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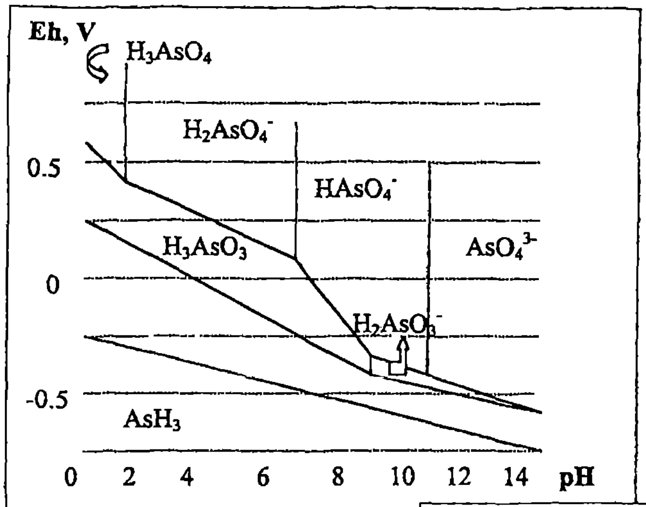

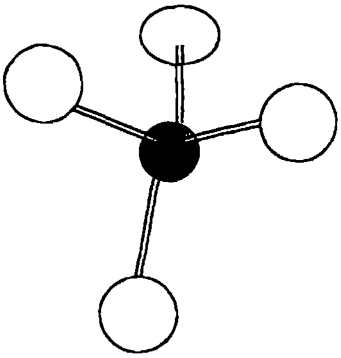

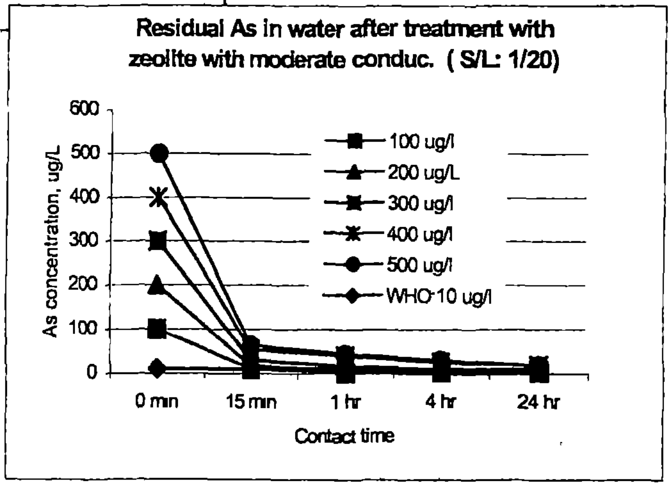

Arsenic Removal from Groundwater by Conditioned Zeolite

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Arsenic removal from groundwater

by conditioned zeolite

by

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ABSTRACT

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ABSTRACT

Arsenic contamination is becoming a problem in many parts of the world especially in the developing countries where millions of humans are chronically exposed to inorganic arsenic in drinking water at levels sufficient to cause severe toxic effects. These problems have stimulated research and development of efforts to define water purification techniques for arsenic removal. The existing processes in water treatment plants are capable of removing significant concentrations of arsenic; the advanced techniques are promising at lab scale but not yet proven at full-scale treatment plants and their use generally requires an entirely new treatment step Therefore, the need exists for a low-cost technology that can be applied in the areas where water treatment facilities are not available and sophisticated technologies are not feasible.

In this research, the feasibility of using a natural zeolite (clinoptilolite), to remove arsenic(V) from groundwater was studied. The performances of unconditioned and conditioned zeolite in removing arsenic(V) were compared. It was found that, in 15 minutes, the conditioned zeolite performed better with the efficiency of 77% to 89% compared to less than 7% efficiency of the unconditioned one. For conditioned zeolite, effects of parameters such as initial concentration of arsenic, contact time, solid-liquid ratio and conductivity of zeolite in water were investigated. The study showed that significant removal of arsenic took place within 15 minutes. Experiments were carried out for water samples with arsenic concentrations ranging from 100 µg/L to 500 µg/L. For the samples with 100 µg/L and 500 µg/L initial concentrartions, the removal efficiencies were 90% and 87% respectively, which showed that the initial concentration of arsenic is not very important for the removal efficiency. The solid-liquid ratio and the conductivity of zeolite play noticeable role in the removal process. The application of this method to groundwater showed that the arsenic removal was also affected by other factors such as the composition and pH of the water.

In conclusion, this research demonstrates the potential of conditioned zeolite in removing arsenic from groundwater.

Chapter 1
Introduction

1.1 Arsenic in drinking water

Interactions between water and human health are complex. Humans use water for many purposes, of which drinking is the most important. We need water in sufficient quantities and of good quality. Human health may be affected by the ingestion of contaminated water and by the use of contaminated water for purposes of personal hygiene and recreation. For drinking water, the most important requirement is that it is free from harmful substances.

Arsenic contamination is becoming a problem in many parts of the world: Bangladesh, India, Taiwan, Canada, Hungary, Chile, China, Argentina, Mexico, Thailand, Australia, Philippines, United Kingdom, United States, Mongolia and more. Millions of humans are chronically exposed to inorganic arsenic (As) in drinking water at levels sufficient to cause severe toxic effects which include dermal lesions that is most commonly observed, black foot disease, cancer of skin, bladder and possibly liver as well as adverse effects on the cardiovascular system. The high content of arsenic in deep-well water used for drinking in the southwest part of Taiwan has been linked to black-foot disease and other internal cancers (*Shen, 1973*). In West Bengal, India, it is estimated that more than 800,000 people from 312 villages are drinking arsenic-contaminated water, and amongst them at least 175, 000 people show arsinical skin lesions (*Das et al., 1996*). More than 21 million people in Bangladesh are drinking water containing arsenic above the WHO standard (10 µg/L) especially in the southwest part near the border of West Bengal of India (*Karim et al, 1997).* In 1987 health problems attributable to arsenic were first highlighted in a district in the south of Thailand where total arsenic concentration in surface water was in the range of 4.8- 583 µg/L. Over 1000 cases of arsenic induced skin disorders were confirmed including several arsenical skin cancers (*Williams, 1997*; *Choprapawon, 1998*).

Arsenic is one of the most common and important trace elements whose toxic and medical properties have been known for centuries. It is naturally distributed throughout the earth's biosphere and can be found just about anywhere. Humans are exposed to arsenic from air, soil, dust, food, and water by inhalation, ingestion and absorption through the skin and mucous membranes. In water, arsenic is introduced through the dissolution of minerals and ores, from industrial effluents and via atmospheric deposition. Based on sufficient evidence for carcinogenicity in humans, inorganic arsenic compounds are classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans. Taking the potential hazards into consideration, WHO lowered the guideline value for arsenic in drinking water from 50 µg/L to 10 µg/L in 1993 (*WHO, 1993).*

1.2 Arsenic removal and the research need

Health and environmental concerns regarding arsenic contamination in drinking water have stimulated significant research and development of efforts to define water purification techniques for arsenic removal, mostly for application in the water treatment plants. These include ion exchange, iron-oxide-coated sand, reverse osmosis, activated carbon, and activated alumina. These techniques are promising at lab scale but not yet proven at full-scale treatment plants for low-level arsenic removal, and their use generally requires an entirely new treatment step. The existing processes in water treatment plants such as coagulation with metal salts, lime softening, and Fe-Mn treatment are capable of removing significant concentration of arsenic (*Shen, 1973*; *Gulledge and O'Connor, 1973; Edwards et al, 1994; McNeill and Edwards, 1997*).

Most of the areas facing the problems caused by high level of arsenic in drinking water, are those where there is no piped water supplied, and where isolated communities are dependent on bore holes which provide the only source of water. In most of such areas, the drilling of wells for water reaches the geological strata rich in arsenic without adequate prior geochemical analysis. It is obvious that the available sophisticated techniques for removal of arsenic are not appropriate due to the high cost of installation and operation, high level of technical know-how and the need for well-trained personnel. Therefore, a need exists for a simple technology that can provide cost effective removal of arsenic at village scale.

Zeolites are low-cost minerals that have the capability of adsorption and ion exchange. They were introduced as adsorbents for industrial separations and purification in late 1954. Since then a mass of scientific literature describing their synthesis, properties, structure and applications in ion exchange, adsorption and catalytic process has been generated (*Flanigen, 1984; Klein and Hurlbut, 1993*). Interests in zeolites derive from their structures that have large voids and large internal surfaces. These large surfaces, high mobility of water molecules and variable amounts of cations in the voids and channels become fundamental properties in their use as ion exchanges, molecular sieves and catalysts. Furthermore, the selected zeolite, after treatment with a suitable conditioning agent, was found more effective in the removal activity (*Eberly, 1976*; *Tarasevich, 1994*).

Clinoptilolite, one of the natural zeolites that is available in several places around the world, is widely used in many applications in industries and environmental technologies, such as removal of heavy metals, fluoride, ammonia, some organic compounds etc. *(Flanigen, 1984; Klein and Hurlbut, 1993*; *Tarasevich, 1994*). However, very few publications are available about its use in removing anions. A study by Sakadevan and Bavor (*1998*) showed that clinoptilolite has the capability of phosphate removal.

In this research, the feasibility of using clinoptilolite to remove arsenic from drinking water was studied. It is expected that this method can be applied as a simple and economical technique at village level to reduce arsenic in drinking water to the safe level.

1.3 Objectives

The overall goal of this research is to study the feasibility of using natural zeolites as a low-cost and simple technology for arsenic removal from drinking water. The specific objectives for this research are as follows:

- To compare the efficiencies of conditioned and unconditioned zeolites in removing As(V).
- To determine the capacity of conditioned zeolite for arsenic uptake.
- To investigate the effect of experimental parameters such as contact time, initial As (V) concentration, solid-liquid ratio and conductivity of zeolite on the As(V) removal efficiency.
- To apply the method to natural water.

Chapter 2
Literature Review

2.1 Introduction

This chapter reviews background information about arsenic, the removal technologies for arsenic, and about the zeolites and their applications. The first part of this chapter includes the sources and occurrence of arsenic, its chemistry and mobility in groundwater. It also includes the human health effect of arsenic. Then the removal technologies for arsenic are reviewed and discussed. The final part includes zeolites and their applications.

2.2 Arsenic

2.2.1 Introduction

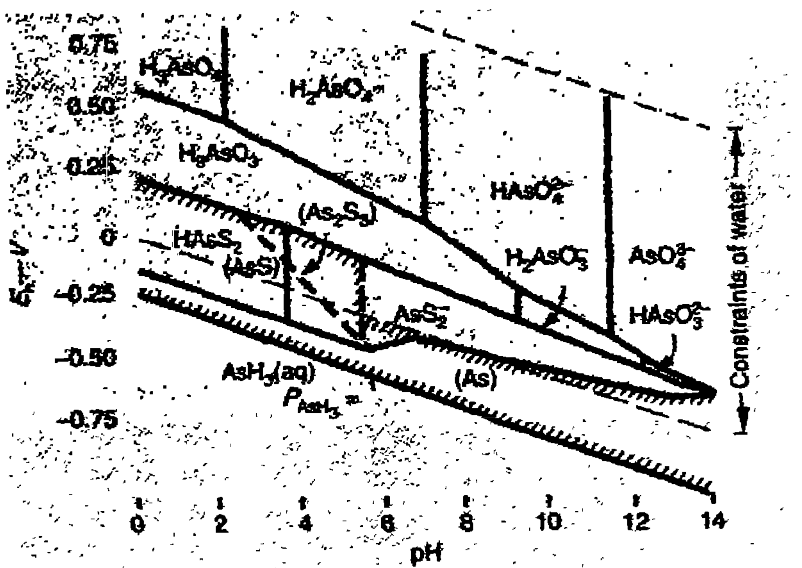
Arsenic was introduced by chance at the beginning of the Bronze Age during some of the earliest melting and refining of copper in the primitive furnaces of the time. In the ancient time, orpiment (As_2S_3) was known and also called 'arsenic' by the Greeks and Romans (*Polmear, 1998*). Arsenic compounds were used in medicine in the Orient 2,000-3,000 years ago (*Newland, 1980*). Arsenic metal was first isolated by the German alchemist, Albertus Magnus in the year 1250 (*Polmear, 1998*).

There is no one distinct source of arsenic in the environment. It can be found just about anywhere. The natural abundance of arsenic is low; it exists as stable compounds of low concentration. Therefore it is not harmful to the environment except for some certain areas where they can be released by natural events such as volcanic activities and water actions (*Reglinski, 1998*). Agricultural and industrial applications have raised the level of arsenic in the biosphere.

