An approach to reduce arsenic from drinking water and rice grain during cooked rice preparation

A **Thesis** submitted
for the partial fulfilment of the continuous assessment of
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UNDERTAKING BY THE STUDENT

I, Urshita Mazumdar hereby declare that this thesis titled "An approach to reduce arsenic from drinking water and rice grain during cooked rice preparation" submitted for the partial fulfilment of the continuous assessment of Master of Technology in Environmental Biotechnology to the School of Environmental Studies (SOES), Jadavpur University, Kolkata – 700032 is record of original work done by me under the guidance of Dr. Tarit Roychowdhury.

This thesis is written in my own words, with reference to several published scientific papers which have been adequately cited from the original sources. It is also to be declared that this thesis does not contain any fictional or misreported data or result.

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Table of Contents

Chapter 7

Chapter 8

OBJECTIVE 2:

Chapter 9

Chapter 10

Chapter 11

Chapter 12

Abstract

Arsenic contaminated water is one of the major threats to present human health. Arsenic polluted water not only affects drinking quality of water but it also affects the rice cultivation and other various cultivation which uses arsenic affected water for irrigation purpose. Rice is one of the major staple foods all over the world. When rice is cultivated using arsenic contaminated water, the rice grains also gets contaminated. As a result its consumption affects human health. In this research an effort has been made to remove arsenic contamination from drinking water and rice grains. For remediation of arsenic contaminated water, iron nanoparticle infused membrane (mFeNP) been used, varying the concentration of iron nanoparticles infused in membrane. A significant reduction of arsenic was observed varying from 28-72% depending on the concentration of ion nanoparticles infused in membranes. For remediation of arsenic from rice grains, the rice grains were cooked in water (As<3µg/L). Rice grains were first washed then soaked and then cooked using water (As<3µg/L). After each step the water was discarded and the arsenic concentrations were estimated for rice grains. It was observed there was significant reduction of arsenic concentration (61-81%) after each step once the water was discarded. Once the cooking was done, the arsenic estimation of cooked rice and TDW (total discarded water) was done. The cooked rice showed appreciable level of arsenic reduction concentration (74-88%) and the TDW had arsenic (30-68µg/L) in it. This shows flow of arsenic from rice grains to water. Two varities of rice grains were taken for the work: - Minikit and Maharaj.

Keywords: Arsenic contamination, remediation, water, iron nanoparticle, membrane, rice grains, cooked rice, arsenic flow.

Chapter 1

Introduction

Introduction

Water is one of the essential substance and key element for survival of lives on earth. It covers about 71% of earth's surface, however when it comes to availability of safe water for various purposes, many people don't have proper access for it. Water quality is one of the factors which determine the suitability of water for a specific use based on chosen physical, chemical, and biological characteristics. Water quality is influenced by a wide range of natural and human influences. The most significant of the natural influences are geological, hydrological and climatic, since these affect the quantity and the quality of water available.

Their influence is usually greatest when existing water quantities are low and maximum use must be made of the limited resource; for example, high salinity is a frequent problem in arid and coastal areas. If the economic and technical supplies are available, seawater or saline groundwater can be desalinated but in many situations this is not possible.

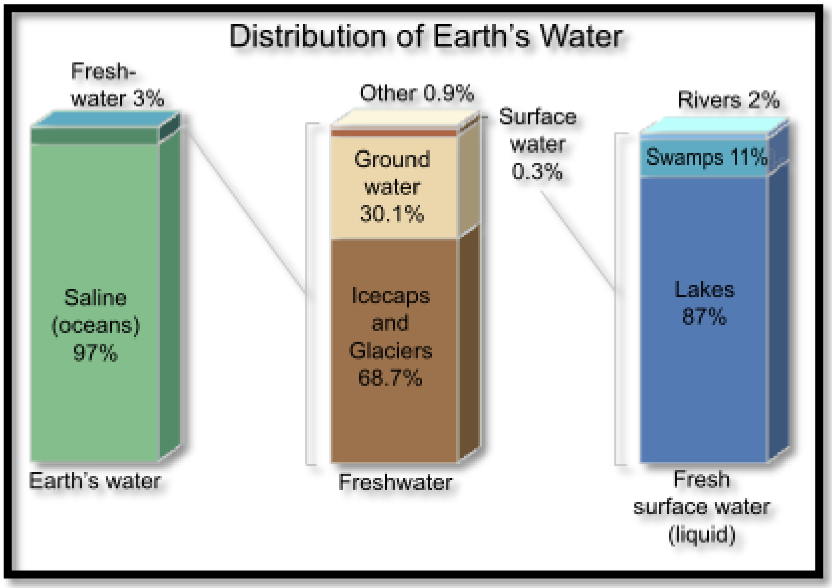


Fig.1.1 Graphical representation of distribution of Earth's water (source: Yaccup et al., 2012)

Thus, although water may be accessible in sufficient quantities, it’s inappropriate quality limits the uses that can be made of it. Although the natural ecosystem is in harmony with natural water quality, any significant changes to water quality will usually be disruptive to the ecosystem (Phadatare et al., 2016).

1.1 Increasing Groundwater contamination

Due to increasing pollution and fall of qualities of various surface water sources, people have started relying upon groundwater. However, groundwater in some regions contain specific ions (such as fluoride) and toxic elements (such as arsenic and selenium) in quantities that are harmful to health and some even cause fatal diseases to the living organisms consuming it or using it for any other purposes, while others contain elements or compounds that cause other types of problems (such as the staining of sanitary fixtures by iron and manganese).

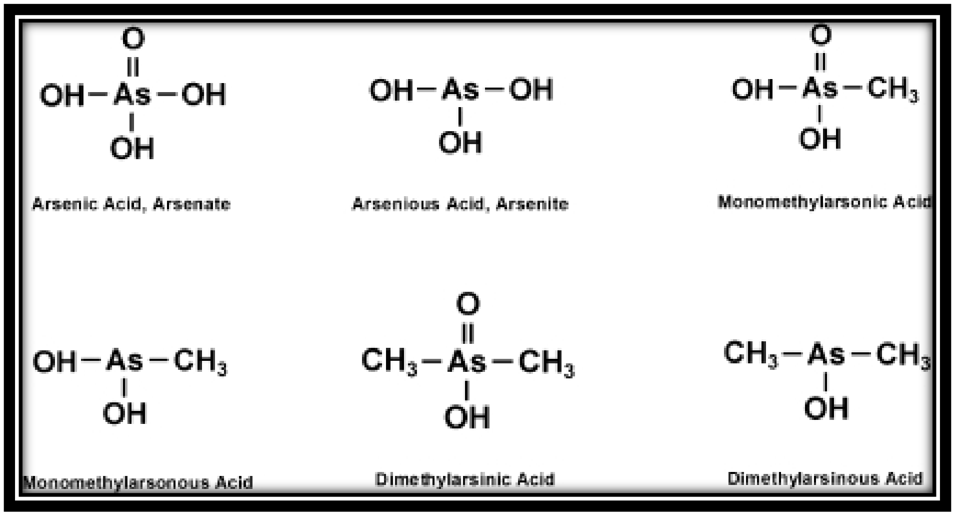
Also use of contaminated water is a serious public health issue as groundwater is used without any kind of treatment. It is polluted with nitrates, heavy metals, and pesticides that can result in cancer, mental retardation. Pesticides and other heavy metals enter the food chain through agricultures, hence it is important to protect the groundwater,” says Nitya Nacob, Programme Director (Water), CSE. It is shortage of proper sewerage that adds to the problem as 78 per cent of sewage percolates back into the ground, this adds while drawing attention to the highly toxic discharges that are drained into rivers in industrial belts, which ultimately find their way into groundwater (Shankar et al., 2014). The pollutant frequently creates a toxic plume within an aquifer. Movement of water and dispersion within the aquifer extends the pollutant over a wider area. Its expanding boundary, often called a plume edge, can interconnect with groundwater wells and to some extent surface waters as well.

1.2 Arsenic and various types of arsenic compound

In current times, arsenic contamination in water sources has become one of the emerging problems around the world. Arsenic is a metalloid with the symbol ‘As’ and atomic number 33. Arsenic appears in many minerals, generally in amalgamation with sulfur and metals, but also as a pure elemental crystal. It is found in both in surface water as well as in groundwater, but the percentage of arsenic contamination is much higher as compared to surface water. Arsenic generally occurs in two oxidation state; one is in trivalent oxidation state and the other one in pentavalent oxidation state.

Table 1: Arsenic compounds of environmental and human relevance

Trivalent oxidation state	**Pentavalent oxidation state**
Arsenite	Arsenate
Arsenic trioxide	Arsenic pentoxide
Mono-methylarsonous acid	Mono-methylarsonic acid
Di-methylarsinous acid	Di-methylarsinic acid
	Tri-methylarsine oxide
	Arsanilic acid
	Arsenobetaine



Arsenic Acid, Arsenate

Arsenious Acid, Arsenite

Monomethylarsonic Acid

Monomethylarsonous Acid

Dimethylarsinic Acid

Dimethylarsinous Acid

Fig. 1.2 Chemical structures of some Arsenic compounds (source: Caumette et al., 2012)

Generally, it is found that the trivalent state of Arsenic is much more toxic than the pentavalent oxidative form of arsenic. Arsenic is also present in gaseous state known as arsine gas, which is most toxic for which inhalation of over 10 ppm is lethal and at concentrations higher than 25 ppm are reported to be lethal in less than an hour after exposure, while over 250 ppm is reported to be instantaneously lethal.

1.3 Arsenic toxicity and its effect on living organisms

When in surface water, Arsenic can be easily removed by the process of sedimentation or other chemical methods since its present in very less quantities. But when present in groundwater, there is special requirement of arsenic treatment. Arsenic (As) is introduced into soil and groundwater during weathering of rocks and minerals followed by succeeding leaching and runoff. It can also be lead into soil and groundwater from anthropogenic sources. Many factors influence arsenic concentration and movement in groundwater, which comprise: Red-ox potential (Eh), adsorption/ desorption, precipitation/dissolution, Arsenic speciation, pH, presence and concentration of competing ions, biological transformation, etc.

Due to scarcity of surface water, it often leads to excess use of groundwater by digging tube wells which leads to fall of water level; thereby the water comes in contact to Arsenic containing minerals leading to contamination. It is a sophisticated problem due to the use of deep tube wells for water supply used in a number of parts of world, causing grave arsenic poisoning to large numbers of people.

Arsenic occurs as a chief constituent in more than 200 minerals and the desorption and dissolution of geologically occurring Arsenic containing minerals and alluvial sediments result in high As concentration in groundwater in deltas and alluvial plains even if the As concentration in the solid phase is not high. The occurrence of metalloid in high concentration in groundwater may be due to ores deposits where Arsenic is present predominantly in sulfide minerals such as arseno-pyrite and pyrite (Mukherjee et al., 2006).

World Health Organization (WHO) has referred Arsenic poisoning as the “the largest mass poisoning in the history of humanity”.

Arsenic, a well-known carcinogen, is considered as one of the world’s most perilous chemicals. Excessive and long-standing (such as 5–10 years) human ingestion of toxic inorganic As from drinking water and food may result in arsenicosis, a common name usually used for As related health problems including skin disorders, internal cancers (bladder, kidney, and lung), skin cancers, diseases of the blood vessels of the legs and feet, possibly diabetes, raise in blood pressure, and reproductive disorders. In terrestrial environment, the inorganic forms of As (such as trivalent arsenite (III) and pentavalent arsenate (V)) are greatly dominant and toxic than the organic forms in general. As put froths detrimental effects on general protein metabolism with high toxicity by reacting with sulfhydryl groups present in cysteine residues. Arsenic pollution in the environment is turning to be a serious public health problem in numerous parts of the world. It is well-established fact that toxicity of arsenite is greater than arsenate, with inorganic As(III) being more toxic than organic As(V).

However, different organic As species represent various intensity of toxicity. For instance, mono-methylarsonic acid and di-methylarsinic acid as final Arsenic metabolites are less toxic than inorganic arsenic, whereas the degrees of toxicity of intermediate metabolites such as mono-methylarsonousacid and di-methylarsinous acid are much higher than inorganic arsenic. In addition, it is well-established fact that continuous exposure to arsenic can lead to arsenicosis, including Blackfoot disease, skin lesions, peripheral vascular disease, and cancers.

Fig. 1.3 Physiological effect of arsenic exposure (source: SenGupta and Greenleaf, 2002)

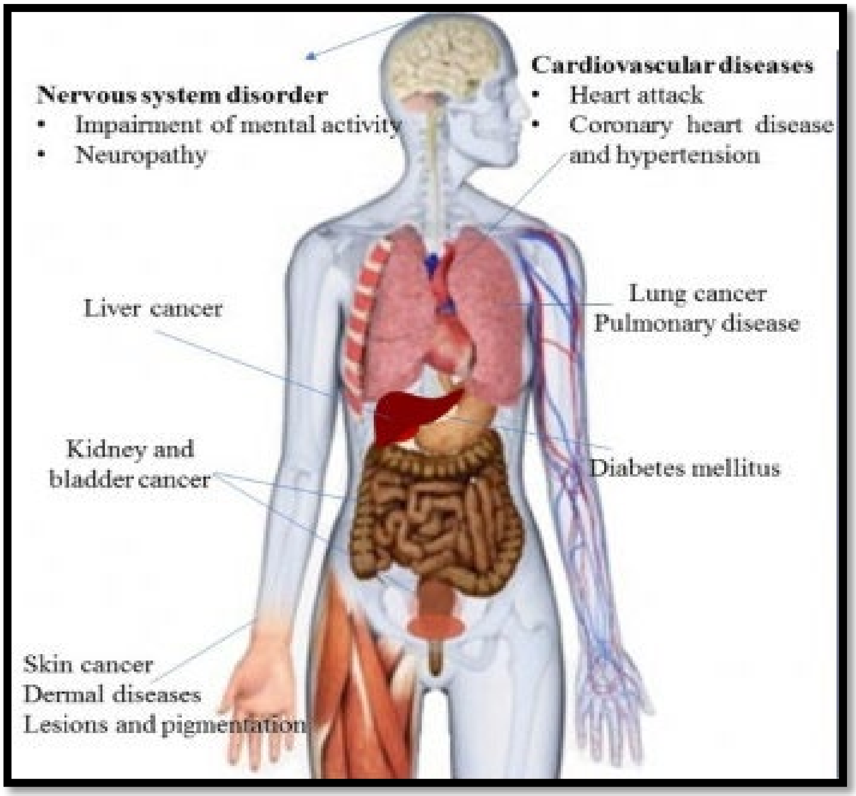


Fig. 1.4 Chronic diseases due to long term arsenic exposure (source: Shahid et al., 2018)

People are exposed to high levels of inorganic arsenic via drinking polluted water, using arsenic contaminated water in food preparation and irrigation of food crops, industrial processes, eating contaminated food. The concentration of arsenic in everyday used water samples from the Public Health Engineering Department (PHED) of tube well and dug well (general depth less than 50 m) in Kourikasa village was found to be as high as 880 μg L^{-1} and 520 μg L^{-1} respectively which is much more than the permissible value of arsenic as set by WHO (10μg/L).

1.4 Timeline Showing some historic events of Arsenic poisoning

1836 Marsh Test for detection of arsenic developed

1842 Dimethyl arsenic acid was detected in the environment

1887 Hutchinson proposes arsenic is human skin carcinogenic.

1942 U.S drinking arsenic standard level was set to 50µg/L.

1975 Environmental Protection Agency set the arsenic standard level in drinking water to 50µg/L.

1980 Arsenic contamination detected in wells of Bangladesh.

1983 First arsenic contamination was detected in Indian groundwater in West Bengal.

1990 Arsenic contamination in India was widespread in West Bengal and later in Bihar, Assam and ……….Bihar and other states.

1993 WHO sets arsenic level in drinking water to 10µg/L.

2000 FDA approves arsenic trioxide for leukemia therapy.

2000 Comprehensive well-testing program was conducted in Bangladesh by British Geological Survey.

2002 EPA lowers arsenic level in drinking water for U.S to 10µg/L.

1.5 Effect of arsenic pollution worldwide

A survey carried out in 2007 established that over 137 million people in more than 70 countries are considerably affected by arsenic poisoning of drinking water. This problem became serious health issue after mass poisoning of drinking water in Bangladesh. Arsenic pollution of ground water is found in many countries all across the globe, including the US (*USAToday.com*, 30 August 2007). Prominent level of As in groundwater has been well acknowledged in Chile, Mexico, China, Argentina, USA, and Hungary (Smedley et al., 2002) as well as in the Indian State of West Bengal, Bangladesh, and Vietnam (*Sun and Williams,* 2008).

About 150 million people around the world are estimated to be affected globally with an increasing prospect as new affected areas are continuously discovered(Mukherjee et al., 2006) .The major arsenicosis affected areas have been reported in large deltas and/or along major river basins across the world (*Williams and Islam,* 2009) such as in Paraiba do Sul delta, Brazil Bengal delta(Mukherjee et al., 2006), Mekong delta, Cambodia (Naito S and Matsumoto et al., 2016), Danube riverbasin, Hungry, Hetao river basin, Mongolia, Duero Cenozoic Basin, Spain, Zenne river basin, Belgium, and Tulare Lake, USA.

