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GROUNDWATER ARSENIC (As) CONTAMINATION AND SIMPLE LOW COST ARSENIC REMOVAL PROCESSES IN TRIPURA

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ABSTRACT: Arsenic (As) is a metalloid. It occurs in almost every fraction of the environment. It is moving in each and every corner of our environment. Levels of arsenic (As) in the environment have become a global concern due to its toxicity and adverse effects on human health and other living beings. It is highly toxic even at low concentrations. It is also carcinogenic. Although, its natural sources are igneous and sedimentary rocks, the anthropogenic source of arsenic (As) plays an important role to maintain its concentration in our environment. The mining, smelting and refining, industrial processes, coal combustion, and waste incineration are released arsenic (As) in the environment. It may undergo cycling processes in the environment after release in the environment. This cycling process occurs depending upon few factors such as its oxidation state, speciation, concentrations and the presence of organic matter, competing ions, and other environmental factors (*e.g.*, pH, redox). This paper reviews the natural and anthropogenic occurrence of arsenic in the environment, toxicity of arsenic and newly invented scientific low cost household and the other chemical processes to remove arsenic (As) and its compounds from arsenic-contaminated water and soils in the world as well as in Tripura.

INTRODUCTION: Arsenic (As) is a naturally occurring, mobilized toxic metalloid. Arsenic (As) is widely distributed in water, soil, air and biota from natural and anthropogenic sources^{1, 2}. It can occur in both organic and inorganic forms. Organic arsenic (As) is associated with carbon and hydrogen. On the other hand inorganic arsenic (As) is associated with iron, cobalt or nickel coupled with sulphide minerals³.

According to the list of comprehensive environment response, compensation, and liability (CERCLA) Act, in US, arsenic (As) is one of the top five toxic chemicals^{4, 5}. There are four oxidation states of arsenic (As) such as arsines and methyl arsines (As³⁻), elemental arsenic (As⁰), arsenite (As³⁺) and arsenate (As⁵⁺), the inorganic form (As³⁺ or As⁵⁺). Among them the inorganic form (As³⁺ or As⁵⁺) of arsenic (As) is highly toxic and mobile in the environment compared to the organic form (As³⁻ or As⁵⁻). The arsenite (As³⁺) is 10 times more toxic than arsenate (As⁵⁺)^{6, 7, 8, 9}.

The main pathways to exposure to arsenic (As) are ingestion, inhalation and skin contact. The harmful effects of arsenic (As) on health are cardiovascular disorders, diabetes and cancer. As it is a known

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human carcinogen it can adversely affect human health even at low concentrations (0.002mg/l)¹⁰.

The widespread contamination and toxicity of inorganic arsenic (As) is an alarming issue as the metalloid does not degrade, nor can it be destroyed in the environment. It circulates around the earth and produces toxicity. As a result arsenic (As) toxicity has received increasing international attention. The observed arsenic (As) levels in the drinking water often exceed the WHO standard guideline (10 µg/l) in more than 42 nations including China, Australia, Cambodia, Vietnam, Bangladesh and India. Approximately 150 million people have been affected by drinking water contaminated with arsenic (As). The levels of arsenic (As) in drinking water in several countries worldwide cause a major public health issue. The arsenic (As) concentration in the north-eastern states of India is greater than 0.05 mg/l, implying that millions of people are at serious risk of as poisoning¹¹.

According to the North Eastern Regional Institute of Water and Land Management (NERIWALM) report 2007, the arsenic (As) levels in Assam, Manipur, Tripura and Arunachal Pradesh were above 300 parts per billion (ppb). According to the World Health Organisation (WHO), uptake of water contaminated with arsenic (As) levels of over 50 ppb can cause skin lesions and even cancer.

A number of simple, sustainable and sophisticated technologies have been developed to remove or minimize arsenic (As) in groundwater. Several physical, chemical and biological processes have been invented to remediate arsenic (As) in water and soil. There is a need to review a systematic and extensive study from sources to removal techniques of arsenic (As) in various environmental conditions. This paper reviews from sources to toxicity of arsenic (As) in the environment and summarizes currently available effective removal technologies of arsenic (As) from soil and water.

