

**A STUDY OF ARSENIC POLLUTION IN GROUND WATER OF
BANGLADESH AND FINDING A METHOD FOR ITS REMOVAL FROM
DRINKING WATER**

**A DISSERTATION IN PARTIAL FULFILMENT FOR THE
REQUIREMENT OF THE DEGREE OF MASTER OF PHILOSOPHY**

SUBMITTED BY

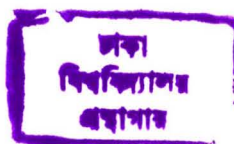
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DECLARATION

Certified that the thesis entitled, "*A Study of Arsenic Pollution in Ground water of Bangladesh and Finding a Method for its Removal from Drinking water*" submitted in fulfillment of Master of Philosophy in Chemistry, Department of Chemistry, University of Dhaka has been completed independently by Mohd. Noor-E-Alam Siddique under our supervisions.

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Dedicated
to
My beloved Grandfathers

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SUMMARY

Arsenic problem is a great threat to our existence. Water supply in Bangladesh is primarily based on ground water sources. Ground water is free from pathogenic microorganism and available in adequate quantity in shallow aquifers. Being aware of the water-borne diseases, when rural people have developed the habit of drinking tube well water, then unfortunately, unacceptable amount of arsenic has been detected in this water in most parts of Bangladesh.

In Bangladesh, the major source of arsenic intake in human body so far known is from drinking water tapping from ground water sources. As per WHO, the provisional guideline value of arsenic in drinking water is 0.01 mg/L. However, in Bangladesh the maximum limit of arsenic in drinking water is 0.05 mg/L. Since arsenic-containing water is odourless, tasteless and colourless, its presence in water cannot be identified without a proper test. This requires extensive studies to detect and quantify arsenic in tube well water of different regions of Bangladesh.

It is so far reported 61 out of 64 districts are contaminated with arsenic and 27-75 million people are at risk of being affected by arsenic. Many arsenicosis patients suffer not only physically but also psycho-socially and economically. The Govt. of the People's Republic of Bangladesh has already been facing problem about the arsenic issue.

In consideration of arsenic pollution, the selecting areas were Hajigong Thana, Muradnagar & Debidwar Thana, Naogaon Municipality area and Kalaskati Union at Bakergong Thana. Depth, exact locations and year of installation of the hand tube well were first recorded. The water samples were collected in a well-stoppered polythene container and few drop of concentrated nitric acid (pH <2-3) were added into the sample for analyzing arsenic content. Graphite Furnace Atomic Absorption Spectrophotometer was used to analyze the water samples.

Most of the tube wells in Hajigong Thana under Chandpur district were contaminated with arsenic. Certain arsenic free deep tube wells (750 -950 feet) were found in this region. About 99% tube wells were extracted water from the aquifer 60 to above 100 feet and high amount arsenic was found in this aquifer. The very significant amount of arsenic concentration was varied among the 29 villages of Hajigong Thana. However, there was no significant variation of arsenic concentration with age of the tube wells.

Muradnagar and Debidwar is 53 km far away from Hajigong. The concentration ranges were 2.6 - 0.83 mg/L in Hajigong and 0.23 - 0.07 mg/L in Muradnagar & Debidwar.

The tube well water of Naogaon Municipality area was free from arsenic (0.01 mg/L) which is within the WHO acceptable limit. The very deep (750 -1100 feet) tube wells were found in Kalaskati under Bakergong Thana. However only one-tube well was found within the depth 105 feet and arsenic concentration was 1.524 mg/L. A linear correlation was found between the arsenic concentration and depth of the tube wells. Higher is the depth relatively lower is the arsenic concentration.

In Bangladesh, the sources and variation of arsenic contamination is due to the changes of geological environment of shallow aquifers.

For consideration of arsenic removal, two types of household waste biomaterials like skin of garlic and rice husk were selected. These materials might uptake in certain extent of arsenic from drinking water. The mitigated water samples analyzed by Ag-DDTC in UV-visible method and also graphite furnace AAS.

Certain amount of arsenic from synthetic water (initial concentration 1000 ppb) was removed by the above biomaterials and the arsenic removing capacity of skin of garlic was better than rice husk. The zero-valent iron removed rest of the arsenic in the water samples. The fine wood charcoal also removed colour and impurities from the mitigated water. pH and conductance of the mitigated water were within the acceptable limit.

For the consideration of field water, initial arsenic concentration in both Hajigong and Singair Thana were 380 ppb and 166 ppb respectively. The arsenic concentration in mitigated water was 0.02 mg/L for the field water of Hajigong and 0.019 mg/L for the field water of Singair after passing through arsenic contaminated 50 L sample water.

In these circumstances, the combination of skin of garlic and zero-valent iron chips might be a method of arsenic removal from drinking water.

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Chapter-1

INTRODUCTION

1.1 General

The environment is the combination of atmosphere, hydrosphere, lithosphere and biosphere; in which these segments interact with man as a life support system and sustained ecological balance. Environmental pollution is the unfavorable alteration or contamination of various components of the environment with harmful wastes originated by the anthropogenic activities and which ultimately has a detrimental effect on environment and produce imbalance in the ecological system.

All living organisms including man are part of the environment and are dependent on all other components of the environment such as air, water, soil etc. Among them water is an important part of our life. All life's on earth depends on water. The total water resources of the world are about 26.6 trillion tons, approximately 94.7% of this occurs in lithosphere (bound water in rocky belt). The surface water, which includes, water of rivers, lakes and pond water together with ground water, is only about 0.03% of water found in the lithosphere. This small fraction of water is mainly used for drinking, domestic, industrial and irrigation purposes. The necessity of utilizing this water is increasing tremendously with the increase of both the population and the industrialization. Due to dispose of the domestic sewage, industrial water, animal excreta, agricultural run off etc. in water body. The accumulation of these objectionable substances gradually changes physical, chemical and biological properties of this surface water. Due to the complex interrelationship in the ecosystem, pollutants that alter a minor part in any sector harm almost all other parts in the ecosystem. As a result, water has borne some diseases like cholera, typhoid; dysentery, yellow fever etc. are frequently observed. This problem is particularly tragic for the children. UNICEF estimated that about 15 million children below the age of 5 die in the developing countries every year mainly due to scarcity of safe water. At this moment, UNICEF suggests that groundwater is free from pathogenic microorganisms and can be safely used for drinking and cooking purposes¹.

The effect of arsenic is included in inorganic arsenic from ancient time. The effects were mostly related to immediate effects following intake of bulk of arsenic at a time and after use of arsenic in smaller doses. Aristotle in 384 –322 A.D knew very efficient poisoning effects of arsenic than the available poisons in that time because of its peculiar relations with many other elements and the colourless and odourless characters when dissolved in water. Poisoning effects of inorganic arsenic were known since 55 AD when Emperor

Nero was poisoned. Napoleon was also said to die from slow arsenic poisoning. Adverse effects of inorganic arsenic were better understood in nearly the end of 18th Century².

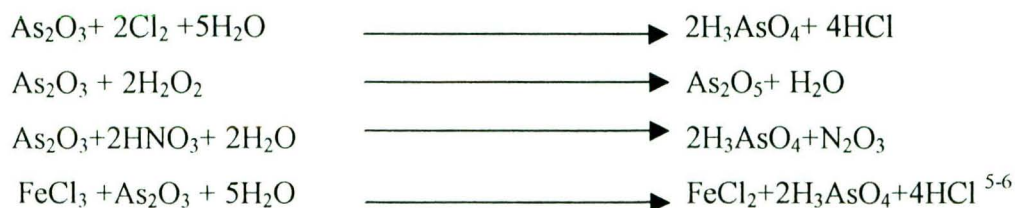
There are reportedly 11 million tube-wells in Bangladesh, which were supplying 97% of the population with safe drinking water. However, recently it has been reported that over half of these wells contaminated with arsenic. Arsenic levels in the affected tube-wells are typically in excess of 0.2 mg/L and in many areas concentrations can exceed 1 mg/L. The British Geological Survey in 1998, found that 35% of the wells they investigated had an arsenic level of over 0.05 mg./L. These estimates that between 25-75 million people are at risk of being affected by contaminated wells³⁻⁴.

1.2 Chemistry of Arsenic

The metalloid arsenic is a p- Block element of the group VB (15) on the periodic table. Arsenic is a metalloid and it shows n-type semi conductor character when it is introduced in silicon and Germanium⁴.

The most common compound of arsenic is As₂O₃ arsenic trioxide, Arsenic sulfide (As₂S₃), metal arsenate, (Na₃AsO₄), and metal arsenite, (Na₃AsO₃) as its aqueous solution behaves as a feebly tri-acidic acid and may contain arsenious acid, H₃AsO₃ or HAsO₂. As₂O₃ exists in three forms, which are (a) vitreous form called amorphous glass, which is colorless, non-crystalline. It has glassy appearance and is therefore called vitreous arsenic. It is slightly soluble in water, (b) octahedral form; it is the common form as it is stable under ordinary conditions and is crystalline. (c) Monoclinic form is also less soluble than amorphous form and is obtained as needle crystals.

An important point is the common valence state of arsenic are As (III) & As (V). As (III) is easily oxidized to As (V), arsenic acid (H₃AsO₄) or arsenate by O₃, H₂O₂, halogens, aquaragia, HNO₃ and hypochlorites (especially in alkaline solution)



1.3 Occurrence

The name arsenic has come from Greek name “Arsenikon”, originally applied to mineral “Orpiment” the most common purer arsenic ore is Realgar (As_2S_2). It occurs in more than 250 arsenic minerals in the rocks. These are arsenopyrite (FeAsS), Arsenolite (As_2O_3), Enargite (AsS_4), Lollingite (FeAs_2), Maucherite (Ni_3As_2), Nickel glance (NiAsS), Niccolite (NiAs), Orpiment (As_2S_3), Rammelsbergite (NiAs_2), Safforite (CoAs_2), Skutterudite ($(\text{Ni}, \text{CoFe})\text{As}_3$), Tennantite [$(\text{Cu}, \text{Fe})_{12}\text{As}_4\text{S}_{13}$] etc. Arsenic also occurs in the soils (1-60 ppm) and traces of arsenic found in some mineral water, in the adult human body (0.1 mg per kg.), in American tobacco (6-30ppm), in the fresh edible parts of shell – fish (7- 90 ppm) and in the yellow fogs⁷.

1.4 Importance of Arsenic

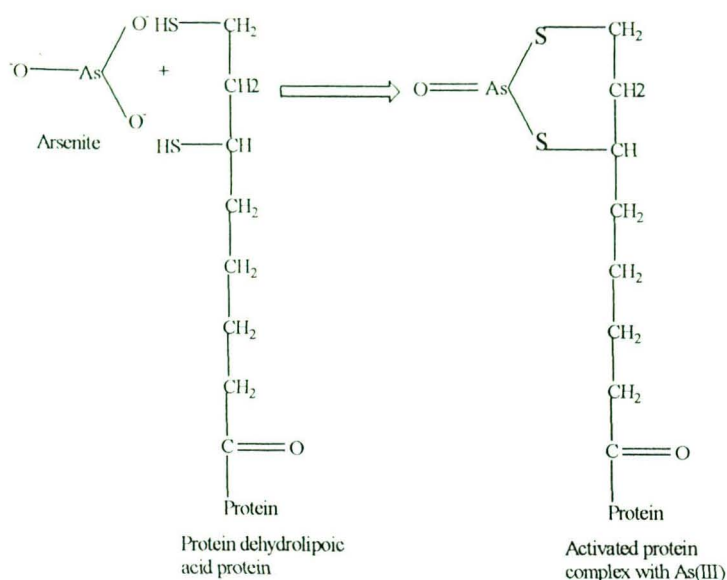
1983 the FAO/WHO joint commission of the Codex Alimentarius established the maximum acceptable daily intake of arsenic as $2 \mu\text{g}/\text{Kg}$ ⁸.

Arsenic is a classical poison; however, it has also been used in medical treatments, and occurred as late as in 1959 on the list of drugs in Sweden. Arsenic tetra sulfide seems to have been used already in antiquity in a paste for ulcer treatment and in 1786, Fowler introduced his solution that contains 1% of As_2O_3 that was used for asthma, psoriasis, rheumatic fever, leukemia, fever, pain, and as a tonic (WHO, 1981; NRC, 1999)⁹.

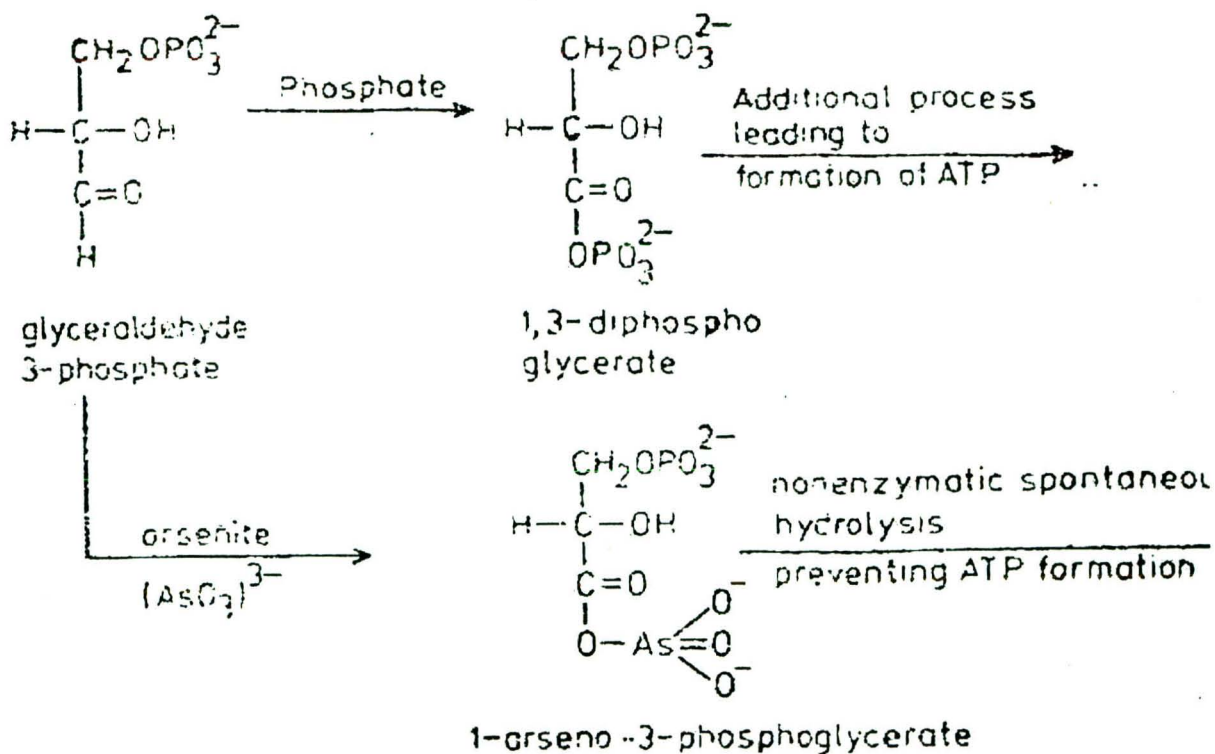
1.5 Chemical Effect of Arsenic in Biological System

Arsenic commonly occurs in insecticides, fungicides and herbicides. Among its compounds, those of As (III) are the most toxic. As (III) exerts its toxic action by attacking –SH groups of an enzyme, thereby inhibiting enzyme action.

The enzymes, which generate cellular energy in the citric acid cycle, are adversely affected. The inhibitory action is based on inactivation of pyruvate dehydrogenase by complexation with As (III), whereby the generation of ATP is prevented.

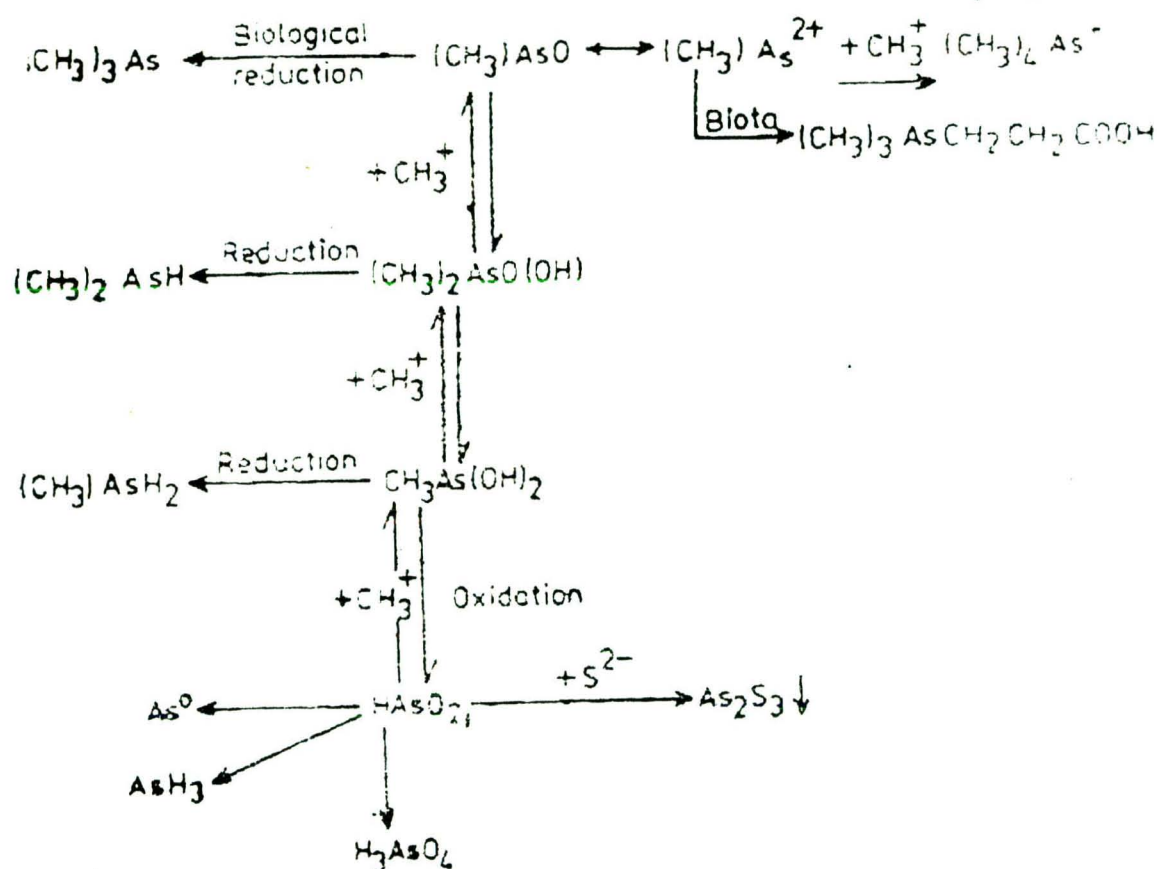


By virtue of its chemical similarity As interferes with phosphorus in some biochemical generation processes. This is observed in the bio-chemical generation of key energy-yielding substance, ATP. An important step in ATP generation is the enzymatic synthesis of 1,3-diphosphoglycerate from glyceraldehydes 3-phosphate. Arsenite interferes by producing 1-arseno-3-phosphoglycerate instead of 1,3-diphosphoglycerate is replaced by arsenolysis hydrolysis to 3-phosphoglycerate and arsenate.



Arsenic (III) compounds at high concentrations coagulate proteins, possibly by attacking the sulfur bonds maintaining the secondary and tertiary structures of proteins. There are three major biochemical actions of arsenic are coagulation of proteins, complexation with coenzymes and uncoupling of phosphorylation¹⁰.

On the other hand in human body, arsenic compounds have not formed deoxyribonucleic acid (DNA) adducts (i.e. bound to DNA) nor caused point mutations. Thus, indications are that the mode of action does not involve direct reaction with DNA.



Trivalent inorganic forms inhibit enzymes, but arsenite and arsenate do not affect DNA replication. However arsenic indirectly affects DNA, including chromosomal changes. Arsenic induced chromosomal abnormalities could possibly come from errors in DNA repair and replication that affect gene expression; that arsenic may increase DNA hypermethylation and oxidative stress; that arsenic may affect cell proliferation (cell death appears to be nonlinear); and that arsenic may act as a co-carcinogen. Arsenite

causes cell transformation but not mutation of cells in culture. It also induces gene amplification (multiple copies of DNA sequences) in a way that suggests interference with DNA repair or cell control instead of direct DNA damage⁹.

1.6 Arsenic in Bangladesh

The most villagers drank water from hand –dug wells or natural ponds that they often shared with bathing cows and buffaloes until 1970's. Cholera and diarrhea diseases flourished in this water and each year hundreds of thousands of death originated in the earthen pitchers that villagers carried to their porches.” Prior to 1970's people died of cholera and diarrhea but no one noticed the symptoms of arsenic poisoning¹¹. There is little doubt that origin of groundwater arsenic poisoning in Bangladesh is geological but the UK/ DFID statement on the age of the arsenic poisoning in ground water in Bangladesh contradicts the historical medical evidences. In 1999, University of Arkansas, U.S.A reported that prior to the 1970's hundreds of thousands of people in 28000 villages of Ganges Delta drink water from 280,000 hand –dug wells. The wells were about one to two meters in diameter and about eight meters deep. We know of no difference in the inorganic and organic quality of water from tube wells and hand- dug wells. Both extract water from subsurface geological formations i.e. ground water and from about the same depth. Tube wells are made of steel or plastic and hand-dug wells are constructed with concrete rings which are simply a big hole in the ground. Before tube wells were drilled as many as 25-40 people collected their drinking water from one single hand-dug well. If conditions were the same after the tube well were drilled as when the dug wells used the hand –dug well water would have been poisoned by arsenic in the same geologically contaminated areas where the poisoning are existed today. If ground water arsenic contamination had been present for thousands of years, as suggested by the UK report, then both shallow hand-dug wells and tube wells would extract arsenic contaminated water and would have impacted water users with arsenic poisoning before 1975. If the UK/DFID statement were true, then prior to 1965, the people who had been poisoned by arsenic. Prior to 1975 there was no evidence that arsenic poisoning had affected people in Bangladesh, therefore, it appears that the groundwater arsenic poisoning in Bangladesh is a recent environmental episode and began after 1975¹¹.

