PERFORMANCE EVALUATION OF JUTE BIOCHAR FOR REMOVAL OF ARSENIC FROM CONTAMINATED WATER

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of the requirements for the degree

Master of Engineering in
Water Resources and Hydraulic Engineering

Submitted by

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This thesis work is dedicated to my parents.

CERTIFICATE OF RECOMMENDATION

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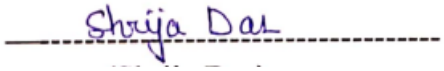
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Abstract

Arsenic is a carcinogenic metalloid that is toxic to humans. The range of arsenic concentrations found in natural waters varies from 0.5 mg/L to 5,000 mg/L. The threshold concentration for safe uses of drinking water is 10 lg/l established by many organizations. Arsenic contamination was detected in the groundwater of different states of India such as West Bengal, Jharkhand, Bihar, Chhattisgarh, Uttar Pradesh and Assam with more than 50 million people residing in arsenic affected areas in India.

Arsenic contaminated groundwater is the primary source of water for irrigation, drinking, cooking and allied purposes in such areas. Due to its high toxicity in the dermal and nervous systems, novel methods of arsenic remediations is to be studied which do not cause large waste generation, require high capital and energy requirements, cause incomplete contaminant removal from water and require high operational and maintenance requirements that are a disadvantage of conventional methods.

The objective of the present study is to evaluate the performance of biochar for removal of arsenic from contaminated water. Arsenic remediation was studied for raw jute biomass and jute biochar pyrolysed at 800℃ under anaerobic conditions. The removal efficiency for three different initial concentrations were determined for different filtration rates and thickness of filter media. The absorption process of arsenic onto biochar is a complex process following different mechanisms for various modifications. However, pristine unmodified biochar has shown effectiveness in arsenic remediation without addition of further reagents if filtration was conducted with multiple layers of filter paper, thereby increasing rate of filtration and thickness of filter media. As jute biomass is cheap and readily available it can be widely employed for mitigation of arsenic in contaminated water.

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Appendix A:

List of Abbreviations

mm	millimetre	mg/l	milligram per litre
cm	centimetre	g/l	gram per litre
m	metre	min	minute
µg	microgram	hr	hour
kg	kilogram	DD	Double Distilled
g	gram	As	Arsenic
ml	millilitre	As (III)	Arsenite
l	litre	As (V)	Arsenate
ppm	parts per million	UV	Ultraviolet
ppb	parts per billion		

WHO	World Health Organization
BIS	Bureau of Indian Standards
EPA	Environmental Protection Act

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CHAPTER- 1

INTRODUCTION

1.1 Introduction-

Arsenic is a natural constituent of the Earth's crust and the 20th abundant element, with an average arsenic content in the continental layer from 2 to 3 mg/kg (Tanaka, 1988). Arsenic has more than 200 mineral forms, including arsenates (60%), sulphides and sulfosalts (20%), and arsenides, arsenates, oxides, silicates, and arsenic in its native form . The common minerals are arsenopyrite (FeAsS), realgar (As4S4), and orpiment (As2S3). Realgar (As4S4) and orpiment (As2S3) are the two crucial reduced forms of arsenic and the oxidised form is arsenolite (As2O3). Other naturally occurring arsenic minerals are loellingite (FeAs2), safflorite (CoAs), and niccolite (NiAs).

Arsenic is introduced in water through dissolution of such minerals and ores, due to erosion and weathering. Anthropogenic activities resulting in discharge of untreated industrial effluents from metallurgical, ceramic, dye and pesticides manufacturing industry into water sources has resulted in increased arsenic levels both in surface and ground waters.

Due to the acute and chronic toxicity of arsenic especially to dermal and nervous systems in humans, arsenic removal is of great significance. The most frequently used remediation methods are coprecipitation with iron and aluminium salts; adsorption onto activated alumina, carbon or activated bauxite; ion-exchange, reverse osmosis and electrocoagulation. Adsorption technology is gaining importance as a sustainable, cost-effective, user friendly and effective method. Biochar, a carbonaceous and stable product, synthesised by the pyrolysis of abundant, inexpensive and freely available solid waste materials derived from agricultural and food-industry byproducts ,as feedstock in an inert atmosphere. It has been used for arsenic removal from contaminated aqueous media, such as oak wood biochar, sewage sludge biochar, Douglas fir biochar, cotton stalk biochar, grape seeds biochar, rice husk and municipal solid waste biochars, waste plant litter biochar, and peanut shell biochar

1.2 History-

Arsenic was known in the form of certain compounds before it was clearly identified as a chemical element. In the 4th century BC, Aristotle called the mineral realgar, a sulphide of arsenic, as sandarache. In the 1st century CE, the writers Pliny the Elder and Pedanius Dioscorides both described the bright yellow dye orpiment, As2S3 as auri pigmentum,. By the 11th century CE three compounds of arsenic were recognized- white (As4O6), yellow (As2S3), and red (As4S4). The element was first isolated in the 13th century by Albertus Magnus,

who named it arsenicum. The first clear report of the free element was made in 1649 by Johann Schroeder, a German pharmacist, who prepared arsenic by heating its oxide with charcoal. In the Middle Ages, arsenic gained notoriety as an effective homicidal agent, because of its toxicity and frequency of its use. Arsenic is often referred to as the "king of poisons".

By the 18th century, arsenic was well known as a unique metalloid. Until the 1850s, arsenic remained a popular poison as it was readily available and was odourless and tasteless, and undetectable in food or beverages. The visible symptoms of acute arsenic poisoning were nausea, vomiting, diarrhoea, and abdominal pain which were easily confused with other common diseases at the time such as cholera and pneumonia.

1.3 General chemistry of Arsenic-

Arsenic constitutes 0.00005% of the Earth's crust with an average concentration of 1-2mg/kg and is the 20th most abundant element, 14th most abundant element and the 12th most abundant element in the Earth's crust, seawater and human body respectively. It is denoted by the atomic symbol As, has the atomic number 33, the atomic weight 74.9 and is a metalloid in Group 15 of the periodic table. It has allotropic forms of both yellow, grey and black arsenic. It is solid at room temperature and sublimes at 616℃.

Its mean concentration in the crust is 1.8ppm; in soils 5.5 to 13 ppm; in streams less than 2ug/L, and in groundwater it is generally less than 100g/L. It occurs naturally in sulphide minerals such as pyrite.

The common oxidation states of arsenic are 5 (existing as arsenates), 3(existing as arsenites and organoarsenic compound) and -3(existing as arsenides and intermetallic compounds). Arsenic is commonly found in groundwater as forms in different proportions - trivalent arsenite and pentavalent arsenate. Arsenite is generally found in groundwater as neutral molecules of AsO_3 whereas arsenate is found as anions of AsO4- in the pH 4-10.

Its mean concentration in the crust is 1.8ppm; in soils 5.5 to 13 ppm; in streams less than 2ug/L, and in groundwater it is generally less than 100g/L. It occurs naturally in sulphide minerals such as pyrite. Arsenic is used in alloys with lead, in storage batteries, and in ammunition.

Arsenic compounds are widely used in pesticides and in wood preservatives. Aqueous arsenic in the form of arsenite, arsenate, and organic arsenicals may

result from mineral dissolution, industrial discharges, or the application of pesticides. The chemical form of arsenic depends on its source.

Arsenate exists in four forms in aqueous solution based on pH-

H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ & AsO_4^{3-}

Similarly, arsenite exists in five forms-

$H_4AsO_3^+$, H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$ & AsO_3^-

Ionic forms of arsenate are common at pH>3, and arsenite is neutral at pH<9 and ionic at pH>9. The valence and species of soluble arsenic are crucial in evaluating conventional arsenic removal technologies. (Wang, 2000).

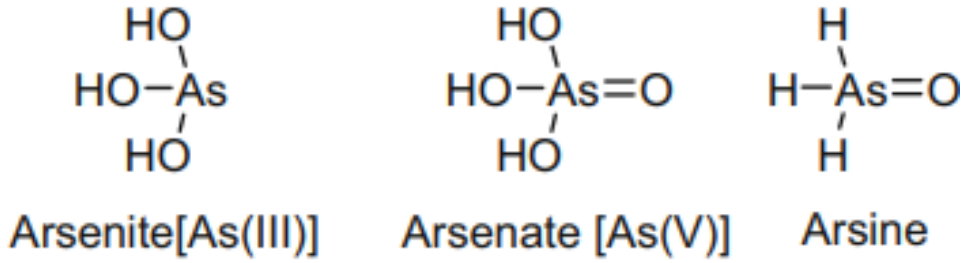


Fig. 1.1: Chemical structure of commonly found arsenic compounds

1.4 MINERALOGY-

1.4.1 Arsenic Oxides-

The affinity of arsenic to bond with other elements and species indicates its rarity as a native element, with the occasional exception in hydrothermal ores. The simple arsenite oxides, arsenolite and claudetite form naturally as secondary weathering products of arsenic sulphides and are also the oxidation products of the roasting of arsenic ore minerals or coal. Condensation of combustion vapours

forms “white arsenic” powder characteristic of arsenic trioxide (National Research Council 1977).

Arsenic trioxides are moderately soluble in water and are a component in insecticides. A large number of alkali, alkaline-earth, and metal arsenite salts can be made by linking arsenite oxyanion groups to a variety of monovalent and divalent cations These compounds are sparse in the natural environment, occurring occasionally in hydrothermal ores at mildly reducing conditions, but have synthesised for industrial use as pigments, curing agents and pesticides for a long time. Copper arsenite (Scheele’s green), following its discovery in 1775 and was used extensively as an insec-ticide. The solubility of arsenite salts depends on the type of cation in the compound, with alkali arsenites being the most soluble and metal arsenites being the least soluble.

Copper, lead, and calcium arsenates were extensively used as herbicides and insecticides from the 1870s to 1970s (Nriagu 2002). Copper arsenate— in the form of chromated copper arsenate (CCA) solutions—continues to be used as a wood preservative in many countries (Katz and Salem 2005). The widespread and extensive use of arsenate and arsenite compounds in agriculture and industry has added a significant load of arsenic that may participate in biogeochemical activity to surface environments.

Arsenolite As_2O_3,

Claudetite As_2O_3

1.4.2 Arsenic Sulphides-

Arsenopyrite, orpiment, and realgar are the widely found arsenic sulphide minerals, occurring typically in hydrothermal and magmatic ore deposits. As a pigment and dye, orpiment was used in ancient times for its golden colour (from Latin auri). Realgar (from Arabic rahj al ghar, “powder of the mine”) was a common red pigment for paints and dyes in paintings and manuscripts. It is unstable in air and alters to pararealgar, a yellow orange powder, seen now in old, unrestored paintings or manuscripts that have a yellow or orange hue over the original red (Clark 1999). Other transition metals, such as Co, Ni, and Cu, also combine with arsenic and sulphur to form a range of arsenic sulphides and sulphosalts.

Arsenopyrite FeAsS

Cobaltite CoAsS

Gersdorffite NiAsS

Orpiment As_2S_3

Realgar As_2S or AsS_4

1.4.3 Metal Arsenides-

A wide range of metal arsenides are known, generally with the form MeAs-n, where n = 1, 2, or 3 and Me is a metallic element. The well-known industrial semiconductor GeAs is an example. In nature, the most common arsenides form with Fe, Co, Ni, and Cu but are rare and found occasionally in hydrothermal and magmatic ore deposits in association with sulphide minerals. They often react with sulphide minerals such as pyrite, pyrrhotite, marcasite, and galena.

Löllingite $FeAs_2$

Nickeline or Niccolite NiAs

Nickel Skutterudite $NiAs_2$

Rammelsbergite $NiAs_2$

Safflorite $CoAs_2$

Skutterudite $CoAs_2$

1.4.4 Organic and Biological compounds-

Arsenic is able to bind to a variety of organic ligands with different coordination geometries and its greater redox potential than phosphorus is why mechanisms of arsenic toxicity in living organisms are still incompletely understood despite much investigation (Carter et al. 2003). A large number of organoarsenic compounds are found in the environment due to biomethylation. Ehrlich synthesised hundreds of organoarsenic compounds to combat syphilis, which had reached epidemic levels and empirically isolated Salvarsan, the chemical structure of which is a mixture of cyclic As–As compounds with aminophenol

groups. In the 20th century, organoarsenic compounds were produced and manufactured for a range of applications. For example, synthetic alkyl- and arylarsenicals were used as insecticides and pesticides.

1.5 Arsenic contamination in the environment-

Arsenic is symbolised by 'As', has the atomic number 33, atomic weight 74.92 is classified chemically metalloid of the nitrogen group (Group-15 [Va]) of the periodic table. The typical oxidation states for arsenic are : -3, found as arsenides (alloy-like intermetallic compounds), +3 found as arsenites (in organoarsenic compounds), and +5 found as arsenates (stable inorganic arsenic oxy compounds). Arsenic is found as compounds with oxygen, chlorine, sulphur, carbon and hydrogen on one hand, and with lead, gold and iron on the other. It is found in inorganic form in minerals such as in sulphide ores as arsenopyrite or in organic form. Inorganic arsenic compounds are more widespread and toxic and are known human carcinogens.

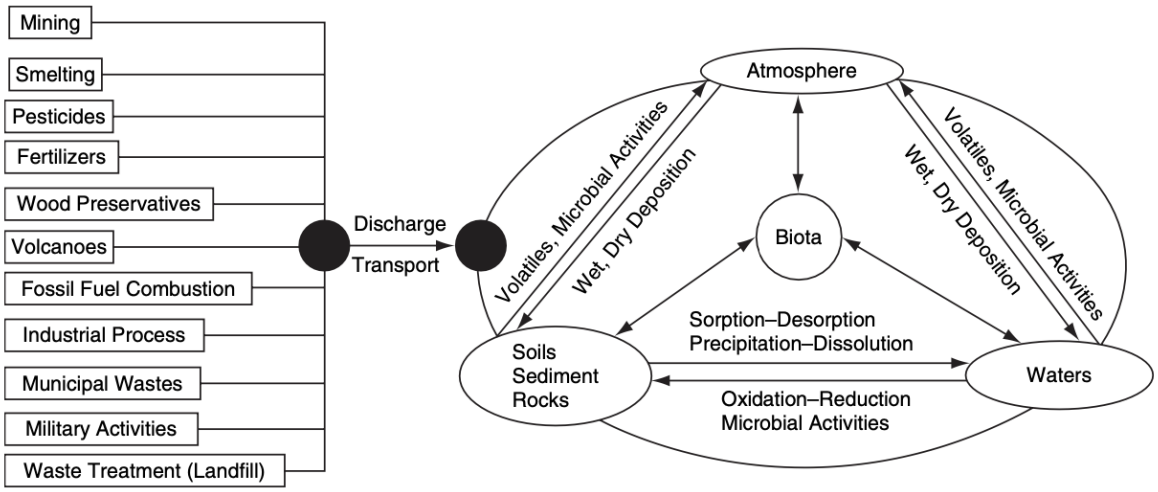


Fig 1.2: Sources and distribution of arsenic in the environment (Wang and Mulligan, 2006)

1.5.1 Arsenic distribution in air-

The concentration of As in the atmosphere was found in the 1980's to be between 0.8 × 106 kg and 1.74 × 106 kg, with a distribution of 85% in the north hemisphere

and 15% in the south hemisphere. Arsenic can be released from soils into the atmosphere due to microbial metabolism, due to volcanic activity, low temperature volatilization, wind erosion, forest fires and sea spray. Of the anthropogenic sources , the significant sources are metal production and burning of fossil fuels. Two thirds of the arsenic emissions to the atmosphere are due to anthropogenic sources. Copper production due to mining activities and the conversion of the metallic sulphides and pyrites by Cu-smelting and refining was the main anthropogenic emission source of As,. Pyrites contain up to a 10% in weight of arsenic that is released during roasting of pyrites. The production of other metals such as lead, zinc and steel also causes emission of arsenic. Coal burning is the second source of As emission. The average arsenic content in coals has been estimated to be 9.0 ± 0.8 mg/ kg for bituminous coals up to several thousands mg/ kg in some coals. Petroleum represents a minor emission source, of 0.26 mg /kg. The sum of Cu- smelting and coal burning causes 60% of the anthropogenic arsenic emission to the atmosphere worldwide . A detailed inventory of anthropogenic As emissions was done by the EU.

The mean worldwide concentration was estimated at 2.8 ng/m3 . This concentration of arsenic is increasing due to the increasing industrial activity in the world with China as a significant emitter of arsine gas and arsenic into the atmosphere. The atmospheric emission from coal combustion in China was reviewed to have a mean value of 51 ng/m3 in 44 main Chinese cities.

The first regulation for arsenic in ambient air was adopted by the EU in 2005 with a target value of 6 ng/m3 in PM10 . China has established a National Ambient Quality Standard (NAAQS) with a similar value of 6 ng/m3 . New Zealand adopted a value of 5.5 ng As m3 and Canada of 10 ng/m3. However, most of the countries do not have national legislation about arsenic in ambient air, although permissible exposure limits are usually limited to 10 mg/m3 of inorganic arsenic and 0.05 ppm of arsine gas for occupational workers in the United States. One of the lacks of the actual legislation regarding ambient air, is that it referees just to the total arsenic content, not considering the different species with distinct toxicity.

1.5.2 Arsenic distribution in soil-

There are several “hot spots” where soils have very high concentrations of As caused by natural geochemical enrichment and long-lasting ore mining and processing. The majority of soil As pollution was caused in a period before extensive statutory controls over arsenic emissions.

Acid sulphate soils that were formed by the oxidation of pyrite in sulphide-rich terrains have concentrations of arsenic with an average of 8 to 45 mg/kg arsenic in acid sulphate soils due to the weathering of pyrite rich shales . Concentrations in the overlying leached horizons were low with concentration between 1.5 - 8.0 mg/kg due to volatilization or leaching of arsenic to lower levels. Arsenic levels are higher in areas with mining operations due to the natural weathering of arsenic rich minerals . The background arsenic concentration of soil in such areas can vary from 4 to 150 mg/kg with concentration ranging from 754 to 9580 mg/kg in areas of high mining activity.

The major proportion of arsenic compounds in soils and sediments are in the form of arsenite and arsenate. Under oxidising conditions, inorganic arsenic is in the form of pentavalent arsenate. $H2AsO_4$ is the most stable species between pH 2 and 7, while HAsO42 is the most stable species above pH 7. As(V) can be reduced to As(III) under moderately reducing conditions, which is found in submerged soils (Masscheleyn *et al*., 1991; Reynolds et al., 1999). H_3AsO_3 is the prevalent species within the normal soil pH range of 4 to 9. Gaseous arsine AsH_3 can be formed under extremely reduced conditions (Challenger, 1945). Biotransformation and methylation of arsenic occur naturally as a result of microbial activity. The methylated arsenic species such as MMA(V), DMA(V) and TMAO is widely found in soils.

Arsenic in soils and sediments is usually found as complexes with iron, aluminium, and manganese hydroxides and oxides in clays, and mineral oxyanions such as sulphates, phosphates and carbonates. The grain size of particles controls the distribution and mobility of arsenic. Fine grains can adsorb the bulk arsenic onto their surface because they are of larger surface areas. Clay minerals and hydroxides and oxides of iron, aluminium, and manganese are a major source and sink for arsenic. Iron hydroxides, such as goethite (a-FeOOH) and ferrihydrite (h- FeOOH), are commonly found in soil and affect the mobility of arsenic.

Arsenic is a natural constituent of the Earth's crust and the 20th abundant element, with an average arsenic content in the continental layer from 2 to 3 mg As/kg (Tanaka, 1988; Cullen and Reimer, 1989). Arsenic is found in 200 mineral forms, including arsenates (60%), sulphides and sulfosalts (20%), and arsenides, arsenates, oxides, silicates, and arsenic in its native form . Crucial As-containing minerals are arsenopyrite (FeAsS), realgar (As_4S_4), and orpiment (As_2S_3). Realgar (As_4S_4) and orpiment (As_2S_3) are the two common reduced forms of arsenic and the oxidised form is arsenolite (As_2O_3). Other naturally occurring arsenic minerals are loellingite ($FeAs_2$), safflorite (CoAs), niccolite (NiAs),

rammelsbergite ($NiAs_2$), arsenopyrite (FeAsS), cobaltite (CoAsS), enargite (Cu_2AsS_4), gersdorffite (NiAsS), and glaucodot ((Co,Fe)AsS)

From its origin in the ores, inorganic As enters into soils where its concentration depends on parent rocks, man-made activities, climate, forms of As, and redox conditions of the soil (Yan-Chu, 1994).

Rock type	Arsenic concentration (range, mg/kg)
Igneous rocks	
Ultrabasics	0.3–16
Basalts	0.06–113
Andesites	0.5–5.8
Granites/silicic volcanics	0.2–13.8
Sedimentary rocks	
Shales and clays	0.3–490
Phosphorites	0.4–188
Sandstones	0.6–120
Limestones	0.1–20
Coal	
Bituminous[a]	9.0 ± 0.8
Lignites[a]	7.4 ± 1.4
Peat	16–340

Table 1.1: Natural abundance of As in the crust (Jacks and Bhattacharya, 1998)

1.5.3 Arsenic distribution in water-

Arsenic is released into the environment due to: (1) geogenic processes and (2) anthropogenic activities. Arsenic released in the environment due to natural processes such as weathering of rocks and sediments, hydrothermal ore deposits, volcanic eruptions, geothermal activities, forest fire, wind-blown dust, and sea-salt spray may be transported over long distances as suspended particulates or gaseous forms through water.

In deep sea water, arsenic is in the form of arsenate As(V) [HAsO24-] species and its average concentration was found to be 1.7mg/l - 8 mg/l at a salinity of 3.6% (Bruland, 1983) and the global median of arsenic in seawater is 3.7 mg/L.

Arsenic concentration in water varies in different water bodies. Due to geographical speciation there is a great diversity in arsenic contents of rivers, lakes and groundwater around the world and any generalised data contradicts each other as fresh water with arsenic can contain from hundred

microgram to thousands of microgram of arsenic per litre of water (Chappell et al., 2001).

The concentration of arsenic in groundwater depends on the mineralogical characteristics of the aquifer. Arsenic containing aquifers can release arsenic compounds into the water by being weathered which depends on physicochemical properties of the groundwater as water causes the weathering of aquifers. Arsenic enters groundwater by reductive dissolution of arsenic rich iron oxyhydroxides in dispersed phases in aquifers which are released from the weathering of arsenopyrite (Nickson et al., 2000). Arsenic is found in reduced conditions in the alluvial aquifers of West Bengal, India and Bangladesh (Ahmed et al., 2004). The major part of the world contains the oxidised forms of arsenic in groundwater due to oxidation of arsenic-rich minerals.

High levels of arsenic was detected in rivers with geothermal water sources or by contamination from anthropogenic sources. In the Yellowstone National Park, Madison River was detected with 250–370 mg/l of dissolved As (Jones et al., 1999). , and in Gegogan Lake region of Nova Scotia, a site contaminated by gold mine tailings, had arsenic concentration in suspended particles from 1500 to 5000 mg/kg (Wong et al., 1999).

In the Andean range of South America, due to release of geogenic arsenic from volcanic rocks and volcanic ash falls, hot springs, sulphide ore deposits and other geothermal activities (Bundschuh et al., 2006) high levels of arsenic 200–900 mg/l was detected in the river water of northern Chile. Arsenic released from the weathering and dissolution of the rocks of the volcanic chain,was mobilised by the snow melt and rain and entered the river water.
In Bangladesh, dissolved arsenic concentrations vary between 0.7 and 1.1 mg/l in Padma River, while in Meghna River, the concentrations vary between 0.6 and 1.9 mg/l (Bhattacharya et al., 2002). In China, dissolved As concentrations in the Huanghe River were found to increase from 1.4 -- 1.5 mg/l upstream to 2.3 -- 2.4 mg/l in the water downstream of the river (Zhang, 1995).

1.5.4 Bioaccumulation of As in plants and crops-

Food is one of the routes of human exposure to As and other trace elements.
Soil is a main source of trace elements for plants both as micronutrients and pollutants. Inorganic arsenic is toxic to plants and inhibits phosphate uptake necessary for growth as there is a chemical similarity between arsenate and phosphate ions which causes uptake of arsenate by plants, which then inhibits

phosphorus uptake (Dixon, 1997) This reduces the yield of production, reduces growth and may be may be lethal to the plant.
The high levels of As in groundwater in the region of SouthEast Asia, especially in Bangladesh and West Bengal in India have caused difficulties as the the use of groundwater for irrigation purposes caused significant contamination of paddy and agricultural soils with arsenic (Bhattacharya et al., 1997; Huq et al., 2006).

1.5.5 Total arsenic exposure-

Human exposure to arsenic can be through dermal and inhalation exposure routes, or food and drinking water routes which are the principal causes of human exposure to arsenic (WHO, 2011). The International Agency for Research on Cancer classified arsenic and inorganic arsenic compounds as known carcinogens of Group 1 based on sufficient evidence of carcinogenicity in humans (IARC, 1973).
From 13,608 samples analysed, 7623 samples corresponding to drinking water and 5985 to different types of food, in particular rice and rice based products, were found to have inorganic arsenic. Children and infants were exposed to 0.58 and 1.20 μg/kg of inorganic arsenic per day in biscuits, rusks and cookies for children and cereal-based food for infants. Adults were exposed to 200 μg/kg in polished or white rice, to 250 μg/kg in parboiled rice and unpolished rice, 300 μg/kg in rice waffles, rice wafers, rice crackers and rice cakes . Additionally, Codex Alimentarius has adopted through the years different MLs for tAs (10 μg/L for natural mineral water; 100 μg/kg for edible fats, oils (including fish oils), fat spreads and blended spreads; 500 μg/kg for food grade salt), and, more recently, for iAs (200 μg/kg for polished rice, and 350 μg/kg for husked rice)

1.5.6 Standards for arsenic content in drinking water-

Different countries have different standards for arsenic in potable water. WHO norms for drinking-water quality in 1958 for allowable concentration of arsenic was at 200 μg/L. In 1963, it was reduced to 50 μg/L. Due to adverse health reports arising from different parts of the world the guidelines were revised and permissible limits were reduced from 50 μg/L to 10 μg/L (10 ppb) in 1993 India set the maximum permissible limit for arsenic to 50 μg/L.

