

“Pure water is the world’s first and  
Foremost medicine”

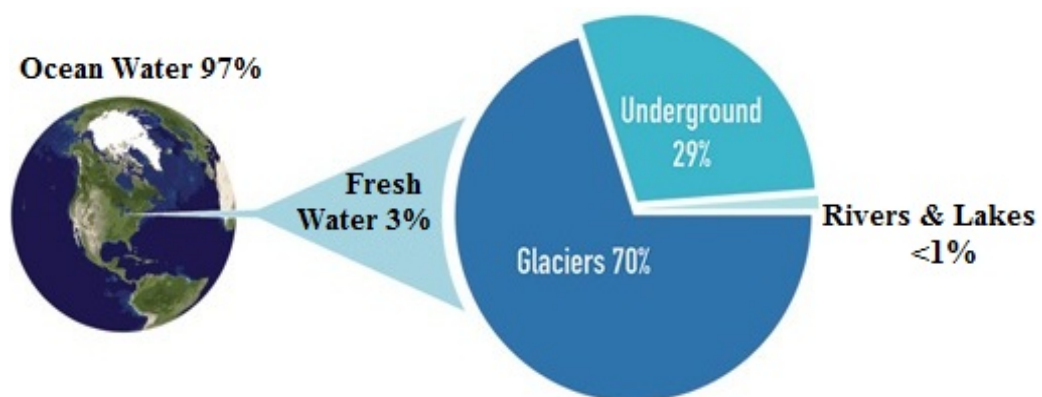
- Slovakian Proverb

## 1.1 General Aspect

Water is the driving force of all the nature. In some organisms, 90% of the total body weight is due to the presence of water. In human being, water is composed of the major portion of many organs such as brain and heart (73%), lungs (83%), skin (64%), muscles and kidneys (79%), and bones (31%) [1]. A mere 2% drop in the water level of the body can cause lose in alertness of brain and the body to feel fatigued [2].

The vital roles played by water to keep us all going are-

- Serves as a vital nutrient to the building blocks of organisms i.e., the cell.
- Maintains the internal body temperature by means of sweating and respiration
- Helps in the metabolism of carbohydrates and proteins, etc. and transport many essential particles via the bloodstream
- Helps in the waste disposal of body in the form of urin
- Helps in absorbing shocks of brain, spinal cord, and fetus
- Forms saliva
- Water acts as lubricants for the joining of different parts and helps the brain in preparing many hormones and neurotransmitters.
- Takes part in all the reactions occurring inside the body



**Figure 1.1** Water distributions on earth’s surface

Water covers most of the earth's surface (~71%) and the major part of it is present in oceans. Rest of it is present in different forms in the air (as water vapor), rivers and lakes, icecaps and glaciers, ground as soil moisture and in aquifers [3]. Water is never sitting still. Due to the water cycle, our planet's water supply is constantly moving from one place to another and from one form to another.

### **1.2 Fresh Water Scarcity and its global impact**

Out of all the water on earth, surprisingly most of them are not useful for drinking purposes, being saline in nature; fairly 2.5–2.75% is fresh and out of which very small fraction is available for useful purpose. In addition to scarcity, fresh water is not evenly distributed [4]. Furthermore, due to different anthropogenic activities, the fresh water sources are reducing day by day [5]. Lack of the fresh water sources harm the environment in several ways like loss of many species, increased salinity, nutrient pollution, loss of floodplains etc.

The lack of drinkable water is measured in terms of Falkenmark Water Stress Indicator [6]. According to it, if the annual water supplies per person per year are less than 1,700 cubic meters, then the respective country/region is said to experience “water stress”. If the value drops below 1,000 cubic meters, then the later faces “water scarcity” [7]. At present, around one fifth of the world's population is affected by water scarcity and it has been identified as one of the top three global risks by industry, government, civil society and academic institutions [8]. One of the major impacts of fresh water scarcity is that human population has become largely dependent on groundwater sources for consumption, agriculture, energy production and other uses.

### **1.3 Use of Ground Water Sources and its Consequences**

Groundwater is pooled below the earth's surface and can provide a usable quantity of water through wells or springs. Until recent history, ground water was not a highly utilized resource. But availability of the conventional sources decreased tremendously due to pollution, climate changes or increased demand. Changes in knowledge, technology and funding have allowed for focused development into abstracting water from groundwater resources. The risk of microbial contamination and turbidity are much lesser in ground water than surface water. Today, groundwater supplies cover nearly half of all drinking water worldwide [9]. Groundwater has

become crucial for the livelihoods and food security of 1.2 to 1.5 billion rural households in the poorer regions of Africa and Asia [10].

But the risk involved in using groundwater is that it has exposed human population to different harmful contaminants like heavy metal ions, arsenic, microbial, fluoride, etc. [11,12]. Arsenic, heavy metal ions like iron, lead, copper, etc., are mostly prevalent in groundwater through different natural processes and sometimes due to different anthropogenic activities. The later includes industrial effluents, use of fertilizers, pesticides and herbicides in crop fields etc. [13]. They can cause these metals to pass through the earth's surface and contaminate the ground water. According to a study by Central Ground Water Board (CGWB), in India, 276 districts have been found to be dependent on groundwater contaminated with fluoride, 387 districts are with nitrate and another 87 districts have high levels of arsenic. Moreover, impermissible limits of heavy metal ions in the groundwater of 113 districts across 15 states are also found [14]. The health threat due to those harmful toxic contaminants, especially Arsenic in the groundwater is most notorious.