2.2.2 Chemistry of arsenic

Arsenic (As) belongs to Group VA, in the periodic table, which comprises the elements nitrogen, phosphorus, arsenic, antimony and bismuth. Arsenic has atomic number of 33 and atomic mass of 74.9216. The stable form (element) is crystalline, brittle and has a grey, metallic lustre, but this form is not common in the environment. Rather arsenic is usually found combined with one or more other elements such as; oxygen, chlorine, and sulphur (*Karim, 1997; Carmal and Norman, 1998).*). Arsenic is usually described as metalloids or semi-metals since it has some properties associated with metallic behaviour. Arsenic exists entirely as the single isotope ^{75}As and in oxidation states of –3, 0, 3, and 5 (*Pontius, 1994*; *Carmalt and Norman, 1998)*. Soluble arsenic occurs commonly in inorganic forms as arsenate (As(V)) and arsenite (As(III)). Arsenic trioxide (As_2O_3) is only slightly soluble in water, forming arsenous acid (H_3AsO_3) and exists in neutral form in a wide range of pH. Arsenic pentoxide (As_2O_5) is readily soluble in water forming arsenic acid (H_3AsO_4) which exists primarily as the anionic species ($H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}) at pH higher than 2. The thermodynamic predictions of the equilibrium chemistry of inorganic arsenic species are shown in Figure 2.1 (*Edwards, 1994,* reprinted and cited from Ferguson and Garvis, 1972).

Figure 2.1 Thermodynamic predictions of the equilibrium chemistry of inorganic arsenic species



Arsenate [As(V)] is anionic above about pH 2 and is thermodynamically favored in oxygenated waters. Arsenite [As(III)] is nonionic at pH values less than about 9.6, is anionic at higher pH, and is thermodynamically favored in anoxic waters. Stability diagram at 25° C, 1 atm with 10^{-5} M total arsenic, and 10^{-3} M total sulfur. Solid species enclosed in hatched area, indicating < $10^{-5.3}$ M solubility.

2.2.3 Sources and occurrence of arsenic

2.2.3.1 Natural sources of arsenic

Arsenic is naturally distributed throughout the earth's crust at an average concentration of 1.5-2 mg/kg. Igneous and sedimentary rocks contain varying amount of arsenic. Sedimentary iron ores and manganese ores are quite high in arsenic with average 400 mg/kg and up to 1.5 %, respectively (*Carmalt and Norman, 1998*). Over 245 arsenic bearing minerals have been identified which occur mainly as sulphides and which are usually associated with ores containing copper, lead, zinc, gold and silver. The most common ores are shown in Table 2.1 (*Carmalt and Norman, 1998*).

Table 2.1 The most common arsenic bearing ores

Common ores	Formula
Asenopyrite	FeAsS
Realgar	As_4S_4
Orpiment	As_2S_3
Arsenolite	As_2O_3
Energite	Cu_3AsS_4

Arsenic is found in many soil and sediment. In soil, arsenic originates primarily from the rocks, which were weathered to form that soil. Soils contain from 0.1 to 40 mg/kg As naturally. Soil overlying sulphide-ore deposits contain arsenic at several hundred mg/kg and are present as the unweathered sulphide minerals or in an inorganic anion state. Inorganic arsenate is bound mainly to iron and aluminum (W*oolson, 1982*).

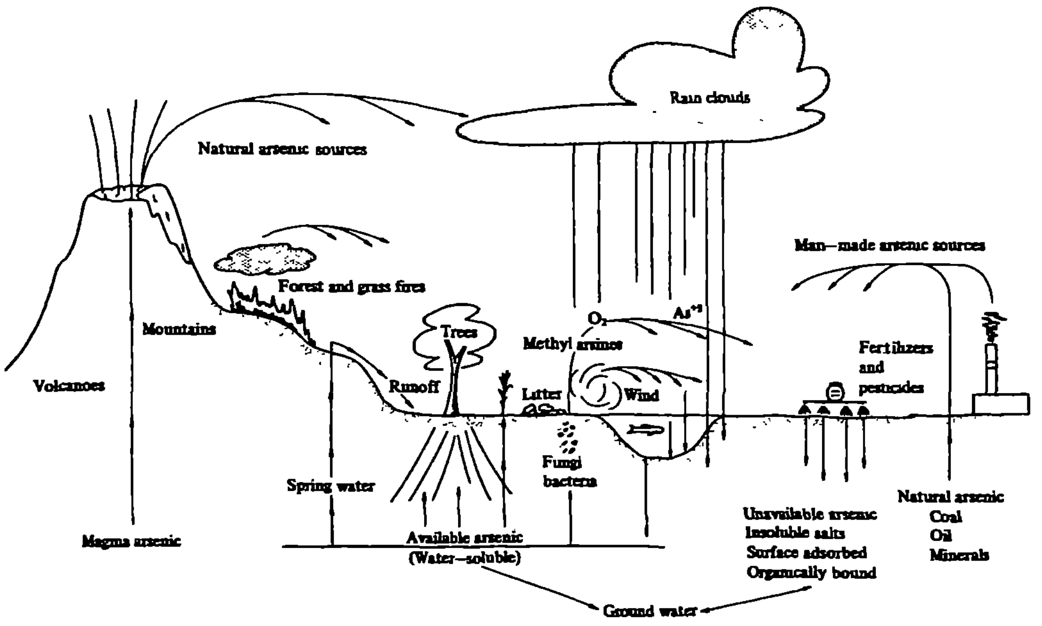
Arsenic is present in all waters and has a mean dissolved content of 1.7 µg/L in river water. (*Woolson, 1982*). Seawater contains 1.45-1.75 µg/L (*Carmalt, and Norman, 1998*). The arsenic content of water in lakes, rivers, wells, and springs varied greatly. Most of arsenic present there is naturally although some may have been added through pesticide usage. High content of arsenic in hot springs is notable. Extremely high arsenic concentrations have been reported in some groundwaters from areas of thermal activity (*WHO, 1996*). Arsenic is also transported by forest fire and volcanic action.

2.2.3.2 Anthropogenic sources

In addition to the natural erosion processes, smelters, industrial and agricultural applications have increased the quantity of arsenic in the environment. Arsenic is present in all copper, lead, and zinc sulphide ores and is carried along with those metals in the mining, milling, and concentration processes. Arsenic trioxide (As_2O_3) is widely used in commerce and agriculture. The world production of arsenic trioxide was about 50,000 tons/year (*Carmalt and Norman, 1998*). It is a basic raw material for herbicides, fungicides, insecticides, algicides, sheep dips, wood preservatives, feed additives and human and veterinarian medicines. The other human activities increase the worldwide atmospheric deposition of arsenic. These include the use of fossil fuel in power plants, coal conversion technologies, and oil shale conversion.

The environmental transfer of arsenic from natural and man-made sources is illustrated in Figure 2.2 (*Newland, 1980*)

Figure 2.2 Environmental transfer of arsenic



2.2.3.3 Mobility of arsenic in ground water

Arsenic is introduced into groundwater mainly through the dissolution of minerals and ores. Dissolution of arsenic and its transport in water occurs when the redox-potential value is around zero. Where there is iron, as found i.e. in the River Ganges delta in India and in the Netherlands, the behaviour of arsenic in groundwater is linked to iron (*Das, 1996*; *Zuurdeeg, 1998*). Dissolved arsenic occurs commonly in inorganic forms as arsenate (As(V)) and arsenite (As(III)) but under reducing conditions, as generally found in groundwater, As(III) is predominant (*WHO, 1996*; *Karim, 1997*; *Carmalt and Norman, 1998*). An increase in pH may increase the concentration of dissolved arsenic in water. (*WHO, 1996*). Although both organic and inorganic forms of arsenic have been detected, organic species (methylated arsenic compounds) are rarely present at concentration higher than 1 µg/L (*Pontius, 1994*; *Karim, 1997*).

2.2.4 Human-health effects of arsenic

2.2.4.1 Standards and guidelines

Arsenic is one of the most common and important trace elements whose toxic and medicinal properties have been known for centuries. Arsenic is an essential element to some animal species (*Pontius et al., 1994; WHO, 1996*). Trace amounts of arsenic are found in human body, and as cited by Carmalt and Norman (*1998*), Emsley (1991) reported that arsenic is essential to humans but Pontius et al. (*1994*) and WHO (*1996*) concluded differently that no evidence is available that it is essential to human.

Current findings on associated health risks of arsenic, increased incidence of skin cancer and possible internal cancer risks, stimulate the set-ups of standards or revisions of existing standards for maximum level of arsenic in drinking water in many countries. The WHO guideline value for As is reduced from the former level of 0.05 mg/L to 0.01 mg/L in 1993. India (*Das et al., 1996*) and Bangladesh (*Karim et al, 1997*) have a limit of 0.05 mg/L. In 1996, Germany reduced the level from 0.040 mg/L to 0.01 mg/L (*Hildebrandt and Holzel, 1997*). In the United States, the reduction of the limit from 0.05 mg/L, which is in effect since 1974, to a new range of 0.002-0.02 mg/L, is under amendment (*Frey and Edwards, 1997*).

2.2.4.2 Environmental levels and human exposure

Humans are exposed to arsenic from air, soil, dust, food, and water by inhalation, ingestion and absorption through the skin and mucous membranes. The levels of arsenic in air range from 0.4 to 30 ng/m^3 Higher concentrations are found in the areas of industrial sources (*WHO, 1996*). Food is a significant source of dietary intake of human. Studies in Canada indicate that arsenic content in many foods is mainly inorganic arsenic, however, fish, fruits and vegetables primarily contain organic arsenic (*Pontius, 1994*). It is estimated that 25% of intake of arsenic from food is inorganic and 75% is organic (*WHO, 1996*). Natural water contains 1-2 μg As/L except in the areas of natural sources. In the areas where geochemical conditions favour arsenic dissolution, ground water used for drinking purpose becomes an important source of arsenic exposure (*Pontius, 1994; WHO, 1996*).

2.2.4.3 Toxicity of arsenic in humans

The toxic effects of arsenic in drinking water on human health have been reported in several countries such as Taiwan, Thailand, India and Bangladesh. In general, inorganic arsenic species is more toxic than organic species. Arsenic(III) is about 10 times more toxic than arsenic(V) (*Reglinski, 1998*). Arsenic(V) carries a long term effect due to its reduction to arsenite (III) which when combines strongly with sulphur will affect key enzymes. The toxicity of arsenicals decrease as follows: arsines > arsenites > arsenoxides >arsenates > pentavalent organic compounds > arsonium metals > metallic arsenic (*Anonymous, 1979; WHO, 1996*).

The adverse effects of arsenic can be classified as acute and chronic effects. Acute effect occurs when high-concentration of arsenic is ingested in short time. Chronic effect is a long-term toxicity caused by accumulated arsenic after ingestion of low concentration of arsenic for long time.

- **Acute toxicity**

The acute toxicity of arsenic in humans is a function of the rate of removal from the body. The severity of the effect depends primarily on the level of ingestion. The average daily intake of arsenic is 0.04-1.4 mg. High-dose arsenic ingestion (5-50 mg) can lead to various health problems (*Carmalt and Norman, 1998*). The lethal dose (LD_{50}) in humans ranges from 1.5 mg/kg of body weight (arsenic trioxide) to 500 mg/kg of body weight (dimethylarsenic acid (*WHO, 1996*). The effects include vomiting, diarrhoea, redness and swelling of the eyelids and scrotum, erythema over the entire body, and loss of nails and hair, muscular pain, numbness and tingling of the extremities, muscular cramping, deterioration in motor and sensory responses. Death may occur from cardiovascular collapse (*Gulledge and O'Connor 1973*; *Pontius et al., 1994; WHO, 1996).*

- **Chronic toxicity**

The most common signs of long-term, low-level arsenic exposure from drinking water are dermal lesions that occur after minimum exposure periods of approximately 5 years. These include change in skin pigments, hyperkeratoses and ulcerations (*Pontius et al., 1994; WHO, 1996*). Another common disease is blackfoot disease that is found in many countries where ground water is used as drinking water. Other effects include cardiovascular system neurological, and diabetes mellitus (*Pontius et al., 1994*).

Based on sufficient evidence for carcinogenicity in humans, inorganic arsenic compounds are classified as carcinogenic to humans (*WHO, 1996)*. Studies have been conducted on cancer risk from chronic exposure of arsenic. The mechanism of action, however, is not well understood.

The chronic effects of arsenic in drinking water, as reported in some countries are summarised in Table 2.2.

Table 2.2 Arsenic levels in groundwater and arsenic-related health problems as reported in some countries

Country	As concentration in groundwater in the problem area (mg/L)	Diseases/ health problems	References
Argentina	0.5-1.5	chronic arsenic diseases skin cancer	*Pontius, 1994; Das et al., 1996*
Bangladesh	up to 1	skin disease cancer	*Karim et al., 1997*
Chile	0.8	dermatological manifestation	*Borgono and Greiber, 1971 (cited by Das et al, 1996)*
India	>0.5	skin disease cancer	*Das et al., 1996*
Taiwan	0.6-2	blackfoot disease, internal cancers	*Shen, 1973*
Thailand	up to 0.6	skin cancer skin lesions	*Choprapawon, 1998*

2.3 Arsenic removal technologies

2.3.1 Introduction

Health and environmental concerns regarding arsenic contamination in drinking water have stimulated significant research and development of efforts to achieve treatment processes that can effectively remove arsenic in drinking water to levels below the national standards or WHO guideline value. Arsenic can be removed by a number of available technologies, the choice of which depends on the amount of water to be treated, the amount of arsenic present and the presence of other contaminants, and others.

In the following details, conventional and advanced technologies are reviewed.

