

An experiment was conducted to compare the adsorptive capacity of modified rhyolite with some of the other existing arsenic removal media. The isotherm data for those existing media were obtained from a plot in the literature (Xu et al., 2002). Similar experimental conditions were maintained and an isotherm was plotted with the zeolite made from minus No. 200 material, with chemical treatment, along with the data obtained for the other media that had been tested for arsenic removal. The other media included:

- Aluminum loaded P1 type Shirasu zeolite
- Aluminum loaded $P1'$ type Shirasu zeolite
- Aluminum loaded coral lime
- Activated carbon

- Basic lanthanum carbonate
- Lanthanum hydroxide
- Activated alumina

Rock samples of weights 0.05, 0.1, 0.2 and 0.35 g were contacted with 100 ml of the arsenic contaminated water for 16 hours. An initial concentration of 1.6 mM was used for this experiment. The obtained results are plotted as an isotherm along with the data for the other adsorbents. The isotherm for the modified rhyolite had an R^2 value of 0.8034. The modified rhyolite proved to be superior in terms of capacity to the other adsorbents as it could be seen in Figure 14. The data used for preparing the plot (Figure 14) is given in Appendix G.



Medium: Zeolite made from minus No. 200 material, with chemical treatment

Amount of medium used = 0.05, 0.1, 0.2 and 0.35 g

Influent concentration =1.6 mM

Volume of arsenic solution used = 100 ml

Contact time = 16 hours

Figure 14: Comparison with other media

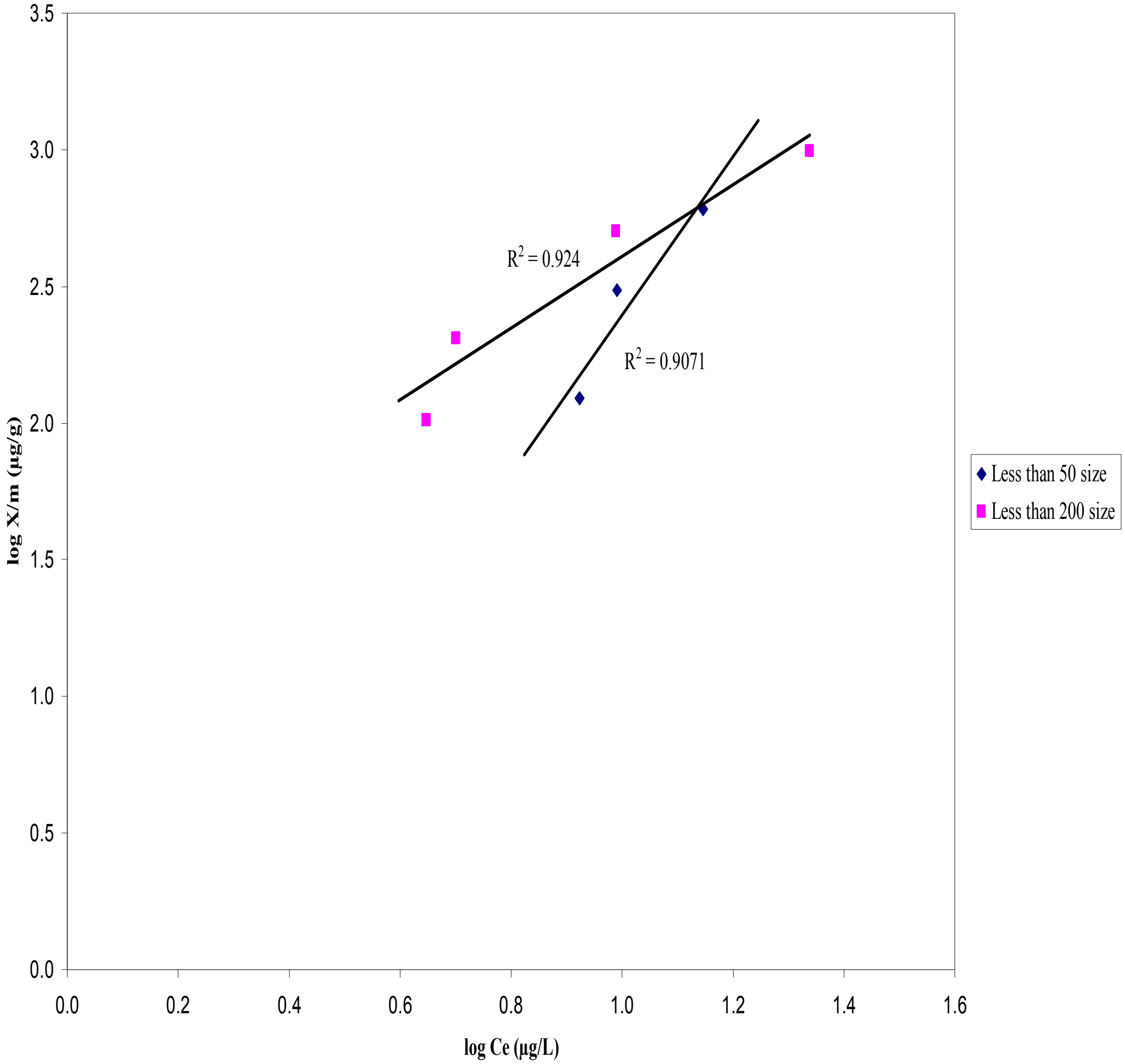
(Data from Xu et al., 2002 compared to data from this study)

A Freundlich isotherm was prepared to determine the capacities of zeolite made from minus No. 50 material and minus No. 200 material, with chemical treatment. The isotherm was prepared using the data obtained from previous experiments. The isotherm is shown in Figure 15 and the data used is given in Appendix H. The Freundlich isotherm constants obtained are reported as in Table 11.

Table 11: Freundlich Isotherm Constants of Media

Adsorbent	**K (µg/g)**	**1/n**
Minus No. 50 material	245.5	2.903
Minus No. 200 material	416.9	1.313
Activated alumina	250	0.05
Al-loaded P1 type shirasu zeolite	182.8	0.13
Al-loaded P1′ type shirasu zeolite	131.86	0.14

Table 11 shows that the zeolite made from minus No. 200 material, with chemical treatment has a very high removal capacity than the conventionally used media like activated alumina and the novel adsorbent Al-loaded shirasu zeolite.



Media: Zeolite made from minus No. 200 material and minus No. 200 material, with chemical treatment

Amount of medium used = 0.5 g

Influent conc. = 317 ppb (minus No. 50 material) and 516 ppb (minus No. 200 material)

Volume of arsenic solution = 100 ml

Contact time = 3 hours (minus No. 50 material) and 10 minutes (minus No. 200 material)

Figure 15: Adsorptive capacity of the medium

Non-zeolite and zeolite made from minus No. 200 material, with chemical treatment rock samples were subjected to desorption with hydrochloric acid and then checked for readsorption potential by contacting them with a fresh arsenic solution. The kinetic experiments done with the zeolite made from minus No. 200 material showed a depression in pH i.e., H^+ ions were liberated into water. HCl was used as the desorption fluid to make up for the lost H^+ ions from the adsorbent.

Different weights of the rock samples were treated with 100 ml arsenic solution of an initial concentration 279.3 ppb for 10 minutes. The rock samples contacted with arsenic solution were than subjected to desorption by contacting them with 100 ml of 0.04 M HCl solution for 10 minutes. The desorbed rock samples were than washed with distilled water. The samples were than contacted with a fresh arsenic solution to check for arsenic readsorption. One hundred milliliters (100 ml) of an arsenic solution with a concentration of 291.4 ppb was then shaken with the desorbed rock samples for 10 minutes in an effort to evaluate the readsorption potential. The results obtained are tabulated as in Table 12.

The results of the study (Table 12) showed that the zeolite and the non-zeolite medium had an average desorption of 64.09 % and 61.15 % of the arsenic adsorbed, respectively. The experiment also showed that the adsorbent is capable of readsorbing arsenic after being desorbed with HCl.

Table 12: Desorption and Readsorption with HCl

Influent conc. used for adsorption = 279.3 ppb

Influent conc. used for readsorption = 291.4 ppb

Adsorbent	Weight of medium (g)	As Adsorbed on to the adsorbent (ppb)	As Desorbed (ppb in HCl solution)	As Readsorbed on to the adsorbent (ppb)
Zeolite	0.05	276.8	182.1	67.4
	0.1	277.8	161.3	75.6
	0.25	278.5	180.5	93.4
	0.5	279.3	189	159
Non-Zeolite	0.05	274.6	164.5	40.6
	0.1	277.2	162.8	74.5
	0.25	278.3	159.6	76
	0.5	278.3	191.2	195

Another study to check desorption and readsorption of arsenic was done with both hydrochloric acid and sodium hydroxide solutions of concentration 0.04 M. Xu et al. (2002) had proposed that Al-loaded shirasu zeolite removed arsenic from water due to exchange of As(V) ions for OH^- ions. Hydroxyl ions were liberated into water from the shirasu medium. With the mechanism being unclear for the modified rhyolite and the suspicion that modified rhyolite might have the same removal mechanism as Al-shirasu zeolite, desorption with NaOH solution was done, with HCl being the other desorption fluid used.