Meaning of Metalloid:

- Elements that share properties of metals and non-metals.
- Metalloids are located between metals and non-metals on the periodic table.

- The elements found along the step like line between metals and non-metals of the periodic table.
- The metalloids are boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), tellurium (Te), polonium (Po) and astatine (At). They are also called semi-metal.

Characteristics of Arsenic (As): The name “arsenic” is thought to come from “arsenikon”, the Greek name for the yellow pigment orpiment. Arsenic (As) was discovered approx 1250 by Albertus Magnus. It is a silver grey brittle, crystalline semi- metal or metalloid. It exists in three allotropic forms such as yellow, black and grey. The basic physical and chemical characteristics are given below:

TABLE 1: THE BASIC PHYSICAL AND CHEMICAL CHARACTERISTICS OF ARSENIC (As)

Name	Arsenic
Symbol	As
Atomic number	33
Relative atomic mass (Ar)	74.92160 (2)
Standard State	Solid at 298K
Colour	Metallic grey
Classification	Semi-metallic
Group in periodic table	15
Period in periodic table	4
Block in periodic table	p-block
Electron shell structure	2, 8, 18, 5
Electron configuration	[Ar]3d ¹⁰ 4s ² 4p ³
Valence	3, 5
Boiling point	Sublimes at 612 °C
Melting point	817 °C at 28 atm
Vapour pressure	1 mmHg at 372 °C
Density/specific gravity	5.727 at 14 °C

Sources of Arsenic (As): Different natural and anthropogenic sources are deemed responsible for arsenic (As) contamination in groundwater. Arsenic (As) is a major constituent in more than 200 minerals¹². The desorption and dissolution of naturally occurring arsenic (As) bearing minerals and alluvial sediments result in high arsenic (As) concentration in groundwater in deltas and alluvial plains even if the arsenic (As) concentration in the solid phase is not high^{13, 14}. In groundwater, arsenopyrite and pyrite contain arsenic (As) in excess concentration¹⁵. The main anthropogenic sources of arsenic (As) are burning of fossil fuels, mining, use of arsenical fungicides, herbicides, insecticides and wood preservatives¹⁶. Most arsenic (As) is produced as a by-product of copper and lead refining.

Permissible Limit of Arsenic (As): Permissible limits of arsenic (As) in drinking water according to United State Environment Protection Agency (USEPA), World Health Organization (WHO),

Indian Standard Institution (ISI), Central Pollution Control Board (CPCB) and Indian Council of Medical Research (ICMR) are compared¹⁷.

TABLE 2: PERMISSIBLE LIMITS OF ARSENIC (As) IN DRINKING WATER ACCORDING TO UNITED STATE ENVIRONMENT PROTECTION AGENCY (USEPA), WORLD HEALTH ORGANIZATION (WHO), INDIAN STANDARD INSTITUTION (ISI), CENTRAL POLLUTION CONTROL BOARD (CPCB) AND INDIAN COUNCIL OF MEDICAL RESEARCH (ICMR)

Name of the heavy metal	Symbol	USEPA	WHO	ISI	ICMR	CPCB
Arsenic (mg/l)	As	0.05	0.05	0.05	0.05	No relaxation

Uses of Arsenic (As): Arsenic (As) is a well-known poison. Arsenic compounds are sometimes used as rat poisons and insecticides but their use is strictly controlled. Arsenic is used as a doping agent in semiconductors (gallium arsenide) for solid-state devices. It is also used in bronzing, pyrotechnics and for hardening shot. The most important use of arsenic is in the preservation of wood. It is used in the form of a compound called chromated copper arsenate (CCA). CCA accounts for about 90 percent of all the arsenic used in the United States. It is added to wood used to build houses and other wooden structures.

Global Scenario of Arsenic (As) Contamination: The arsenic (As) contamination in drinking water of Taiwan, China, Chile, Argentina, Mexico, India, Hungary Bangladesh, USA and Thailand are red alarming for the world. More than 20 Country along with India, is in the midst of a large scale

thread cause by chronic mass toxicity through arsenic (As) contamination of ground water. However the largest mass of population in the world affected by chronic arsenic (As) toxicity due to drinking of arsenic contaminating ground water belongs to Bangladesh, India and China.