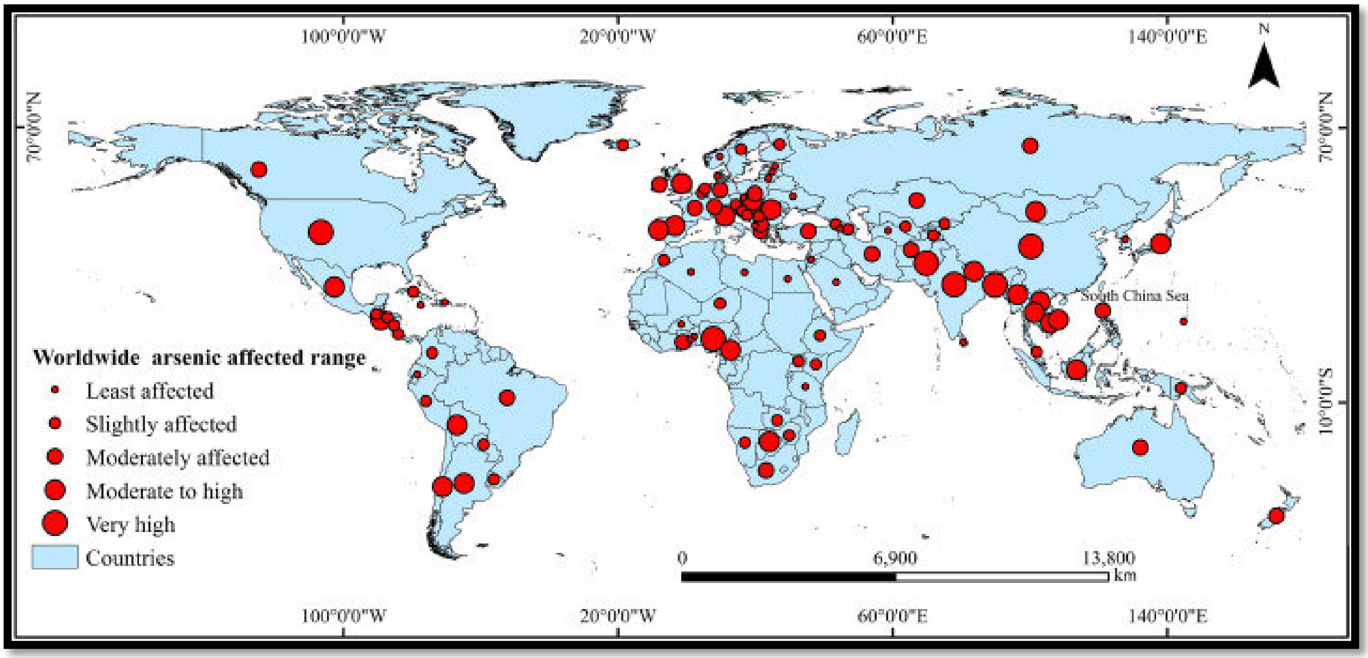


Fig. 1.5 Arsenic affected areas worldwide (Source: Shaji et al., 2021)

Arsenic contamination in groundwater in the Ganga- Brahmaputra aluvial plains in India and Padma-Meghna aluvial plains in Bangladesh and its consequences to the human health have been reported as one of the world's greatest natural groundwater disasters to the mankind. In India, seven states namely- Uttar Pradesh, Jharkhand, Bihar, West Bengal, in the flood plain of the Ganga River; Manipur and Assam in the flood plain of the Brahamaputra and Imphal rivers and Rajnandgaon village in Chhattisgarh state have so far been reported affected by Arsenic contamination in groundwater above the permissible limit of 10 µg/L.

People in these affected states have constantly been exposed to drinking Arsenic polluted hand tube-wells water. With every new investigation, more Arsenic affected villages and people suffering from Arsenic related diseases are being discovered, and the issues are getting complicated by a number of unknown reasons. These fluvial plains signify Holocene aquifers of recent alluvial sediments and have the paths originated from the Himalayan region (*Gupta, S. K. (2014)*).

1.6 Scenario of arsenic contamination in Indian subcontinent

In India Arsenic pollution in ground water was first reported in West Bengal in 1978 and it includes79 blocks in 8 districts among 26 districts where arsenic concentration in ground water surpassed 50 µg/L. According to the recent report of the Central Ground Water Board (CGWB), 21 states across the country have pockets with arsenic levels more than the Bureau of Indian Standards' (BIS). Pre decided tolerable threshold of 0.01 milligram per liter (mg/L). According to Das et al., 2015, this trouble is increasing rapidly and in 2006 almost 3235 villages were affected including Howrah, North 24 Parganas, Nadia, Murshidabad, South 24 Pargana, and Burdwan, Hooghly and Maldah districts. The harshly affected districts are Murshidabad, Nadia, Maldah, North and South 24 Parganas, Burdwan, Howrah and Hooghly. In module of this study, the numbers of affected blocks under the affected districts were too high.

Almost all the district consists over 50% to 100% arsenic contaminated block(Mukherjee and Sengupta, 2009).People are exposed to high levels of inorganic arsenic via drinking polluted water, using arsenic contaminated water in food preparation and irrigation of food crops, industrial processes, eating contaminated food. The concentration of arsenic in everyday used water samples from the Public Health Engineering Department (PHED) of tube well and dug well (general depth less than 50 m) in Kourikasa village was found to be as high as 880 μg L^{-1} and 520 μg L^{-1} respectively which is much more than the permissible value of arsenic as set by WHO (10μg L^{-1}). Rice is the chief food for more than half the world's population. It supplies about 20% of the global dietary energy supply to humans. Arsenic contamination of groundwater in many South (S) and Southeast (SE) Asian countries, the arsenic hot spots in the world, and irrigation with arsenic-contaminated groundwater in rice cultivation has resulted in high arsenic buildup in rice grains.

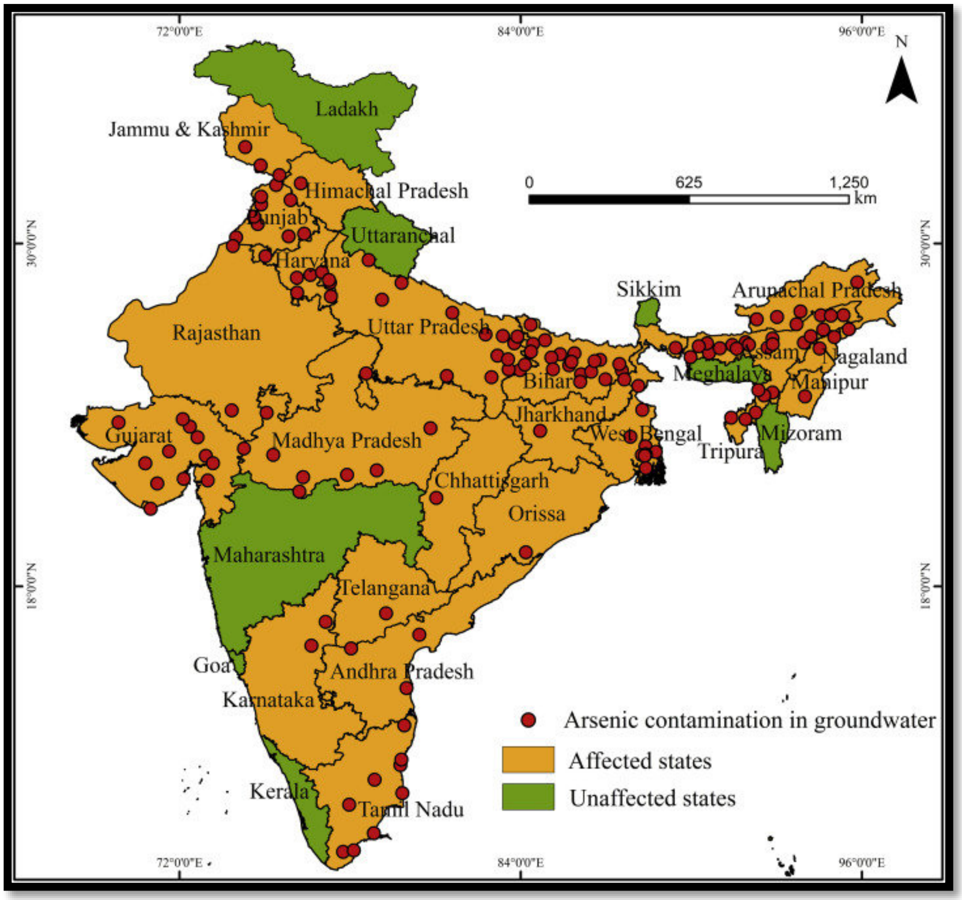


Fig. 1.6 Indian map showing arsenic affected area (Source: Shaji et al., 2021)

In addition, cooking rice with arsenic-contaminated water increases its quantity in cooked rice. In arsenic-endemic S and SE Asian countries, rice is considered as one of the major sources of arsenic exposure. The major portion of arsenic in Asian rice is inorganic arsenic (iAs) species. The toxicity, bioavailability, and bioaccessibility of iAs is the highest among arsenic species. Therefore, Asian rice is regarded as to be a health risk for the population of this area as well as for the populations of other regions who consume imported rice from arsenic-polluted Asian countries (Bhattacharya et al., 2015).The study signifiess that the average accumulation of As in rice grain increases with a decrease of grain size (ELS: 0.04; LS: 0.10; MS: 0.16; and SB: 0.33 mg kg^{-1}), however people living in the rural villages mostly favor brown colored SB type of rice because of its lower cost (Halder et al., 2012). Immediate consideration should be given to review the possibility of accumulating arsenic in soils through irrigation-water and its subsequent entry into the food-chain through various food crops and fodders. As per a researches conducted by Bihar Pollution Control Board, the arsenic contamination has found its way into the food chain mainly observed in rice, wheat and potatoes. Arsenic contamination in groundwater has been an increasing concern in different parts of the country. The number of arsenic affected habitations in India has amplified by 145% in last five years (2015-2020).

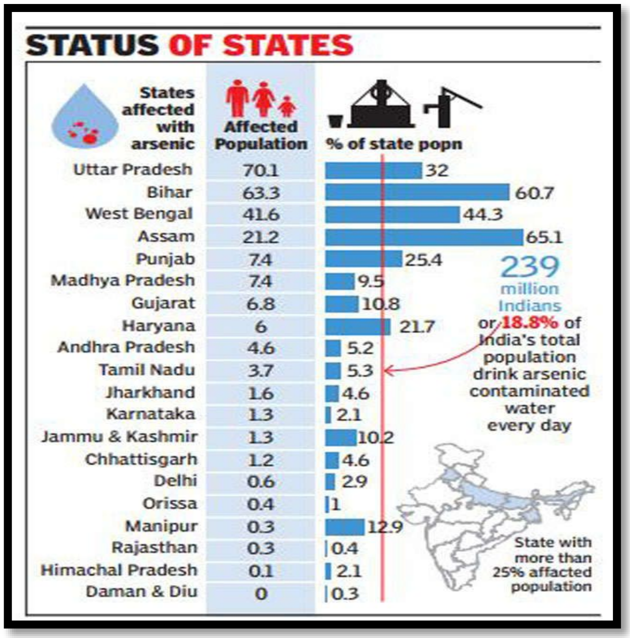


Fig. 1.7 Bar graph representing percentage population of Indian states effected with arsenic (Source: Times Of India, Dec 24, 2017)

In spite of different research studies on As buildup in rice grain which is present till date, an concentrated scrutiny on the specific interaction between As and micronutrients, such as Se and Zn in rice system is undoubtedly an underexplored phenomenon. Fascinatingly, there is a contradictory relation between Se and As regarding As carcinogenicity along with their presence in periodic table as next door neighbors (Rossman and Uddin, 2004). Concurrently, as per Williams et al., 2009a, Zn content in rice grain generally decreases with the increase of As content. So, micronutrients' precise influence on arsenic accumulation, uptake, assimilation and distribution would assist to assess rice quality as well as to develop technologies for reduction of As content in different variety of uncooked and cooked rice grain during cooking. Therefore, keeping in concern the above particulars, an attempt has been made in this paper to remediate As contamination, from water and rice grains irrigated in contaminated water using various traditional and advanced technologies.

Chapter 2

Arsenic Contamination in Surface and Ground water

2.1 Route for arsenic contamination in drinking water

Arsenic occurs naturally as a trace component in many rocks and sediments. It occurs in combination with many minerals mostly sulphur:- such as Realgar (AsS), Orpiment (As_2S_3), Nickolite (NiAs) and many others. Whether the arsenic is released from these geologic sources into groundwater depends on the chemical form of the arsenic, the geochemical conditions in the aquifer, and the biogeochemical processes that occur.

Arsenic from soil and rock can dissolve into groundwater and enter drinking water wells. For most people, food and water are the biggest sources of exposure to arsenic. There are two forms of arsenic:

- Inorganic arsenic is formed when arsenic combines with metals and elements other than carbon. Inorganic arsenic is the type found in contaminated drinking water, and is the most harmful type of arsenic. This type of arsenic is also found in rice, cereal grains and other foods.
- Organic arsenic is formed when arsenic combines with carbon. It is the most common type of arsenic found in food. It is common in fish and shellfish, and is less harmful to health than inorganic arsenic.

Arsenic also can be released into groundwater as a result of human activities, such as mining, and from its various uses in industry, in animal feed, as a wood preservative, and as a pesticide.

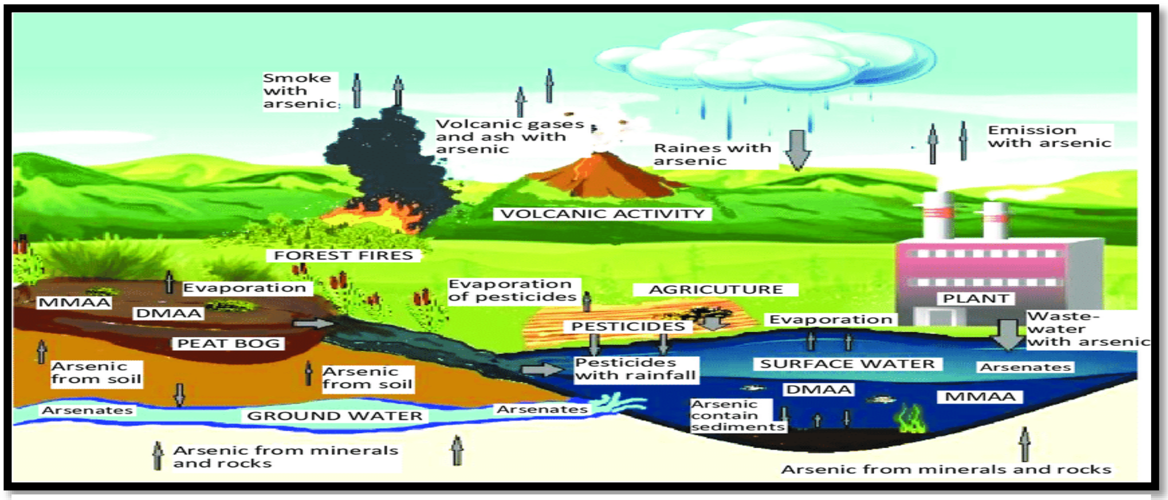


Fig. 2.1 Sources of arsenic contamination in water (Source: Litynska et al.2017)

In drinking-water supplies, arsenic poses a problem because it is toxic at low levels and is a known carcinogen. The U.S. Environmental Protection Agency (EPA) standard for arsenic in drinking water is 10 micrograms per liter (µg/L). The EPA has a federal drinking water standard of 10 µg/L for public water systems serving places where people live, work, go to school, and receive childcare. These systems take action to reduce arsenic if levels exceed the standard.

2.2 Literature Review

Ground water is a key source of drinking water, and elevated concentration of arsenic in ground water has been associated with various negative health effects in humans (Bhattacharya et al., 2001). Arsenic in drinking water is considered one of the most significant environmental causes of cancer in the world. Consequently, since 1963, the World Health Organization has recommended limits to the maximum concentrations of arsenic in drinking water. In 1963, their recommendation was of 50 µg/L, but after new evidence relating low arsenic concentrations with cancer risk, the World Health Organization further reduced their recommendation to 10 µg/L in 1992. Contamination of ground water is one of the major pathways of human exposure to inorganic arsenic and the risk of arsenic contamination is generally much higher in ground water than that in surface water (Argos et al., 2001).

Elevated concentrations of arsenic have chiefly resulted from natural sources, such as erosion and leaching from geological formations or anthropogenic sources. In addition, arsenic use for industrial purposes, mining activities, metal processing, and pesticides and fertilizers are other major sources of contamination. The duration of arsenic exposure in India is uncertain, but it is thought that the problem began in the late 1960s when digging of tubewells commenced as part of a state-wide irrigation plan (Bagla et al., 1996). Because groundwater was cleaner than water from tanks, ponds and the polluted Ganges river, many inhabitants switched to using tubewell water. The contamination of groundwater with arsenic was first detected in 1978, and the first arsenic poisoning cases were reported in the early 1980s (Mazumdar et al., 1988).

Most of the affected villages are located along the western side of the Ganges river. A survey conducted by Das et al., 1995 which was limited to regions with levels >50µg/L, indicated that the arsenic concentration was generally between 50 to 500 µg/L in the drinking water supplies. However, concentrations have reached nearly 3000 µg/Lin some villages. In present times in West Bengal in a district called Murshidabaad out of 26 blocks, 20 blocks are affected with arsenic poisoned ground water grave situation.

There are several methods available for removal of arsenic from water in large conventional treatment plants. The most commonly used technologies include oxidation, co-precipitation and adsorption onto coagulated flocs, lime treatment, adsorption onto sorptive media, ion exchange resin and membrane techniques (Cheng et al., 1994; Hering et al., 1996; Kartinen and Martin, 1995). Previously experiments have been carried out where iron oxide coated sand and limestone has been used as filtration agent for removal of arsenic from drinking water (Devi et al., 2014).Membrane filtration can remove a number of contaminants from water. Removal of arsenic by membrane filtration is highly dependent on the species of arsenic and the properties of the membrane. Also ferric salts have been found to be more effective in removing arsenic than most other components on a weight basis and effective over a wider range of pH. In both cases pentavalent arsenic can be more effectively removed than trivalent arsenic. Thus oxidation of As(III) to As(V) is thus required as a pretreatment for efficient removal. Thus synthesized iron nanoparticle infused membrane, has been presented in this study for remediation.