At the initial stage after detection of arsenic, arsenic containing raw materials might be the source of contamination. In 1993, arsenic was first detected in Bangladesh. Later on it was reported that the use of electrical poles of Rural Electric Board (REB) treated with

corrupted copper arsenic (CCA) to protect these from termites and fungal deterioration might be the source of ground water pollution with arsenic. But subsequently this idea was not found valid because such sources cannot account for widespread distribution of arsenic in the country¹².

In Bangladesh the first reporting of the presence of arsenic in ground water in Baraghoria union at Chapai-Nawabgonj was made by the Department of Public Health Engineering in 1993¹³⁻¹⁴. This was actuated by the prediction by the School of Environmental Science, Jadavpur University, Kolkata, as because West Bengal has arsenic problem with ground water. Gradually the incidence of arsenic was detected in southwestern and southeastern parts of Bangladesh and the prediction came true¹⁵.

Bangladesh is now threatened by mass arsenic poisoning that endangers the lives of millions of people not only in rural areas but also in some urban areas like municipalities. At the end of the year 2001, it is so far been reported that 61 districts out of 64 and 28 municipalities affected and also 265 Thanas were being the most affected. It is also believed that 26 millions people are of risk of contacting arsenicosis and 12,0000 were recorded for cases of arsenicosis in the country¹⁶.

1.7 Arsenic Hazards in Bangladesh

During 1983 and 1987 Dr. K.C. Shaha, Professor of Dermatology (Retired) of School of Tropical Medicine, Kolkata conducted surveys in the seven districts of West Bengal of India. In 1983, Dr. Shaha identified patients poisoned by arsenic who had been drinking tube well water with concentration of arsenic ranging from 10.0- 1.25 ppm and a mean concentration of 0.32 ppm. According to Dr. Shaha's survey the time required for the symptoms of arsenic poisoning to appear varies from six months to two years and is dependent on age.

In 1996 the Asian Arsenic Network (AAN) conducted skin examinations on 167 people from West Bengal of India who had drunk tube-well water for a period from 4 months to 45 years. The largest group (63) drank the tube well water for 6-10 years. One hundred sixty three people out of one hundred sixty seven (97.6%) ranging in age from 3-80 years, were found to have skin lesions related to arsenic poisoning. Based on Dr. Shaha's survey, the AAN estimated the beginning of arsenic contamination in West Bengal began

around 1980-1981. It is so far known that no such survey have been conducted in Bangladesh; however, in West Bengal we have seen evidence of poisoning after months of drinking of arsenic contaminated water. Infants and the young are more susceptible than adults.

High concentration may cause poisoning over a shorter period of time. A recent UK/DFID reports states: "There is clearly a very serious problem of arsenic in ground water in southern and eastern part of Bangladesh. In terms of the population-exposed Bangladesh has the most serious groundwater arsenic-poisoning problem in the world.

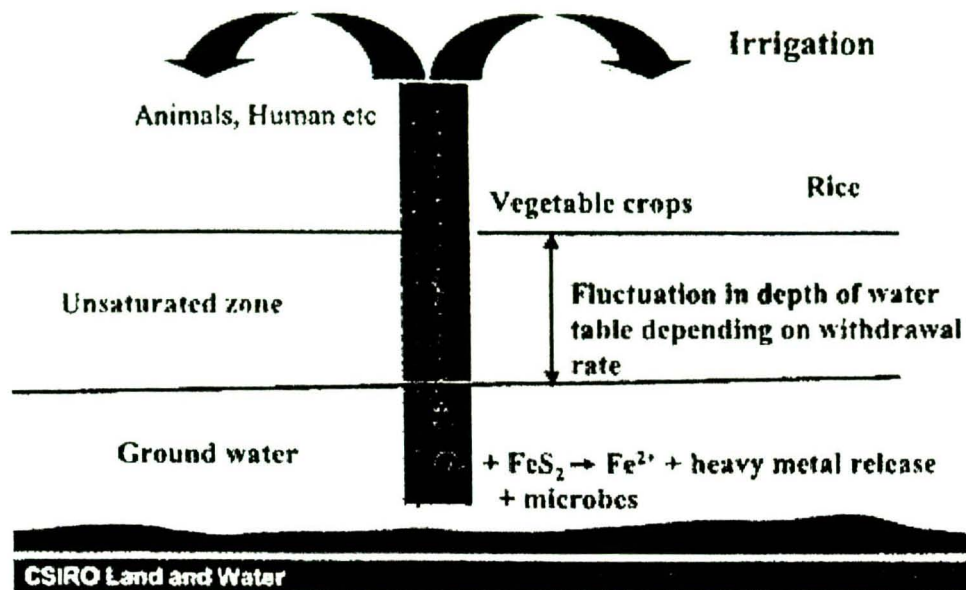
Descriptions of the problem are complicated by large variability at both local and regional scales. The arsenic is of geological origin and is probably only apparent now because it is only in the last 20-30 years that groundwater has been extensively used for drinking water in the rural areas. However, the arsenic has probably been present in the groundwater for thousands of years¹⁷.

Now the people of Bangladesh are continuously getting exposed to the arsenic toxicity causing serious health hazards, which is very alarmingly engulfing vast region. At this moment the contamination of the underground water has become a great challenge for making provision of safe drinking water to the majority of the population. The health hazards due to this contamination have raised the serious concern of public health. Arsenic in the form of arsenite and arsenate are known as carcinogen and have got, affinity to deposit in hair, nail, bone and found in liver, spleen, kidney and lungs as well¹⁸⁻¹⁹.

1.8 Probable Source of Arsenic in Bangladesh.

Presently, two theories about the arsenic poisoning in Bangladesh are known. In 1996, Dipankar Das conducted a geochemical survey in the six districts of West Bengal bordering the western part of Bangladesh. These districts are Malda, Murshidabad, Bardhaman, Nadia, North 24-Paragan and South –24 Pargana. They did a subsurface investigation with some laboratory analysis and observed the presence of arsenopyrite minerals in the sediments. They stated that the source of arsenic in groundwater and in the soil is from pyrite minerals containing arsenic.

Arsenic transfer pathway



However, they did not discuss how arsenic is released in groundwater form arsenopyrite. They cited the oxidation of pyrite process presented in the literature from the U.S. However, in their conclusions they state that: “The way that arsenic enters the groundwater in these six districts is not well understood. Our borehole analyses show arsenic –rich FeS_2 in sediment layers. Since pyrite (FeS_2) is not soluble in water, the question therefore arises as to how arsenic from pyrites enters the water. Although pyrite is not soluble in water, it decomposes when exposed to air or in aerated water. A probable explanation may be that the changes of geochemical environment due to high withdrawal of groundwater might have resulted in the decomposition of pyrites to ferrous sulfate; Ferric sulfate and sulfuric acid and thus arsenic in pyrites becomes available. Our mineralogical study by XRD (X-ray defraction) shows the presence of FeSO_4 in one sample. The group that studied arsenic in the groundwater of the western USA reported: “mobilization of arsenic in sedimentary aquifers may be, in part, a result of changes in the geochemical environment due to agricultural irrigation. In the deeper subsurface, elevated arsenic concentrations are associated with compaction caused by groundwater withdrawal”. If the time of arsenic contamination is after 1975 in Bangladesh, a probable explanation is that the changes in geochemical environment due to the high withdrawal of ground water resulted in the decomposition of pyrites to oxides of iron, arsenic, sulfuric acid; these oxides are soluble in water containing sulfuric acid. In the reducing conditions below the water table and in the presence of organic matter non-poisonous oxides of arsenic are reduced to poisonous oxide forms. The UK/DFID report mentioned that the

oxidation of arsenic pyrite is not a major cause of groundwater arsenic poisoning in Bangladesh rather they postulated an 'arsenic adsorption and oxy-hydroxide reduction' hypothesis as the main cause of ground water arsenic poisoning in Bangladesh. The UK/DFID states that: "a number of anthropogenic explanations have been given for the occurrence of arsenic in groundwater. While it is possible that some may explain isolate cases of arsenic contamination, none of the anthropogenic explanations can account for the regional extent of groundwater in Bangladesh and West Bengal.

There is little doubt that the source of arsenic is of geological. The arsenic content of alluvial sediments in Bangladesh is usually in the range 2-10 mg/kg; only slightly greater than typical sediments (2-6mg/kg). However, it appears that an unusually large proportion of the arsenic is present in a soluble form. The high groundwater arsenic concentrations are associated with the grey sands rather than the brown sands. There is a good correlation between extractable iron and arsenic in the sediments and a relatively large proportion (often half or more) of the arsenic can be dissolved by acid ammonium oxalate, an extract that selectively dissolves hydrous ferric oxide and other poorly ordered oxides. It therefore appears likely that a high proportion of the arsenic in the sediments is present as adsorbed arsenic. This would not be true of arsenic in the present primary minerals such as arsenic- rich pyrite. The greatest arsenic concentration is mainly found in the fine-grained sediments especially the grey clays. A large number of other elements are also enriched in the clays including iron, phosphorus and sulfur. In Chapai-Nawabganj, the clays near the surface are not enriched with arsenic to any greater extent than the clays below 150 m, in other words, there is no evidence for the weathering and deposition of a discrete set of arsenic- rich sediments at some particular time in the past. It is not yet clear how important these relatively arsenic- rich sediments are for providing arsenic to the adjacent sandier aquifer horizons. There is unlikely to be a simple relationship between the arsenic content of the sediment and that of the water passing through it. "The origin sources of arsenic probably existed as both sulfide and oxide minerals. Oxidation of pyrite in the source areas and during sediment transport would have released soluble arsenic and sulfate. The sulfate would have been lost to the sea but arsenic, as As (V), would subsequently have been absorbed by the secondary iron oxides formed. These oxides are present as colloidal- sized particles and tend to accumulate in the lower parts of the delta.

The finer-grained sediments tend to be concentrated in the lower energy parts of the delta. This is likely to be responsible for the greater contamination of arsenic in the south and east of Bangladesh. The map of arsenic contaminated ground water shows that highly contaminated areas are found in the catchments of the Ganges, Brahmaputra and Meghna rivers¹³⁻¹⁷.

1.9 The Global Perspective of Arsenic Pollution

The problems of high arsenic levels in water experienced in widespread regions across the globe: Argentina, Chile, Finland, France, Germany, Hungary, India (West Bengal), Inner Mongolia, Northern China, Thailand, UK and the USA (Arizona, Illinois, New Hampshire, New Mexico, Southern California).

The concentration of arsenic occurring in the environment is highly variable. Soil has been reported to contain 0.03-0.25 ppm, plants 0.023-0.25 ppm, sea water 0.0001-0.08 ppm, fish food 3-170 ppm, wine 0.008-0.085 ppm and urban air up to 0.00049 or 0.63 microgram/m³. Some areas in the World are reported to have very high concentrations of arsenic in drinking and large populations exposed in the following table.

Table 1. Arsenic Concentration in Drinking water in Different Parts of the World, and the Size of populations potentially exposed is given below:¹⁸⁻¹⁹

Country	Concentrations in water µg/L	Number of individuals	Year of exposure
Argentina	up to 800	20000	1983-81
Bangladesh*	up to 2040	>67 million	1970-still
Chile	up to 800	130000	1958-70
China	up to 800	>400	1969-still
India	up to 3400	1 million	1978-still
Mexico	up to 800	200000	1963-83
Taiwan	up to 600	>100000	1961-85
Thailand	up to 800	no data	1987-88

* Drilling of wells started in the late 1960s; first cases of keratosis known around 1993.

Several epidemiological studies demonstrated the association of arsenic poisoning with the arsenic concentration in drinking water, which ranges from 0.6-1.2mg/ L in China, 0.2 to 1.7 mg/L in Argentina, 0.3 to 1.8 mg/L in West Bengal, India, and 2.7 mg/L in Taiwan.

Several studies indicate that there is a significant relationship between the correlation between increase of arsenic in soil and arsenic accumulation in plants. However, no specific attempt has yet been made in order to address issues like relationship between the arsenic contamination in groundwater and the arsenic affect on bio-diversity and human health so far ²⁰.

1.10 Socio-economic Background of Rural Bangladesh

Bangladesh is a developing country. The socio-economic status of Bangladesh is similar to that of other developing countries. The prominent ethnic groups in this country are Muslims and strong religious beliefs are prevalent among various communities. Family ties, here are as strong as in other Asian countries. Most of the people are ignorant about various aspects of public health a wide range of superstitions and false beliefs being prevalent in these communities. These low levels of socio-economic norms, aggravated by the sudden changes of victim's skin due to arsenicosis (spotted or diffuse melanosis and /or palmo- planter keratosis, etc.) makes the perception level of the common people more lower which ultimately leads to social refusal and cultural discrimination. Bangladesh apprehended that better economic conditions leading to maintain better nutritional status of population might have a role to prevent arsenicosis, at least partly.

There are several reports which showed that patients of arsenicosis are to face many problems: the neighbours avoids the adults, children are refused to play with other, and the adolescent girls are often not married due to social discrimination (Bangladesh Arsenic Control Society's observation at Charghat) and few arsenic victims are even kept isolated from the surrounding communities in Samta Village, Jessore. These findings are consistent with that of the observation from Dhaka Community Hospital: they reported that arsenicosis patients suffer not only physically but psycho-socially and economically. They are deprived of their job, wages and refused from the job being treated as unproductive and thus these victims becomes the burden for the household, family and the society. Not only, that the arsenic victims are turned up into a sort of sources of teasing psychogenic irritation and neglected by the neighbourhood communities.

Moreover, the Dhaka Community Hospital observed that friendships and /or marriage broke down among arsenic affected pairs considering falsely that arsenicosis are contagious, infectious and or inherited (DCH Report: Seminar on ‘ Arsenic Disaster in Bangladesh Environment’ Jan, 1997), Political Commitment of a society and Government Support of a country including lack of community concerns and social mobilization were observed as the major problems in facing the challenge of chronic arsenic poisoning in a district of Thailand²¹.

1.11 Techniques use for Determination of Arsenic

Analytical chemistry has made phenomenal progress in developing sensitive methods for the determination of trace elements in water. Not too long ago the limits of detectability were at the parts per billion levels. Now, determinations of trace elements are routinely carried out at low parts per billion concentrations, and several methods with detection limits in the parts per trillion ranges are available. As analytical methods for the determination of trace elements are extended to ever lower concentrations, increasing attention must be paid to matrix interferences. Inter laboratory calibration exercises are no guarantee that such interferences are detected, unless several independent analytical techniques are employed.

Several methods are available, which can be relied upon to give “ total arsenic” concentration irrespective of the nature of the chemical compounds containing arsenic. The method are neutron activation analysis, X-ray fluorescence spectroscopy, plasma emission spectroscopy, perhaps flame and flameless atomic absorption spectroscopy, hydride vapor generator AAS, graphite furnace AAS, Ag-DDTC and Molybdenum blue in UV-visible spectroscopy, polarography and Field-test kit etc²².

1.12 Best Available Technology for Removing Arsenic

Technologies for removal of arsenic from drinking water already exist as incidences of arsenic contamination in ground water have already been reported from various parts of the world. The safe drinking water act states that each National Primary Drinking Water Regulation (NPDWR) has a maximum contaminant level (MCL) and shall list the technology, treatment techniques, and other means that the administrator finds to be

feasible for purposes of meeting the MCL. The technologies are judged to be a Best Available Technology (BAT) when the following criteria are satisfactorily met:

1. The capability of a high removal efficiency;
2. A history of full scale operation;
3. General geographic applicability;
4. Reasonable cost based on large and metropolitan water systems
5. Reasonable service life;
6. Compatibility with other water treatment process; and
7. The ability to bring all of the water in a system into compliance

Environmental Protection Agency (EPA) has reviewed several technologies as BAT candidates for arsenic removal, e.g., ion exchange, activated alumina, reverse osmosis, nanofiltration, electrodialysis reversal, coagulation assisted micro filtration, modified coagulation/ filtration, conventional iron and manganese removal and several emerging technologies. The maximum percent of arsenic removal that can be reasonably obtained from these technologies is also shown in the following table.

Table 2. Best available technologies and removal rates

Treatment technology	Maximum percent removal
Ion exchange	95
Activated alumina	95
Reverse osmosis	>95
Modified coagulation /filtration	95
Modified lime softening (pH>10.5)	90
Electrodialysis	85
Oxidation/filtration	80

These removal efficiencies are for arsenic (V) removal, pre-oxidation may be required. In water, the most common valence states of arsenic are As (V), or arsenate, As (III) or arsenite. As (V) is more prevalent in aerobic surface waters and As (III) is more likely to occur in anaerobic ground waters. In the pH range of 4 or 10, As (V) species (H_2AsO_4^- and $\text{H}_2\text{AsO}_4^{2-}$) are negatively charged, and the predominant As (III) compound (H_3AsO_4) is neutral in charge. Removal efficiencies for arsenic (V) is much better than removal of As (III) by any of the technologies evaluated because the arsenate species carry a negative charge and arsenite is neutral under these pH conditions. To increase the removal efficiency when As (III) is present, pre-oxidation to the As (V) species is necessary.

As (III) may be converted through pre-oxidation to As (V) using one of several oxidants like chlorine, potassium permanganate, hypochlorites and ozone are effective in oxidizing As (III) to As (V). For any arsenic removal from drinking water chlorination may be required for oxidation of As (III).

Ion exchange can effectively remove arsenic using anion exchange resins. It is recommended as a BAT primarily for site with low sulfate because sulfate is preferred over arsenic. Sulfate will compete for binding sites resulting in shorter run lengths. Due to much shorter run lengths than activated alumina, anion exchange must be regenerated because it is not cost effective to dispose of resin after one use. It is very difficult for Bangladeshi people to regenerate the resin.

Activated alumina is an effective arsenic removal technology; however, the capacity of activated alumina to remove arsenic is very pH sensitive. High removals can be achieved over a broad range of pH, but shorter run lengths will be observed at higher pH. Activated alumina can be operated in one of two ways. The activated alumina can either be disposing of or regenerated after the media exhausted. Under the regeneration option, strong acids and bases are used to remove arsenic from the media so that it can be used again to remove arsenic. Because arsenic is strongly adsorbed to the media, only about 50-70 % of the adsorbed arsenic is removed. The disposable activated alumina option can be operated both at the optimal pH of 6 and at higher natural water pH values. Activated alumina media in most cases is used to remove arsenic in drinking water systems with arsenic above 50 ppb.

Reverse osmosis can provide removal efficiencies of greater than 95% when operating pressure is ideal. Water rejection (on the order of 20-25%) may be an issue in water-scarce regions and any prompt systems employing reverse osmosis to seek greater levels of recovery. Water recovery is the volume of drinking water produced by the process divided by the influent stream. Increased water recovery is often more expensive, since it can involve recycling of water through treatment units to allow more efficient separation of solids from water. Based on the cost of the process, it is unlikely that reverse osmosis would be installed solely for arsenic removal.

Modified coagulation /filtration is an effective treatment process for removal of arsenic (V) according to laboratory, pilot plant, and full-scale tests. The type of coagulant and dosage used affects the efficiency of the process. Below pH of approximately 7, removals with alum or ferric sulfate/chloride are similar. Above pH of 7, removal with alum decrease dramatically (at a pH of 7.8, alum removal efficiency is about 40%). Other coagulants are also less effective than ferric sulfate/chloride. Systems may need to lower pH or add more coagulant to achieve higher removals.

Modified lime softening operated within the optimum pH range greater than 10.5 is likely to provide a high percentage of arsenic removal. Systems operating lime softening at lower pH will need to increase the pH to achieve higher removals of arsenic. Coagulation/filtration and lime softening are unlikely to be installed solely for arsenic removal. Systems considering installation of one of these technologies should design the process to operate in the optimal pH range if higher removal efficiencies are needed for compliance.

Some technologies are currently being promoted for application in Bangladesh. They claim to be effective in removing arsenic from tube well water. These are new and in development stage. The effectiveness, viability and sustainability of the technologies under field conditions in Bangladesh are yet to be ascertained before their adsorption and scale-up thereof. Some of the technologies so far tried both in laboratory and at field level.

Auto-attenuation, which needs collection of ground water from the wells and allowing it stand for a specific period of time. Ground water having high concentration of dissolved iron is readily oxidized and that adsorb arsenic. The auto-oxidation of Fe^{2+} to Fe^{3+} generates favorable substrate with surface reactive sites for the adsorption of unchanged As (III) as well as anionic As (V) species. The test result showed that it needs further modification for high-arsenic ground water.