Zeolite made from minus No. 200 material, with chemical treatment, was contacted with 100 ml of a 293 ppb arsenic solution for 10 minutes. The rhyolite samples with the adsorbed arsenic on them were treated with either 100 ml of 0.04 M HCl or NaOH solution for 10 minutes. The rock samples desorbed of arsenic were then retreated with 100 ml of an arsenic solution at the same initial concentration. Desorption and readsorption steps were done twice to determine the arsenic readsorption capacity of the modified rhyolite after each desorption step. The results obtained from the two cycles are given in Table 13.

As shown in Table 13, the first cycle had a desorption percentage of 42.4 % with HCl and 59 % with NaOH. Al-loaded Shirasu zeolite had desorption a of 25 % with 0.04 M HCL and 71 % with 0.04 M NaOH. An Al-loaded chelating resin desorbed 60-70 % of the arsenic adsorbed with NaOH of 2 M or more, but the desorption agent was not able to desorb arsenic from Ce-, Fe- and Zr-loaded resin (Trung, 2001).

Table 13: Desorption and Readsorption with HCl and NaOH

	Weight of medium (g)	Desorption fluid : HCl			Desorption fluid: NaOH		
		As Conc. (ppb)	Percent (%)	pH	As Conc. (ppb)	Percent (%)	pH
Adsorption (ppb adsorbed)	0.1	287.7	96.45	5.64	289.3	97	5.6
	0.25	293.6	98.44	5.02	293.8	98.48	5.16
	0.5	293.2	98.29	4.84	295	98.88	4.81
Desorption (ppb desorbed)	0.1	105.2	36.57	1.61	178	62.18	12.45
	0.25	142	48.36	1.63	172	58.58	12.45
	0.5	124	42.29	1.7	165.5	56.11	12.43
Readsorption (ppb adsorbed)	0.1	279.7	93.78	6.38	175.3	58.77	6.78
	0.25	291.9	97.84	5.59	182.9	61.3	6.9
	0.5	291.3	97.66	4.98	180.4	60.47	7.55
Desorption (ppb desorbed)	0.1	227.1	-	1.6	178.8	-	12.61
	0.25	194.2	-	1.71	164.6	-	12.42
	0.5	246.7	-	1.92	196.5	-	12.32
Readsorption (ppb adsorbed)	0.1	197.2	66.1	6.47	177.8	59.6	7.48
	0.25	171.9	57.62	6.34	175.3	58.77	7.06
	0.5	189.9	63.66	6.97	181.8	60.95	6.98

Medium: Zeolite made from minus No 200 material, with chemical treatment

Concentration of Arsenic solution used = 298.3 ppb

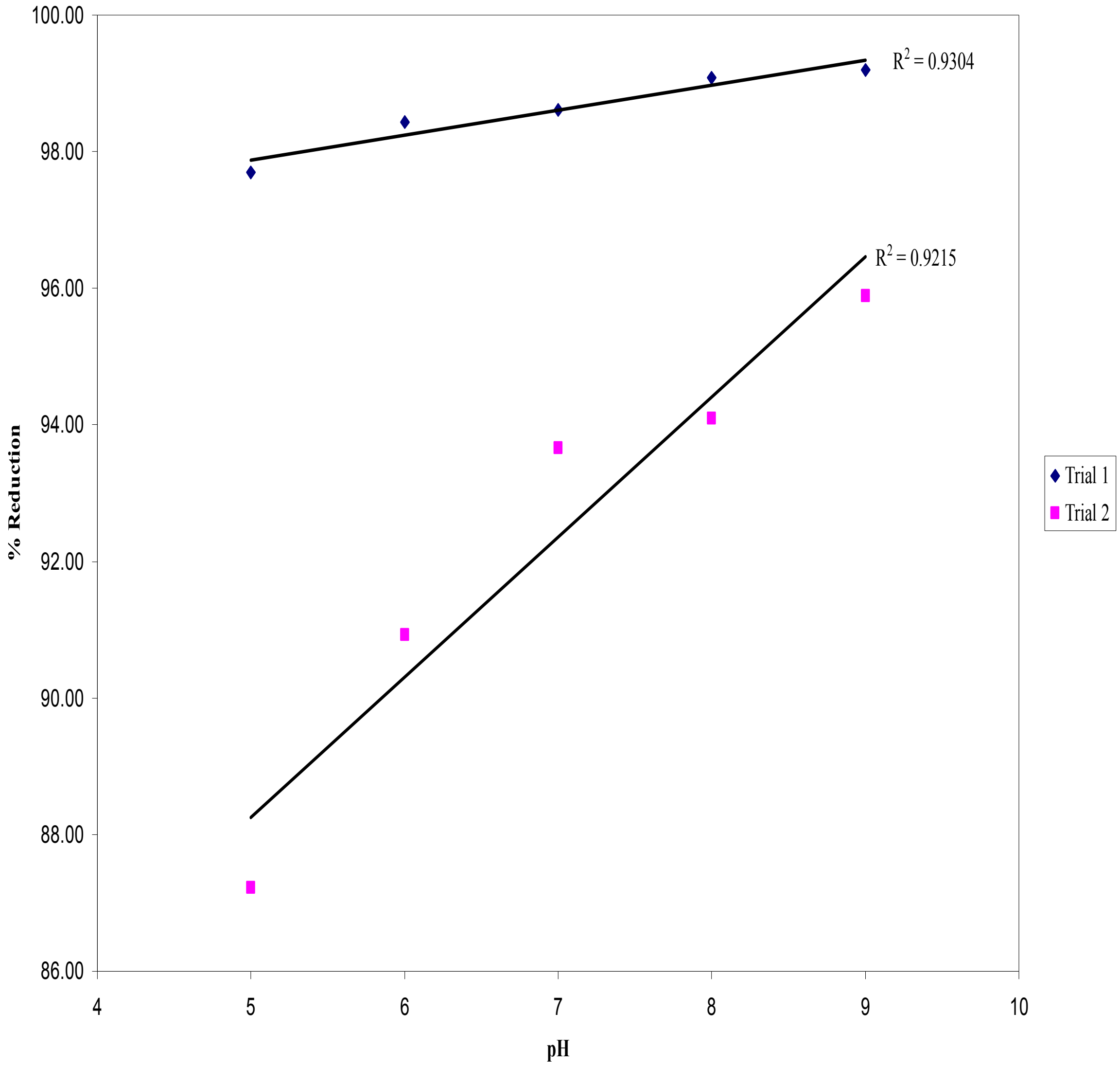
Volume of arsenic and desorption solution used = 100 ml

Contact time = 10 minutes

The proposed removal medium had readsorptions of 96.5 % and 60.2 % for the HCl and NaOH desorbed samples respectively for the first cycle. Al-loaded Shirasu zeolite had readsorptions of 85 % and 94 %, respectively for the HCl and NaOH desorbed medium. The modified rhyolite samples were able to readsorb arsenic after two desorption cycles. The adsorption of arsenic onto the NaOH desorbed samples remained the same (at about 60 percent) after the two desorption cycles. Though the HCl desorbed samples had a significant reduction in capacity of arsenic after the second desorption cycle, it was not able to reach below the 10 ppb standard. Hence it would be wise to use it as a once through system.

An experiment was done in duplicate to determine the effect of pH on arsenic removal by modified rhyolite. Zeolite made from minus No 200 material, with chemical treatment was used to study the effect in a pH range of 5 to 9. The reason behind the selection of this pH range was that the typical pH values of drinking water are in the range 6.0 to 9.0. Modified rhyolite samples of 0.5 g were contacted with 100 ml of arsenic solution with initial concentrations 487.6 and 528.7 ppb with pH 5, 6, 7, 8 and 9 for a period of 10 minutes.

Figure 16 contains the results obtained from the two trials performed which show an increase in % reduction of As(V) with increase in pH. The data used for the plot is given in Appendix I. This trend is completely opposite to the results shown by Xu and Yuan (Xu et al., 2002 and Yuan et al., 2002). However, La-loaded resin had shown increased % reduction with increase in pH in the range 4 to 10 (Trung, 2001).



Medium: Zeolite made from minus No. 200 material, with chemical treatment

Amount of medium used = 0.5 g

Influent concentrations = 487.6 ppb (Trial 1) and 528.7ppb (Trial 2)