A nanoparticle is a small particle that ranges between 1 to 100 nanometers in size. Nanoparticle synthesis can be performed by various methods such as physical, chemical, and biological approaches. Generally, the physical and chemical methods are considered the best to get uniform-sized nanoparticles with long-term stability. Recent advances in nanoscience and nanotechnology have led to the development of a number of nanoparticles for the environmental remediation of various contaminants from groundwater (Zhang et al., 2003). Due to their high specific surface area and reactivity, nanoparticles are considered as a suitable option for fast removal of contaminants from aqueous solution (Huber et al., 2005).

Based on this early study, the use of nanomagnetite particles for the removal of arsenic from water appears to be promising: a very high rate of adsorption was observed, with the limit of As concentration for drinking water achieved after only 300 min (Jain and Singh, 2012). Previously experiments have been carried out where iron oxide coated sand and limestone has been used as filtration agent for removal of arsenic from drinking water (Devi et al., 2014). Fe_2O_3 nanoparticles. Iron oxide as a nano-adsorbent is able to remove arsenic five to ten times more effectively than their micron-size counterparts. Tuutijärvi et al. (2009) reported that the adsorption capacity of As(V) was as high as 50 mg g^{-1} when γ-Fe_2O_3 nanoparticles were prepared.

Membrane filtration can remove a number of contaminants from water. Removal of arsenic by membrane filtration is dependent on the species of arsenic and the properties of the membrane. Hydrogels membranes are described as three-dimensional cross-linked hydrophilic polymers with a very high intrinsic content of water. Hydrogels holds a specific shape once they are cast and set after cross-linked. They have the latent ability of imbibing large quantities of water or hydrophilic fluids without themselves dissolving in them. . Among the vast array of hydrogels membrane, hydrogels prepared using poly (vinyl alcohol) (PVA) blended with polysaccharides and some other synthetic polymers are attractive alternatives because of the abundance of such polymers, ease for chemical alteration or derivatization, and in most cases satisfactory biological compatibility (Kamoun et al., 2014). For the arsenic removal, in present study iron nanoparticles was infused in the membrane. The membrane for this experimental approach was prepared using PVA. PVA's melting point is approximately 220–230 °C for fully hydrolyzed grades and 180–190 °C for partially hydrolyzed ones. Additionally, the great film forming, adhesion, good mechanical and optical properties, O_2 barrier capability in low humidity, non-toxicity, biocompatibility and partial biodegradability and relatively easy nanocomposite preparation capabilities render PVA valuable candidate material in diverse and demanding applications (Sapalidis et al.,2020).

Due to these properties, PVA has found its way in a wide spectrum of technological fields ranging from biomedical to construction. Indicative applications include fibers, water soluble packaging, and protective colloid in emulsion and suspension polymerization, adhesives and so on (Halima et al., 2016). Practical applications of PVA based membranes require that it should be cross-linked prior to use in order to retain the structure and mechanical properties, especially in water related processes; studies have also shown that cross-linking can induce minimum effects on the thermal and mechanical properties, or even their deterioration (Krumova et al., 2000).

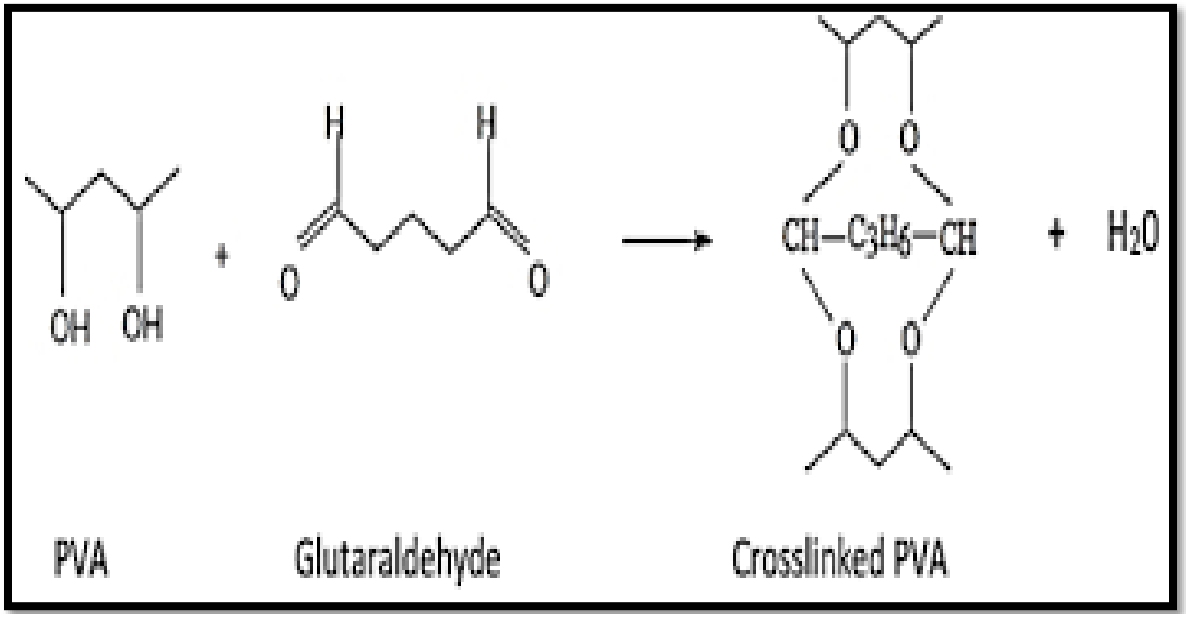


Fig. 2.2 Reaction between PVA and Glutaraldehyde (Source: Distantina et al.; 2017)

As a membrane material, PVA is considered attractive due to the following advantages: hydrophilicity, water permeability, good mechanical properties, thermal and chemicals resistance, anti-fouling potential, and film forming ability. On the negative side, PVA is permeable to ions, has a high degree of swelling, compacts under pressure, and shows low flux when it is highly crosslinked (Sapilidis et al., 2018). Furthermore, poly (vinyl alcohol) has attracted a lot of research interest as a membrane for separations, especially in water treatment due to its low biofouling tendency (Pendergast, 2012); a known issue that affects various membrane processes.

Keeping all this in view PVA synthesized membrane with infused iron nanoparticles is being used for the remediation of arsenic polluted water.

Chapter 3

Arsenic Contamination in rice grains

3.1 Route for arsenic contamination rice grains

Arsenic can get into water supplies used for irrigation purposes via natural deposits in earth's crust or through agricultural or industrial. It is well known fact that naturally occurring arsenic dissolves out of certain rock formation when ground water levels drop considerably. Some industries in the United States discharge thousands of pounds of arsenic into the environment every year. Once ejected, arsenic stays in environment for a long period of time. Arsenic is removed from the air by rain, snow and gradual settling. Once the arsenic comes in contact with the ground or surfaces of any water bodies, arsenic slowly sips into the groundwater.

Also elevated levels of arsenic in farm wells and other sources of water may come from certain arsenic containing fertilizers used for farming or other arsenic containing chemicals released from various industrial discharges. Often arsenic contaminated water from such sources is used for irrigation of rice plants; thereby the rice plants take up the arsenic contaminated water via phosphate transporters, since phosphate and are analogous to each other and mostly compete for the particular adsorption sites.

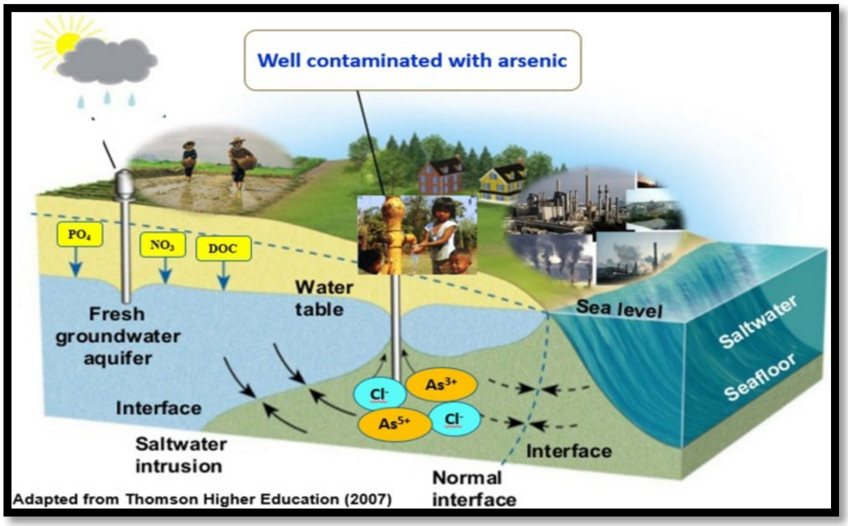


Fig. 3.1 Flow of arsenic from soil to groundwater
(Source: Boonkaewwan et al., 2021)

The rice plants use this adsorbed arsenic contaminated water for its growth, maturation and development of rice grains. As a result the rice grains also get contaminated arsenic (As). Rice usually gathers more arsenic than any food crops. In fact, it is the single biggest food source of inorganic arsenic, which is the more toxic form.

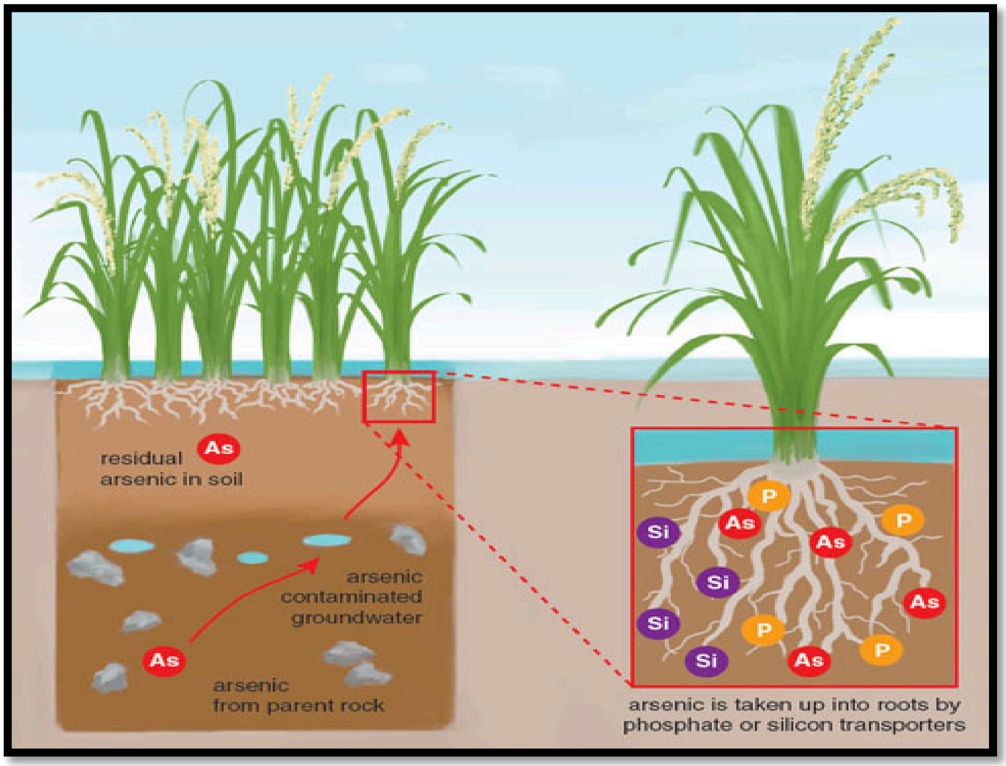


Fig. 3.2 Transportation of Arsenic into Rice grains (Source: Yosim et al., 2015)

Generally, the average translocation factor for arsenic in rice grains is almost around 0.8, which is quite higher than other crops, like barely (0.2) and wheat (0.1). In certain areas the arsenic contaminated water is also for the cooking purposes thereby increasing the arsenic content of cooked rice.

Arsenic in rice is one of the serious issues for many people around the globe. A large part of the world's population depends on rice as a major food source, and millions of people might be at the danger of developing arsenic-related health issues.

3.2 Literature Review

Anthropogenic arsenic poses one of the major noteworthy public health challenges, distressing 140 million people over more than 70 countries in the world (WHO, 2018). In specific, inorganic arsenic (iAs) is a group 1 carcinogen as advised by the International Agency for Research on Cancer (IARC). Also, iAs is included within the list of top 10 chemicals, of r group of chemicals, of significant public health concern by the World Health Organisation (WHO 2016). Intake of As contaminated water and food directs to Arsenic toxicity which affects millions of people throughout the world. Plants take up As through polluted water, which is ultimately stored in grains that are in turn eaten by humans which leads to serious health effects. In specific, rice, the chief food for more than 50% of the world's population, has shown the tendency to accumulate iAs in more substantial amounts than other cereals (Carey et al., 2019; Liao et al., 2018; Meharg et al., 2008; Nunes and Otero, 2017). In regions where arsenic exposure via drinking water is least, rice and other foods rich in iAs can add up considerably to human arsenic ingestion (54–85%) as shown in a US-based study (Kurzius-Spencer et al., 2013). In the same way, in the UK, arsenic exposure because of drinking contaminated water is not widely reported except in private water supplies in Cornwall (Middleton et al., 2016). However, in the UK reports have shown that arsenic exposure through the consumption of rice and rice products are more significant. Almost 90% of households in the UK purchase rice; consumption of rice has increased by 450% since the 1970s, majorly due to the growing Asian based population and food diversification over the period of time (Schenker, 2012; Rice Association).

In UK the per capita rice consumption is approximately 5.6 kg y^{-1} (i.e., 0.015 kg d^{-1}) which is slightly more than across the European Union (4.9 kg y^{-1}) (OECD, 2015; Schenker, 2012); however, it varies considerably across the UK population.

For example, Asian ethnic groups constitute 7.5% of the total population in England and Wales, and according to National Diet and Nutrition Survey (NDNS Years 1–9, 2008/09–2016/17), 42–43% of the tested UK population have rice in their diet over a period of four days. In comparison to Asian countries, it was 73–78% for sub-population of Asian or Asian British ethnicity over the same period. Across the sampled UK population of rice consumers, adults (16+ years of age) consumed almost 0.036 kg d^{-1}, while children and infants (0–15 years of age) have rice intake amount of 0.021 kg d^{-1}.The adults of the tested sub-population of Asian or Asian British ethnicity consumed 0.047 kg d^{-1}, on the other hand children and infants of Asian or Asian British ethnicity consumed 0.028 kg d^{-1} (NatCen Social Research, 2019).

The trouble of arsenic pollution in groundwater is now well documented in most of the S and SE Asian countries as discussed in the earlier parts. Rice is the staple cereal crop produced in this territory, particularly in Bangladesh and West Bengal (India), which uses groundwater for irrigation purpose during dry season. Recently, it has become evident that arsenic-polluted irrigation water is adding significant quantity of arsenic in the topsoil and in rice, which pose grave threat to sustainable rice cultivation in these two countries (Brammer and Ravenscroft, 2009; Dittmar et al., 2010;Khan et al., 2009; Khan et al., 2010a; Khan et al., 2010b; Meharg and Rahman, 2003). Since the agro-ecological and hydrogeological environment of the S and SE Asian countries are broadly parallel, irrigation of arsenic-contaminated groundwater is supposed to generate alike effects on paddy rice of this region. Furthermore, paddy rice is considered to be one of the chief and probable exposure sources of arsenic for people (Meharg and Rahman, 2003; Mondal and Polya, 2008; Pillai et al., 2010; Rahman et al., 2008a; Singh et al., 2010; Tuli et al., 2010; Williams et al., 2006; Zavala and Duxbury,2008) because of its rising deposition in the topsoil from irrigation water and its successive uptake in rice grain (Dittmaret al., 2010).

Irrigation with arsenic-contaminated groundwater may specifically influence rice cultivation in terms of production and contamination. There may be two main causes for this — i) a large quantity of underground water containing peak level of arsenic has been irrigated for rice cultivation in for the most parts of S and SE Asia during arid season and ii) rice is the crop that is most vulnerable to arsenic toxicity (Brammer and Ravenscroft, 2009).

The uptake of monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) has also been to take place in plants via Lsi1.Inorganic and organic As species differ in their mobility. Due to the reduction of rainfall in this area, also in monsoon season, the reliance on groundwater for rice cultivation is likely to be increased in the upcoming years in order to enhance crop production to meet the demands of the ever-increasing population. This routine will increase additional arsenic accumulation in topsoil. Latest instances have been found in recent times in different places of Asia including Lao People Democratic Republic, Cambodia, Myanmar and new regions in China (The International Conference on Water Quality Arsenic Mitigation,2004), Nepal (Shrestha et al., 2003), Vietnam (Berg et al.,2001), Pakistan (Nickson et al., 2005) and Lower Mekong(Stanger et al., 2005).

In India, the Ganga-Meghna-Brahmaputra (GMB) river basin is one of the most terribly arsenic (As) polluted regions due to the presence of excessive concentrations of the toxic metalloid within the top 50 m depth of aquifers in India (Ahmed et al., 2004; Mukherjee and Bhattacharya, 2001; Singh, 2006).Geochemical characteristics of aquifers in areas drained by these three rivers have reportedly shown natural groundwater As contamination (Bhattacharya et al., 2010; McArthur et al., 2001; Mukherjee et al., 2008). Groundwater arsenic contamination in the Bengal delta has been referred as the largest chemical poisoning in history (Smith et al., 2000). Groundwater is one of the prime sources of water for drinking and cooking and various domestic purposes in many parts of Bengal affected with arsenic contamination.