Country/Institution	Allowable level of Arsenic in drinking water
US-EPA, USA	10 µg/L or 10 ppb
Australia	7µg/L or 7 ppb
Canada	25 µg/L or 25 ppb
BIS, India	50 µg/L or 50 ppb
Latest, WHO's norm (1993)	10 µg/L or 10 ppb

Table 1.2: Standards for arsenic in drinking water in different countries

1.6 Sources of arsenic contamination-

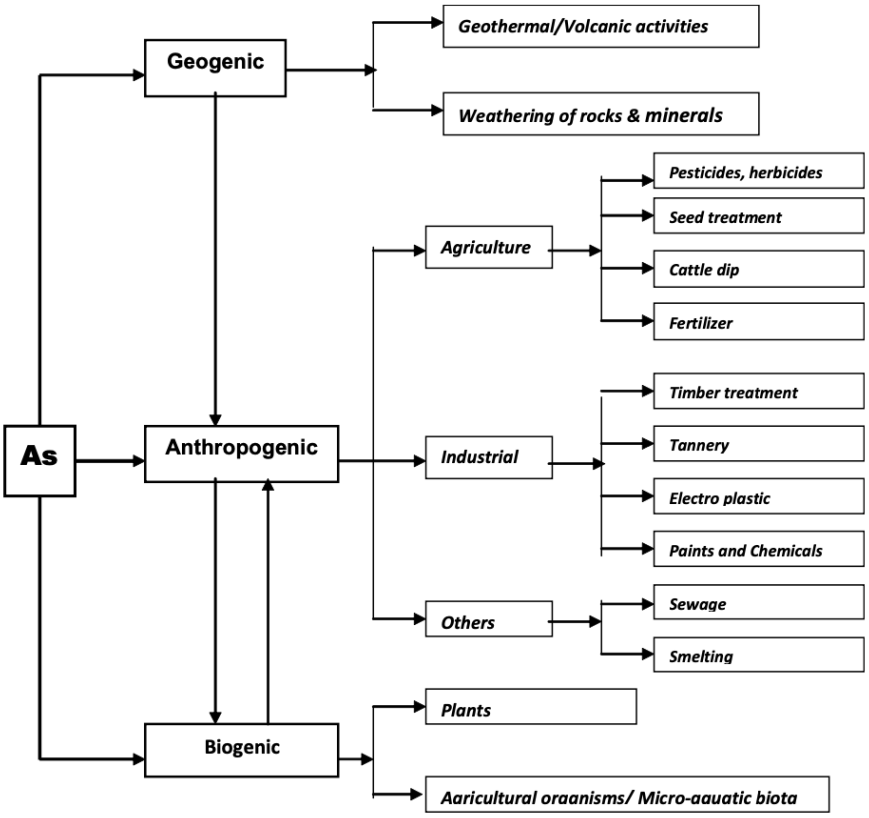


Fig 1.3: Major sources and routes of arsenic in soils and water (Sparks et al., 2005)

1.6.1 Anthropogenic sources-

Mining, smelting and ore processing, pesticides, fertilisers, timber curing, pharmaceutical plants, chemical industries, thermal power plants using coal or peat, wood preservation industries using CCA (chromated copper arsenate) and incinerations of preserved wood wastes contribute large quantities of arsenic contamination annually in the environment (Nriagu and Pacyna, 1988). Some examples are arsenic acid H_3AsO_4 which was used to defoliate cotton bolls before harvesting and as a wood preservative, As_2O_3 and which was used to decolourize glass and manufacture pharmaceuticals and sodium arsenite NaH_2AsO_4 which was used in agricultural insecticides, pesticides, and herbicides.The global annual emissions of arsenic to the atmosphere was estimated to be 19kt (range 12–25.6kt), but in soil and aquatic environments estimated was 82 and 42 kt, respectively (Nriagu and Pacyna, 1988). However, there has been a significant decrease in the atmospheric emission of arsenic in Europe, from 5 kt in 1986 to 0.6 kt in 1995 due emission regulations (Pacyna et al., 1995).

The release of arsenic from different sources is often cited in the literature (Boyle and Jonasson, 1973; Berdowski et al., 1997), but there is still lack of information on atmospheric emission of arsenic in eastern regions of the Indian subcontinent. Average concentration of arsenic in Indian coal ranges up to 3.72 mg/kg, with a maximum value of 40 mg/kg (e.g. Sohagpur coalfield, Northeastern India) (Khandekar et al., 1999; Warwick et al., 2001). Hence, it is believed that coal combustion in Eastern India is one of the major sources of anthropogenic arsenic emission in the environment. There are several metallurgical plants, cement factories, incineration and chemical industries in eastern and Northeast India which contribute to the emission of arsenic into the environment. However, there is no data available, on the exact tonnage of arsenic entering the environment. A secondary leading industry near greater Kolkata, West Bengal, releases arsenic to the environment. The maximum concentration in soil of that area was reported to be 9740 ± 226 mg/kg while the minimum was 17.5 ± 0.52 mg/kg (Chatterjee and Banerjee, 1999). Leaching of arsenic in groundwater is also expected in the vicinity of areas of landfills containing waste and hazardous waste piles (Boyle and Jonasson, 1973; Tripathi et al., 1997; Pandey et al., 1998). The use of fertilisers and insecticides also causes high concentration of arsenic in soil compartments. There is a lack of information on the anthropogenic deposition of arsenic, within the extensive alluvial tract of the Ganga-Brahmaputra river basin. The arsenic-affected areas are the parts of the lower delta plain of the Ganges and

foothills of Brahmaputra and Barak valley. The sources of arsenic are natural or may partly stem from anthropogenic activities like intense exploitation of groundwater, application of fertilisers, burning of coal and leaching of metals from coal-ash tailings. However, it has been contemplated that the Ganges-Brahmaputra basin has rather been undisturbed by anthropogenic sources compared to industrialised countries, where river basins have generally been affected by industrial activities (Huang et al., 1992).

1.6.2 Geogenic sources-

Chakraborti et al. analysed over 125,000 water samples from hand drawn tube wells for arsenic from the Bengal basin in the School of Environmental Sciences at the Jadavpur University, Kolkata, India. They reported that the arsenic levels in the affected areas varied between <1 and 1300 mg/l. No mono and dimethylarsonic acids in the groundwater of West Bengal, India were detected. The sedimentary aquifers of the Bengal Delta Plain in West Bengal and the bordering country of Bangladesh, the alluvial aquifers of the Terai belt of Nepal, the Indo Gangetic plains of Uttar Pradesh, Bihar and Jharkhand states of India and the Brahmaputra plains of Assam have documented evidence of As concentrations above the national drinking water standard of 50 mg/l and well above the WHO guideline value of 10mg/l . In groundwater, inorganic arsenic is found as arsenate and arsenite. Arsenite is more mobile and toxic for living organisms. Arsenate is adsorbed to a greater extent by sediments and arsenite is less strongly adsorbed under reducing conditions.The adsorption capacity on the mineral surfaces is controlled by geochemical parameters such as pH, Eh, ionic composition, and mineral type. Redox reactions in the aquifers increase the mobility through dissolution of the iron oxides that transfer significant amounts of As into the aqueous phases (Bhattacharya et al., 1997).
Mechanisms of As-mobilisation in the Bengal Delta Plain is postulated to be due to the principal redox reactions controlling As release in the groundwater in the area.Arsenic containing aquifers can release arsenic compounds into the water by being weathered which depends on physicochemical properties of the groundwater as water causes the weathering of aquifers. Arsenic enters groundwater by reductive dissolution of arsenic rich iron oxyhydroxides in dispersed phases in aquifers and oxidation of arsenopyrite (Nickson et al., 2000). Arsenic is found in reduced conditions in the alluvial aquifers of West Bengal, India and Bangladesh (Ahmed et al., 2004).

Two hypotheses describing the probable mechanisms of arsenic mobilisation in groundwater with reference to Holocene aquifers like in West Bengal and Bangladesh are-

1. Mobilisation of arsenic due to the oxidation of **arsenopyrite**- Insoluble Arsenopyrite FeAsS, are oxidised if exposed to atmosphere, releasing soluble arsenite , sulphate (SO 2 -), and ferrous iron (Fe2+). The released arsenite is partially oxidised to arsenate by microbial reactions (Bose and Sharma, 2002). The chemical reaction is given by-

$$\mathbf{FeAsS + 13\ Fe^{3+} + 8\ H_2O \longrightarrow 14\ Fe^{2+} + SO_4^{2-} + 13\ H^{+} + H_3AsO_4\ (aq.)}$$

2. Dissolution of arsenic **iron oxyhydroxides** (FeOOH) in reducing conditions- Under oxidising conditions, inorganic species of arsenic are predominantly retained in the solid phase through interaction with FeOOH coatings on soil particles. Under reducing conditions, such as fermentation of peat, dissolution of FeOOH coatings releases inorganic arsenic resulting in release of Fe_2+, As_3+, and As_5+ present on such coatings (Nickson et al., 2000). The chemical reaction is given by-

$$\mathbf{8FeOOH - As_{(s)} + CH_3COOH + 14\ H_2CO_3 \longrightarrow 8\ Fe^{2+} + As_{(d)} + 16\ HCO_3^{-} + 12\ H_2O}$$

The dissolved arsenic is released in the aquifers.

The same release mechanisms of arsenic into the groundwater may not apply in the arid and semi-arid regions of the world. In Latin America, where groundwater arsenic is mostly found in oxidising aquifer environments and in the Argentine Chaco-Pampean Plain at least 1.2 million people are exposed to arsenic mobilised from volcanic ash dispersed in the alluvial sediments (Bhattacharya et al., 2002). . The underlying mechanism for arsenic mobilisation is related to desorption from oxyhydroxides of Al, Mn, and to a lesser extent Fe due to changes in pH and Eh of the adsorbent.

Country/region	Area affected	Depth of well	Arsenic concentration (μg/l)	Mechanism of contamination
Bangladesh, BDP (61 districts)	118 012 km^2	8–260 m	<2–900	Reduction of Fe-oxyhydroxides/sulfide oxidation (?) in alluvial sediments
India, West Bengal, BDP (8 districts)	34 000 km^2	14–132 m	<1–1300	Reduction of Fe-oxyhydroxides/sulfide oxidation (?) in alluvial sediments
China, Xinjiang Inner Mongolia (HAB)	4800 km^2	Shallow/deep	<50–1860	Reducing environment in alluvial sediments
Taiwan	_	Deep	Up to 1820	Oxidation of pyrite in mine tailings
Thailand (10 districts)	10 districts	Shallow	120–6700	Oxidation of mine wastes and tailings
Ghana	1600 km^2	70–100 m		Oxidation of arsenopyrite in mine tailings
Argentina (Chaco-Pampean Plains)	10 million km^2	Shallow aquifers	100–4800	Volcanic ash with 90% rhyolitic glass
Chile	_	Shallow and deep wells	100–1000	Volcanic ash

Table 1.3: Reasons for arsenic contamination in groundwater from selected parts of the world (Naidu and Bhattacharya, 2006)

1.6.3 Social problem-

Arsenic contaminated groundwater can disturb the socioeconomic conditions of a country. Skin disorders resulting from arsenicosis look like leprosy, resulting in marginalisation and ostracism of such people. People with black spots on their skin are discriminated against in gaining employment and affected children are not allowed to attend school. People with arsenic poisoning are deprived socially and economically in many affected areas (Biswas et al., 1998). UNICEF launched the ‘‘Facts for Life’’ program to promote awareness about the need for sensitivity such as children and women being marginalised if they have signs of arsenic poisoning.

1.6.4 Treatment of affected patients -

There is no cure for a patient suffering from the toxicity of arsenic. The affected patient may not recover if the source of arsenic exposure is not removed. Chelating agents such as D-penicillamine, dimercaptosuccinic acid, and dimercaptopropane succinate have been prescribed for chronic arsenic toxicity. These medicines are effective at the early stage of poisoning. It has also been reported that protein- rich diets and vitamins C and E may reduce the pain of arsenicosis.

1.6.5 Removal of arsenic from drinking water:

In developing countries, treatment technology such as reverse osmosis is not affordable for the majority of the population , and families have to consume arsenic contaminated well water and surface water with disease-causing microbes.
Selection of treatment technology depends on the form of arsenic in water and the oxidation technique for converting arsenite to arsenate . In developing countries, selection of remediation methods also depends on costs and social acceptability by the population to be served. Viable solutions are to comply with the existing framework of groundwater use and land use pattern in the region.

1.7 Magnitude and extent of arsenic contamination in groundwater-

1.7.1 Global distribution-

Most of the cases of arsenic toxicity in the mediaeval and early modern age were caused by arsenic intake through medicine, smelting or genocidal activities. Around the middle of the 20th century arsenic poisoning was detected from some countries where people ingested arsenic contaminated water. This toxicity was detected on a mass scale, not the mere individual cases.

Arsenic was found to a large extent in the alluvial aquifers of the Indian states of West Bengal, Assam, Bihar, Jharkhand, Uttar Pradesh and in Bangladesh. Parts of other countries like Nepal, China, Mongolia, Myanmar, Thailand, Taiwan, Vietnam, Cambodia, Sri Lanka, Pakistan, Afghanistan, Japan, Hungary, Ghana, Mexico, Bolivia, and Argentina are also affected by arsenic toxicity. Arsenic in soil or water beyond the safe limit have been detected in parts of Iran, Australia, New Zealand, parts of the European Union, Iceland, Brazil, Canada and the U.S.A (Mukherjee et al., 2006). Globally, more than 150 million people are affected due to consumption of arsenic contaminated drinking water (Ministry of Water Resources and River Development and Ganga Rejuvenation, 2014).

Country/region	Groundwater As concentration in μg/L (1 μg/L = 0.001 mg/L)	Approximate size of population at risk
India	<10–3200	70,400,000
Bangladesh	<1–2500	32,000,000
China (Mainland China)	50–2000	>2,300,000
Vietnam	1–3050	>100,000
Thailand	1–>5000	15,000
Taiwan	10–1820	200,000
Inner Mongolia	<1–2400	600,000
Argentina	<1–9900	2,000,000
Chile	100–1000	400,000
Mexico	8–620	400,000
Hungary, Romania	<2–176	400,000
Greece	1–1840	150,000
Spain	<1–100	>50,000
U.K.	<1–80	minimal
U.S.A., Canada	<1–>10,000	minimal
Ghana	<1–175	<100,000

Table 1.4: Groundwater arsenic concentrations and approximate number of affected people in some countries (Mukherjee et al., 2006; Ministry of Water Resources and River Development and Ganga Rejuvenation, 2014)

1.7.1.1 Bangladesh-

In Bangladesh alone out of its total 64 districts, 60 districts have groundwater arsenic contamination above WHO guideline value of 10μg/L. The major affected districts with arsenic concentrations more than 50 μg/L were- Satkhira, Munshiganj, Chandpur, Lakshmipur, Noakhali, Gopalganj, Madaripur, Rangpur (Panchagarh, Kurigram, Lalmonirhat, Nilphamari, Dinajpur), Bagerhat, Faridpur, Rajshahi (Joypurhat, Naogaon), Shariatpur, Meherpur and Barisal (Barguna, Bhola, Patuakhali) districts.

1.7.1.2 China-

Geospatial information and climate data, land use data, suggest that 19.6 million people in China are exposed to arsenic contamination. Arsenic pollution was detected in Beijing, Guangdong, Gansu, Henan, Hunan, Heilongjiang, Inner Mongolia, Jilin, Jiangsu, Liaoning, Ningxia, Qinghai, Sichuan, Shandong, Shanxi, Taiwan, Xinjiang, Yunnan and Zhejiang (Xia et al. 2019).

1.7.1.3 Vietnam-

Arsenic contamination in tube well water and human arsenic exposure in four districts -Tu Liem, Dan Phuong, Ly Nhan, and Hoai Duc in the Red River Delta. With concentrations in the range of in the range of <1 to 632 μg/L

Most of the world's arsenic contaminated groundwater is due to the rock water interaction. The majority arsenic affected provinces are in young unconsolidated sediments of Quaternary age and of the Holocene epoch. (<12 thousand years). The deposits with the arsenic contaminated aquifers can broadly be grouped into : (i) large alluvial and deltaic plains such as the Bengal delta, the Yellow River plain, the Irawaddy Delta, Red River Delta, and (ii) inland closed basins in arid or semi-arid setting such as the Argentina, Mexico, Chile). These aquifers do not contain high concentration of arsenic bearing minerals, but have chemical and hydro geological conditions for mobilization and retention of arsenic in solution.

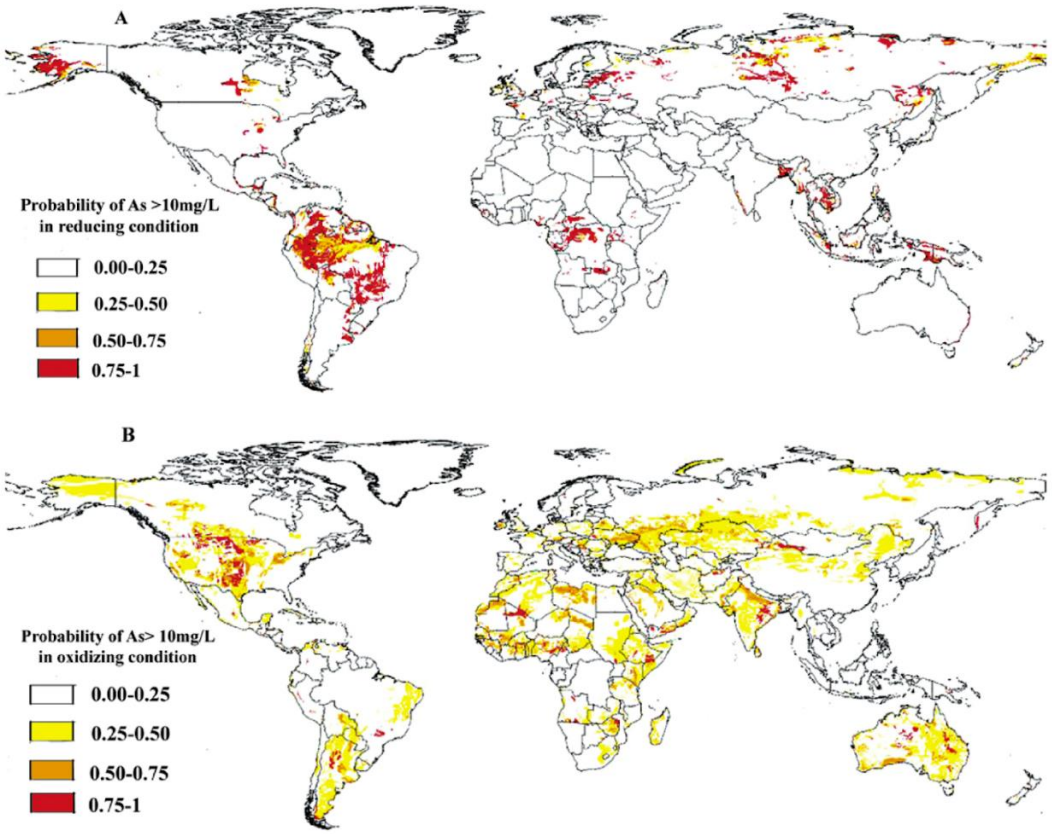


Fig 1.4: a) arsenate distribution and b) arsenite distribution in groundwater due to geogenic contamination (Amini et al., 2008).

1.7.2 Magnitude and extent of distribution in India-

The demographic survey of the affected areas and analysis of water samples by School of Environmental Studies, Jadavpur University (analysis of 211,955 water samples) and CGWB, State PHED, WB and Bihar, estimated that more than

13.85 million people were exposed to groundwater contaminated with arsenic above 10 µg/L, in which more than 6.96 million people were exposed to levels above 50 µg/L, with total population of these areas around 50 million. A large number of live-stock were also exposed to arsenic contaminated groundwater. Which was also used for agricultural irrigation in the arsenic affected areas. The people were also exposed to arsenic through the food chain in contaminated areas and in uncontaminated areas due to the open market (CGWB, 2008).

The arsenic affected areas of India lie in the alluvial plains and delta of the Ganges-Brahmaputra river system, from the Himalayas in northern India and downstream in a roughly southeasterly direction through the states of Uttar Pradesh, Bihar, Jharkhand and West Bengal where the main branch passes into Bangladesh and several distributaries pass through the state of West Bengal to the sea. It was found along the banks of the tributaries also originating from the Himalayas, Yamuna, Ramganga, Sarda and Ghaghara which join the Ganges in Uttar Pradesh and the Great Gandak which joins the Ganges in Bihar. In Assam, the Brahmaputra enters the state in the far northeast and flows roughly south-westerly through the length of the state until it turns to the south and enters Bangladesh in the district of Dhubri.

Mitigation of the problem in most states has taken approaches to supply arsenic-safe water. These include: piped water supply schemes based on surface water and deep groundwater; deep handpumps; refurbishment of large diameter open wells; rainwater collection; and community and domestic filters.

State	No. habitations	Population	Habitations affected	Population in affected habitations	% of affected population
Assam	88,099	29,658,323	3,726	1,236,964	9.6
Bihar	110,234	99,454,050	1,077	1,666,039	12.9
Haryana	7,948	18,407,573	45	142,944	1.1
Jharkhand	120,067	26,899,888	130	115,862	0.9
Karnataka	60,248	40,277,798	21	47,141	0.4
Kerala	11,883	26,874,598	3	7,651	0.1
Maharashtra	100,066	64,445,038	1	87	0.0
Meghalaya	10,475	2,667,743	1	169	0.0
Odisha	156,468	35,652,623	2	42	0.0
Punjab	15,384	17,989,668	492	590,103	4.6
Rajasthan	121,648	50,806,731	3	0	0.0
Tripura	8,723	4,491,866	1	1,118	0.0
Uttar Pradesh	260,801	168,768,908	262	159,572	1.2
West Bengal	105,905	74,637,222	8,066	8,950,460	69.1

Table 1.5: Arsenic affected habitations and populations in India, (Ministry of Drinking Water and Sanitation, 2017)

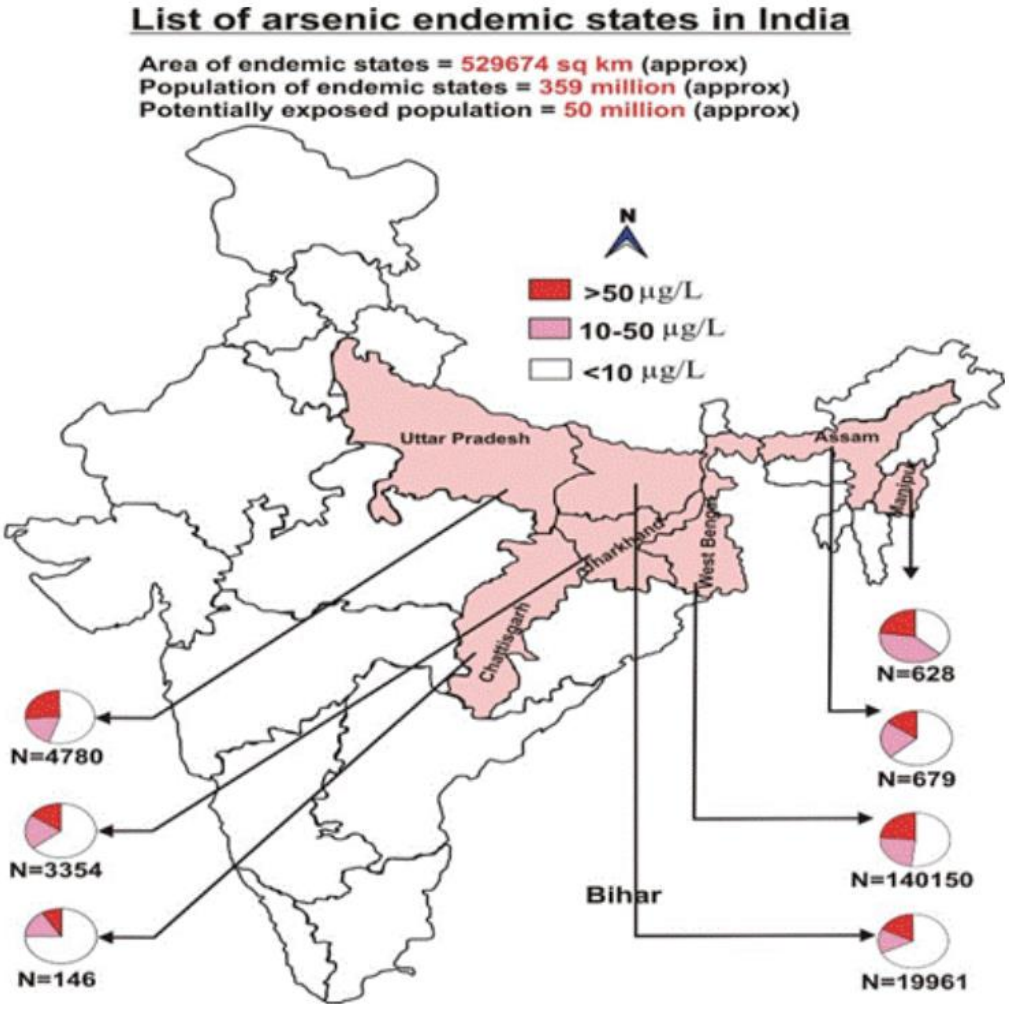


Fig 1.5: Summary of arsenic distribution in India, (CGWB, 2008)

1.7.2.1 Magnitude of Arsenic distribution in West Bengal-

169698 samples from hand tubewell from the state of West Bengal were collected and analysed by the School of Environmental Study, Jadavpur University. 45.97% and 22.94% of these samples had arsenic concentration more than 10 ug/L and 50 ug/L respectively. Of the analysed samples, 3.3% had arsenic concentrations above 300µg/L, the concentration indicating noticeable arsenical skin lesions. A total of 187 (0.13%) hand tube-wells from which samples were taken were highly contaminated (> 1000 µg/ L). From these samples, the maximum arsenic concentration (3700 µg/L) was found in Ramnagar village of GP Ramnagar II, Baruipur block, in South 24-Parganas district. From a preliminary survey of 10073 people, from this state, 10118 had arsenical skin lesions, arsenic neuropathy and fatal pregnancy outcomes like spontaneous abortion, stillbirths, preterm birth and low birthweight. Around 100

million people had been diagnosed with subclinical symptoms of arsenicosis. Arsenicosis was also caused by consumption of contaminated rice and vegetables like green papaya, arun(Colocasia), spinach, long beans, potatoes, radish, carrots, brinjals, lettuce.
In West Bengal, in 1983 there were only 33 villages in four districts that were reported to have arsenic concentration greater than 50 ug/lt. In 2008, 3417 villages in 9 districts were reported to have arsenic concentration greater than 50 ug/lt.

Table 1.6: A summary of the survey report for arsenic contamination in all the 19 districts in West Bengal.
(School of Environmental Studies, Jadavpur University, 2008)

Parameters	West Bengal
Area in sq. km.	88,750
Population in million	80.2
Total number of districts (no. of district surveyed)	19 (19)
Total number of water samples analyzed	1,40,150
% of samples having arsenic > 10 μg L^{-1}	48.1
% of samples having arsenic > 50 μg L^{-1}	23.8
Maximum arsenic concentration so far we analyzed (μg/L)	3700
No. of severely arsenic affected districts *	9
No. of mildly arsenic affected districts*	5
No. of arsenic safe districts*	5
Total population of severely arsenic affected 9 districts in million	50.4
Total area of severely arsenic affected 9 districts in sq. km.	38,861
Total number of blocks/ police station	341
Total number of blocks/ police station surveyed	241
Number of blocks / police station having arsenic >50μgL^{-1}	111
Number of blocks / police station having arsenic >10μgL^{-1}	148
Total number of village	37910
Total number of village surveyed	7823
Number of villages/paras having arsenic above 50 μgL^{-1}	3417
People drinking arsenic contaminated water >10 μgL^{-1} (in million)	9.5
People drinking arsenic contaminated water >50 μgL^{-1} (in million)	4.6
Population potentially at risk from arsenic contamination > 10 μg L^{-1} (in million)	26
No. of districts surveyed for arsenic patients	9
No. of districts where arsenic patients found	7
Villages surveyed for arsenic patients	602
Number of villages where we have identified people with arsenical skin lesions	488

Based on the arsenic concentrations found in water samples from hand drawn tube wells in the 19 districts of West Bengal the severity of contamination has been classified into three categories: Severely affected (>300 µg/L), mildly affected (between 10 and 50 µg/L, and unaffected (< 10 µg/L). Nine districts - Malda, Murshidabad, Nadia, North 24-Parganas, South 24-Parganas, Bardhaman, Howrah, Hooghly and Kolkata, had more than 300 µg/L arsenic concentrations in tube well water samples and were categorised as severely affected. From 135,555 samples analysed from these nine districts 67,306 (49.7%) had arsenic concentrations above 10µg/L and 33,470 (24.7%) above 50 µg/L.

From topographical surveys , it was noticed that the 9 severely affected districts with concentration > 50 µg/L are in a linear track along the river Bhagirathi (the stretch of the river Ganga that passed through Kolkata). Most of the affected areas lie along the left side of the river in the direction of groundwater flow. The groundwater flow direction in those areas is towards the south-east direction, and the affected areas also in the same region. The geological formations in these areas were of recent alluvial deposits of the Quaternary age. Arsenic contaminated groundwater in the strata lie largely in the intermediate zone depth that ranges from 15m to 50 m.