2.3.2 Conventional removal technologies

In most conventional technologies, processes existing for other purification purposes are applied for removing arsenic. Several researches have been focused on improving the efficiency of coagulation with metal salts since these technologies are available in most water treatment facilities. Other technologies include Fe-Mn oxidation, lime softening, and slow sand filtration.

2.3.2.1 Arsenic removal by coagulation/adsorption with metal salts

Coagulation with metal salts (ferric chloride, alum) is one of the most common processes in the water treatment plants to reduce turbidity and particles by removing non-settling and slow-settling solids from source waters (*Masschelein, 1992*). It has been recognized as an effective method for removing As from source waters and is perhaps the most effective method for large-scale treatment plants.

The studies carried out on the removal of As by coagulation showed that ferric chloride was more effective than alum. Shen (*1973*) found that ferric chloride gave the best effect on removal of arsenic (at an initial concentration 1.72 mg/L) compared with aluminium sulphate, ferrous sulphate and lime. In the full- scale study carried out by Scott et al. (*1995*), when the source water containing 1.6 µg/L was treated with 3-10 mg/L of ferric chloride (18.5-61.7 µM Fe(III)/L), arsenic removal of 82- 96 percent were achieved. Alum was less effective than ferric in removing arsenic. Alum dosed of 6, 10, and 20 mg/L (20.2, 23.6, and 67.3 µM Al(III)/L), reduced the arsenic concentration of 2.15 µg/L by 23, 45, and 69 percent. In the same study when the arsenic removal in bench-, pilot-, and demonstration-scale studies were compared (Figure 2.3a and 2.3b.), more variables at different scale were found with alum treatment than in ferric chloride.

Figure 2.3a. Arsenic removal in water with bench-, pilot-, demonstration-, and full-scale ferric chloride coagulation

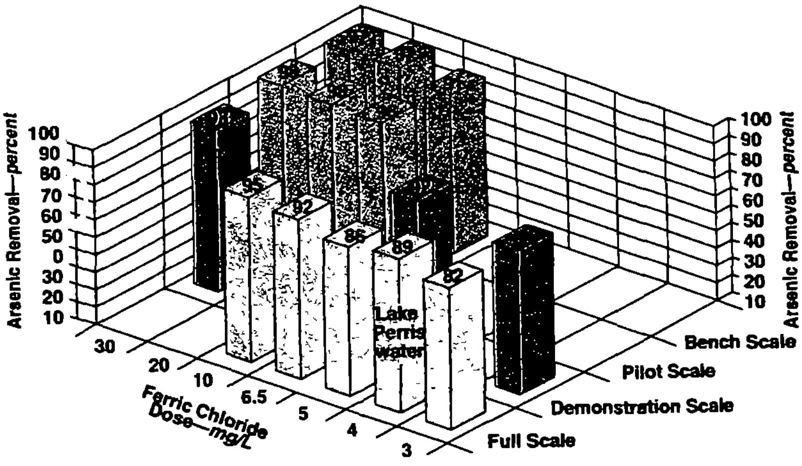
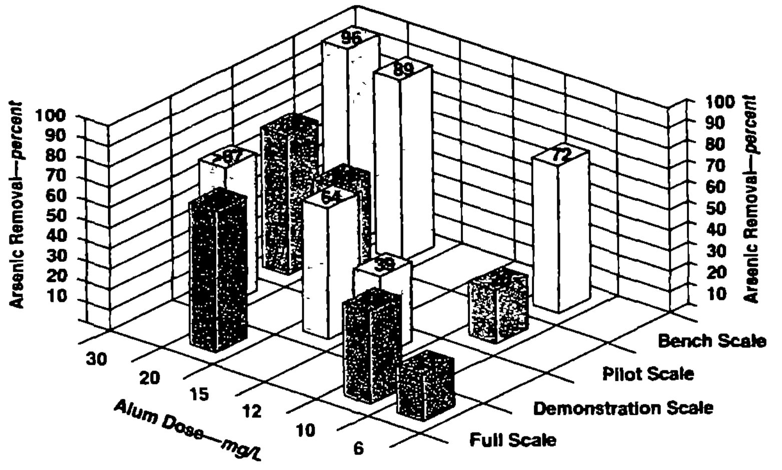


Figure 2.3b. Arsenic removal in water with bench-, pilot-, demonstration-, and full-scale alum coagulation



The study by Gulledge and O'Connor *(1973)* showed that arsenic adsorption on ferric hydroxide exceeded the adsorption on aluminum hydroxide. However, Edwards (*1994*) observed equal effectiveness between iron and aluminum coagulants in removing As(V) at pH 7.5.

Initial arsenic(V) concentration does not seem to affect the removal by ferric chloride or alum . Studies carried out by Edwards (*1994*) and Hering et al. (*1996*) showed that the removal of arsenic by ferric chloride or alum is independent of initial arsenic(V) concentration. Hering et al. (*1996*) showed that during treatment with 4.9 mg/L ferric chloride, arsenic removal percentages remained nearly constant while the influent arsenic concentration varied from 2.0 to 100 μg /L. Edwards (*1994*) found that percentage arsenate removals are independent of initial arsenate concentration for all aluminum dosages and when iron dosages are > 10 μM.

The effect of pH on arsenic removal was studied widely (*Gulledge and O'Connor, 1973; Edward, 1994; McNeill and Edwards, 1995; Hering et al., 1996*). Gulledge and O'Connor (*1973*) observed a noticeable decrease in removal of As (initial concentration of 50 μg /L) at pH 8.0 for both ferric and aluminum coagulants and suggested that it might be the result of the change in anionic form of the arsenic(V) from $H_2AsO_4^-$ to $HAsO_4^{-2}$. Alternatively, at the higher pH, the hydroxyl ion may begin to compete for the exchange sites on the ferric and aluminum precipitates. McNeill and Edwards (*1995*) found that reducing the coagulation pH from 7.4 to 6.8 improved removal of particulate aluminium, thereby enhancing soluble As(V) removal during treatment.

The species of arsenic also affect the removal efficiency. Better removal was observed for As(V) than for As(III) (*Shen, 1973, McNeill and Edwards, 1995; Hering et al., 1996*). Shen (*1973*) showed that if oxidation by chlorine was used before coagulation by ferric chloride, the result was better than by coagulation alone. Hering et al. (*1996*) observed higher removal percentage of As(V) than for As(III) in both coagulation and adsorption by ferric chloride. The other factor found to have effect on the efficiency of removal is the composition of source water. Hering et al. (*1996*) observed that when sulphate was added, the removal efficiency of As(III) by ferric chloride decreased whereas no change was observed in the case of As(V). In the same study it was observed that the removal of As(V) at an initial concentration of 20 μg/L was increased during coagulation with 4.9 mg/L ferric chloride and in the presence of 3.0 mM calcium at pH 9.0. It was also observed that the presence of calcium counteracted the slight competitive effect of phosphate.

The mechanisms of As removal are not definitely known yet. Shen (*1973*) suggested that the removal of As is via chemical binding (i.e., with the iron ion) rather than physical adsorption, while Gulledge and O'Connor (*1973*) and Edwards (*1994*) concluded that the removal is through physical adsorption, precipitation, and co-precipitation. The bench-scale studies conducted by Hering et al. (*1996*) demonstrated that adsorption is an important mechanism governing arsenic removal during coagulation although other processes, such as co-precipitation with ferric hydroxide and the oxidation of As(III) to As(V) may influence the efficiency of arsenic removal.

2.3.2.2 Other techniques

In Fe-Mn oxidation process, the arsenic removal is achieved via co-precipitation or adsorption reactions during the formation of hydroxides. No arsenic is expected to be removed by soluble Mn(II) or Fe(II). Edwards (*1994*) predicted that removal of 2 mg/L as Fe(II) could achieve a 0 75 μg/L soluble effluent concentration from a 10-μg/L As(V) initial concentration via adsorption alone. Removal of arsenic during manganese precipitation is relatively ineffective when compared with iron. In general, arsenic removal is controlled by the quantity of iron removed ($Fe(OH)_3$ formation) but is relatively independent of the quantity of manganese removed (MnOOH formation).

Lime softening and sand filtration can remove arsenic. In the lime softening process, As(V) removal is controlled by $Mg(OH)_2$ formation (*Dutta and Chaudhuri, 1991*; *McNeill and Edwards, 1995*). Insignificant soluble As(V) removal occurred during calcite precipitation. Shen (*1973*) showed that sand filtration can remove arsenic from water. Slow sand filtration gave better results than rapid filtration, however, the filtration was run too short- only 5 days.

2.3.3 Advanced technologies

Current advanced treatment options for As removal in water treatment plant show promising results in laboratory. However, these methods are limited to pilot scale or small scale and mostly not yet proven at full-scale treatment plants. Moreover, their use generally requires an entirely new treatment step.

2.3.3.1 Activated carbon

Activated carbon is found effective for the removal of both As(V) and As(III). The ability of activated carbon to adsorb arsenic depends on the arsenic oxidation state and pH of the water (*Rajakovic 1995*; *Tokunaga and Uthiumi, 1997*). A study by Rajakovic (*1995*) shows that activated carbon adsorbed arsenic(V) with a saturation adsorption capacity of 0.27 mmole per g. By impregnation of activated carbon by copper, the sorption process for arsenic(III) species was significantly improved. The used carbon, however, is difficult to be regenerated (*Tokunaga and Uthiumi, 1997*).

2.3.3.2 Iron-oxide-coated sand

This process was studied in a laboratory scale by Joshi and Chaudhuri (*1996*) to be used in small systems or home-treatment units for removing As(III) and As(V) from ground water. The results showed that at an initial concentration of 1.0 mg/L As(III) and As(V), breakthrough empty-bed volumes at the WHO guideline value of 10 μg /L were in the range 163-184 and 149-165 per cycle for As(III) and As(V), respectively. The study, however, did not address the effect of some important factors, such as possible selectivity of As(III) and As(V) over one another for removal, water pH, concentration and type of competing anions, and cations that sorb and surface charge of the medium or form soluble arsenic complexes.

2.3.3.3 Other techniques

Reverse osmosis technique can be used effectively to remove arsenic. However, this process is slow and operated under limited conditions and the cost for maintenance is very high (*Tokunaga and Uthiumi, 1997*). Ion exchanger can remove arsenic from water but it is not practical with large-scale application due to its cost and complex operation. Anion exchange may be the method of choice provided that the sulphate and total dissolved solids (TDS) levels are not too high because sulphate is preferred over chloride and arsenate by the typical strong-base resins used in the process (*Clifford, 1995*).

2.4 Zeolites and their applications

2.4.1 Introduction

The name *zeolite,* meaning *boiling stone* in Greek, was given by a Swedish mineralogist, Cronstedt in 1756 after he observed that a new mineral lost water easily when heated. There are now about 46 natural zeolites, many of which show close similarities in composition, association, and mode of occurrence (*Dyer, 1995*). Over the past 40 years zeolites have become the focus of intensive activity and growth in applications in industrial and environmental technologies.

2.4.2 Zeolite structures and properties

2.4.2.1 Zeolite structures

Zeolite is a framework aluminosilicate with cations (most commonly Na, Ca, and K), and H_2O in the generally large voids of the framework. The framework structure of zeolite consists of corner-linked tetrahedra that form three-dimensional four connected nets. At the centres of tetrahedra lie small T atoms (Al and Si) and at the corners lie oxygen atoms. The corner sharing of tetrahedra requires twice as many oxygen atoms as T atoms (*Smith, 1976; Klein and Hurlbut, 1993;)*. Figure 2.4 illustrate $[SiO4]^{4-}$ tetrahedron and linked chain of tetrahedra and Figure 2.5 stereodiagram of framework topology of heulandite (*Meier et al., 1996*). The water molecules are weakly bound by hydrogen bondings to anionic framework atoms. Cations and water molecules can move freely in the interconnecting spaces or channels. The general formula of zeolite is $M_{x/n}[(AlO_2)_x(SiO_2)_y]_wH_2O$ where M is cation, n is cation valence, w is the number of water molecules and y/x for natural zeolite has values of 1-5 depending upon the structure.

Figure 2.4 $[SiO4]^{4-}$ tetrahedron (black circle Si) and linked chain of tetrahedra

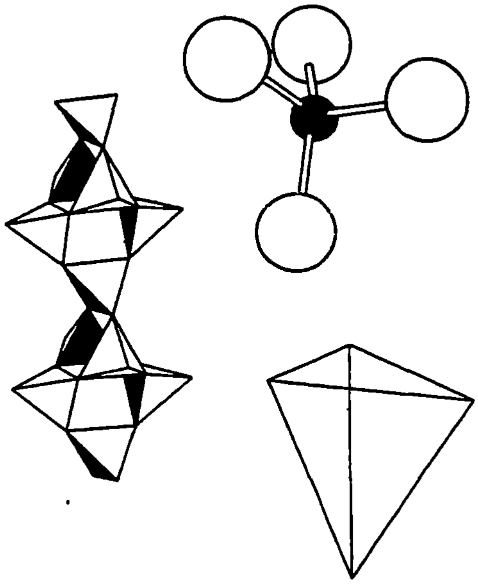
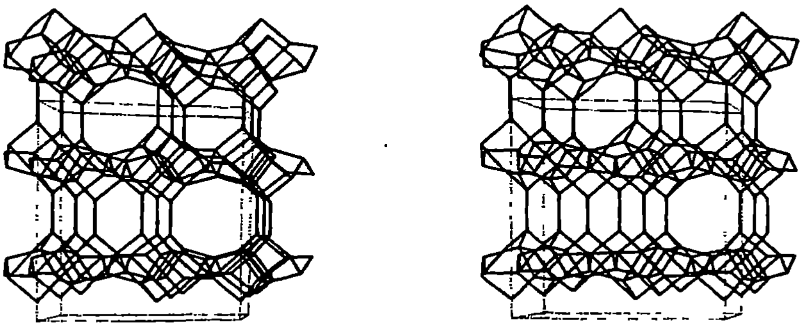


Figure 2.5 Stereodiagram of framework topology of heulandite. The dotted lines show one unit cell.



