

Arsenic Contamination Status in Water Resources of India and Its Treatment Strategies

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Abstract Safe drinking water is both a basic requirement for good health and a human right. In many places of the world, fresh water is already in short supply due to rising population, urbanisation and climate change and will become much more restrictive in the next century. Among the various other contaminants of drinking water, arsenic has proven to be one of the most toxic due to its hazardous nature and adverse effects on living being and is therefore considered as one of the biggest environmental threats. The path followed by As in our environment, ultimately reach and affect our ecology as a whole. This paper presents an overview of the highly toxic arsenic existence in drinking water around the globe with a detailed view of India and the various treatment techniques followed by remedial measures along with their advancement.

Keywords: arsenic contamination, water resources, India, treatment

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1. Introduction

Arsenic or As, a metalloid present in group V of the periodic table is one of the highly toxic metals present in our environment in traces. Physically appearing as a metal, this element is 20th among the most abundant elements that are present in the earth's crust which raises concern with respect to the environment as well as human health. The use of arsenic has been wide and varied since the earliest of times in the form of drugs or poison due to its abundance. It is without a doubt, a major environmental threat proven to be deadly. Consumption of water contaminated with arsenic is a major contributor to health hazards [1].

The occurrence of arsenic in water is due to natural as well as anthropogenic activities. Weathering and mixing rocks and ores rich in arsenic, volcanic eruptions and other various natural processes contributes majorly to the addition of arsenic in surface and groundwater. Arsenic-contaminated water produced from industries, water from wells dug deep in arsenic-rich earth crust, food and runoff water contaminated with arsenic-based pesticides, burning of arsenic rich fossil fuels, mining and many more activities lead to exposure of humans and environment to this highly toxic substance [2].

Arsenic exists in nature in organic as well as inorganic forms. The inorganic form is more widespread and more toxic which has acute as well as chronic effects. Its presence in water has no effect on the physical appearance of water, even at a high concentration, which makes it

difficult to detect without complex techniques. It has come to light that consumption of drinking water with arsenic (inorganic) present in low amounts for a long period of time is fatal [3]. Due to the presence of high amount of arsenic in the earth's crust makes ground water the most vulnerable to arsenic contamination. The dominant role played by ground water in fulfilling drinking water demand around the world, makes its contamination in arsenic rich areas deadly for the exposed population due to its high solubility and mobility in water [4] and. In light of the fact that millions of people are poisoned by the arsenic present in groundwater which is used as drinking water, for irrigation, food processing etc. removing arsenic from contaminated soils and waters or immobilizing it to prevent bioavailability, is of utmost importance [5].

2. Role of Industries

The majority of industries are responsible for the deposition of one or another trace metal in the soil and water ecosystems. In the past, 82,000 metric tons/year worldwide was the anthropogenic contribution of As in the environment [1]. Trace metals in soils are mainly obtained from coal combustion ash residues and general surface waste of commercial products.

Wood preservation is done by chemicals such as CCA (Chromated Copper Arsenate) and other As-based chemicals. These are water soluble and their incineration contaminates the soil around wood preservation facilities [6]. Production of ammunition, pigments, insecticides,

rat poison, semiconductors etc, contributes towards dissolution of As in the environment.

Since a long period of time, the use of arsenic has been prevalent in the production of pesticides, fungicides, herbicides etc, in the inorganic form such as arsenic trioxide, arsenic acid, arsenates of calcium, copper, lead and sodium and arsenites of sodium and potassium [7].

3. Widespread of Arsenic Poisoning

The devastating effects of arsenic toxicity can already be seen in many countries worldwide due to water contaminated with arsenic. Bangladesh, India, Nepal, Cambodia, Myanmar, Taiwan, Mongolia, Vietnam, China, Afghanistan, Pakistan, Argentina, Mexico, Chile and the United States are the countries exposed to arsenic toxicity [8]. Globally, more than 300 million people are estimated to be poisoned by arsenic and as many as 180 million are among those living in the Ganga-Meghna-Brahmaputra plains which has an area of approximately 500,000 km² and a population of over 500 million [9]. Data indicates that Asian regions are more vulnerable to arsenic toxicity than other regions around the world. South-east Asia has been facing a great rise in problems related to arsenic contamination through ground water. Globally, crop quality and the impact of As on yield are major concerns, particularly for rice [10]. Rice is the staple food of majority of Asian countries and studies in the EU have indicated that in non-seafood diets, it is the primary source of exposure to arsenic [4].