Parknikar (1998) describe two types of metal-microbiological interactions that can be used for arsenic removal. SORAS is a simple method that uses irradiation of water with sunlight in PET or other UV-transparent bottles to reduce arsenic level from drinking water. Khair (1999) found Bijaypur clay from Mymensingh and processed cellulosic materials to be capable of adsorbing both As (III) and As (IV) in solutions acidified with

vinegar or HCl. The bucket treatment unit was developed by DPHE-Danida and is being under the Arsenic Mitigation Pilot Project.

BSCIR (1999) has developed a low cost arsenic filter. The technology consists of adding a floc forming composition to the arsenic contaminated water followed by stirring and settling. The chemicals that used for settling are composed of iron oxide, alum, activated charcoal and CaCO_3 , which are to be mixed in definite proportions, homogenized and micronized.

Activated alumina is a granulated form of aluminum oxide (Al_2O_3) with very high surface area, in the range of 200-300 m^2/g . This high surface area gives the material a very large number of sites where sorption can occur, and activated alumina has been widely used for removal of fluoride. It was early discovered that activated alumina could remove arsenic from water. The kinetics of arsenic removal onto the alumina surface is slower than ion exchange resins, and some arsenic leakage is often noted in activated alumina systems.

Table 3. The available technologies for arsenic removal in Bangladesh is as follow:

TECHNOLOGY	PROCESS
Alcan Enhanced Activated Alumina (AL)	Adsorption to enhanced activated alumina (AAFS-50)
Ardasha Filter (AR)	Passive sedimentation and adsorption to clay/carbonized organic matter candle
BUET Activated Alumina (BUET)	Oxidation, adsorption to sand filter and activated alumina
DPHE/Danida 2-bucket System (DPHE/DANIDA)	Oxidation, coagulation and adsorption through sand candle
GARNET Home-made Filter (GARNET)	Passive coagulation with iron (from brick chips) and adsorption to sand
Sono 3-kolshi Method (SONO)	Passive coagulation with Fe and/or adsorption to sand matrix
Stevens Institute Method (STEVENS)	Enhanced coagulation and co-precipitation (ferrous sulphate), filtration and adsorption to sand filter
Tetrahedron (TETRAHEDRON)	Ion exchange resin

In recent years, elemental or zero-valent iron has received considerable attention as a reactive medium for treatment of a wide variety of contaminants in water, including chlorinated hydrocarbons, chromium, nitrate and radionuclides (EPA2002, USA). One of the chief advantages of ZVI-based treatment technology is their adaptability to passive flow-through application, which can be significantly less costly to operate and maintain than traditional pump-and-treat systems. Although ZVI based technology are presently available for some contaminants, many other applications are still under development and testing.

In this consideration, there was no up-to-date research of arsenic mitigation with zero-valent iron with sulfur releasing biomaterials.^{9, 23-36}

1.1.3 Aim of the Study

The environmental hazards soaring high consciousness among peoples and equally getting momentum to find the fact and extent of this debacle¹. Now Bangladesh facing hazardous condition due to the contamination of arsenic in the tube well water.

Considering arsenic pollution in ground water of Bangladesh; four different places were selected to study the arsenic pollution and also finding a method for removal of arsenic from drinking water.

In consideration of arsenic pollution, the selecting areas were Hajigong Thana, Muradnagar & Debidwar Thana, Naogaon Municipality area and Kalaskati Union at Bakergong Thana. The tube well water samples from different depths and different locations of sampling sites were collected and analyzed by the GF-AAS.

For consideration of arsenic removal, two types of household waste biomaterials like skin of garlic and rice husk were selected. These materials might uptake in certain extent of arsenic from dinking water. The mitigated water samples analysed by Ag-DDTC in UV-visible method and also graphite furnace AAS.

Chapter-2

THEORETICAL ASPECTS

2.1 UV-Visible Spectrophotometer

2.1.1 **Theory:** When a molecule absorbs ultraviolet/visible light of a particular energy, it is assumed that a first approximation of only one electron is promoted to a higher energy level and that all other electrons are unaffected. The excited state thus produced is formed in a very short time (of the order of 10^{-15} s) and a consequence is that during electronic excitation the atoms of the molecule do not move.

The most probable ΔE transition would appear to involve the promotion of one electron from the highest occupied molecular orbital to the lowest available unfilled orbital, but in many cases several transitions can be observed, giving several absorption bands in the spectrum. Not all transitions from filled to unfilled orbitals are allowed, the symmetry relationship between the two orbitals being important, and where a transition is 'forbidden', the probability of that transition occurring is low, and correspondingly the intensity of the absorption band is also low.

UV-visible spectrophotometer is consisting of a light source, double beams (reference and sample beams), a monochromator, a detector, and amplification and recording devices. The source usually incorporates a tungsten filament lamp for wavelengths greater than 375nm, a deuterium discharge lamp for values below that and a solenoid-operated mirror, which automatically deflects light from either one as the machine scans through the wavelengths.

All UV-visible spectrophotometers are ratio recording; the ratio between reference beam and sample beam intensities (I_0/I) is fed to a pen recorder. The recorder trace is invariably absorbance (A) against wavelength (λ), and most instruments record linearly over the range 0-3 absorbance units³⁷

2.2 Spectrophotometric Method of Arsenic Analysis

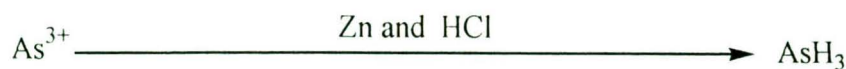
Trivalent arsenic reacts with silver-diethyldithiocarbamate [$\text{Ag-SCSN}(\text{C}_2\text{H}_5)_2$] to form a red color complex, which absorbs at 535 nm.



This is standard and reliable method for arsenic determination in water at the ppb (parts per billion) concentration level.



By adding Zn to this solution, the arsenic is reduced further to arsenic hydride.



In this reaction chloroform and 1% morpholine is used to dissolve the Ag-DDTC. A scrubber containing glass wool impregnated with $\text{Pb}(\text{CH}_3\text{COO})_2$ solution is used to remove sulfide ion which interfere the reaction³⁸.

2.2.1 Modification of Ag-DDTC Method

Nitrogen gas (99.997%) was passed into the conical flask to drive off quickly arsine gas produced by chemical reduction to the Pyrex tube where Ag-DDTC absorbs arsenic gas. Due to the passage of nitrogen gas, the reaction is very rapid and the signal of arsenic is reproducible.

2.3 Atomic Absorption Spectrophotometer

2.3.1 Theory: Atomic absorption spectroscopy is based on the excitement of atoms. This is the term used to describe the situation when an atom is raised its ground state to a higher energy level. Atoms have a positively charged nucleus surrounded by an electron cloud, with each electron occupying a different energy around the nucleus. There is a ground state, which represents the minimum energy level for an electron. If the atom absorbs energy, this causes excitement and electrons are raised temporarily to higher energy levels. The source of energy may be heat or light (photons). Several energy levels are possible, but usually, only the first level is of concern, since very few electrons are excited beyond E_1 unless the temperature is very high. The electrons further from the nucleus require the least amount of energy for the transition from E_0 to E_1 .

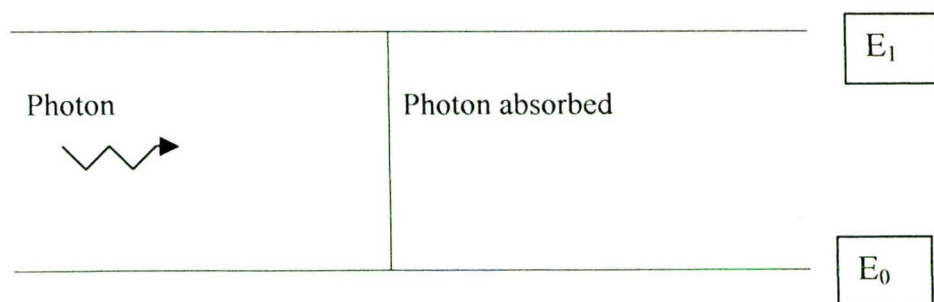
In particular, metallic and semi-metallic elements have outer electrons, which are loosely bound to the nucleus and require low energy to excite whereas other elements require very high energy for transition from E_0 to E_1 .

Therefore the range of elements, which can be studied by conventional atomic absorption spectrophotometer technique, is limited.

If too much energy is supplied, the electron may be raised to higher energy levels E_2 , E_3 and a stage is reached at which the electrons break up completely and ionization occurs. Therefore enough energy must be supplied but not too much. For each atom of an element the energy gap (E_0-E_1), for a particular electron is the same and unique to that element.

As mentioned above the energy source can be heat or light. The light of an exact wavelength must be used to excite the atom of a specific element. This is the reason why the atomic absorption technique is so selective.

For atomic absorption, a flame forms a cloud of free atoms. Photons of a specific wavelength (dependent on the element being studied) are passed through the cloud and the cloud absorbs a proportion. The proportion absorbed is function of the concentration of the element in the cloud. It should be noted that as well as the source photons passing through the cloud; there will also be emission of photons on the same atoms in the flame being excited and then returning to the ground state. It is essential for atomic absorption work that these should be distinguished from the source photons. The source photons are produced as an alternation signal, whereas the emitted radiation is continuous signal.



2.3.2 Measurement of Concentration:

The proportion of source photons absorbed is proportional to the concentration of the element corresponding to that wavelength. This derived from Lambert and Beer's law. This may be written as

$$kL = \log I_0/I_t \text{ or } A = \log I_0/I_t$$

Where, k = absorption co-efficient

L = length of the absorbing cell

I_0 = incident light

I_t = transmitted light.

Beer's law is a development of this. If $\log I_0/I_t$ is an expression of absorbance and if kL is proportional to the number of atoms in the cell, then absorbance is proportional to concentration. However, this is not always true. It usually holds only for dilute solutions. So at low concentration, there is a linear relationship between absorbance and concentration, but at higher concentration it is non-linear and large errors can be introduced. Therefore, for atomic absorption work, the best results are obtained from the range, often samples must be dilute. So that Beer's law is observed.

2.4 Interferences: Atomic absorption spectroscopy is a technique, which highly specific, with few problems of interference. Those, which do occur, can be classified as either spectral or non-spectral.

2.4.1 Spectral Interference: These occur when some of the light absorption is due to a species other than the element being studied. Since the instrument is highly sensitive, spectral interferences are rarely caused by the overlap of resonance lines. More common is background absorption due to undissociated molecules in the matrix material. This can be overcome by using a continuous source which is usually a deuterium lamp positioned at right angle to the element lamp ray path. A mirror deflects this light from the deuterium lamp. So that it passes through the flame and can be detected by the photo multiplier. This light will not be absorbed by atomic absorption, but will be partly absorbed by background adsorption.

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2.4.2 Non-spectral Interference: There are two main types of interferences in this category chemical interference and ionization interference. Chemical interference occurs when the sample contains a component, which forms a thermally stable compound with the analyte element. This prevents complete atomization. An example of this in the measuring of calcium in the presence of phosphate will not dissociate completely in air acetylene flame. As a result the concentration of phosphate increase and the absorption by calcium decreases. This can be overcome by either (i) Using a hotter flame (Nitrous oxides-acetylene) or by (ii) Adding an excess of a releasing agent.

Ionization interference is associated with hotter flames of with more easily ionized elements, particularly the alkali metals and alkaline earth metals such as sodium, potassium, magnesium and calcium. This effect can be overcome by adding an excess of an element, which is easily ionized; this suppresses the ionization of the analyte element.

For example, if calcium is the analyte, potassium could be added to a concentration of 2000 mg/L to act as an ionization suppressant.

2.5 Application of Beer's Law in UV-Visible Absorption Spectroscopy

Beer's law is the basis of all quantitative application of UV-Visible spectroscopy. Generally a method of calibration or standardization is used for determining the concentration of the analyte. Beer's law will generally hold over a wide range of concentration if the structure of the colored ion or of the colored non-electrolyte in the dissolved state does not change with concentration. Small amounts of the electrolytes, which are chemically unreactive with the colored compound, do not usually affect the light absorption large amounts of electrolytes may result in a shift of the maximum absorption and may also change the value of the absorptivity.

Discrepancies are usually found when the colored solute ionize, dissociates or associate in solution. Since the nature of the species in solution will vary with the concentration. The law does not hold when the colored solute forms complexes the composition of which depends upon the concentration. Beer's law holds strictly for monochromatic radiation. But no instrument can attain such resolution of wavelength. A straight line passing through the origin indicates conformity to the law. The slope of the spectrum increases as the concentration is increased, with the result that the fractions of each wavelength observed may change, particularly if the instrument setting should drift over the period of the measurement. A negative deviation in the absorbance versus concentration plot will in these cases be observed. The greater is the slope of the spectrum the greater is the deviation.

This instrument is designed to measure each source alternately. The element plus background absorb the analyte element ray, whereas the background only absorbs the deuterium ray. The instrument measures both and subtracts the deuterium reading from the analyte reading to give a corrected value.

$$(\text{Element plus background}) - (\text{background}) = \text{Element absorbance}^{39}$$

2.6 Graphite Furnace Atomic Absorption Spectrophotometry (GF-AAS)

Electrothermal Atomizers:

Electrothermal atomization is usually performed with a graphite furnace although vertical crucible furnaces and open filaments have been employed. Electrothermal (non flame) atomizers offer several attractive features that complement flame AAS.

1. Only small amounts (10^{-8} to 10^{-11} absolute) of analyte are required.
2. Solid can be analyzed directly, often without any pretreatment.
3. Small amount of liquid samples, 5 to 100 μL
4. Background noise is very low.
5. Sensitivity is increased because the production of free analyte atoms is more efficient than with a flame.

On the negative side, matrix effects are usually more severe, and precision, typically 5% to 10% compares unfavorably with that of AAS and FES.

2.6.1 Principle: After insertion of the sample onto a platform mounted within the electrothermal atomizer, a heating sequence is initiated to take the sample through three steps: dry, ash chars, and atomize.

- (i) In the drying cycle, the sample is heated for 20 to 30 seconds at 110 $^{\circ}\text{C}$ to evaporate any solvent or extremely volatile matrix components.
- (ii) The ash or char step is performed at an intermediate temperature (often 500 $^{\circ}\text{C}$) to volatilize higher boiling point matrix components and to pyrolyze matrix materials that will crack and carbonize. The latter would be fats and oils. Loss of analyte may occur if the ashing temperature is too high or is maintained for too long.
- (iii) In the atomization step, maximum power is applied to raise the furnace temperature as quickly as possible to the selected atomization temperature. The analyte residue is volatilized and dissociated into free atoms that will absorb light from the ASS source. The transient absorption signal must be measured rapidly.

2.6.2 Matrix Modifier: Palladium (II) nitrate is a useful chemical modifier that stabilizes many elements to temperatures several hundred degrees higher than possible otherwise. Palladium modifies the analyte element by converting it to a more thermally stable species. This lessens analyte volatility and permits a higher temperature for the ash step,

which more efficiently removes bulk matrix constituents without loss of analyte element. Thus palladium reduces signal dependency on the sample composition and produces greater consistency in absorption analyte signals.

The greatest temperature shifts are achieved for these elements: As, Bi, Ga, Ge, P, Pb, Sb, Te and Tl.

2.6.3 Arsenic Measurement:

In FES the lines most frequently used are at 228.8 and 234.90 nm. A hydrocarbon species in the flame is required, supplied either by the fuel gas or by an organic solvent.

The most sensitive lines in AAS are at 189.04, 193.76 and 197.20 nm. To minimize absorption by the flame gases, a helium (entrained air)- hydrogen flame is preferable. Otherwise, a lean air-acetylene flame is used; the line at 193.76 nm is best. Serious interference arise from these elements; Al, Cr, Mg, Mo, Ni, Sn, Ti and nitrate.

The best approach is chemical vaporization as AsH_3 into a GF-AAS as this procedure offers the maximum sensitivity and freedom from interferences⁴⁰⁻⁴².

Chapter-3

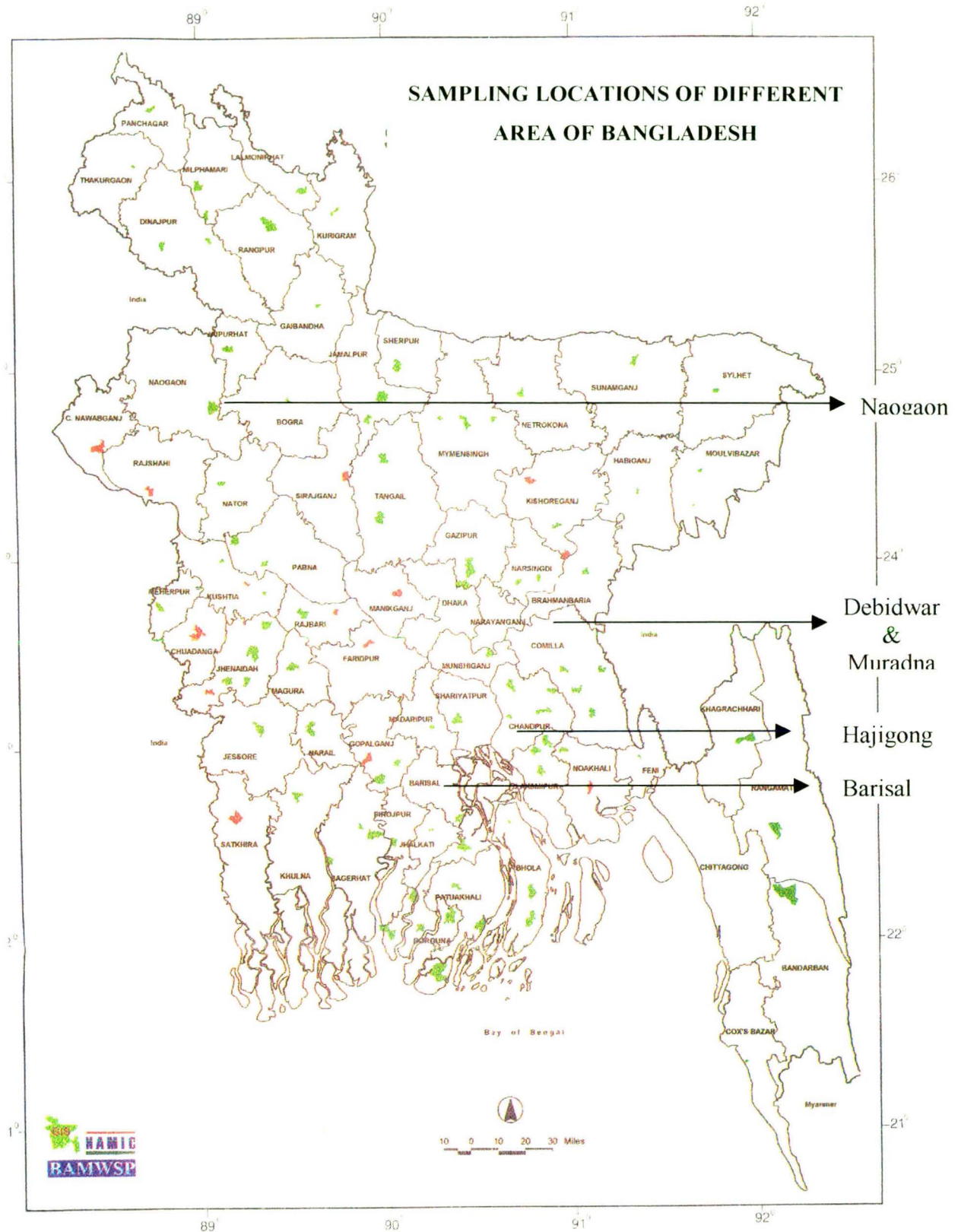


Fig 1: MAP OF BANGLADESH

Map of Hajiganj Upazila

**Fig-2: SAMPLING LOCATIONS OF
HAJIGONG**

EXPERIMENTAL

3.1 A Short Description of the Study Areas

Arsenic in ground water and soil is no longer a localized problem. The latest survey has confirmed the worst fears in this regard by listing arsenic contamination in Bangladesh to be the biggest in the world.

Muradnagar and Debidwar Thana in Comilla district were one of the sampling locations. These Thanas were situated in the northern part of the Comilla district. The river Gomti is flowing along the Thanas. 12 tube well water samples were collected from those Thanas.

Naogaon municipality area was considered as one of the sampling area. Prior to 1998, most of the people used tube well water for drinking purpose. The river Jumuna (local name 'Chotto Jumuna') flows near the municipality area. 10 samples were collected from different locations of the area. Kalaskati union at Bakergong Thana was also a sampling site. It is the southern part of the Barisal district. 10 samples were collected from this place.

Hajigong Thana at Chandpur district was 53 kilometers away from Comilla district. The river Dakatia flows near the Thana. 29 villages of Hajigong Thana were considered as the sampling stations.

3.2 Collection of The Water Samples

3.2.1 Containers: The samples were collected in polythene containers. These containers were washed with 5% HNO_3 and then washed with distilled de-ionized water and finally with the tube well water at the sampling sites for several times before collecting samples.

3.2.2 Depth, Year of Installation and Red Colour Marked:

The information about depth of the tube well, year of installation of tube well and also red or green marked were collected from the local inhabitants by supplying questionnaires.

3.2.3 Preservation of Water Samples:

The tube well water samples were preserved by adding HNO_3 and kept pH of the water samples within pH range 2 – 3.

3.3 Spectrophotometric Measurement of Arsenic

Arsine (AsH_3) generation followed by complexation with silver -diethyldithiocarbamate [$\text{Ag-SCSN}(\text{C}_2\text{H}_5)_2$] solution: Arsenic reacts with a solution of Ag-DDTC, complex with morpholine in chloroform to form soluble red complex, which has an absorption maximum at 535 nm. This forms the basis of the method.