Districts	Area in km^2	Population	Total no. of blocks	No. of blocks surveyed	No. of blocks with As >10 µg/L	No. of blocks with As >50 µg/L	No. of samples analyzed	Distribution of total samples in different arsenic concentration (µg/L) ranges									Max. As. conc. (µg/L)
								≤3	4 -10	11-50	51-100	101-200	201-300	301-500	501-1000	> 1000	
Highly affected																	
North-24-PGS	4094	8934286	22	22	22	21	54368	22221	3129	13001	6403	5531	2249	1308	477	49	2830
South-24-PGS	9960	6906689	29	17	12	11	8333	4407	427	1141	743	741	327	305	212	30	3700
Murshidabad	5324	5866569	26	26	25	24	29668	11471	2244	8042	3267	2366	941	884	382	71	3003
Nadia	3927	4604827	17	17	17	17	28794	11431	2613	9810	2265	1520	630	360	152	13	3200
Maldah	3733	3290468	15	14	13	9	4449	1754	373	810	488	559	183	163	97	22	1904
Haora	1467	4273099	14	12	12	7	1471	889	226	192	87	41	22	12	1	1	1333
Hugli	3147	5041976	18	17	16	11	2212	1469	346	251	77	52	14	2	1		600
Kolkata	185	4572876[a]	141[b]	100[b]	65[b]	30[b]	3626	2224	855	345	85	75	27	10	5		800
Bardhaman	7024	6895514	31	24	12	7	2634	2091	79	244	86	89	27	11	6	1	2230
Sub Total	38861	**50386304**	172	149	129	107	135555	57957	10292	33836	13501	10974	4420	3055	1333	187	
Mildly affected																	
Koch Bihar	3387	2479155	12	5	4	1	474	403	57	13	1						54
Darjiling	3149	1609172	12	4	3	0	562	502	50	10							19
Dinajpur (N)	3140	2441794	9	7	6	2	990	817	57	112	4						68
Dinajpur (S)	2219	1503178	8	6	2	1	452	398	47	6	1						51
Jalpaiguri	6227	3401173	13	7	4	0	445	355	74	16							27
Sub Total	18122	**11434472**	54	29	19	4	2923	2475	285	157	6						
Unaffected																	
Bankura	6882	3192695	22	17	0	0	279	279									<3
Birbhum	4545	3015422	19	11	0	0	718	718									<3
Purulia	6259	2536516	20	15	0	0	314	314									<3
Medinipur (E)[c]	14081	9610788	25	10	0	0	182	182									<3
Medinipur (W)			29	10	0	0	179	179									<3
Sub Total	31767	**18355421**	115	63	0	0	1672	1672									
Grand Total	88750	**80176197**	341	241	148	111	140150	62104	10577	33993	13507	10974	4420	3055	1333	187	

Table 1.7: Summary of distribution of arsenic contamination in individual blocks, West Bengal (Chakraborti et al. 2008)

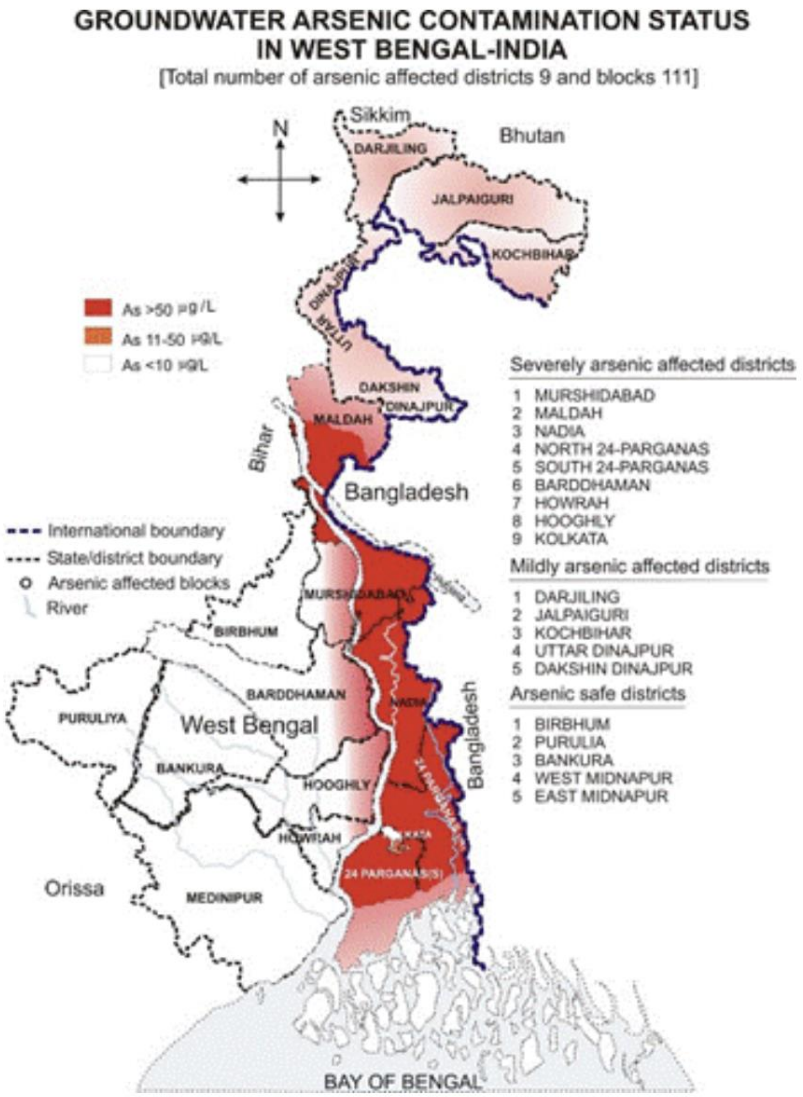


Fig 1.6: Arsenic Contamination in Groundwater in West Bengal, (Chakraborti et al. 2008)

1.7.2.2 Magnitude of Arsenic contamination in Bihar-

In 2002, groundwater arsenic contamination was detected in two villages, Barisban and Semaria Ojhapatti in the Bhojpur district of Bihar in the Middle Gangetic Plain. The area was located in the flood-prone belt of Sone-Ganga inter-fluvial region. Investigations conducted by Central Ground Water Board and Public Health Engineering Department, Bihar indicated contamination averaging 0.178 µg/L in the adjoining villages, affecting the hand pumps, which are usually at 20-40 m below ground surface. By the year 2008, 15 districts of 38 districts, covering 57 blocks were exposed to groundwater with arsenic contamination

above 50 μg/L. These districts were Buxar, Bhojpur, Patna, Lakhisarai, Saran, Vaishali, Begusarai, Samastipur, Munger, Khagaria, Bhagalpur, Darbhanga, Purnea, Katihar, and Kishanganj. These districts were distributed linearly along the river Ganges in Bihar except in three districts - Darbhanga, Purnia, and Kishanganj, which were isolated and scattered with no distinct routes of connection to one another. It was also estimated that the districts lying in the area where Ganga and its tributaries, originating from the Himalayas, shifted in course of time, would be arsenic contaminated . The geological formations in the affected areas are of Quaternary period, consisting of multi-aquifer systems mixed with medium to fine sands having occasional coarse grained followed by medium sand, pebble and gravel.

Sl. No	District	Block	Population of affected Block
1	**Patna**	1.Maner	201345
		2.Danapur	325457
		3.Bakhtiarpur	172531
		4.Barh	162381
2	**Bhojpur**	1.Barhara	194439
		2.Shahpur	185911
		3.Bihea	139374
		4.Koilwar	169564
		5.Udwant Nagar	132258
		6.Arrah	369644
3	**Begusarai**	1.Matihani	127090
		2.Begusarai	418614
		3.Barauni	228026
		4.Balia	148155
		5.Sabehpur Kamal	155057
		6.Bachwara	153699
4	**Khagaria**	1.Khagaria	295480
		2.Mansi	74297
		3.Gogri	243303
		4.Parbatta	192212
5	**Samastipur**	1.Mohiuddin Nagar	142472
		2.Mohanpur	88930
		3.Patori	143832
		4.Vidyapati Nagar	122240
6	**Bhagalpur**	1.Jagdishpur	471457
		2.Sultanganj	200123
		3.Nathnagar	122120
7	**Saran**	1.Sonepur	220271
		2.Dighwara	107912
		3.Chapra Sadar	363036
		4.Revelganj	99010
8	**Munger**	1.Jamalpur	181751
		2.Dharhara	104037
		3.Bariarpur	92406
		4.Munger	297741
9	**Katihar**	1.Mansahi	62581
		2.Kursela	52997
		3.Sameli	67261
		4.Barari	220955
		5.Manihari	149250
		6.Amdabad	132107
10	**Buxar**	1.Brahmpur	163855
		2.Semary	181003
		3.Chakki	34133
		4.Buxar	229521
11	**Vaishali**	1.Raghopur	187722
		2.Hajipur	349694
		3.Bidupur	207421

Table 1.8: Summary of arsenic affected areas in Bihar (School of Environmental Studies, Jadavpur University, 2004)

District	No. blocks affected	Total sources tested	Sources 10–50 μgL^{-1}	Sources > 50 μgL^{-1}	% Sources 50 μgL^{-1}	District population
Begusarai	6	6,288	2,645	221	3.5	2,349,366
Bhagalpur	3	4,516	439	680	15.1	2,423,172
Bhojpur	6	5,420	1,007	1,430	26.4	2,243,144
Buxar	4	6,916	734	1,116	16.1	1,402,396
Katihar	6	9,926	1,808	1,223	12.3	2,392,638
Khagaria	4	8,175	1,735	760	9.3	1,280,354
Munger	4	2,026	101	103	5.1	1,137,797
Patna	4	4,989	396	275	5.5	4,718,592
Samastipur	4	6,492	1,667	1,001	15.4	3,394,793
Saran	4	3,795	273	134	3.5	3,248,701
Vaishali	5	8,080	1,292	221	2.7	2,718,421
Total	50	66,623	12,097	7,164	10.8	27,309,374

Table 1.9: Summary of arsenic affected areas in Bihar (School of Environmental Studies, Jadavpur University, 2004)

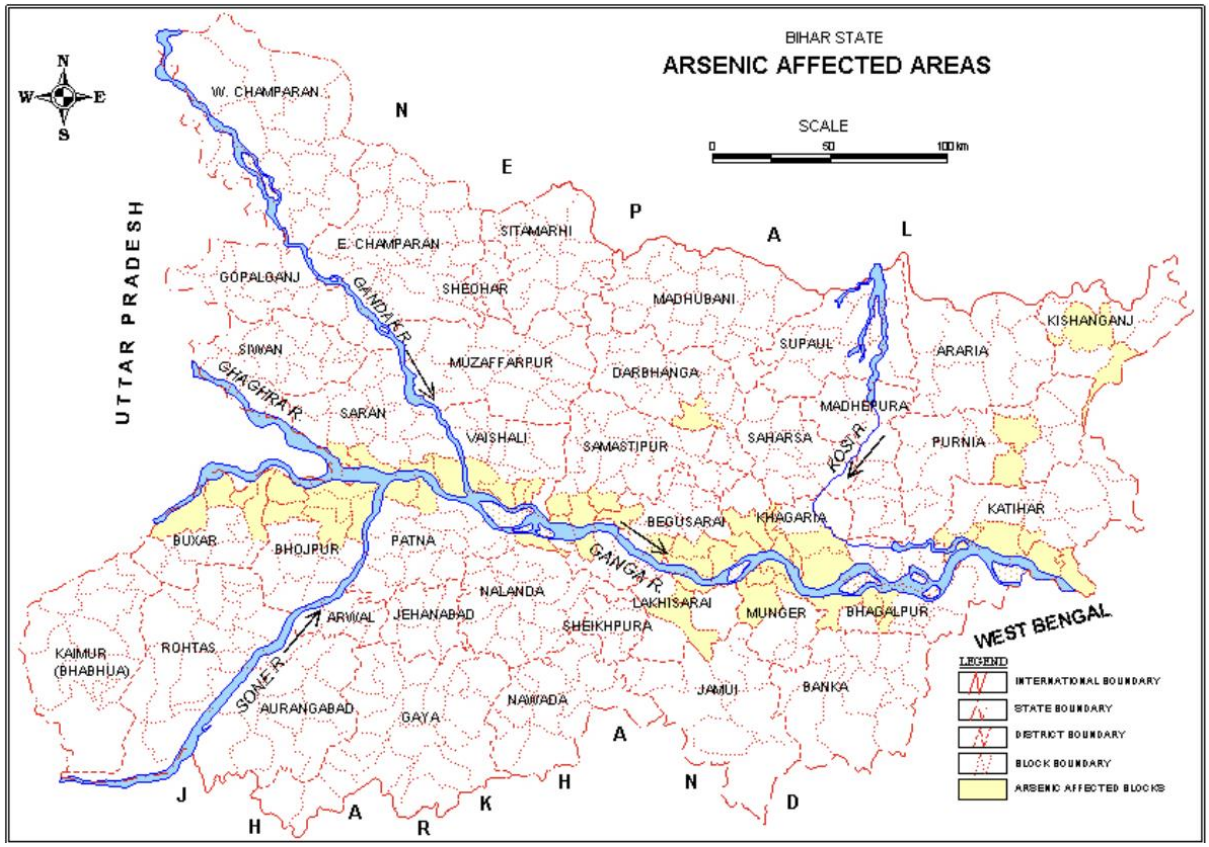


Fig-1.7: Arsenic Contamination in Groundwater in Bihar, (Chakraborti et al. 2008)

Reasons for arsenic contamination in groundwater from selected parts of the world (Naidu and Bhattacharya, 2006)

1.7.2.3 Magnitude of Arsenic Contamination in Uttar Pradesh -

Groundwater arsenic contamination in Uttar Pradesh was first detected in 2003 by SOES, Jadavpur University from a survey of 25 villages in the Ballia district. With further surveys, two more districts, Gazipur and Varanasi were found to have arsenic groundwater contamination. As of 2008, 3 districts covering 69 villages in 7 blocks in Uttar Pradesh were found to have arsenic groundwater contamination, with people who used water from hand pump operated tube wells suffering from arsenical skin lesions. These tube wells tap ped groundwater from shallow aquifers about 20-30 m below ground level. All the arsenic affected districts in UP and 12 districts in Bihar were aligned along the linear direction of the river Ganga.

District	*No. blocks affected*	*Total sources tested*	*Sources >50 μgL^{-1}*	*Sources >50 μgL^{-1}*	*% Sources >50 μgL^{-1}*	*District population*
Bahraich	2	151	47	20	13.2	2,381,072
Ballia	12	5,651	1,492	246	4.4	2,761,620
Balrampur	1	789	27	18	2.2	1,682,350
Chandauli	1	149	2	1	0.7	1,643,251
Faizabad	1	1,691	37	3	0.2	2,088,928
Ghazipur	2	353	63	12	3.4	3,037,582
Gorakhpur	10	4,403	376	76	1.7	3,769,456
Kanpur Nagar	1	357	2	1	0.3	4,167,999
Kheri	6	5,032	1,775	104	2.1	3,207,232
Meerut	1	112	0	1	0.9	2,997,361
Sant Ravidas Nagar	1	312	0	4	1.3	1,353,705
Unnao	1	1,126	12	3	0.3	2,700,324
TOTAL	39	20,126	3,833	489	2.4	31,790,880

Table 1.10 Summary of arsenic affected areas in Uttar Pradesh, (Ahmad et al. 2004)

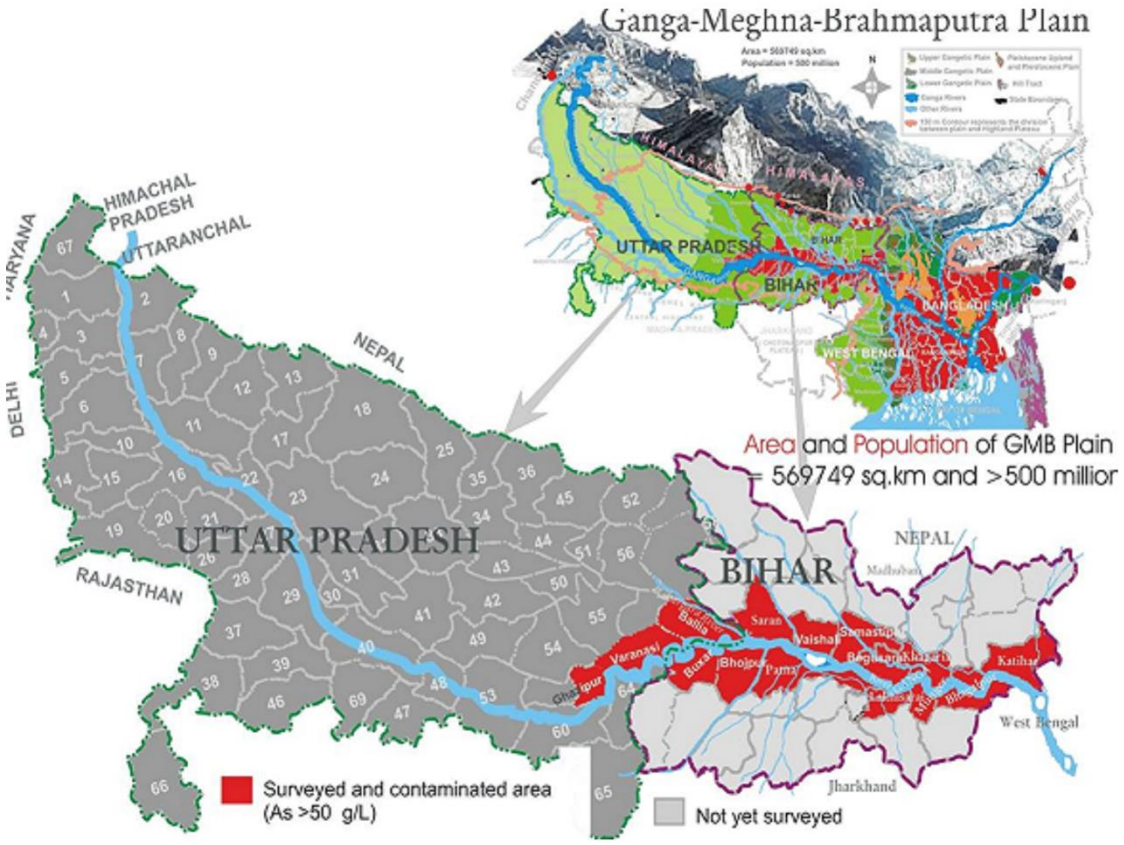


Fig-1.8: Arsenic contamination in 3 districts in Uttar Pradesh and 15 districts in Bihar (School of Environmental Studies, Jadavpur University, 2008)

1.7.2.4 Magnitude of Arsenic Contamination in Jharkhand-

During 2003-2004, groundwater arsenic contamination above 50 µg/L was first reported by SOES, Jadavpur University in the Sahibganj district of Jharkhand, in the middle Ganga plain. In 2007, it was confirmed by CGWB through detailed investigation. Arsenic contamination is close to the Ganges river and in those areas where the Ganga River shifted during the recent past. The hand pump tube-wells of depth range 25-50 m below ground water table were reported to be contaminated, and the affected areas had similar geological formations as in adjoining Bihar and West Bengal. The dug wells with shallow depth were reported by CGWB in 2008 to be free from arsenic contamination.

District	*No. blocks affected*	*Total sources tested*	*Sources 10–50 μgL^{-1}*	*Sources >50 μgL^{-1}*	*% Sources >50 μgL^{-1}*	*Population of affected blocks*
Sahibganj	2	9007	338	336	3.7	271,092
Total	2	9007	338	336	3.7	271,092

Table 1.11 Summary of arsenic affected areas in Jharkhand, (School of Environmental Studies, Jadavpur University, 2004)

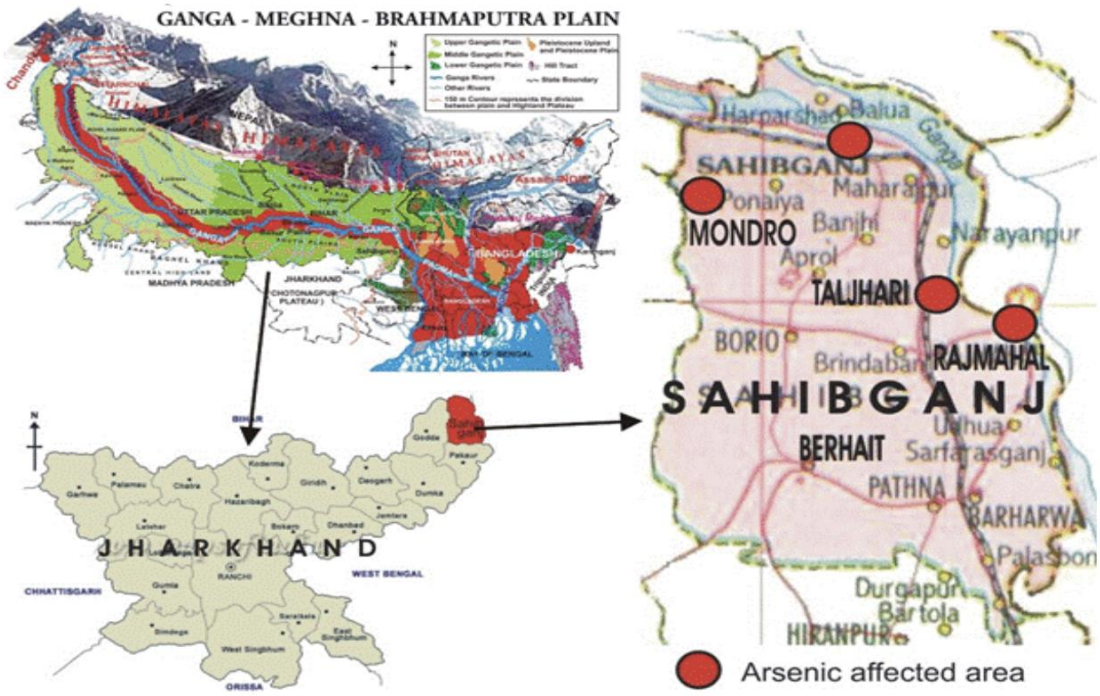


Fig- 1.9: Areas with Arsenic Contamination in Jharkhand, (School of Environmental Studies, Jadavpur University, 2008)

1.7.2.5 Magnitude of Arsenic Contamination in Assam and Manipur in the North Eastern Hill states-

From the seven states in the North eastern Hill States, Manipur, Mizoram, Assam, Tripura, Arunachal Pradesh, Nagaland, and Meghalaya, groundwater arsenic contamination was reported from Assam and Manipur states. A preliminary survey detected that hand tube well water in flood plains of these two states had arsenic contamination above 50 µg/ L and the magnitude was much less as compared to Ganga-Padma- Meghna plain. Recently, UNICEF reported arsenic contamination from Assam and found arsenic contamination in 18 out of 23 districts of Assam above 50 µg/L. SOES, Jadavpur University reported groundwater arsenic contamination from Manipur. The valley districts of Manipur were found to be arsenic contaminated. These districts were Kakching, Imphal east, Imphal west, and Bishnupur. The area of these 4 districts was 10% of the total area of Manipur but about 70% of total population resided in these 4

districts. In Manipur, at present people do not use hand tube well water for drinking, cooking and agricultural purposes. As a result arsenic patients have not been identified from states of Manipur and Assam.

District	No. blocks affected	Total sources tested	Sources 10-50 μgL^{-1}	Sources > 50 μgL^{-1}	% Sources > 50 μgL^{-1}	District population	Projected population at risk
Barpeta	5	130	21	7	5.4	1,647,201	-
Bongaigaon	3	100	15	6	6.0	904,835	-
Cachar	7	210	68	59	28.1	1,444,921	-
Darrang	4	254	92	9	3.5	1,504,320	-
Dhemaji	5	539	128	83	15.4	571,944	-
Dhubri	6	435	130	21	4.8	1,637,344	-
Goalpara	2	145	11	3	2.1	822,035	-
Golaghat	5	268	67	30	11.2	946,279	-
Hailakandi	4	159	45	11	6.9	542,872	-
Jorhat	6	224	96	24	23.1	999,221	-
Kamrup	1	261	39	1	0.4	2,522,324	-
Karimganj	6	811	150	61	7.5	1,007,976	-
Lakhimpur	5	218	50	9	4.1	889,010	-
Marigaon	1	271	40	2	0.7	776,256	-
Nagaon	1	314	55	1	0.3	2,314,629	-
Nalbari	5	148	25	14	9.5	1,148,824	-
Sibsagar	3	206	72	15	7.3	1,051,736	-
Sonitpur	3	227	34	6	2.6	1,681,513	-
TOTAL	72	4920	1138	362	7.4	22,413,240	-

Table 1.12 Summary of arsenic contamination in districts of Assam, (Nickson et al., 2007)

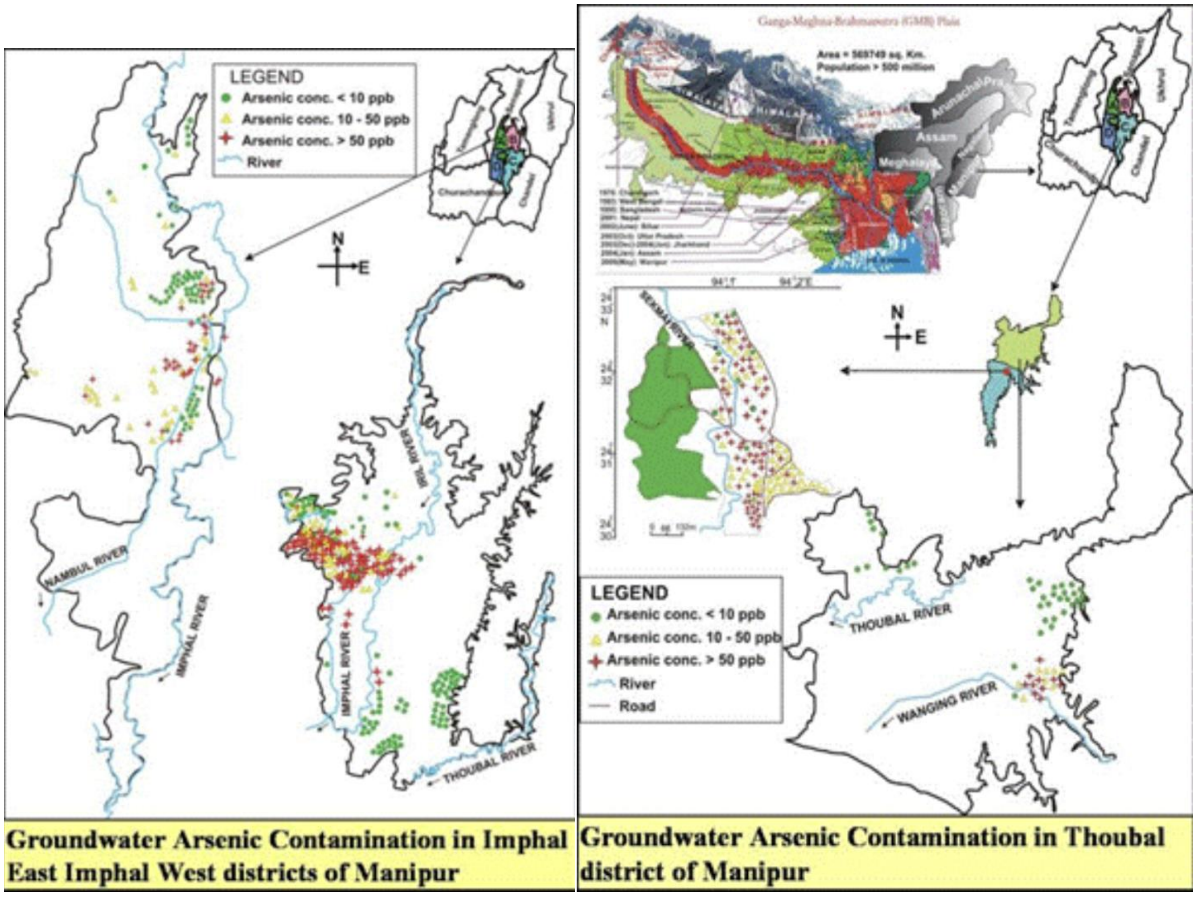


Fig-1.10: Areas with Arsenic Contamination in Manipur, (School of Environmental Studies, Jadavpur University, 2008)

1.7.2.6 Magnitude of Arsenic Contamination in Chhattisgarh-

Apart from the flood plain areas of Ganga-Brahmaputra-Barak rivers, groundwater arsenic contamination was detected from Rajnandgaon district of Chhattisgarh state. A few hundred people had arsenical skin lesions from affected villages. One cancer patient and many patients with keratosis were identified.