The two worst arsenic contamination affected regions are Bangladesh and West Bengal. As per reports, Bangladesh is the biggest arsenic catastrophe in the world with more than half the population under the risk of arsenic toxicity [11]. Bangladesh went through a surge in the installation of tube wells by the government and international aid organizations due to the severe decline in mortality rate because of the widespread of diarrheal diseases. The tube wells were an alternative that tapped into pathogen-free aquifers, convenient and cheap which further increased its number as people began private installation. The over-withdrawal of ground water led to changes in the geochemical properties and redox condition of it, which led to the release of arsenic from the minerals in the aquifer. Chronic exposure to arsenic led to an epidemic of arsenicosis, a couple decades later [12,13].

4. Overview of India

In India, multiple states such as West Bengal, Bihar, Uttar Pradesh, Jharkhand, Assam, Chhattisgarh, and Manipur are affected by arsenic poisoning. In recognition of the severe health problems caused by groundwater arsenic in India, the Indian Bureau of Standards revised the national limit for arsenic in drinking water from 50 µg/l to 10 µg/l in 2003. The current BIS standard limit for arsenic in drinking water is 0.01 to 0.05 mg/l [14].

5. West Bengal

In the Bengal Delta Plain, arsenic is believed to have accumulated during the late Quaternary age, with alluvial

sediments containing arsenic deposited by the Ganga, Brahmaputra, Meghna and other smaller rivers flowing across the Bengal Delta Plain into the Bay of Bengal. During the oxidation process, the arsenic is adsorbed as oxyanions on oxyhydroxides of iron, aluminium, and manganese, which are then mobilised in the alluvial aquifers where the oxyhydroxides dissolve under the influence of the reducing environment, releasing the arsenic in the groundwater [15].

In West Bengal alone, around 6.5 million of the population is exposed to arsenic contaminated drinking water with As concentration exceeding 50 µg/l [16]. The reducing environment present in the alluvial sediments exposes the ground water to arsenic, this ground water is accessible to the population and makes them vulnerable to effects of arsenic toxicity. The region has an affected area of 4800 km² with arsenic concentration <50-1860 µg/l. In the last 18 years of survey, reports show that 3500 blocks from 90 villages have been arsenic affected. As per Mukherjee *et al.*, [17], an average 85% of the 30,000 biological samples that were collected from the arsenic affected regions of West Bengal had arsenic content above normal level.

6. Bihar

The state lies in the middle Ganga plain and partly in the upper Ganga plain [16]. The first report of arsenic contamination came from Semaria Ojha Patti village of Shahpur, a block of Bhojpur district in 2002. The current situation has risen to 16 districts and 61 blocks with more than 10 million people under the risk of arsenic poisoning [18]. The constant increase in the number of affected regions demands effective actions by the government with respect to arsenic mitigation programs. As per intensive research done by Mukherjee *et al.* [17], analysis of 9,597 samples show 39.02% of them contained arsenic >10 µg/L and 23% contained >50 µg/L and 5.5% of 4513 people screened for arsenic skin lesions were registered with skin lesions. In a study conducted by Singh *et al.* [19], the cancer risk (CR) and hazard index (HI) exceeded both, the minimum and maximum acceptable ranges indicating an increase in cancer susceptibility in the population exposed to arsenic contaminated sources. In accordance to a study conducted by Kumar *et al.* [20], in Simri village of Buxar district, the amount of arsenic detected in the ground water was reported to be 1929 µg/l and the amount detected in the blood of the subject was 664.7 µg/l. Hyperkeratosis on sole and palm, hyperpigmentation and melanosis in the skin of the body were the effects observed in the population of this region. In addition to this, diseases like diabetes, hypertension, loss of appetite, dysentery, abdominal pain, breathlessness, hormonal imbalance, mental disability and cancer were also prevalent in the region. A mere handful of mitigation structures exist in villages of the state, therefore, most of the population are forced to drink arsenic-contaminated water [20].

7. Uttar Pradesh

In 2002, the state lying in the middle and upper Ganga plain was suspected with arsenic contamination. Study

done by Ahamed *et al.*, [21], verifies presence of arsenic contamination in Ballia, Varanasi and Ghazipur districts. The arsenic concentration above 300 ppb was found in only 10% of the samples studied but due the overuse of ground water for agricultural and drinking purposes, this value has risen to as much as 44.4% of the samples. Arsenic concentration ranging from 5.40 to 15.43 ppm was found to be present in the soil samples of the districts of Uttar Pradesh, this range is toxic and particularly to sensitive crops. The report from Srivastava *et al.* [22] suggests that soil samples collected from 15-30 cm depth constituted high arsenic concentration than the ones from 0-15 cm depth. Even the sources of irrigation water had an alarming level of arsenic and irrigation of crops with such high arsenic concentrated water for a long period of time (10-20 years or more) causes contamination of the soil and affect the crops severely. Crops and loss by volatilization appear to diminish the accumulated arsenic in soil only by small amounts. High concentration of arsenic in soil and water in the region puts the population at risk and demands immediate actions.