3.3.1 Preparation of Ag-DDTC Solution for Arsenic Absorption

The solution was prepared by dissolving 0.75 g Ag-DDTC in a solution of 1 mL of morpholine dissolved in 100 mL of chloroform (CHCl_3). Then it was kept in a round bottom quick fitted flask covering with aluminum foil and preserved at 4°C in a refrigerator.

3.4 Zn/HCl Method

3.4.1 Principle

Inorganic arsenic is reduced to arsine, (AsH_3), by zinc in acid solution in a Gutzeit generation (modified). The arsine is then passed through a scrubber containing glass wool impregnated with lead acetate solution and into an absorber tube containing Ag-DDTC dissolved in chloroform or pyridine. In the absorber arsenic reacts with the silver salt, forming a soluble red complex suitable for photometric measurement.

3.4.2 Interference

Although certain metals- Cr, Co, Cu, Hg, Mo, Ni, Pt and Ag interfere in the generation of arsine, the concentration of these metals normally present in the sample do not interfere significantly. Antimony salts in the sample form stibine, which interferes with color development by yielding a red colour with maximum absorbance at 510 nm.

3.5 Preparation of Necessary Solution and Reagents

3.5.1 Preparation of Lead acetate Solution

10 g of pure lead acetate, [$\text{Pb}(\text{CH}_3\text{COO})_2$] was dissolved in 100 mL distilled de-ionized water.

3.5.2 Preparation of Potassium iodide Solution

15 g potassium Iodide (KI) was dissolved in 100 mL distilled de-ionized water.

3.5.3 Preparation of Stannous chloride Solution

10 g stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) was dissolved in 100 mL distilled de-ionized water.

3.6 Procedure

3.6.1 Treatment of Sample

50 mL sample was taken into a clean generator bottle (quick fitted 100 mL conical flask) adding successively, 5 mL 1:1 HCl, 5 mL KI (15%) solution and 8 drops SnCl_2 reagent.

3.6.2 Preparation of Scrubber and Absorber

Cotton was impregnated in the scrubber with lead acetate solution and 4 mL Ag-DDTC reagent was taken with a pipette in absorber tube.

3.6.3 Arsenic Generation and Measurement

Adding 1 g Zn-dust to generator, it was connected with scrubber absorber immediately. All connection must be fitted tightly. Allowing 30 min, for complete evolution of arsine and pouring solution absorber into a 1 cm cell, the absorbance was measured at 535 nm, using the reagent blank as the reference.

3.6.4 Preparation of Standard Curve for Arsenic Measurement

Standard curve was prepared for total arsenic in concentration 5, 10, 15, 20 and 40 ppb. Then the standard curve was prepared plotting the amount of arsenic (in ppb) along X-axis and absorbance along Y-axis.

The arsenic content of water was then measured with the help of the curve.

Table 4: data for spectrophotometric measurement of arsenic

Sl No	Absorbance	Concentration (ppb)
1	0.007	5.0
2	0.014	10.0
3	0.030	15.0
4	0.065	20.0
5	0.112	40.0

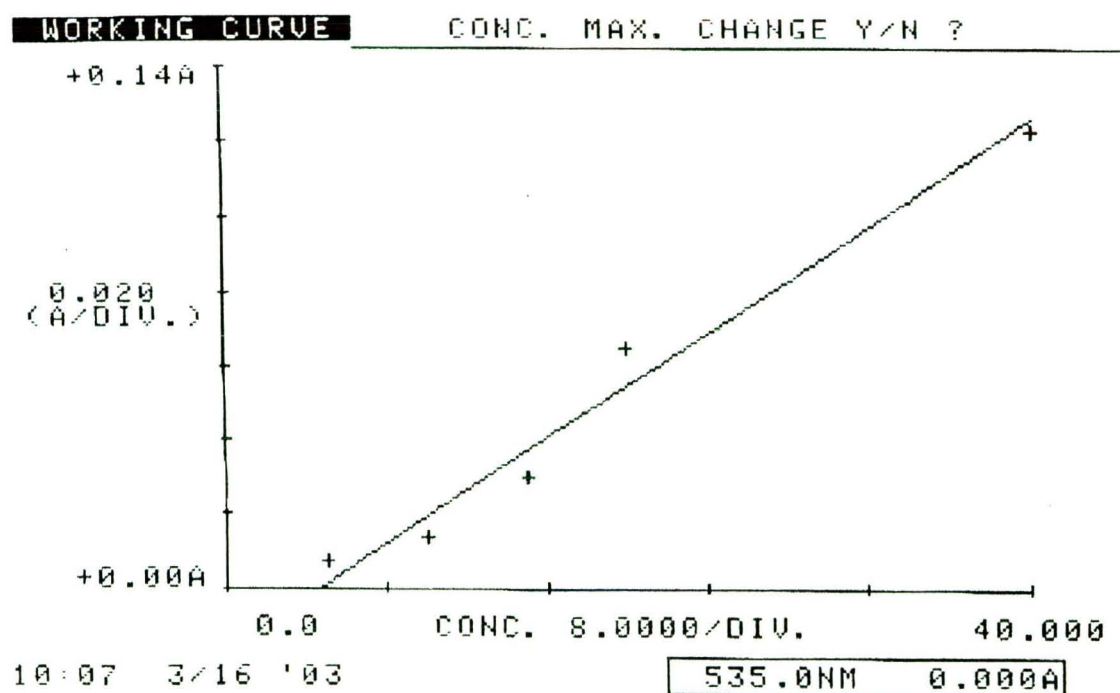


Figure-3: Calibration curve of arsenic concentration

3.7 AAS-Graphite Furnace for Measurement of Arsenic

Graphite furnace atomic absorption spectrophotometry is

- A technique to minimize dilution during atomization of the analyte prior to its determination with atomic absorption spectrometry.
- A technique with more interferences than the more reliable flame atomization.
- A technique with high sensitivity and very good detectability but not so good throughput and precision.

3.7.1 Procedure

Instrumentation

Three components make up an electrothermal atomizer: the work head, the power unit, and the controls for the inert gas supply. A heated graphite atomizer consists of a hollow graphite cylinder 28 mm long and 8 mm in diameter, the interior of which is coated with pyrolytic graphite. Electrodes at each end of the cylinder are connected to a power supply. A metal housing surrounding the furnace is water-cooled to allow the entire unit to be rapidly restored to ambient temperature after each run. Inert gas usually nitrogen (99.997 %), enters the cylinder at both ends and exists through the samples introduction port at the center of the cylinder. The gas flow removes the matrix components vaporized during the ashing step (to prevent subsequent vaporization during the atomization step and thereby large background absorption signal) and prevents oxidation of the graphite cylinder during the heating cycles. Liquid samples are introduced with a micro-syringe through the small opening in the top of the cylinder and place on a thin graphite plate or platform that is located within the cylinder. Care must be taken not to scratch the pyrolytic graphite surface.

The steps of a graphite furnace atomization

- 5-100 μ L samples
- Drying
- Ashing
- Atomization
- Burnout
- Cool

Atomization curve

Ashing curve

Interference

Modifier

Background correction

Platform

Steps in graphite furnace atomization -1:

- The samples introduction
- The sample is injected usually between 10-30 μL but some times the range could be extended to 100 μL .
- This is preferably made up of dilute nitric acid as matrix
- Sometimes solid samples are introduced

The drying step

- To volatilize the sample solvent
 - Use some degrees above the solvents boiling point (for water use 110°C) and about the same time in seconds as the injected volume in μL
 - Check that the solvent only volatilizes and not boil, otherwise bad reproducibility may occur

Steps in graphite furnace atomization -2:

Ashing of the sample

- May be the most important step
- Remove sample matrix without losing the analyte
- Highly dependent on both the analyte and sample matrix.
- Every new sample type should be optimized
- Inorganic matrix more difficult, because higher temperature is needed.

The atomization step 3:

This step is to vaporize and atomize the analyte.

- The vaporization pressure of the analyte dominates the supply of analyte atoms inside the tube.
- The convection of expanding gas and diffusion dominate the throughput of analytes out of the tube.
- Rapid heating is necessary for good sensitivity.

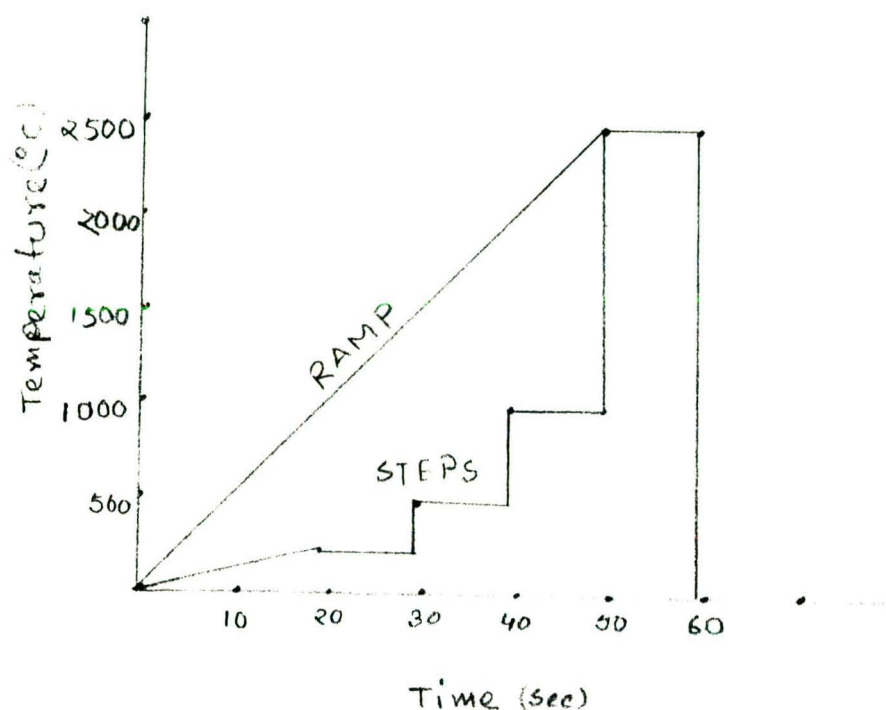
The steps in graphite furnace:

The burnout step

- It is used for taking away parts of the samples not completely volatilized during atomization
- temperature in the range $2700 - 3000^{\circ}\text{C}$ is most often used.
- If not completely vaporization of the sample is achieved. The sensitivity will slowly decrease and the imprecision increase.

Steps in graphite furnace atomization

Temperature program



Ashing curve

The ashing curve is the function of absorbance versus ash temperature for analyte

- It is prepared in the same way as the atomization curve, but the atomization temperature is set at its maximum value. The ashing temperature is stopped from 300°C to no more absorbance are registered.
- Do it once again with sample and may be with modifier
- Measure also the background.

Last cooling step

- Its purpose is to cool down the furnace temperature

The atomization step 4:

An atomization curve is the function of absorbance versus atomization temperature for the analyte

- Start with pure standards.
20 μL with peak absorbance in the range 0.2 –0.5. A low ashing temperature (300 $^{\circ}\text{C}$) and make atomization temperature from 800 to 2400 $^{\circ}\text{C}$
- Do it once again with the sample and may be with modifier.

3.7.2 Interference

The graphite furnace atomization technique is much more prone to interferences than the flame which depends on higher concentration of non-analytes.

- Physical
Change in surface properties of the graphite tube influence the atomization rate
- Spectral
Molecular absorption –light scattering
- Non spectral or chemical
Molecular binding between analyte and matrix
Less volatile compound forms.
Reactions with graphite tube.

3.7.3 Interference and How to Avoid Them:

Ashing with the optimal temperature

- Matrix modifiers
Thermal stabilization of analyte and vaporization of interfering materials during the ashing step.
Increase volatility of interfering compound
Decrease volatility of interfering compound and selection vaporization during the atomization step.
- Platform
Vaporization to high and more uniform furnace temperature
- Background correction
Elimination of unspecific absorbance.

3.7.4 Modifiers:

Thermal stabilization of analyte

- Ni or Mg to keep Se or As and make it possible to increase ashing temperature 800 $^{\circ}\text{C}$.

Increase volatility of interfering compound

- Ammonium sulphate or ammonium nitrate to increase volatility of chloride
- $\text{NaCl} + \text{NH}_4\text{NO}_3 \longrightarrow \text{NaNO}_3(\text{s}) + \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$

Decreased volatility of interfering compound

- Lanthanum to make sulphate stable and interfere with arsenic.

Continuously deuterium lamp background correction:

Background correction with continuously deuterium lamp

- The absorption of non-specific light is measured with a deuterium lamp and subtracted from the analytical signal from the line source.

3.7.5 Temperature Programming for Arsenic Determination:

Stage	1	2	3	4	5	6
Temperature	120	250	400	600	2500	0
Time	20	30	10	10	03	30
Step/RAMP	RAMP	RAMP	Step	Step	Step	Step
Gas	03	03	03	03	0	03
Recorder	-	-	-	0	-	30
Peak	-	-	-	27	6	-
End	-	-	-	-	-	6.

3.7.6 Preparation of Standard Curve for Arsenic Measurement with GF-AAS:

Standard curve was prepared for total arsenic in concentration 10, 20, 30, 40 and 50 ppb. Then the standard curve was prepared plotting the amount of arsenic (in ppb) along X-axis and absorbance along Y-axis. The arsenic content of water was then measured with the help of the curve.

Table: data for GF-AAS measurement of arsenic

Sl No	Absorbance	Concentration (ppb)
1	7	10.0
2	14	20.0
3	20	30.0
4	25	40.0
5	28	50.0

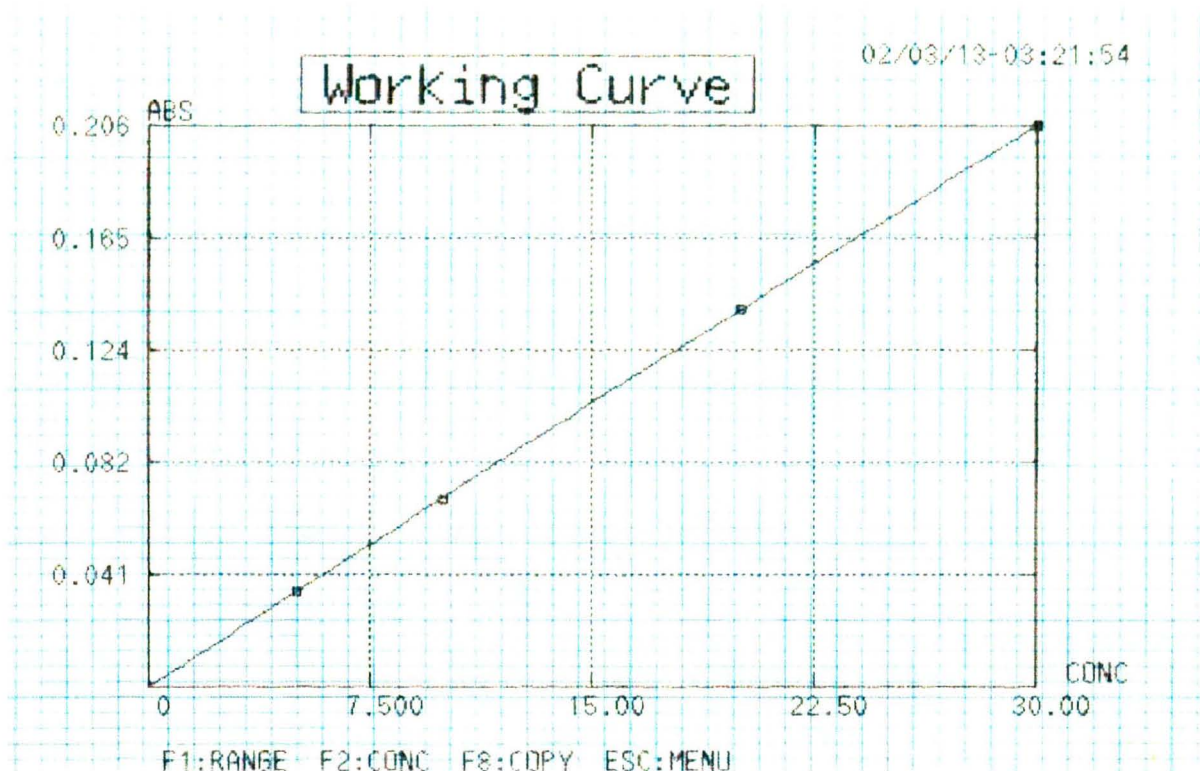


Figure-4: Calibration curve of arsenic concentration

3.8 Processing of Biomaterials

3.8.1 Skin of Garlic:

Skin of garlic was collected from Kawran Bazar local market, and then it was washed with de-ionized water for removing dust particles.

75 g skin of garlic, 5 g belching powder, and 500 mL de-ionized water taken in 1 L beaker. The mixture was boiled for 30 min to remove the colored materials from the skin of garlic. Then it was dried in oven at 110 °C temperature to remove the moisture and then it was ready to act as adsorbent for arsenic.

3.8.2 Rice Husk:

Rice husk was collected from Naogaon local market, and then it was washed with de-ionized water for removing dust particles. 75 g rice husk, 5 g belching powder, and 500 mL de-ionized water taken in 1 L beaker. The mixture was boiled for 40 minutes to remove the colored materials from rice husk. Then it was dried in oven at 110 °C temperature to remove the moisture and then it was ready to act as adsorbent for arsenic.

3.8.3 Construction of Arsenic Mitigation Plant

Arsenic mitigation plant consists of five buckets system. Top of the buckets was contained biomaterials, second bucket was contained iron chips, third and fourth bucket was contained wood charcoal, and fifth bucket acted as a arsenic mitigated water reservoir.

3.8.4 Technique for Arsenic Removal

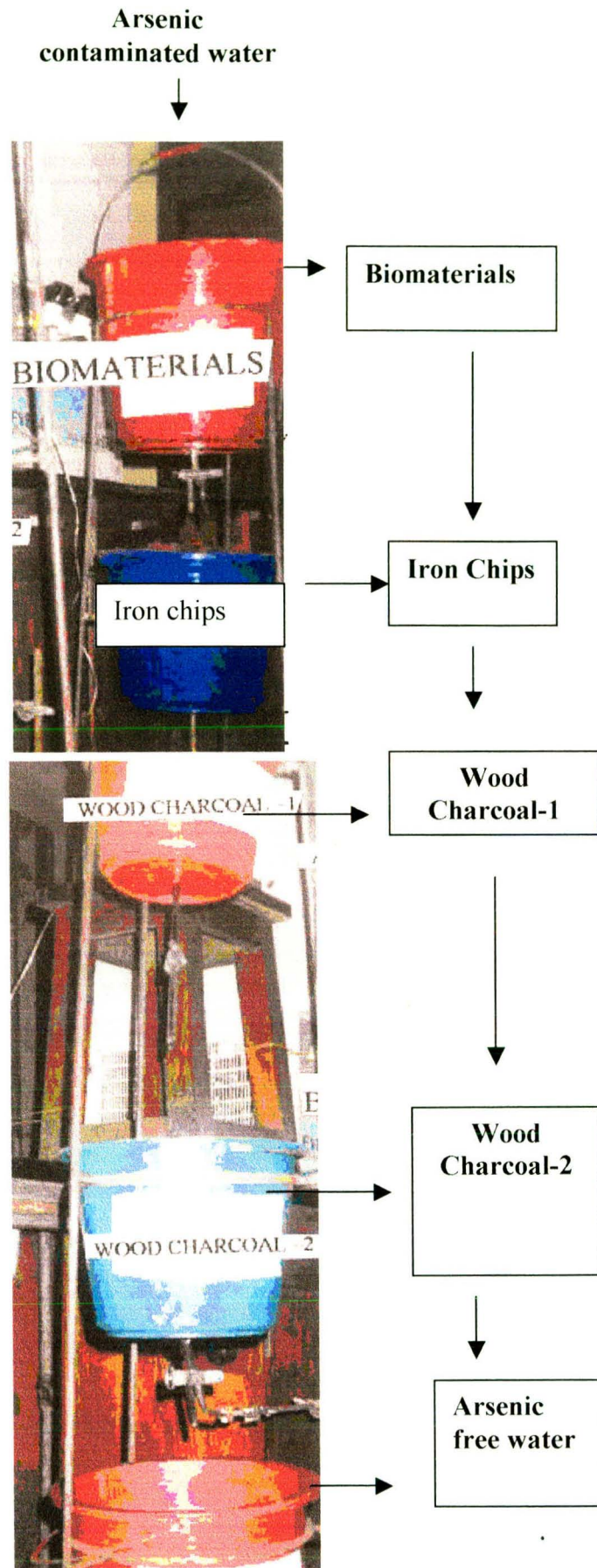
The concentration 1000 ppm has made by 1.320 g arsenic trioxide granular salts (As_2O_3 E.Merck) dissolved in 1 L de-ionized water. Taken 5 mL from 100-ppm solution in 50 L de-ionized water to make 1000 ppb synthetic water. 10 L synthetic water was poured in the first bucket that contained biomaterials.

The effluent was collected from first bed after passing 10 L of synthetic water to examine the maximum uptake of arsenic. The first bed was drained into second bed that contained iron chips. The color mitigated water then was poured in third bucket that was drained in the fourth bucket. Finally color and arsenic free drinking water stored in fifth reservoir.