Beside intake of arsenic contaminated water, arsenic also gets into human body due to eating vegetables and crops grown in the arsenic polluted field and cultivated with As contaminated water (Naidu and Bhattacharya, 2009; Rahman et al., 2009). Presence of great level of As in rice (Oryzasativa L.) and human exposure to As through rice consumption is a worldwide health issues (Kumarathilaka et al., 2019). The continuous accumulation of arsenic in rice contamination, that is grown in the arsenic contaminated zones of Bengal Delta, which is eaten by the people as one of the staple meal, exposes the whole population to the threat of arsenic contamination (Halder et al., 2014; Roychowdhury, 2008a; Samal et al., 2011; Smith et al., 2006).

It has been found that there is great As accumulation (mean = 143 ± 76 µg/kg; range =2–557 µg/kg) in rice grain cultivated via groundwater irrigation from 25 villages in 4 districts of Bangladesh (Rahman et al., 2009). Mandal et al., (2019) showed in their study from West Bengal, India that As concentration in cooked rice(n = 100) ranged from 31.5 to 80 µg/kg(median = 47.8 ±10.5 µg/kg) and 219–664 µg/kg (median = 349 ± 100 µg/kg) in comparison to raw rice As concentration of 105–510 µg/kg (median: 223 ±89 µg/kg) when cooked with As safe water (0.5 µg/l) and As rich groundwater samples (median = 132 ± 33 µg/l; range = 90–230 µg/l), respectively.

Inorganic As has been found as the most prevalent species in both raw (93.8%) and cooked rice (88.1%) from rural Bengal (Halder et al., 2014). Rice contains high concentrations of arsenic in comparison to other crops and represents a major source of As intake in human diets. Yet, unceasing exposure to As has the potential to cause several forms of cancer and countless other serious negative health effects in humans. The bio accessibility of As in humans refers to the portion of dissolved As, due to gastrointestinal absorption (Zhuang et al. 2016). Reproducible and cost-effective in vitro digestive methods are usually used to measure As bio accessibility of cooked rice in humans (Laparra et al. 2005; Sun et al. 2012; Zhuang et al., 2016). Basically, in vitro digestive methods can imitate both enzymatic and physico-chemical processes of the human digestive tract. Studies correlated to the simulated gastrointestinal digestion (i.e. using artificial gastrointestinal digestion) have shown that inorganic As species in cooked rice were greatly bio accessible in humans (63–99%) (Laparra et al., 2005).

The undigested portion of fibre in rice may go through a microbial fermentation process in the colon. Sun et al. (2012) observed a reduction of As bio accessibility in the simulated colon (i.e. simulator of the human intestinal microbial ecosystem (SHIME) reactor). Calatayud et al. (2018) also found that the percentage of As bio accessible fraction reduced from 36% to 14% (oral) and from 117% to 89% (colon), due to the existence of salivary bacteria along the gastrointestinal digestion.

However, the toxicity of As relies majorly on its chemical environment, with the inorganic forms of As (As(III) and As(V)) being the most toxic, followed by monomethylarsonic acid(MMA) and dimethylarsinic acid (DMA), while the other organic forms of As are usually considered to be mostly non-toxic (*Li and Zhou,2013*). Therefore, the possible toxicity of As depends not only on the total As concentration, but also on the species of As existing in a given food sample (*Li and Zhou, 2013*).

To formulate an accurate hazard assessment method, one must also take into count the bio-availability of toxic elements, as total concentration is not necessarily a useful indicator of toxicity in humans. Bio-availability refers to the capability of an element to be absorbed into the systemic circulation system. Therefore, rice eating is the major source of As exposure and it signifies a major health threat in terms of persistent toxicity of As to the populations of Bengal delta drinking As free groundwater (Biswas et al., 2019; Halder et al., 2013, 2014; Meacher et al., 2002; Tsuji et al., 2007). Urinary levels of As are also considered to be a legitimate measure of As exposure (i.e. through mass balance approach) through rice consumption (Banerjee et al. 2013; Davis et al. 2012; Meharg et al. 2014). Following the ingestion, As excretes via the kidneys as inorganic As and metabolites of methylated As species (i.e. MMA (V) and DMA(V)). Numerous studies have shown that 40–60% of rice-derived total As excretes through the urine (He and Zheng 2010; Meharg et al. 2014).

Parallel analyses have also proved that the consumption of As rich rice causes high As excretion in humans (Gilbert–Diamond et al. 2011; Heand Zheng 2010). For example, Meharg et al. (2014) found that intake of 300 g of rice per day increased total As in urinary excretion by 730%in adults. In the subject of As speciation, Meharg et al. (2014) established that DMA(V) was the principle As species (90%) in the urine of individuals who has consumed rice containing inorganic As and DMA(V) at a ratio of 1:1. The end metabolite of As conversion in humans is DMA (V) (Li et al. 2013).

Therefore, it is possible to have DMA (V) as the most prominent As species in human urine (Li et al., 2013). However, As excreted in urine does not reflect entire bioavailability of As since As species can stay in the body but can also be excreted as faeces. Significant variations in total arsenic concentrations in different fractions of raw rice (hull, endosperm, polished rice, whole rice, and bran) have been accounted in literature (Rahman et al., 2007) studied total arsenic concentrations in different fractions of parboiled and non-parboiled raw rice gathered from arsenic-contaminated regions (Satkhira district) of Bangladesh. Results revealed that arsenic concentrations in non-parboiled raw rice were significantly elevated than those in parboiled rice.

The maximum arsenic concentrations were in husk (in the range of 0.7–1.6 µg g^{-1} d. wt.) followed by bran (0.6–1.2 µg g^{-1} d. wt.), whole grain (0.5–0.8 µg g^{-1} d. wt.), and polished rice (0.3–0.5 µg g^{-1} d. wt.). Thus, the array of arsenic concentrations in rice fractions was husk >bran>whole rice>polish rice (Rahman et al., 2011). Paddy, that is cultivated using As-polluted irrigation water, is further subjected to post-harvest processing called parboiling using contaminated water for cooking of parboiled rice grain on a domestic scale (average =184 µg/L; range = 40–366 µg/L; n = 10) (Chowdhury et al., 2018b). This result into an additional entry of As in parboiled rice grain. A large section of the aforesaid population consumes parboiled rice mainly short-bold (SB) brown rice as their staple food. The rice grains that are mainly available in rural Bengal have been differentiated into four categories, like short-bold (SB), medium-slender (MS), long-slender (LS) (all these three categories fall under brown coloured rice) and extra-long slender (ELS) (falls under white coloured Indian Basmati) on the basis of their average length and length to breadth ratio (Halder et al., 2012). It is necessary to lessen the risk of arsenic exposure to population through rice consumption (Carlin et al., 2016; Islam et al., 2016).

Total arsenic concentration (tAs) in food products includes comparatively extremely high toxic inorganic (iAs) forms (i.e., AsIII and AsV) as well as less toxic organic (oAs) forms (e.g., dimethyl arsenic acid (DMA) and traces of monomethylarsonic acid (MMA)); all these arsenic species are usually found in rice (Islam et al., 2016; Meharg et al., 2008; Nortonet al., 2013).

Rice is majorly grown under flooded soil conditions that are favourable to the reduction of AsV to AsIII. The resulting lower valent species, arsenous acid (H_3AsO_3; pKa 9.2), is soluble in flooded soil and easily bioavailable to rice for intake in the plant parts including grains (Bakhat et al., 2017; Islam et al., 2016). From irrigation to parboiling, the total procedure carried out in As-polluted water in most of the cases, thus brings about an effect adding up to a high exposure risk for the countryside population. It has been also revealed that the concentration of entire arsenic content and of arsenic species may be altered during the preparation of food for human consumption. The quantity of studies on this regard is still inadequate and the observed ambiguity is high. Studies have made it known that rinsing rice before cooking can affect the amount of As in the grain. Naito et al. showed that an absolute washing of rice before cooking reduced As up to 29% (Naito et al. 2015).The As lost during washing was mainly inorganic. DMA loss was insignificant. Raab et al. found that rinsing rice before cooking only reduces As by 13–15% in basmati rice, but only decreased As by 1–4% in white long grain, brown and parboiled rice (Raab, Baskaran, et al. 2009). These studies measured the following sources of variability: (i) the arsenic amount in the water used for cooking (no arsenic; low arsenic content; high arsenic content); (ii) the consequence of rinsing the raw rice; and (iii) water-to-rice ratio (ranging between 1:2 and 1:10). Percentage of total arsenic residual after cooking was the chief indicator, with only a small portion including speciation. The mean arsenic content of cooked rice reduces as the water-to-rice ratio increases, as long as additional water is discarded, indicating a obvious dilution effect. (Atiaga et al., 2020). During rice cooking two fundamental processes take place: intake of arsenic by rice from As polluted water and removal through the washing and discard water. When the amount of intake surpasses the released amount; the total As quantity in cooked rice is more than that in raw rice and vice versa.

So it was observed, up to a specific concentration of arsenic in cooking water the total arsenic content in cooked rice was less than that in raw rice, and after the equilibration point it increases. The overall arsenic in cooked rice is less than in raw rice at arsenic concentration 10 g/L (WHO provisional guideline value); but at 50 g/L As(standard for many developing countries) an average of 35–40% increase was observed (Sengupta et al., 2006).

Excess water cooking reduced total As and iAs in parboiled rice more than either long grain polished or brown rice. During parboiling rice starch granules are gelatinised, protein bodies are broken and fat content is lowered (Misaki and Yasumatsu, 1985). Water-soluble vitamins and elements move about from the bran layer to the endosperm during parboiling. One possible cause why As and iAs leach more competently from parboiled rice may be because parboiling rice allows easier movement of elements and nutrients into and out of the endosperm due to internal arrangement changes in starch, protein and fat constituents (Gray and Conklin, 2016). However, only a small numbers of studies have focused on the effects of post-harvesting technologies and cooking methods to reduce As quantity in raw and cooked rice grains in As endemic areas. Taking this into consideration, this literature review article discusses possible causes for high levels of As in cooked rice and potential post-harvesting and cooking techniques to decrease As levels in cooked rice.

Chapter 4

Aims & Objectives

The objective of the work is to reduce arsenic from drinking water and rice grain during cooking of rice.

The work is basically divided into two segments.

- Attempt to remove arsenic from arsenic contaminated water using membrane filtration technique.
- Approach to remove arsenic from rice grains during cooking of rice.

4.1 Removal of arsenic from arsenic contaminated water

- To prepare a membrane containing lab synthesised iron nano-particles infused within the membrane.
- Treatments of the arsenic contaminated water with the help of the prepared iron nano-particles infused membranes.
- To analyse the water quality parameters of the arsenic contaminated raw water and treated drinking water.

4.2 Removal of arsenic from arsenic grains during rice cooking

- To remediate arsenic from rice grains during cooking process use of relatively arsenic safe water is used.
- The remediation to be done using arsenic safe water in different ratios (1:3 and 1:6) along with pre followed step of washing and soaking of rice grains to be carried out.

OBJECTIVE 1:

AN APPROACH TO REMEDIATION OF ARSENIC CONTAMINATED WATER USING IRON NANOPARTICLES INFUSED MEMBRANE

Chapter 5

Materials and Method

5.1.1 Chemicals Used:

- Poly(vinyl alcohol) (powder form)
  [LOBA CHEMIE PVT. LTD.]
- Corn starch
  [Herald Food and Commodities PVT. LTD.]
- Glutaraldehyde
  [Spectrochem PVT. LTD.]
- Ph capsules
  [Ph 7 and Ph 9 Capsules]
- Iron Nanoparticles
  [Lab synthesized by $FeCl_3$ and NaOH]

5.1.2 Instruments:

- Magnetic Stirrer with hotplate
  [LIMCO]
- Incubator
  [INCON, Model BOD-INC. Sl No. 03475/6]
- UV-Vis Spectrophotometer
  [Thermo Scientific (ORION Aquamate 8000]
- Atomic Absorption Spectrophotometer
  [AA140FI- HG- AAS (Flow Injection Hydraulic Generation Atomic Absorption Spectrophotometer)]

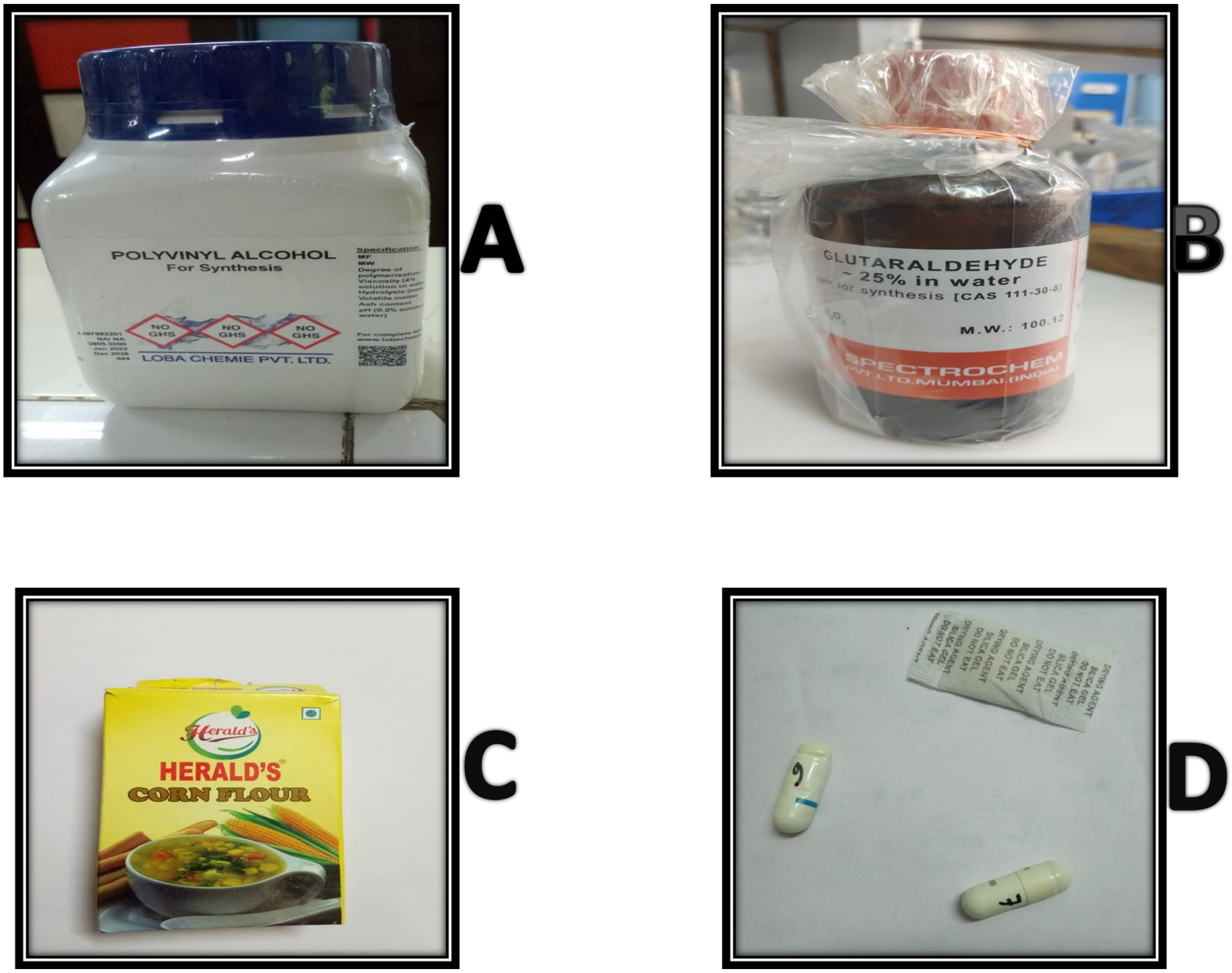


Figure 5.1 Chemicals used in the experiment. A: Poly (vinyl alcohol) (powder form), B: Glutaraldehyde , C: Corn Starch Powder, D: pH capsules(pH -7 and pH-9)

5.2 Preparation of iron nanoparticles

1. $FeCl_3$ solution of 0.1 M strength was prepared.
2. 1 M NaOH stock solution was prepared.
3. The $FeCl_3$ solution was heated at 80ºC followed by the drop by drop addition of 1 M NaOH to maintain its pH at 7.00.
4. The solution was heated while maintaining a pH of 7.00 till most of the solvent part was evaporated leaving behind the synthesized nanoparticles.
5. The nanoparticles were collected and washed using double distilled water via shaker and then centrifuged.
6. After the washed nanoparticles solution was centrifuged, the supernatant was discarded and the pellet or the nanoparticles were collected.
7. The washing steps were repeated 4-5 times in order to gain as much as purity possible.
8. After repeating the washing steps, double distilled water was again added to the iron nanoparticles and heated till all the liquid is evaporated and the nanoparticles are dried in order to obtain it in fine powder form.

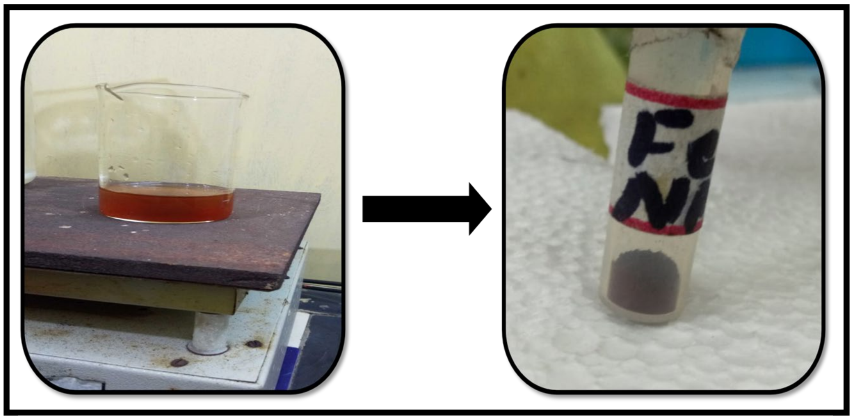


Figure 5.2 Preparation of iron nanoparticles

5.3 Quantitative analysis of the synthesized Iron nanoparticles (FeNPs)

UV-Vis Spectroscopy

The formation and completion of the synthesis of iron nanoparticles was monitored and characterized by UV-Visible spectroscopy. The formation of the iron ions in the solution was monitored by sampling of aliquots and monitoring the UV-Visible spectra at 250-350 nm range operated at a resolution of 1 nm. Distilled water was used as a blank.