8. Jharkhand

The state has tropical type of climate. Therefore, high temperature and humidity prevails which increases the need of water among the population. In a study conducted by Alam *et al.* [23], Bicarbonate was the major anion present in ground water samples taken from districts of Jharkhand, by carbonating arsenic sulfide minerals, bicarbonate anion causes arsenic to leach into groundwater. In the pre-monsoon and post-monsoon season, arsenic concentration was higher than that in the monsoon season which can be assumed to be the outcome of dilution by increase in precipitation reaching the aquifers. Arsenic concentration in Badi Kodderjana was found to be 133µg/l followed by Dehari, Ghat Jamni and Keswa in the post-monsoon season. Dehari was reported with 115µg/l of arsenic concentration in the pre-monsoon season which indicates high contamination in some areas.

The areas around the banks of Ganga consisted of high arsenic concentration. A large number of fields are present in the alluvium deposited zone. Arsenic levels are directly proportional to the depth of ground water and shows positive connection with phosphate concentration. Phosphate in ground water is the result of percolation of agricultural runoff that contains fertilisers; it helps in the release of arsenic in ground water. Children and adults were found to be at the same high risk of cancer when drinking water containing arsenic (4.63E-03 in adults and 4.45E-03 in children). The vast population comprising of adults as well as children exposed to high risk requires immediate mitigation strategies from arsenic contaminated water sources [23].

9. Toxicity of Arsenic

Arsenic commonly occurs in two oxidation states in our environment, trivalent (Arsenite) and pentavalent (Arsenate) form. The trivalent form, Arsenite is 60 times

more toxic and the one prevalent in drinking water [15]. Arsenic poisoning refers to the adverse effects shown in humans after exposure to arsenic either in high concentration or in low concentration for a prolonged period. It affects the sulphhydryl group of cells by interfering with their enzymes, their respiration, and their mitosis, making it a protoplasmic poison. The arsenic that enters our body is mostly absorbed by the gastrointestinal tract and the lungs which further add it to the blood. The erythrocytes carry around 95 to 99% of the absorbed arsenic to the various organs of the body [2]. According to analysis done by Rahman *et al.*, [24], when arsenic toxicity begins to develop, it takes six months to two years or more of exposure. The amount of arsenic ingested, the amount of arsenic in the water, and the nutritional status all play crucial role in its development.

Arsenicosis, which is a result of consumption of arsenic contaminated ground water, was first detected in 1993 and rising at an alarming rate [11]. Arsenic is now widely recognized as a human carcinogen, which contributes to the high incidence of skin and other types of cancers in populations exposed to high levels of As in drinking water [25]. As-containing compounds were classified by the International Agency for Research on Cancer (IARC) as group 1 carcinogens [26].

10. Acute Arsenic Toxicity

Exposure to high concentration in a short period of time is termed as acute. Gastrointestinal irritation along with difficulty faced in swallowing, abnormally low blood pressure, thirst and convulsions are some of the adverse effects of acute exposure to high dose of arsenic orally. Cardiovascular collapse may even lead to death [27]. As stated by the Risk Assessment Information System database, "The acute lethal dose of inorganic arsenic to humans has been estimated to be about 0.6 mg/kg/day" [15].

11. Chronic Arsenic Toxicity

Long term exposure is termed as chronic. There is a gradual onset of non-specific symptoms like abdominal pain, diarrhoea, and sore throat. It leads to disease affecting multiple systems of the body and Malignancy is the most serious one. Accumulation of arsenic absorbed by the body happens in the liver, kidneys, heart, and lungs, with more minor accumulations occurring in the muscles, nervous system, gastrointestinal tract, spleen, and lungs. Typically, arsenic affects the nails, hair and skin as it gets deposited in keratin-rich tissues. Hyperpigmentation, palmar and solar keratosis are the commonly seen effects. In addition to cardiovascular disease, there is an increased risk of peripheral vascular disease, respiratory disease, diabetes mellitus, and neutropenia. Because of chronic arsenic exposure, individuals can suffer from mental retardation and developmental disabilities, including physical, cognitive, psychological, sensory and speech impairments [8].