People residing in newly identified states with arsenic contamination are in greater danger, as many will not be aware of arsenic contamination in the hand tube-wells and will unknowingly continue drinking arsenic contaminated groundwater. In arsenic contaminated areas, arsenic contaminated groundwater is used for agricultural irrigation resulting in arsenic in the crops in that area. Along with the direct consumption of arsenic in drinking water, the food chain, particularly contaminated rice followed by vegetables, contributes to ingestion

of arsenic. This indicates that the effects of this contamination are far-reaching; sustainable solutions to reduce contamination will reduce future environmental, health, socio economic and socio-cultural hazards.

Even after spending a large amount of money for providing arsenic safe water to the villagers from contaminated hand tube-wells and other sources, the overall result indicates the requirement of more concentrated and focused efforts in planning to cope with such a large calamity. Attempts made so far to counter the menace of groundwater arsenic contamination, to identify the causes, to provide arsenic free drinking water to people dependent on groundwater supply, to reduce the arsenic related social and socio-economic problems and to develop cost effective technology for eradication of arsenic contamination have proven inadequate, fragmented and less responsive. There is a need for adopting a holistic approach to resolve solutions considering management of science-society-resources together, but not merely healing the pain externally. Proper watershed management, possibility of tapping of freshwater aquifer linking to proper aquifer management, in-situ remediation of

the problem and economical utilisation of all available alternative safe sources of water needs to be explored. To combat the arsenic crisis, we need to be aware and educate the villagers of the dangers of arsenic toxicity and the importance of using arsenic safe water. This can only be achieved by active community participation and whole-hearted support from government and arsenic researchers.

1.8 Plan of Action-

In order to mitigate arsenic menace in the state, a number of remedial measures had been started and implemented according to the recommendations of the expert committee constituted by the Government. The measures and steps have mainly been concentrated on-

- Supplying arsenic free drinking water to the entire population in the arsenic contaminated areas by alternate freshwater sources and by treating contaminated groundwater using arsenic removal techniques.
- Identifying extent and nature of arsenic contamination in groundwater
- Establishment of causes and mobilisation mechanism
- Mitigation strategies
- Research & Development studies for devising cost effective remediation technology and for developing sustainable groundwater resources management strategies.

The effectiveness of the counteractive measures and steps, initiated by the Government, in remediation of the problem and understanding the physical processes, needs a critical appraisal to ensure its effective implementation in other arsenic contaminated areas.

1.8.1 Steps and measures taken by the Government-

- Since 1992, the Govt. of West Bengal has taken a number of preventive steps and measures to mitigate the hazard of groundwater arsenic menace,
- such as public awareness programs, devising and demonstrating some of the results acquired from scientific analysis.
- Some of the important steps taken are as follows-
- The infected hand pumps and tube wells, which were being used for domestic supply in the arsenic affected areas, have been identified and put into hold for further use
- 'Arsenic Task Force', consisting of technical experts in the state, has been constituted to prepare an arsenic mitigation action plan for the aquifers in the arsenic contaminated districts;
- A 'Master Plan' under the guidance of the 'Arsenic Task Force' was prepared to supply arsenic free water to the arsenic affected villages using surface water, and groundwater based schemes with Arsenic Treatment Unit.

- Public Health Engineering Department, Government of West Bengal has established chemical laboratories in each district for detecting arsenic content in groundwater.
- A number of surface water based schemes have been put into operation with provision of chemical treatment of arsenic
- Arsenic treatment plants, based on various treatment technologies to remove arsenic contaminated groundwater, have been installed in many places and put into operation if there was no access to other sources of potable water supply
- Arsenic free deeper aquifers and wells were investigated and constructed by CGWB by state agencies for public water supply
- Arsenic content in food and their effect after ingestion has been analysed.

- R & D studies focusing on understanding sources and causes, geochemical processes, mobilisation of arsenic, impact on food chains, social and health hazards, have been initiated.

Despite such steps and measures, the task of ensuring potable water supply in many areas is difficult due to-

- lack of proper coordination
- poor operation and maintenance of arsenic removal devices
- unsatisfactory performance of the arsenic removal filters used in the devices.

The source of irrigation in most of the arsenic affected areas is groundwater from shallow aquifers within 100 m below ground level. With no alternate source of arsenic free irrigation water, rural people continue to tap arseniferous aquifer causing, mobilisation of arseniferous groundwater to freshwater zones, spreading of the sources by the cycling process of water and use of fertilisers and pesticides, transport through food chains, causing further contamination.

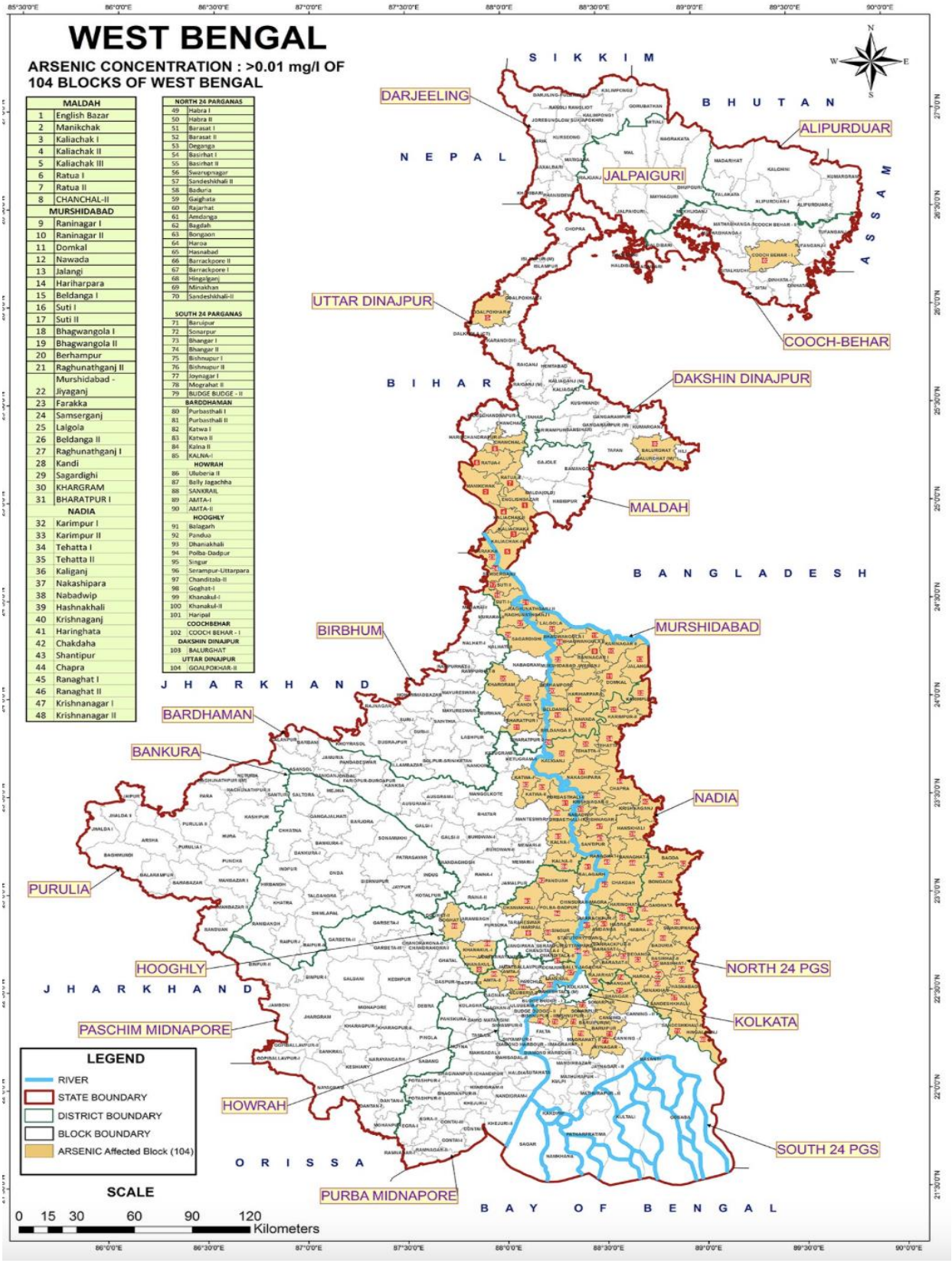


Fig 1.11: Distribution of Arsenic affected areas (WBPHED)

CHAPTER-2
OBJECTIVE AND SCOPE OF WORK

2.1 Objective of the study:

The foremost objective of the study is to evaluate the efficiency of bioadsorptive technology in the removal of arsenic from contaminated groundwater. The study also includes :

- Sources, occurrence and mobilisation mechanisms of arsenic in groundwater.
- Extent and magnitude of arsenic contamination.
- Impact of arsenic pollution on human health and the environment.
- An action plan for mitigation of arsenic contamination in groundwater.
- An overview of the effectiveness and suitability of different arsenic remediation technologies.
- Arsenic removal from contaminated groundwater using biochar as adsorption media.

2.2 Scope of work:

To remove arsenic by using biomass and biochar media and using SDDC method to determine concentration of arsenic before and after removal. The concentration of arsenic in different solutions were 0.1 mg/L, 0.2 mg/l and 0.3 mg/l which simulates the concentration of arsenic found in different groundwater sources.

Using both pristine biomass and biochar to evaluate removal efficiency of arsenic from solutions of three different initial concentrations.

To assess the relation between removal efficiency and concentration of solution used.

CHAPTER-3
LITERATURE REVIEW

Literature review-

PK Sharma *et al.* (2022) summarized effective and feasible methods of arsenic adsorption using biochar that was both pristine and modified, synthesised using pyrolysis under anaerobic conditions having high surface area, microporosity and enhanced functional groups, and highlighted the scope of biochar adsorbents in commercial and industrial scale. From a list of adsorbents, the removal efficiency and adsorption capacity of palm based magnetite composite biochar, at 227.6 mg/g and 67%, and iron modified microfibrillated cellulose at 184.4 mg/g was found to be highly usable for industrial purposes. Other biochar media such as fungal tea biomass treated with ferric chloride and amino modified nano cellulose impregnated with ferric oxide was 100% efficient for removal of arsenite and 77% for arsenate in under 2 hrs with adsorption capacities of 23.6 mg/g and 26mg/g. Peanut shell biochar pyrolysed at 450 ℃ for 2 hrs had a removal efficiency of 99% for arsenite and 95% for arsenate. Removal efficiency was also pH dependent as it varied from 85% at pH 2 and 78% at pH 6 for arsenate using C. fiscula leaves biochar. Presence of ions such as phosphate, silicates, bicarbonate, sulphate, carbonate and chloride which arereleased into water due to anthropogenic activities reduce adsorption of arsenic ions as similarity in structural shape, surface charge and particle size cause competition at same adsorption site.

Moreno-Bárcenas *et al*. (2022) investigated the removal of arsenic utilizing activated jute stalks immobilized with nanoparticles of zero-valent iron over graphene oxide. It resulted in reduction of the total arsenic content from 350 ppb to 34 ppb indicating 90% adsorption by the activated fibre. The individual spherical nZVI nanoparticles with sizes between 17–20 nm form agglomerates due to their high surface The nanoparticles were synthesized from Fe(NO3)3·9H2O could be applied to low-income populations lacking robust infrastructure, such arsenic treatment plant can be adopted by developing countries.

Bashir *et al*. (2020) examined arsenic removal from biochar in unmodified and composite forms and the effect of pH, biochar dose on removal effectiveness, and its physicochemical properties. Various adsorbent media were used for the removal of arsenic in original form and as composites of iron, sulphide, activated

carbon, ferrihydrites, nano particles, flyash, and zerovalent iron coated particles. Biochar was produced by using fast pyrolysis, slow pyrolysis, gassification, and carbonation at different temperatures. It was noted that pristine pinewood chips pyrolyzed at 700°C and zinc modified biogas residue pyrolyzed at 700 °C had the highest surface area available for removal. Other adsorbents used were cotton stalk biochar, grape seed biochar, rice husk biochar, peanut shell biochar and municipal waste biochar. The surface was often modified and impregnated with other media such as zerovalent iron ZVI and aluminium nanoparticles. It was recorded that increasing the temperature of pyrolysis 300°C to 700°C of perilla leaf biochar increases surface from 3.2 m^2/g to to 473 m^2/g. A difference in surface area with rising temperature is due to different amounts of hemicellulose, cellulose and lignin which leads to different, physical and chemical properties . It was also recorded that at higher temperature, volatile organic compounds evaporate, increasing concentration of basic cations which facilitate absorption of arsenic. Fourier transform. Infrared spectroscopy was used to study the property, properties of functional groups and compare changes before and after arsenic absorption. it was seen the spectral peak of iron impregnated biochar was in the wave number interval 1900 cm-1 but after arsenic absorption, it shifted to 881 cm-1 indicating the role of iron in absorption. X-ray diffractometer or XRD used to study the crystalline structures of biochar and x-ray photoelectron spectroscopy or XPS was used for the surface analysis of arsenic and biochar.

Benis *et al.* (2020) reviewed the treatment of aqueous arsenic using biochar and included 63 physical and chemical methods that were used to modify biochar to improve its morphological, textural, chemical, surface and structural properties. From several samples, including biochar prepared from sewage sludge digestate, cotton stalks, jute stick, pine wood shavings, coal blending, jute sticks the greatest sorption capacity (As(V): 30.9 mg/g) was found in chemically treated municipal solid waste that was pyrolysed at 600 °C under inert atmosphere and mixed with KOH solution. A comparison of arsenic adsorption by composite biochar included Fe-composite Rice husk, municipal wastes, corn cob, rice husk, de-alginated macroalgae Gracilaria, sawdust, tea residue, Zn composite biogas waste. It was observed that cotton pyrolysed at 800 °C under inert atmosphere, mixed with $FeCl_3$ and Na_2SO_4 solution, and ultrasonicated had a sorption capacity as high as 93.94 mg/g. The principal removal mechanisms that were identified were - ion exchange, redox transformation, hydrogen bond formation , reaction with functional groups, surface complexation, precipitation and electrostatic attraction.

Mondal *et al.* (2020) examined the effects of impregnation of ZnO on biochar derived from agricultural residual biomass to improve its arsenate and lead adsorption capacities. Corn cob and coffee husk were pyrolysed in mild conditions and ZnO was precipitated onto the biochar creating a composite which was comprehensively characterised, describing their textural, chemical, surface, morphological and structural properties. The crystal structure of prepared adsorbents was analysed by XRD and the diffractograms showed combination of amorphous and crystalline structure. The wide diffraction peaks present at 12.2°, 23.6° and 43.2° were due to the amorphous phase of the biochar and these peaks were seen in all the biochars (pristine and ZnO modified). ATR-FTIR spectra of the materials revealed various functional groups and it was found that there were similar functional groups on the surface of all the biochar samples.The peaks at 880 cm−1 were due to aromatic C–H groups, at 1100 cm−1 due to ether group C–O–C, at 1560cm−1 due to alkene C=C, at 1700cm−1 due to to carbonyl group C=O, confirming that pyrolysis was achieved under anaerobic conditions as most of oxygen-based functional groups were removed as seen from low intensity spectral bands. X-ray fluorescence (XRF) found the content of Zn in ppm and the biochar samples contained less than 0.01% ZnO confirming its amorphous nature from XRD diffractograms. Due to better textural properties and morphological structure of corn cob, penetration of zinc precipitate was better and improved microporosity. Kinetic and equilibrium adsorption tests showed improved affinity of arsenate to ZnO composite biochar which was attributed to increase in active sites for metal adsorption, with corn cob biochar having greater effectiveness at an adsorption capacity of 9.622 mg/g while coffee husk composite have an adsorption capacity of 1.989 mg/g.

Ahmad *et al.* (2020) studied mechanisms of arsenate removal in ferric based co precipitation low pressure membrane filtration systems. The effect of feed water composition and pore size, dosage of ferric hydroxide was studied. Effluent samples from rapid sand filter was used, polymeric polyethersulphone (PES) and polyvinylpyrrolidone (PVP) fibre membranes of two different pore sizes 200nm and 20nm were used. A scanning electron microscope (SEM) was used to obtain images of the inner surface, cross section and study membrane fouling. Feed solution was pumped at 8.3 mL/min and ferric chloride stock solution at 0.3 mL/min. The hydraulic residence time (HRT) between application of coagulant and filtration was 1 minute. Duration of filtration was 1 hour for each cycle, with a total of 6 cycles. Arsenic, iron, calcium, phosphate were measured using inductively coupled plasma mass spectrometry (ICP- MS). It was observed that without dosing the effluent with ferric chloride stock solution,

no arsenate was removed as the small sized anions passed through both UF and NF membranes and due to the negative surface charge on the membranes. With increasing dosage of stock solution, arsenate dosage also increased. The presence of calcium cations in feed water promotes formation of ferric precipitates in the form of ternary complexes. The presence of phosphates and silicates competes with arsenate on adsorption sites of ferric hydroxide and reduces removal. To study fouling mechanisms, SEM-EDX was used which shows deposits of ferric precipitates in irregular layers which was persisting even after backwash with ultrapure water. This was because some ferric particles are deposited in the internal structure and subjected to lower hydraulic shear forces. These cannot be removed by backwashing and contribute to fouling resistance. It is not dependent on pore size as ferric precipitates are larger than UF and NF pores. Fouling resistance was a function of coagulant dosage, composition of feed water and residence time before UF or NF. However, for smaller pore sizes, hydraulic backwash does not effectively remove precipitates that have been immobilised in the deeper structure.) In such cases membrane operation for prolonged periods of time reduces permeability due to internal membrane fouling.

Navarathna *et al.* (2019) investigated the effectiveness of arsenic removal using magnetite (ferric oxide) and douglas fir biochar composite (MBC). The sorption media was gasified at 800-1000 ℃ with a residence time of 1-10 seconds in anaerobic conditions. MBC was synthesized using ferric chloride and hydrated ferric sulphate and batch sorption was carried out using 10 mg/L arsenite solution. The samples were isolated and oven dried at 40 ℃ for 2 hrs. SEM for MBC indicates that morphological changes due to precipitated ferric oxide particles on surface were seen with a reduction in surface area from 670.4 m2/g to 320.1 m2/g due to precipitation on the carbonaceous surface which diminishes adsorption onto the microporous surface. However it was seen that there was preferential adsorption onto the magnetite precipitates instead of the carbonaceous surface with no arsenite adsorption on the pristine biochar surface between pH 2-12. The adsorption capacity of MBC was found to be 8.3mg/g and that of pristine biochar was negligible. From initial concentrations of 5, 10 and 20 mg/L solutions greatest removal efficiency was seen at 20mg/L due to formation arsenic iron stoichiometric compounds that cause greater removal. The Sips isotherm capacity indicated increasing adsorption capacity at higher temperature due to multilayer adsorption.

Upadhyay *et al*. (2018) compiled available data on arsenic levels in rice from various sources. It was revealed that the concentration of arsenic in crops varied even across a single field with highest concentration near the irrigation inlet. The arsenic contamination in different species of rice, maize, sorghum, millets, potato, beans, chickpeas, lentils, brinjal, carrot, tomatoes, cabbage, coriander, had been noted with especially high concentration in prawns, crabs, and mushrooms. Processed food including puffed rice, soy milk and infant cereal also contained concentrations above recommended limits. The studies indicate the scale of arsenic contamination in rice, wheat, corn and several other food items that are necessary in regular diets. A routine sampling of soil, water, food for total arsenic, using subsidized and safe protocols like bio sensors or nano sensors that can be used in developing countries without large capital investment may be required to act as data for regulatory and policy-making purposes ensure safe food.

Ratnaweera *et al.* (2017) investigated the effects of doubling filtration comprising of nano-filtration and reverse osmosis in the complete removal of arsenite from drinking water. A bench scale RO unit consisting of polyamide thin film composite RO membranes by Filmtec Co. from Dow model TW30- 4040 was used. The feed water was pumped by booster pumps and was pretreated and passed through coarse filters before membrane treatment. Flow rate was controlled by two valves. It was found that the optimum conditions for arsenic removal were at 1310kPa -1448kPa operating pressure, and pH of 6-8. Filtrate flow was fixed at 200L/hr. Experiments were undertaken to ascertain if second filtration increases efficiency of arsenite removal. The concentration of arsenic was measured by Agilent 8800 Inductively Coupled Plasma Mass Spectrometry. Ion exchange resin Dowex 21K XLT with styrene DV8 gel charged with chloride was used to separate arsenate from arsenite, after passing through resin, samples only contained arsenite. It was found that arsenite removal efficiency after first filtration was 60% - 80% but after second filtration it was 98%, which was higher than that of other membrane technologies.

Jayasinghe *et al.* (2015) outlined the effects of arsenic on different organ systems in the human body with a main focus on respective disease conditions. It was noted that arsenic causes epigenetic changes in utero and genetic mutations in the body. In the integumentary system the important characteristic features of arsenic exposure are skin lesions, melanosis, keratosis and pigmentation. Skin lesions were usually detected 5–10 years after the exposure. Skin pigmentation was reported in 66% patients out of 156 patients encountered

with arsenic exposure through drinking water sources. High arsenic exposure had been associated with cardiovascular diseases and atherosclerosis, hypertension, arrhythmia and change in blood pressure. Exposure to arsenic also causes autoimmune diseases, anaemia, diabetes, haemolysis, immunosuppression, hepatic toxicity, pancreatis, renal toxicity, and lung tumorigenesis. Development of cancer in skin, lung, liver, bladder, kidney and prostate due to arsenic has been extensively established.

Asadullah *et al*. (2013) examined removal of arsenic using biochar prepared from jute stalks in both pristine and modified from. Corchorus capsularis stalk was collected, washed and open air dried for two days to remove unbound moisture and then cut into 1cm size with grinding machine and sieved into 1milimeter size. The jute was evaluated with both proximate and ultimate analysis. From proximate analysis volatile fraction fixed carbon and ash yield of jute was 78%, 21% and 0.6% respectively. According to ultimate analysis the elemental composition of jute was 49.79% carbon 6.02% hydrogen , 41.37% oxygen 0.1% nitrogen, 0.05% chloride and 0.05 % sulfur by weight respectively. The jute was steam pyrolysed at 800 ºC for one hour, washed with distilled water and oven dried at 105ºC for 12 hour. For preparation of iron composite of bio char 10% ferric sulphate solution, 5% sodium hypochlorite solution was added and calcined at 500ºC under inert atmosphere. The surface area of biochar sample was measured at -196ºC using surface area analyser AUTOSORB -1 to find microporosity. The surface functional group was analyzed by perkin Elmer spectrum FTIR spectrometer and recorded spectra were between 4000 and 450 centimeter-1. It was found that chemically activated biochar using phosphoric acid had higher BET surfaces of 1624 meter sq/gram has compared to Physically activated biochar using steam with bet surface area of 750 meter square per gram. During physical activation the burn off percentage was 88% and yield was 12% while the burnoff percentage was 51% and yield was 49% resulting in micro porous structure with highest surface area and high porosity. Arsenic was operated using column filtration. It was seen that adsorption capacity was higher in 150 microgram/ gram than 100 micrograms/gram. The adsorption of arsenic of biochar surface depends on flow rate concentrations those ph and temperature. It was found that for the same residence time a flow rate of 45 mL/ minute remove acceptable amount of arsenic . It was also observed that at higher ph adsorption was decreased as positive charge on surface was converted to negative charge by deprotonation due to hydroxyl ion and the arsenate was electro-statically repelled . Change in temperature did not caused variation in arsenic adsorption. The highest adsorption capacity of 1320 microgram/ gram was seen in clacined

biochar with iron contain of 5.5% due to affinity of iron to surface functional group and arsenic.

Bhargav *et al.* (2013) evaluated the removal of arsenate from municipal water supply utilizing magnetite nanoparticles (Fe3O4) with size less than 30 nm, and applying external magnetic fields. At optimized pH Fe304 nanoparticles were coated with stoichiometric mixture of ferrous and ferric salts and carboxymethyl-β-cyclodextrin (CM-β-CD) which form surface functional groups. The sorption of arsenate takes place, following pseudo-second order mechanism, on these aggregates which are removed with help of external magnetic field as magnetite nanoparticles remain non magnetised and can be reused.

Glocheux *et al*. (2013) used Acidified Laterite (ALS), a cost effective industrial by-product of sulphuric acid generated during the production of Ferric Aluminium Sulphate (FAS) by acid leaching treatment as an adsorbent , and also used raw laterite for comparison in the arsenic adsorption experiments and elemental analysis, surface chemistry, pore texture parameters, PZC, and SEM was conducted to analyse physico-chemical properties. From adsorption isotherm and kinetics data modelled using the pseudo first and pseudo second order kinetic models maximum loading capacities of raw laterite for arsenite and arsenate ions were revealed to be 127.8 μg g−1and 301.2 μg g−1and that of acidified Laterite for arsenite and arsenate ions to be 171.7 μg g−1and 923.6 μg/g, 3 and 5 times higher than that of raw laterite due to higher surface area, microporosity and presence sulphate functional groups on the ALS surface. At 1 g/L of ALS, 94% removal was noted for [As(V)] 0 = 1 ppm while only 35% was removed by the raw laterite.

Oehmen *et al.* (2011) studied the removal of arsenic through a hybrid anion exchange membrane - coagulation process and the quality of the water so obtained as compared to a conventional coagulation- filtration process. In this study there was no secondary contamination from the addition of coagulants and pH controlling reagents. Anion exchange membranes from Fumatechs, Ionics and Polymer Chemie Altmeier were used. The concentration of arsenic was determined by inductively coupled plasma atomic emission spectrometry (ICP- AES). Membranes were stored in 0.5M NaCl solution which exchanges chloride anion with arsenic cation. Two coagulants were tested ferric chloride FeCl3 and aluminium chloride AlCl3. IEM was conducted for 45 hr.

Due due Donnan exclusion the transport of arsenic ions through the membrane to the receiving compartment is encouraged by the excess of Cl- ions. A coagulant is added to the receiving compartment, which keeps concentration of arsenic ions in receiving compartment low, driving more arsenic ions into the compartment. Therefore the coagulant added acts as both precipitant and source of counter ions for more arsenate transport, achieving two purposes by the addition of one chemical. Due closed circuit receiving compartment, recovery of arsenic and its disposal by (incineration or landfilling) is optimised. As arsenic is found in aqueous solution as H2AsO4 and HAsO4 2-, a suitable ion exchange medium is required that can transport arsenic in both monovalent and divalent forms. The Ionics membrane was tested to be most suitable in terms of arsenate flux, mechanical strength. AlCl3 as a coagulant reduces incrustation on membrane and increases its design life. This because of the charges of the precipitate which are repelled from positively charged membrane. The pH was 6.5 to 7.5 It was concluded that the Ionics AR04-UZRA anion exchange membrane was most suitable due to high flux of both monovalent and divalent forms of arsenate in aqueous solution H2AsO4- and HAsO4 2- . The use of suitable coagulant also increases arsenate flux per membrane area due to reduced scaling. The IEM process can also be operated over extended periods with minimal maintenance and no secondary contamination due to additional coagulants and pH controllers in closed circuit.