Morphological studies of Iron nanoparticles using scanning electron microscopy (SEM)

A SEM was employed to analyze the morphology and size details of the iron nanoparticles that were formed. The sample for the analysis was the powdered form which was obtained after lyophilization of the concentrated extract (solution) of the synthesized iron nanoparticles.

5.4 Testing the arsenic sequestration capacity of iron oxide nanoparticles

1. Arsenic contaminated water sample was prepared in lab with strength of 100 ppb or 100 µg/L of arsenic in 10 mL of water.
2. 10 mg of iron nanoparticles was added to the prepared arsenic contaminated water and kept overnight.
3. Next day the solution was filtered to remove the sediments formed over night and then the arsenic content was checked.

5.5 Preparation of PVA-corn starch composite membrane

PVA-corn starch based composite membrane was prepared containing the iron nanoparticles with the idea of developing efficient delivery systems for natural products or synthesized nanoparticles mostly for remediation applications. For this purpose, PVA was blended with corn starch, and prepared into thin matrices through the conventional solution casting method.

5.6 Solution casting method for membrane preparation:

Solution casting is the method by which the polymer is dissolved in one or more volatile solvents (organic or water) to get a homogeneous solution with a low viscosity. The solution may either spread on a substrate or cast into a mold. Solvent casting technique is one of the oldest as well as the versatile and easy techniques used for the preparation of polymer casts.

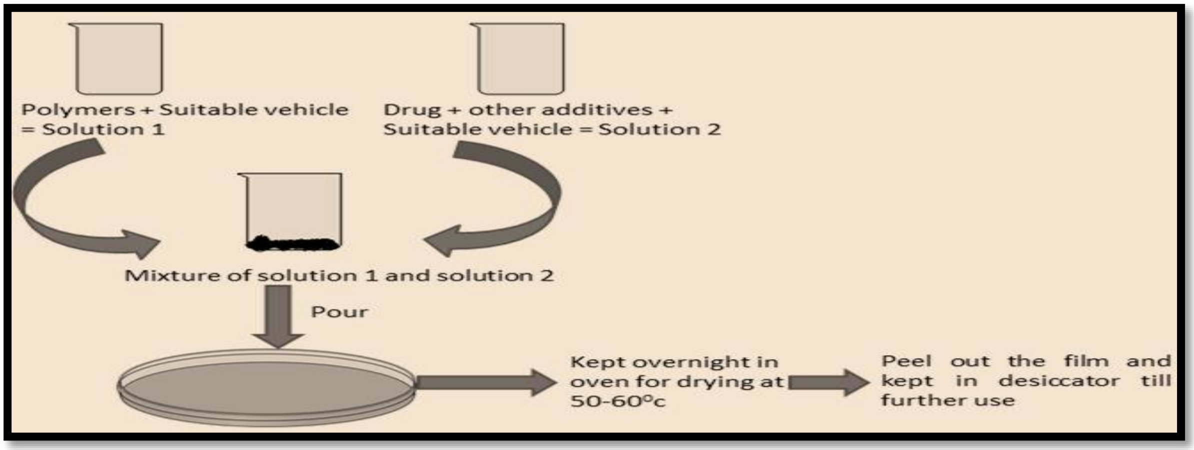


Figure 5.3 Schematic diagram of solution casting method (Source: Kumar and Teotia, 2019)

5.7 Procedure for synthesizing the membrane are as follows:

- 5% stock solution of PVA was prepared in distilled water
- Separate stock solution of 2.5% corn starch was prepared in distilled water.
- 10 mL of PVA solution and 10 mL of the corn starch solution was blended thoroughly using a hot magnetic stirrer.
- 1 mL of 0.4% glutaraldehyde solution was added as the cross-linking agent.
- After 30 min on the magnetic stirrer at 50°C, the contents were poured in a glass plate and kept in a 37°C incubator for 24-48 h. The film is carefully removed and stored in -20°C for future use.

5.8 Studies on PVA-corn starch (composite) membrane

Determination of swelling behavior

In order to measure the swelling degree of PVA-corn starch membrane, samples were cut into 2cm×1cm pieces and dried at 37°C in a vacuum oven for 6 h, the weight of driedsample was determined (We). The dried samples were soaked in different pH buffer solutionsof pH 4, pH 7 and pH 9.2, incubated at 37°C during which they were weighed at every 30 min followed by 1 h intervals (till there is no subsequent weight change, i.e., the matrices have reached equilibrium swelling). The weight of the swollen pieces was designated as (Ws). Theexcess moisture was wiped from the surface of the swollen pieces with tissue paper before weighing. The water uptake of membrane was determined using the following equation:

$$\textit{Water uptake or swelling ratio SR (\%)} = \frac{Ws - We}{We} \times 100$$

Determination of hydrolytic degradation

In order to measure the degree of hydrolytic degradation of PVA-corn starch membrane, the swollen pieces in the different pH buffer solutions after completion of swelling study, were transferred into a hot air oven and dried for a period of 24 h at 37°C. The final weights of the membrane pieces after incubation were recorded (Wd). The formula:

$$\textit{Hydrolytic degradation}(\%) = \frac{We - Wd}{We} \times 100$$

5.9 Preparation of iron nanoparticles infused membrane (mFeNP)

After the stability and characterisation of membrane was confirmed, the iron nanoparticles were infused into the membrane in three varying concentration. Those concentrations were:-

1. 1 mg/mL of iron nanoparticles in membrane
2. 2 mg/mL of iron nanoparticles in membrane
3. 0.5 mg/mL of iron nanoparticles in membrane

Thereafter fixing the concentration of iron nanoparticles to be infused, 3 sets of membrane were prepared in following way-

1. 5% stock solution of PVA was prepared in distilled water.
2. Separate stock solution of 2.5% corn starch was prepared in distilled water.
3. 10 mL of PVA solution and 10 mL of the corn starch solution was blended thoroughly using a hot magnetic stirrer. To it the required dose of the respective nanoparticles was added(1 mg/mL, 2 mg/mL and 0.5 mg/mL respectively into 3 membranes).
4. 1 mL of 0.4% glutaraldehyde solution was added as the cross-linking agent.
5. After 30 min on the magnetic stirrer at 50°C, the contents were poured in a glass plate and kept in a 37°C incubator for 24-48 h. The film is carefully removed and stored in -20°C for future use.

Once the membranes were prepared, the **pH dependent swelling behavior and hydrolytic degradation were again checked for all the 3 sets of membranes**.

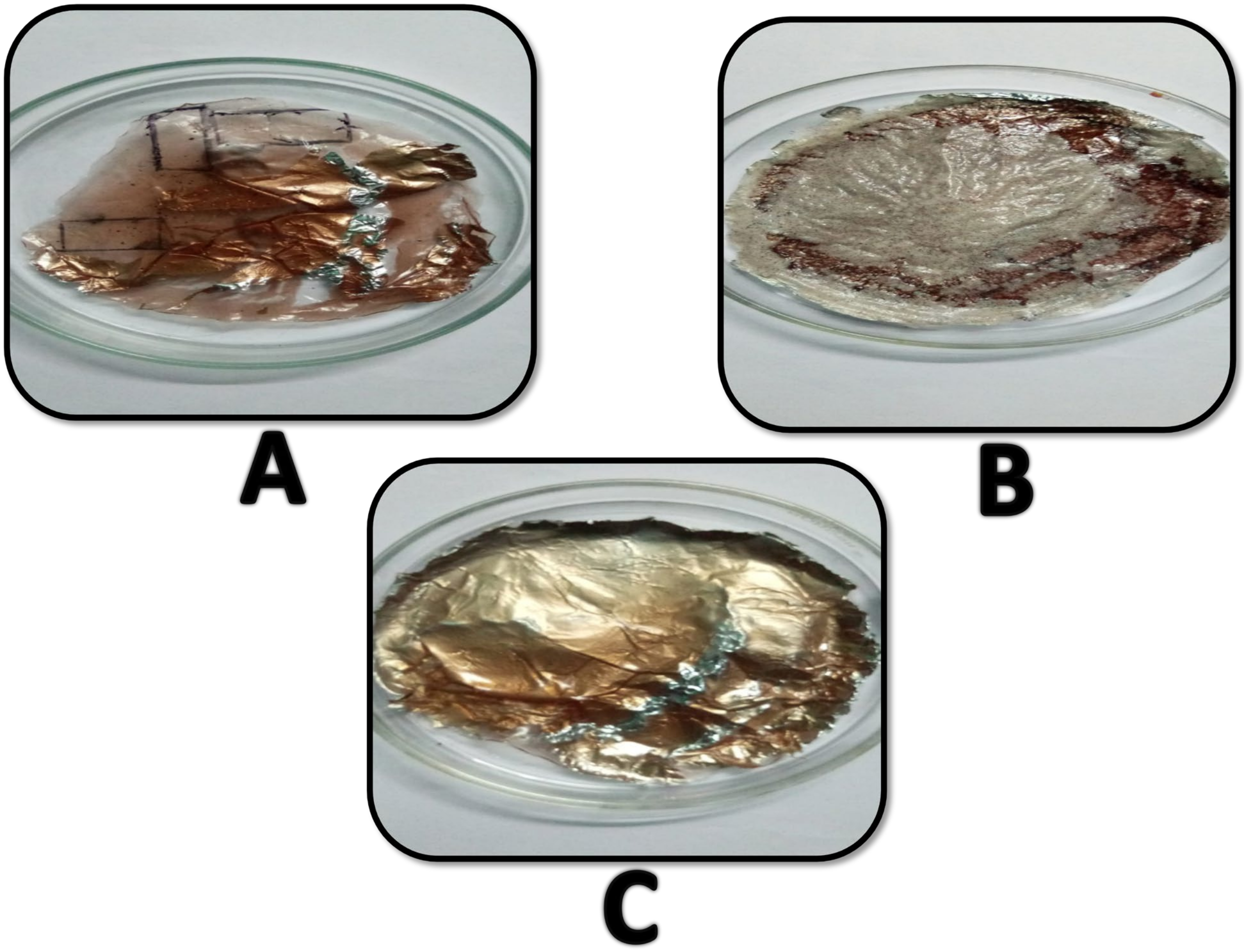


Fig.5.4 Iron nanoparticle infused membrane (mFeNP). A: 1 mg/mL of iron nanoparticles in membrane, B: 2 mg/mL of iron nanoparticles in membrane, C: 0.5 mg/mL of iron nanoparticles in membrane.

5.10 Testing the arsenic sequestration capacity of iron infused membrane (mFeNPs)

First a stock solution of arsenic (containing pentavalent and trivalent form) of 100 ppb is prepared. Another stock solution of pentavalent arsenic 100 ppb is prepared.

The three membranes were labelled as follow:

A- 1 mg/mL of iron nanoparticles containing membrane
B- 2 mg/mL of iron nanoparticles containing membrane
C- 0.5 mg/mL of iron nanoparticles containing membrane

Each membrane was cut out into 2 pieces; one piece of membrane was added to 10 mL of arsenic (containing pentavalent and trivalent form) of 100 ppb solution and another piece of membrane is added to pentavalent arsenic 100 ppb solution.

In the above mentioned way, two sets for each labelled membrane (mFeNPs) were prepared. All the samples were kept overnight and next they were filtered and stored for arsenic ananlysis.

5.11 Total As Analysis

A Varian model AA140 (USA) was used for the total As estimation of all the liquid and digested solid samples by FI-HG-AAS method (Roychowdhury, 2008a). Details of instrumentation, optimization conditions and methodology of FI-HG-AAS system were as reported earlier(Das et al., 1995; Samanta et al., 1999; Roychowdhury, 2008a, 2010).

Chapter 6

Results And Discussions

6.1 Synthesis and characterization of synthesized FeNPs

1. UV-Vis Spectrophotometry:

The completion of the formation of FeNPs was monitored by sampling of small aliquot of the reaction mixture and scanning under a UV-Visible spectroscope in the 250-350 nm range. The spectroscopy shows a peak at 294 nm. Electrons absorb the UV rays and gets excited to higher state. This leads to the surface vibration of electron resulting in formation of peak at 294 nm.

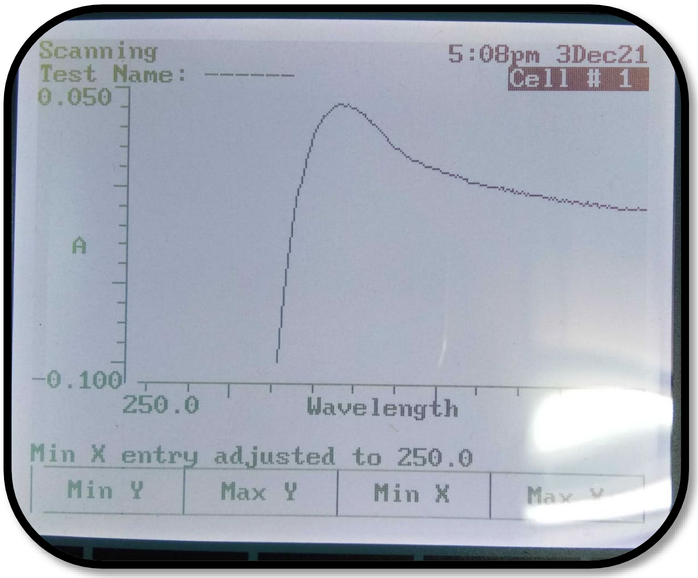


Fig.6.1 UV spectrophotometer showing peak at 294 nm for iron nanoparticles

2. Morphological studies of iron nanoparticles using scanning electron microscopy (SEM)

The SEM results show that the iron nanoparticles were in the size distribution in between 50.52 nm to 74.84 nm, with mean particle size of 60.46 ± 2.94 nm. According to particle size the nanoparticles were less than 100 nm, so nano-scale particles size could be achieved. These particles are responsible for sequestration of arsenic from arsenic contaminated water.

Elemental mapping analysis shows that carbon, potassium, nitrogen, silicon, platinum and iron are present as shown in figure number 6.4.