As per Saha's classification of stages of clinical features of arsenic toxicity, it occurs in four main stages [2]:

- Pre-clinical/asymptomatic stage
- Clinical/symptomatic or overt stage
- Internal complication
- Malignancy

12. Arsenic Cycling (Environment)

Deposition of arsenic can be either naturally or anthropogenically, but either way it cannot be degraded or destructed once released. Therefore, As cycles in the environment. Globally, mankind is a crucial element of the bio-geochemical cycling of As.

As is present in the sedimentary and igneous rocks (avg As levels: igneous-1.5, sandstone-2.6 and shale-14.5 mg/kg) [7]. The factors that affect the As concentration in these rocks are:

1. Type of rock
2. Chemical and structural aspects
3. Organic and inorganic components
4. Redox potential

Predominantly, Arsenite (As^{3+}), Arsenate (As^{5+}) and organic arsenic are found in the soil. A very small percentage of the total is found in its natural form, form of amorphous iron and aluminum oxides. Reduced redox conditions in soil cause arsenic to be released from arsenic containing iron hydroxide. If there is sulfide present, arsenic may precipitate as arsenic sulfide, but excessive arsenic may be released into the environment. Dry weather causes arsenic to remain fixed in the soil matrix, so soils containing arsenic tend to have a higher content during the dry season. Arsenic concentration tends to be higher in alluvial soil as compared to sandy soil indicating that clay plays a crucial role in arsenic fixation.

Aerobic environmental condition supports inorganic As in readily binding with organic as well as inorganic components of soil (like clay, iron and manganese dioxide), hence, existing in Arsenate state. Whereas, in anaerobic condition, it exists in less toxic volatile forms due to degradation into DMAA (Dimethyl arsenic acid) and MMAA (Monomethyl arsenic acid) by anaerobic bacteria [7].

A major concern is generation of waste from coagulation-based systems and from systems based on absorptive filtration and other techniques (e.g., ion exchange). The waste from the coagulation-based system contains coagulated flocs of alum or iron salt, rich in arsenic and is primarily slurry. These arsenic rich wastes are generated from households or community-based As removal systems [28]. Effluents from domestic wastewater, coal burning power plants and sewage sludge act as a major source of As in the aquatic environment [1].

The Arsenic pumped with tube well water can undergo different processes such as:

1. Redox and microbial processes leading to transformation
2. Various biological transformation volatilizing As into the atmosphere
3. Undergo absorption-desorption, the loss of water through evaporation and evapotranspiration leaves arsenic and other minerals in topsoil on irrigated agricultural land. As is expected to accumulate in

surface soils as this arsenic is unlikely to be dissolved or washed away by flood or rainwater in an oxidized condition due to its affinity for iron, manganese, aluminum, and other minerals in soil. This process may lead to washing away of As by surface runoff or its leaching in the ground water.

4. Consumption by plants, thus entering the food chain [28].

13. Arsenic Cycling (Human Metabolism)

The metabolism of As in biological species, humans as well, has evolved and likely to be converted from the most toxic form to less toxic form followed by the cells accumulating or excreting it, like other heavy metals. The inorganic form of arsenic is methylated into MMA (monomethylarsonic acid) which further changes into DMA (dimethylarsinic acid) with the help of SAM (S-adenosyl-methionine), catalysed by methyltransferases in the presence of glutathione. Methylation threshold hypothesis states that the methylation capacity begins to decline after exposure of inorganic arsenic, thus increasing the harmful effects of inorganic As. To control the rate of metabolism of As, reduction of As from pentavalent to trivalent form plays an important role as the trivalent form are preferred as substrates in methylation mechanism. With the increasing levels of inorganic arsenic, excretion of DMA comes to an end after a short period of time (few days) while MMA levels remain elevated. This indicates the presence of two successive methylating-enzyme activities [29].

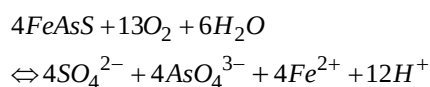
Conversion of arsenic to less toxic methylated forms takes place in the liver and getting excreted by the urine. It undergoes a triphasic model of time periods: 28 h, 59 h and 9 days. Continuous decline in methyl leads to DNA hypomethylation and simultaneously malignant transformations take place. DNA hypomethylation aids abnormal gene expression that leads to carcinogenesis. MMA was found to be methylated to DMA adversely by chronic exposure to arsenic, though the exact physiological basis of the reduced rate of methylation isn't yet understood. Metabolic methylation of inorganic arsenic is a genotoxic-enhancing process as it constitutes initiation of DNA damage and DNA single-strand breaks due to the inhibition of repair polymerization [29].