Volume of arsenic solution used = 100 ml

Contact time = 10 minutes

pH range: 5 to 9

Figure 16: Effect of pH

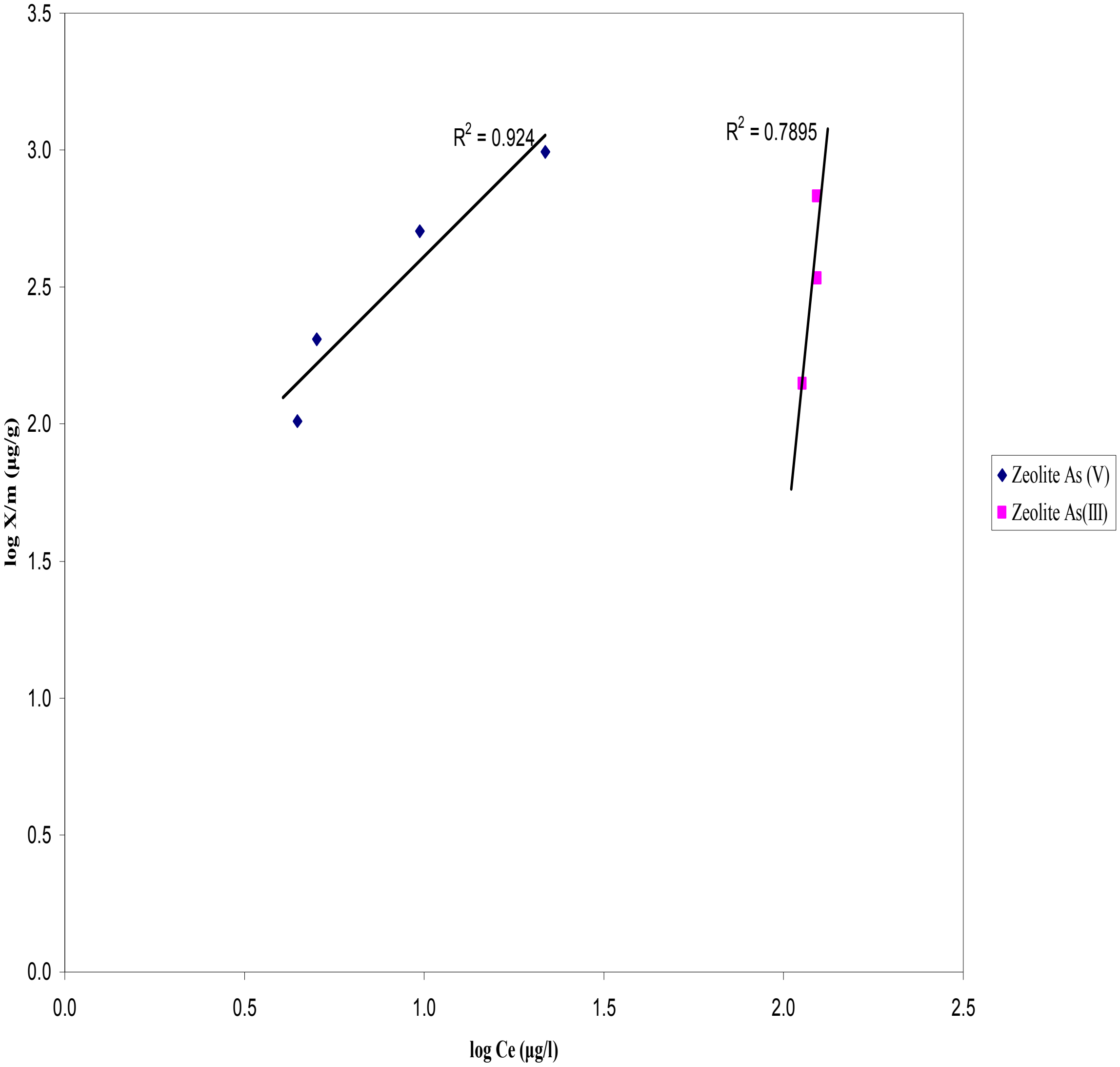
Experiments were conducted with zeolite made from minus No. 200 material, with chemical treatment to determine the effect of competing ions (sulfate, phosphate and nitrate) on arsenic removal. The results of the competing ions experiments are given in Table 14. Increase in sulfate and nitrate ion concentration had no effect on arsenic removal. Though there was not any impact of the phosphate ions for smaller Initial Molar Ratios (IMRs), a little impact was seen at higher IMRs.

Table 14: Effect of Competing Ions

IMR	**mM of As(V)**	**mM of Anion**	**Final As(V) concentrations (ppb)**		
			Phosphate Initial conc* = 473 ppb	**Sulfate** Initial conc* = 473 ppb	**Nitrate** Initial conc* = 450 ppb
0	0.0016	0	6.824	7.5	5.3
1	0.0016	0.0016	4.978	5.3	5.29
3	0.0016	0.0048	6.286	5.6	4.78
5	0.0016	0.008	8.136	6	7.82
10	0.0016	0.016	8.274	5.3	9.42
20	0.0016	0.032	9.4	4.1	8.13
30	0.0016	0.048	11.71	6.61	6.241

* Initial As(V) concentration of the solution used

The novel medium, modified rhyolite proved to be highly efficient in removing As(V) based on the previous experiments. An experiment was performed to determine the ability of the medium to remove As(III). Zeolite made from minus No. 200 material, with chemical treatment of weights 0.05, 0.1, 0.25 and 0.5 g was contacted with 100 ml of arsenic solution with an initial concentrations of 516 ppb As(V) and 464 ppb As(III) for 10 minutes.



Medium: Zeolite made from minus No 200 material, with chemical treatment

Amount of medium used = 0.05, 0.1, 0.25 and 0.5 g

Influent concentration =516 ppb (As V) and 464 ppb (As III)

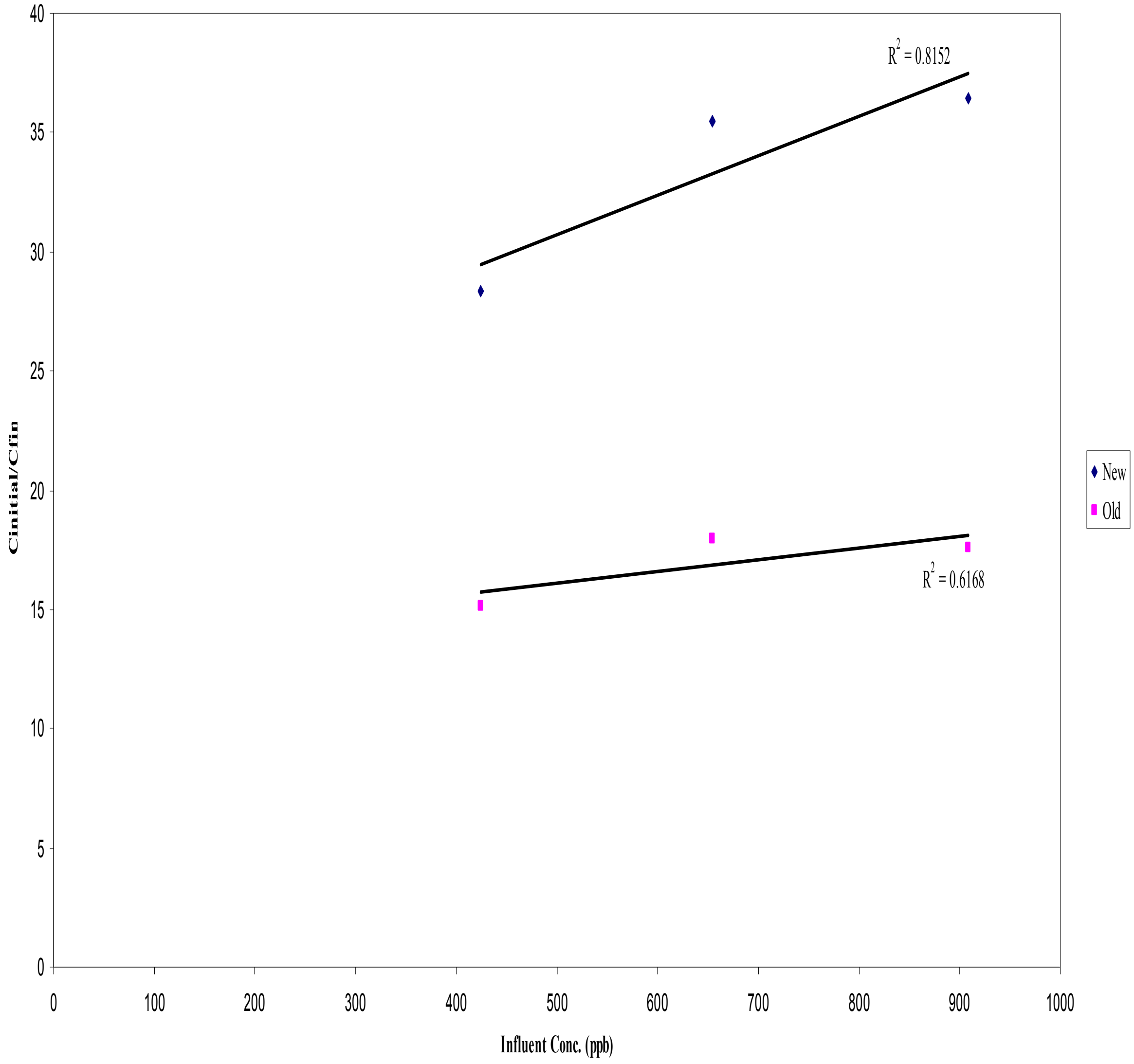
Volume of arsenic solution used = 100 ml

Contact time = 10 minutes

Figure 17: Arsenic (V) vs Arsenic (III)

Though the medium is capable of removing As(III), it is not as efficient as it is in As(V) removal. Figure 17 clearly illustrates the difference in the capacity of the medium in removing As(III) and As(V). The data for plotting the isotherm is given in Appendix K.

An experiment was performed to determine if the aging of the medium had any effect on the removal efficiency of arsenic. A freshly prepared modified rhyolite sample and a sample prepared two months prior to the preparation of the fresh sample were used for the study. Half a gram samples of the two zeolites made from minus No 200 material, with chemical treatment were contacted with arsenic solutions of concentrations 654, 908 and 424 ppb for 10 minutes. The results obtained were plotted in a graph of initial concentration vs $C_{initial} / C_{final}$ as in Figure 18. Appendix L has the data used for the plot. The data showed a decrease in removal capacity with aging of the medium.