Nickson *et al*. (2007) collated data on arsenic in groundwater in the in the Ganges-Brahmaputra river basin. Testing was done using SDDC method and Merck Spectrophotometer Model UV1. In West Bengal, water from 132,262 government installed handpumps in 8 districts had been tested and around 25.5% of samples contained arsenic at concentrations greater than 50 µ gL−1 and 57.9% at concentrations greater than 10 µgL−1. Similar studies were conducted in in Assam and 5,729 government handpump sources in 22 districts had been tested for arsenic. 6.3% of sources were established to contain arsenic at concentrations greater than 50 µgL−1 and 26.1% at concentrations greater than 10 µgL−1. In Bihar, on the river Ganges upstream of West Bengal, 66,623 sources from 11 districts have been analysed and water samples from 10.8% of sources were revealed to contain arsenic at concentrations greater than 50 µgL−1 and 28.9% at concentrations greater than 10 µgL−1. Upstream of Bihar in Uttar Pradesh, , to date water samples from 20,126 government-installed handpump sources have been tested and 2.4% of the samples tested were found to contain arsenic at concentrations greater than 50 µgL−1 and 21.5% at concentrations greater than 10 µgL−1.

Rengaraj *et al*. (2004) studied the effectiveness of mesoporous alumina in removing arsenic from aqueous solution as compared to activated alumina. Adsorption is a more economical and safer method of arsenic production than co-precipitation, ion exchange or membrane filtration. Activated alumina (AA) which is prepared by dehydroxylating aluminium hydroxide with surface area of 200 m^2/g is the most common adsorbent for arsenic. However it has irregular pores and is kinetically slow.In comparison, Mesoprous alumina (MA) has a larger surface area 307 m2/g, uniform and highly interlinked pores, greater physical and chemical stability. Adsoption of arsenate by MA was found to be 7 times higher (121 mg of As(V)/g and 47 mg of As(III)/g was adsorbed). 0.05 M NaOH was the the most effective desorption agent. The studies show that the essential parameter in adsorption of arsenic is not surface area, but uniform pore size, pore interconnectedness, and chemical stability. Mesoporous arsenic was found to be a better adsorbent for arsenic than activated alumina based on these parameters.

Singh *et al.* (2003) experimented on activated alumina for removal of arsenite from contaminated water and the effects of dose, pH, and contact time and found arsenic removal was dependent on pH and temperature and that the highest adsorption of 94.4% was attained in the pH range of 6-8 and 96.2% removal at pH of 7.6. The adsorption process followed first order kinetics and the regression analysis of the equilibrium data fitted the Langmuir, Friendlich, and Dubinin–Radushkevich DR adsorption isotherm model. It was established that the uptake of arsenite increases with the lapse of time and the adsorption was rapid in the first 6 hrs after which the rate slowed down as the equilibrium approached. Their experimental result suggest that adsorption of arsenite on activated alumina is a complex mechanism where both surface adsorption and intra-particle diffusion contribute to the rate determining step of adsorption kinetics. The adsorption process was spontaneous and decreased with increase in temperature showing exothermic nature of the adsorption.

Roychowdhury *et al* (2002) investigated the amount of total arsenic in food composites, collected from arsenic-affected areas of the Murshidabad district, West Bengal and established that highest mean arsenic concentrations were potato skin (292.62 mg/kg), pumpkin, gourd, radish leaves and other edible herbs 212.34 and 294.67 mg/kg, arum leaf (331 and 341 mg/kg), papaya (196.5 and 373 mg/kg), rice (226.18 and 245.39 mg/kg), wheat (362 mg/kg), cumin (209.75 mg/kg), brinjal (490 mg/kg), coriander (334.5 mg/kg) and turmeric powder (297.33 and 280.9 mg/kg) in the Murshidabad district. The

other highest mean arsenic concentrations in individual food composites are radish (145 mg/kg) and for Jalangi block, and, five spices (122 mg/kg) and cow's milk (170 mg/l) for Domkal block. For cooked food, the highest mean arsenic concentrations were in (374.17 and 666.57 mg/ kg), freshwater fish (830 mg/g), and pulses (900 mg/kg). block, are rice (183 mg/kg), coarse wheat flour (80 mg/kg), turmeric powder (334.67 mg/kg), five spices (247 mg/kg), beans (200 mg/kg) and green chilli (130 mg/kg).

Das *et al.* (2000) developed a household device for removal of arsenic from contaminated water consisting of a filter made of purified fly ash with binder, tablet containing iron salt, oxidizing agent and activated charcoal, two earthen jars or plastic jars. One use was sufficient for 20 litres of contaminated water having arsenic concentration of 1000 g/l. The sludge produced after removal of arsenic was rich in arsenic and was disposed in soil with cow dung and arsenic was eliminated as volatile arsenic species through the microbes in the cow-dung. After successful laboratory testing, several units were taken to arsenic affected villages in six districts of West Bengal and tested with contaminated hand tube-wells (arsenic range 300-950 ug/l) from about 100 families and it was recorded that the efficiency was 93 to 100%. This "Filter Tablet System" was suitable for emergency in affected villages for West Bengal India and Bangladesh.

Gonzalez *et al*. (1999) conducted experiments on arsenic adsorption on natural solids. The natural adsorptive media used were zeolites and volcanic stone such as tosudite, cristobalite, calcite, quartz and mica. These were activated in acid wash (2 M HCl at 50°C for 2 hrs and kept in solution for 24 hrs then washed with water and dried at 200 °C after pH of 5 was obtained. The AgNO3 test for chloride is to be negative.) The sorption experiments were carried out in batches at 20°C . It was kept in equilibrium for 7 days then kept in ultrasonic bath. The adsorption arsenate and arsenite was measured daily for 12 days. After 24 hrs, the arsenite concentration was significantly reduced in zeolite adjusted with 0.0001 M HCl and 0.0001 M LiOH. as compared to activated zeolite. The stability, dominance and susceptibility of removal of arsenic depends on pH of aqueous solution. From the ICP-MS chromatogram, it is seen, arsenate is quickly adsorped and 99% arsenate was removed. It was seen that when ultrasonic treatment is applied arsenite adsorption increases by 80%. The role of decationation by washing with HCl acid was also examined. On removal of cations such as sodium and calcium and dealumination, thermal stability and catalytic activity changes, and more mesopores are available for adsorption.

Synthetic mordenite ZS-M had a removal efficiency of 75%, natural clinoptilite ZMS had a removal efficiency of 56%.

Bajpai and Chowdhuri (1999) investigated the removal of arsenic from groundwater by manganese coated sand. Manganese dioxide coated sand was prepared by oxidation of manganous ion with potassium permanganate in presence of sand under alkaline conditions by using sodium hydroxide solution. The mixture was rinsed with distilled water and dried at 105ºC. EDAX spectra was used to study the kind of coating formed on sand particles and electron micrograph to study the uniformity of coating. The groundwater used in the tests had pH 7.5 - 7.8, alkalinity 250 - 260 mg of CaCO3/L, hardness 160 - 200mg of CaCO3/L. The molybdenum blue spectrophotometric method was used to measure arsenite and arsenate . The removal kinetics of arsenite was more rapid and the bulk of removal took place in an hour, while the kinetics of arsenate removal was slower and the bulk of removal took place in an hour. This indicates the effectiveness of this methodology in removal of arsenite. Ten cycles of such tests were conducted, each with 74 mins contact time. There was no leaching of arsenite or manganese from column. This technology has been successfully used as a home removal unit in developing areas, although external parameters such as attrition of manganese dioxide coated sand, fouling, orifice blocking.

Hering *et al*. (1997) analysed that except the co-precipitation and adsorption methods other methods are not economically feasible for village level use. Co precipitation method was found to be ineffective if the arsenic concentration of was higher than 0.35 mg/L, as the removal efficiency of coagulation is in between 80% to 85%. Treated water needed a secondary treatment to meet the recommended standards. In terms of cost effectiveness, the adsorption procedure was more suitable than ion-exchange or member separation. There were a number of adsorbents such as activated carbon, activated alumina, and ferric hydroxide that were used. In terms of availability, reliability and economy, activated alumina was the best suited alternative. Arsenate removal effectiveness by either ferric chloride or alum was relatively unaffected by change in source water composition below pH 8. At pH 8 and 9, the efficiency of arsenate removal by ferric chloride was decreased in the presence of
natural organic matter. The pH range for arsenate removal with alum was lesser than with ferric chloride. For 20 g/L, final arsenate concentrations in the water was less than 2 ug/L with both coagulants at pH 7. Removal of arsenite

from water using ferric chloride was less effective and more strongly influenced by source water composition than removal of arsenate . The presence of sulphate at pH 4-5 and natural organic matter at pH 4 -9 reduced the efficiency of arsenite removal by ferric chloride. It was noted that arsenite could not be removed from water by coagulation with alum.

Nriagu *et al*. (1988) reviewed the distribution of arsenic in soil and grounwater. The average annual global atmospheric emission of As from natural sources was noted to be about 12Mt (million metric tons) taking into account wind-blown dust from weathered continental crust, forest fires, volcanoes (20–40%), sea spray, hot springs, and geysers. In sedimentary environments, As occured as sorbed oxy-anions in oxidized sediments, with concentrations of 0.6 and 120 mg/kg in sand and sandstones and 490 mg/kg in shale and clays. Arsenic concentrations was found to be between 0.7 and 1.1 mg/l along the Padma River, while in Meghna River, the concentrations were between 0.6 and 1.9 mg/l. Mining, smelting and ore processing, pesticides, fertilizers, pharmaceutical and chemical industries, thermal power plants using coal or peat, timber processing and preservation industries using CCA, and incinerations of preserved wood wastes release large quantities of arsenic to the environment. In general 19 kt (range 12–25.6 kt) of arsenic was released into the atmosphere per year. 82 and 42 kt into the soil and aquatic environments.

Gupta and Chen (1978) discussed of pH, salinity, type of adsorbents on efficiency of arsenic removal. The samples collected were filtered through 0. 45um membrane and analysed by atomic adsorption spectrometry with deuterium arc. The adsorbents tested were activated alumina, activated bauxite and activated carbon. It was observed that arsenate constitutes 10%to 40% of the aqueous solution in slightly reducing condition that is commonplace in most groundwater. Groundwater has a greater concentration arsenite and surface water has a combination of arsenate and arsenite. It was found that arsenic was removed by activated alumina at an exponential rate, and much

quicker than the other two adsorbents. 50% of the arsenate was removed in the first 10 minutes. Rates of arsenite removal was much slower and merely 6% of arsenite was removed by activated alumina in the first 10 minutes. Arsenate adsorption by activated bauxite and activated alumina was found to be most effective in the pH range 4-7 with with decrease in adsorption above pH 7. Activated carbon worked better between the acidic range pH 3-5 with sharp

decline at increased and decreased pH values. Arsenite adsorption did not vary much with pH except decline sharply after pH 9.

CHAPTER-4
EFFECT OF ARSENIC ON HEALTH

4.1 Introduction-

As a metalloid , arsenic exists in various allotropic forms such as elemental, sulphide, oxide and carbonate form . Exposure to inorganic arsenic through consumption of contaminated food, water, and air causes adverse effects on human health. Low doses and long term exposures of arsenic leads to a range of medical complications termed as “arsenicosis”.

Arsenic exposure is a result of geogenic or anthropogenic sources. Ingestion, inhalation and skin absorption are some of the crucial routes for arsenic entering the human body. Both arsenate and arsenite are speedily and substantially absorbed from the gastrointestinal tract. The absorption rates of sodium arsenate, sodium arsenite and arsenic trioxide are higher than arsenic trisulphide, lead arsenate and inorganic tetravalent arsenic due to their molecular size. Trivalent compounds are more water soluble than pentavalent arsenic compounds and therefore are more toxic in nature. Reduced (trivalent As(III)) and maybe oxidised (pentavalent As(V)) forms of arsenic, are absorbed and accumulated in tissues and body fluids (Ueki et al., 2004). Arsenic concentration in the body is relatively constant but widely distributed in organs such as skin, lungs, liver and kidneys. In the liver, inorganic arsenic is reduced from pentavalent to trivalent form by enzymatic or non-enzymatic (glutathione) processes. About 70% of arsenic, both organic and inorganic, is excreted through the renal system by urine. Inorganic arsenic (iAs) is retained in the body for longer than organic arsenic and the excretion process of iAs takes longer and causes more damage.

Disease	Global background mortality rates[a] (deaths/ 100 000 persons)	Mortality rates in regions where As ≥ 300 µg/l (deaths/100 000 persons)	Number of As-related deaths annually, worldwide[b]	Reference
Cancers	114	350	28 000	Wu et al. (1989)
Cardiovascular diseases	137	165	13 200	*Ibid.*
Cerebrovascular diseases	89	130	10 400	*Ibid.*

Table 4.1 Estimates of annual As-related mortality (WHO, 2004)

Low to moderate levels of arsenic consumption (10–300g/L) through drinking water causes skin lesions, circulatory disorders, neurological disorders , diabetes, respiratory diseases, hepatic and renal dysfunction including mortality due to chronic diseases. Depending on the type of arsenic exposure, acute or chronic, there are a range of symptoms. Symptoms of acute exposure develop more rapidly, causing organ damage and sometimes death, while clinical symptoms of chronic arsenic exposure develop over a long period of exposure, causing disfigurement of extremities and malignant tumours.
Various complications involving dermatological effects, cardiovascular effects, pulmonary disorders, reproductive effects, neurological effects have been reported in adults and children due to arsenic exposure specifically via drinking water.

Inorganic arsenic consumption can cause tumorigenesis in skin, bladder, kidneys, lungs and liver along with other circulatory and neurological complications. While organic arsenic compounds commonly found in seafood are less toxic than inorganic arsenic .Effects of arsenic exposure are distinctly divided into four stages.

4.2.1 Effects of arsenic on the integumentary system -

Skin and its appendages including hairs and nails form the integumentary system. Skin is more vulnerable to arsenicosis and the initial symptoms are first seen in the integumentary system. Skin abnormalities are the major indicator of arsenicosis. It was noted that men are more likely to develop arsenic induced skin disorders compared to women. Some of the important features of arsenic exposure are **skin lesions, melanosis, keratosis and pigmentation**. These features are used to diagnose chronic arsenic exposure. However, skin lesions usually develop 5–10 years after the beginning of exposure. Skin pigmentation and **thickening and nodule formation on the palm and sole** were reported in 66% patients out of 156 patients with arsenic contamination through drinking water sources (As concentration of 0.05 -- 3.2 mg/L) in West Bengal, India (Mazumder et al., 1998).
Hyperpigmentation was recorded in 54.4% palms and 39% soles and relatively low keratosis in 23.2% palms and 17.6% soles with arsenic exposure Apart from skin, arsenic deposition in other keratin rich areas of the body such as nails leads to formation of **distinct white lines (Mee's lines) in the nails** of fingers and toes . **Alopecia** is a common clinical symptom of chronic arsenic exposure. Arsenic is a group 1 carcinogen and on chronic exposure causes **non-melanoma skin**

cancer (NMSC), basal cell carcinoma (BCC) and squamous cell carcinoma (SCC), (Cohen and Moore 2007).

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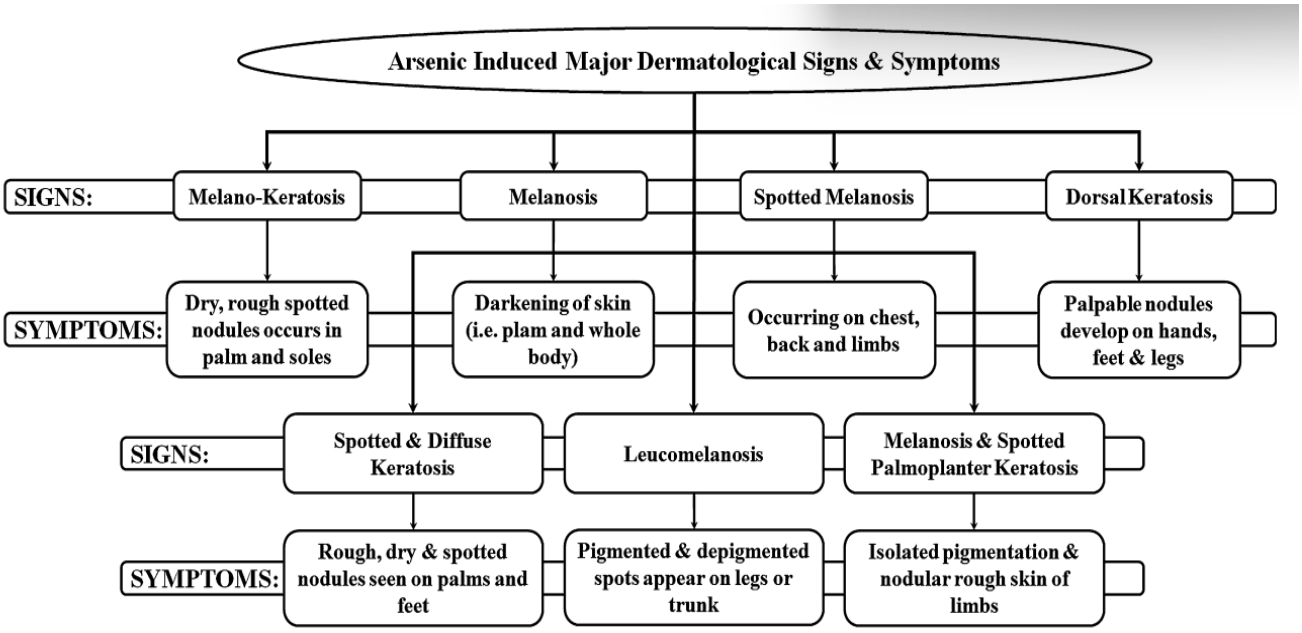


Fig-4.1: Classification of arsenic caused dermatological diseases based on the type of symptoms. (Saha *et al*. 1999



Fig-4.2: Arsenic induced melanosis and Aldrich Mee's Lines on hands.

4.2.2 Effects of arsenic on the nervous system-

Arsenic species are distributed in all parts of the brain and cross the blood brain barrier easily. The highest accumulation was observed in hypophysis (pituitary gland) Development of neurological complications due to acute and chronic exposure of arsenic is rather quick and in the form of symmetrical sensorimotor neuropathy as sensory nerves are more vulnerable to arsenic than motor nerves with short axons. Some of the very common clinical symptoms include paraesthesia, pain and numbness in the soles of the feet caused by reduced capabilities of neurons to detoxify Reactive Oxygen Species (ROS) and produce glutathione. Oxidative stress is the major cause of arsenic induced neurotoxicity. In severe conditions, inactivation of crucial enzymes that governs the cell function may be hindered. However, the most important mechanism involved in arsenic induced neurotoxicity is the dismantling of the cytoskeletal framework by altering protein composition of the cytoskeleton and by hyper-phosphorylation of proteins. Arsenic also causes neuronal apoptosis by activation of p38 and c-Jun N-terminal kinase-3 (JNK3) mitogen-activated protein kinases. Neuropsychological studies confirm **severe impairment of memory and verbal learning skills upon arsenic exposure** (Vahidnia et al., 2007). Development of **neurobehavioral disorders and cognitive dysfunction**, **altered levels of neurotransmitters such as dopamine, norepinephrine,** acetylcholine, glutamate, gamma-aminobutyric acid and 5-hydroxytryptamine, central and **peripheral neuropathy, encephalopathy with gradual loss of brain function and activity over time, headache, hallucinations, seizures and coma** are noted in long-term low level arsenic exposure. Peripheral neuropathy was the predominant neurological complication in patients exposed to arsenic contaminated ground water in West Bengal, India (Mukherjee et al., 2003).

4.2.3 Effects of arsenic on the respiratory system -

Arsenic exposure by either drinking water or from atmospheric conditions lead to respiratory complications over time, leading to **lung dysfunction and increased mortality**. Arsenic dust or fume inhalation during mining or milling of ores often produces respiratory complications such as **chronic cough, shortness of breath, blood in sputum, laryngitis, bronchitis and rhinitis**. A correlation between urinary arsenic levels and serum Clara cell protein (CC16) levels were found, CC16 acts as a novel biomarker for respiratory illness. High urinary arsenic levels showed decreased lung function. Recent prospective cohort studies found low to moderate levels of arsenic exposure in Bangladesh population resulted in impaired lung function and tuberculosis. In utero and childhood exposure of arsenic through drinking water caused long term lung

damage, decrease in forced vital capacity and a restrictive spirometry pattern and non-malignant lung diseases.

4.2.4 Effects on the cardiovascular system-

High arsenic exposure and cardiovascular diseases (CVD) including **concord atherosclerosis, hypertension, and arrhythmia.** Long-term inhalation of inorganic arsenic causes adverse effects on the cardiovascular system including heart and blood vessels increasing morbidity and mortality rate. Arsenic exposure causes **atherosclerosis**, has a strong correlation causing mortality and causes atherogenicity. Arsenic induces a range of pathophysiological events that causes **atherosclerosis, hypertension, arrhythmias and ischemic heart diseases** Arsenic exposure causes gene expression of mediators influencing inflammation including interleukin-8 and tumour protein p53 have shown joint effects on susceptibility of carotid atherosclerosis upon arsenic exposure >50 mg/L. Arsenic exposure increases calcium sensitization, phosphorylation of myosin light chain, oxidative stress resulting in decreased antioxidant mechanisms leading to **hyper contraction in blood vessels**.

4.2.5 Effects of arsenic on the hematopoietic system –

Arsenic contamination affects the hematopoietic system including bone marrow, spleen and erythrocytes. Greater arsenic accumulation was noted in the spleen with 2–3 times higher accumulation compared to other organs such as heart, liver and kidney. The majority of the arsenic binds to haemoglobin and accumulates in the erythrocytes inducing **haemolysis,** curtailing longevity of erythrocytes **reducing healthy erythrocytes** and causing **anaemia.**

4.2.6 Effects of arsenic on the immune system-

Distinct disruptive signs of innate immunity due to inorganic As exposure has been recorded. Arsenic exposure on macrophages reduces its capabilities, thereby **increasing susceptibility toward infections**. The major underlying mechanism causing impaired functions of macrophage is due to malfunction in unfolded protein response (UPR) signalling pathway due to arsenic exposure. Arsenic exposure induces a range of autoimmune diseases including diabetes, atherosclerosis and non-melanoma skin cancers. Inorganic arsenic also impairs

the development, activation, proliferation and function of lymphocytes, causing **oxidative damage, apoptosis, DNA strand damage, modification of DNA bases**, crosslinking proteins, lipid peroxidation. It has been established that arsenic exposure causes **hypertrophy of liver and spleen, chronic inflammation** and can also lead to **various forms of cancer.**

4.2.7 Effects of arsenic on the endocrine system –

Arsenic is a well-known disruptor of the endocrine system, including thyroid, thyroid hormone, pancreas, and disrupts hypothalamic-pituitary-adrenal axis. Impaired thymic functions were noted in prenatal exposure possibly via arsenic induced oxidative stress and apoptosis. Arsenic accumulates in pancreas and decreases the secretion of insulin, glucagon and viability of the cells.. High blood glucose levels due to insufficient insulin production by pancreatic cells is the distinct reason for the heterogeneous disorder causing **diabetes.**

4.2.8 Effects of arsenic on hepatic system-

Accumulation of arsenic in liver following repeated exposures causes **hepatic toxicity, ascites, jaundice, or enlargement of liver** and in critical cases **hepatic fibrosis, non-cirrhotic portal fibrosis, cirrhosis and liver failure**. In many cases, liver enlargement was noted with elevated levels of globulin, alkaline phosphatase, alanine aminotransferase and aspartate aminotransferase in population exposed to arsenic (0.05–3.2 mg/L) in West Bengal, India. It also

causes amyloid formation, damages and causes malfunction of pancreatic cells and induces diabetes. In fat and muscle, arsenic alters gene expression increased insulin resistance and decreased insulin sensitivity.

4.2.9 Effects of arsenic on reproductive system and development-

Arsenic is a teratogen and affects the development of the foetus. With increasing dose and duration of arsenic exposure there is increasing **growth retardation and foetal death**. Arsenic exposure through drinking water causes **pregnancy complications, spontaneous abortion, preterm birth, stillbirths, low birth weight, birth defects, foetal loss and premature delivery.**

4.2.10 Arsenic exposure induced epigenetic modifications-

Epigenetic changes have been correlated with a wide range of diseases involving cardiovascular, neurological complications and metabolic diseases including impaired foetal growth, foetal death, birth defects, impaired cognition and also vulnerability toward various diseases.

4.2.11 Arsenic exposure and cancer development –

Arsenic is a group-1 carcinogen as classified by the International Agency for Research on Cancer(IARC) with supporting evidence of inducing carcinogenicity in humans. Arsenic exposure causes **tumorigenesis of skin, lung , bladder, liver, and prostates**.

Skin cancer due to high contamination of arsenic in drinking water has also been observed in China, Bangladesh and India resulting in major types of **non-melanoma skin cancer (NMSC), basal cell carcinoma (BCC) and squamous cell carcinoma (SCC).** Consumption of water from drilled wells contaminated with arsenic provided evidence of increased vulnerability toward **bladder and kidney cancer**.

Agency	Carcinogenicity Classification	Description
International Agency for Research on Cancer	1	Known human carcinogen
National Toxicology Program	–	Known human carcinogen
U.S. Environmental Protection Agency	Group A	Known human carcinogen

Table- 4.2 Inorganic arsenic is listed as a human carcinogen (IARC 2004).

4.3 Stages of clinical manifestations in arsenic toxicity-

Clinical manifestations of the stages of arsenic toxicity are- (1) Preclinical stage – initial stage of arsenic toxicity with high levels of arsenic metabolites in biological samples but no signs of clinical symptoms. (2) Clinical stage – with confirmed arsenic toxicity based on biological sample analysis, the stage of developing visible clinical symptoms such as major and minor dermatological disorders. (3) Internal complications stage – in this stage major internal organs develop non-dermatological symptoms. (4) Malignancy stage – development of tumour and other complications in various organs of the body and eventual death.