14. Chemistry of Arsenic

Soil – The lithology of parent rocks determines the background As content in soil. Various factors comprising of the Climatic and geomorphic characteristics affects the availability and dispersal of arsenic in soil, such as [6]:

1. Rainfall
2. Surface runoff
3. Rate of infiltration
4. Level of ground water and its fluctuation
5. Redox potential
6. pH
7. Soil mineralogy
8. Grain size
9. Composition of clay minerals

Weathering of arsenopyrite and other primary sulphide minerals leads to the exposure of soil environment to arsenic. Oxidation of S^{2-} to SO_4^{2-} and As^{III} to As^V due to reduction of O_2 occurs in the presence of dioxygen and water. The reaction can be written as:



In reducing environment, arsenous acid ($H_3As^{III}O_3^0$) prevails over a wide range of pH and at pH >9.0, arsenous acid occurs in protonated forms ($H_3As^{III}O_3^-$).

In an oxidizing environment and higher pH, pentavalent As prevails, at pH >7.0, in $HAsO_4^{2-}$ form and at pH <7.0, in $H_2AsO_4^-$ form.

Trivalent As is more mobile and toxic as compared to pentavalent As in soils. MMA and DMA are volatile and readily moves by reaction of arsenous acid with methylcobalamin in the presence of anaerobic bacteria but their unstability in oxidizing conditions returns them into the soil in inorganic forms. While soil exhibits a high affinity for As, it may take an extremely long time for soils to retain this element to levels below toxicological concern [6].

Water—Ground water contributes majorly to the addition of As in the environment. Leaching and weathering of geological formation rich in As, mining and waste and even thermal springs and geysers located in several regions consisting of high level of As results in the rise of As level in natural waters. Inorganic As prevails in ground water in trivalent (arsenite) and pentavalent form (arsenate), arsenite being more toxic and mobile. Inorganic As is biomethylated by reduction into less toxic forms such as DMAA and MMAA in the aquatic environment by the action of prokaryotes and eukaryotes. Bio-methylation refers to mobilizing of arsenic from aquifers to ground water by degradation of organic matter and conversion of As^V into more soluble As^{III} species [10].

15. Arsenic Remedial Methods

i) Oxidation techniques

The conventional methods developed for removal of arsenic contamination are allegedly more effective when done in a two-step procedure which includes the first step to be the oxidation of arsenite into arsenate followed by using technologies for the removal of arsenate i.e., the second step. The given approach is adopted as majority of the technologies available are more effective for treating arsenate rather than arsenite [30]. Oxidation of arsenite can be accomplished with oxygen, ozone, free chlorine, hypochlorite, permanganate, hydrogen peroxide, and fulton's reagent. However, in developing countries, atmospheric oxygen, hypochloride, and permanganate are commonly used for oxidation [31]. Oxidation process plays a significant role in removing arsenic from anoxic groundwater, since arsenite is the dominant form of arsenic when pH is close to neutral. Various oxidants used for the conversion of arsenite into arsenate are as follows:

- Active chlorine oxidizes As in deionized water completely when the initial concentration is >300µg/l.
- Chlorine dioxide results in 86% oxidation in ground water after an hour of contact with some metals assisting to catalysis.
- Monochloramine results in 60% oxidation in ground water after around 18 hours.
- Hypochlorite completely oxidizes As(III) in ground water if the concentration is 500µg/l.
- Hydrogen peroxide's oxidizing efficiency in fresh water and sea water increases when the pH increases to 10.3.
- Potassium permanganate completely oxidizes As(III) in ground water after a minute.
- Photocatalytic oxidation efficiently oxidizes As(III) in ground water. UV dose of 2000 mJ/cm² gives an 85% yield that shows increase in UV dose leads to an increase in efficiency.
- Insitu oxidation refers to the pumping of oxygenated water into ground water aquifer in order to reduce the As concentration to <10µg/l [31].

(ii) Coagulation and Flocculation

Coagulation refers to the neutralization of the forces that keep the colloids apart, thus destabilizing them. Positively charged coagulants such as $Al_2(SO_4)_3$ and $FeCl_3$ reduces the negative charge i.e., zeta potential of the colloids resulting in collision and thus, enlargement.

Flocculation, flocs (large mass particles) are bridged by the action of polymers and binding of particles form large clumps. Polymer chain segments absorb on different particles and aid in particle aggregation. Particles can be destabilized either by bridging or charge neutralization as an anionic flocculant reacts with positively charged suspensions [32,30].