Medium: Zeolite made from minus No. 200 material, with chemical treatment

Amount of medium used = 0.5 g

Influent concentrations = 424, 654 and 908 ppb

Volume of arsenic solution used = 100 ml

Contact time = 10 minutes

Figure 18: Effect of Aging

A TCLP analysis was done to check the leaching ability of the arsenic adsorbed on to the modified rhyolite medium (zeolite made from minus No 200 material, with chemical treatment). Two samples of the adsorbent weighing 0.75 g were treated with arsenic solutions of concentrations 342 ppb and 525 ppb. The arsenic solution had a final concentration of 23 ppb and 28.7 ppb for the influent concentrations of 342 ppb and 525 ppb, respectively, after being contacted with the adsorbent for 10 minutes. The TCLP test was done and the resulting solution was analyzed for As(V). Table 15 has the results obtained for the TCLP analysis.

Table 15: TCLP Analysis

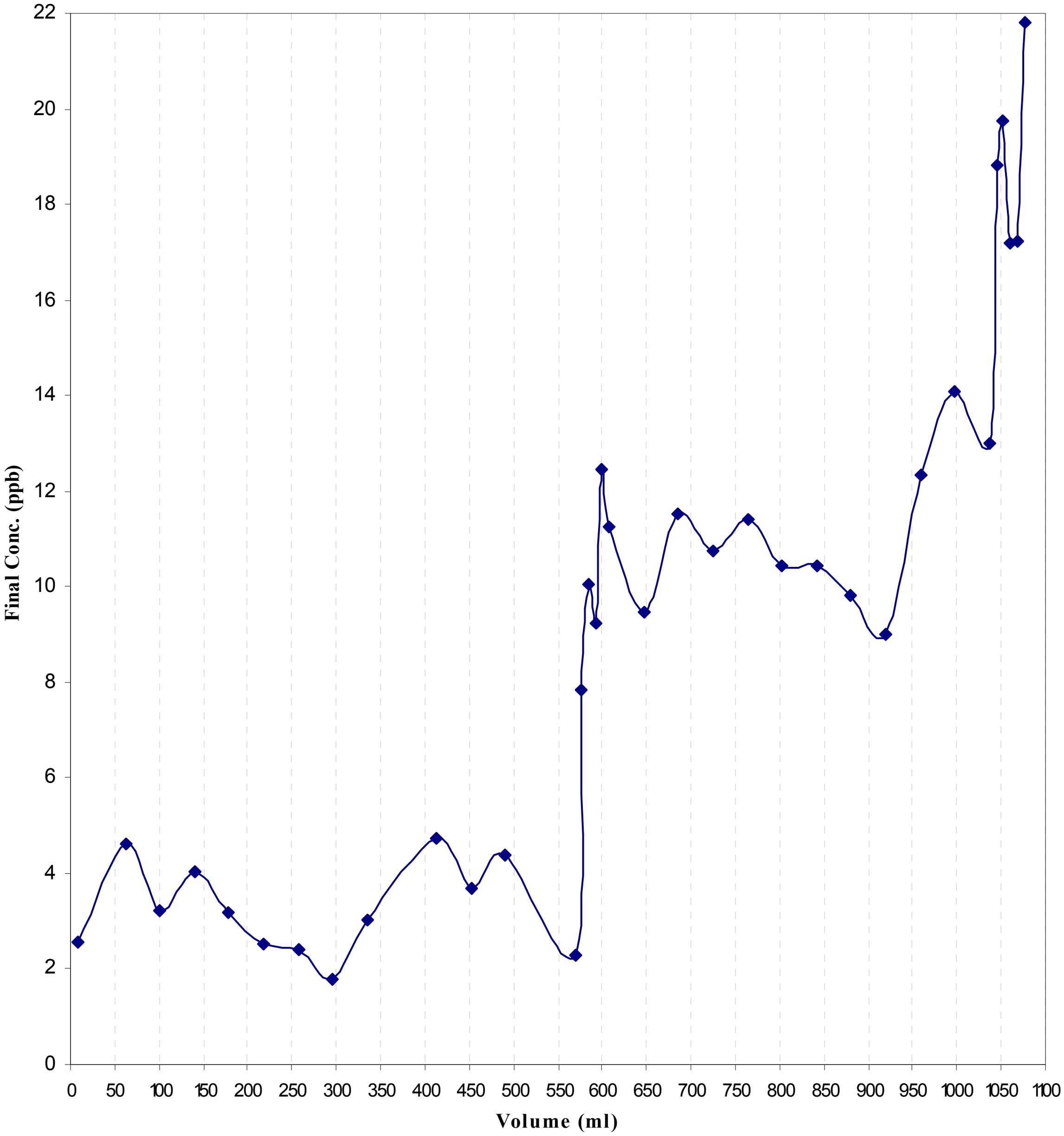
Mass of adsorbent (g)	Initial As conc. (ppb)	Final As conc. (ppb)	As removed (ppb)	As conc. in the extraction fluid (ppb)
0.75	346	23	323	BPQL*
0.75	525	28.75	496.25	BPQL*

*Below Practical Quantitation Limit

The current TCLP arsenic limit is 1 mg/L (from January, 2006), which is 100 times of the drinking water standard (EPA, 2001). The extraction fluid should have less than or equal to 20 times of the TCLP limit (20 x 1 = 20 mg/L) to pass the test. The extraction fluid analyzed had As(V) concentration was below detection limit. Non-hazardous waste landfills should be able to accept the adsorbent after serving its purpose of removing arsenic from water.

A column study was conducted to determine the operating capacity of the zeolite made from minus No. 200 material, with chemical treatment. An initial concentration of 516 ppb was used for this study. A flow rate of 0.5 ml/min was maintained with a siphon arrangement. Figure 19 shows the results obtained for the column study.

The volume of water that could be treated with the column before it could give an effluent concentration of 10 ppb for an initial concentration of 516 ppb was calculated from the curve in Figure 19. A volume of 950 ml could be treated with this column having 0.5 g of the medium. Hence it would require 200 kg of the medium to treat 100,000 gal/day of groundwater with arsenic concentration 516 ppb. The calculation for determining the amount of the medium is in Appendix L.



Medium: Zeolite made from minus No. 200 material, with chemical treatment

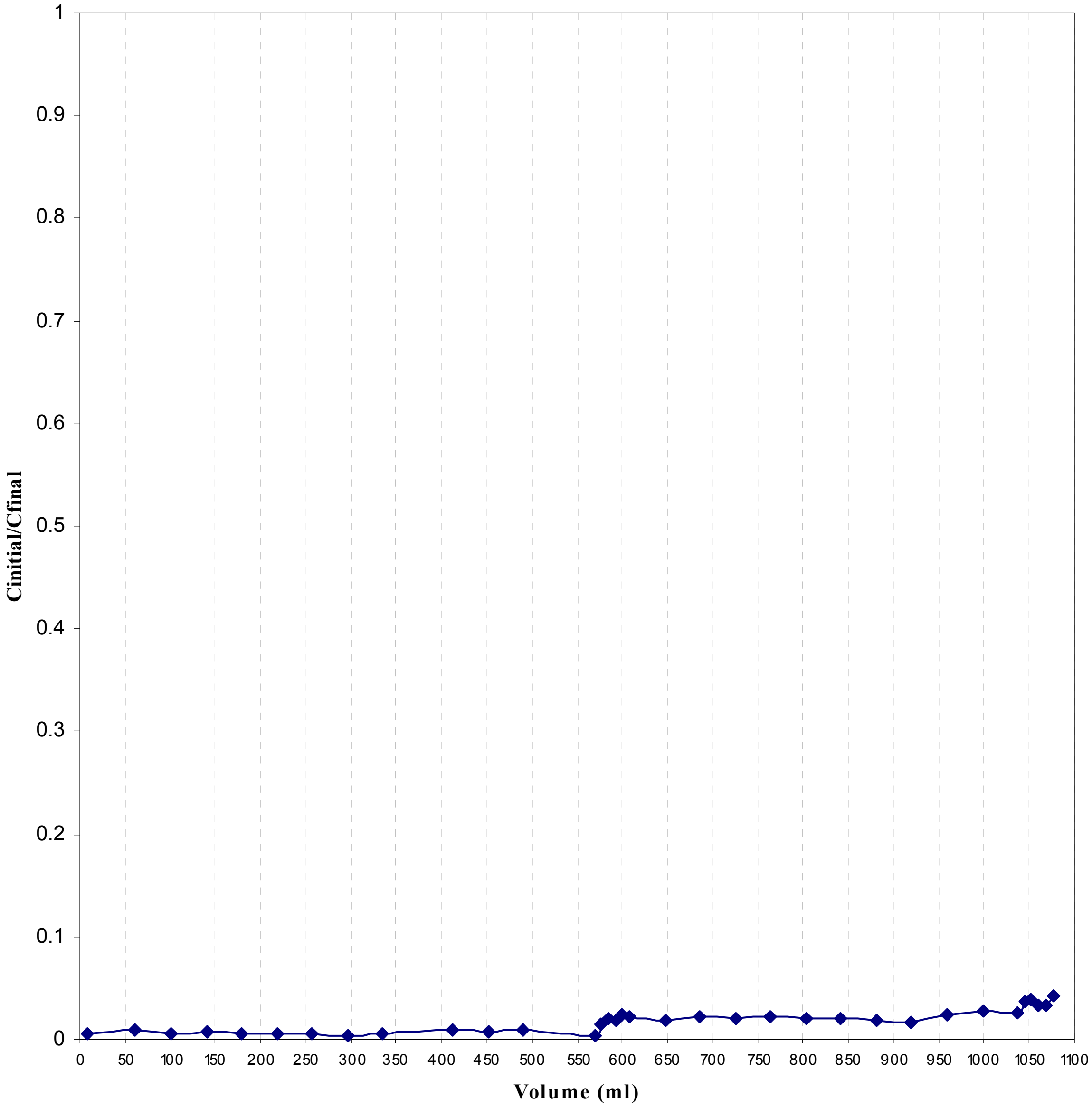
Amount of medium used = 0.5 g

Influent concentration = 516 ppb

Flow rate = 0.5 ml/min

Figure 19: Column Study

The results of the column study were plotted as volume vs $C_{initial}/C_{final}$ as in Figure 20 to determine the operating capacity of the column. The area above the curve up to the breakthrough point (950th ml) represents the operating capacity of the column, which was calculated to be 60.5 mg/g. The data used for plots (Figure 19 and Figure 20) are in Appendix L.