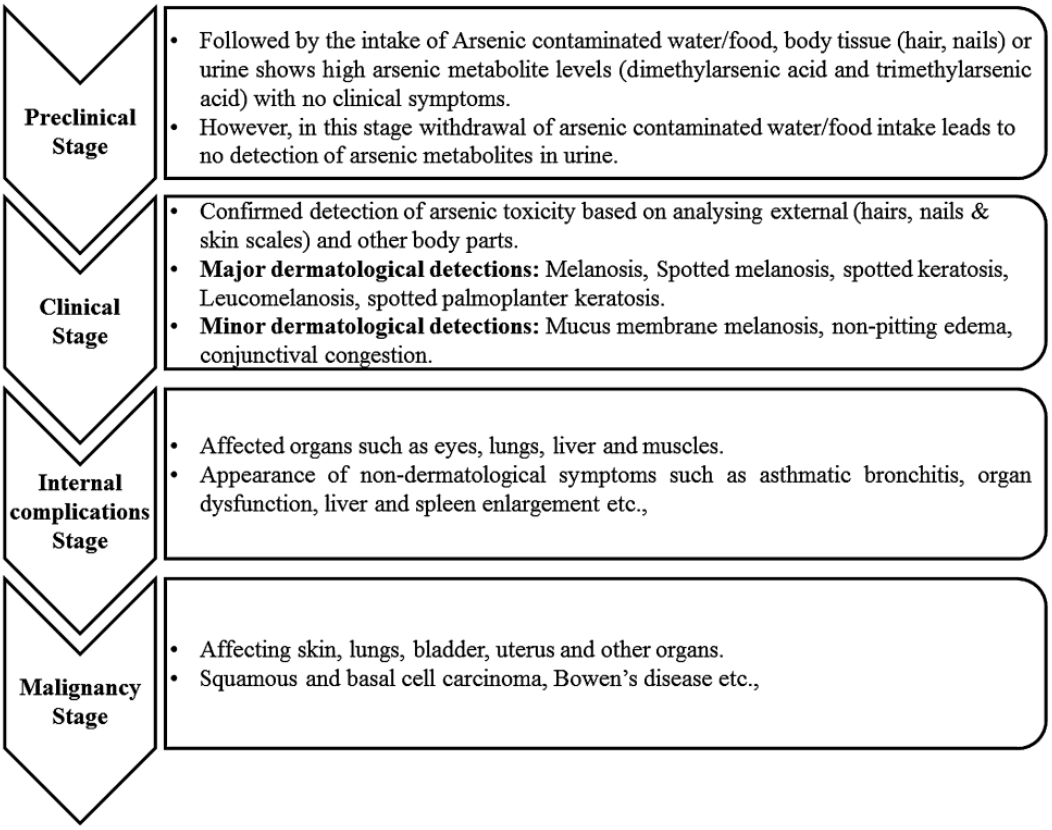


Fig-4.3: Clinical manifestations of the stages of arsenic toxicity (Jayasinghe, 2015)

CHAPTER-5
METHODS OF ARSENIC REMOVAL

5.1 Introduction-

Arsenic is found in aquatic environments in trivalent arsenite or pentavalent arsenate. A range of treatment technologies developed from oxidation, co-precipitation, adsorption, ion-exchange and membrane processes, are used for removal of arsenic from contaminated water. The efficiency and

applicability of the technologies depends on arsenic concentration and differences in source water composition. Some of these methods are simple but produce large amounts of toxic sludge requiring treatment before disposal into the environment, or are not sustainable in terms of economic viability and social acceptability. The requirements of an effective removal methodology are-

- High efficiency for different arsenic concentrations and water compositions.
- Safe technology to ensure ease of use by people.
- Simple operation and maintenance .
- Minimum sludge produced
- Cost effective and socially acceptable

Methods of arsenic removal

Arsenic can be removed from groundwater by the following methodologies

- Co-Precipitation
- Adsorption
- Ion Exchange
- Membrane filtration
- Electrocoagulation

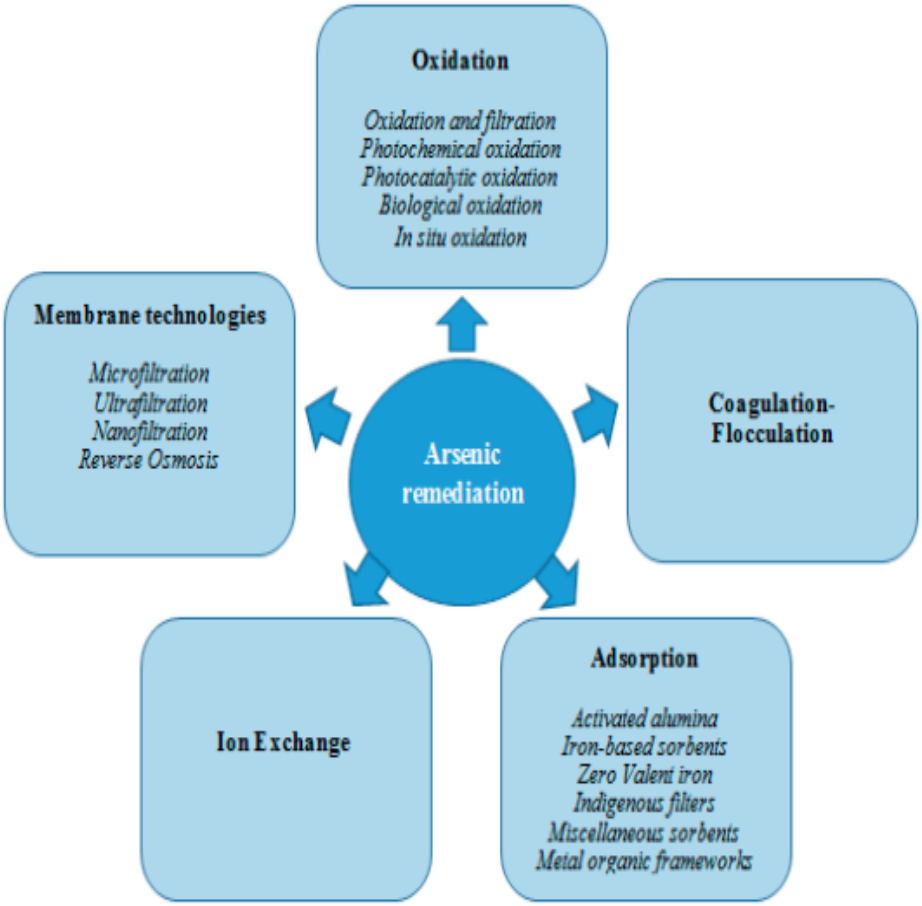


Fig 5.1: Various remedial measures used for the removal of arsenic from water

5.2 Oxidation-

Arsenic is found in groundwater as trivalent arsenite and pentavalent arsenate forms in different proportions. Most treatment methods can remove arsenic in the form of arsenate and an oxidation step as pretreatment is necessary to convert trivalent arsenite to pentavalent arsenate. Arsenite can be oxidised by oxygen, ozone, free chlorine, hypochlorite, permanganate, hydrogen peroxide,

catalytic oxidation, UV irradiation, and Fulton's reagent. Atmospheric oxygen, hypochlorite and potassium permanganate are commonly used for oxidation in developing countries.

- Air oxidation -Very slow and can take weeks for oxidation (Pierce and Moore, 1982)

- UV Radiation: This process is very fast but UV light, by itself is ineffective. If the water has sulphite, UV photo oxidation converts arsenite to arsenate (Ghurye and Clifford, 2001) and requires a high pressure mercury lamp for effective conversion. Natural organic compounds in water are oxidised. In domestic units and in community models,in rural areas, it cannot be used.

- Chlorine dioxide - Ineffective in oxidising arsenite to arsenate

- Chlorine - Fast and effective oxidant, but can produce a toxic by- product like trihalomethane from organic matters (Gallard and Gunten 2002)

- Sunlight- In the presence of sunlight and natural occurring light-absorbing minerals, the oxidation rate of arsenite by oxygen can be increased by ten thousand fold.

- Ozone -Used as an oxidant in developed countries as it is a good oxidant and a strong disinfectant. It also oxidises iron and manganese

- Permanganate is widely used as an oxidant in developing countries as it is relatively stable with a long shelf life, easily available, produces a bacteriostatic effect and effectively oxidises arsenite along with ferrous and manganese ions. The concentration of residual manganese should not exceed 0.5 mg/L (WHO 1993)

5.2.1 Advantages -

- Relatively simple and rapid process.

- Oxidizes other metallic salts and kills microorganisms.

5.2.2 Disadvantage -

- The process removes only a part of arsenic.
- Chlorine, permanganate and ozone are the three effective oxidising agents for oxidising arsenite to arsenate , over a broad range of working conditions in developing countries.

5.3 Co-precipitation -

Co-precipitation has been the most commonly used method to treat arsenic contaminated water in numerous experimental and full scale applications. This technology can reduce arsenic concentrations to less than 50 μg/L and in some cases below 10 μg/L. To remove arsenic by co-precipitation, coagulant such as alum [Al2 (SO4)3.18H2O], ferric chloride [FeCl3] and ferric sulphate [Fe2 (SO4)3.7H2O], are added. Co precipitation occurs if an inorganic contaminant forms an insoluble complex with the coagulant. Ferric salts remove more arsenic than alum on a weight basis and are effective over a wider range of pH. In both cases, pentavalent arsenic is removed more than trivalent arsenic. The aluminium or iron coagulant converts the soluble inorganic arsenic species into insoluble products by precipitation, coprecipitation or adsorption.The steps in the co-precipitation process for removal of arsenic:

- Addition of bleaching powder / hypochlorite,
- Addition of alum / ferric sulphate,
- Rapid mixing of chemical followed by slow mixing,
- Sedimentation, and
- Filtration.

For coagulation and flocculation, aluminium sulphate or ferric chloride or ferric sulphate is added and dissolved in water by stirring rapidly for a few minutes. Aluminium or ferric hydroxide microflocs are formed. The water is slowly stirred for a few minutes for agglomeration of micro-flocs. The micro-particles and negatively charged ions are then electrostatic attachment. As arsenite is non-ionized form, it is not removed. Oxidation ofarsenite to arsenate , is required as a pretreatment for efficient removal by addition of bleaching powder (chlorine) or potassium permanganate. The following three chemical precipitation processes are normally used:

i) Enhanced Lime Softening,

ii) Conventional Gravity Coagulation/Filtration, and

iii) Coagulation Assisted Micro-filtration.

5.3.1 Advantages

- This is a conventional and frequently used method, already in use in many water treatment facilities.
- No monitoring is required.
- The chemicals required are easily available and of low cost.
- The process has been tested in both pilot and full scale applications.
- Arsenic removal efficiency is independent of the initial arsenic concentration.

5.3.2 Disadvantages -

- The procedure can be used over a narrow pH range and coagulant dosage.
- Disposal of arsenic contaminated coagulant sludge which is toxic poses difficulties.
- The presence of competing ions such as sulphates and phosphates reduces effectiveness.
- Safe storage of chemicals needs technical skill..
- Arsenic needs to be oxidised by pretreatment using suitable oxidising measures to convert arsenite to arsenate for effective removal.
- Disinfection is required to remove microorganisms
- Secondary treatment is necessary to meet the arsenic standard in BIS guidelines.

5.4 Adsorption-

Adsorption technology can reduce arsenic concentrations to less than 50 μg/L in general and in some cases even below 10 μg/L. Its effectiveness depends on a variety of untreated water contaminants and characteristics. It is used treat groundwater and drinking water due to its cost effectiveness, ease of handling, sludge free operation and regeneration capability.

In adsorption technology, contaminants concentrate at the surface of a sorbent, reducing their concentration in the bulk liquid phase. The adsorption media is usually packed into a column and the contaminants are adsorbed, as the

contaminated water is passed through the column. As adsorption sites are filled, the column must be regenerated or disposed of and replaced with new media.

The common adsorption media are-

- Activated alumina (AA)
- Activated Carbon (AC)
- Iron Based Sorbents (Granular Ferric Hydroxide, Iron Coated Sand)
- Indigenous Filters
- Cartridge Filters
- Oxides and clay mineral
- Bauxite, hematite and feldspar
- Synthetic anion exchange resins
- Iron oxide coated sand(IOCS)

The main factors affecting adsorption are suspended or precipitating solids and competition for adsorption sides with other constituents like silica, fluorides, sulphates and phosphates. Arsenic adsorption processes produce wastes from regeneration or spent media that might require treatment or disposal.

There are several filters that use indigenous material such as red soil, oxidised iron, clay minerals, iron ore, iron scrap or fillings and processed cellulose materials as arsenic adsorbent.Some of the filters manufactured using these materials are :

- Sono 3-Kolshi Filter,
- Granet Home-made Filter,
- Chari Filter,
- Adarsha Filter,
- Shafi Filter
- Bijoypur Clay or Processed Cellulose filters.

5.4.1 Advantages -

- Can be used at household level, as no specialised skill is required.
- This method is cost effective depending on the absorbent used.
- No sludge is produced and there are no disposal difficulties.

5.4.2 Disadvantages -

- Periodic regeneration or replacement of the adsorbent is required depending on the adsorbent.
- These methods may be expensive depending on the sorbent.
- Bacteria or fungi may grow on the adsorbent surface .
- Effectiveness depends upon the contaminant type, concentration and adsorbent used.

5.5 Ion Exchange-

Ion exchange is a physical-chemical process in which ions are exchanged between a solution phase and solid resin phase. The solid resin is an elastic three-dimensional hydrocarbon network, containing a large number of ionizable groups electrostatically bound to the resin. These groups are exchanged for ions of similar charge in solution that have a stronger exchange affinity for the resin. Strong base anion exchange resins are used for arsenic removal and pre- oxidation is necessary as ion exchange raisins can remove arsenate. This technology can reduce arsenic concentrations to less than 50 μg/L in general and in some cases to below 10 μg/L. Its effectiveness is sensitive to a variety of untreated water contaminants and characteristics. It is used less frequently than precipitation/co precipitation. And it is most commonly used to treat ground water and drinking water.

The main factors affecting ion exchange performance are fouling the resins with suspended or precipitating solids and competition with other anions, particularly, sulphates and phosphates.

5.5.1 Advantages -

- This effectiveness of this methodology does not depend on pH changes in water.
- Low maintenance and operation cost, except the addition of sodium chloride resin every few weeks.
- Systems can treat the water supply of an entire community..
- Low capital cost.

5.5.2 Disadvantages -

- Ion exchange efficiency can be reduced by competition with other anions (sulphate, nitrate, phosphate) and pretreatment to remove ions may be necessary.
- Bicarbonate removal during the ion exchange process reduces the pH and increases the corrosiveness of the treated water.
- If ion exchange is used beyond the point of sulphate exhaustion, the removed arsenic can be released back into the treated water.
- Treated water can have very low pH and high levels of chloride, which causes the water to be very corrosive.

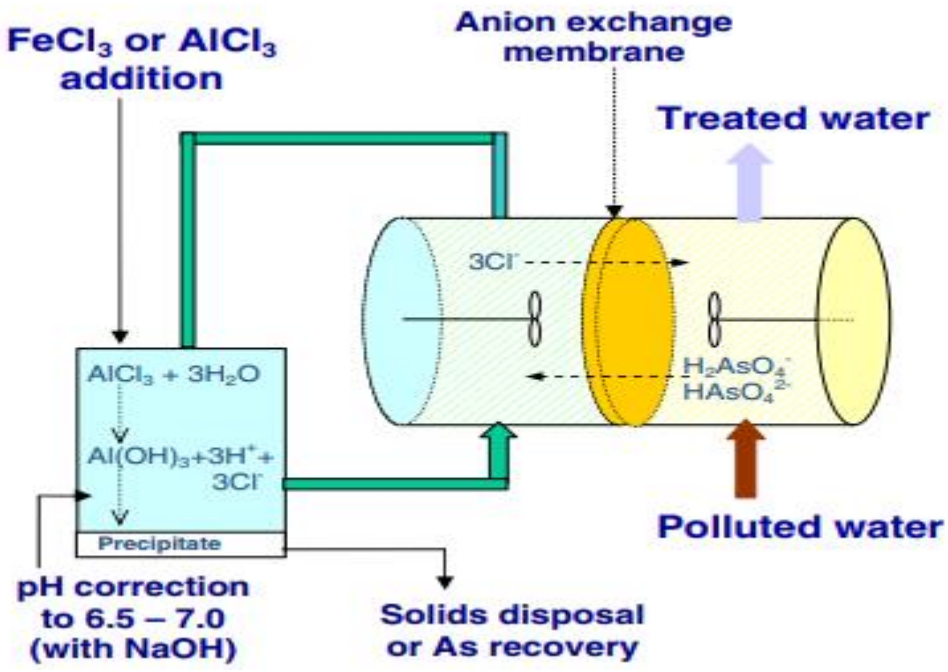


Fig-5.2: Schematic diagram of arsenic removal by ion exchange method

5.6 Membrane Technology-

Membrane technology can remove a broad range of contaminants from water. As it also produces a larger volume of residuals and tends to be more expensive than other arsenic treatment technologies, it is used less frequently than co

precipitation, adsorption and ion exchange despite maintaining simplicity and ease of operation.

In this process, water is allowed to pass through special filter media which physically retain the impurities present in water. The water is to be free from suspended solids and the arsenic in pentavalent form. Most membranes, however, can not withstand oxidising agents, so pretreatment is required.

There are four types of membrane processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). All the four processes are pressure-driven and are categorised by the size of the particles that can pass through the membrane pore size of the membrane (EPA, 2000). The force required to drive fluid across the membrane depends on the pore size.

Arsenic species dissolved in water tend to have relatively low molecular weights, NF and RO membrane processes are able to effectively treat dissolved arsenic (EPA, 2000). NF is less efficient than RO in removing dissolved arsenic from water. MF can be used with co precipitation to remove solids containing arsenic.

5.6.1 Advantages -

- Membrane technologies have ease of operation and maintenance and can be very effective at the household and community level.
- The effectiveness of removal does not depend on pH if within range of 4-8.
- The process requires less space.
- The process does not require the addition of chemicals.
- No solid waste produced due to this technology.
- The process can remove a broad range of contaminants from water including nitrates, phosphates, other heavy metals, microorganism, suspended solids, pesticides, dyes and hydrocarbons.
- Disposal of used membranes is simple.

5.6.2 Disadvantages-

- High capital and maintenance cost
- Membrane technology is pressure driven and requires a power source that may not be available.
- Pressure, flow rate, and pH is to be controlled.
- BIS values are not met for high initial arsenic concentrations.
- Loss of influent water (20-25%) causes difficulty in water-scarce regions.
- Pretreatment of the water may be necessary for removing salts and hardness.
- Pre treatment involving oxidation is required for converting arsenite to arsenate in a way that does not damage membrane
- More highly contaminated wastewater is produced as effluent due to this process.
- Membrane fouling reduces effectiveness.

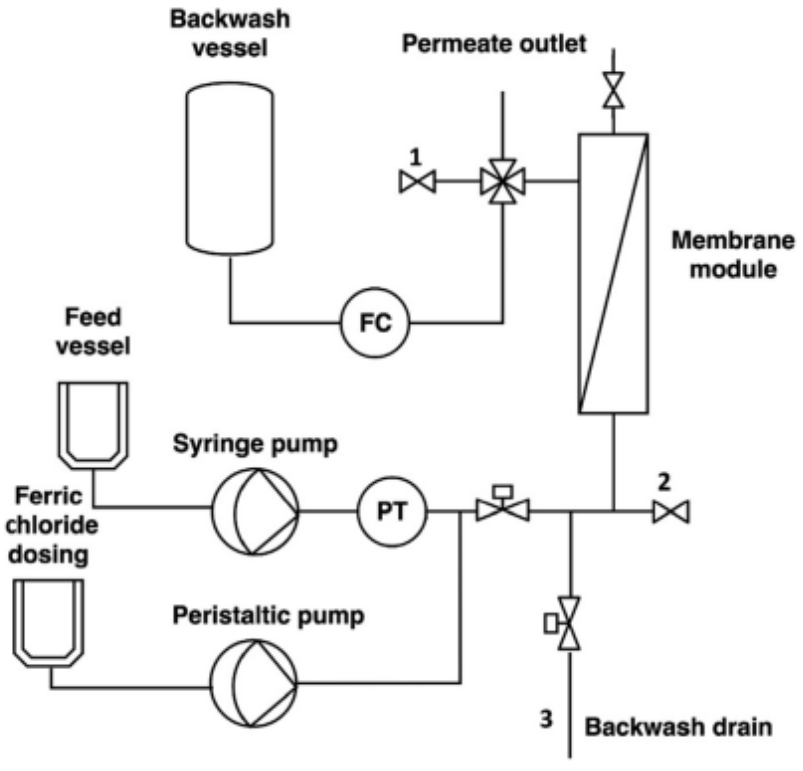


Fig-5.3: Schematic diagram of arsenic removal by membrane technology

Technology		Advantages	Disadvantages
Chemical precipitation	<30% for arsenite and >90% for arsenate	Relatively low capital cost, simple in operation, common chemicals are available and can work over a wide range of pH,	Produces toxic sludge. Pre-oxidation may be required, which can produce harmful disinfection by-product. Mainly removes arsenate , medium removal of arsenite . Chemicals dosing, oxidation step, sedimentation and filtration is needed.
Sorption techniques	<30% for arsenite and >95% for arsenate	Relatively well know and commercially available. High removal efficiency for arsenate Easy operation and handling. More cost effective. Additional chemical and sludge free. Improves taste and odour. No harmful by-products.	Absorption bed gets exhausted. Periodic replacement of absorbent material. Yet to be standardized. Produces toxic solid waste. Pre-oxidation and filtration are required.
Ion exchange	<60% for arsenite and >97.9% for arsenate	Well-defined medium and capacity. The process is less dependent on pH of water. Exclusive ion-specific resin to remove arsenic.	Highcost medium. Requires high-tech operation and maintenance. As (III) is difficult to remove. Exhausted resin regeneration. Applicable for low TDS. Life of resin.
Membrane techniques	<55% for	Well defined and high removal efficiency. No	Very high capital cost. Pre-treatment is needed.

	arsenite and >96% for arsenate	toxic solid waste is produced. Capable for removal of other contaminants and microorganisms. Chemical free.	High water rejection. High-tech operation and maintenance. Toxic wastewater is produced. Multiple membranes are required. Efficiency is less for removal of arsenite . Membranes are prone to scaling and fouling. Produce highly contaminated waste water.

Table-5.1 An overview of arsenic removal methods

An overview of arsenic removal methods (Mondal et al., 1998)

CHAPTER-6
DETERMINATION OF ARSENIC IN WATER

6.1 Introduction-

In order to measure arsenic in water samples, the arsenic is to be converted into its simple derivatives like arsenic trichloride or pentachloride which can be reduced to arsine gas by action of zinc and dilute hydrochloric acid. These derivatives are to be free from interfering substances such as nitrate, copper, silver, mercury, cobalt, nickel, molybdenum and palladium.

6.2 Laboratory Methods

•UV double beam Spectrophotometric Silver Diethyldithiocarbamate Method
•Hydride generation Atomic Absorption Spectrophotometric Method
•Electro thermal atomic absorption spectrometric method
•Inductively coupled plasma (ICP) emission spectroscopy method
•Inductively coupled plasma (ICP) mas spectroscopy method
• Mercuric Bromide Stain Method

6.3 Sampling and Filtration

Plastic bottles are to be used for arsenic sampling. If dissolved and suspended arsenic is measured separately, the sample is to be filtered immediately. A known volume of sample is filtered through a 0.45 µm filter paper. The filtrate is preserved by reducing pH to below 2 with concentrated nitric acid. 1.5 mL of concentrated nitric acid is added per litre of filter. The membrane filter is retained for analysis and measurement of suspended arsenic. If total arsenic has to be measured , the sample is not filtered, but preserved immediately with concentrated nitric acid. The maximum holding time for samples after preservation is 6 months (EPA).
Filter paper containing suspended arsenic particles are dissolved with concentrated nitric acid .

6.4 Double Beam Spectrophotometric Silver Diethyldithiocarbamate Method-

The methodology for the determination of arsenic colourimetrically with silver diethyldithiocarbamate was developed and reported by Vasak and Sedivec in 1952 . The analytical procedure is unchanged till date except for the use of chloroform instead of pyridine. It is the most widely used of the four methodologies approved by the EPA for the evaluation of arsenic concentrations

in water supply or water pollution analyses. The complete apparatus is called a "Gutzeit generator", but "arsine" or "hydride generator" are also used.

6.5 Principle-

Total arsenic in groundwater usually contains inorganic arsenates (AsO3) and arsenates (AsO4). Arsenates in the water sample are reduced from pentavalent form to trivalent arsenite by potassium iodide (KI) solution, hydrochloric acid (HCI) and stannous chloride (SnCl2). The arsenite is additionally reduced by granular zinc, hydrochloric acid and stannous chloride (SnCl2) in a Gutzeit generator, to arsine(AsH3), a colourless, volatile gas. The arsine obtained passes through a scrubber containing lead acetate [(CH3COO)2Pb] solution soaked in glass wool where sulphurated hydrogen(H2S), if generated, is arrested. Arsine is then passed through a U-tube where it reacts with silver diethyldithiocarbamate (C5H10NS2Ag) dissolved in morpholine-chloroform system, to produce an orange-red complex which strongly absorbs at 520 nm in a properly calibrated spectrophotometer . Since the intensity of the color of the complex is directly proportional to the concentration of arsenic present in the water sample (Beers Law), the concentration of arsenic can be determined by measuring the absorbance of the complex using a spectrophotometer.

6.6 Reduction of Arsenate to Arsenite

Only inorganic arsenic(III) is quantitatively reduced to arsine under the conditions of the method. Therefore, arsenic(V) must be reduced to arsenic(III) before the final reduction step. This is accomplished by the acidification of the

sample with concentrated hydrochloric acid and the subsequent addition of potassium iodide and tin(II) chloride. If the digestion step is performed, all of the nitric acid must be expelled to ensure it will not interfere in the arsenic(V) reduction. The sample is set aside for fifteen minutes to allow for quantitative reduction. However, in the 1.5 M HC1 matrix that is produced, the reaction is very rapid. The reactions involved are as follows:

6.7 Apparatus-

• Arsine generator, scrubber and absorber assembly: A 200 ml two necked flask to carry the scrubber closed with a rubber septum, or by a screw cap with a hole at the top for insertion of a TFE-faced silicone septum.. Absorber tube of 30 ml capacity is fitted to the scrubber and it is filled with silver diethyldithiocarbamate

solution. Rubber or cork stoppers are not to be used as they absorb arsine gas. The glass equipment is cleaned with concentrated nitric acid.
• Photometric equipment: Spectrophotometer for use at 520 nm with 1 cm clean dry cell.

6.8 Reagents-

•Concentrated Hydrochloric acid (38%)
•KI solution (15%): 15 gm of Potassium Iodide (KI) is diluted to 100 ml with D/D water.
Stannous chloride solution (40%): 40 gm of SnCl2.2H2O is dissolved in 25 ml concentrated HCI and diluted to 100 mL with D/D water..
•Lead acetate solution (10%): 10 gm of Pb(CH3COO)2. 3H2O is diluted to 100 mL with D/D water..
•Zinc, 2-3g granules, arsenic free.
• Silver diethyldithiocarbamate solution: 1 ml morpholine (C4H9NO) is dissolved in 70 mL Chloroform (CHCl3).
0.30 gm silver diethyldithiocarbamate, (AgSCSN(C2H5)2), is added. Solution is shaken in a stoppered flask until most is dissolved. Solution is diluted to 100 mL with chloroform. Solution is kept in a cool (4°C) store in a tightly closed brown bottle in a refrigerator for 24-48 hours before use.

•Standard arsenite solution: 0.1734 g NaAsO is dissolved in water and diluted to 1000 ml with water.

•Standard arsenate solution: 0.416g NaHAsO4.7H20 is dissolved in water and diluted to 1000ml.