2.4.2.2 Zeolite properties

Some typical properties of most common zeolites are shown in Table 2.3 (*Sherman, 1984*).

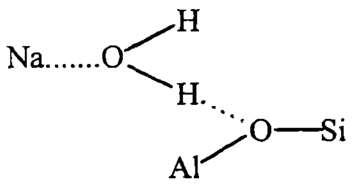
Table 2.3 Typical properties of some zeolites

Zeolite type	Pore opening, (hydrated form) A°	Typical SiO_4/Al_2O_3 mole ratio	Typical max theoretical cation exchange capacity (Na^+ form, anhydrous) meq/g
Clinoptilolite	4.0 x 5.5 and 4.4 x7.2 and 4.1 x 4.7	10	2.6
Chabazite	3.7 x 4.2 and 2.6	4	4.9
Mordenite	6.7 x 7.0 and 2.9 x 5.7	10	2.6
LINDE X	7.4 into alpha cage and 2.2 into beta case	2.5	6.4

Zeolites are relatively stable over a very broad range of conditions. The evidence is the presence of natural zeolites formed millions of years ago and the current formation and persistence of vast quantities of certain zeolites, especially philipsite and clinoptilolite present in shallow sediments on the floor of the oceans. At the pH levels of natural surface water (pH6-10), most zeolites are relatively stable and dissolve only very slowly (*Sherman, 1984*).

When water is added to a zeolite, highly polarizing cations tend to surround themselves with water molecules or even to disproportion a water molecule into a hydroxyl which bonds to the cation and a proton which condenses with a framework oxygen. (*Smith, 1976*). The infrared studies suggest that the water molecule interacts directly with the cation through the oxygen atom at different locations in the structure (Figure 2.6) (*Ward*, 1976).

Figure 2.6 Interaction of water with zeolite



In general zeolite containing cations of Group IA (Na, K etc) are non acidic. Introduction of divalent cation into zeolite introduced simultaneously structural hydroxyl group and acidity is detected. Addition of water increases the acidity (*Ward*, 1976).

2.4.3 Natural and synthetic zeolites

2.4.3.1 Natural zeolites

The first zeolite minerals were obtained from vesicles and fractures in basalts. The vesicles resulted from bubbles arising during emplacement of the basaltic liquid, and the zeolite formed by later precipitation from fluids that permeated the basalts . The bulk composition of the host rock correlates with that of the zeolites. Thus, mordenite and other Si-rich zeolites occur in rocks supersaturated in silica while faujasite, chabazite, gmelinite, and other Si-poor zeolites occur preferentially in rocks deficient in silica (*Smith, 1976*). Large deposits of zeolite have been found in the western USA and in Tanzania as alterations of volcanic tuff and volcanic glass (*Klein and Hurlbut, 1993*). During the last 3 decades, vast deposits of zeolite were found worldwide in sedimentary and low-grade metamorphic rocks. These Zeolites are mined commercially in USA, Cuba, Hungary, Bulgaria, Japan, Slovakia, South Africa, Italy, Russia, Indonesia and Korea (*Dyer, 1995*). Important natural zeolites include natrolite ($Na_2Al_2Si_3O_{10}.2H_2O$), chabazite ($Ca_2Al_2Si_4O_{12}.6H_2O$), heulandite ($CaAl_2Si_7O_{18}.6H_2O$), clinoptilolite ($(Na,K)_6[Al_6Si_{30}O_{72}].20H_2O$), and stilbite ($NaCa_2Al_5Si_{13}O_{36}.14H_2O$), etc. Other zeolites of lesser importance are phillipsite, harmotome, gmelinite, laumontite, scolecite and thomsonite (*Klein and Hurlbut, 1993; Dyer, 1995)*.

2.4.3.2 Synthetic zeolites

The high selectivity of clinoptilolite for ammonium ion in wastewater treatment and other applications generated interest in developing synthetic zeolites (*Flanigen, 1984*). In the synthetic zeolite the aperture and channel sizes may be controlled by a sort of template synthesis- the zeolite is synthesized around a particular organoammonium cation. This yields channels of the desired size (*Huheey et al., 1993*). Synthetic zeolites are often designated by a letter such as zeolite F, zeolite X and zeolite Y. The most important parameters in synthesis are cation and Si/Al ratio (*Flanigen, 1984*). Zeolites with high

Si/Al ratio are of high interest in commercial aspect. The best known of these products is ZSM-5 which can be made with a Si/Al ratio in the range 2-50 (*Dyer, 1995*).

2.4.3.3 Clinoptilolite

Clinoptilolite is a natural zeolite having the same framework topology as heulandite. The composition of clinoptilolite is $(Na,K)_6[(AlO_2)_6(SiO_2)_{30}].20H_2O$ with void fraction of 0.34 (*Dyer, 1995*). Vast quantities of clinoptilolite were found in shallow sediments on the floor of the oceans. (*Sherman, 1984*). It can also be found in hydrologically open system where percolation of meteoric water through tuff layers creates a series of vertical zones as seen in the John Day Formation in Oregon and Otahue in Hawaii. Clinoptilolite also forms in geothermal occurrence typified by those in Iceland, Yellowstone Park in the United States and Wairakei in New Zealand (*Dyer, 1995*).

When clinoptilolite is heated, irreversible dehydration commences at about 300°C, becomes appreciable at about 500 °C and completes at about 900 °C (*Taborsky, 1993*). In water, like other natural zeolites, clinoptilolite is very stable in the pH range 6-10. Its weight loss at pH 11, 10, and 9 are 1.1, 0.4 and 0.15% respectively (*Sherman, 1984*).

The high Si/Al ratio of clinoptilolite attracts much attention from researchers as a high Si/Al ratio means large void volume as well as hydrophilic property. Treatment of clinoptilolite with acid increases its porosity and adsorption capability. Clinoptilolite is used in many application especially ion exchange technologies due to its characteristics and availability. However, very few publications are available about the use of clinoptilolite in removing anion. A study by Sakadevan and Bavor (*1998*) showed that clinoptilolite has the capability of phosphate removal. Applications of clinoptilolite as well as other natural and synthetic zeolites are summarized in section 2.4.4.

2.4.4 Zeolite applications

2.4.4.1 Introduction

Zeolites were introduced as adsorbents for industrial separations and purification in late 1954. Since then a mass of scientific literature describing their synthesis, properties, structure and applications in ion exchange, adsorption and catalytic process have been generated (*Flanigen, 1984; Klein and Hurlbut, 1993*). Interests in zeolites derive from their structures. They have large voids and large internal surfaces, which control most of their useful properties. High mobility of water molecules and variable amounts of cations in the voids and channels become fundamental properties in their use as ion exchanges, molecular sieves and catalysts.

2.4.4.2 Ion exchange

The cations (such as Na^+, K^+, and Ca^{2+}) are only loosely bound to the tetrahedral framework and can be removed or exchanged easily by washing with a strong solution of another ion. Zeolites exhibit differential affinity for diverse cations with involve many complex interactions and factors including ionic shape and size. In this regard, however, Dyer *(1995)* observed that zeolites with an open structure and high Si/Al ratio prefer unhydrated cations (e.g. Cesium (Cs) uptake in clinoptilolite) whereas those with Si/Al close to unity often take up the small, more hydrated cations (e.g. Ca into zeolite A). Taborsky *(1993)* suggested that valence, although itself is not a conclusive determinant of relative affinities, may be used as a rule of thumb.

The use of clinoptilolite, chabazite, and mordenite for the removal and recovery of cesium and strontium radioisotopes in the nuclear industry was among the earliest applications of zeolites as ion exchangers (*Smith, 1976; Flanigen, 1984)*. clinoptilolite is very selective to Cs. In 1986, clinoptilolite from Bulgaria was dropped by air to help control the nuclear accident at Chernobyl. In soil, clinoptilolite has been used to reduce Cs-uptake by plants. (*Dyer, 1995*).

This ability for cation exchange is the basis for many applications as shown (examples) in Table 2.4

Table 2. 4 Ion exchange application

Application	Zeolite(S) used	References
Detergent builder	clinoptilolite zeolite A, zeolite X	*Dyer, 1995*
Radioisotope control	clinoptilolite mordenite LINDE AW-500	*Smith,1976,* *Flanigen, 1984*
Removal of NH_4^+	LINDE F, LINDE W clinoptilolite	*Flanigen, 1984,* *Dyer, 1995*
Heavy metals removal	clinoptilolite chabazite	*Flanigen, 1984;* *Ouki and Kavannagh, 1997*
Slow release fertilizers	clinoptilolite	*Flanigen, 1984,* *Huang and Petrovic, 1994*

2.4.4.3 Uses of zeolites as molecular sieves

When a zeolite is heated, the water in the channel ways is given off easily and continuously as the temperature rises, leaving the structure intact. About 80 to 90% of all the water is lost from the structure below about 350^0 C without collapse of the framework (*Klein and Hurlbut, 1993)*. The dehydration of zeolite structure is reversible. Zeolites in their dehydrates state can absorb other molecules whose size is smaller than the overall size of the zeolite channels allowing larger molecules to pass through. This property of most zeolites is known as "molecular sieving".

When dehydrated zeolite is immersed in water it can completely be rehydrated. This property allows zeolites to be used as desiccants, such as in the removal of water from gaseous hydrocarbons and petroleum. (*Flanigen, 1984*; *Klein and Hurlbut, 1993)*.

Applications of zeolites as molecular sieve include desiccants, gas purification, and gas separation.

2.4.4.4 Zeolites as catalysts

The commercial application of zeolites in hydrocarbon catalysis was introduced in the 60's when zeolite X was used in catalytic cracking of crude to produced liquid fuels (*Flanigen, 1984*). Synthesised zeolite ZSM-5 with high Si/Al have received much attention in commercial application due to its unique crystal structure with 0.6 nm pores outlined by 10-membered rings of oxygen that make it catalytic shape selective (*Flanigen, 1984*). Present applications of zeolites in catalysis include hydrocarbon conversion, hydrogeneration and dehydrogeneration , hydrodealkylation, methanation, shape-selective performing, dehydration, organic catalysis, and inorganic reaction.

Chapter 3
Materials and Methods

3.1. Experimental materials and apparatus

3.1.1 Experimental materials

- Natural zeolite: provided by 'SELOR/ROSCON'
  Clinoptilolite with particle size 1-200 μm (unconditioned and conditioned with calcium chloride)
  Heulandite
- Ceroxon
- Synthetic water (prepared by spiking appropriate amount of As(V) solution (see Section 3.4.1.1) in demineralized water.

3.1.2 Batch experiment apparatus

- Stirring set (200 rpm): C6F VELP Scientifica
- Centrifuge (18 000 rpm): MSE High Speed 18
- Polyethylene (PE) containers or beakers; 500 ml, 1000 ml
- Filter paper with 0.5-1.49 μm pore size: Schleicher & Schuell GF6 glass fibre papers
- Polyethylene syringes: 40 ml.
- Other borosilicate glassware (beakers, volumetric flasks, pipettes etc.)

3.2 Analytical materials

3.2.1 Chemicals and reagents

- Arsenic pentoxide (As_2O_5), 99.999%: Acros
- Demineralized water
- Nitric acid (HNO_3), AR grade: Merck
- Nickel nitrate ($Ni(NO_3)_2$), AR grade: Merck

3.2.2 Analysis instruments and devices

- Atomic absorption spectrophotometer (AAS): Perkin Elmer 1100 B with graphite furnace and HGA 300 Programmer
- Flame AAS: Perkin Elmer 3110
- Ion chromatography (IC): DIONEX Series 4500i
- pH meter: Metrohm 691
- Conductivity meter: WTW LF 340

- Borosilicate glassware (beakers, volumetric flasks, pipettes etc.); all glassware were cleaned with nitric acid and rinsed with demineralized water before use.
- Micro pipette

3.3 Experimental methods

3.3.1 Preparatory experiments

3.3.1.1 Basic properties of unconditioned and conditioned zeolite

In the experiments, use was made of zeolite (see 3.1.1). The conditioned zeolite (or unconditioned zeolite) was stirred in demineralized water, using solid/liquid (S/L) ratio of 1/20, for 10 minutes, then the solution was separated from zeolite by filtration (with the GF6 fibre filter). Iron and calcium in the filtrate were measured by Flame AAS, sulphate and chloride by IC, pH by the pH meter and electrical conductivity (EC) by the conductivity meter.