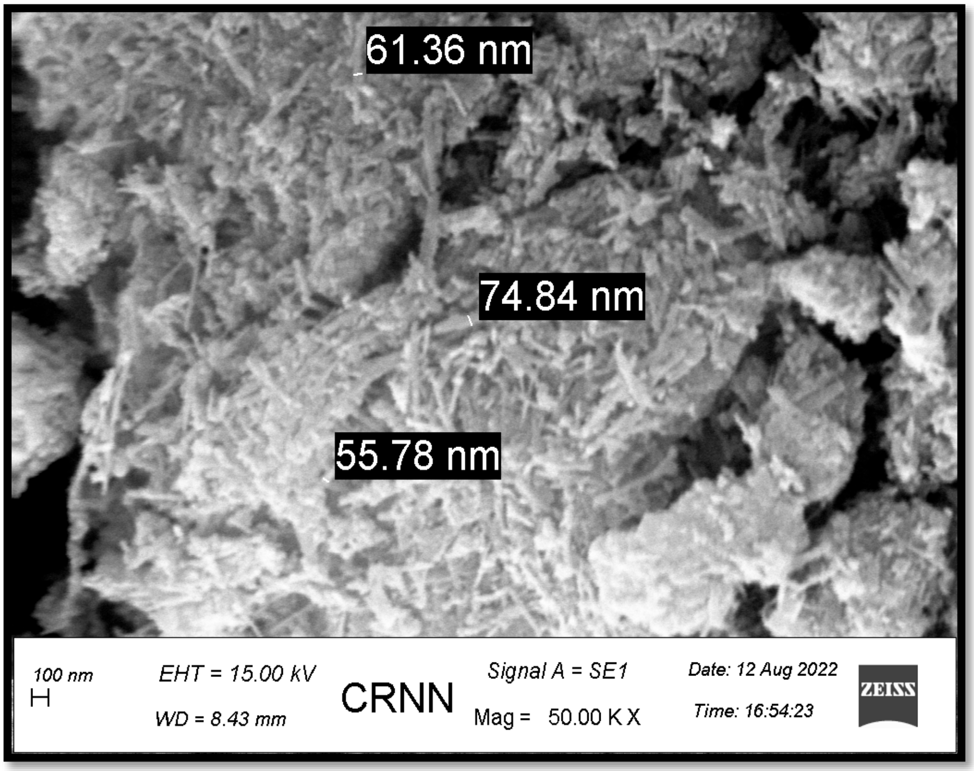


Fig 6.2 SEM for lab synthesized iron nanoparticles obtained via SEM analysis

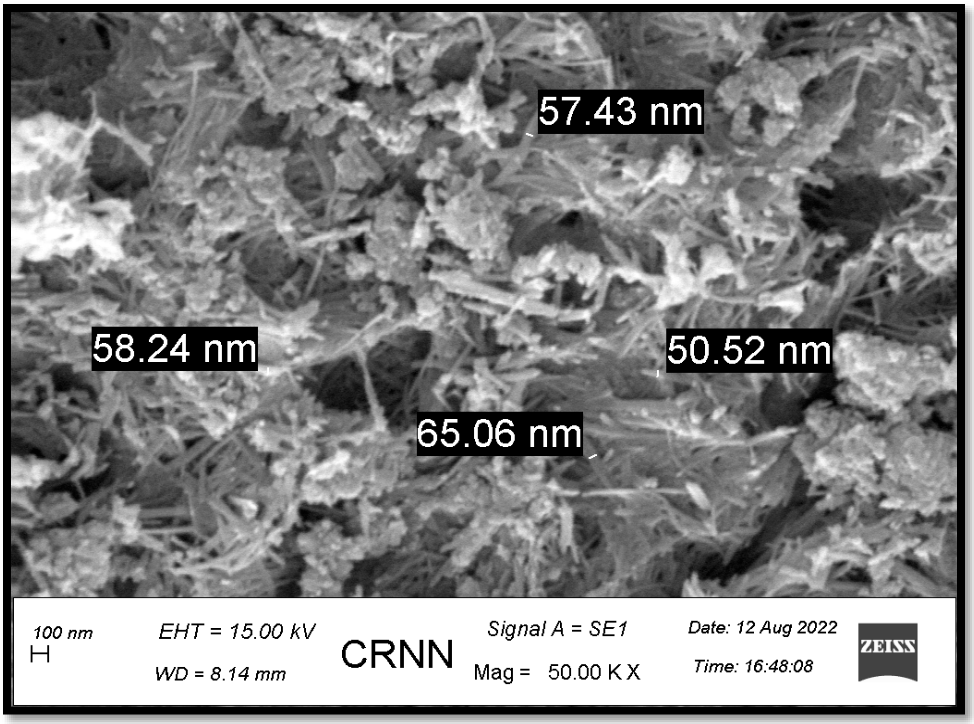
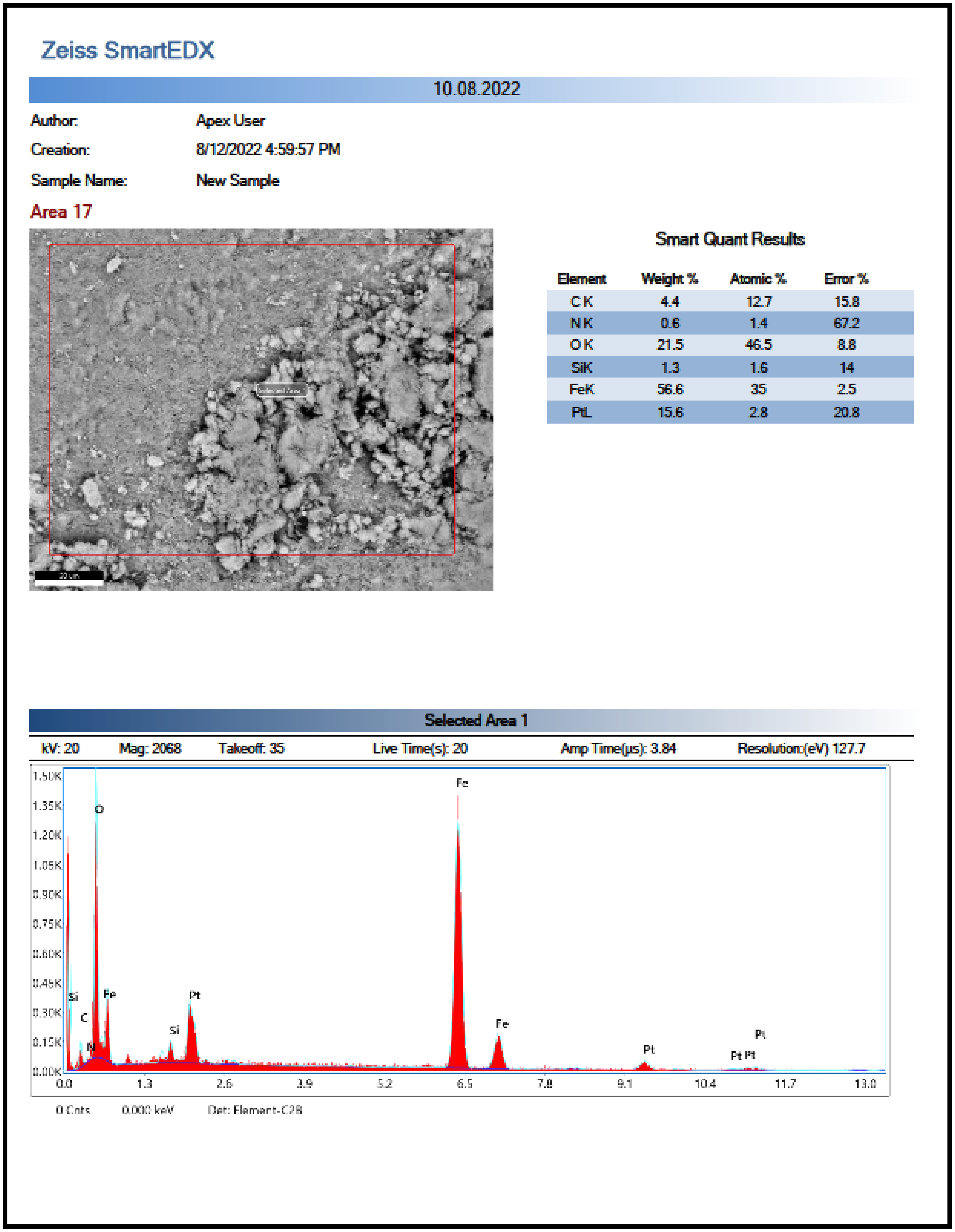


Fig. 6.3 SEM result for lab synthesized iron nanoparticles obtained via SEM analysis



Zeiss SmartEDX

10.08.2022

Author:	Apex User
Creation:	8/12/2022 4:59:57 PM
Sample Name:	New Sample

Area 17

Smart Quant Results

Element	Weight %	Atomic %	Error %
C K	4.4	12.7	15.8
N K	0.6	1.4	67.2
O K	21.5	46.5	8.8
SiK	1.3	1.6	14
FeK	56.6	35	2.5
PtL	15.6	2.8	20.8

Selected Area 1

kV: 20 Mag: 2068 Takeoff: 35 Live Time(s): 20 Amp Time(µs): 3.84 Resolution:(eV) 127.7

0 Cnts 0.000 keV Det: Element-C2B

Fig. 6.4 Elemental mapping analysis result for lab synthesized iron nanoparticles obtained via SEM analysis

6.2 Characterization of PVA-corn starch blended membrane

Estimation of swelling and degradation behavior

Swelling behaviour is a characteristic of membranes defined as the property of a material to imbibe large amounts of a liquid without dissolving in it. The swelling property of the PVA- corn starch thin hydrogel matrix was determined as a function of time, at three physiological pH conditions; namely a neutral pH of 7 and an alkaline pH of 9.2. At pH 6.5 to 8.5, As III is present as uncharged arsenious acid, H_3AsO_3, under reducing conditions, whereas As V is present in the form of singly and doubly charged $H_2AsO_4^-$ and $HAsO_4^{2-}$ anions in oxidizing waters. Thus, processes that remove anions (e.g., anion exchange and activated alumina adsorption) are suitable for removing As (V) and As (III). It has also been seen Arsenic (III) removal efficiency increased with iron and was best removed at pH 7.12 (Devi et al., 2014). So while measuring the swelling properties of membranes, it was conducted under basic condition. Thus Ph 7 and 9 was taken into consideration in order to study swelling properties.

It was observed that the matrix pieces started losing their structural integrity to a certain degree beyond incubation for 24 h for ph 9.2. However, this was not the case upon incubation at pH of 7. It was possible to retrieve the swollen matrix pieces from the buffer maintained at pH 7 up to 48 h. The PVA-corn starch matrix showed maximum swelling of 350 ± 10.7 % at pH 7 and 903 ± 9.40 % at pH 9.2, after incubation for 12 h. This indicates that the membrane is most useful to help in remediation of arsenic effected groundwater, since the average pH of groundwater samples with arsenic concentrations greater than 10 μg/L is only 7.6 (Podgorski et al., 2017).

After iron nanoparticles were infused into the membranes at various concentrations, the swelling percentage were checked at pH 7, the percentage of swelling by few percentage but the structural integrity remained intact for all throughout.

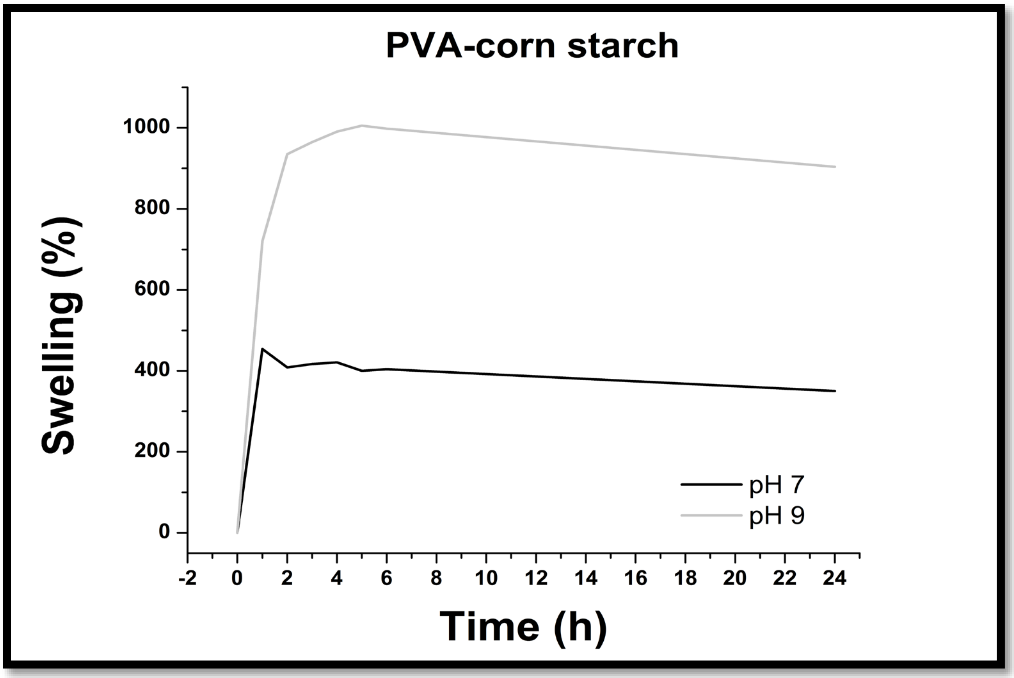


Fig. 6.5 Swelling percentage graph for lab synthesized membrane

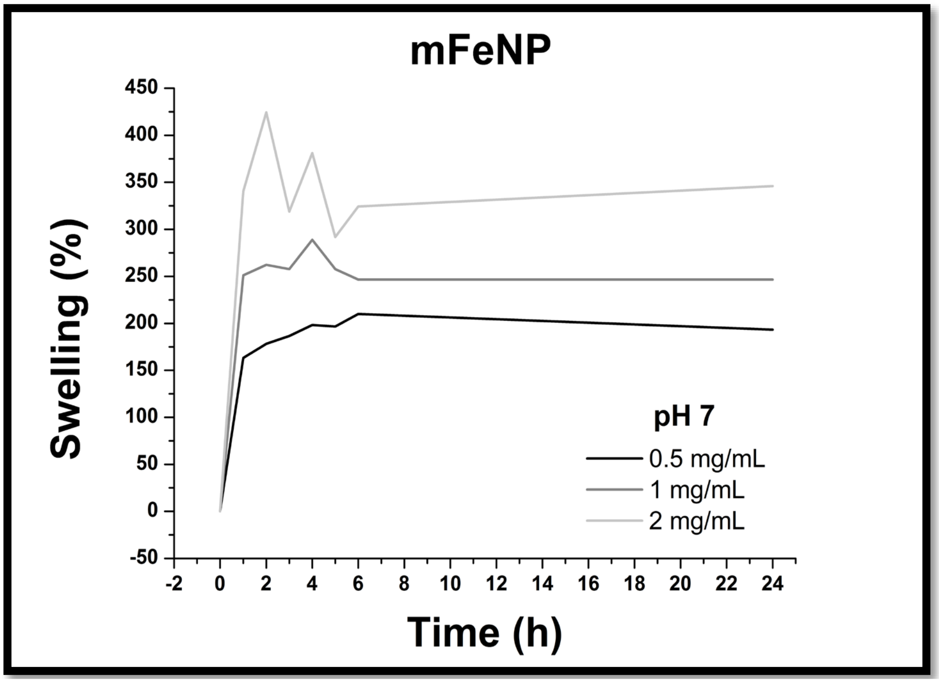


Fig. 6.6 Swelling percentage graph for mFeNP at various iron nanoparticles concentration

6.3 Estimation of arsenic content after treatment of arsenic contaminated water by mFeNP

After treating the arsenic contaminated water samples with mFeNP over night, next day the arsenic content was of the water were estimated after filtration.

Initially the arsenic content of water was 100 ppb.

Table 2 Arsenic concentrations in water after being treated by mFeNP

Sample Name	**Arsenic Concentration(ppb/µg/L) (initial)**	**Arsenic Concentration(ppb/ µg/L) (after treatment)**	**% Reduction in Arsenic concentration(after treatment)**
As- water Fe Nanoparticle	100	31.7	68.3
As- water mFeNP(0.5 % Fe conc.)	100	72.7	27.3
As-V water mFeNP(0.5 % Fe conc.)	100	60.4	39.6
As- water mFeNP(1 % Fe conc.)	100	51.24	48.6
As-V water mFeNP(1 % Fe conc.)	100	40.5	59.5
As- water mFeNP(2 % Fe conc.)	100	28.85	71.15
As-V water mFeNP(2 % Fe conc.)	100	26.85	73.15

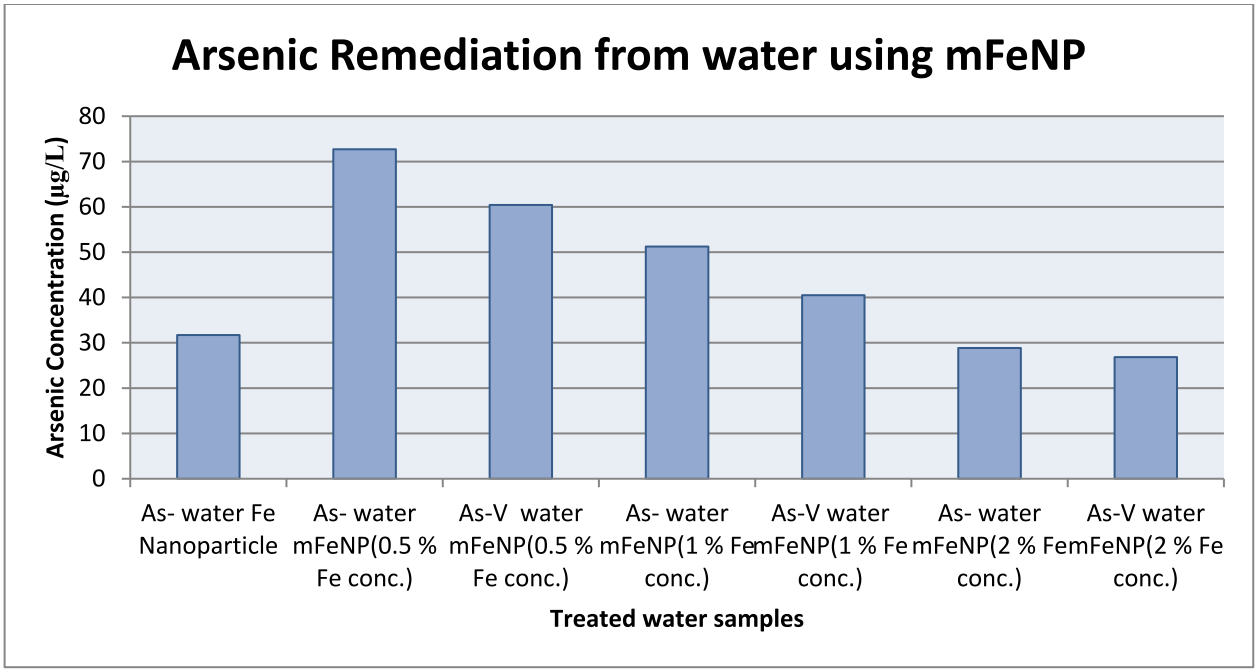


Fig. 6.7 Graph showing concentration of arsenic in contaminated water after being treated with mFeNP

Chapter 7

Conclusion

Conclusion

In this study it is revealed that iron nanoparticles and the novel formulated iron nanoparticle infused membrane (mFeNPs) both can reduce the arsenic concentration in water to an appreciable level. Both show comparable effective results. Thus it can be concluded that mFeNp can serve as an effective remediation method for removal of arsenic from water.

Addition of direct iron nanoparticles is not preferable since iron nanoparticles can form colloidal emulsion and along with it becomes difficult to remove since it needs to be filtered number of times in order to remove the nanoparticles completely. On the other no leaching out of iron nanoparticles from membrane occurs during the remediation process of arsenic contaminated water and along with this it is also economical, since it can be easily synthesized with readily available materials. So mFeNP can be considered effective and more preferable for remediation of arsenic contaminated water.

Along with this the treated water is suitable for general uses purposes but cytotoxicity of the water is also needed to be checked before it can be labelled as absolutely fit for drinking for drinking purposes.

Chapter 8

Future Work

The results discussed in the previous sections are simply stepping stones upon which a huge foundation can be build towards a novel arsenic remediation via membrane system. As such there are certain test and variation of chemical elements used for mFeNP composition which can be performed as a continuation to this study.

- **Cytotoxic study**

  Cytotoxic study should be done to learn about potential toxicity which might have be there after filtration, in order to confirm absolute safety of water for drinking and other biological and agricultural purposes.

- **Varying concentration of iron nanoparticles in mFeNP**

  The concentration of iron nanoparticles infused in membrane can be further varied upto a admissible level in order to check if the variation of iron nanoparticles quantity in mFeNP can increase the remediation percentage of arsenic contamination in affected water.