Scenario of Arsenic (As) Contamination in India as well as Tripura: According to the investigations of Central Ground Water Board (CG WB) reveals that arsenic (As) contamination (>0.05 mg/L) is affecting the states of West Bengal, Bihar, Uttar Pradesh, Assam, Chhattisgarh. The Bengal Delta Plain (BDP) covering Bangladesh and West Bengal in India is the most dangerous case of groundwater arsenic (As). The water of the West Tripura, Dhali and North Tripura is contaminated with arsenic (As)¹⁸. The concentration of arsenic (As) in groundwater of this areas is in between 65-444 g/l.

TABLE 3: ARSENIC CONTAMINATED AREA OF TRIPURA

District	Location	Arsenic (mg/l)
West Tripura	Jirania	191
Dhalai	Salema, Halhali, Halhooli, Kamalpur, Joyanagar	65 - 444
North Tripura	Sanitala, Rajbari, Dharma Nagar	122 - 283

The Symptoms of Arsenic (As) Toxicity: The children are often more affected than the adults in the arsenic (As) contaminated areas. Most of the people from a poor socio-economic background are suffering from arsenic (As) skin lesions. The common features were noted (1983 - 2006) from the arsenic endemic areas of India: (i) Skin itching to sun rays, burning and watering of eyes, weight loss, loss of appetite, weakness, lethargy and easily fatigued limited the physical activities and working capacities. (ii) Chronic respiratory complaints were also common. Chronic cough with or without expectoration was evident in more than 50%.

(iii) Gastrointestinal symptoms of anorexia, nausea, dyspepsia, altered taste, pain in abdomen, enlarged liver and spleen, and ascites (collection of fluid in abdomen). (iv) Moderate to severe anaemia was evident in some cases. (v) Conjunctival congestion, Leg edema was less common. Various types of skin manifestations and other arsenic toxicity were observed from melanosis, keratosis, hyperkeratosis, dorsal keratosis, and non pitting edema to gangrene and cancer. Arsenic (As) induces cardiovascular dysfunctional¹⁹, diabetes mellitus²⁰, neurotoxicity, nephrotoxicity and hepatotoxicity²¹, carcinogenicity²², reproductive toxicity²³.



FIG. 1: ARSENOICOSIS PATIENT

Removal of Arsenic (As) from Groundwater:

Dangerous public concerns have been raised worldwide due to ingestion of arsenic (As) contaminated surface and groundwater. There are a number of techniques to remove arsenic (As) from the water²⁴. In recent years, sustainable, low cost and efficient techniques have gained more attention. Commonly used remediation techniques for arsenic (As)- contaminated water include oxidation, lime treatment, chemical precipitation / coagulation, ion exchange, adsorption, bioremediation, phytoremediation, hybrid membrane process (nanofiltration and ultrafiltration) and electro dialysis²⁵⁻²⁷. Oxidation is a simple method. It converts arsenite to arsenic. This can be obtained by oxidizing arsenic (As) contaminated water with oxygen, hypochlorite, free chlorine, hydrogen peroxide and permanganate. Other conventional oxidation methods are storage of water for about two weeks, reducing 50% of the arsenic concentration in water and solar oxidation. Arsenic (As) in subsurface water is removed by injecting oxygenated water and ferric chloride into an anaerobic aquifer²⁸. Atmospheric air and chemical oxidation are simple and low cost methods that aid in the removal of arsenic (As) in rural areas.