3.3.1.2 Effect of filtration and centrifugation on As in solution

Before the actual experiments with zeolite were carried out, the selection of the separation technique had to be made. Therefore the effect of each technique on As was carried out to define whether filtration or centrifugation was appropriate for separating the As solution from the solid phase (zeolite) after the required contact time was reached.

- **Effect of filtration** :

A solution containing 98 µg As/L (see 3.1.1: synthetic water) was filtered through GF6 fibre filter with the help of air suction and the filtrate was collected in a glass tube. The first filtrate was filtered through a GF6 filter after which the second filtrate was filtered again through a new GF6 to obtain the third filtrate. Each filtrate was stored in a polyethylene bottle, and analysed for As within 1 day by graphite furnace AAS with maximum temperature of 2300 °C as described in Section 3.4.2. The As concentration in the filtrate was compared with the As in the initial solution before filtration. The experiment was repeated with solutions containing 95 µg As/L and 300 µg As/L.

- **Effect of centrifugation (18000 rpm):**

To see the possible effect of uptake or release of As by centrifuge tubes, a solution containing 100 µAs/L was centrifuge at 18000 rpm for 10 minutes, and measured for As as described in Section 3.4.2.

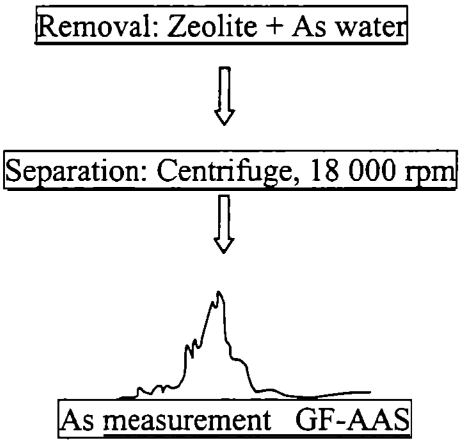
3.3.2 Removal of As by conditioned and unconditioned zeolite

3.3.2.1 Removal of As by unconditioned zeolite

Based on the results of previous preparatory experiments (see Figures 4.1, 4.2 and Table 4.2), the following experiments were carried out using centrifugation at 18000 rpm as the separation method. In the whole research, batch experiments were conducted in duplicate.

Fifty gram of unconditioned zeolite was added to the polyethylene beaker containing 1000 ml of synthetic water with 316 μg As/L (S/L ratio1/20); the suspension was stirred continuously at 200 rpm. Then about 20 ml of the water/zeolite suspension was collected by a syringe at 15 minutes, 1, and 4 hours and transferred to a centrifuge tube. It was then centrifuged for 10 minutes. The supernatant was separated from zeolite by a Pasteur pipette and determined for As as described in Section 3.4.2. The experimental set up is shown in Figure 3.1.

Figure 3.1 The set up diagram for As removal batch experiment



3.3.2.2 Effects of contact time and initial As concentration using conditioned zeolite.

The conditioned zeolite used in the following experiments (3.3.2.2 – 3.3.2.4) was washed with demineralized water to remove excess Ca and Cl (thus reduce EC) as follows: the dried zeolite was stirred in demineralized water with S/L ratio 1/20 for 15 minutes and centrifuged for 10 minutes until the pre-fixed EC values were attained. In the following experiments, the washed conditioned zeolites having different EC values are referred to low EC zeolite (<100 μs/cm), moderate EC zeolite (100-200 μs/cm), and high EC zeolite (500 –600 μs/cm).

The procedure was as described in 3.3.2.1 using moderate EC zeolite, with a S/L ratio 1/20, synthetic water with initial As concentration of 100 μg/L, and with 15 minutes, 1, 4, and 24 hours contact times. The experiment was repeated for the synthetic water with initial As concentration of 200, 300, 400, and 500 μg/L.

3.3.2.3 Effects of solid-liquid ratio and conductivity of conditioned zeolite

The procedure was as described in 3.3.2.1. The S/L ratios were 1/20, 1/15 and 1/10 for low EC zeolite; 1/20 and 1/10 for moderate and1/20 and 1/10 for high EC zeolites. The contact times were 15 minutes, 1 and 4 hours. The initial As concentration was 300 μg/L for each experiment.

3.3.2.4 Capacity of zeolite on arsenic uptake

The capacity of zeolite for arsenic(V) was estimated by using the conditioned zeolite with high EC. The procedure is as described in Section 3.3.2.1 and is described in detail, together with the results, in Table 4.3. In each step, a certain amount of As was added to zeolite/water suspension. After the appropriate contact time, 20.0 ml of the suspension was collected and centrifuged, after which the solid material was returned to the beaker, and demineralized water was added to compensate for the sampling volume. The supernatants after centrifugation were then analysed for As, so that the As uptake by the zeolite could be calculated after each step. This was continued until the maximum As uptake by the zeolite had been reached.

3.3.2.5 Removal of As in natural water by conditioned zeolite

The groundwater samples from Bangladesh had been treated with hydrochloric acid to pH below 1.5 before being transported to IHE. Prior to the experiment, the samples were adjusted with 1M NaOH to pH about 7. The groundwater samples from Hungary were used as received. The experiments were carried out as described in Section 3.3.2.1.

The experimental parameters used in Section 3.3.2 are summarised in Table 3.1

Table 3.1 Experimental parameters used in Section 3.3.2

Experiment	Zeolite used	S/L ratio	Initial As conc., μg/L	Contact time	Results
3 3 2.1 Removal of As by unconditioned zeolite	unconditioned zeolite	1/20	316	15 min., 1, and 4 hr	Fig. 4.3
3 3 2 2Effect of contact time and init As concentration	moderate EC zeolite	1/20	100, 200, 300, 400, 500	15 min, 1, 4 and 24 hr	Fig. 4.4a and 4.4b
3 3.2 3 Effect of solid-liquid ratio and conductivity of zeolite	low EC zeolite moderate EC high EC	1/20, 1/15, 1/10 1/20, 1/10 1/20, 1/10	300	15 min, 1, and 4 hr	Fig. 4.5
3 3 2.4 Capacity of zeolite	high EC zeolite	1/50	-	-	Table 4.3
3.3 2.5 Removal of As in natural water ▪ from Bangladesh ▪ from Hungary	moderate EC	1/20	 425, 1320 224, 232	15 min, 1, and 4 hr	 Fig. 4.6, Table 4.4 Fig 4.7, Table 4.6a-4.6c

3.3.3 Removal of As by alternatives materials

The alternative materials used in this study were heulandite and a synthetic xonolite (ceroxon). The procedure was as described in Section 3.3.2.1 using these materials instead of zeolite. The parameters used are shown in Table 3.2.

Table 3. 2 The parameters used in the removal of As by alternative materials

Material	Initial concentration of As, µg/L	Contact time	S/L ratio	Result
Heulandite	343	15 min., 1 hr	1/20	Figure 4.8
Ceroxon	318	15 min., 1 hr	1/20	Figure 4.8
Ceroxon	343	15 min., 1 hr	1/50	Figure 4.8

3.4 Analysis methods

3.4.1 Preparation of standard solutions and samples

3.4.1.1 Standard solutions:

The As(V) stock solution of 1000 mg/L was prepared by dissolving 0.1534 g As_2O_5 in 100.0 ml demineralized water; this was stored in a refrigerator. The As(V) primary standard of 10.0 mg/L was prepared from the stock solution by diluting 1.0 ml to 100.0 ml with 0.1 M HNO_3. The secondary standard of 1.0 mg/L was prepared from the primary standard. This standard was used within 2 weeks. The working standards of 0, 20, 40, 60, 80 µg/L As(V) were prepared by diluting the appropriate volumes of the secondary standards with 0.1 M HNO_3. The 0 µg/L solution was used as the blank standard. The working standard solutions were freshly prepared before every experiment.

3.4.1.2 Samples

The supernatant obtained from the As removal experiment (section 3.3.2 and 3.3.3) was pre-treated with 1 M HNO_3 to adjust pH to about 2 (3 drops/10 ml sample) and with $Ni(NO_3)_2$ (100 µl/ 10 ml sample) as a matrix modifier.

3.4.2 Arsenic measurement

3.4.2.1 Standard solutions

The analysis for As was carried out according to the Standard Methods (*Eaton et al., 1995*) by using AAS with graphite furnace. The temperature programme is given in Annex I.

Each standard solution (20 µl) was injected to the graphite tube of the AAS and heated to 2300°C in steps according to the pre-set program. The analysis of each standard was done in triplicate to verify the method precision. The linear analytical curve was then constructed in the AAS (plot of the average peak areas of the standard solution versus concentration of the working standards).

3.4.2.2 Samples

Each sample was analysed using the same procedures as the standard solutions, and at least in duplicate or until reproducible results were obtained ($\leq$ 10% variation). The As concentration in the sample was read directly from the AAS. For the samples with higher concentration than those of the most concentrated standard solution; these were diluted in 0.01 M HNO_3 and reanalysed.

3.4.2.3 Limit of detection (LOD)

The blank standard was analyses for As in 10 replicates. Then the results were calculated for standard deviation (SD). LOD was obtained as 3xSD of the blank. In this study, the LOD was thus found to be 6 µg As/L.

Chapter 4
Results and Discussion

4.1 Preparatory experiments

4.1.1 Quality control in the laboratory

In order to assure the quality of experimental results, a comparison of analysis results (As concentrations) with a recognised laboratory was carried out. Three samples of As were prepared differently and sent to the Netherlands Organization for Applied Scientific Research (TNO) in Utrecht for As measurements.

Sample 1: demineralized water was spiked with As(V)
Sample 2: demineralized water was spiked with As(V), then filtered through GF6 glass fibre filter.
Sample 3: demineralized water was spiked with As(V), mixed with unconditioned zeolite and stirred for 10 minutes then filtered through GF6 glass fibre filter.

The results from IHE laboratory and TNO are compared in Table 4.1

Table 4.1 The results of As measured by two laboratories

Sample No.	Results (As, µg/L)		Difference ±%
	TNO	IHE lab.	
1	35.0	38.0	7.9%
2	12.0	12.7	5.5%
3	10.0	<6	~66.7%

As shown in Table 4.1 above, the results from the two laboratories are in good agreement for samples 1 and 2, whereas the results for sample 3 differed significantly. The reason for this difference is possibly due to the fluctuation and uncertainty near the limit of detection. In general, it can be concluded that the analysis results obtained in this research are acceptable.

4.1.2 Basic properties of unconditioned and conditioned zeolites

The basic properties of unconditioned and conditioned zeolites, after adding demineralized water (see 3.3.1.1) are compared as shown in Table 4.2. These results show that the EC of conditioned zeolite was very high and not suitable for treatment of drinking water. The high value of EC is mainly due to the excess amount of $CaCl_2$ used for conditioning the zeolite. Therefore, in this research, conditioned zeolite was rinsed by demineralized water to remove excess $CaCl_2$ (see 3.3.2.2).

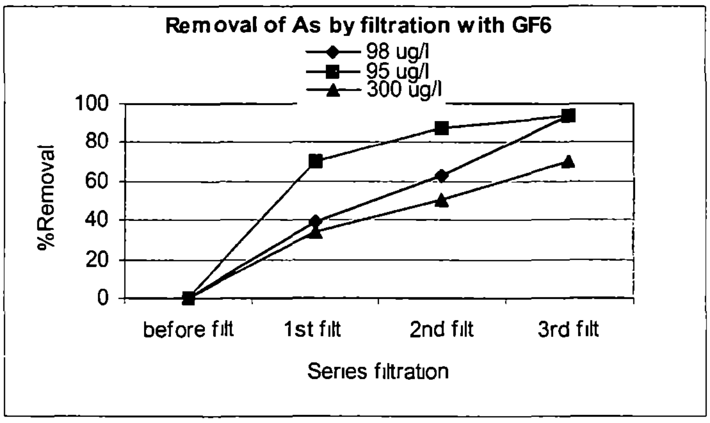
Table 4.2 Some basic properties of unconditioned and conditioned zeolites (S/L ratio: 1/20)

Solution	pH	EC, µs/cm	Fe, mg/L	Ca, mg/L	SO_4, mg/L	Cl, mg/L
Unconditioned zeolite	7.5	95	0.36	3.4	22	4
Conditioned zeolite	6.7	2600	0.11	370	25	750
Demin. water	7.7	1.5	-	-	-	-
Tap water	8.0	480	-	-	-	-

4.1.3 Effects of filtration and centrifugation on As.

The results of the effects of filtration and of centrifugation are shown in Figure 4.1 and Figures 4.2a and 4.2b respectively.

Figure 4.1 Series filtration of As containing water by GF6 fibre filter, at initial As concentrations 95, 98 and 300 µg/L.



The Figure 4.1 shows that after each filtration 20 to 60 % of As was retained on the filter. Therefore filtration is not a suitable method. With centrifugation, no marked differences in As concentration between before and after centrifugation were observed as shown in Figure 4.2a. This indicated that there was no adsorption of As on the wall of the centrifuge tubes.