6.9 Procedure-

- Treatment of sample: 35 ml sample was pipetted out into a clean conical flask of Gutzeit generator bottle, 5 ml conc HCl acid, 2 ml KI solution and 0.5 ml of stannous chloride was added successively with thorough mixing. 15 minutes was allowed for reduction of arsenate to arsenite.

$$2KI + H_3AsO_4 + 2HCl = H3AsO_3 + I_2 + H_2O + 2KCl$$
$$SnCl_2 + I_2 + 2Cl^- = 2I^- + SnCl_4$$
$$2HCl + H_3AsO_4 + SnCl_2 = H_3AsO_4 + SnCl_4 + H_2O$$

- Preparation of scrubber and absorber: Glass wool in the scrubber was soaked with lead acetate solution. 5 ml Silver diethyldithiocarbamate solution was pipetted into the absorber tube.
- Arsine generation and measurement: 3-4 gm zinc granules were added to the generator and scrubber- absorber assembly was tightly connected immediately. 30 minutes was allowed for complete evolution of arsine. The solution was directly poured from the absorber into a 1 cm cell and absorbance was measured at 520 nm by spectrophotometer.

$$H_3AsO_3 + 6H^+ + 6e^- = AsH_3 + 3H_2O$$

$$As + 3H^+ + 3e^- = AsH_3$$

$$H_3AsO_3 + 3H^+ + 3e^- = As + 3H_2O$$

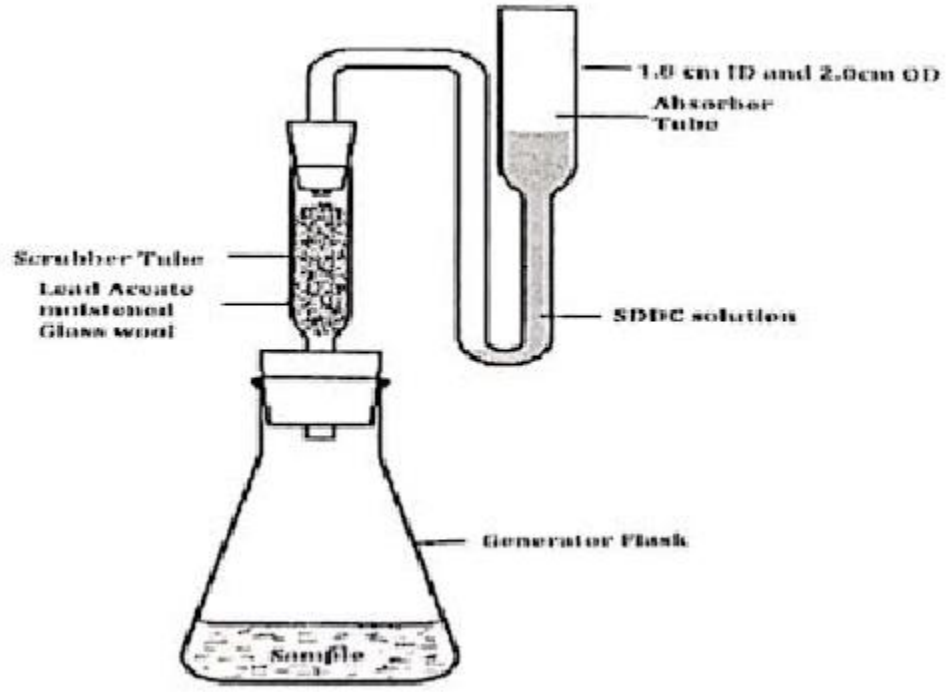


Fig-6.1: Arsine gas generator and absorber assembly

CHAPTER-7

EXPERIMENTAL STUDY ON THE REMOVAL OF ARSENIC USING BIOCHAR

7.1 Introduction-

Various methodologies are used for arsenic remediation from contaminated water- adsorption, reverse osmosis, oxidation, precipitation, coagulation, ion-exchange, and membrane filtration. These technologies remove more arsenate than arsenite, which is neutral at pH below 9.2, and arsenite is not removed by adsorption, ion-exchange, and precipitation (Johnston et al., 2001). These methods can also remove colour, bacteria, phosphate, hardness, fluoride, manganese, turbidity, odour, and colour. However, these mitigation methods have limitations, due to high cost of resin, skilled operation and maintenance, sludge disposal, and production of toxic wastes, requirement of large plant area, high operational and maintenance costs, high energy requirement and capital investment. Novel technology with higher efficiency, multi-functionality, high flexibility, and regenerative capacity is required. Materials such as zero valent carbon, nanocomposites, inorganic nanoparticles, graphene based materials, biochar and metal oxides can remove heavy metals from contaminated water (Fuertes et al., 2007). These particles have better activated, catalytic, electrical, optical, and magnetic features, and higher surface area, higher porosity, electro-potential charges, and surface functional groups, as compared to bulk material of similar composition (Sarkar et al., 2012). Due to its broad range of use, high efficiency, cost effectiveness, no sludge production, and ease of operation; adsorption is a comprehensive measure for arsenic removal from water.

7.2 Biochar-

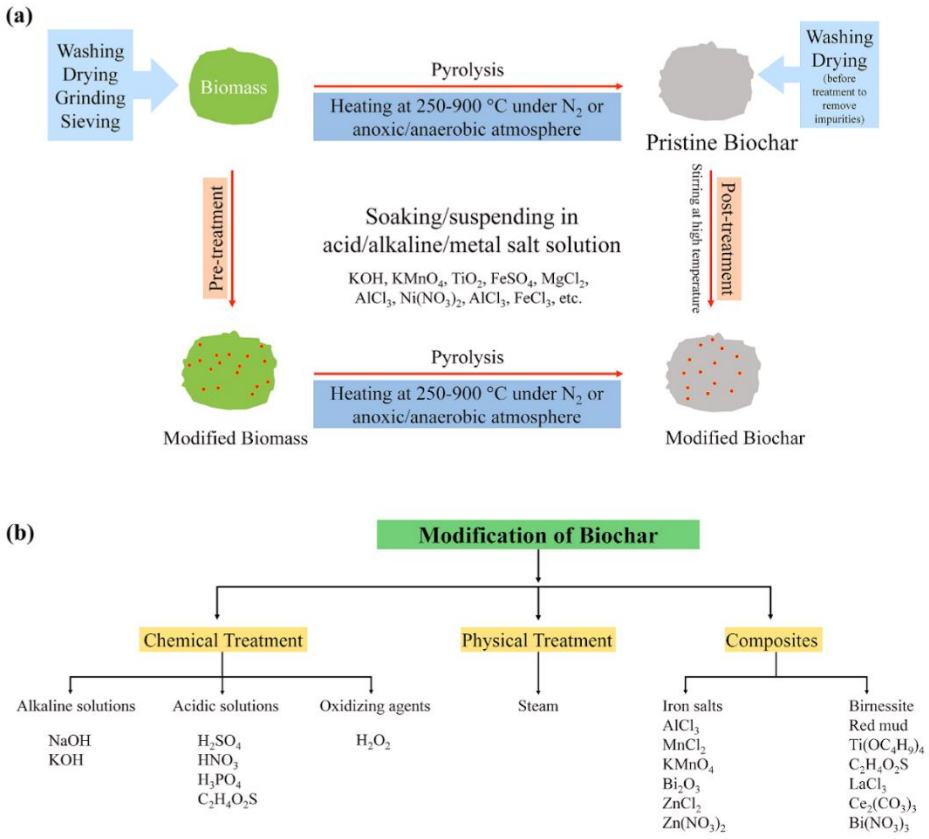
Biochar is a stable, solid carbonaceous black compound that possesses high surface area, diverse surface functional groups, and dual-porosity synthesised from biological feedstock pyrolysed under inert conditions. Various types of feedstocks, including distiller grain, bioenergy crops like grass, wood chips and pellets, tree bark, and bagasse from the sugarcane industry, dairy manure, sewage sludge, chicken litter, olive mill waste, and paper sludge are used for the synthesis of biochar.

7.2.1 Synthesis of biochar-based materials-

Biochar is a solid, carbonaceous, renewable, stable, black compound synthesised from biomass under inert environment, usually through slow pyrolysis in the temperature range of 300–700 ◦C for long durations. Biomass feedstock characteristics and various parameters such as pH, temperature, pyrolysing conditions, adsorbent dose, affect physical and chemical properties. Biomass used for biochar production consists largely of three organic components,

cellulose, hemicellulose, and lignin. Hemicellulose consists of branched chain polysaccharides, and decomposes at a temperature between 220 and 315 ◦C (Yang et al., 2007). Cellulose, has an unbranched polysaccharide structure, and decomposes at a temperature range between 200 and 400 ◦C . Lignin has a wide decomposition temperature range of 200–900 ◦C due to complex macromolecular structures.

Due to these components, the yield and properties of biochar differ as these components behave differently during the synthesis of the biochar under different conditions.



(a) Summary for production of biochar using pre- and post-treatment and (b) different treatment approaches for modification of biochar.

Fig-7.1: Summery of synthesis of biochar by different methods (PK Sharma et al., 2022)

These modifications improve the physio-chemical properties and surface morphology of the biochar, increasing adsorption efficiency. Some common metal salts are FeCl3, MnCl4, AlCl3 , FeSO4 and acids, like H2SO4, HCl and HNO3 applied during pre-treatment of biomass. Synthesis of biochar performed under devolatilizing gases, like N2, causes the porous structure on biochar, and the dual-porosity directly affects the water holding capacity, cation exchange capacity, mechanical stability, and the density of the biochar (Chesworth, 2008). The synthesis method used and feedstock type affects the surface area, porosity,

biochar yield, ash content, carbon, hydrogen, nitrogen, sulphur, and oxygen contents of the biochar. Increase in pyrolyzing temperature (>600 ◦C) increases the surface area and carbon percentage (Wang et al., 2017), but low temperature (300–400 ◦C) increases the quantity of biochar (Qian et al., 2013).

7.2.2 Mechanisms-

Several biochar samples synthesised from different biomasses, such as rice husk, sewage sludge, solid waste, oakwood, and pinewood, perilla leaves, paper mill sludge derived biochar, tea waste, almond shell biochar, wheat straw derived biochar, potato peel and rice husk ash, and bagasse fly ash can be used for As removal in aqueous solution.The surface of biochar contains functional groups, such as –OH, –COOH, –C– O and –NH+, that facilitate to removing metalloids from the aqueous media. Possible adsorption mechanisms for arsenic include electrostatic attraction, surface complexation, ion exchange, and precipitation (Niazi et al., 2018). Biochar has higher oxygen-based functional groups, which causes surface complexation with As and shifts in spectral bands after adsorption, such as from –CO to ester, –OH and –COOH groups.

There are different mechanisms for the adsorption of arsenite and arsenate by biochar due to the numerous surface functional groups on the biochar surface. The adsorption of arsenite and arsenate onto the surface of pristine biochar is less due to the negative charge and low anion exchange of most biochars. Biochar requires modification for increased removal of arsenic from water. Biochar with surface modifications causes the formation of surface complexes by strong intermolecular interactions (Rajapaksha et al. 2016) which removes arsenic. Surface complexation or precipitation, oxidation and reduction, electrostatic interactions, ion exchange, and enhancement of surface functional groups are the major mechanisms that cause arsenic adsorption on biochar surfaces (Tan et al. 2016). Increasingly, investigations have focused on enhancing biochar capacity by the extensive use of acids or bases, metal ions or oxides, such as Fe, hydrous ferrous oxide (FeO), MnO2, and Fe–Mn oxides.

The high surface areas of biochar and the large number of electron donor surface functional groups such as COOH, phenolic groups on the surfaces can increase the reduction of arsenate to arsenite (Choppala et al., 2016). The π-electrons on biochar surface functional groups transfer to arsenate, and cause oxidation of carbon material (Choppala et al., 2016).

$$AsO_4^{3-} + 2H^+ + 2^{e-} \rightarrow AsO_3^{3-} + H_2O$$

The oxidation of arsenite to arsenate in the presence of positive species such as Fe in metal impregnated biochars (Bakshi et al., 2018) increases efficiency of removal by adsorption of the newly formed arsenate on the biochar (Asadullah et al., 2014). Persistent free radicals (PFRs) on biochar increases the rate of redox reactions (Ruan et al., 2019) and functional groups of biochar can facilitate the oxidation of arsenite to arsenate

.

Surface functional groups on biochar act as electron acceptors and oxidise arsenite into the less mobile and less toxic arsenate.Microscopic and spectroscopic studies revealed that persistent free radicals on biochar caused oxidation of arsenite to arsenate. The redox reactivity on modified biochars increases the rate of arsenic from water . Arsenic species undergo redox reactions in the presence of strong oxidising agents such as O2, H2O2, MnO4 and reducing agents, such as Fe, Al, Zn, Mn, Mg, on the biochar surface.

Zong et al. examined the possible role of active functional groups on biochar in the conversion of arsenite to arsenate as a function of varying pH and oxygen conditions and found that conversion of arsenite to arsenate took place under acidic and neutral conditions by OH and H2O2 produced from activation of O2 by phenolic –OH groups and persistent free radicals. Arsenite oxidation under alkaline conditions was caused by free radicals, i.e., quinoid H2O2.
Future research is required to provide new insights into the role of these redox-active species on biochar-based materials responsible for oxidation of As(III) to As(V) and vice versa over a wide pH range under both anoxic and oxic conditions.

Bakshi et al. (2018) found that arsenite was adsorbed more on Fe-modified biochar. Wongrod et al. (2019) identified that arsenite was adsorbed more on a H2O2-modified biochar. The speciation of arsenic is an important factor in the adsorption process. There are no clear trends in the biochar sorption capacity for either arsenite or arsenate in the current literature. Biochar adsorbent induced redox reactions is the governing mechanism of arsenic sorption.

7.2.3 Influence of biochar doses on arsenic adsorption-

It is required to optimise the adsorbent (biochar or modified bio- char) dose for maximum adsorption of arsenic by keeping the initial As concentration and pH constant (Yadav et al., 2014). With an increase in biochar dose, the removal efficiency increases up to the optimum level and all active sites on the biochar surface area are occupied and saturated (Sanyang et al., 2016). Ali et al. (2014) reported that removal efficiency increases from 84 to 95% for arsenate and from 79.9 to 95% for arsenite at biochar dosage of 1.5–3 g/L. Verma and Singh (2019)

identified the optimum biochar doses for arsenic removal ranging from 1 to 5 g/L at constant pH and temperature.The adsorption efficiency of arsenic depends upon biochar doses, which increases up to the saturation level of active sites, thereafter, negligible changes were observed.

7.2.4 Influence of arsenic concentration on adsorption-

The adsorption capacity of biochar based materials depends on initial arsenic concentration in the aqueous solution. At fixed biochar dose and low initial arsenic concentration, arsenic ions can have active sites available onto the biochar surfaces. With an increase in As concentration without increasing the biochar doses, adsorption decreases due to less availability of active sites for As ions and intra-competition within As ions (Yadav et al., 2014).

Nham et al. (2019) identified that the removal efficiency of As decreased from 92.8 to 78.6% with an increase in initial As concentration from 4 to 30 mg/L, using iron-modified biochar. To determine the influence of sorbate, Sanyang et al. (2016) analysed the arsenic concentrations of 1–150 mg/L keeping other parameters like pH, adsorbent dose, and contact time constant. Adsorption rapidly increased from 0.423 to 27.56 mg/g for 1–100 mg/l As concentration, due to the availability of active sites for sorption of arsenic. Further increase in As concentration from 100 to 150 mg/L had no such increase in adsorption of As ions, which indicates that biochar had attained an equilibrium state in which the active site would have exhausted and competition between As ions would have increased. As the adsorbate concentration increased, the progressive saturation of the active site led to a stage when there was no further increase in adsorption .

7.3 Sustainability and reusability of biochar-based adsorbents-The stability, regeneration, and reusability of novel biochar based sorbents are significant for social, environ- mental, and economic perspectives. Pristine and modified biochars are novel adsorbents, having high adsorption capacities for remediation of heavy metals, resulting in low investment costs and potential applicability for wastewater treatment. The feasibility and cost-effectiveness of biochar-based materials mainly depend upon regeneration and reusability for specific sorption/desorption cycles. Rahman et al. (2021) applied (NH4)2SO4, HNO3, and NaOH as desorbing agents and found that HNO3 and NaOH were more significant as compared with (NH4)2SO4 and that regeneration efficiencies were decreased from the first to third cycles.

CHAPTER-8

ANALYTICAL PROCEDURE FOR ARSENIC REMOVAL USING JUTE BIOCHAR

8.1 Materials required

8.1.1 Apparatus required

- 3 conical glass flasks
- Pipette
- Glass rod.
- Glass funnel.
- Measuring cylinder
- Electronic weighing machine
- Stop watch
- Whatmans filter
- Shaker at 200 rpm
- Muffle furnace at 105 °C
- Jute biochar pyrolyzed at 800°C
- Double beam UV spectrophotometer

8.1.2 Reagents required

- Double Distilled water
- Arsenic stock solution (concentration 100 mg/l).
- Hydrochloric acid 37%
- SDDC solution

8.2 Sampling-

All chemicals used were AR/GR grade and were used without additional purification. All solutions were prepared with double distilled water in the Water Quality Laboratory of School of Water Resources Engineering. Glass and plastic apparatus were acid washed before use. All secondary standard stock solutions or solutions of low concentrations were prepared for each experiment from the concentrated, primary stock solutions.

From the primary stock solution for arsenic prepared from sodium arsenate, 10 ppm solution was prepared in the Water Quality Laboratory. Before preparing the sample, the container was rinsed five times with the water to be filled.

8.3 Preparation of solutions of required concentrations-

From 100 mg/L stock solution, 10 mL of solution was pipetted and mixed with 90 ml distilled water in a measuring cylinder to yield 100 mL of solution with

concentration of 10 mg/L. The solution was transferred to a conical flask and kept in a cool, dry place at about 4°C.
The solutions with concentrations 0.1 mg/L, 0.2 mg/L, and 0.3 mg/L were prepared by taking 1 mL, 2 mL and 3 mL respectively from the 10 mg/L solution with a pipette and mixing with 99mL, 98 mL, and 97 mL distilled water respectively in a measuring cylinder and transferring to a conical flask.
These solutions were freshly prepared for every experiment.

8.4 Preparation of biomass-

Jute mill solid wastes or jute caddies were collected from a jute industry located in Howrah, West Bengal, India and used as feedstock for biomass and biochar. The jute stalks were cut with a pair of scissors to a length of about 1 cm.

8.5 Preparation of biochar-

Jute stalks were soaked in 1:1 dilute sulfuric acid in 1:5 weight ratios for 1 h for carbonization and activation. The biomass turned to deep brownish black slurry that was washed 3 times to remove the excess H2SO4 and thermally decomposed by pyrolysis at a temperature of 800°C in anaerobic condition. The resultant biochar was washed several times with hot distilled water. The washed biochar was oven-dried, then ground to size of 1 cm length, and stored in an airtight container for further use.

8.6 Batch adsorption of arsenic –

Batch mode adsorption experiments were performed to evaluate the arsenic adsorption ability of the raw biomass and synthesised biochar. The adsorption studies were carried out in stoppered glass conical flasks containing 100 mL of arsenic solution with 3 different initial concentrations and 1g of prepared biochar which was shaken at 200 rpm for 3 hrs at room temperature. At the end of the experiment the solutions were filtered using two layers of Whatman no.42 filter paper.

8.7 Experimental procedure-

All batch adsorption experiments were carried out in stoppered glass conical flasks containing 100 mL of arsenic solution prepared from stock solution and distilled, unionised water without any pH adjustments.
100 mL of 10 mg/L arsenic solution was prepared from 100 mg/L primary stock solution by diluting with water and stored in a cool dry place at about 4°C in a stoppered conical flask. This solution was used to prepare 0.1 mg/L, 0.2 mg/l and 0.3 mg/L solution as and when required.

No oxidising agent added to the solution for the conversion of arsenite to arsenate. 1 g of biomass- jute stalks cut into 1 cm size was weighed on an electronic weighing machine and added to each conical flask. 100 ml arsenic solution of three different initial concentrations of 0.1 mg/L, 0.2 mg/l and 0.3 mg/l was added to the flask. The flasks were stoppered tightly and placed in a shaker at 200 rpm for 3 hrs at room temperature.
The flasks were removed from the shaker and filtered using Whatman filter paper. The filtrate obtained was transferred to clean acid washed conical flasks. 35 mL of this solution was used for arsenic measurement using the SDDC method.
This was repeated using 1 g of jute biochar for solutions of 0.1 mg/L, 0.2 mg/l and 0.3 mg/l arsenic concentrations respectively.

8.8 Arsenic analysis method-

Total arsenic content was measured using the Silver Diethyldithiocarbamate double beam spectraphotometer method.that is based on the absorption of light as a function of wavelength. All spectrophotometers have a light source that generates light of specific wavelengths. The DR6000 uses Tungsten (visible range), deuterium (UV range) as source lamp.

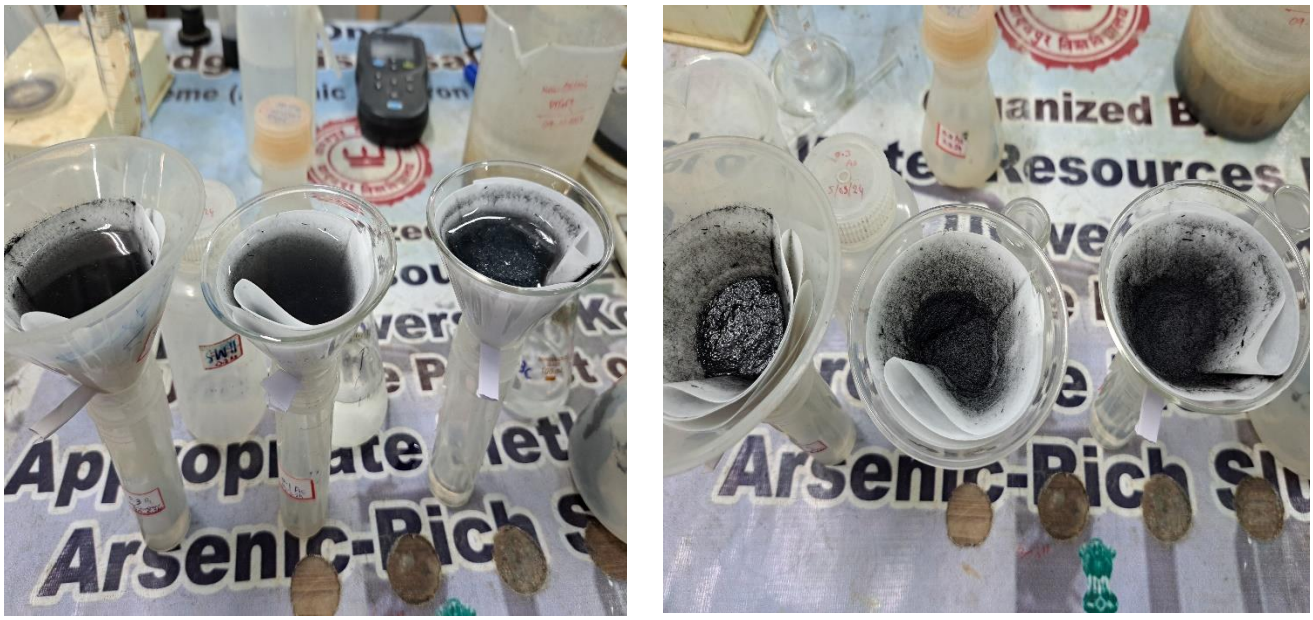


Fig-8.1: Filtration of arsenic solution after adsorption by jute biochar.



Fig-8.2: Arsine gas generator and absorber assembly for arsenic measurement



Fig- 8.3: Shaker used at 200 rpm at room temperature for arsenic adsorption on biochar



Fig-8.4: Double beam UV spectrophotometer used for arsenic determination



Fig-8.5: Arsine gas generator and absorber assembly for arsenic measurement

8.9 Results, Analysis and Discussion –

Result and analysis-

Extent of arsenic removal without using jute or biochar –
Experimental condition
water sample of three different initial concentration is kept in shaker at 200 rpm for 3 hours at room temperature.
Solution is filtered with one layer of Whatman's filter paper.

Set-1
Table 8.1 Arsenic removal in water sample without jute or biochar

Initial arsenic concentration in water sample (mg/L)	Biochar dose (grams)	Filtration Time in (minutes)	Final arsenic concentration in water sample (mg/L)	Removal of arsenic in water sample (%)	Adsorption capacity (mg/g)
0.1	1	30	0.1	0	0
0.2	1	28	0.2	0	0
0.3	1	32	0.3	0	0

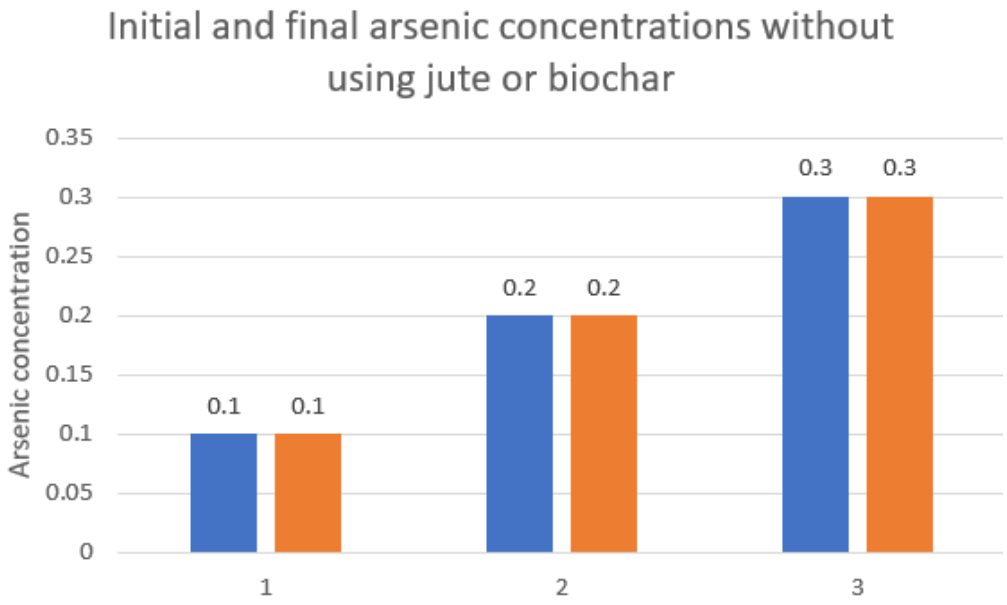


Fig-8.6: Initial and final arsenic concentrations without using jute or biochar

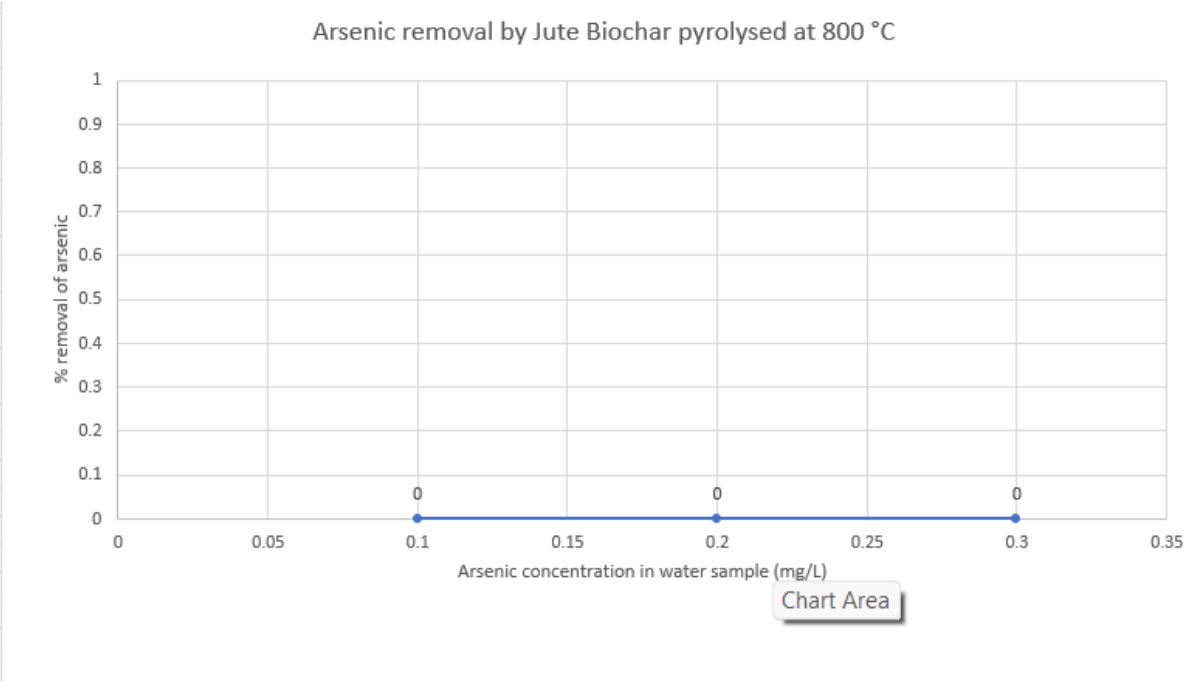


Fig-8.7: Arsenic removal without using jute or biochar

Set-2

Experimental condition
1gram of raw jute biomass was added to each water sample.
Water sample of three different initial concentration is kept in shaker at 200 rpm for 3 hours at room temperature.
Solution is filtered with one layer of Whatman's filter paper.