Medium: Zeolite made from minus No. 200 material, with chemical treatment

Amount of medium used = 0.5 g

Influent concentration = 516 ppb

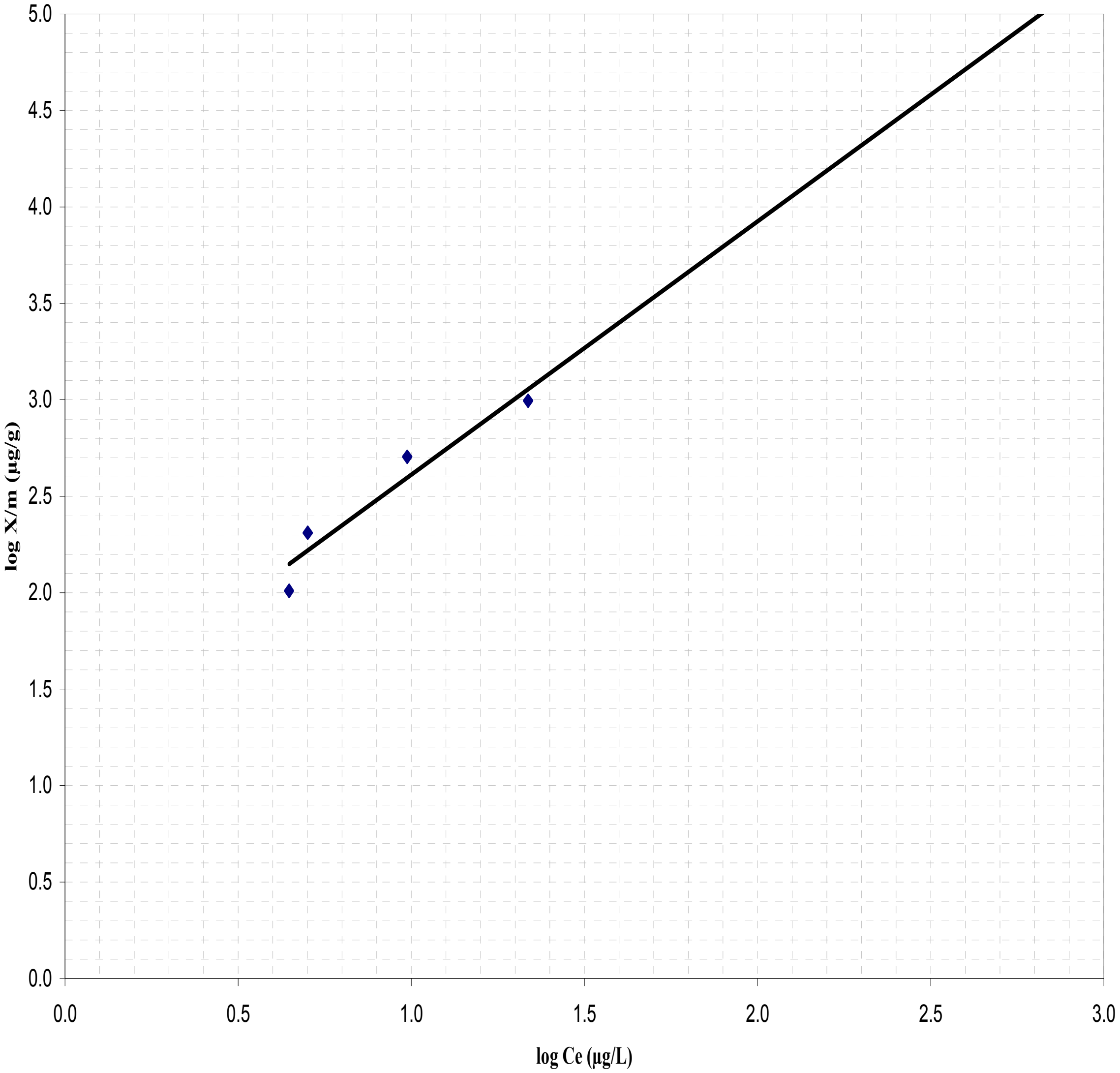
Flow rate = 0.5 ml/min

Figure 20: Operating Capacity of the Column

This operating capacity obtained for the column was compared with the operating capacity for batch operation. For this, an isotherm was plotted using the data for Zeolite made from minus No. 200 material, with chemical treatment, when used in batch study. Figure 21 has the isotherm required for determining the operating capacity of the modified rhyolite material when used in a batch operation. This isotherm in Figure 20 is the same as plotted for the minus No. 200 material in Figure 13. The data used for plotting Figure 21 is in Appendix F.

A perpendicular line drawn from the X axis towards the extended isotherm i.e., from the log value of influent concentration (log 516 = 2.7) would give the corresponding capacity on the Y axis. The operating capacity for an influent concentration of 516 ppb would be 71 mg/g.

The operating capacity obtained for batch operation is close to that obtained for column operation (60.5 mg/g). So it could be concluded the arsenic removal process could be done either by contacting the arsenic contaminated water with the adsorbent or run the contaminated water through a column made of the modified rhyolite.



Medium: Zeolite made from minus No. 200 material, with chemical treatment

Amount of medium used = 0.05, 0.1, 0.25 and 0.5 g

Influent concentration = 516 ppb

Volume of arsenic solution used = 100 ml

Contact time = 10 minutes

Figure 21: Operating Capacity for Batch Operation

The initial thought that modified rhyolite might follow the same mechanism as that of Al-loaded shirasu zeolite was dismissed reviewing the results obtained from various experiments. Al-loaded shirasu zeolite released OH^- ions during the process of arsenic removal (Xu et al., 2002). Kinetic experiments with modified rhyolite showed decrease in pH with time. The reaction mechanism proposed for Al-loaded shirasu zeolite does not involve any release of Al ions into solution. But experimental results with modified zeolite showed release of Al ions into solution from the medium. The decrease in pH might be because of the release of Al ions into the solution. These facts make the removal mechanism of modified rhyolite completely different from that of Al-loaded shirasu zeolite. Table 16 has some of the inferences obtained for both modified rhyolite and Al-loaded shirasu zeolite.

Table 16: Comparison of Modified Rhyolite vs Al-Loaded Shirasu Zeolite

	Modified rhyolite	Al-loaded shirasu zeolite
pH changes during reaction	Decrease in pH	Increase in pH
Release of Al ions	Released	No release as per eqn.(1)
Reaction order	Second order	First order

Engineering Application

Experimental results prove that this novel method is very effective in removing arsenic in its pentavalent form, arsenate. Hence the arsenic in the form of As(III) in groundwater should be oxidized to As(V). The groundwater from wells could be pumped over a series of cascades to aerate the water (Jhonston et al., 2001). Thus the arsenite present gets oxidized to arsenate. However, the kinetics of oxidation of arsenite to arsenate by natural oxidation (25-30 % per 24 hours) is very slow and hence would require other oxidizing agents for complete oxidation (Sarkar et al., 2001). Oxygen, ozone, free chlorine, hypochlorite, permanganate, hydrogen peroxide are some of the commonly used oxidizing agents for this purpose (Ahmed, 2005). The water could then be passed through a filtration bed made of the adsorbent material. Since the adsorbent material is of very small size, this would potentially have a significant problem of head loss. The filtration unit could be backwashed periodically and the backwash water be sent to settling ponds. The wastewater could be decanted off and the sludge removed. Figure 20 gives the schematic diagram of the application option described.

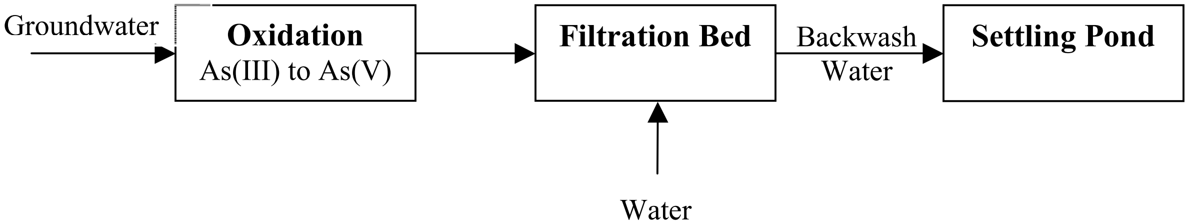


Figure 22: Arsenic removal from water with a filtration bed

Another possibility of using the modified rhyolite medium is to have a contact basin after the aeration the groundwater. The contact basin, with a mechanical mixer, is to provide enough contact between the adsorbent and the water to be treated. This could be followed by a sedimentation basin where the solids could settle down and the residuals be removed periodically. This treatment process could be done as a continuous operation. Figure 21 is a representation of the treatment option with a contact basin.