OBJECTIVE 2:

AN APPROACH TO REMEDIATION OF ARSENIC CONTAMINATED RICE GRAINS FROM COOKED RICE

Chapter 9

Materials and Methods

9.1 Post harvesting procedure

Parboiling of mature whole grains i.e. grain along with its husk of paddy plant is a common post harvesting procedure followed by farmers in rural Bengal. Parboiling of rice is a process involving soaking, steaming and drying of the whole grain with its hull intact. It is generally employed because it imparts health benefits by increasing contents of vitamin and other mineral in the grain. Whole paddy grains are steamed with water in a ratio of 5:1 respectively for 30 min at a temperature of 70-90º C. This concludes the half boiling stage. To obtain parboiled whole grains, the steamed (half boiled) whole grains are subsequently soaked in water at a ratio of 1.2:1 and allowed to stand undisturbed overnight. Next day, the soaked grains were subjected to boiling at 70-90º C for 30 min, which concludes the full boiling stage. These full boiled whole grains are finally subjected to sun drying treatment which converts them to parboiled whole grains, followed by mechanical dehusking to separate the edible part (parboiled rice grain) from the husk (Chowdhury et al.,2018)

Fig. 9.1 Parboiled rice grains(Source: Wikipedia; parboiled rice)

9.2 Study Area

In this research, the study area taken into account is Gaighata (22.93°N 88.73°E), which is a community development block that forms an administrative division in Bangaon subdivision of North 24 Parganas district in the Indian state of West Bengal. This area has been reported to be affected with high levels of arsenic contamination in water and foodstuffs (Joardar et al., 2021). Rice grains from the fields of Gaighata, grown by the farmers living over there have been collected for the arsenic analysis. Figure 8.2 shows the location map of the studied areas.

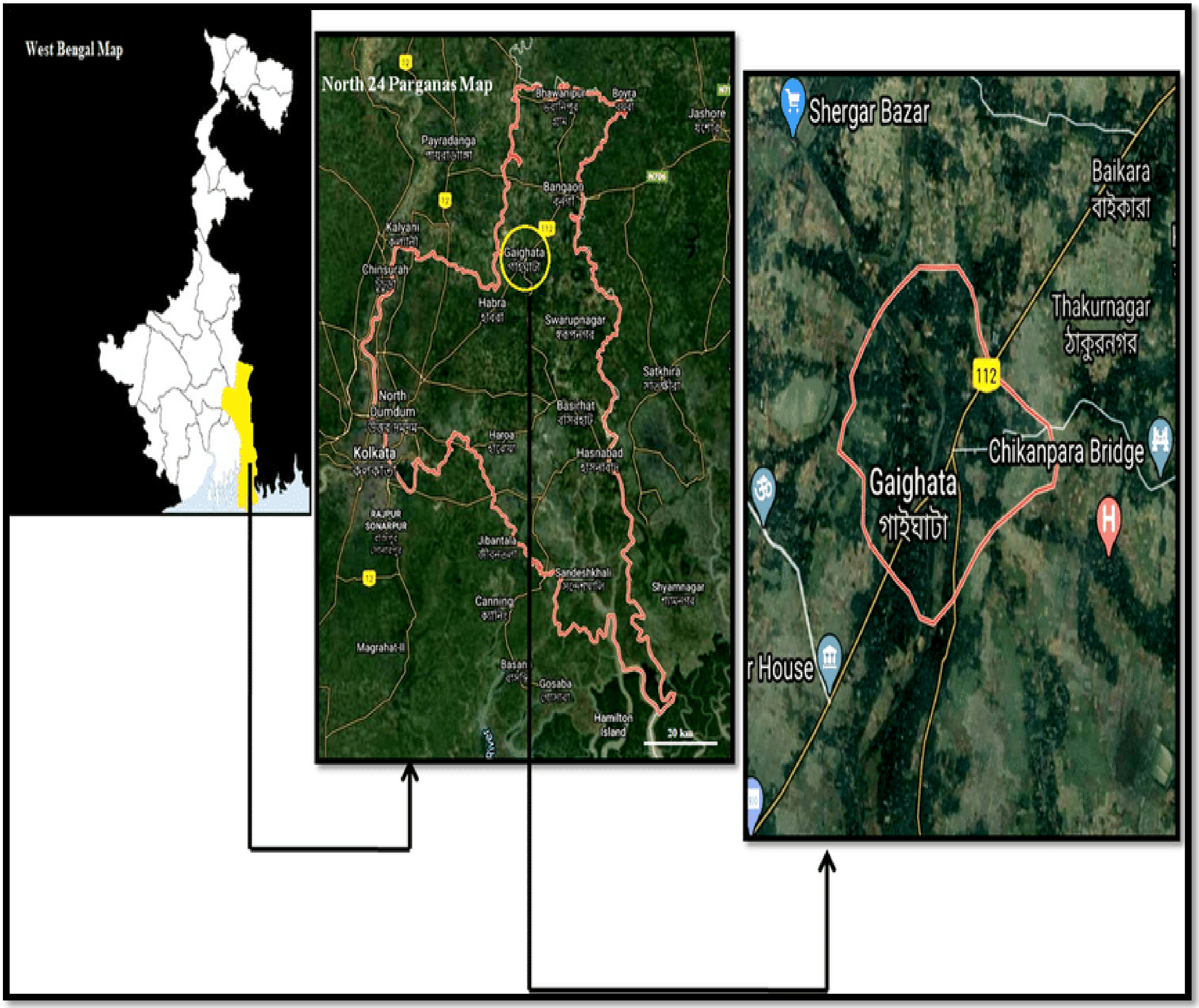


Fig.9.2 Map of Gaighata showing arsenic affected area (Source: Joardar et al., 2020)

9.3 Sample collection and preparation

Raw parboiled rice grain samples were collected in sterile zip-locks, which are harvested by the farmers and consumed by the families living there. All the solid samples were processed for digestion, prior to arsenic estimation. Raw rice grains were processed directly for digestion. Procedures and protocols for rice cooking were followed and parts of wet cooked rice was directly digested and part was dried in a hot air oven at 50 °C for 24–48 h until constant weight was achieved and then digested. All samples were 4º C until analyzed for arsenic estimation.

9.3(a) Varieties of rice grain

Different cultivars of parboiled rice varieties like Minikit and Maharaj were collected from various rural areas cultivated by different farmers.

Fig. 9.3 Collected rice samples

9.3(b) Preparation of cooked rice

The work was carried out at laboratory scale using As-free water (As< 3 μg/L) with parboiled rice grains. Rice grains were taken in two sets of glass beaker, washed with laboratory tap water (As <3 μg/L) for 10 min with rice to water ratio of 1:2, followed by soaking in tap water for 30 min maintaining the ratio of 1:2 before cooking the rice. A part of As can be lost from raw rice grain at the time of washing and soaking before cooking the rice. Some parts of washed rice grains and soaked rice grains were collected and dried and processed for arsenic digestion and estimation. Then 2 sets of soaked rice grains were cooked with 1:3 rice to water ratio and 1:6 rice to water ratio respectively of cooked rice (wet) was directly processed for digestion. After the rice was fully cooked, the excess water was drained (TDW) were collected for As estimation.

9.4 Chemicals, Reagents and Instruments

- **Chemicals Used:**
  - For Overnight Digestion: 2ml of concentrate Nitric Acid (HNO_3)
    1ml of Hydrogen Peroxide (H_2O_2)
  - For estimation purpose: Sodium Borohydride [$NaBH_4$] (Merck);

Potassium Iodide [KI] (Merck);

Hydrochloric Acid (HCl) about 35% (Merck);

Sodium Hydroxide Pellets [NaOH] (Merck)

- **Reagents:**

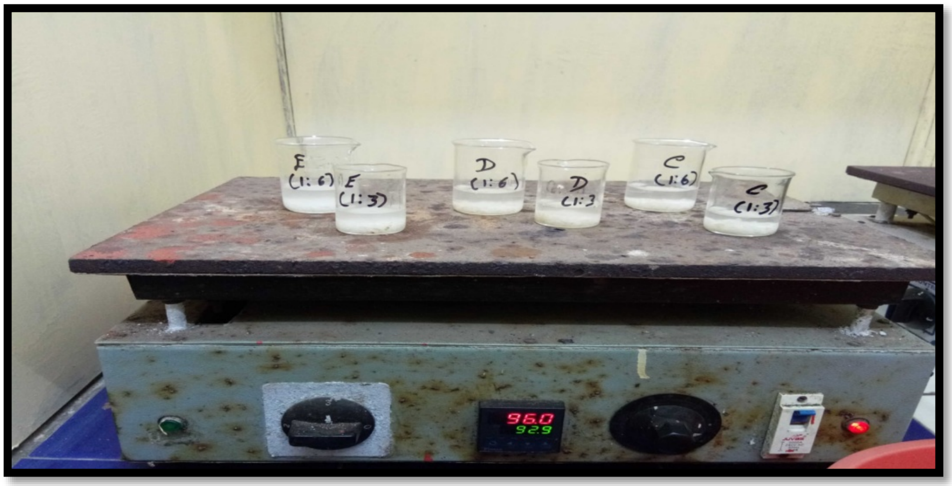
For 500ml of Reductant Solution – 3 gm of $NaBH_4$ + 2.5 gm of NaOH

For 500 ml of Acid Solution – 200 ml of conc. HCl + 300 ml of dd H_2O

For 100 ml of 10% KI – 10 gm KI + 90 ml dd H_2O

Instruments used:

Hot plate:



VARIAN AA140 HG- AAS (Hydride Generation Atomic Absorption Spectrophotometer):

Suction Filtration Unit:

- **Calibration:**

  Calibration curve was prepared using Blank, 10, 20, 30, 40 µg/L of Arsenic Solution

- **Preparation of Samples:**

  To every 5 ml of sample 0.6 ml of 10% KI and 0.4 ml of HCl is added.

  Two procedural blanks were prepared in the same way as the digested samples.

9.5 Digestion

Approximately, 0.02–0.2 g (dry weight) of individual rice grain samples were placed in small beaker with the addition of concentrated HNO3 (96%) and H2O2 (30% v/v) in a ratio of 2:1 and kept for overnight digestion. After that, the digested materials were vaporized by placing them on a hot plate for 1 h at about 90 °C. The vaporized materials were adjusted to a required volume (4–5 ml) with double distilled water and passed through a suction filter (Millipore 0.45 μm). The filtered solutions were then stored for further analysis of arsenic estimation in cooked rice was based on wet and dry weight. The details of sample digestion methodology have been described elsewhere (Roychowdhury, 2010).

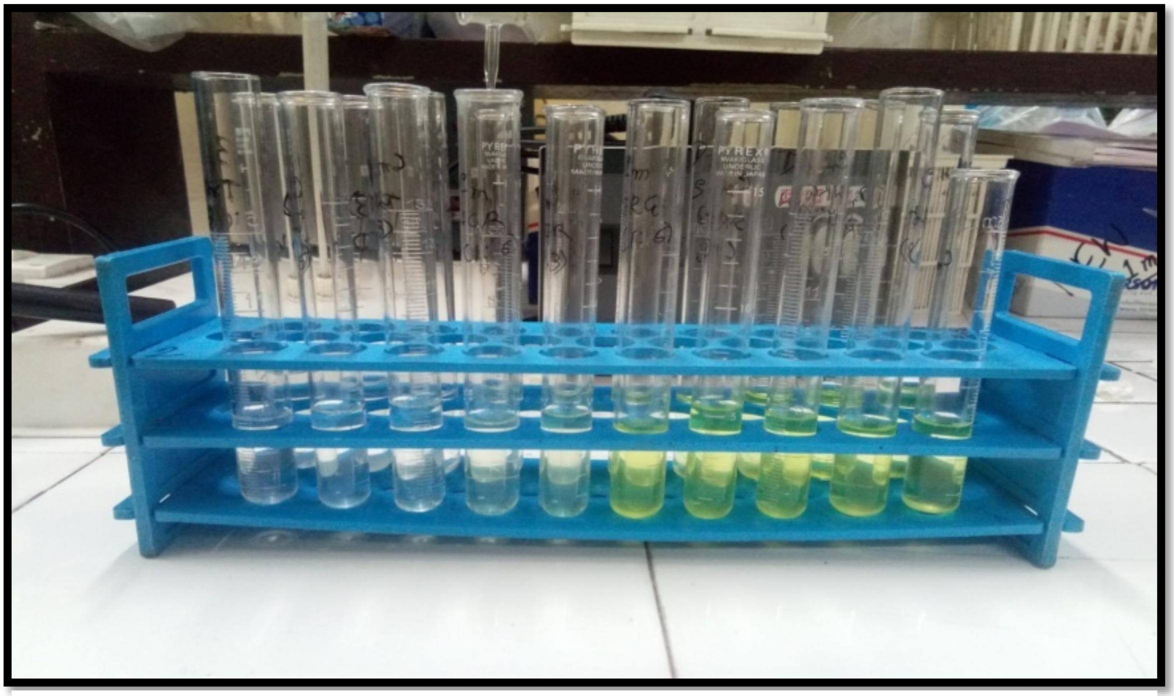


Fig. 9.4 Samples ready for arsenic estimation

9.6 Analysis

9.6(a) Total As

A Varian model AA140 (USA) was used for the total As estimation of all the liquid and digested solid samples by FI-HG-AAS method (Roychowdhury, 2008a). Details of instrumentation, optimization conditions and methodology of FI-HG-AAS system were as reported earlier(Das et al., 1995; Samanta et al., 1999; Roychowdhury, 2008a, 2010).

9.7 Quality control and quality assurance

Quality control and quality assurance were maintained by digesting30% of the solid samples through hot plate digestion method (Chowdhury et al., 2018a). As concentration of a standard reference material [Rice Flour 1568 a(National Bureau of Standards. Gaithersburg, MD, USA)] was analyzed via digestion protocols. Hot plate digestion showed 84 to 86% recovery. Quality control tests were also performed by analyzing duplicates and random repeats of certain samples. Quality control tests by analyzing duplicates which showed ± 8% variation.

Chapter 10

Results and Discussions

10.1 Parboiled rice grain

Higher accumulation of As has been reported in parboiled rice grain compared to their raw variety due to parboiling with As-contaminated water at domestic scale which contributes to additional As(Chowdhury et al., 2018b; Rahman et al., 2007). However, it is of paramount importance to carry out the steaming process in low-As water for preparation of parboiled rice, which often becomes difficult in domestic scale from As affected areas. Additionally, it is of utmost importance of cooking As contaminated parboiled rice in low-As water. In the absence of low-As water, it is necessary to quantify the threshold value of As in cooking water above which the parboiled rice grains will start to accumulate water As.

During the cooking process of parboiled rice grains with lab scale tap water, the movement of As from rice grain to water was evaluated in this study.

Arsenic concentrations of the parboiled raw rice grains of Minikit variety ranged from 197 to 549 µg/kg (average 294 ± 170 µg/kg, n = 4).Post-cooking, the As concentrations in the rice grains (wet condition, average 78 ± 18 µg/kg for rice to water cooking ratio 1:3)(wet condition, average 57 ± 24 µg/kg for rice to water cooking ratio 1:6) decreased by 61–84% with respect to raw rice grain for rice to water cooking ratio 1:3 and for rice to water cooking ratio 1:6 it decreased by 74-82%. It can also found that during the cooking process most arsenic gets reduced when the rice grains is cooked in a ratio of 1:6 water to rice grains after being soaked for 30 mins. The reduction percentage is almost 72-74%.

However arsenic concentrations of the parboiled raw rice grains of Maharaj variety ranged from 48 to 108 µg/kg (average 86 ± 29 µg/kg, n = 4).Post-cooking, the As concentrations in the rice grains (wet condition, average 23 ± 10 µg/kg for rice to water cooking ratio 1:3)(wet condition, average 16 ± 10 µg/kg for rice to water ooking ratio 1:6) decreased by 63–89% with respect to raw rice grain for rice to water cooking ratio 1:3 and for rice to water cooking ratio 1:6 it decreased by 68-85%. It can also found that during the cooking process most arsenic gets reduced when the rice grains is cooked in a ratio of 1:6 water to rice grains after being soaked for 30 mins. The reduction percentage is almost 11-88%.

Arsenic concentration in cooked rice can vary based on various factors like its geographical origin, cultivar, cooking water and the cooking method used (Mondal and Polya, 2008; Mondal et al., 2010). In this study, when laboratory tap water (As< 3 µg/L) was used for cooking, As in cooked rice decreased consistently for both Minikit parboiled rice (Fig.10.2) and Maharaj parboiled rice (Fig.10.1) respectively.

For both Minikit and Maharaj Rice grains, it was observed that the total discarded water termed as TDW, collected after cooking process shows an arsenic concentration of 58.3 ± 51.2 µg/L for Minikit rice cooked in rice to water ratio of 1:3 and 54.5 ± 59.4 µg/L for Minikit rice cooked in rice to water ratio of 1:6, similarly for Maharaj rice 5.85 ± 3.5 µg/L cooked in rice to water ratio of 1:3 and 7.57 ± 8.15 µg/L cooked in rice to water ratio of 1:6.