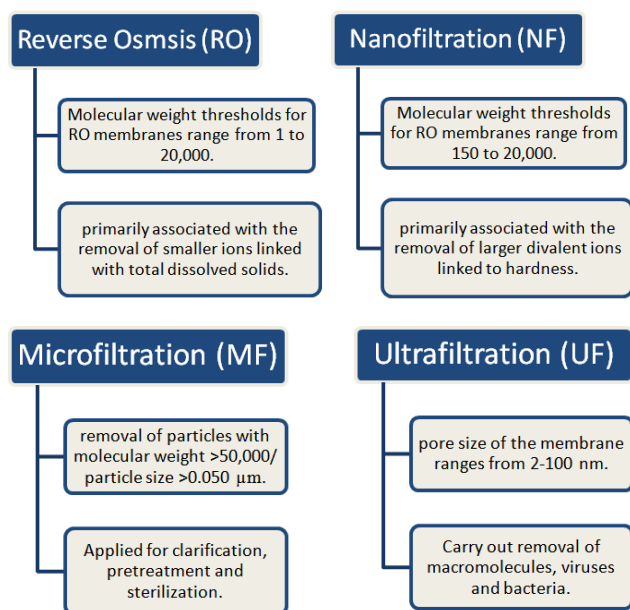
The given processes and action of chemicals on As leads to conversion of dissolved As into an insoluble solid which is precipitated whereas the soluble As species are brought to metal hydroxide phase and undergoes co-precipitation followed by filtration/sedimentation of the solid. Coagulants such as Ferric Chloride, Alum, Zirconium (IV) chloride, etc are used for the removal of As.

The viability of this process is low due to the formation of As concentrated sludge as an end result which arises the issue of further pollution as there is a lack of affordable/cheap treatment methods for the sludge.

(iii) Membrane filtration

Various selectively permeable synthetic membranes are available, the membrane is structured with billions of pores that are selective in nature such that they allow some molecules pass through, whilst others are excluded or rejected. In order for water to pass through the membrane, a pressure differential between the feed and permeate sides is needed and the force required is dependent on the pore size. There are four kinds of membrane processes that fall under the categories of low and high pressure driven processes, such as microfiltration (MF) and ultrafiltration (UF) under low pressure membrane processes (5-100 psi) and reverse osmosis (RO) and nanofiltration (NF) under high pressure membrane processes (50-150 psi) [5,30,34].

- Ozone oxidizes complete As present in ground water rapidly (within 20 minutes) whereas oxygen takes up to five days for 57% conversion.



(iv) Adsorption

Removal of a substance from a liquid of gaseous phase is carried out by a solid in the process of adsorption. The existence of Van der Waals forces and electrostatic forces between the molecules of the adsorbate and the atoms constituted in the adsorbent surface give rise to the process of physical adsorption. The course of adsorption includes division of a substance from one stage joined by its gathering or fixation at the outer layer of another. Adsorption has been accounted for as the most broadly involved procedure for arsenic expulsion due to its few benefits including somewhat high arsenic expulsion efficiencies, simple activity, also, dealing with, cost-adequacy, and no ooze creation. Be that as it may, adsorption of arsenic firmly relies upon the framework's fixation and pH. At low pH, arsenate adsorption is leaned toward, while for arsenite, most extreme adsorption can be acquired between pH 4 and 9. Additionally, debased water doesn't just hold back arsenic; it is generally joined by different particles, like phosphate and silicate, contending for the adsorption locales. Beside the framework's conditions, the viability of adsorption in arsenic expulsion can likewise be upset by the sort of adsorbent itself [33].

Iron and its mixtures have major areas of strength to absorb As. Iron documenting channels can eliminate arsenite from aqueous solutions with a proficiency of >99% to levels underneath the necessary limit of 10 µg/l with an absence of maintenance for quite some time (8 months).

Activated alumina has been utilized for specific adsorption of As(V) and its adsorption limit can be all around as high as 0.112 gm of As/gm. The ideal pH an incentive for amplifying adsorption of arsenic on activated alumina is acidic (pH-6). Various other adsorbents for the expulsion of As incorporate activated carbon, iron filings blended in with sand, goethite and gibbsite, lignite, Ganga sand, feldspar, ferrihydrite and hydrous ferric oxides, hematite, kaolinite-humic corrosive buildings, actuated red mud and red mud treated with seawater (Baux-sol), zeolites and other wastes generated from industries [5].