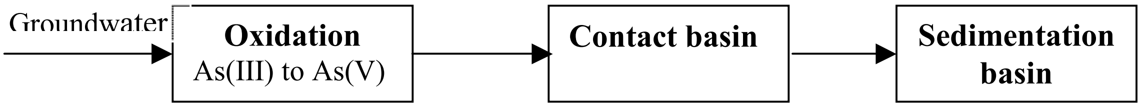


Figure 23: Arsenic removal from water with a contact basin

CHAPTER VI

CONCLUSIONS

Arsenic a long known toxic element in water has been implicated in skin and internal carcinogenesis. The EPA requires the community water system to be under compliance with the current arsenic standard of 10 μg/L in January, 2006. The new MCL will largely drive and dictate the installation of arsenic removal processes. The novel medium, modified rhyolite was able to achieve the EPA drinking water standard in 6 minutes from an initial concentration of 300ppb. The arsenic removal process with modified rhyolite follows second order kinetics. Modified rhyolite was found to have a very high adsorption capacity (417 μg/g) compared to many other adsorbents. The efficiency of arsenic removal by the modified rhyolite slightly increased with increase in pH. Competing ions like sulfate, nitrate and phosphate did not have any effect on arsenic removal. The potential to be regenerated is limited with modified rhyolite and would be wise to use it as a once through medium. The medium passed the TCLP analysis and hence could be disposed off without any concern. Faster adsorption, greater adsorption capacity and very little effect on arsenic adsorption by change in pH and presence of competing ions would make this adsorbent material attractive for future applications.

The mechanism of arsenate removal is not very clear. It was observed that the arsenic contaminated water has aluminum ions in it after being treated with the medium. Though, it could be proposed that arsenic removal is likely due to the exchange of aluminum ions in the medium with arsenic ions in water, exchange of cations with oxyanions makes the proposed mechanism questionable. Further research work to determine the mechanism of the removal process should be conducted. Pilot studies to check the feasibility of the application options described could be done.

REFERENCES

1. Adedge Technologies (2003). “Health Effects of Arsenic.” <http://www.adedgetechnologies.com/technology/aboutarsenic.htm> (May 8, 2005).
2. Ahmed, Feroze M. (2001). “An Overview of Arsenic Removal Technologies in Bangladesh and India.” Proc., BUET-UNU International Workshop on Technologies for Arsenic Removal from Drinking Water of the UNU-NIES International Workshop, Dhaka, Bangladesh.
3. Ali, M. Ashraf, A.B.M Badruzzaman, M.A. Jalil, Hossain M. Delwar, M.M. Hussainuzzaman, M. Badruzzaman, O.I.Mohammad, O.I., N. Akter (2001). “Development of Low-cost Technologies for Removal of Arsenic from Groundwater.” Bangladesh University of Engineering and technology, 2001.
4. Aragon, Alicia, Bruce Thomson, Joe Chwirka (2002). “Rapid Small-Scale Column Testing for Arsenic Adsorption Media.” Proc., 9th Annual International Petroleum Environmental Conference, Albuquerque, NM, October 2002.
5. Bellack, Ervin (1971). “Arsenic Removal from Potable Water.” Journal AWWA, 63, 454-58.
6. Bhaumik, A., Samanta S., Mal N.K. (2004). “Efficient Removal of Arsenic from Polluted Ground Water.” Journal of Applied Sciences, 4(3), 467-471.

7. Breck, Donald W. (1974). “Zeolite Molecular Sieves: Structure, Chemistry, and Use.” John Wiley & Sons, Inc.
8. Chwirka, Joseph D., Bruce M.Thomson, John M.Stomp III (2000). “Removing Arsenic from Groundwater.” Journal AWWA, Vol. 92, Issue 3, 79-88.
9. Das, H.K (1998). “Alternative Source of Arsenic Removal.” The Daily Star <http://www.slowsandfilter.com/arsenic.html> (September 20, 2005).
10. Deng, Youjun, James B. Harsh, Markus Flury and Jeffrey S. Boyle (2005). “Mineral Transformation in Soils Reacted with Simulated Hanford Tank Solutions.” American Journal of Soil Science Society, 69, 531-538.
11. Dousova, B., V. Machovic, D. Kolousek, F. Kovanda and V. Dornicak (2003). “Sorption of As(V) Species from Aqueous Systems.” Water, Air and Soil Pollution, 149, 251-267.
12. EPA (1999). “Analytical Methods Support Document for Arsenic in Drinking Water.” EPA -815-R-00-010.
13. EPA (2000). “Technologies and Costs for Removal of Arsenic from Drinking Water.” EPA 815-R-00-028, Office of Water.
14. EPA (2005). “ List of Drinking Water Contaminanats and MCL’s.” <http://www.epa.gov/safewater/mcl.html> (December 05, 2005)
15. EWRI Currents (2004). “The Newsletter of the Environmental & Water Resource.” Institute of the American Society of Civil Engineers, 6(1).
16. Focazio, M.J., A.H. Welch, S.A. Watkins, D.R. Helsel, and M.A. Horn (1999). "A Retrospective Analysis on the Occurrence of Arsenic in Ground-Water Resources of the United States and Limitations in Drinking-Water-Supply

Charecterizations." U.S. Geological Survey Water-Resources Investigation, Report 99-4279.

17. Foster, Robert J., Walter A. Gong (1976). "Merill Physical Science Series." Bell & Howell Company, Ohio.
18. Frank, P. and D. Clifford (1990). "Project Summary: Arsenic (III) Oxidation and Removal from Drinking Water." EPA/600/S-2-86/021.
19. Frazer, L. (2005). "Metal Attraction: An Ironclad Solution to Arsenic Contamination." Environmental Health Prospective, Vol. 113, No. 6, 398-401.
20. Freemantle, Michael (2005). "Arsenic Rooted from Water." Chemical & Engineering News, 83 (14), 12.
21. French, Derek K (2005). "Arsenic in the Environment." Environmental Science and Engineering, <http://www.esemag.com/0105/arsenic.html> (March 23, 2005).
22. Hering, Janet G. Pen-Yuan chen, Jennifer A.Wilke, Menachem Elimelech (1997). "Arsenic Removal From drinking Water During Coagulation." Journal of Environmental Engineering, Vol. 123, No. 8, August 1997, 800-807.
23. Hoffmann, Stephen (2002). "EPA regs favor firms with cost-effective arsenic removal methods." Water Investment Newsletter, <http://www.thebullandbear.com/resource/RI-archive/2002/0102-epa.html> (March 25, 2005)
24. "Igneous Rocks (2005)." Encarta Encyclopedia Article, <http://encarta.msn.com/encyclopedia_761555655/Igneous_Rock.html> (August, 2005)

25. Jhonston, Richard, Han Heijnen (2001). “Safe Water Technology for Arsenic Removal.” Proc., BUET-UNU International Workshop on Technologies for Arsenic Removal from Drinking Water of the UNU-NIES International Workshop, Dhaka, Bangladesh.

26. Lamn, Steven H. (2001). “Health Effects of Arsenic.” <http://www.nab.usace.army.mil/projects/WashingtonDC/springvalley/arsenic/LammPresentation.pdf> (March 12, 2005).

27. Lin, Tsair-Fuh, Jun-Kun Wu (2001). “Adsorption of Arsenite and Arsenate within Activated Alumina Grains: Equilibrium and Kinetics.” Water Resources, 35(8), 2049-2057.

28. MacPhee, Michael J., Gail E. Charles, David A. Cornwell (2001). “Treatment of Arsenic Residuals from Drinking Water Removal Processes.” EPA 600/R-01/033, Environmental Engineering & Technology, Inc., Newport News, VA.

29. National Academy of Science (1997). “Arsenic: Medical and Biological Effects of Environmental Pollutants.” <http://www.nap.edu/catalog/9003.html> (April 23, 2005)

30. “Online Chemical Engineering Information.” Green Chemistry with Zeolite Catalysis, <http://www.cheresources.com/zeolitezz.shtml> (March 28, 2005).

31. Poole, Barika R. (2001). “Point-of-Use Water Treatment for Arsenic Removal through Iron Oxide Coated Sand: Application for the Terai Region of Nepal.” Dept. of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA.

32. Pickard, Brian, Muhammad Bari (2004). "Feasibility of Water Treatment Technologies for Arsenic and Fluoride Removal from Groundwater." Proc., AWWA Water Quality Technology Conference.
33. PUREFLOW Filtration Systems, Bulletin A2.9432.4 (2005). " The Removal of Arsenic from Potable Water." <http://www.mhrahome.org/media/arsenic/vendor/pureflow_bulletin.pdf> (May 5, 2005)
34. Report On Carcinogens, Eleventh Edition (1980). "Arsenic Compounds, Inorganic." Substance Profiles, <http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s015arse.pdf> (May 2, 2005).
35. Roberts, Freddy L., Prithvi S. Kandhal, E. Ray Brown, Dah-Yinn Lee, Thomas W. Kennedy (1996). "Hot Mix Asphalt Materials, Mixture Design, and Construction." Second Edition, NAPA Education Foundation, Lanham, Maryland.
36. Saask, Aapo (2002). "The Arsenic Challenge." Green pages, <http://www.eco-web.com/cgi-local/sfc?a=/editorial/index.html&b=/editorial/04099.html> (August 12, 2005).
37. Saha, J.C., K. Dikshit, M. Bandyopadhyay (2001). "Comparitive Studies for Selection of Technologies for Arsenic Removal from Drinking Water." Proc., BUET-UNU International Workshop on Technologies for Arsenic Removal from Drinking Water of the UNU-NIES International Workshop, Dhaka, Bangladesh.