Coagulation is a traditional way of removing arsenic (As) from water contaminated with arsenic (As). The arsenic (As) contaminated water is treated by the addition of ferric sulfates, ferric hydroxide, hydrated lime, alum or ferric chloride. Ferric salts are known to be good coagulants. As^{5+} can be easily removed by coagulation process by the addition of coagulants and formation of aluminium or ferric floc. But, As^{3+} requires further

treatment either by oxidation, filtration or the addition of bleaching powder (chlorine) or potassium permanganate. Mixture of alum and chlorine showed 90% removal efficiency of arsenic at pH 7²⁹. After coagulation changes in pH, phosphate and silicate levels occur. As the coagulation process involves the use of simple chemicals, only a low capital cost and pre-treatment (oxidation) are required for complete removal of arsenic. Arsenic (As) is generally associated with iron (Fe). So, an excellent sustainable remediation technology for removing of arsenic (As) is co-precipitation of arsenic (As) with iron (ferric sulphate)³⁰.

Adsorption is an important technique of removing arsenic (As) from the water contaminated with arsenic (As). Adsorbents like activated carbon, hydrous metal oxides, ion exchanger resin, activated red mud, zeolite and ferruginous manganese ore are used to remove smell, colour, organic and inorganic pollutants. The pH is determined the arsenic (As) Arsenic (As) speciation. It is an important indicator in arsenic (As) removal by adsorption. The commercially available absorptive filtration media are activated alumina, activated carbon, kaolinite clay, hydrated ferric oxide, titanium oxide, indigenous filters and many other natural and synthetic filters. It has been reported that they remove arsenic (As) effectively. Another technique of removal of arsenic (As) involves injection of electric current (EC) into aqueous medium containing electrodes. It is also a practiced sustainable method used to treat the contaminated water.

In the aqueous medium the anode produces metal cations and the cations oxidize metal to oxides, creating flocculation, coagulation and settling. The 75% of arsenic (As) was removed by the Electro-coagulation technique at 20V³¹. Arsenic (As) is removed by the electro coagulation with iron and aluminium electrodes to the US EPA drinking water standard³². This method is suitable for a rural area due to absence of any chemicals. This is a simple and cost effective method although it requires frequent changes of the electrodes.

Phytoremediation of arsenic (As) in water is occurs with the aid of water plants to detoxify arsenic (As) present in water in combination with electro-chemical technique. The *Eichornia crassipes* (water hyacinth) and *Rhaphidophyceae chattanello* plants have the capacity to absorb arsenic (As) by their shoots. The arsenic (As) metal can be extracted through an electrochemical method.

The main membrane techniques such as reverse osmosis, nanofiltration, ultrafiltration and electro-dialysis are commonly used to treat arsenic (As) -contaminated water. At low and high pressure, reverse osmosis removes dissolved solids. It has been reported that the removal efficiency of arsenic (As) in hybrid membrane techniques is higher than the conventional membrane techniques. It is extremely expensive. This technique requires high operation and maintenance. It produces toxic wastewater³³.

Studies on the use of engineered magnetic nanoparticles (NP) (nano zero-valent iron (NZVI), magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃) and hydrous cerium oxide (HCO)) in removing arsenic (As) from arsenic (As)-contaminated water is gaining lot of preference due to their high removal efficiency, fast kinetics, reduction, adsorption and magnetic property. However, this technique is relatively much expensive. The nano-particles with NZVI can be desorbed in the presence of phosphorus present in the ground water or by addition of phosphate into groundwater and reused³⁴⁻³⁷.

CONCLUSION: This review has summarized the present scenario of arsenic (As) contamination in the different parts of India as well as Tripura, a Northeast state. Various types of skin problems,

melanosis, keratosis, hyperkeratosis, dorsal keratosis, non-pitting edema and cancer can be observed in people of these regions. But still the proper health measures cannot be followed these arsenic affected areas. In the absence of alternate source of arsenic (As) free irrigation water, people of the arsenic (As) affected areas have continued to explore new water sources, resulting in further intensification of the problem.

This exhibits that the effects of this occurrence have far-reaching consequences. Sooner we search permanent solutions to solve the problem; otherwise in future it induces environmental, health, socio-economic and socio-cultural hazards. Despite these reports from different governmental and non-governmental institutes, research centres, survey studies is still unsuccessful in providing safe drinking water to the people of these states. A long-term environmental planning and integrated research is required to mitigate the danger of arsenic (As) poisoning.

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