The complete separation of the liquid phase (solution) from the solid phase (zeolite) was observed from the duplicate experiments as shown, for instance, in Figure 4.2b which was replotted from the results from the experiment in 3.3.2.2. The variation between the two identical experiments was less than 5%.

Figure 4.2a Effect of centrifugation tubes on As compared with filtration

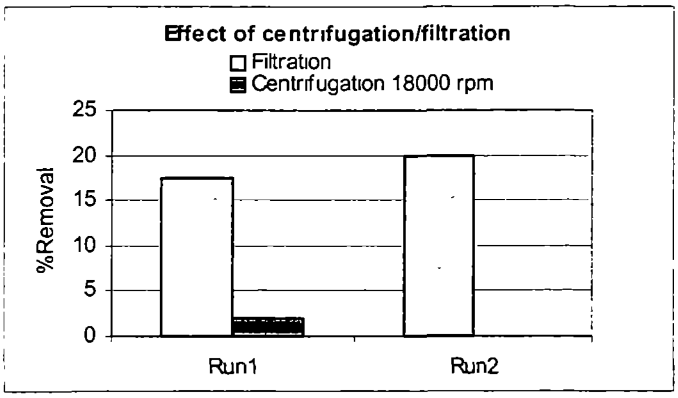
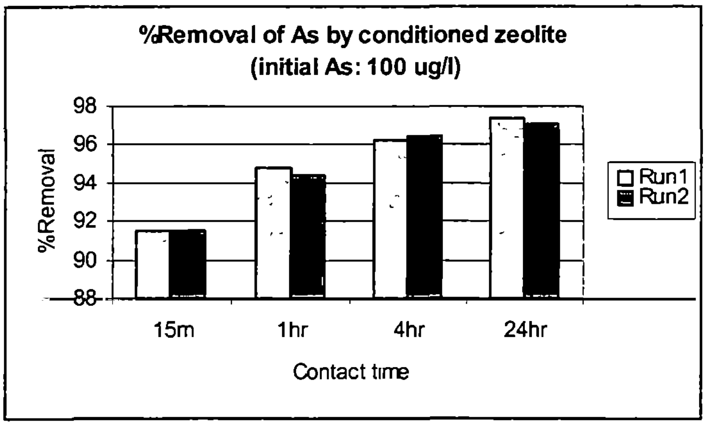


Figure 4.2b Results of the duplicate experiment on removal of As by conditioned zeolite, using 18000 rpm centrifugation as the separation technique



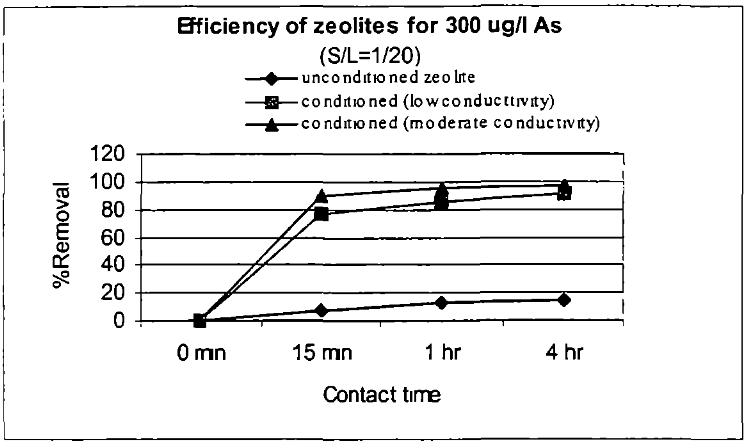
4.2 Removal of As(V) in synthetic water by conditioned and unconditioned zeolites

4.2.1 Efficiency of conditioned zeolites in removing As(V), compared with unconditioned zeolite

The comparison of the efficiencies between conditioned and unconditioned zeolites is shown in Figure 4.3 and is given in Table II.3 in Annex II.

The results show that the As removal efficiencies of conditioned zeolites with both low and moderate EC values were much higher than that of unconditioned zeolite. At 15 minutes contact time, 77.3% and 89.0% removal efficiencies were obtained respectively for conditioned zeolites with low and moderate EC values. For the same contact time, the removal efficiency of unconditioned zeolite was found to be only 6.7%. Similarly, for unconditioned zeolite the maximum efficiency obtained at 4 hours was also very low (14.3%) compared to 91.0 % and 97.0 % of the conditioned ones. During the experiments, the pH values of the solutions with conditioned and unconditioned zeolites were in the ranges of 5.0 – 5.8 and 8.1 – 9.1 respectively.

Figure 4.3 Efficiency of unconditioned zeolite, conditioned zeolite with low EC and zeolite with moderate EC.



The reasons for the higher efficiency of conditioned zeolites to remove As(V) might be as follows:

- Unconditioned zeolite used in this experiment is in the monovalent-cation form with more K than Na in its structure (see Annex III). These cations occupy the space in the channels. After being modified with $CaCl_2$, some K^+ ions and/or Na^+ ions were replaced by Ca^{2+}ions. The decrease in the number of cations in the zeolite ($2K^+$ are replaced by Ca^{2+}) results in more clear pathway fraction through the three-dimensional network of channels for the entry of guest ions such as $H_2AsO_4^-$ ions, and thus improves the adsorption of As(V). This phenomenon was previously described by Eberly (*1976*) in the removal of n-paraffin and N_2 by zeolite A; when Na^+ in zeolite A was replaced by Ca^{2+}, better adsorption was obtained.

- The pH of zeolite in water and the form of As(V) seemed to play role in the As removal. According to the Eh-pH diagram shown in Figure 2.1, at pH between 2 and 7.5 most of As(V) exists as $H_2AsO_4^-$ and between 7.5 and 11.5 as $HAsO_4^{2-}$. At pH above neutral, OH^- ions generate and compete with $HAsO_4^{2-}$ for the adsorption sites on zeolite surface. Since the pH of the solution in the case of unconditioned zeolite was well above neutral the phenomenon of OH^- ions might be responsible for the comparatively low As removal efficiency.

- The direct formation of calcium arsenate might take place. In this case formation of $Ca(H_2AsO_4)_2$ can remove more As(V) than the formation of KH_2AsO_4 or NaH_2AsO_4.

4.2.2 Effect of contact time and initial As concentration on the removal efficiency

The results are shown in Figure 4.4a and 4.4b and are tabulated in Table II.4 in Annex II. During the removal process the pH of all solutions were between 5.6 to 6.0. It is clearly seen that the contact time did not play a major role on the removal efficiency. Most of the removal took place within 15 minutes. The percentage removals of As from 100 μg/L, 200 μg/L, 300 μg/L, 400 μg/L and 500 μg/L samples during the first 15 minutes were 90, 91.5, 90, 86.5 and 87.2 respectively. This showed that the initial concentration of As is not very important for the removal efficiency. The residual concentration of As(V) in the samples of 100 μg/L was 10 μg/L, which is the safe level recommended by WHO. For initial As concentration of 200 μg/L and 300 μg/L, it needs 15 minutes to1 hour and 1 to 4 hours respectively to bring As to the safe level. For 400 μg/L and 500 μg/L samples, more than 24 hours are required.

Figure 4.4a Residual As in water after contact with conditioned zeolite

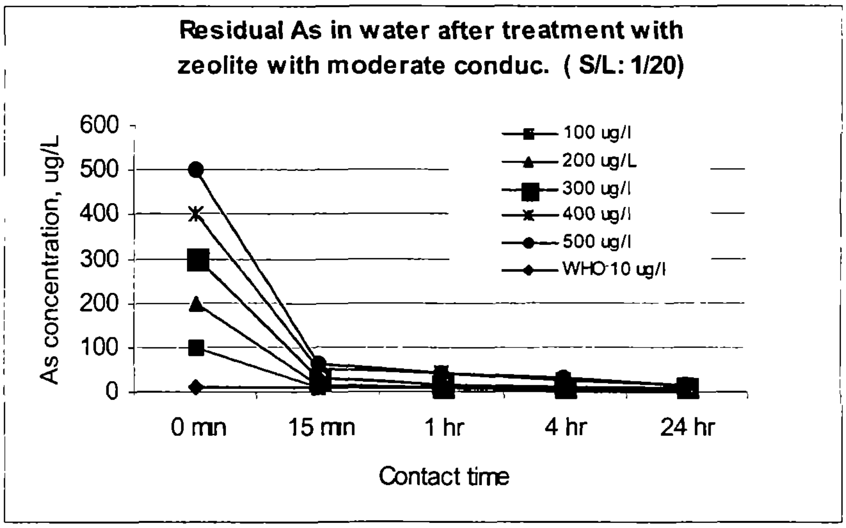
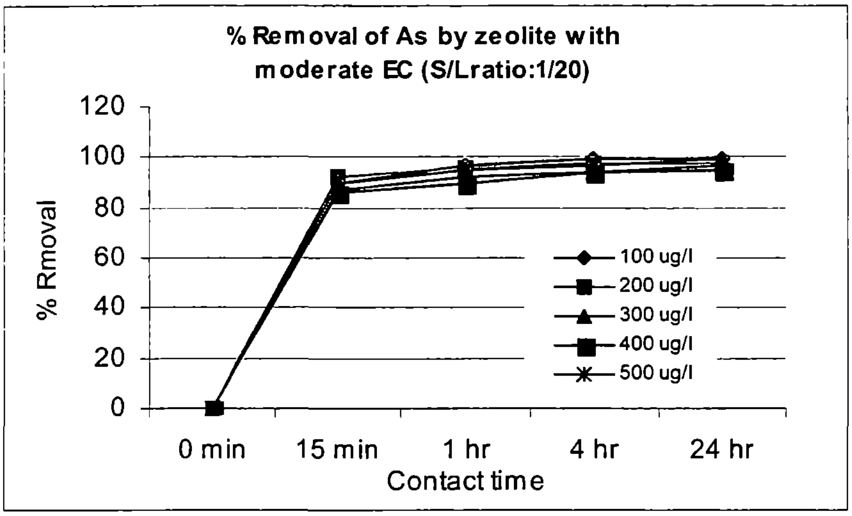


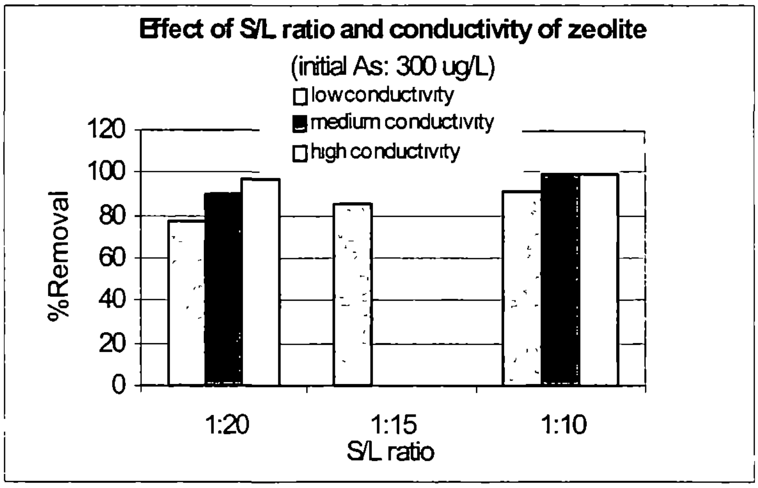
Figure 4.4b %Removal of As and contact time



4.2.3 Effect of solid-liquid ratio and conductivity of zeolite on the removal efficiency

The results of these experiments with low, moderate and high EC zeolites at 15 minutes contact time are illustrated in Figure 4.5 and given in Table II.5 to II.7 in Annex II. When there was more zeolite in the solution (high S/L ratio), the removal efficiency was higher. For the conditioned zeolite of low EC, at 15 minutes contact time and initial As concentration of 300 µg/L, the efficiencies for S/L ratios 1:20, 1:15, and 1:10 were 77.3%, 85.3%, and 91.3% respectively. For moderate and high EC zeolites, less increase in removal efficiency was observed with the increase in S/L ratio.

Figure 4.5 Effect of S/L ratio and conductivity of zeolite



Comparing the efficiencies of the different EC zeolites with the same S/L ratio, it was observed that zeolite with higher EC gave higher efficiency. In 15 minutes, for S/L ratio of 1/20 the observed efficiencies were 77%, 90% and 97 % respectively for low, moderate and high EC zeolites.

It is likely that some Ca^+ ions, which were bound loosely in the structure of conditioned zeolite, dissolved in water resulting in the increasing EC. The question may arise whether dissolved Ca^+ reacted with As(V) and was precipitated. Therefore, an experiment was carried out to show whether or not the As(V) was removed via precipitation of calcium arsenate. Conditioned zeolite of high EC was stirred in demineralised water with S/L ratio of 1/20 for 1 hr and then centrifuged at 18 000 rpm for 10 minutes. The supernatant was separated from zeolite for Ca measurement and for experiment with As(V). When As(V) was added to the supernatant, to make a solution containing about 300 µg/L As, and mixed well, no precipitation of calcium arsenate was observed. Therefore, it can be concluded that precipitation did not play a role and that higher EC actually indicated higher Ca^{2+} in the zeolite structure, and accordingly, higher removal was obtained.