38. “Sandstone Chemical Properties (2005). ” <http://www.granite-sandstone.com/sandstone-chemical-properties.html> (August 14, 2005).
39. Sarkar, Anisur Rehman, Omar Twabur Rehman (2005). “Insitu Removal of Arsenic – Experience of DPHE-Dandia Pilot Project. “ <www.unu.edu/env/Arsenic/Sarkar.pdf>, December 2005.
40. Sato, Y., M. Kang, T. Kamei, Y. Magara (2002). “Performance of Nanofiltration for Arsenic Removal.” Water Research, Vol. 36, Issue 13, 3371-7.
41. Scott, Jeanette (1980). “Zeolite Technology and Applications: Recent Advances.” Noyes Data Corporation, New Jersey.
42. Selecky, Mary, Bill White, Gregg Grunenfelder (2003). “Guidance Document: Arsenic Treatment for Small Water Systems.” DOH PUB. # 331-210, Washington State Department of Health, Olympia, Wasington.
43. Severn Trent Technologies (2004). “Arsenic Treatment and Arsenic Removal.” Water Purifications and Solutions, <http://www.severntrentservices.com/water_purification/filtration_products/arsenic.jsp> (March 20, 2005).
44. Sing, Tony Sarvinder, K.K Pant (2004). “Equilibrium, Kinetics and Thermodynamic Studies for Adsorption of As(III) on Activated Alumina.” Separation and Purification Technology, 36, 139-147.
45. Sing, Tony Sarvinder and K.K. Pant (2001). “Removal of Arsenic from Water Using Activated Alumina.” Research Journal of Chemistry and Environment, 5(3), September 2001.

46. Thirunavukkarasu, O.S., T. Viraraghavan, K.S. Subramanian (2003). "Arsenic Removal from Drinking Water Using Granular Ferric Hydroxide." Water SA, 29(2).
47. Thirunavukkarasu, O.S., T. Viraragavan, K.S. Subramanian, O. Chaalal, M.R. Islam M.R. (2005). "Arsenic Removal in Drinking Water- Impacts and Novel Removal Technologies." Energy Sources, 27, 209-219.
48. Tiemann, Mary (2001). "Arsenic in Drinking Water: Recent Regulatory Developments and Issues." National Council for Science and the Environment, CRS Report RS20672.
49. Tiemann, Mary (2001). "RS20672: Arsenic in Drinking Water: Recent Reguatory Developments and Issues, CRS Report for Congress." <http://www.ncseonline.org/NLE/CRSreports/water> (May 9, 2005).
50. Trung, Do Q., Chu X. Anh, Nguyen X. Trung, Yuta Yasaka, Masanori Fujita and Minoru Tanaka (2001). "Preconcentration of Arsenic Species in Environmental Waters by Solid Phase Extraction Using Metal-loaded Chelating Resins." Analytical Sciences, 17.
51. USGS (2005). "Volcano Hazards Program – Reducing Volcanic Risk." US Department of Interior, Menlo Park, California. <http://volcanoes.usgs.gov/Products/Pglossary/rhyolite.html> (April 23, 2005).
52. Vance, David B. (2001). "Arsenic - Chemical Behavior and Treatment." 2 The 4 Technology Solutions, <http://2the4.net/arsenicart.htm> (Mach 8, 2005).

53. Veenstra, John, Gary Kinder and Greg Holland (2004). "Removal of Arsenic from Drinking Water." Proc., Oklahoma Water 2004, Environmental Institute Oklahoma State University, Oklahoma.
54. Wang, Lili, Wendy E. Condit, Abraham S.C. Chen (2004). "Technology Selection and System Design USEPA Arsenic Demonstration Program Round 1." EPA/600/R-05/001.
55. Wegelin, Martin, Daniel Gechter, Stephan Hug, Abdullah Mahmud, Abdul Motaleb (2000). "SORAS – A simple arsenic removal process." 26th WEDC Conference, Dhaka, Bangladesh. <http://www.sandec.ch/WaterTreatment/Documents/SORAS.pdf> (Mach 5, 2005)
56. Xu, Yan-hua, Tsunenori Nakajima and Akira Ohki (2002). "Adsorption and Removal of Arsenic(V) from Drinking Water by Aluminum-Loaded Shirasu-Zeolite." Journal of Hazardous Materials, B92, 285-297.
57. Yuan, Tao, Jiang Yong Hu, Say Leong Ong, Qi Fang Luo and Wern Jun Ng (2002). "Arsenic Removal from Household Drinking Water by Adsorption." Journal of Environmental Science and Health, A37(9), 1721-1736.
58. Zeo Agronomic Technology (2004). "Natural and Synthetic Zeolites." <http://www.zeoinc.com> (March 25, 2005).
59. "Zeolite Molecular sieve." <http://www.gracedavison.com/eusilica/Adsorbents/product/zeolite_molecular_sieve.htm> (Marsh 20, 2005).

APPENDICES

APPENDIX A

Kinetics – Non-zeolite made from greater than 50 mesh size, with chemical treatment

Time (hours)	Effluent Conc. (ppb)
0	357.2
0.5	243.4
1	249
1.5	251.5
2	238.2
2.5	250.8
3	245.9
5	223.1
7	238.8
9	227.6
11	211.3
16	222.3
24	222.3
48	229.6

APPENDIX B

Kinetics – Non-zeolite made from less than 50 mesh size, with chemical treatment

Time (hours)	Effluent Conc. (ppb)	pH
0	336	7.55
0.5	69.96	7.45
1	39.36	7.39
1.5	24.23	7.44
2	15.01	7.37
2.5	10.32	7.46
3	7.02	7.44
9	5.596	7.58
24	4.7222	7.82
48	4.656	7.88

APPENDIX C

Kinetics – Non-zeolite made from less than 200 mesh size, with chemical treatment

Trial I:

Time (minutes)	Effluent Conc. (ppb)	pH
0	298.1	6.45
2	9.74	4.72
4	7.028	4.67
6	6.879	4.63
8	4.582	4.74
10	4.79	4.77

Trial II:

Time (minutes)	Effluent Conc. (ppb)
0	269.2
1	33.4
2	17.79
4	11.16
6	10.53
8	8.72
10	5.39

Trial III:

Time (minutes)	Effluent Conc. (ppb)	pH
0	336.8	6.8
0.5	43.34	4.92
1	28.22	4.95
1.5	24.93	4.72
2	20.61	4.93
4	12.95	4.73
6	10.23	4.75
10	6.26	4.74

APPENDIX D

Investigation of Mechanism of Adsorption

Time (min)	Effluent Conc. (ppb)			% Removal		
	Zeolite w/ Chem Treatment	Raw Rhyolite	Zeolite w/o Chem. Treatment	Zeolite w/ Chem Treatment	Raw Rhyolite	Zeolite w/o Chem. Treatment
0	420	420	493	0.00	0.00	0.00
1	22.25	127.2	124.6	94.70	69.71	74.73
2	19.19	130.4	125.1	95.43	68.95	74.62
4	17.53	127.4	123.1	95.83	68.67	75.03
6	12.04	131.2	127.8	97.13	68.76	74.08
8	11.36	133.2	124.3	97.30	68.29	74.79
10	10.91	131	124.8	97.40	68.81	74.69

APPENDIX E

Investigation of Mechanism with Feldspar and Sandstone

Adsorbent	m (g)	Ce (µg/L)	X (µg)	X/m (µg/g)	log X/m (µg/g)	log Ce (µg/L)
Modified Rhyolite	0.5	0.16	54.104	108.208	2.034	-0.796
	0.25	8.39	30.81	123.245	2.091	0.924
	0.1	9.785	30.672	306.72	2.487	0.991
	0.05	13.98	30.252	605.04	2.782	1.146
Unmodified Feldspar	0.5	168.4	14.81	29.62	1.472	2.226
	0.25	208.4	10.81	43.24	1.636	2.319
	0.1	246.7	6.98	69.8	1.844	2.392
	0.05	275.3	4.12	82.4	1.916	2.440
Unmodified Sandstone	0.5	182.3	13.42	26.84	1.429	2.261
	0.25	206.1	11.04	44.16	1.645	2.314
	0.1	270.3	4.62	46.2	1.665	2.432
	0.05	291	2.55	51	1.708	2.464
Unmodified Rhyolite	0.5	134.7	19.03	38.06	2.130	1.581
	0.25	140	18.5	74	2.146	1.869
	0.1	151.6	17.34	173.4	2.181	2.239
	0.05	154.8	17.02	340	2.190	2.532