3.9 Field Trial For Arsenic Removal

The tube well water samples were collected from Toragore at Hajigong Thana in Chandpur district and DPHE Bhaban's tube well from Singair Thana at Manikgong district.

The physical parameters and arsenic contents were first determined in real samples before pouring into buckets. The arsenic was measured with UV-visible spectrophotometer and eletrothermal atomizer. Then it was poured in the first bucket followed by the above-mentioned procedure.



Chapter-4

RESULTS AND DISCUSSION

Among the 141-tube-wells water of Hajigong Thana, the mean, median, mode, standard deviation, variance and range of these results is 0.507 mg/L, 0.423 mg/L, 0.540 mg/L, 0.389 mg/L, 0.152 mg/L and 2.52 mg/L respectively.

The range of arsenic concentration 2.52 mg/L indicates that its concentration lies in the range 0.08 to 2.60 mg/L. The mode value 0.540 indicates that it is the highest frequencies and about 8.5 % cover of the value in this distribution.

In a symmetrical distribution, the mean, median and mode are alike. However, arsenic concentration of the tube well water samples in Hajigong Thana is a skewed distribution (1.912), that arsenic concentration of a tube well differs from one to another. In an asymmetrical distribution, mode value (0.540 mg/L) is greater than mean value (0.507 mg/L).

Karl Pearson's⁴³ coefficient of skewness of this distribution is 1.912 that implies that it is a negative asymmetrical skewed distribution. In this distribution mean (0.507) is pulled toward the low valued items and also contains some values that are much smaller than the majority observations. So it indicates that the concentration ranges which are between (0.080 to 0.507 mg/L) has a maximum number i.e. about 60% of the values lies in the concentration range.

In this distribution, the kurtosis value is 5.67, which is greater than 3 that means it is a "leptokurtic" type of curve. This type of curve shows that the certain values in the distribution are two or three times greater than mean value. So it is about 40% of the data of this distribution, which is within the range (0.51 to 2.60 mg/L).

The variation of arsenic concentration of 29 villages in Hajigong Thana that represents arsenic contents which are varied from tube wells of different locations. Among these villages, the average concentration of arsenic was high in Toragore (1.1 mg/L) near Hajigong Thana and the lowest value of arsenic content was in the village Notohara (Figure-6 & 7). However all tube wells water of these villages is above the Bangladesh acceptable limit (0.05 mg/L).

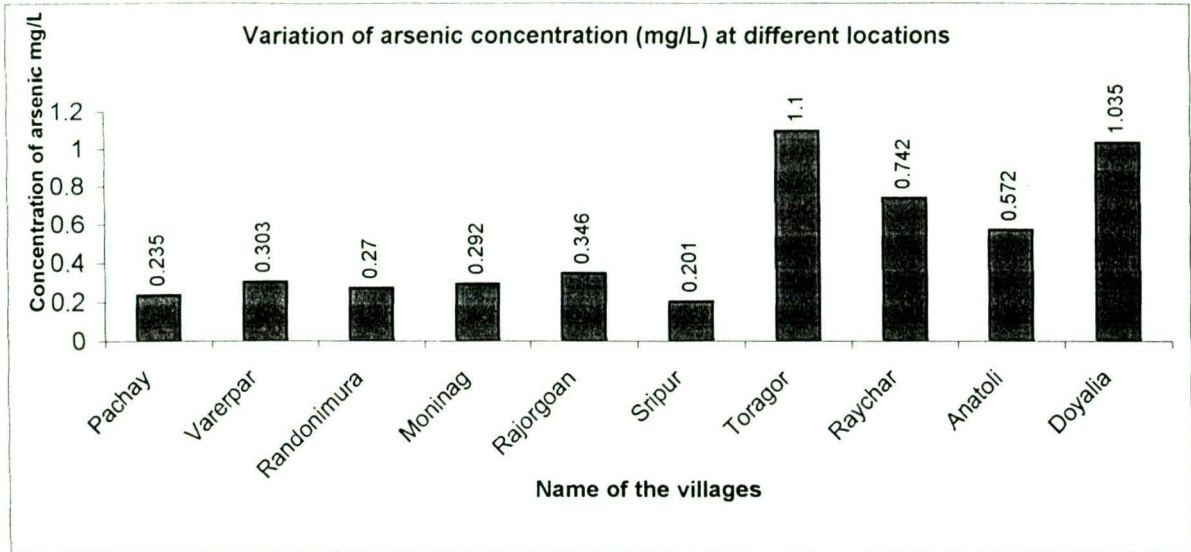


Figure-6

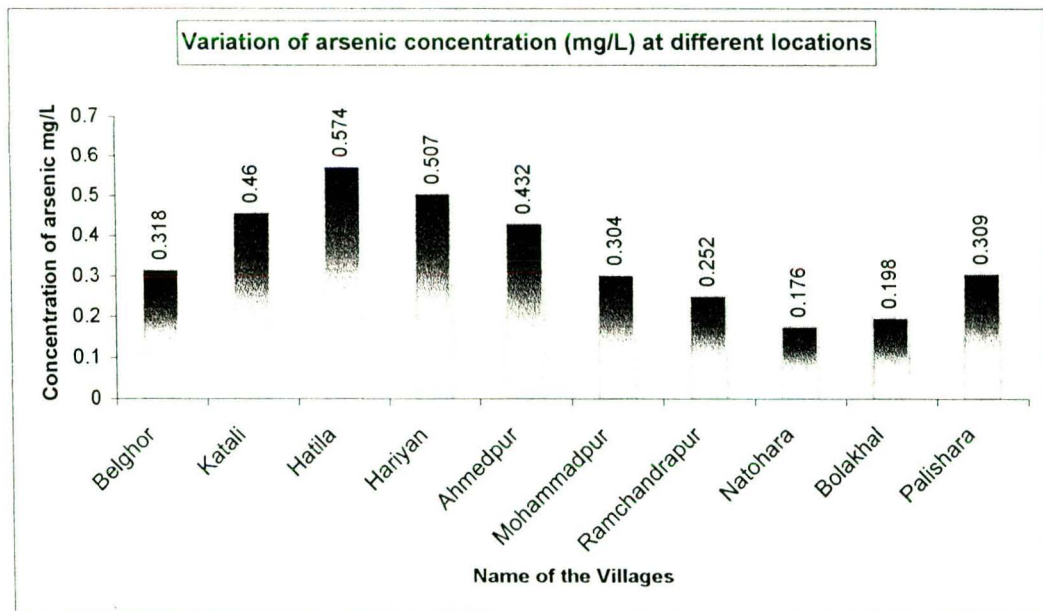


Figure-7

The variation of arsenic concentration was plotted with depth of the different tube wells (Figure-8). The depth of most tube well were from <60 feet to >100 feet. It is shown that in the lower and higher depth of the tube wells, arsenic contents were found in smaller amounts.

The concentration of arsenic was increased with the increase of depth from 60 feet to 100 feet. This indicates high percentage of water was withdrawn from these aquifers. However, > 100 feet, concentration of arsenic was low due to the less number of tube well. Hence, low amount of water was withdrawn at these aquifers.

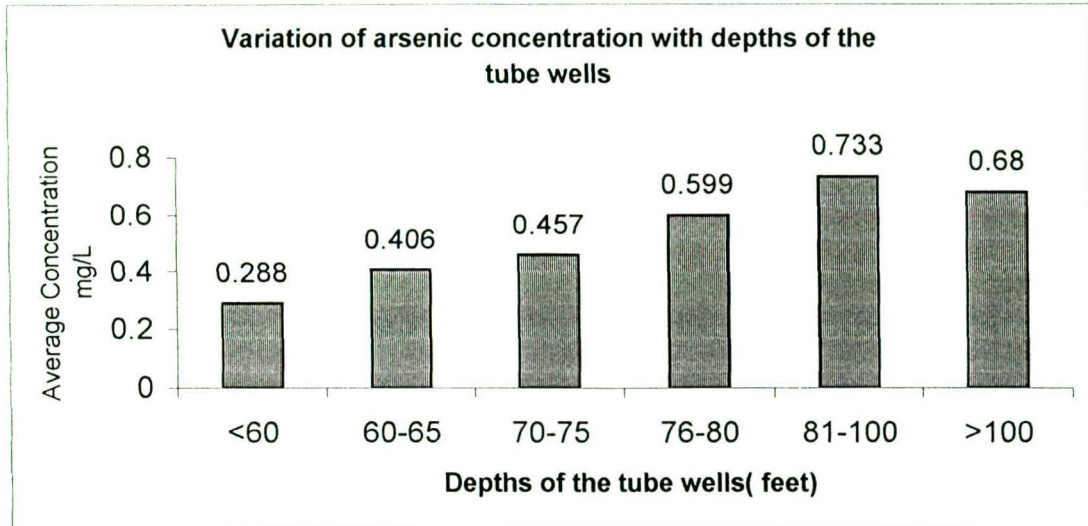


Figure-8

The variation of arsenic concentration with age of the tube well was also considered. The arsenic contents from older well were relatively lower from newer one which is shown in the bar diagram (Figure-9). It may be stated that aged tube wells extracted arsenic from geological sediments for several years, as a result lower concentration of arsenic were found from these types of tube wells.

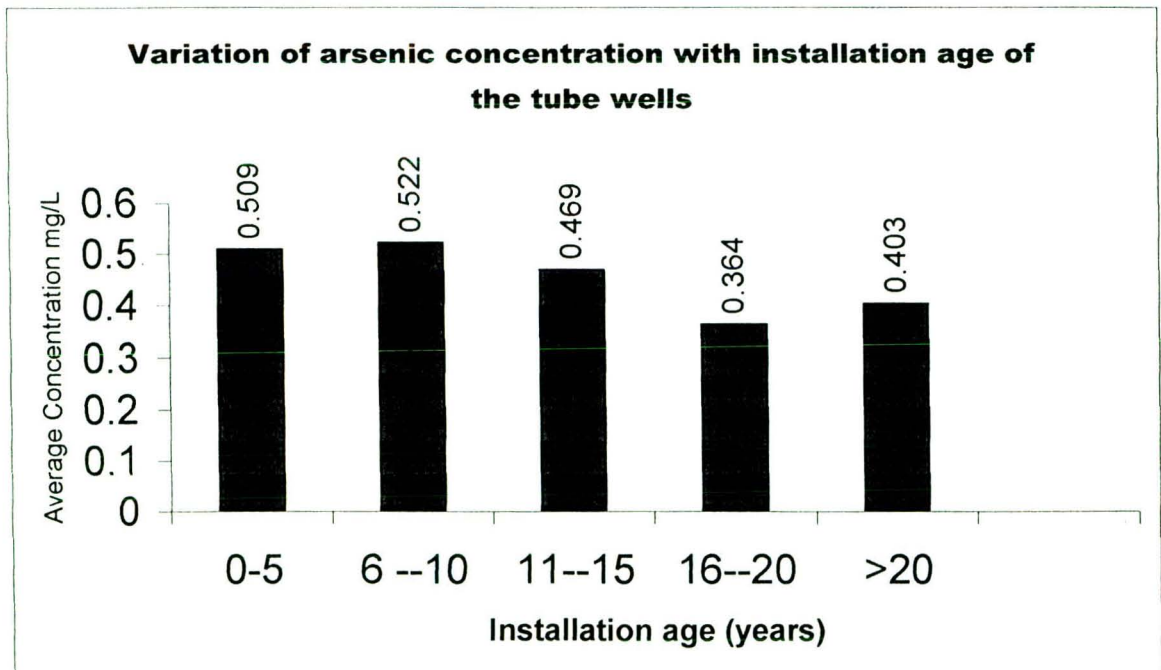


Figure-9

Average arsenic concentration was high with the age of the tube wells (6-10) years. This value gradually decreases with increasing age. However, the water extractable capacity (>20 years age) of tube well has already lost, as a result arsenic concentration was high of those tube wells.

The arsenic concentrations were classified into different classes. These are: very safe level (< 0.01 mg/L), safe level (0.01 -0.05mg/L), harmful level (0.051 - 0.1 mg/L), dangerous level (0.1 - 0.9 mg/L) and very dangerous level (>1.0 mg/L). All 141-tube wells are contaminated with arsenic (Figure-10)

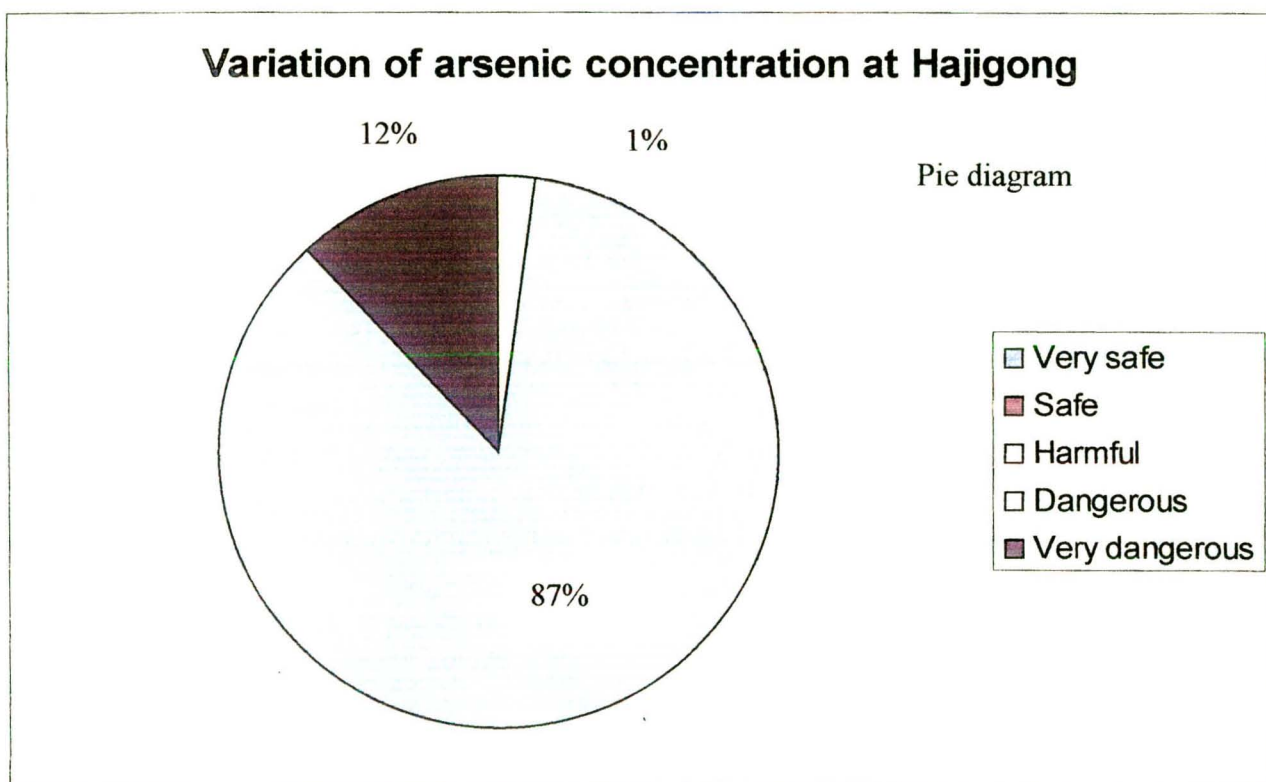
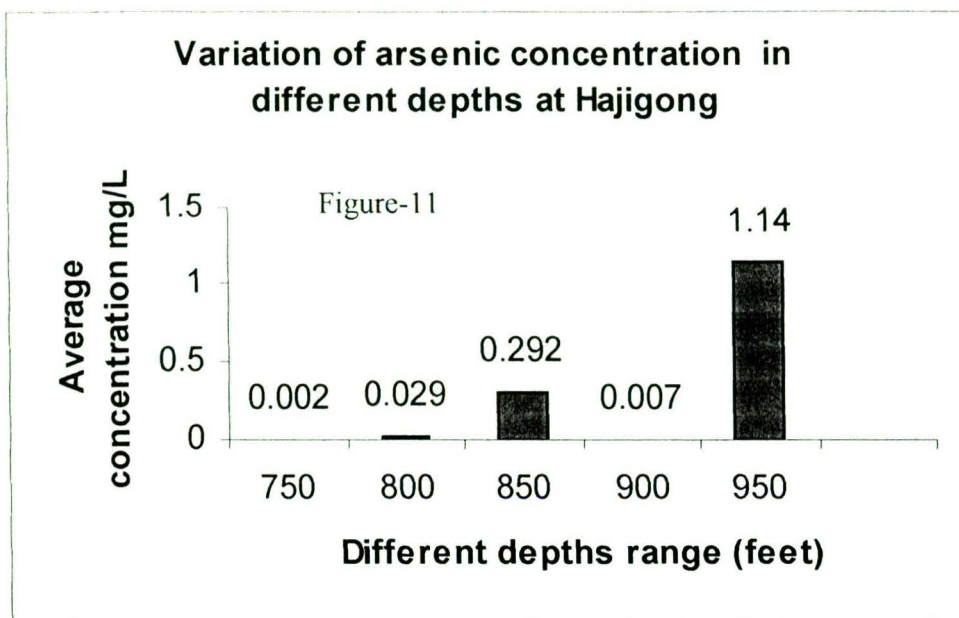


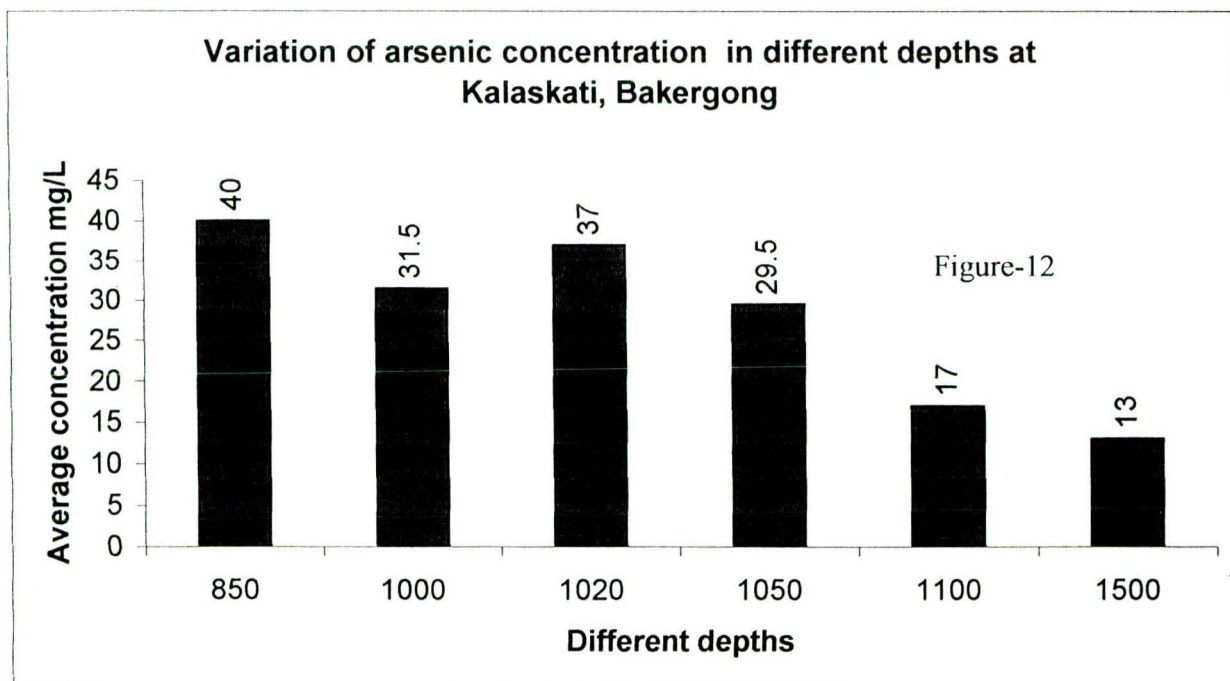
Figure-10

Sample water was also collected from very deep tube wells water in Hajigong Thana (Table-5). Among nine (9) tube wells, only 6-tube well water was safe for drinking (Figure-11). This is because about 1500 families depend on the water of these tube wells and they were withdrawing a heavy amount of water every day; as a result, these tube wells were gradually contaminated with arsenic.



Out of 12 water samples of Debidwar and Muradnagar Thana in Comila district were collected and analyzed. 7 samples were beyond the Bangladesh acceptable limit (0.05 mg/L). The concentration range was 0.014 mg/L to 0.185 mg/L. Only two tube wells water were dangerous level of arsenic, five waters were harmful and rest five tube well water samples were arsenic safe for drinking (Table -2).

Twelve water samples from different sites of Naogaon Municipality area were collected. All tube well water samples were arsenic free with the WHO guide line value (0.01mg/L, Table-3).



Most of the tube wells of Kalaskati Union under Bakergong Thana of Barisal district were very deep (depth > 850 feet). Only one tube was found of lower depth with arsenic content 1.52 mg/L (Table-4) and rest nine tube well waters were arsenic free which is safe for drinking. The variation of arsenic concentration in this area depends on depth. A linear correlation of arsenic concentration with depth was found (Figure-12). Higher were the depth relatively lower was the arsenic concentration of the tube wells water in Kalaskati Union.