Table 3: Arsenic concentration in various phases of cooked rice

Rice Grain	**Arsenic concentration (µg/kg)**						
	RRG	**WRG**	**SRG**	**WCR**		**TDW(µg/L)**	
				1:3	**1:6**	**1:3**	**1:6**
Minikit A	197	189	184	75.4	50.2	58.9	57.6
Minikit B	207	169	164	56.7	42.4	40.6	68.4
Minikit C	225	213	175	78.2	44.3	43.6	30.8
Minikit D	549	370	346	102	94.2	90.2	61.3
MaharajAm	48.3	31.9	20.1	17.7	11.1	4.7	3.9
MaharajBm	107	84.5	62.7	11.4	16.9	15.1	12.6
Maharaj Cm	108	41.1	38.9	34.6	34.4	2.3	1.4
Maharaj Dm	81.9	33.9	32.2	30.1	3.61	1.3	12.4

Table: 4 Statistical interpretation of arsenic concentration in cooked rice

Rice Grain (variety)	Phases of cooking	Mean (As conc. in µg/kg)	Median (As conc. in µg/kg)	S.D(As conc. in µg/kg)	Range(As conc. in µg/kg)	
					Min	**Max**
	RRG	294	216	170	197	549
	WRG	235	201	92.1	169	370
Minikit	**SRG**	218	180	86.2	164	346
	WCR (1:3)	78.1	76.8	18.7	56.7	102
	WCR(1:6)	57.8	47.3	24.5	42.4	94.2
	TDW(1:3)	58.3	51.2	22.7	40.6	90.2
	TDW(1:6)	54.5	59.4	16.4	30.8	68.4
	RRG	86.5	94.6	28.2	48.3	108
	WRG	47.8	37.5	24.7	31.9	84.5
Maharaj	**SRG**	38.5	35.5	17.9	20.1	62.7
	WCR (1:3)	23.5	23.9	10.7	11.4	34.6
	WCR(1:6)	16.5	14.0	10.7	3.60	34.4
	TDW(1:3)	5.85	3.5	6.3	1.3	15.1
	TDW(1:6)	7.57	8.15	5.7	1.4	12.6

- *RRG- Raw rice grains*
- *WRG- Washed rice grains*
- *SRG- Soaked rice grains*
- *WCR- Wet cooked rice grains*

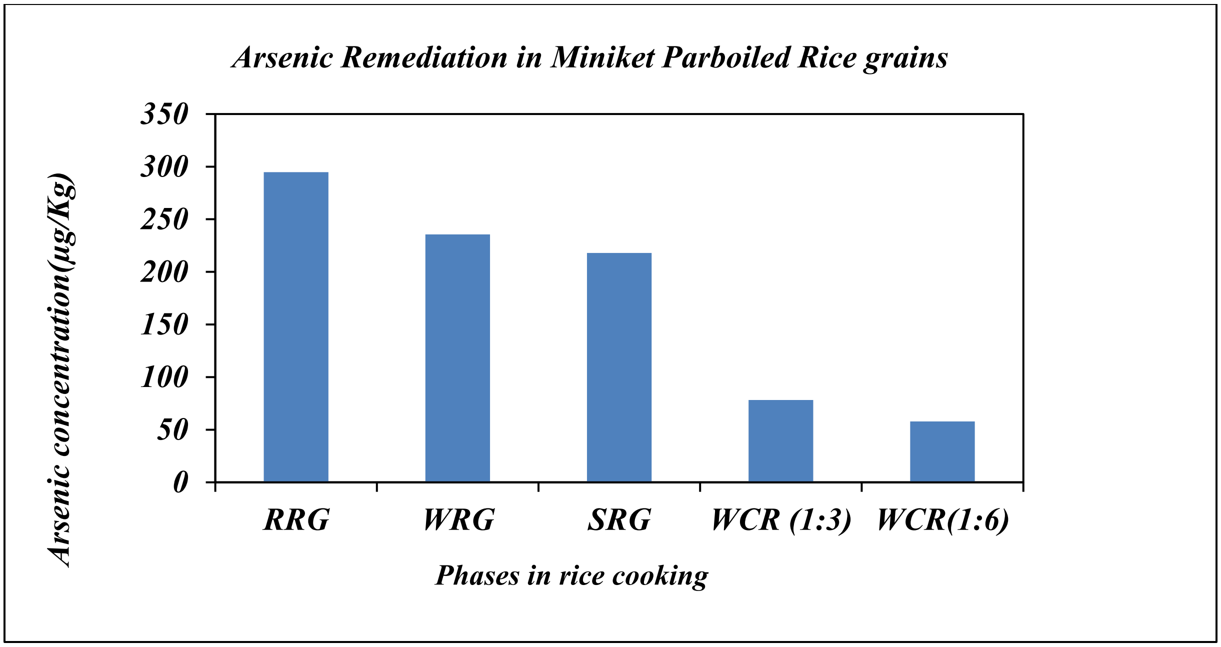


Fig.10.1 *Arsenic Remediation in Minikit Parboiled Rice Grain*

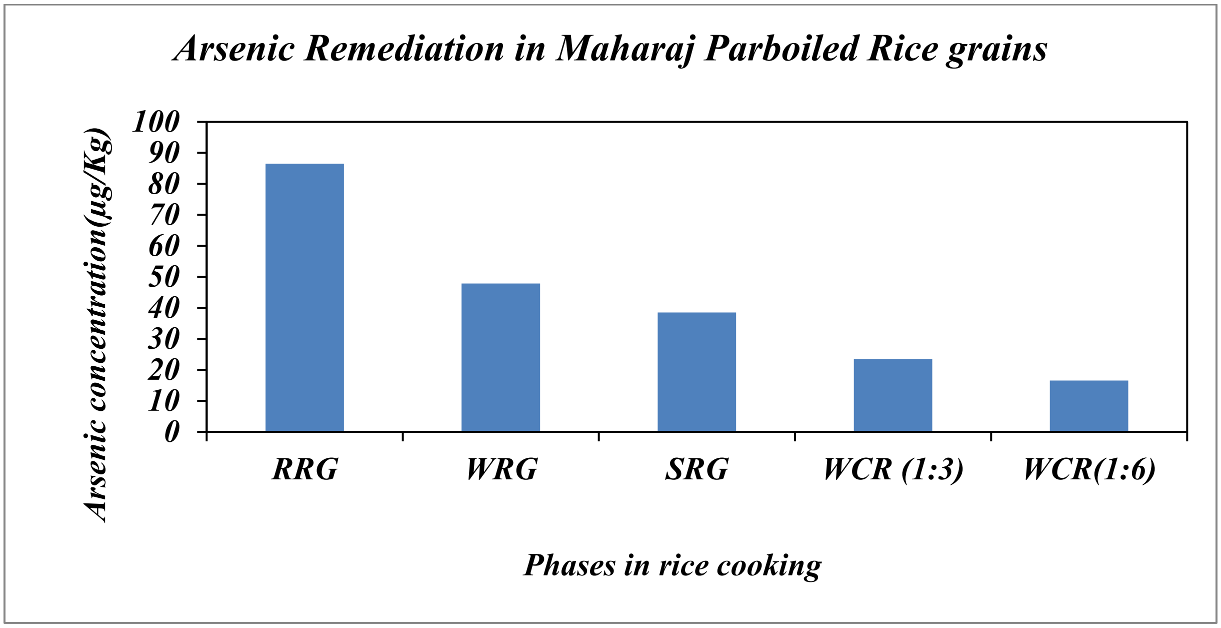


Fig.10.2 *Arsenic Remediation in Maharaj Parboiled Rice grain*

Table: 5.a Percentage increase or decrease of arsenic concentration in cooked rice

Rice Grains	RRG	WRG	% decrease RRG to WRG	SRG	% decrease RRG to SRG	% decrease WRG to SRG
Miniket A	197	189	4.13	184	6.43	2.39
Miniket B	207	169	18.4	164	20.4	2.49
Miniket C	225	213	5.47	175	21.9	17.4
Miniket D	549	370	32.4	346	36.8	6.50
Maharaj Am	48.3	31.9	33.9	20.1	58.3	36.9
Maharaj Bm	107	84.5	21.2	62.7	41.5	25.7
Maharaj Cm	108	41.1	62.0	38.9	64.1	5.44
Maharaj Dm	81.9	33.9	58.6	32.2	60.6	4.90

Table: 5.b Percentage increase or decrease of arsenic concentration in cooked rice

Rice Grains	WCR(1:3)	WCR(1:6)	% decrease RRG to WCR(1:3)	% decrease RRG to WCR(1:6)	% decrease SRG to WCR(1:3)	% decrease SRG to WCR(1:6)
Miniket A	75.4	50.2	61.7	74.5	59.1	72.7
Miniket B	56.7	42.4	72.6	79.5	65.5	74.2
Miniket C	78.2	44.3	65.3	80.3	55.5	74.7
Miniket D	102	94.2	81.3	82.8	70.4	72.8
Maharaj Am	17.7	11.1	63.2	76.9	11.9	44.8
Maharaj Bm	11.4	16.9	89.3	84.2	81.7	73.1
Maharaj Cm	34.6	34.4	68.1	68.1	10.9	11.3
Maharaj Dm	30.1	3.61	63.2	95.5	6.51	88.8

Table: 6 Statistical interpretation of Percentage increase or decrease of arsenic concentration in cooked rice

Rice Grains	% decrease in arsenic	Mean	S.D.	Median	Range	
					Min	Max
	RRG to WRG	15.1	13.2	11.9	4.13	32.4
	RRG to SRG	21.4	12.4	21.2	6.43	36.8
	RRG to WCR(1:3)	70.2	8.68	68.9	61.7	81.3
Minikit Parboiled	RRG to WCR(1:6)	79.3	3.47	79.9	74.5	82.8
	WRG to SRG	7.22	7.10	4.50	2.39	17.4
	SRG to WCR(1:3)	62.6	6.66	62.3	55.5	70.4
	SRG to WCR(1:6)	73.6	1.01	73.5	72.7	74.7
	RRG to WRG	43.9	19.6	46.2	21.2	62.0
	RRG to SRG	56.1	10.0	59.4	41.5	64.0
	RRG to WCR(1:3)	70.9	12.4	65.6	63.2	89.3
Maharaj Parboiled	RRG to WCR(1:6)	81.2	11.6	80.6	68.1	95.5
	WRG to SRG	18.2	15.7	15.5	4.90	36.9
	SRG to WCR(1:3)	27.7	36.0	11.4	6.51	81.7
	SRG to WCR(1:6)	54.5	34.0	58.9	11.3	88.8

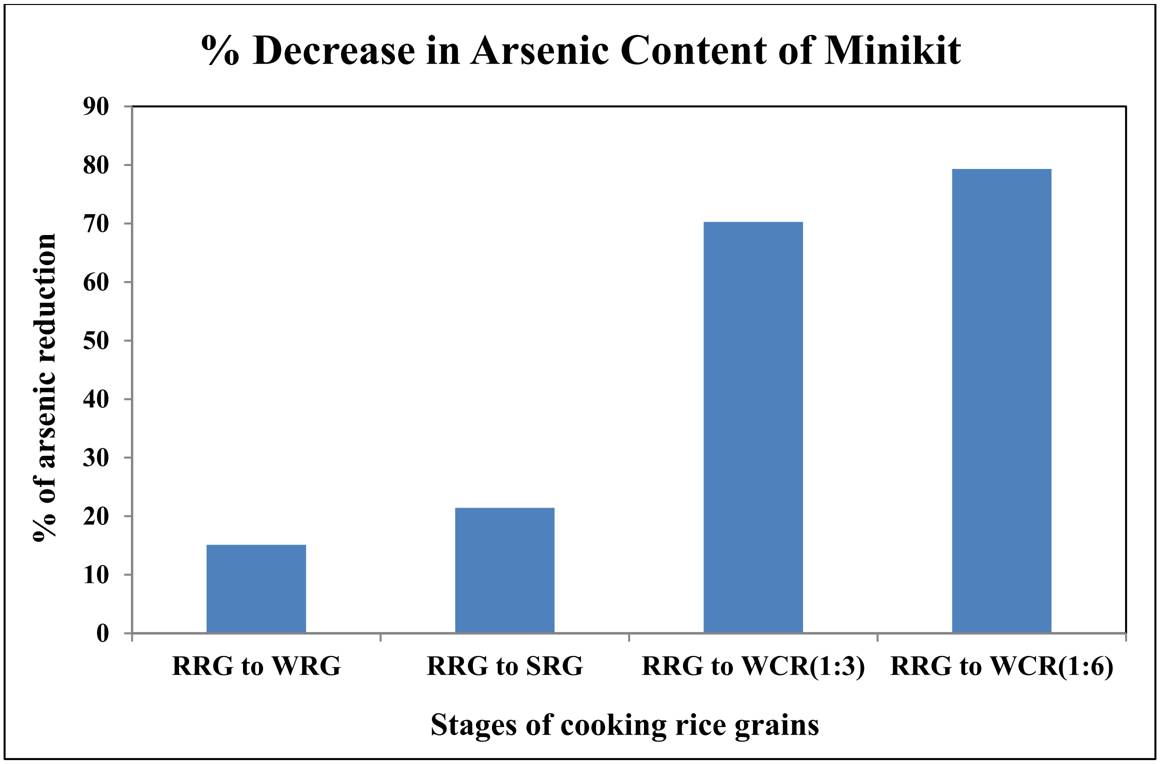


Fig.10.3 Percentage Decrease in Arsenic concentration of Parboiled Minikit Rice grain

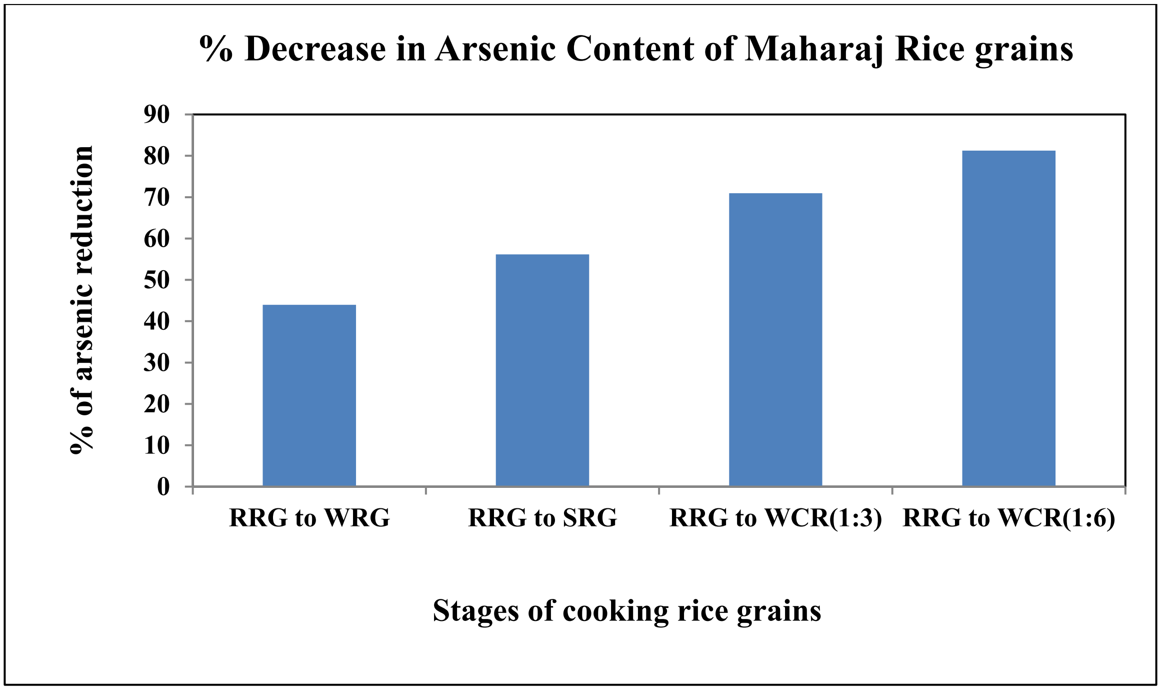


Fig. 10.4 Percentage Decrease in Arsenic Content of Parboiled Maharaj Rice grain

10.2 Arsenic movement direction between rice grain and cooking water

Rice is the staple diet of a large portion of the Asian population. This staple cereal is very often cultivated with As-contaminated groundwater in GMB plain and the rice grains accumulate high amount of As(Meharg et al., 2009; Sun et al., 2008; Torres-Escribano et al., 2008), in comparison to other agricultural products (Das et al., 2004; Schoof et al., 1999). The concentration of As can vary widely depending on the variety of rice (Booth, 2008) and geographical location (Meharg et al., 2009). Rice is by far the largest dietary source (50–70% of th etotal meal) of As for the populations consuming As free drinking water (Chatterjee et al., 2010; Meharg and Rahman, 2003).Arsenic movement direction between rice grain and water used for cooking depends on several factors like initial rice grain As concentration, cooking method, cooking water As concentration, rice cultivar. From Table 4, it can be well concluded that the arsenic from rice grains are drained out through excess water, since the TDW taken out after cooking process shows an arsenic concentration of 58.3 µg/L for Minikit rice cooked in rice to water ratio of 1:3 and 54.5 µg/L for Minikit rice cooked in rice to water ratio of 1:6, similarly for Maharaj rice 5.85 µg/L cooked in rice to water ratio of 1:3 and 7.57 µg/L cooked in rice to water ratio of 1:6.

10.3 Impact of cooking water Arsenic concentration on rice cultivar

For majority of the parboiled rice grains and different cultivars in this study, As moves from rice to water provided low-As (laboratory tap water) water is used for cooking. Based on the study results, lab tap water where As concentration < 3 μg/L was used for cooking rice was able to decrease As in cooked rice, for both parboiled Minikit rice grain (Fig. 10.1) and parboiled Mahraaj rice grain (Fig.10.2).

Chapter 11

Conclusion

Conclusion

Thus through this study it can be found that higher concentration of arsenic is present in Minikit varieties of parboiled raw rice grains in compare to the Maharaj parboiled raw rice grains varieties.

However, cooking these rice grains in As free or low As water, reduces the arsenic content in quiet a significant amount. Analyzing the arsenic content in each phase of cooking also shows that most amount of As reduction is seen when excess amount of water is used to cook the rice (in this study 1:6 rice to water is used for cooking). Interpreting the statistical data of percentage increase and decrease of arsenic content in parboiled rice grains it was also revealed that percentage reduction of arsenic in Minikit parboiled rice grains is higher than the Maharaj parboiled rice grains.

Thus following a simple, cost effective, household technique with help of low As content water the arsenic content in parboiled rice grains, which is the common rice variety used as staple diet in most parts of urban and rural areas, the arsenic percentage can be reduced to significant amount, if cooked properly in more amount of water.

Chapter 12

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