APPENDIX F

Isotherm – Zeolite vs Non-Zeolite

Adsorbent	m (g)	Final conc. Ce (µg/L)	As Adsorbed (µg/L)	X (µg)	X/m (µg/g)	log X/m (µg/g)	log Ce (µg/L)
Zeolite	0.05	21.76	494.14	49.414	988.28	2.995	1.338
	0.1	9.74	506.16	50.616	506.162	2.704	0.988
	0.25	5.02	511	51.088	204.35	2.310	0.701
	0.5	4.44	511.46	51.146	102.292	2.010	0.647
Non – Zeolite	0.05	44.88	470.12	47.012	940.24	2.973	1.652
	0.1	21.42	494.5	49.448	494.48	2.694	1.331
	0.25	17.16	498.74	49.874	199.496	2.300	1.235
	0.5	15.29	500.61	50.061	100.122	2.001	1.184

APPENDIX G

Comparison with Other Adsorbents

Adsorbent	X (mM)	m (g)	X/m (mM/g)	Ce (mM)	log X/m (μg/g)	log Ce (mM)
Rhyolite	0.1594	0.35	0.4554	0.0025	-0.3416	-2.5979
	0.1582	0.2	0.7912	0.0037	-0.1017	-2.4364
	0.1581	0.1	1.5812	0.0038	0.1990	-2.4220
	0.1576	0.05	3.1524	0.0043	0.4986	-2.3681

Adsorbent	log Ce (mM)	log X/m (mM/g)	Adsorbent	log Ce (mM)	log X/m (mM/g)
Al-loaded P1 type Shirasu Zeolite	-1.725	-1.1	**Activated Alumina**	-0.8143	-1
	-0.625	-1		-0.4643	-0.779
	-0.15	-0.95		-0.0786	-0.86
	0	-0.9		0.25	-0.75
Al-loaded P1′ type Shirasu Zeolite	-0.9	-1.2		0.4643	-0.657
	-0.243	-1.15		0.5893	-0.6214
	-0.0643	-1.1	**Basic Lanthanum Carbonate**	-1.0357	-0.857
	0.043	-1.07		-0.6964	-0.5
Al-loaded Coral Lime	-1.6143	-2.428		-0.2143	-0.4286
	-0.757	-2.316	**Lanthanum Hydroxide**	-0.5	-0.2857
	-0.5714	-2.2632		-0.0357	0
Activated Carbon	-0.6964	-1.7857		0.232	0.1786
	-0.3214	-1.5		0.3929	0.1786
	-0.0357	-1.379		0.5	0.2714
	0.25	-1.1286		0.6071	0.2929
	0.4643	-1		-	-

APPENDIX H

Adsorptive Capacity of the Adsorbent

As Species	m (g)	Ce (µg/L)	As Adsorbed (µg/L)	X (µg)	X/m (µg/g)	log X/m (µg/g)	log Ce (µg/L)
Less than 200 mesh size	0.05	21.76	494.14	49.41	988.28	2.995	1.338
	0.1	9.74	506.16	10.62	506.16	2.704	0.988
	0.25	5.02	510.88	51.1	204.35	2.31	0.701
	0.5	4.44	511.46	51.15	102.29	2.01	0.647
Less than 50 mesh size	0.05	13.98	302.5	30.25	605.4	2.782	1.146
	0.1	9.785	306.7	30.67	306.72	2.487	0.991
	0.25	8.39	308.1	30.81	123.24	2.091	0.924
	0.5	0.16	541	54.1	108.21	2.034	-0.796

APPENDIX I

Effect of pH

	pH	Effluent Conc. (ppb)	Removal Efficiency (%)
Trial 1	5	11.25	97.69
	6	7.664	98.43
	7	6.75	98.62
	8	4.439	99.09
	9	3.9	99.20
Trial 2	5	67.55	87.22
	6	48	90.92
	7	33.5	93.66
	8	31.25	94.09
	9	21.75	95.89

APPENDIX J

Arsenic (V) vs Arsenic (III)

Initial concentration of As (V) = 516 ppb

Initial concentration of As (III) = 464 ppb

As Species	M (g)	Ce (µg/L)	As Adsorbed (µg/L)	X (µg)	X/m (µg/g)	Ce (µg/L)	log X/m (µg/g)	log Ce (µg/L)
Arsenic (V)	0.05	21.76	494.14	49.41	988.28	21.76	2.995	1.338
	0.1	9.74	506.16	10.62	506.16	9.74	2.704	0.988
	0.25	5.02	510.88	51.1	204.35	5.02	2.31	0.701
	0.5	4.44	511.46	51.15	102.29	4.44	2.01	0.647
Arsenic (III)	0.05	123.6	340.5	34.05	681	123.6	2.833	2.092
	0.1	123.9	340.2	34.02	340.2	123.9	2.532	2.093
	0.25	112.7	351.4	35.14	140.56	112.7	2.148	2.052
	0.5	136.8	327.3	32.73	65.46	136.8	1.816	2.136

APPENDIX K

Effect of Aging

Adsorbent	Initial Conc.(ppb)	Final Conc. (ppb)	$C_{initial}/C_{final}$
New	908.3	24.95	36.4
	654	18.45	35.45
	424	14.97	28.32
Old	908.3	51.57	17.61
	654	36.4	17.97
	424	28.04	15.12

APPENDIX L

Column Study

Volume (ml)	C_{final} (ppb)	C_{eff}/C_{inf}
7.4	2.578	0.004997
62	4.61	0.008936
101	3.22	0.006242
140	4.05	0.00785
179	3.179	0.006162
218	2.536	0.004916
257	2.4	0.004652
296	1.791	0.003472
335	3.041	0.005895
413	4.751	0.009209
452	3.667	0.007108
491	4.383	0.008496
569	2.271	0.004402
576.8	7.842	0.015201
584.6	10.04	0.019461
592.4	9.221	0.017874
600.2	12.45	0.024133
608	11.26	0.021826
647	9.483	0.018381
686	11.54	0.022369
725	10.75	0.020837
764	11.39	0.022078
803	10.43	0.020217
842	10.44	0.020236
881	9.822	0.019039
920	8.991	0.017428
959	12.32	0.023881
998	14.09	0.027311
1037	13	0.025199
1044.8	18.82	0.03648
1052.6	19.74	0.038263
1060.4	17.19	0.03332
1068.2	17.23	0.033398
1076	21.8	0.042256

Calculation of media required for 100,000 gal/day:

Volume of water that could be treated before breakthrough with 0.5 g of media = 950 ml

Amt of medium required to treat 100,000 gal/day = 100,000gal/day x (0.5g / 950 ml)

= 3.785×10^8 ml/day x (0.5 g / 950 ml)

= 200 kg

VITA

Vinoth Manoharan

Candidate for the Degree of

Master of Science

Thesis: INVESTIGATION OF A NOVEL APPROACH FOR ARSENIC REMOVAL FROM WATER USING MODIFIED RHYOLITE

Major Field: Environmental Engineering

EDUCATION

Master of Science, Environmental Engineering December 2005
Oklahoma State University, Stillwater, OK **GPA: 3.64**
Bachelor of Technology, Chemical Engineering April 2002
Perriyar University, TN, India **GPA: 3.75**

INTERNSHIP

Operations Specialist, the Stover Group Summer 2005

- Operated and maintained a 1.25 MGD wastewater treatment plant of CP Kelco, Okmulgee.
- Sampled, performed laboratory analyses periodically and made necessary process changes as indicated by the tests.
- Supervised and participated in maintenance and modification of the wastewater treatment facilities; Maintained manuals, reports and logs detailing plant operation for compliance.

EXPERIENCES

Graduate Teaching Assistant, OSU Fall 2004 – Spring 2005

- Assisted Instructor with class presentations and teaching materials, and in preparing student evaluations and on field trips.
- Performed experiments and made instructional presentations on Instructor's discretion; Graded assignments, examinations and maintained student records.

LEADERSHIP ACTIVITIES

Chair person, Organizing Committee, FACE, National Level Symposiums, 2000 & 2001.
Student Organizer, Chemical Engineering Professional Development Programs, 2000 - 2002.

Name: Vinoth Manoharan Date of Degree: December, 2005

Institution: Oklahoma State University Location: Stillwater, Oklahoma

Title of Study: INVESTIGATION OF A NOVEL APPROACH FOR ARSENIC REMOVAL FROM WATER USING MODIFIED RHYOLITE

Pages in Study: 111 Candidate for the degree of Master of Science
Major Field: Environmental Engineering

Arsenic ranks twentieth among the most abundant elements in the earths crust. Arsenic has been identified as a human carcinogen. Arsenic in groundwater has become a huge concern globally and in the United States. USEPA proposed the final arsenic rule, which lowered the arsenic standard from 50 ppb to 10 ppb and requires the community water systems to comply with the new standard before January, 2006. Modified rhyolite, the proposed novel adsorbent could reduce arsenic in water from 300 ppb to concentrations below 10 ppb in 6 minutes. This novel medium had very a high removal capacity for As(V). The removal of As(V) was slightly dependent on pH in the range 5 – 9. The arsenic removal process follows second order kinetics. The presence of competing ions had no effect on arsenic removal efficiency by the medium. The practical application of this medium was assessed by multiple cycles of sorption and desorption. TCLP analysis done to check the leaching potential of the medium proved to be favorable and hence this medium could be safely disposed in non-hazardous waste landfills. A column study was conducted and the operating capacity of the column was compared with batch operation. Engineering applications of this novel media are discussed.

ADVISOR’S APPROVAL: Dr. John N. Veenstra.