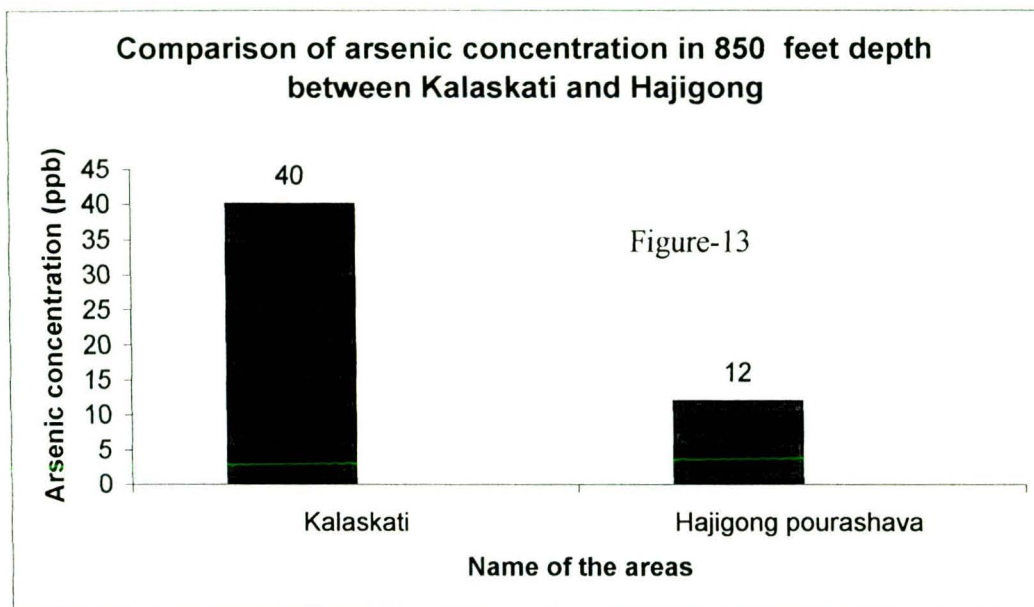


Figure-13

The two tube wells of same depth (850 feet) of which is in Hajigong Municipalities area and another is Kalaskati Union of Bakergong Thana were chosen for comparative study (Figure-13). An Arsenic content was found in higher amount (0.04mg/L) at Kalaskati Union of same depth than at Hajigong Thana (0.012 mg/L).

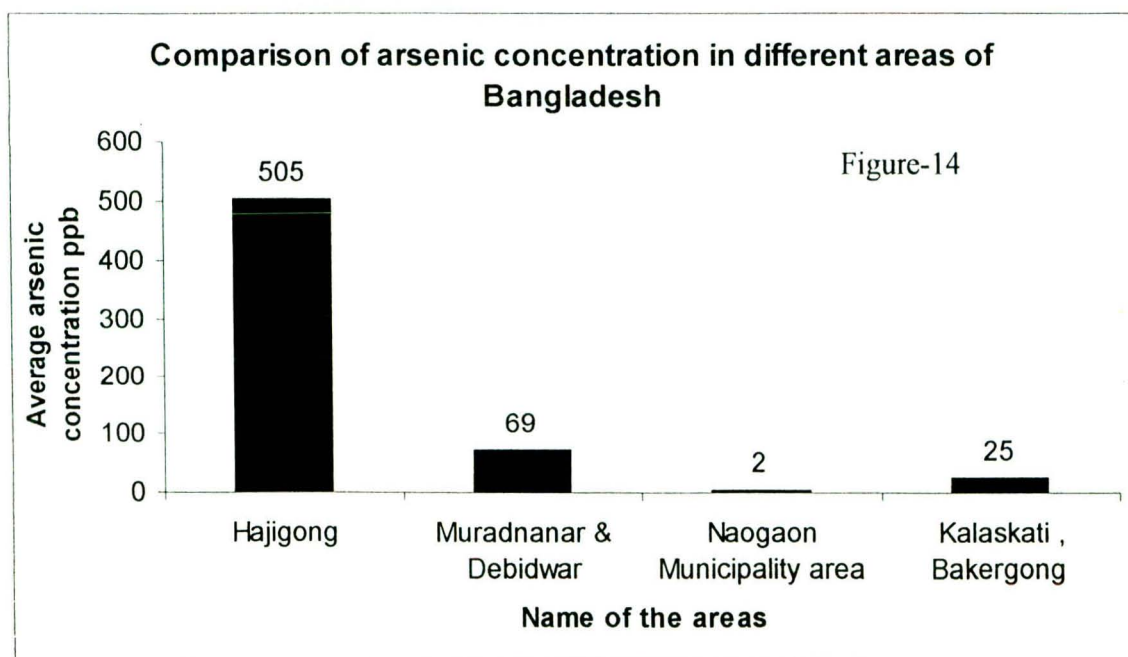


Figure-14

Comparing four selected locations of Bangladesh such as Hajigong Thana, Debidwar & Muradnagar Thana, Naogaon Municipality area and Kalaskati Union under Bakergong Thana, the average arsenic concentration was found in higher amount at Hajigong Thana (Figure-14).

It has been noted that the sources of arsenic in tube well water is geological phenomenon and its variation and deviation with different parameters depends on the changes of geological environment of sediments and different rocks.

In different countries the potential source of arsenic contamination is different. It was recognized that the source of arsenic is geological deposits in Bangladesh. There are two-prevailing hypothesis, one is pyrites oxidation due to the high withdrawn of water from shallow aquifer (40-300 feet) and another is oxy-hydroxide reduction due to a natural process and it seems that arsenic in groundwater has been present for thousands of years. Most of the arsenic affected area of Bangladesh and West Bengal, India, lie on the Quaternary Alluvial plains of the Bengal Basin such as the Ganges flood plain, the Meghna flood plain and the Brahmaputra flood plain. The arsenic bearing sediments from Himalayan and Garo-Rajmahal Hill has been carried by the Padma, the Meghna and the Brahmaputra rivers for thousands of years⁴⁴. As a result arsenic deposition is high at the lower stream of the above rivers.

Hajigong and Bakergong Thana under Chandpur and Barisal district respectively are situated at the lower stream of the Padma, the Meghna and the Brahmaputra rivers. This may be the reason of high arsenic concentration in these regions.

On the other hand, Debidwar and Muradnagar are under Comilla district and is 53 Kms faraway from Chandpur district, the arsenic concentration was relatively lower in this region than those of the above two regions. The Naogaon district is situated at the northern part of Bangladesh and it is not within the above flood plains, the tube well water is within the safe limit of arsenic for drinking purpose. The above-mentioned statement is needed for further examination.

In this study, skin of garlic which is first processed with bleaching powder for removing colour and dust materials. It was then used as adsorbents for removal of arsenic from

synthetic 1000 ppb water solution. The arsenic uptake capacity was determined after passing 10 L synthetic water through bed containing skin of garlic. About 96% arsenic was taken by one Kg skin of garlic from 10 L of water. The uptake capacity was gradually decreased with increasing the volume of water. About 45% arsenic was adsorbed by one Kg skin of garlic after passing 50 L of synthetic water (Table-6).

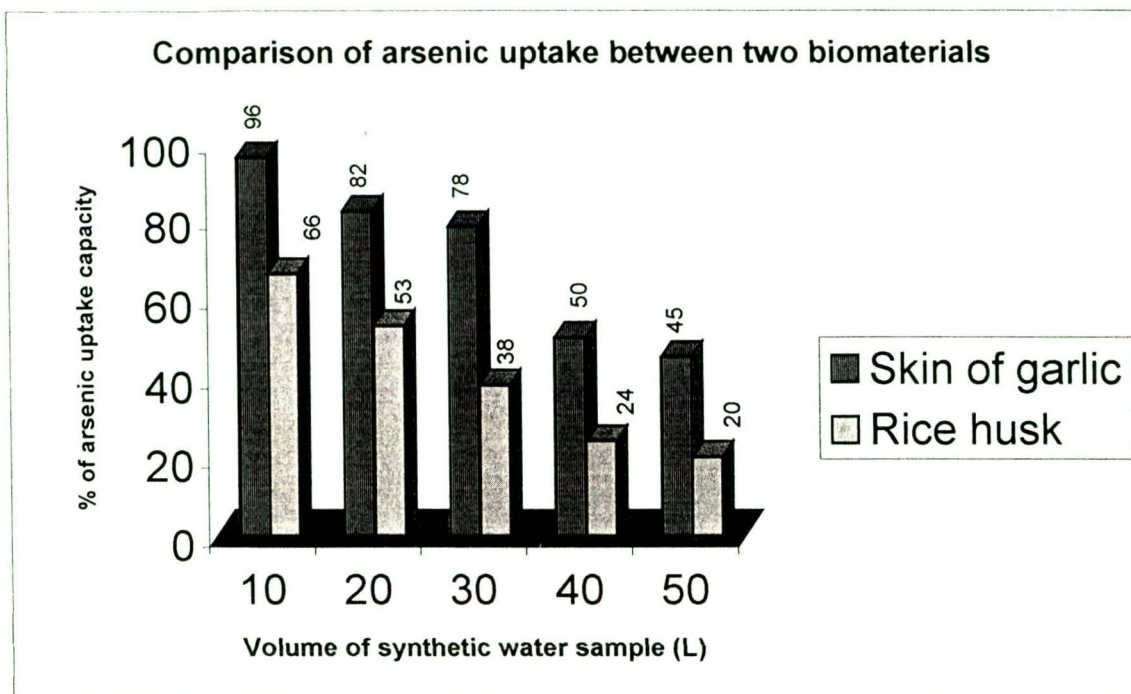


Figure-15

In consideration of rice husk, after 10 L synthetic water passed, the arsenic uptake capacity was about 66%, which was gradually decreased to 20% arsenic uptake after passing the 50 L of water. (Figure-15, Table-7)

The water from first bed falls into the second bed containing iron chips. Again arsenic concentration was determined after 10 L of water. The result of arsenic concentration after passing 10 L was 10 ± 0.5 ppb which was acceptable limit of World Health Organization (10 ppb) and finally its concentration was 16 ± 0.1 ppb after the 50 L water passed through the second bed which was the acceptable limit (0.05 mg/L) for Bangladesh (Table -8). This water from first bed contained rice husk that percolated into the second bed contained iron chips. The result of arsenic concentration after passing 10 L of water was 19 ± 0.8 ppb. (Figure-16, Table-9)

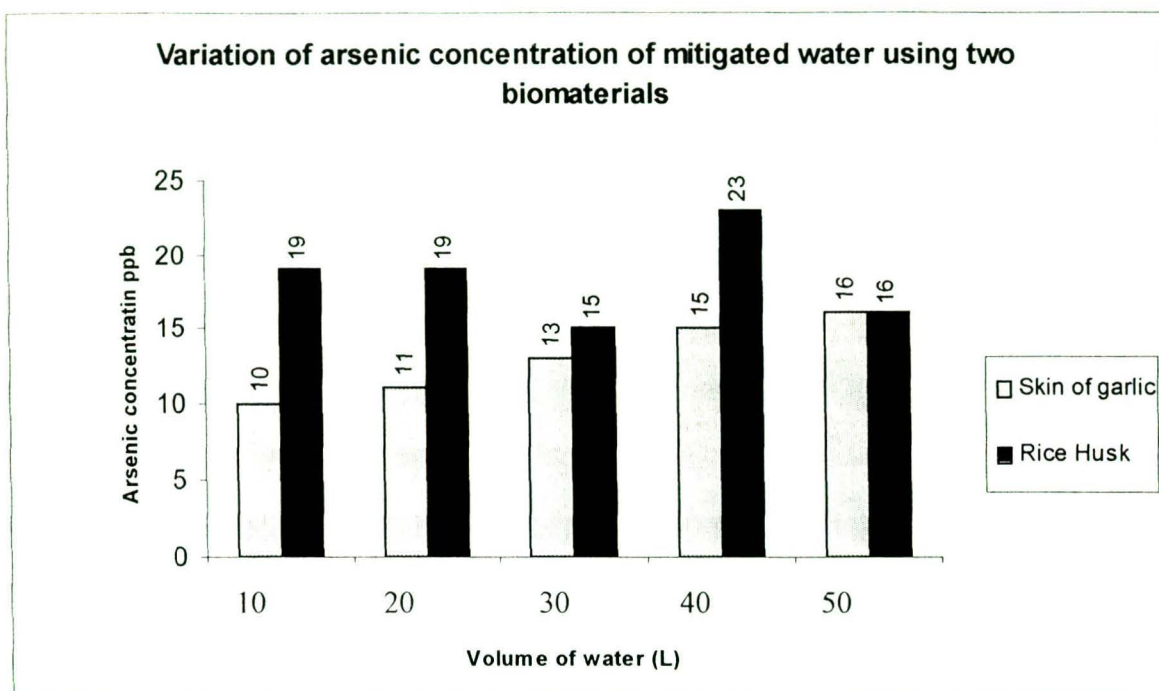
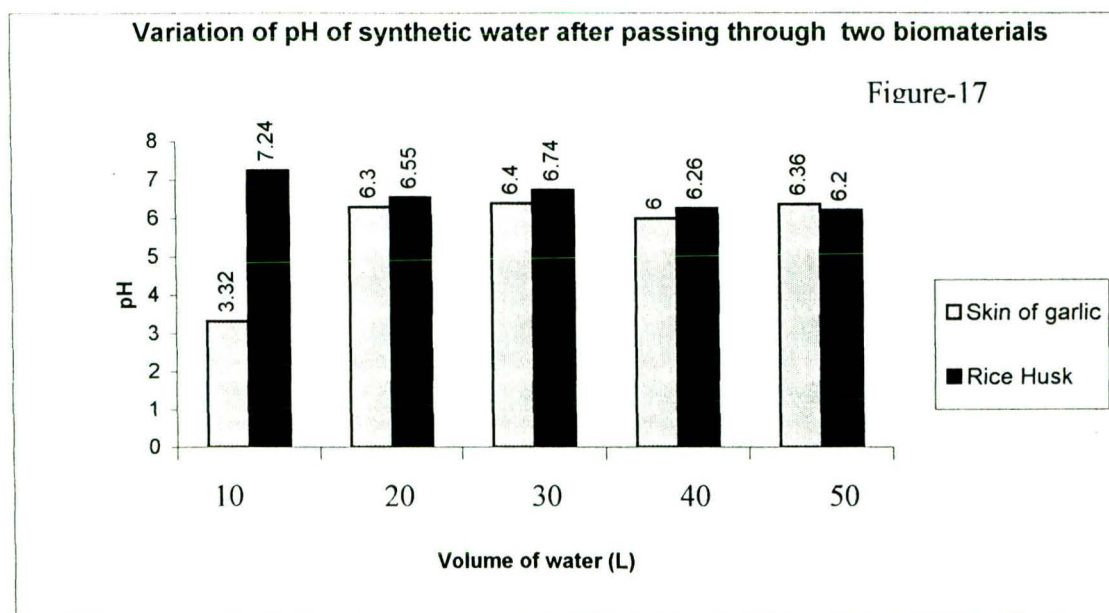


Figure-16

The pH of water samples after passing through 10 to 50 L water in the first bed containing biomaterials were varied from 3.32 to 6.36 for skin of garlic and 7.24 to 6.20 for rice husk is shown in the Figure-17. There is wide variation of pH between two biomaterials at first fraction of effluent (10 L).



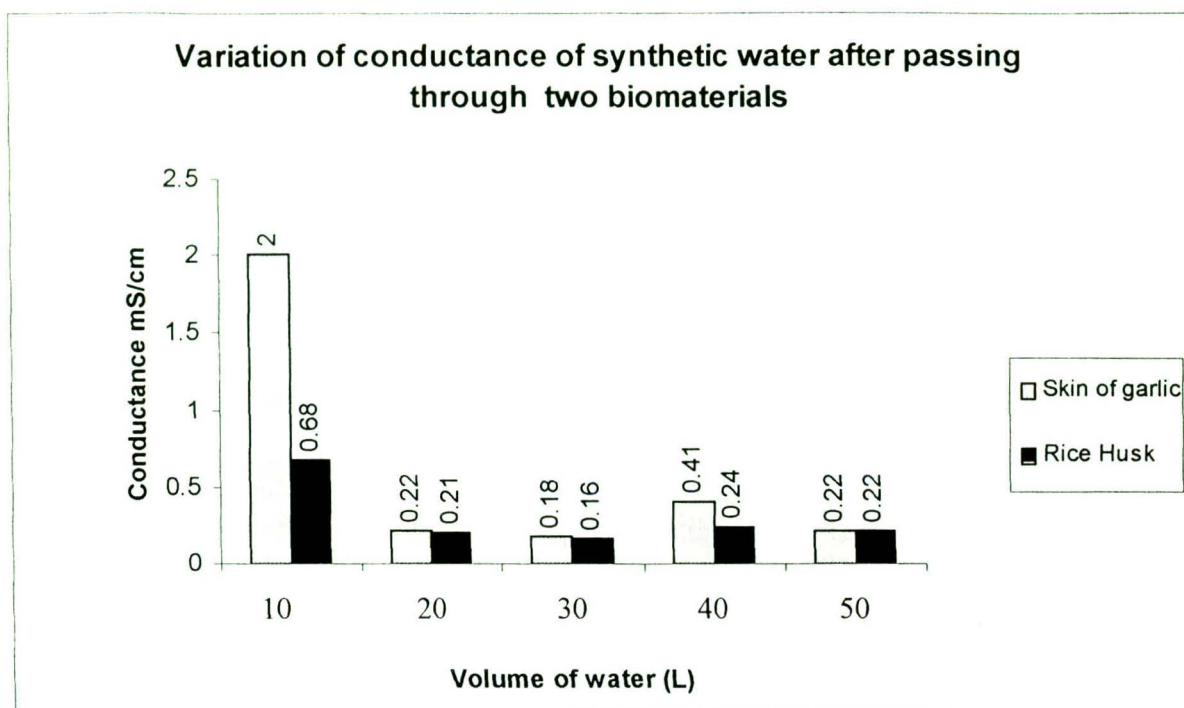


Figure-18

The conductance of water samples after passing through 10 to 50 L water in the first bed containing biomaterials were varied from 2.00 to 0.22 mS/cm for skin of garlic and 0.68 to 0.22 mS/cm for rice husk is shown in the Figure-18. There is also wide variation of conductance of two biomaterials at first fraction (10L) water. The conductance of first fraction (10 L) was high that indicate this fraction is more turbid than other four fractions (Figure-19, Table- 6&7).

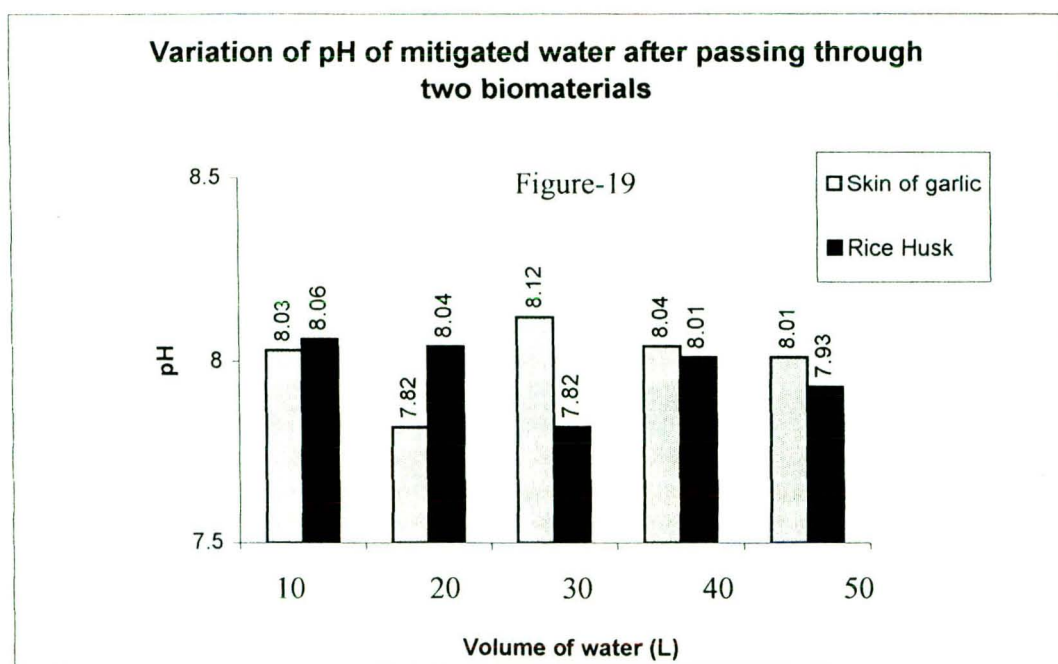


Figure-19

The pH of the arsenic mitigated water was within the range 7.82 to 8.12 and conductance was 0.34 to 1.8 mS/cm in both the cases. These waters are small extent of basic character that is within the permissible limit of drinking water. The conductance of mitigated water using skin of garlic was higher than using rice husk (Figure-20, Table-8 & 9).