(v) Ion Exchange

Ion exchange is a physical/chemical process that involves exchanging ions retained electrostatically on the

surface of a solid for ions of similar charge in a solution. The exchange of cations or anions between the pollutants and the exchange medium removes ions from the aqueous phase. The matrix is a cross-linked polymer skeleton that these resins are built on. This matrix is typically made out of polystyrene that has been cross-linked with divinylbenzene. There are mainly four types of resins depending upon the attached charged functional group to the matrix by covalent bonding: Strongly acidic, weakly acidic, strongly basic, weakly basic [34].

Strong base resins are commonly employed for arsenic treatment because dissolved arsenic is frequently in an anionic state, while weak base resins are effective across a narrower pH range. The technology's effectiveness is affected by a range of impurities; organics, suspended particles, calcium, and iron, for example, can create fouling in untreated water. As a result, it's usually used on groundwater and drinking water, which are less likely to have fouling pollutants. Ion exchange capacity is a measure of the number of exchange sites, similar to adsorption capacity, and is commonly measured in milliequivalents (meq) per mL (wet volume, including pore spaces). Because of partial regeneration and contaminant leakage, the operational capacity of resins under environmental circumstances is always less than the quoted exchange capacity [5,34].

16. Nanomaterial Based Arsenic Removal

Bioremediation, ion exchange, membrane filtration, and adsorption are just a few of the arsenic removal technologies that have been employed. These chemical procedures are easy, but they have the drawback of producing vast volumes of hazardous sludge, which must be treated before being disposed of in the environment. Adsorption is the most efficient and environmentally beneficial way for removing arsenic among these technologies because of its ease of use, economic effectiveness, and environmentally benign procedure [35].

Nanoscience and nanotechnology advancements have paved the path for the creation of different nanomaterials for polluted water cleanup. Nanoparticles have received substantial environmental interest as new adsorbents of pollutants such as heavy metals and arsenic from aqueous solutions due to their high specific surface area, high reactivity, and high specificity [30]. A nanomaterial possesses special biological, physical, and chemical properties due to its extreme modification. Engineered magnetic nanoparticles (MNPs) offer a lot of potential in therapeutic, biological, and environmental applications because of their numerous unique characteristics [35]. For the treatment of arsenic-contaminated water, carbon nanotubes and nanocomposites, titanium-based nanoparticles, iron-based nanoparticles, and other metal-based nanoparticles are among the most utilised and researched nanoparticles.

16.1. Carbon Nanotubes

The carbon nanotubes (CNTs) are cylindrical tubes made from graphene sheets that have been seamless rolled into tubes. They are available in single-walled (SWCNT)

and multiwall carbon nanotubes (MWCNT), with the latter being the more affordable option. They are highly suited for numerous applications due to their unique qualities such as high aspect ratio, exceptional mechanical, electrical, and thermal capabilities. CNTs also have excellent sorption capabilities for a variety of organic and inorganic ions. After treatment with oxidants, CNTs have been shown to be efficient in the adsorption of a variety of organic compounds and metal ions [30].

As per a project carried out by Addo S and Mitra S, the ability of iron oxide-MWCNT (Fe-MWCNT) to remove arsenic was compared to that of multiwall carbon nanotubes (MWCNT) and functionalized multiwall carbon nanotubes (f-MWCNT). Fe-MWCNT has a substantially greater adsorption capacity for arsenic for both As(III) and As(V) (1723 g g⁻¹ and 189 g g⁻¹ respectively) than MWCNT (10 g g⁻¹ and 23 g g⁻¹ respectively) and f-MWCNT (3 g g⁻¹ and 9 g g⁻¹ respectively). Thus, it was concluded that MWCNT might be used as a platform for generating potentially effective environmental clean-up technologies if the surface is modified appropriately [36].

16.2. Titanium Based Nanoparticles

To improve the adsorption characteristics of TiO₂, many nanostructures with varied compositions have been produced, such as homogeneous structures (hydrous titania, crystalline and granular) or heterogeneous structures (Ce-Ti, Zr-Ti, and Fe-titania, among others). Because of their high surface area to volume ratio, corrosion resistance, non-toxicity, and stability, TiO₂ based nanomaterials/nanocomposites demonstrated greater affinity for both forms of arsenic [31].

When 1ppm arsenite solution is treated with mixed impregnated chitosan bead (MICB) (Al₂O₃ TiO₂) under UV light, arsenite is entirely changed into arsenate after 15 minutes, according to a kinetic study.

Filtration-steam hydrolysis was used to create a TiO₂-carbon nanotubes network filter. Because the titania-CNT filter has a wide surface area, it has a higher adsorption capacity for both inorganic and organic forms of arsenic. Arsenite and arsenate adsorption on the constructed filter followed pseudo first order kinetic processes, with the rate of reaction being 127 times faster on TiO₂-CNT filter than granular titania [33].