4.2.4 Capacity of conditioned zeolite for As(V) uptake

The result of the experiment is shown in Table 4.3. The observed capacity of zeolite for As(V) uptake is 62 µg As(V)/g, that is 0.0008 mmole/g. This capacity is very low compared to 0.27 mmole/g capacity of activated carbon as found by Rajakovic (*1995*) (see Section 2.3.3.1). Therefore, in practice it does not seem cost effective to use this conditioned zeolite. However, this experiment was stopped when As adsorption remained constant without adding new As. Furthermore, the variation of pH during the experiment was not considered. Therefore, this value may not be the really maximum capacity. By adding new As(V) continuously, higher capacity may be achieved.

The zeolite used in this study was conditioned for other purposes rather than for the removal of As. It is also expected that higher capacity for As(V) can be obtained from zeolite which is conditioned specifically for As.

Table 4.3 Procedure and result for capacity of conditioned zeolite (see Section 3.3.2.4)

I	II	III	IV	V	VI	VII	VIII	IX	X	XI
	Zeolite (g)	Starting vol ml	ml As (1000 mg/L) added	As in starting sol. ug/L	Contact time	ml of sample collected	As in final sol ug/L	As uptaken by zeolite (ug)	As accumulated in zeolite (ug)	Capacity of zeolite (ug As/g Zeo)
1	25	1000	-	-	15 m	20	-	-	-	-
2	24.5	980	0.5	510	1 h	20	38	472	472	19.3
3	24.5	960+40 =1000	0.5	500+38 =538	1 h	20	238	300	772	30 9
4	24 5	980+20 =1000	0.5	500+238 =738	1 h	20	473	265	1037	42 3
5	24.5	980+20 =1000	0.5	500+473 =973	1 h	20	886	87	1124	45.9
6	24.5	980+20 =1000	0.5	500+886 =1386	1 h	20	1344	42	1166	47.6
7	24.5	980	-	1344	1 h	20	1239	105	1271	51.9
8	24.5	960+20 =980	-	1239	1 h	20	1234	5	1276	52.1
9	25	980+20 =1000	0.5	500+1234 =1734	overnight (14 h)	20	1491	243	1519	**62.0**
10	24.5	980	-	1491	1 h	20	1533	0	1519	**62.0**
11	24.5	960+20 =980	-	1533 or 1491	1 h	20	1491	0	1519	**62.0**
12	24.5	960+20 =980	-	1491	2 h	20	1512	0	1519	**62.0**
13	24.5	960+20 =980	-	1512	3 h	20	1528	0	1519	**62.0**

4.3 Removal of As in natural waters by conditioned zeolite

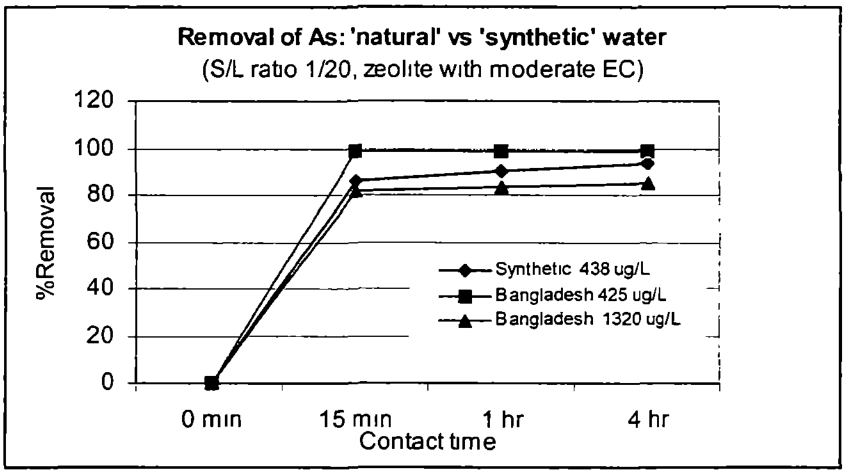
4.3.1 Groundwater from Bangladesh

The results for the removal of As from groundwater from Bangladesh are shown in Table 4.4 and are illustrated in Figure 4.6. Within 15 minutes, the removal of As from groundwater containing 425 μg As/L was completed whereas only 86% of As was removed from synthetic water with similar concentration (438 μg/L). For groundwater with 1320 μg As/L, the removal was 82% in 15 minutes, after which the removal process slowed down markedly with only 85 % removal after 4 hours. For both natural waters, the pH during the process decreased from 7.2 before mixing with zeolite to 6.6, 5.3 and 5.1 at 15 minutes, 1 and 4 hours contact time respectively.

Table 4.4 Residual As and % removal in water from Bangladesh after treatment with moderate EC zeolite (S/L ratio 1/20, initial As concentration 1320 μg/L and 425 μg/L)

Contact time	pH	Conductivity ms/cm	Residual As, μg/L	% Removal	Residual As, μg/L	% Removal
0 min	7.2	>3	1320	-	425	-
15 min	6.6	>2.5	240	82	<<6	>99
1 hr	5.3	>2.5	226	83	<<6	>99
4 hr	5.1	>2.5	194	85	<<6	>99

Figure 4.6 Removal of As from groundwater from Bangladesh compared with the synthetic water with similar As concentration



It is clearly seen that the As removal from Bangladesh waters resulted not only by the zeolite uptake but also by some other factors. The samples had been pre-treated by hydrochloric acid and some other pretreatments might have occurred in which As(III) was oxidised to As(V). The analysis for iron contents of these waters (Table 4.5) show that water containing 425 μg As/L and 1320 μg As/L contain 13.6 mg Fe/L and 5.6 mg Fe/L respectively. It was therefore suspected that the process of As removal was positively affected by the presence of iron. To confirm this, water containing 425 μg As/L (with pH 7.2, adjusted prior to the experiment) was left overnight after which a brown precipitate was clearly seen at the bottom of the container. Then the As concentration in the supernatant was measured. It was found that the supernatant contained only 29 μg/L As. This implies that in the As removal process by zeolite, a significant percentage of As must have been removed by the co-precipitation with iron hydroxide and only partly by zeolite.

Table 4.5 Iron content in groundwater from Bangladesh

	Synthetic water	Groundwater sample no. 1	Groundwater sample no. 2
As, μg/L	438	425	1320
Fe, mg/L	0	13.6	5.6

4.3.2 Groundwater from Hungary

The experiment was repeated with two samples of groundwater from Hungary having As concentrations of 224μg/L and 232 μg/L, with pH 7.9 and 8.2 respectively. The result, as shown in Tables 4.6a, 4.6b and 4.6c, illustrated in Figure 4.7, shows that the As removal from these samples was very low compared to the removal from the synthetic water at an initial pH 5.6.

At 15 minutes, only 22% As removal was achieved from both samples of Hungary water whereas the removal was 96% in the case of synthetic water. The As concentration could not be reduced further; on the contrary, As was released back to the solutions. At four hours contact time the overall removal of As was only 12% and 7%. Unlike the case of Bangladesh water, the pH of the solution of natural waters increased slowly with contact time, that is from about 8 before mixing with zeolite to 8.5-8.6 in 4 hours.

Table 4.6a Residual As and % removal in water from Hungary after treatment with zeolite (initial As concentration· 224 μg/L As)

Contact time	pH	Conductivity μs/cm	Fe mg/L	Residual As μg/L	% Removal
0 min	8.2	666	1.2	232	0
15 min	8.3	758		181	22
1 hr	8.4	734		179	23
4 hr	8.5	730		204	12

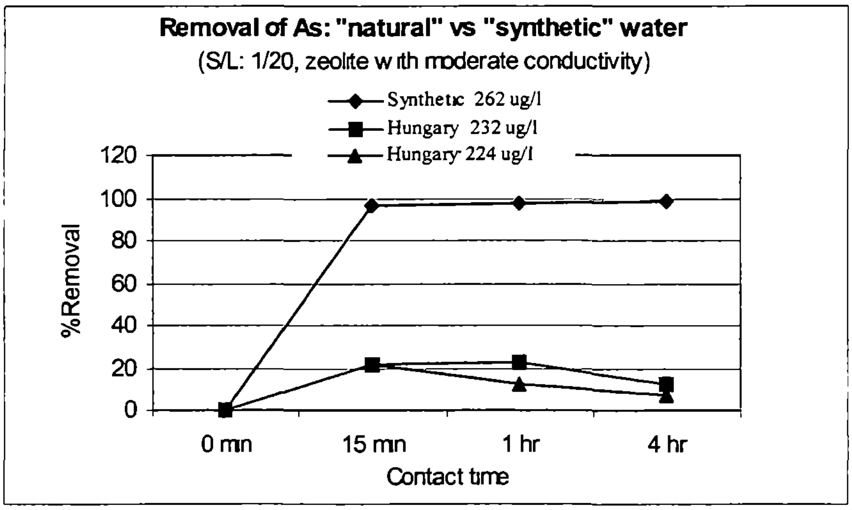
Table 4.6b Residual As and % removal in water from Hungary after treatment with zeolie (initial As concentration: 224 µg/L As/)

Contact time	pH	Conductivity µs/cm	Fe mg/L	Residual As µg/L	% Removal
0 min	7.9	672	0.04	224	0
15 min	8.3	764		175	22
1 hr	8.5	727		197	12
4 hr	8.6	739		209	7

Table 4.6c Residual As and % removal in synthetic water after treatment with zeolite (initial As concentration: 262 µg/L As).

Contact time	pH	Conductivity µs/cm	Fe mg/L	Residual As µg/L	% Removal
0 min	5.6	1.4	0	262	0
15 min	5.7	171		10	96
1 hr	6.0	198		8	97
4 hr	5.7	228		5	98

Figure 4.7 Removal of As from synthetic water and Hungarian waters at required contact times



In contrast with groundwaters from Bangladesh and with the synthetic As water, the efficiencies of As removal in groundwater from Hungary were very low. This noticeable difference in efficiencies could be due to the following reasons:

- The synthetic water used in the experiment contained only As(V) whereas groundwater generally contains more As(III) than As(V) (see Section 2.2.4) Since the groundwater samples from Hungary were not pre-treated as the Bangladesh waters (see Section 4.3.1), the As(III) possibly existed more than As(V) in Hungary samples. In the pH range 2-9, As(III) exists in neutral form that cannot be adsorbed easily.

- An increase in pH increases the concentration of dissolved arsenic in water, as observed in many studies (*WHO, 1996*). In Hungary waters, OH^- can compete with As(V) which exists as $HAsO_4^{-2}$, for the adsorption sites. The number of OH^- ions increased with increasing pH resulting in the desorption of As(V) to the solution. A similar behaviour was observed on phosphate adsorption in sediment in a study by Rippey (1977), cited by Kelderman (*1995)* This low adsorption of As at pH above 8 was observed in other removal processes as well (*see Section 2. 2.1).*

- Finally, other factor affecting the removal of As may be the presence of different substances, especially competitive ions such as phosphate, which will compete for adsorption sites on zeolite, or humic substances which bind strongly with As thus interfering the As removal by zeolite.

4.4 Analysis of adsorption isotherm

Adsorption is usually characterized by the Freundlich and Langmuir equations (*Sakadevan and Bavor, 1998; Kelderman, 1998; Zhang, 1995).* Therefore, in this study, the resulting data of the experiments on the removal of As were analysed for the validity of these two isotherms . The data used were from the experiments of synthetic water with moderate- EC zeolite (S/L ratio 1/20) at 4 hours contact time assuming that the equilibrium was nearly obtained.

- The Freundlich adsorption isotherm empirical equation:

$$x/m = k\, c_e^{1/n}$$

In this case, x is the amount of As adsorbed from the solution (g), m is the amount of zeolite used (g), c_e is the concentration of As in the solution at equilibrium (mole/l) and k and 1/n are constants. This equation can be written in the log-form as

$$\log (x/m) = \log k + (1/n) \log c_e$$

The validity of this isotherm was tested by plotting log (x/m) versus log c_e. The result is shown in Figure 4.8. The linear trend-line plotted shows a good fit with the R-square value of 0.9692.

- The Langmuir adsorption isotherm equation

$$c_e/(x/m) = 1/k_1 + (k_2/k_1)c_e$$

in which k_1 and k_2 are constants.

The validity of this isotherm was tested by plotting $c_e/(x/m)$ versus c_e The results are shown in Figure 4.9. The R-square value of 0.9775 was obtained for the linear trend-line plotted.

Figure 4.8 Freundlich adsorption isotherm for As removal by conditioned zeolite.