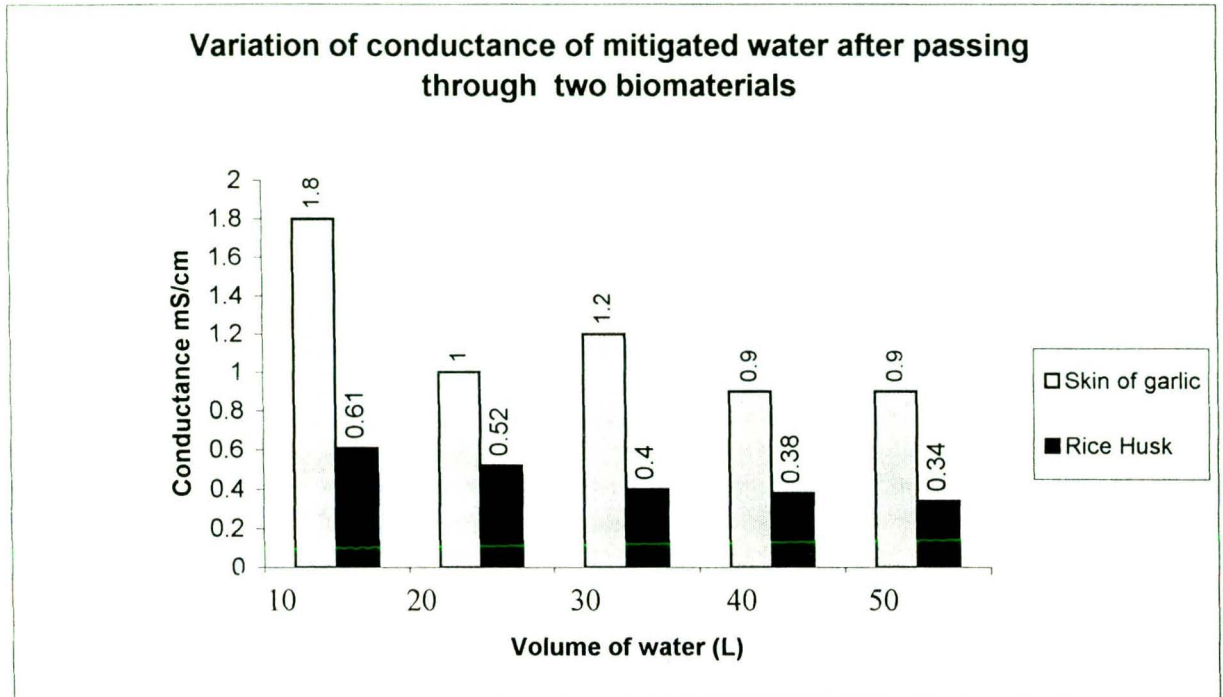


Figure-20

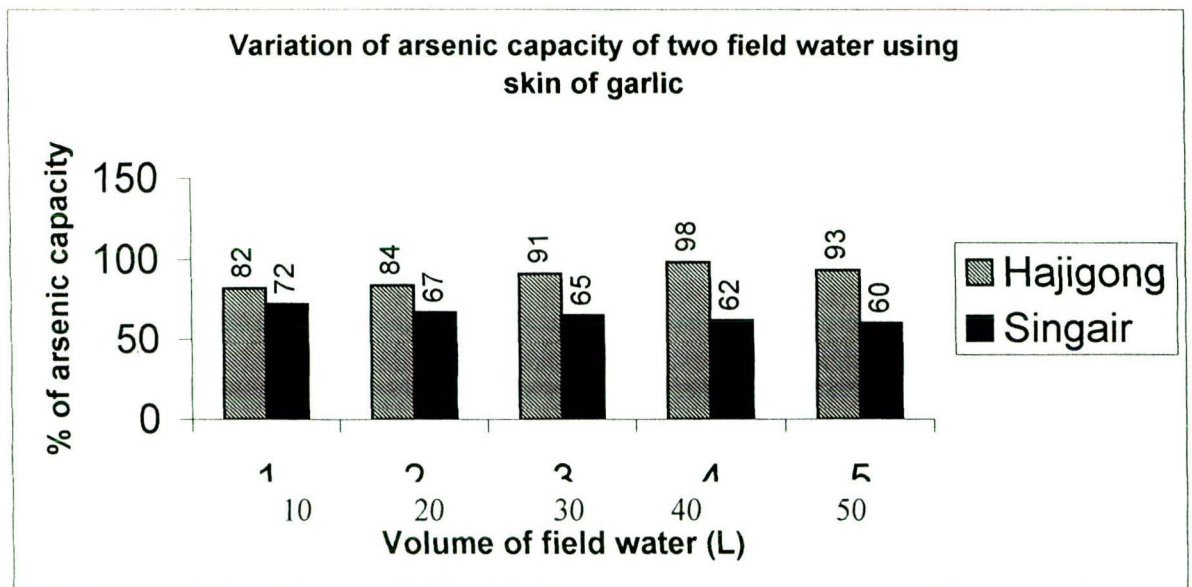


Figure-21

The arsenic uptake capacity was determined after passing 10 L synthetic water through bed containing skin of garlic of two-field water in Hajigong and Singair Thana. The initial arsenic concentration of Hajigong and Singair Thana was 377 and 166 ppb respectively. About 82% arsenic was taken by one Kg skin of garlic from 10 L of water. The uptake capacity was gradually increase with increasing the volume of water up to 40 L then 93% in 50 L water passing through the first bed for field water of Hajigong. However, about 72% arsenic was taken by one Kg skin of garlic from 10 L of field water. The uptake capacity was gradually decreased with increasing the volume of water (Figure-21).

About 60% arsenic was adsorbed by one Kg skin of garlic after passing 50 L of field water of Singair Thana.

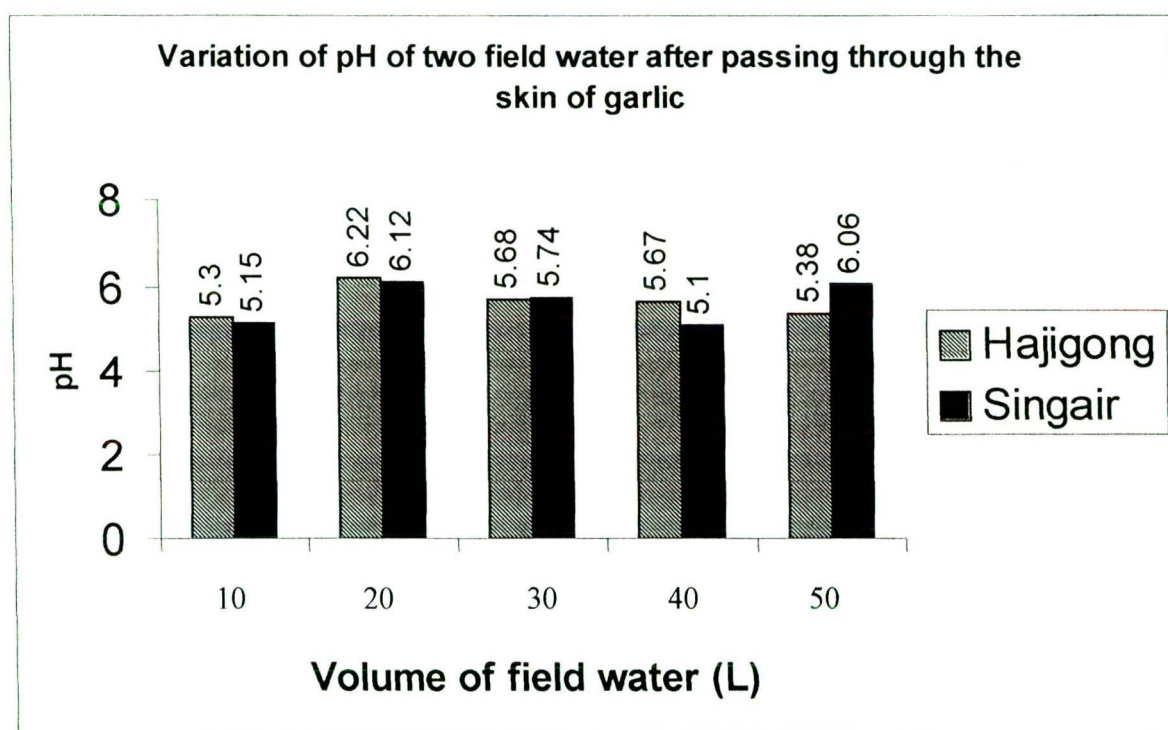


Figure-22

The pH of water samples after passing through 10 to 50 L water in the first bed containing biomaterials were varied from 5.3 to 6.22 of skin of garlic for field water of Hajigong and 5.1 to 6.06 of field water for Singair thana is shown in Figure-22. The conductance of water samples after passing through 10 to 50 L water in the first bed containing biomaterials were varied from 0.5 to 2.2 mS/cm for skin of garlic of field water Hajigong Thana and 0.7 to 1.8 mS/cm of field water for Singair Thana is shown in the Figure-23 (Table-10 & 11)

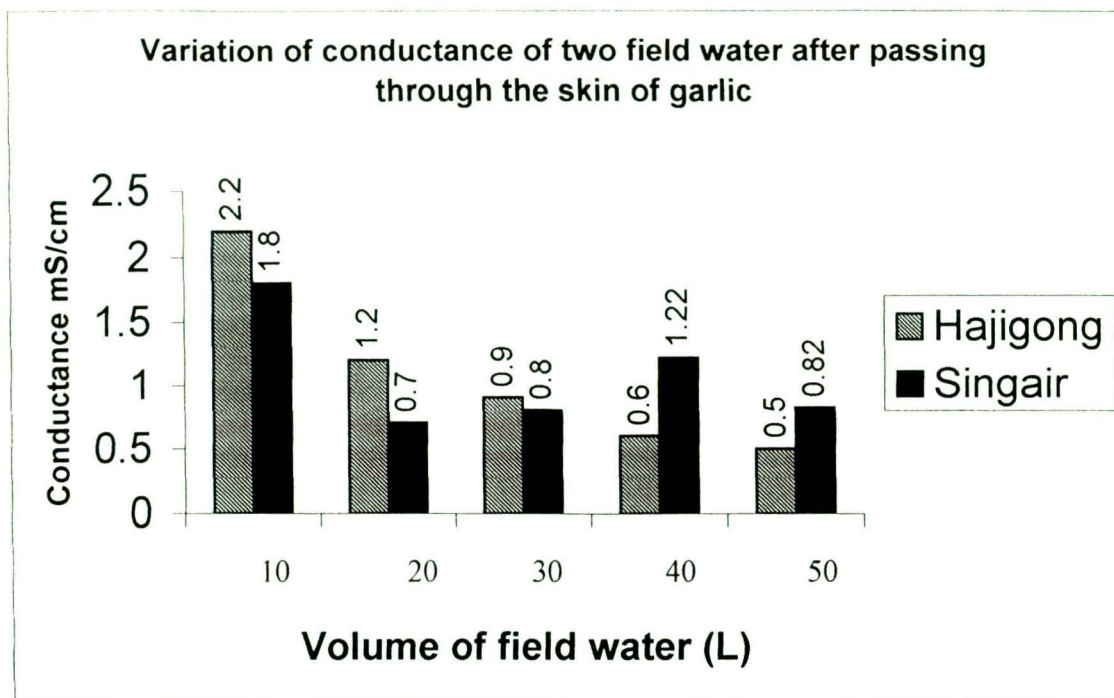


Figure-23

The pH of the arsenic mitigated field water in Hajigong Thana was within the range 7.82 to 8.06 and 7.36 to 7.76 of field water for Singair Thana is shown in the Figure-24. The water of Hajigong Thana was small in acidic character than water of Singair Thana which is within the acceptable limit.

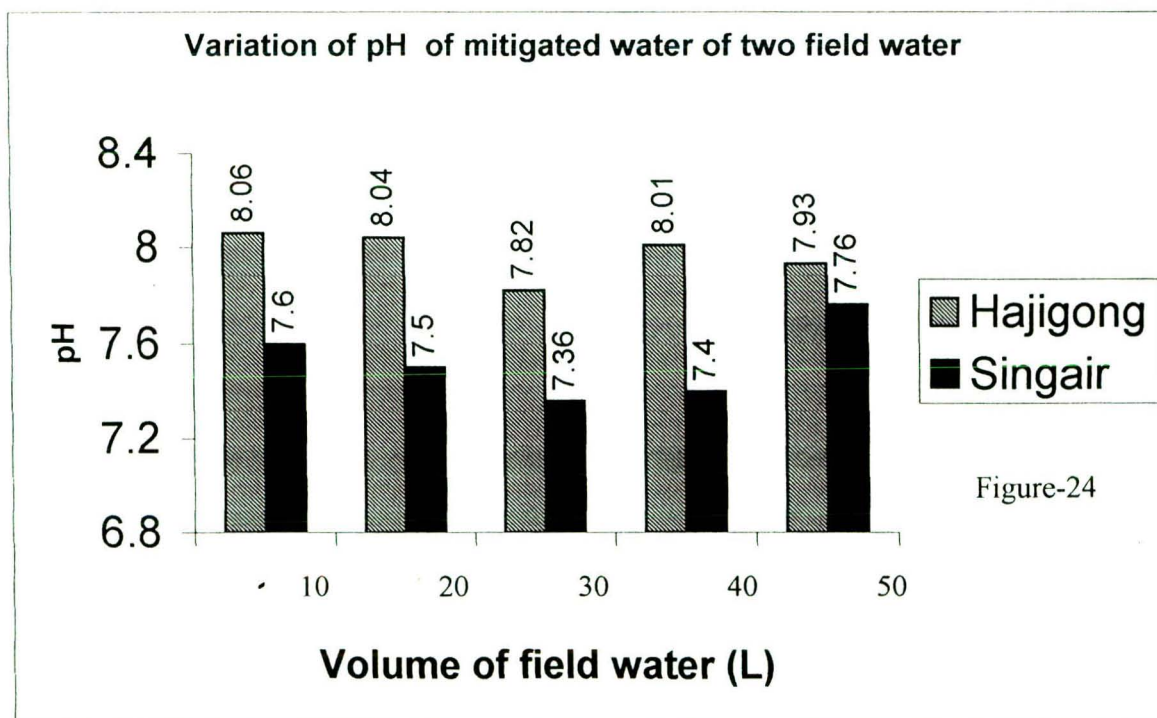


Figure-24

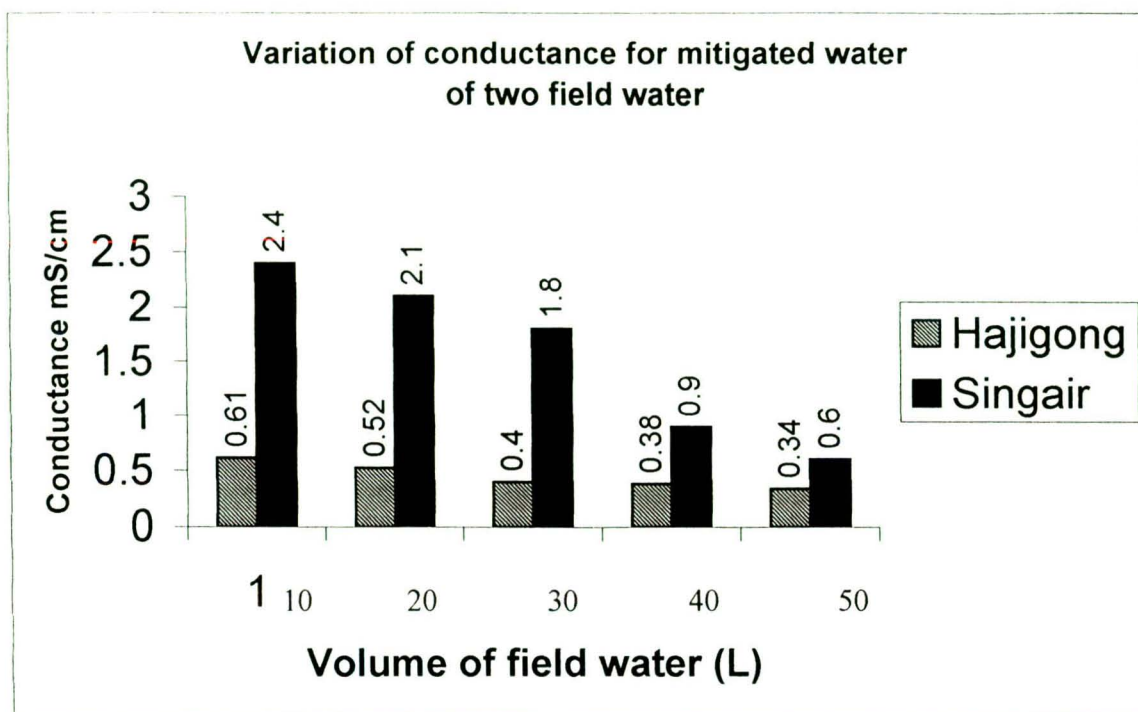


Figure-25

The conductance of the arsenic mitigated of field water of Hajigong Thana was within the range 0.34 to 0.061 mS/cm and 0.6 to 2.4 mS/cm of field water Singair Thana is shown in the Figure-25. The conductance of mitigated water of the field water of Hajigong Thana was less than water of Singair Thana.

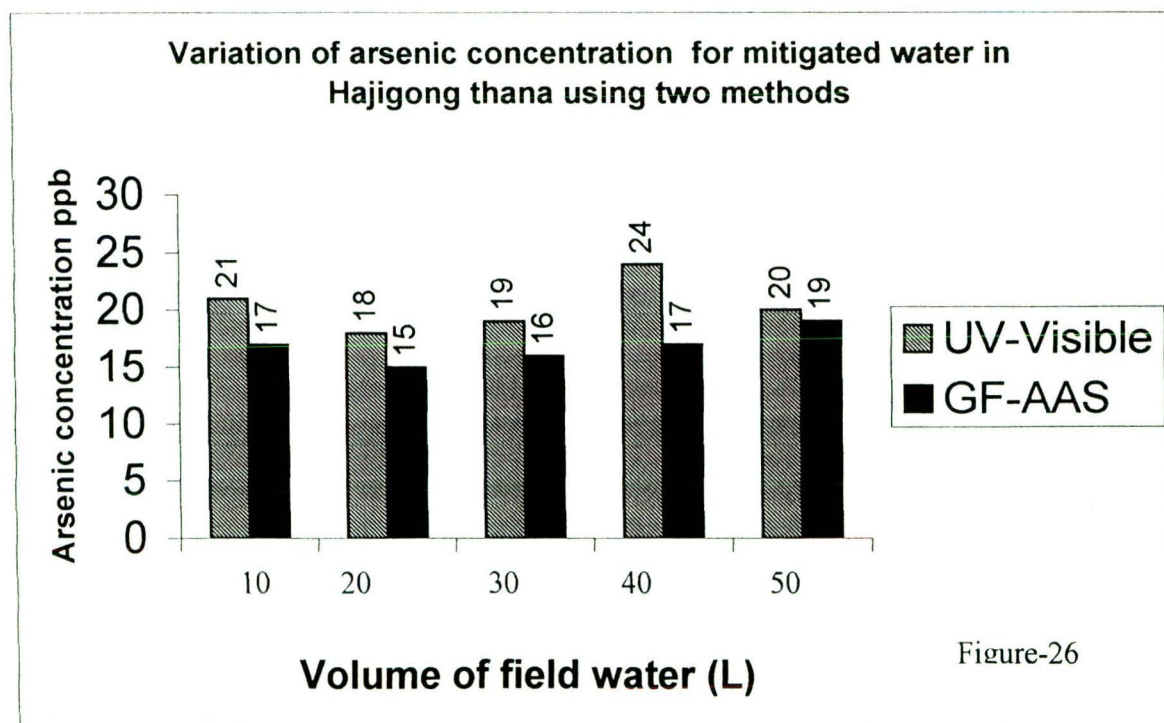


Figure-26

The initial arsenic concentration of the field water of Hajigong Thana was 377 ppb and 380 ppb by using the methods of UV-visible and GF-AAS respectively. However, arsenic concentration of mitigated water of Hajigong Thana was also determined by two methods which is shown in the Figure-26. Arsenic concentration in GF-AAS method was very low than UV-visible spectrophotometric method.

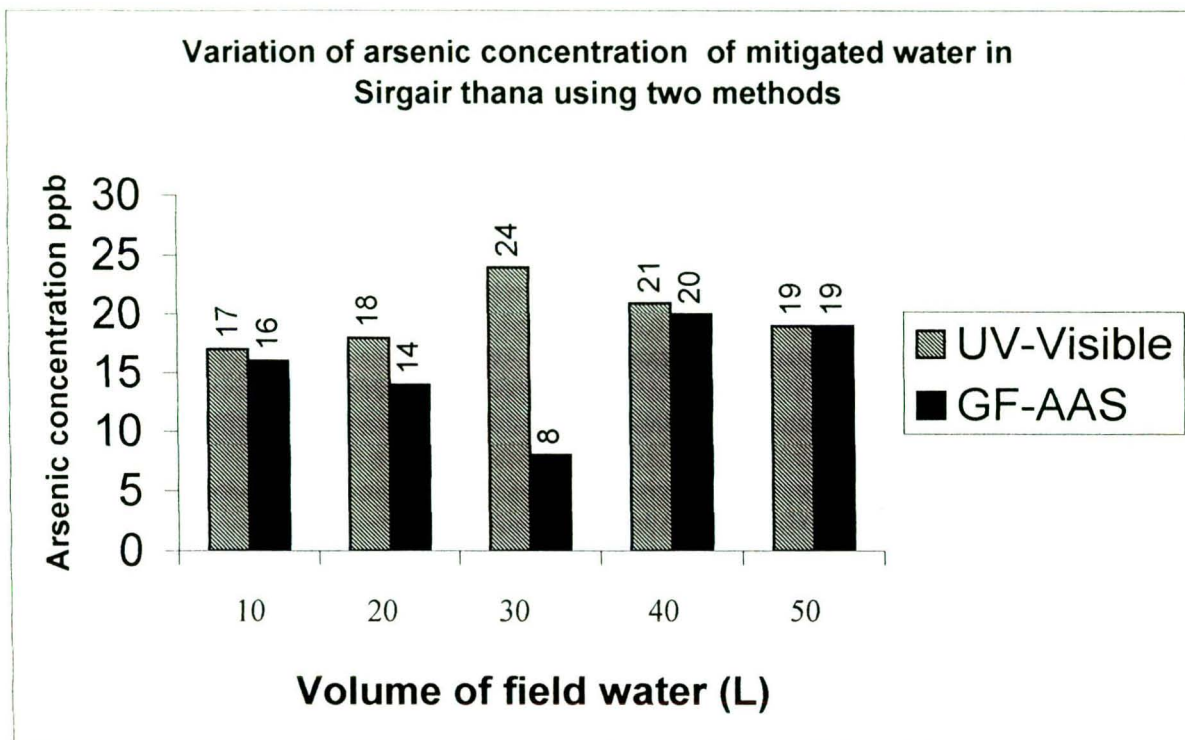


Figure-27

The initial arsenic concentration of the field water of Singair Thana was 160 ppb and 166 ppb by using the methods of UV-visible and GF-AAS respectively. The same phenomenon was also observed for the field water of Singair Thana (Figure-27, Table-12 & 13).