Table-8.2 Arsenic removal in water sample using raw jute

Initial arsenic concentration in water sample (mg/L)	Biomass dose (grams)	Filtration Time in (minutes)	Final arsenic concentration in water sample (mg/L)	Removal of arsenic in water sample (%)	Adsorption capacity (mg/g)
0.1	1	26	0.147	- 47	-0.0047
0.2	1	24	0.246	-23	-0.0046
0.3	1	29	0.374	-24	-0.0074

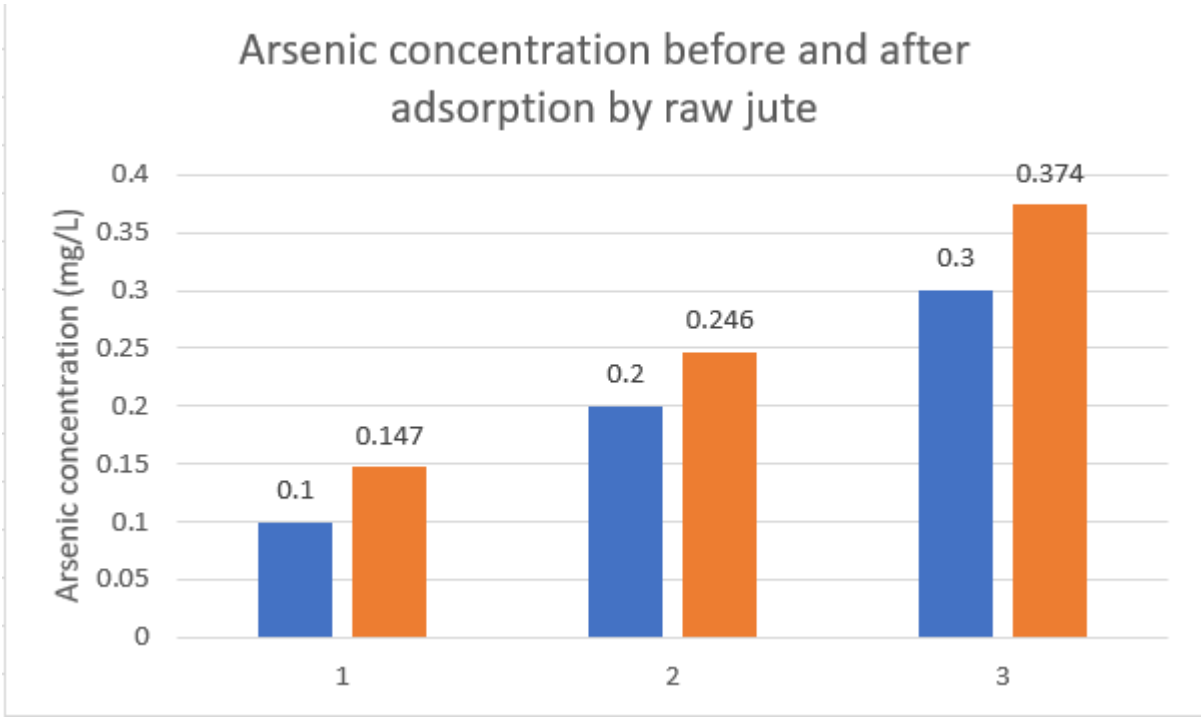


Fig-8.8: Arsenic concentration before and after adsorption by raw jute

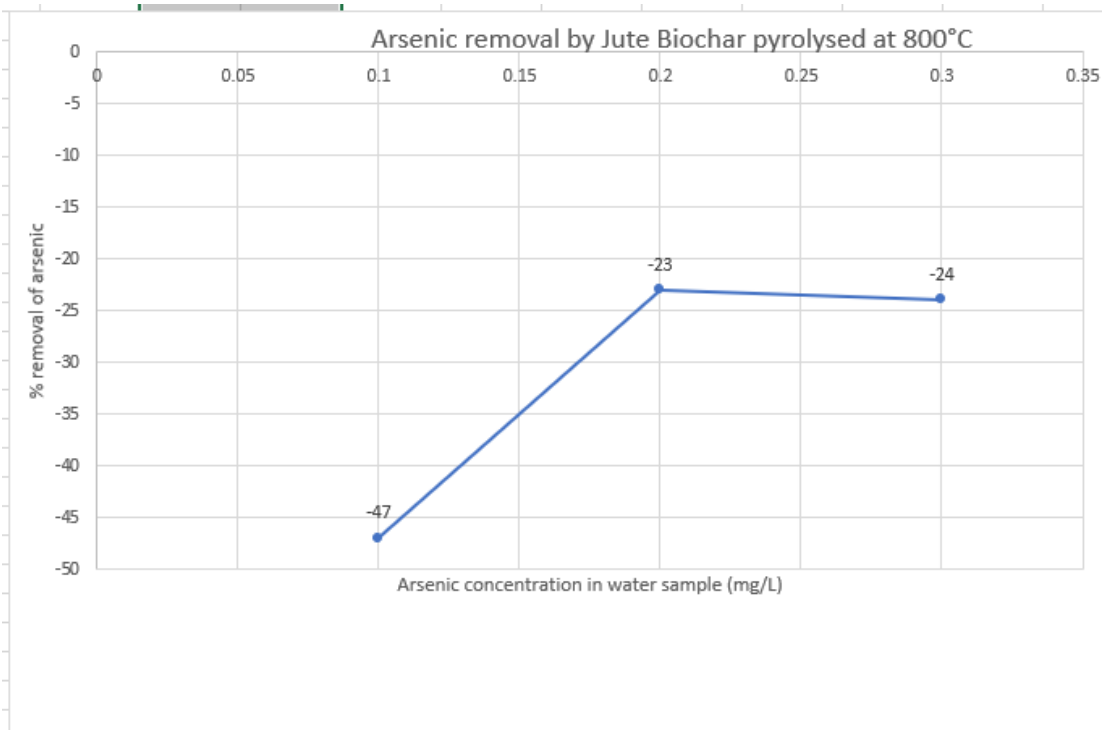


Fig-8.9: Arsenic removal by biochar pyrolyzed at 800°C

Set-3

Experimental condition -
1gram of jute biochar pyrolyzed at 800°C was added to each water sample.
Water sample of three different initial concentration is kept in shaker at 200 rpm for 3 hours at room temperature.
Solution is filtered with one layer of Whatman's filter paper.

Table 8.3 Arsenic removal in water sample using biochar pyrolyzed at 800°C

Initial arsenic concentration in water sample (mg/L)	Biochar dose (grams)	Filtration Time in (minutes)	Final arsenic concentration in water sample (mg/L)	Removal of arsenic in water sample (%)	Adsorption capacity (mg/g)
0.1	1	26	0.127	- 27	-0.0027
0.2	1	24	0.538	-169	-0.0338
0.3	1	29	1.697	-463	-0.1397

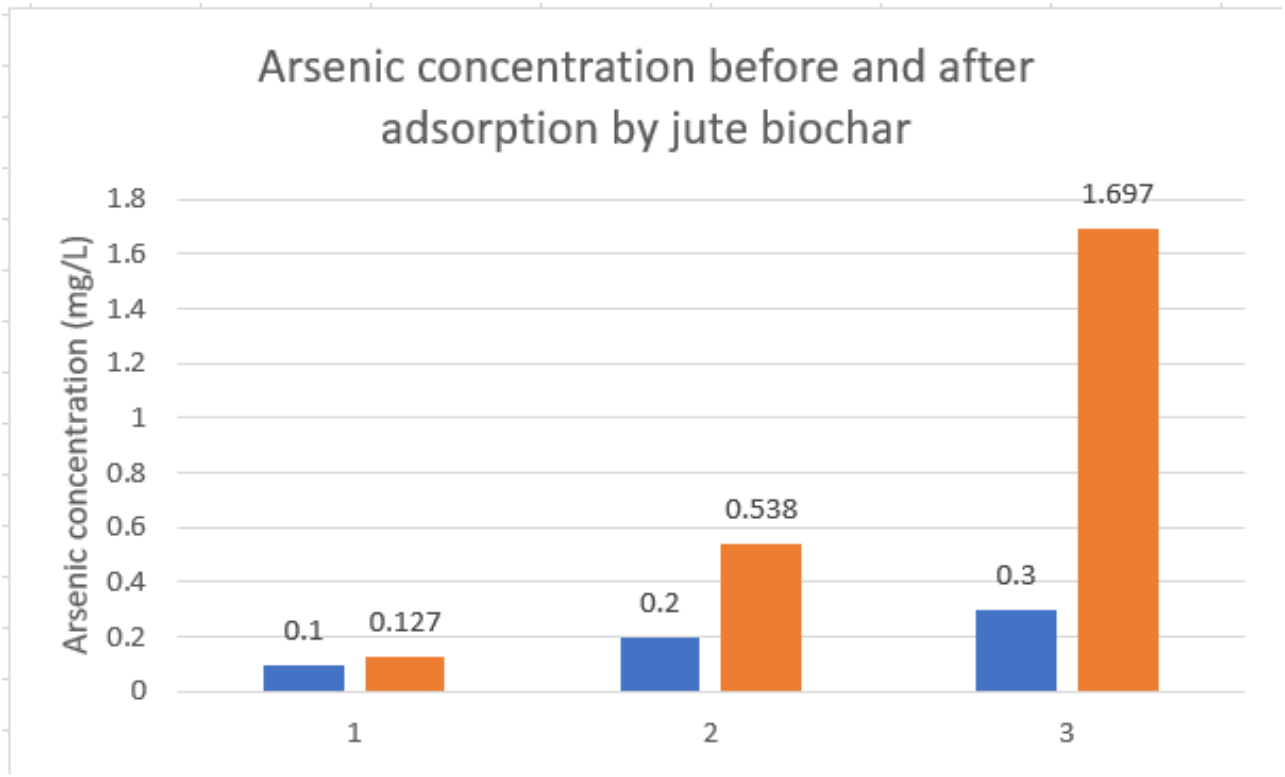


Fig-8.10: Arsenic concentration before and after adsorption by jute biochar

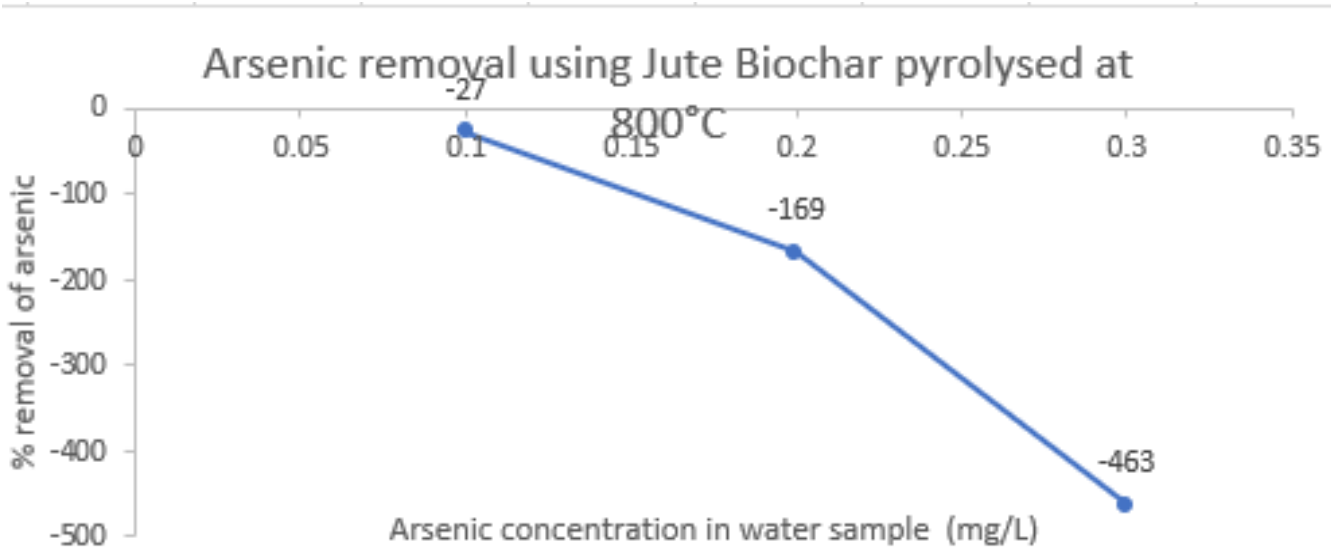


Fig-8.11: Arsenic removal by biochar pyrolyzed at 800°C

Set-4

Experimental condition -
1gram of jute biochar pyrolyzed at 800°C was added to each water sample.
Water sample of three different initial concentration is kept in shaker at 200 rpm for 3 hours at room temperature.
Solution is filtered with two layers of Whatman's filter paper.

Table-8.4 Arsenic removal in water sample using biochar pyrolyzed at 800°C

Initial arsenic concentration in water sample (mg/L)	Biochar dose (grams)	Filtration Time in (minutes)	Final arsenic concentration in water sample (mg/L)	Removal of arsenic in water sample (%)	Adsorption capacity (mg/g)
0.1	1	53	0.027	73	0.0073
0.2	1	75	0.091	54.5	0.0109
0.3	1	56	0.0591	80.3	0.02409

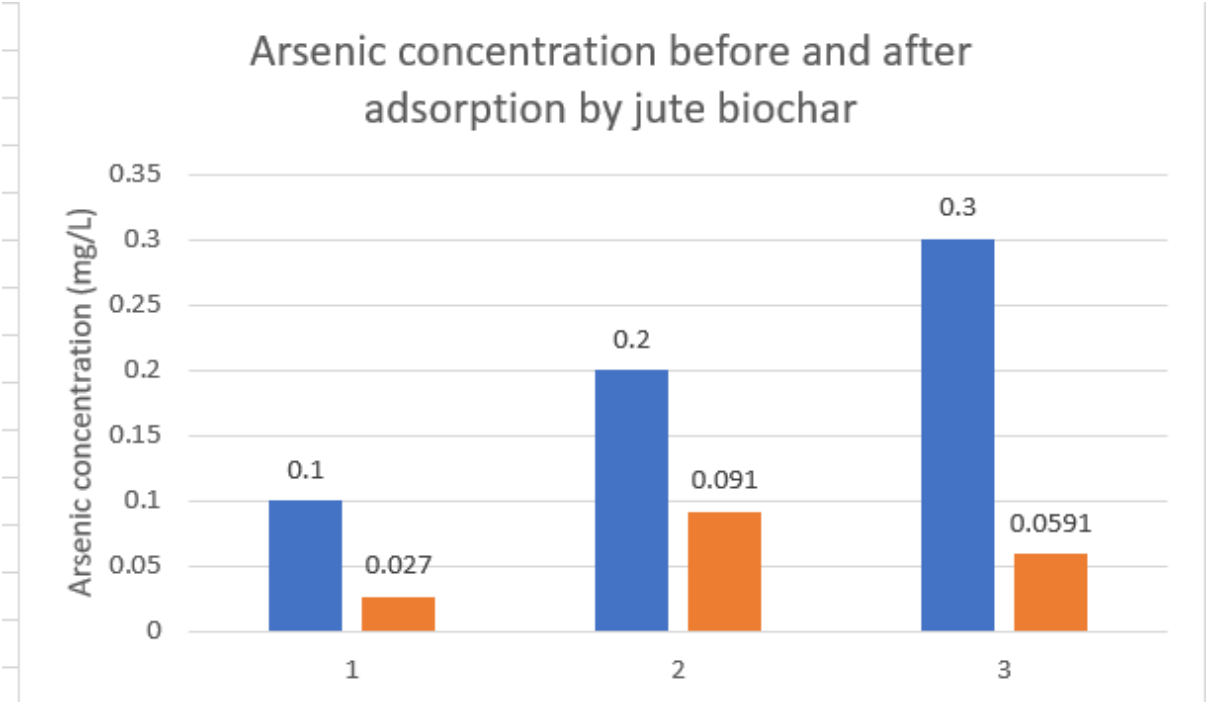


Fig-8.12: Arsenic concentration before and after adsorption by biochar

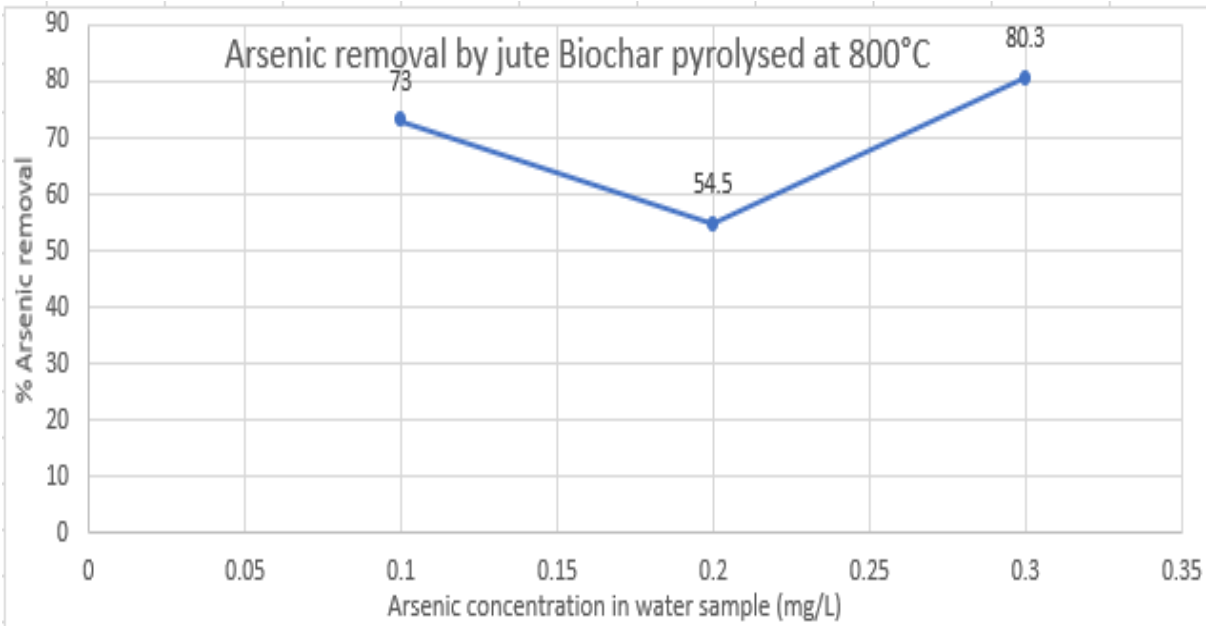


Fig-8.13: Arsenic removal by biochar pyrolyzed at 800°C

Set-5

Experimental condition -
1gram of jute biochar pyrolyzed at 800°C was added to each water sample.
Water sample of three different initial concentration is kept in shaker at 200 rpm for 3 hours at room temperature.
Solution is filtered with three layers of Whatman's filter paper.

Table-8.5 Arsenic removal in water sample using biochar pyrolyzed at 800°C

Initial arsenic concentration in water sample (mg/L)	Biochar dose (grams)	Filtration Time in (minutes)	Final arsenic concentration in water sample (mg/L)	Removal of arsenic in water sample (%)	Adsorption capacity (mg/g)
0.1	1	30	0.001	99	0.0099
0.2	1	28	0.046	77	0.0154
0.3	1	32	0.014	95.33	0.0286

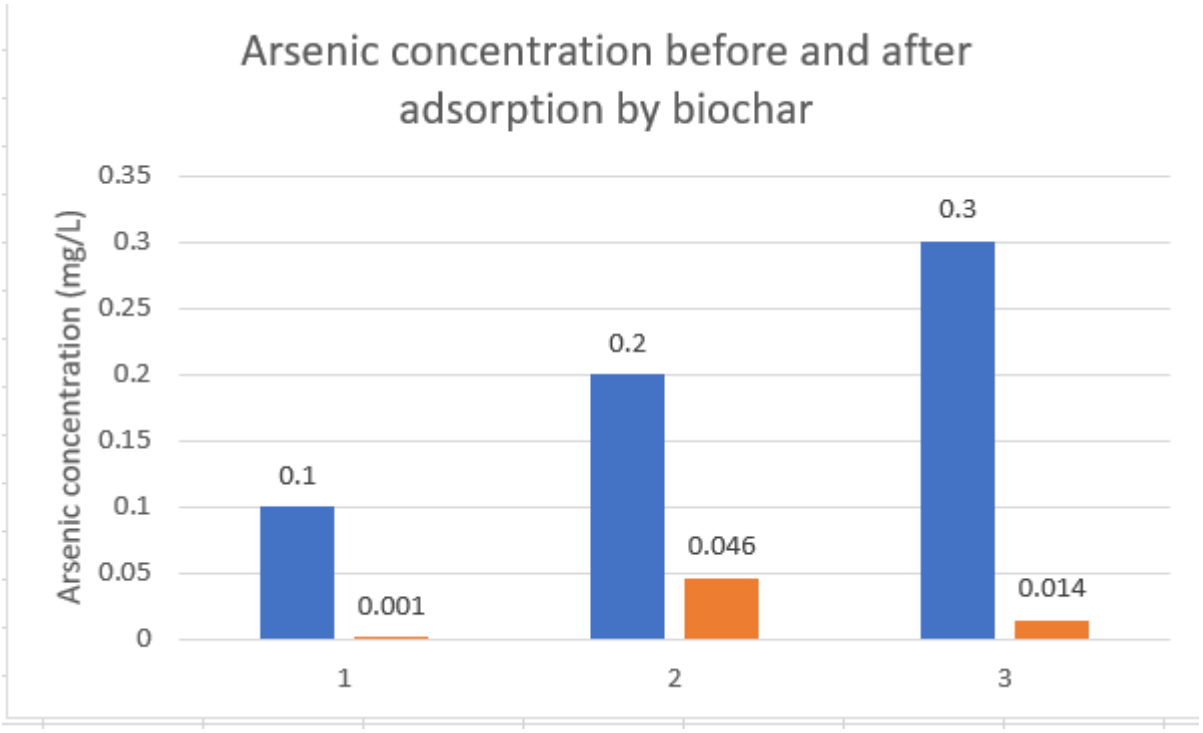


Fig-8.14: Arsenic concentration before and after adsorption by biochar

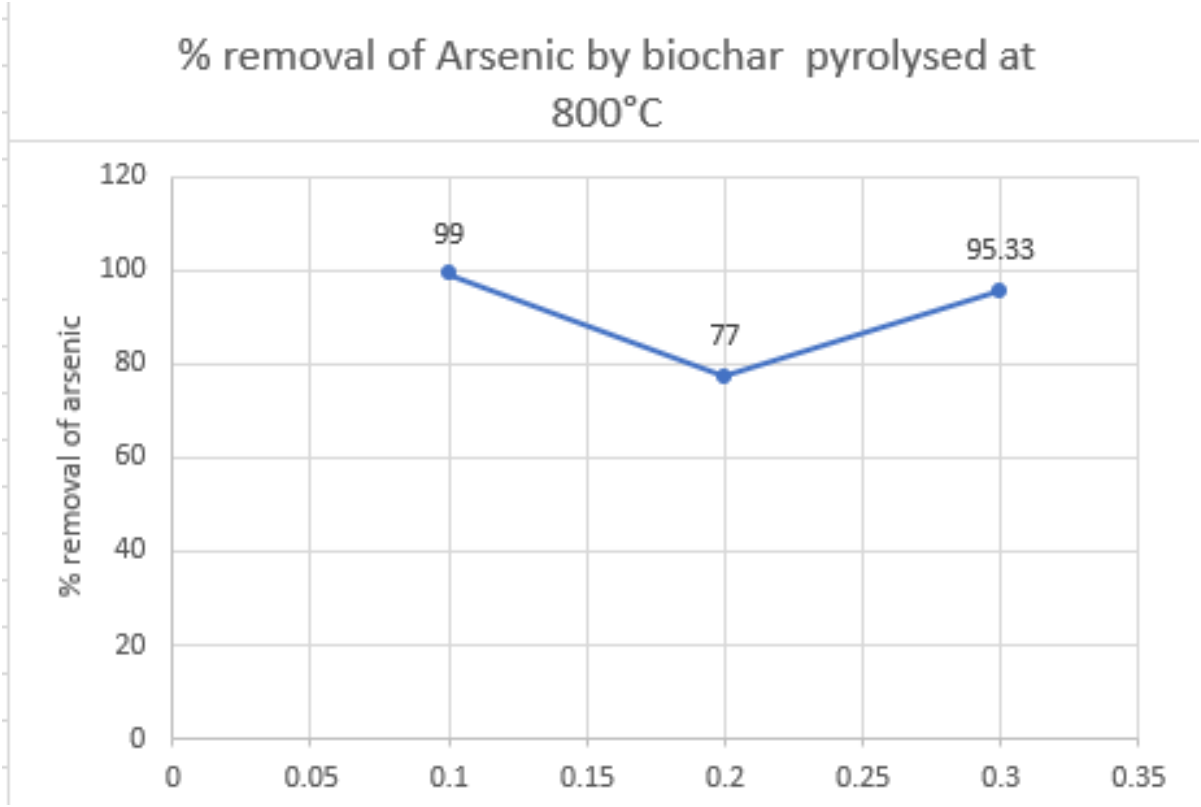


Fig-8.15: Arsenic removal by biochar pyrolyzed at 800°C

8.10 Future scopes, and recommendations-

Several countries require clean drinking water; therefore, biochar can play a significant role in providing clean water without As that does not require conventional water treatment. Action calls for on-site and low-cost As removal techniques and monitoring in As-affected regions with pilot-scale research to encourage use of modified biochars and avoid economic losses due to As-contaminated water on human and animal health. For interdisciplinary and technological advancement, biochar-based sorbents are environmentally sound technologies and can contribute to achieving sustainable development goals.
There are some potential future research aspects, for future studies using biochar-based sorbents for As removal from contaminated water:

• Adsorption experiments are usually conducted only at laboratory scale, involving mono-element systems and using simulated arsenic spiked solutions. In real systems, using drinking water or industrial wastewater, various elements, anions and cations may be found with arsenic , causing competition for sorption

on the surface of biochar. These aspects should be taken into account for the application of biochar-based sorbents in environmental remediation of real arsenic contaminated water.

• Until now, no specific and detailed study has been focused on biochar interaction with arsenic species in sulphide rich water systems.

• Concerning modified biochars, research on new functionalized, biochar or nano zero metal composites and nano-particle-impregnated biochars is warranted. Modification with amide functional groups on biochar surface may have a significant contribution in removing arsenic from water, although only limited research has been focused on these aspects.

• There is limited work available concerning a thorough cost-benefit assessment of the biochar production and application for arsenic removal from water so that the viability of its use in practical terms may be evaluated properly.

• After adsorption completion development of proper methods for the management and safe disposal of the spent biochar is required.

CHAPTER-9

CONCLUSION

Conclusion

Arsenic is a carcinogenic metalloid that is toxic to humans. It occurs naturally in ores and minerals and can be mobilized by weathering reactions and biological activity and leading to contamination of surface or groundwater aquifers. Anthropogenic contamination due to discharge and disposal of arsenic containing compounds causes greater concentrations. Due to the severe toxicity of arsenic a limit of 10 ppm was prescribed.

It is crucial to develop suitable and effective technologies for the remediation of arsenic contaminated water due to widespread contamination and high toxicity of arsenic, without large waste generation, high capital and energy requirements, incomplete contaminant removal from water and high operational and maintenance requirements that are a disadvantage of conventional methods. Biochar is a pyrogenic carbon material synthesized by combustion of biomass under anaerobic conditions. Due to its high surface area and cation exchange capacity, biochar can be used for soil improvement, carbon sequestration removal of arsenic from aqueous solution and reduce their mobility and bioavailability in soils. Unlike traditional methods, adsorption by biochar is a sustainable, cost-effective, user-friendly and effective method for arsenic remediation.

From the above study, it was found that although biomass cannot remove arsenic, biochar has shown effectiveness in arsenic remediation in pristine, unmodified form without addition of further reagents if filtration was conducted with multiple layers of filter paper. Jute biomass is cheap and readily available compared to materials required for conventional remediation methods and can be widely employed for mitigation of arsenic in contaminated water.

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