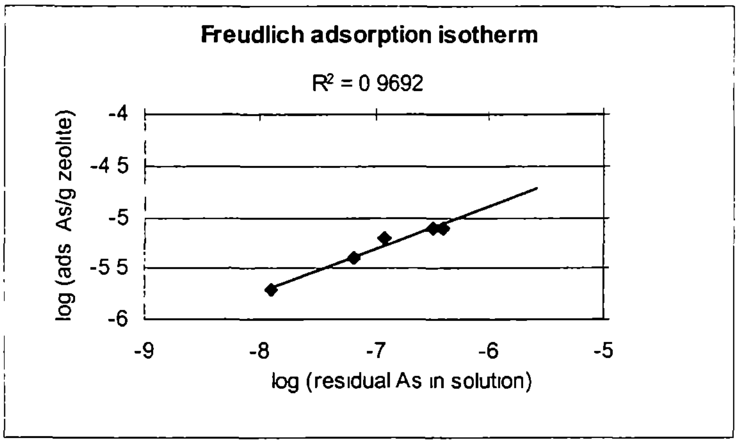
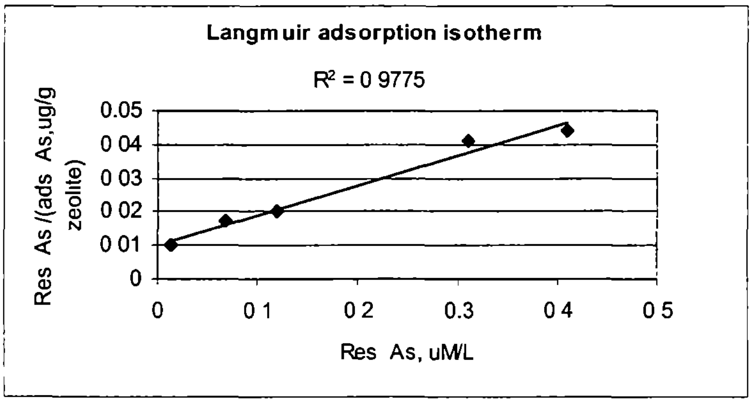


Figure 4.9 Langmuir adsorption isotherm for As removal by conditioned zeolite.

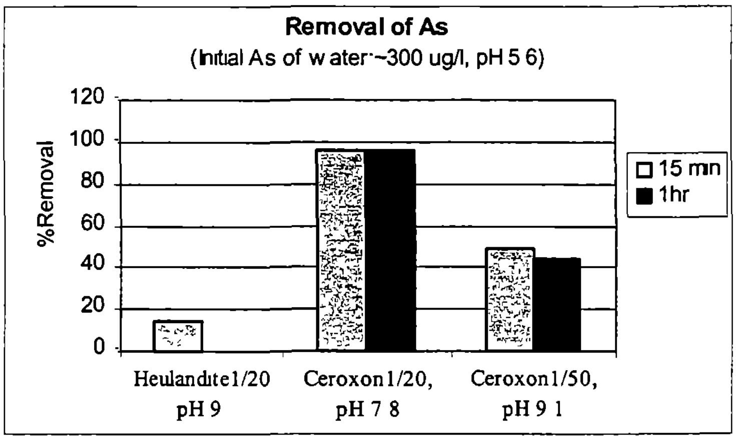


Having R-squared values of 0.9692 and 0.9775 respectively, the analysis results obey both Freundlich and Langmuir adsorption isotherms. A study carried out by Sakadevan and Bavor (*1998*) also showed that adsorption for phosphate by clinoptilolite follows Freundlich and Langmuir isotherms. An experiment carried out by Zhang (*1995*) on adsorption of smelly organic compounds using clinoptilolite also revealed that the adsorption follows the Freundlich and Langmuir isotherms. The adsorption of As following Langmuir isotherm is observed in other materials such as activated carbon, and haematite (*Rajakovic, 1992; Singh et al., 1988*).

4.5 Removal of As by alternative materials

The results of As removal from the synthetic water by heulandite and ceroxon are shown in Figure 4.10 and given in Tables II.8 to II.10 in Annex II. At 15 min, the removal percentage by heulandite (S/L ratio 1/20), ceroxon (S/L ratio 1/20) and ceroxon (S/L ratio 1/50) were 14, 15, 96, and 49 respectively. At 1 hour contact time, As was released back to the solution in the cases of heulandite. For ceroxon, at 1 hour no notable change in the removal efficiency was observed.

Figure 4.10 Removal of As(V) by heulandite and ceroxon



Among the two different materials, ceroxon is the better material for removal of As(V). Even with the S/L ratio 1/50, ceroxon removed much more As(V) than heulandite with S/L ratio 1/20. The key factors might be the composition and pH of the materials. Ceroxon has 6 Ca in its molecule with 2 OH groups. In water, ceroxon might be unstable and its OH^- was fast replaced by $H_2AsO_4^-$ or $HAsO_4^{2-}$. Heulandite is a natural Ca-zeolite. When it is added with water, the high pH (9.1) will result in generation of OH- which interfere the adsorption of As(V) (as described earlier in Section 4.3.2), although at the very beginning of the removal, some As(V) was adsorbed but later it was released back to the solution.

Within the limited experiments, ceroxon seems to be more effective than conditioned zeolite in removing As(V). However, other factors should be considered such as dissolution of ceroxon in water, pH, cost and so on.

Chapter 5
Conclusions and Recommendations

5.1 Conclusions

1. In this research, the feasibility of using a natural zeolite (clinoptilolite), to remove As(V) from groundwater was studied. The performances of unconditioned and conditioned zeolite in removing As(V) were compared. It was found that, in 15 minutes, the conditioned zeolite performed better with the efficiency of 77.3% to 89.0% compared to 6.7% efficiency of the unconditioned one. This study demonstrates the potential of conditioned zeolite in removing arsenic from water.

2. The As(V) removal by conditioned zeolite obeyed Langmuir and Freundlich adsorption isotherms. Significant removal of As(V) took place within 15 minutes.

3. The capacity of zeolite for As(V) uptake obtained in this study is 62 μg As(V)/g zeolite (0.0008 mmole/g). This capacity is very low compared to the capciaty of activated carbon (0.27 mmole/g) as found in a research by Rajakovic (*1995*). Therefore, in practice it does not seem cost effective to use conditioned zeolite without improvement.

4. In synthetic water, variables affecting the As(V) removal efficiency of conditioned zeolite as observed in this study are conductivity of zeolite and solid-liquid ratio. The contact time and the initial As(V) concentration do not seem to have an important role on the removal efficiency.

5. In addition to the conductivity of zeolite and solid- liquid ratio, the As removal efficiency of zeolite from natural water was also affected by arsenic species, pH and composition (competing or enhancing ions) of the source water.

5.2 Recommendations

In order to obtain a better insight into the arsenic removal by conditioned zeolite, further research is needed. In particular, following recommendations are proposed.

1. The zeolite used in this research was not conditioned specifically for the purpose of As removal. Therefore, it is recommended that the further research should be carried out using zeolites conditioned for As removal.

2. Since the pH of water is found to have effect on the As removal efficiency, it is important to know the pH range at which best efficiency can be obtained. It is therefore recommended to take this factor into consideration to carry out further research.

3. The effects of other ions present in water that may enhance or interfere the As removal process should be studied.

4. This research was performed with batch experiment. It is recommended to conduct further research with column experiment.

5. Further research should include the possibility of regeneration of used zeolite.

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Annex I

Temperature programme for arsenic determination by graphite furnace atomic absorption spectrometer

Step	Temperature °C	Ramp °C/sec.	Hold time sec
1	90	5	10
2	110	10	10
3	130	10	10
4	450	10	10
5	850	10	20
6	1300	10	10
7	2300	0	5
8	30	2	2

Annex II-1

Tables of Experimental Results

Table II.1 Effect of centrifugation at 18 000 rpm on As compared with filtration with GF6 glass fibre paper

	Run 1		Run 2	
	As, (µg/L)	%Removal	As, (µg/L)	%Removal
Without any treatment	100	0	93	0
Filtration	82.6	17.4	80 0	20.0
Centrifugation	98.1	1.9	94.6	-1.7

Table II.2 Removal of As by conditioned zeolite (moderate conductivity), using 18000 rpm centrifugation as the separation technique (S/L ratio 1/20)

Initial As(V) concentration	294 µg/L			
	Res. As (µg/L)		% Removal	
0 min	294		0	
	Run1	Run2	Run1	Run2
15 min	25.0	25.0	91.5	91.5
1 hr	15 3	16.3	94.8	94.4
4 hr	11.0	10.2	96.2	96.5
24 hr	7.5	8.5	97.4	97.1

Table II.3 Residual As (µg/L) in solution and efficiency after treated with unconditioned and conditioned zeolites (S/L ratio 1/20)

Contact time	unconditioned,		Conditioned zeolite (low conductivity)		Conditioned (moderate conductivity)	
	Res. As, (µg/L)	% Removal	Res. As, (µg/L)	% Removal	Res As, (µg/L)	% Removal
0 min	300	0	300	0	300	0
15 min	280	6.7	68	77.3	33	89.0
1 hr	263	12.3	44	85.3	14	95.3
4 hr	257	14.3	27	91.0	9	97.0

Annex II-2

Table II.4 Residual As (μg/L) in water and %removal after in-contact with conditioned zeolite (moderate EC), S/L ratio: 1/20

Initial	100 μg/L		200 μg/L		300 μg/L		400 μg/L		500 μg/L	
	Res. As	% Remov	Res. As	% Remov	Res. As	% Remov	Res As	% Remov	Res As	% Remov
0 min	100	0	200	0	300	0	400	0	500	0
15 min	10	90	17	91.5	30	90	54	86.5	64	87.2
1 hr	<6	>94	9	95.5	16	94.7	40	90	43	91.4
4 hr	<<6	>94	<6	>97	9	97	25	93.8	29	94.2
24 hr	<<6	>94	<6	>97	8	97.3	18	95.5	17	96.6

Table II.5 Residual As (μg/L) in solution after treatment with conditioned zeolite of low conductivity (initial concentration 300 μg/L)

S/L ratio	**1:20**		**1:15**		**1:10**	
	Res. As, μg/L	% Removal	Res. As, μg/L	% Removal	Res. As, μg/L	% Removal
0 min	300	0	300	0	300	0
15 min	68	77.3	44	85.3	26	91.3
1 hr	44	85	22	93	17	94

Table II.6 Residual As (μg/L) in solution after treatment with conditioned zeolite of moderate conductivity (initial concentration 300 μg/L)

S/L ratio	**1:20**		**1:10**	
	Res. As, μg/L	% Removal	Res. As, μg/L	% Removal
0 min	300	0	300	0
15 min	30	90	<6	>99
1 hr	16	94	<6	>99

Table II.7 Residual As (μg/L) in solution after treatment with conditioned zeolite of high conductivity (initial concentration 300 μg/L)

S/L ratio	**1:20**		**1:10**	
	Res. As, μg/L	% Removal	Res. As, μg/L	% Removal
0 min	300	0	300	0
15 min	8	97	<6	>99
1 hr	<6	>99	<6	>99

Annex II-3

Table II.8 Residual As(V) concentration in water and % removal after in contact with heulandite (initial concentration 343 μg/L, S/L ratio 1/20)

Contact time	pH	Conductivity, μs/cm	Res. As, μg/L	% Removal
0 min	5.6	2	343	0
15 min	9.1	86	295	14
1 hr	9.1	96	344	0

Table II.9 Residual As(V) concentration in water and % removal after in contact with Ceroxon (initial concentration 318 μg/L, S/L ratio 1/20)

Contact time	pH	Conductivity, μs/cm	Res. As, μg/L	% Removal
0 min	6.1	2.3	318	0
15 min	7.7	239	12	96
1 hr	7.9	252	12	96

Table II.10 Residual As(V) concentration in water and % removal after in contact with ceroxon (initial concentration 348 μg/L, S/L ratio 1/50)

Contact time	pH	Conductivity, μs/cm	Res. As, μg/L	% Removal
0 min	5.5	2.5	348	0
15 min	9.1	127	179	49
1 hr	9.5	131	194	44

Annex III

Chemical analysis of zeolite (clinoptilolite) before and after modification.

Composition	Raw zeolite (Code. 001.050)	Modified zeolite (Code. 701.050)		
	%	%	Difference	+/- %
SiO_2	73.6950	71.96088	-1.73562	-2.4
TiO_2	0.14617	0.12921	-0.01696	-11.6
Al_2O_3	11.87735	11.37789	-0.49946	-4.2
Fe_2O_3	1.66025	1.55554	-0.10471	-6.3
MgO	0.32007	0.30177	-0.01830	-5.7
MnO	0.02544	0.01123	-0.01421	-55.9
CaO	3.84560	5.08264	1.23704	32.2
K_2O	3.20163	2.84988	-0.35175	-11.0
Na_2O	0.27553	0.43127	0.15574	56.5
P_2O_5	0.02443	0.02471	0.00028	1.1
Total	95.07297	93.72502	-1.34795	-1.4
LOI	9.20000	9.40000	0.20000	2.2
	ppm	ppm		
As	0.609	1.008	0.399	65.5
Co	37.500	34.900	-2.600	-6.9
Cr	2.300	0.800	-1.500	-65.2
Cu	5.129	6.349	1.220	23.8
Ni	6.205	8.137	1.932	31.1
Pb	14.897	8.579	-6.318	-42.4
V	9.000	9.700	0.700	7.8
Zn	33.715	28.572	-5.143	-15.3
Ba	727.200	686.300	-14.900	-5.6
Ga	12.652	12.857	0.205	1.6
Nb	10.424	9.884	-0.540	-5.2
Rb	122.863	117.723	-5.140	-4.2
Sr	306.544	395.567	89.023	29.0
Th	15.781	15.984	0.203	1.3
U	1.724	0.129	-1.595	-92.5
Y	25.061	24.584	-0.477	-1.9
Zr	136.895	132.816	-4.079	-3.0