Arsenic has metalloid properties. It has capacity to attach as a metal with phenolic group of lignin in rice husk and also as a nonmetal with thiol group (-SH) containing substances ($\text{HS-CH}_2\text{-CH=CH}_2$)⁴⁵ in skin of garlic. As a result, the above-mentioned substances can remove certain amount of arsenic from contaminated water. Arsenic uptake capacity of skin of garlic is better than rice husk that may indicate the chemical affinity of arsenic to sulfur is higher than to phenolic group in rice husk.

Arsenic removing sites may be blocked with other species of field water as a result arsenic removal capacity of synthetic water was also better than field water.

CONCLUSION

CONCLUSION

1. Arsenic concentrations of 141 tube wells of Hajigong Thana under chandpur district are not same which indicates that occurrence of arsenic in tube well water is of geological phenomenon such as extent of water withdrawing, population density and present changed of geological environment.
2. High content of arsenic is found in shallow aquifer at Hajigong and its values are low at higher and lower depth of the tube wells. Arsenic concentration is also high of the aged tube wells of age limit between 6 to 10 years that indicates higher numbers of tube wells are present of those types at Hajigong. Certain tube wells which are within depth (750 to 950 feet) are found at Hajigong Thana. Some of these are safe for arsenic and some are contaminated with arsenic.
3. Comparing arsenic concentration of Naogaon Municipality area and Hajigong Thana, the tube wells water of Naogaon municipality area are with WHO guideline value (0.01 mg/L). It indicates that the geological condition of Northern part and Southeast parts of Bangladesh are not same. Comparing the arsenic concentration of Hajigong and Mradnagar and Debidwar Thana, the geological environment is almost same because distance between two places is about 110 Km.
4. In Kalaskati Union, arsenic concentration is low with increasing depth. Comparing two places, Hajigong Thana and Kalaskati Union, arsenic concentration is low in higher depth at Kalaskati and higher concentration in Hajigong at lower depth.
5. In consideration of two biomaterials skin of garlic and rice husk, arsenic uptake capacity of sink in garlic is better than rice husk. It is due to thiol group (-SH) content in skin of garlic and phenolic group in rice husk. Only certain extent of arsenic was removed by the above two biomaterials from the 1000 ppb arsenic containing synthetic water sample. The zero-valent iron chips removed the rest of the arsenic from synthetic water sample.
6. pH and conductance of water which were passed through the biomaterials, zero-valent iron chips and wood charcoal were within the acceptable limit both in synthetic and field water.

7. Comparing the synthetic and field water, arsenic uptake capacity was higher in synthetic than field water. Another species (cations, anions, and small particles etc) of field water may be attached to the arsenic removal sites of two biomaterials.
8. Arsenic content of field and its mitigated water was quantified by the GF-AAS and UV-visible methods. There was no wide range difference between the results of two methods.
9. For mitigation, the available filters are commercialized before they are completely tested for their efficiency, workability, durability and uptake capacity of the ground water available in various endemic areas of Bangladesh. As a result, all commercial filters are failed to meet the challenges for providing arsenic free drinking water.
10. Currently available database on arsenic problem in Bangladesh is very limited and much of the available data are not quality assured. Hence, the nature and the extent of arsenic problem is still largely unknown.

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ANNEXURE (TABLES)

ANNEXURE (TABLES)

Table: 1 Arsenic concentration of ground water samples along with certain description of the tube wells

Serial No.	Sample code	Tube well Identity & Sampling Stations of Hajigong Thana at Chandpur district	Depth of the tube well (feet)	Tube well marked	Year of installation	Arsenic concentration mg/L
1	SM-2	Belghor	70	Red	1985	0.539
2	SM-3	Belghor	70	Red	1987	0.330
3	SM-4	Belghor	50	Unmarked	1987	0.445
4	SM-5	Belghor	60	Red	1970	0.264
5	SM-6	Belghor,	65	Red	1988	0.240
6	SM-8	Belghor	70	Red	1992	0.500
7	SM-9	Belghor	65	Red	1990	0.268
8	SM-10	Belghor	75	Red	1998	0.528
9	SM-11	Belghor	70	Red	1987	0.171
10	SM-13	Belghor	70	Red	1993	0.290
11	SM-14	Belghor	70	Red	1994	0.108
12	SM-15	Belghor	75	Red	1992	0.243
13	SM-16	Belghor	70	Red	1996	0.210
14	SM-17	Katali	70	Red	1985	0.598
15	SM-19	Katali	70	Red	1985	0.539
16	SM-20	Katali	70	Red	1985	0.466
17	SM-22	Katali	70	Red	1985	0.239
18	SM-23	Katali	70	Red	1985	0.467
19	SM-24	Bodorpur	70	Red	1985	0.201
20	MS-25	Alipur	70	Red	1985	0.398
21	ML-63a	Hatila	70	Red	1985	0.638
22	ML-65	Hatila	70	Red	1985	0.557
23	ML-59	Hatila	70	Red	1985	0.639
24	ML-61	Hatila	70	Red	1985	0.621
25	ML-63b	Hatila	60	Red	1980	0.599
26	ML-64	Hatila	80	Red	2000	0.569
27	ML-51	Hatila	70	Red	1997	0.556

Table continued.....

Serial No.	Sample code	Tube well Identity & Sampling Stations of Hajigong Thana at Chandpur district	Depth of the tube well (feet)	Tube well marked	Year of installation	Arsenic concentration mg/L
28	ML-52	Hatila	70	Red	1995	0.567
29	ML-53	Hatila	70	Red	1984	0.421
30	ML-43	Hariyan	72	Red	1994	0.290
31	ML-45	Hariyan	70	Red	1992	0.588
32	ML-46	Hariyan	70	Red	1992	0.653
33	ML-47	Hariyan	70	Red	1992	0.477
34	ML-49	Hariyan	70	Red	1993	0.509
35	ML-50	Hariyan	70	Red	1995	0.527
36	ST-73	Ahmedpur	75	Red	1993	0.232
37	ST-75	Ahmedpur	70	Red	1989	0.332
38	ST-76	Ahmedpur	125	Red	1998	0.631
39	ST-77	Ahmedpur	75	Red	1995	0.511
40	ST-79	Ahmedpur	60	Red	1990	0.152
41	ST-80	Ahmedpur	70	Red	1987	0.600
42	ST-78	Ahmedpur	75	Red	1993	0.571
43	ST-81	Ahmedpur	70	Red	1996	0.410
44	ST-82	Ahmedpur	75	Red	1994	0.309
45	ST-84	Ahmedpur	75	Red	1998	0.572
46	ST-94	Mohammadpur	70	Red	1989	0.587
47	ST-95	Mohammadpur	70	Red	1975	0.579
48	ST-97	Mohammadpur	70	Red	1993	0.227
49	ST-101	Mohammadpur	90	Red	1999	0.480
50	ST-102	Mohammadpur	70	Red	1980	0.193
51	ST-103	Mohammadpur	75	Red	1992	0.273
52	ST-112	Mohammadpur	70	Red	1989	0.240
53	ST-105	Mohammadpur	70	Red	1988	0.119
54	ST-106	Mohammadpur	80	Unmarked	2000	0.117
55	ST-109	Mohammadpur	70	Red	1986	0.225
56	NM-01	Ramchandrapur	65	Red	1970	0.116

Table continued...

Serial No.	Sample code	Tube well Identity & Sampling Stations of Hajigong Thana at Chandpur district	Depth of the tube well (feet)	Tube well marked	Year of installation	Arsenic concentration mg/L
57	NM-02	Ramchandrapur	60	Red	1991	0.232
58	NM-03	Ramchandrapur	55	Red	1993	0.131
59	NM-06	Ramchandrapur	60	Red	1995	0.208
60	NM-07	Ramchandrapur	70	Red	1990	0.125
61	NM-04	Ramchandrapur	70	Red	1993	0.237
62	NM-08	Ramchandrapur	60	Red	1986	0.114
63	NM-09	Ramchandrapur	115	Red	1990	0.333
64	NM-10	Natohara	75	Unmarked	1999	0.307
65	NM-11	Natohara	70	Unmarked	1996	0.107
66	NM-12	Natohara	70	Unmarked	1992	0.116
67	NM-14	Bolakhal	80	Unmarked	1999	0.083
68	NM-16	Bolakhal	70	Red	1997	0.206
69	NM-17	Bolakhal (South)	70	Unmarked	1996	0.219
70	NM-18	Bolakhal	70	Unmarked	1996	0.284
71	NM-20	Khatrabillyie	70	Unmarked	1995	0.114
72	NM-21	Palishara	70	Unmarked	1993	0.245
73	NM-22	Palishara	70	Unmarked	1993	0.493
74	NM-23	Palishara	70	Unmarked	1998	0.331
75	NM-24	Palishara	120	Unmarked	1993	0.116
76	NM-25	Palishara	45	Unmarked	1996	0.664
77	NM-26	Islampur	60	Unmarked	1994	0.368
78	NM-27	Pachay	60	Unmarked	1950	0.261
79	NM-28	Pachay	65	Unmarked	1997	0.248
80	NM-29	Pachay	65	Unmarked	2000	0.196
81	NM-30	Varearpar	70	Red	1993	0.200
82	NM-31	Varearpar	70	Red	1993	0.314
83	NM-32	Varearpar	70	Red	1982	0.352
84	NM-33	Varearpar	70	Red	1998	0.347
85	NM-34	Varearpar	70	Red	1998	0.303
86	NM-35	Kashipur	75	Unmarked	1996	0.137
87	NM-52	Kashipur	70	Red	1998	0.125

Table continued...

Serial No.	Sample code	Tube well Identity & Sampling Stations of Hajigong Thana at Chandpur district	Depth of the tube well (feet)	Tube well marked	Year of installation	Arsenic concentration mg/L
88	NM-37	Belcho	75	Red	1980	0.179
89	NM-39	Randonimora	70	Red	1996	0.116
90	NM-43	Moninag	65	Unmarked	1978	0.117
91	NM-44	Moninag	50	Red	1998	0.116
92	NM-45	Moninag	80	Red	1986	0.653
93	NM-46	Rajargaon	70	Red	1997	0.397
94	NM-47	Rajargaon	90	Red	1996	0.272
95	NM-48	Rajargaon	70	Red	1996	0.292
96	NM-49	Rajargaon	90	Red	1990	0.423
97	NM-51	Sripur	70	Red	1994	0.190
98	NM-52	Sripur,	70	Red	1998	0.117
99	NM-53	Sripur	65	Red	1996	0.201
100	NM-55	Sripur	70	Red	1996	0.296
101	NM-56	Bolakhal	55	Red	1990	0.106
102	NM-38	Randonimora	80	Red	1981	0.432
103	NM-40	Randonimora	70	Red	1985	0.302
104	NM-41	Randonimora	70	Red	1970	0.232
105	HJ-1A	Toragor	160	Red	1988	1.317
106	HJ-1B	Toragor	60	Red	2000	0.706
107	HJ-3A	Toragor	60	Red	1987	1.557
108	HJ-5	Toragor	65	Red	1989	0.410
109	HJ-1	Raychar	150	Red	2000	0.454
110	HJ-2	Utter Raychar	95	Red	1999	1.030
111	HJ-4	Anatoli	75	Red	1998	0.238
112	HJ-5	Anatoli	105	Red	1999	0.692
113	HJ-7	Anatoli	70	Red	1970	0.788
114	HJ-14	Doyalia	80	Red	1990	0.794
115	HJ-30	Doyalia	90	Red	1992	1.052
116	HJ-23	Doyalia	80	Red	1997	0.747
117	HJ-17	Doyalia	75	Red	1996	1.590

Table continued...

Serial No.	Sample code	Tube well Identity & Sampling Stations of Hajigong Thana at Chandpur district	Depth of the tube well (feet)	Tube well marked	Year of installation	Arsenic concentration mg/L
118	HJ-24	Doyalia	60	Red	1988	1.498
119	HJ-27	Doyalia	80	Red	1990	1.322
120	HJ-19	Doyalia	75	Red	1988	1.243
121	HJ-29	Doyalia	80	Red	1992	0.862
122	HJ-15	Doyalia	65	Red	1969	0.379
123	HJ-16	Doyalia	65	Red	1994	1.028
124	HJ-26	Doyalia	75	Red	1970	0.894
125	HJ-25	Doyalia	70	Red	1995	0.780
126	HJ-28	Doyalia	70	Red	1992	1.052
127	HJ-5A	Doyalia	70	Red	1993	0.957
128	HJ-4B	Doyalia	75	Red	1997	1.340
129	HJ-2A	Sodia	90	Red	1989	1.351
130	HJ-3B	Matoyan	90	Red	1996	1.250
131	HJ-1A	Matoyan	110	Red	1999	1.137
132	HJ-20	Matoyan	85	Red	1995	0.958
133	HJ-2B	Matoyan	75	Red	1998	1.118
134	HJ-22	Matoyan	65	Red	1988	0.527
135	HJ-18	Matoyan	105	Red	1990	1.161
136	HJ-102	Matoyan	65	Red	1995	0.569
137	HJ-104	Railway station	95	Red	1993	0.684
138	HJ-109	Toragore	75	Red	1994	2.604
139	HJ-114	Toragore	75	Red	2000	0.609
140	HJ-117	Toragore	85	Red	1992	1.021
141	HJ-118	Toragore	65	Red	1997	0.586

Table 2 Arsenic concentration of ground water samples along with certain description of the tube well

Serial no	Sample code	Sampling station and tube well identity at Debidwar and Murad nagar	Depth of the tube well (feet)	Tube well marked	Year of installation	Arsenic concentration mg/L
1	DS	Debidwar	92	Red	1981	0.185
2	SL	Debidwar	72	Red	1990	0.055
3	TL	Debidwar	165	Red	1997	0.053
4	TL-1	Debidwar	120	Red	1990	0.034
5	ML	Debidwar	75	Untreated	1985	0.074
6	AL	Debidwa	230	Untreated	1998	0.036
7	BL	Debidwar	75	Untreated	1989	0.06
8	NH	Muradnagar	90	Untreated	1988	0.035
9	NH-1	Company gong, Muradnagar	120	Untreated	1987	0.178
10	NE	Muradnagar	100	Untreated	1972	0.041
11	HL	Debidwar,	70	Untreated	1999	0.014

Table # 3 Arsenic concentration of ground water samples along with certain description of the tube well

Serial no.	Sample code	Sampling station and tube well identity at Naogaon Municipality area	Depth of the tube well (feet)	Tube well marked	Year of installation	Arsenic concentration mg/L
1	D1	Bangabaria	65	Untreated	1995	0.0017
2	D2	Per-Naogaon	80	Untreated	1996	0.0030
3	D3	Per-Naogaon	45	Untreated	1978	0.0021
4	D4	Masterpara	40	Untreated	1982	0.0015
5	D5	Naogaon Govt. College	85	Untreated	1995	0.0019
6	D6	Masterpar	80	Untreated	1977	0.0018
7	D7	Chakdeb	50	Untreated	1972	0.0032
8	D8	Naogaon Zilla School	90	Untreated	1980	0.0016
9	D9	South Hat-Naogaon, Kalitola	85	Untreated	1986	0.0031
10	D10	Bhovanipur	70	Untreated	1972	0.0036
11	D11	Saluka	75	Untreated	1992	0.00053
12	D12	Chaktataru	90	Untreated	1990	0.0024

Table #4 Arsenic concentration of ground water samples along with certain description of the tube well

Serial no	Sample code	Sampling station and tube well identity at Kalaskati, Bakergong, Barisal	Depth of the tube well (feet)	Tube well marked	Year of installation	Arsenic concentration mg/L
1	BM-1	Kalaskati	1050	Green	1990	0.028
2	UP-2	Kalaskati	1100	Green	1985	0.017
3	PS-3	Kalashkati	1000	Green	1997	0.029
4	TK-4	Kalaskati	105	Red	1996	1.524
5	KH-5	Kalaskati	1000	Green	1995	0.034
6	KG-6	Kalaskati	1020	Green	1998	0.037
7	KD-7	Kalaskati	1500	Green	1987	0.013
8	MK-8	Kalaskati	850	Green	1998	0.04
9	YB-9	Kalaskati	1050	Green	1990	0.031
10	TR-10	Kalaskati	850	Green	1992	0.004

Table: # 5 Arsenic concentration of ground water samples along with certain description of the tube wells

Serial No.	Sample code	Tube well Identity & Sampling Stations of Hajigong Thana at Chandpur district	Depth of the tube well (feet)	Tube well marked	Year of installation	Arsenic concentration mg/L
142	HJ-6	Anatoli	750	Green	1999	0.002
143	HJ-13	Doyalia	950	Green	1999	1.148
144	ML-62	Hatila	800	Green	1999	0.014
145	ML-48	Hariyan	900	Green	1999	0.007
146	ST -99	Mohammadpur	800	Unmarked	1999	0.0012
147	ST-105	Mohammadpur	800	Green	2000	0.067
148	NM-48	Rajargaon	850	Red	1996	0.292
149	NM-50	Rajargaon	800	Green	1999	0.025
150	NM-42	Hajigong Poursava water supply	850	Green	2000	0.012

Table 6: Uptake capacity of skin of garlic for the synthetic water

Volume of water, L	Effluent conc. ppp	Uptake capacity %	pH	Conductance mS/cm
10	1000	96	3.32	2.00
20		82	6.30	0.22
30		78	6.40	0.18
40		50	6.00	0.41
50		45	6.36	0.22

Table 7: Uptake capacity of rice husk for the synthetic water

Volume of water, L	Effluent conc. ppp	Uptake capacity %	pH	Conductance mS/cm
10	1000	66	7.24	0.68
20		53	6.55	0.21
30		38	6.74	0.16
40		24	6.26	0.24
50		20	6.20	0.22

Table 8: Concentration of arsenic mitigated using used skin of garlic

Volume of water, L	Effluent conc. ppp	Arsenic concentration ppb	pH	Conductance mS/cm
10	1000	10±0.5	8.03	1.8
20		11±0.3	7.82	1.0
30		13±0.1	8.12	1.2
40		15±0.4	8.04	0.9
50		16±0.1	8.01	0.9

Table 9: Concentration of arsenic mitigated water using rice husk

Volume of water, L	Effluent conc. ppp	Arsenic concentration ppb	pH	Conductance mS/cm
10	1000	19±0.8	8.06	0.61
20		19±0.4	8.04	0.52
30		15±0.2	7.82	0.40
40		23±0.7	8.01	0.38
50		16±0.1	7.93	0.34

Table 10: Uptake capacity of Skin of garlic for field water –1 (Hajigong)

Volume of water, L	Effluent conc. ppb	Uptake capacity %	pH	Conductance mS/cm
10	377	82	5.30	2.2
20		84	6.22	1.2
30		91	5.68	0.9
40		98	5.67	0.6
50		93	5.38	0.5

Table 11: Uptake capacity of Skin of garlic for field water –2 (Singair)

Volume of water, L	Effluent conc. ppb	Uptake capacity %	pH	Conductance mS/cm
10	166	72	5.15	1.8
20		67	6.12	0.7
30		65	5.74	0.8
40		62	5.10	1.22
50		60	6.06	0.82

Table 12: Concentration of arsenic mitigated water in field water-1 (Hajigong) determined by UV-visible spectrophotometer and GF-AAS method.

Volume of water L	UV-visible method		GF-AAS method		pH	Conductance mS/cm
	Effluent conc. ppb	Arsenic concentration ppb	Effluent conc. ppb	Arsenic Concentration ppb		
10	377	21±0.2	380	17±0.4	8.06	0.61
20		18±0.5		15±0.2	8.04	0.52
30		19±0.9		16±0.2	7.82	0.40
40		24±0.4		17±0.2	8.01	0.38
50		20±1.0		19±0.9	7.93	0.34

Table 13: Concentration of arsenic mitigated water in field water-2 (Singair) determined by UV-visible spectrophotometer and GF-AAS method.

Volume of water L	UV-visible method		GF-AAS method		pH	Conductance mS/cm
	Effluent conc. ppb	Arsenic concentration ppb	Effluent conc. ppb	Arsenic Concentration ppb		
10	160	17±0.2	166	16±0.56	7.60	2.4
20		18±0.23		14±0.29	7.50	2.1
30		24±0.20		8±0.95	7.36	1.8
40		21±0.56		20±0.2	7.40	0.9
50		19±0.23		19±0.06	7.76	0.6