In the presence of visible light, the removal efficacy of core shell and solid spherical nanostructures of V₂O₅-TiO₂ nanocomposites for As (III) was also compared. Due to its huge surface area, the core shell nanostructure has a higher removal capacity for arsenite than the solid spherical complex [30].

The pH of aqueous media affects the adsorption of both inorganic and organic forms of arsenic on titania-based materials [37].

16.3. Ion Imprinted Based Magnetic Nanoparticles

For arsenite (As(III)) and arsenate (As(V)) adsorption, arsenic imprinted magnetic nanoparticles (IIP) were manufactured utilising a molecular imprinting approach in the presence of iron oxide (Fe₃O₄). As a functional

monomer, N-methacryloyl-(l)-cysteine (MAC) was utilised [35].

According to a research done by Turkmen *et al.* [35], IIP-As (III) and IIP-As(V) are homogeneous nanocomposites with average dimensions of 30–40 nm. The adsorption capacity for As(III) was 76.83 mg/g and for As(IV) was 85.57 mg/g (V). In a pH range of 4–8, IIP nanoparticles demonstrated significant As(III) and As(V) removal capabilities. The ability of the IIP magnetic nanoparticles adsorbents to be recovered and successfully regenerated by simple magnetic-based separation, as well as the ability to withstand intervention by other ions, demonstrate their promise as arsenic removal adsorbents in aqueous and wastewater samples [35].

16.4. Iron Based Nanoparticles

Adsorption on iron-based (IB) is a newer treatment method for arsenic removal, however it is regarded one of the most promising. As a result, a variety of products have been developed, including iron coated sand, modified iron, and iron oxide based adsorbents oxy-hydroxides such as amorphous hydrous ferric oxide (FeOOH), goethite (α -FeOOH), hematite (α -Fe₂O₃), iron-based LDHs, zero-valent iron nanoparticles, iron-doped activated carbon, biocomposite materials, iron-doped polymers and iron-doped mineral oxides. Under natural pH settings, IB media has a considerable affinity for arsenic, according to several studies conducted with this medium [38].

According to preliminary study done by Chiavola *et al.* [39], the limit of As content for drinking water was reached after just 300 minutes, indicating a very rapid rate of As adsorption.

Mineral oxides doped with iron oxy-hydroxide are abundant and inexpensive adsorbents and yield substantial results in immobilizing As present in water [38].

Because of their capacity to remove arsenic five to ten times more efficiently than their micron-sized equivalents, iron oxide nanoparticles are becoming increasingly popular in the field of arsenic removal.

17. Phytoremediation

It covers a range of plant-based remediation techniques such as phytostabilisation, phytoextraction, phytoimmobilisation, rhizofiltration and phytovolatilization among which phytoextraction is most popular due to its eco-friendly, cost effective nature having less negative affect towards surrounding biodiversity [40,41,42,43]. In phytoextraction process, arsenic is extracted from soil or water by roots and transported to above parts of plant, which is further harvested by conventional techniques and can be discarded or recycled. This technique requires plant species which can be cultivated easily, grow rapidly and produce significant biomass, and can accumulate high concentration levels of contaminants. Plants that accumulate more than 0.1% of a contaminant are called hyperaccumulators. In phytoremediation, several factors plays an important role i.e redox conditions of soil, arsenic speciation in soils, and the presence of phosphates etc. [44]. Phytostabilisation is long duration process in which native plant entities having arsenic tolerance are used to

reduce the conflict with local ecosystem [45]. In rhizofiltration method aquatic macrophytes and macro-algae has been used for filtration of contaminated water including, storm water, and other effluents [46]. Phytovolatilisation is another process in which volatile arsenic transpires or diffuse out of their roots, leaves, or stems.

18. Conclusion

Several research works done has led to a big advancement in our approach regarding As removal from drinking water. For the aqueous removal of arsenic contaminants, nanomaterial's offer a very effective, selective, and consistent option. But at the same time strategies for mass-production of nanomaterial's without compromising the characteristics of the substances at manufacturing levels are critical. Nanomaterials, among the several available technologies, have a particularly high effectiveness for the removal of arsenic, which has sparked attention in the educational and manufacturing sectors. More research and development are needed before the materials may be recommended for the successful manufacture of nanoparticles soon.

An immediate need for periodic monitoring of As levels in affected areas and its vicinity and provisions for adequate measures to provide relief to the population suffering is the need of the hour. Arsenic contamination has led to severe damages to life and efficient strategies and programs, prohibition of practices that contributes towards increase in As concentrations are a must to prevent further damages in the future.

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