Water for human consumption is derived from a variety of sources: surface water, groundwater and rainwater, depending on local availability. These sources are variable in terms of arsenic risk. Among these, groundwater has the highest concentration of arsenic [15]. Today, the people of developing countries are mostly affected by heavy metal contaminations including Arsenic as they have become incredibly dependent on groundwater for their day-to-day use.

### ***1.3.1 Chemistry of Arsenic***

Arsenic (As) is an element of group V(b) of the periodic table with atomic number 33. It is a brittle crystalline solid with silvery grey colour. It has an atomic mass of 74.9 amu; specific gravity 5.73 g/cm<sup>3</sup>; m.p. 1090 K (at 28 atm); b.p. 887 K and vapor pressure of 1 Pa at 553 K. Due to its high atomic density and chemical activities, it is considered as heavy metal. It readily undergoes multiple redox reactions [16]. It is widely distributed in the environment (in organic as well as inorganic forms) including plant and animal showing different degrees of toxicity and usefulness [17]. The wide range of chemical nature of this element is attributed to its hard-soft acid/base behavior in its different combined/oxidation state.

### 1.3.1.1 Arsenic Species in Groundwater

Arsenic occurs naturally in water in many parts of the world. Arsenic occurs in both inorganic and organic forms in natural waters. Inorganic arsenic is the result of dissolution from the respecting mineral phase, such as arsenolite ( $\text{As}_2\text{O}_3$ ), arsenic oxide ( $\text{As}_2\text{O}_5$ ) or realgar ( $\text{As}_2\text{S}_2$ ) etc.; It may be present in different oxidation states (-3, 0, +3, and +5), depending upon the pH and redox potential of the soil from where it is released [18-20]. But  $\text{As}^0$  and  $\text{As}^{3-}$  are rare in aquatic environments.

Complex arsenic organic compounds such as tetramethylarsonium salts, arsenocholine, arsenobetaine, dimethyl(ribosyl)arsine oxides and arsenic containing lipids are found in the marine environment. Organic arsenic species occur in natural waters as a result of organo-arsenical pesticides use, as well as through the biomethylation mechanisms of micro-organisms [21].

Distribution of arsenic in ground water varies w.r.t. depth of different aquifers. In a study, Bhusal et al. has reported availability of arsenic at different depths in Makar VDC of Nawalparasi District, Nepal. Water from a depth of 30-70 feet was found to have arsenic in toxic level (>50 ppb) while the horizons of aquifers shallower or deeper than this depth were reported to be safe [22]. In an another study, a depth vs arsenic concentration in Bariswan village, similar results were found and highest concentration (0.062 mg/L) was found in 19 m depth which reduces to 0.013 mg/L at 62 m depth and further to 0.002 mg/L at 200 m below the ground. Again dug wells (<10 m) were found to exhibit low arsenic load (<0.01mg/L) [23].

### 1.3.1.2 Sources of Arsenic Contamination

Arsenic in groundwater occurs as a result of natural geochemical processes or pollution from human activities. Arsenic is naturally present in different types of rocks and sediments as listed in table 1.1. Those rocks and sediments form the ground water aquifers.

**Table 1.1** Arsenic in rock and sediment [24]

Rock or sediment type	Arsenic Content (mg/kg)	
	Average	Range
Sandstone	4.1	0.6 – 120

Limestone	2.6	0.4 – 20
Granite	1.3	0.2 – 15
Basalt	2.3	0.2 – 113
Alluvial sand (West Bengal)	2.9	1.0 – 6.2
Alluvial silt (West Bengal)	6.5	2.7 – 15
Loess (Argentina)	-	5.4 – 18

Arsenic found in rock or sediment is usually immobile. It is triggered to groundwater via certain geochemical processes and conditions [25]. There are mainly four geochemical processes which trigger the release of arsenic from aquifer rocks or sediments into the groundwater as shown in table 1.2.

Arsenic has the uniqueness of sensitivity to mobilize at the groundwaters pH (6.5–8.5) as compared to other metalloids and oxyanion-forming elements such as Se, Sb, Mo, V, Cr, U, Re etc., under oxidizing as well as reducing conditions [26, 27]. A key and complex role is played by iron oxyhydroxide phases in controlling the mobility and fate of arsenic in groundwater [28].

**Table 1.2** Natural geochemical processes of Arsenic release [26]

Process	Characteristic geochemical conditions	Generalized geological environment	Countries	Additional information
<b>Reductive Dissolution</b>	Anoxic groundwater; low levels of dissolved O <sub>2</sub> , NO <sub>3</sub> <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> ; pH~7; high Fe, high Mn, NH <sub>3</sub> and bi-carbonate.	Holocene sediments deposited in floodplain areas of rivers draining geologically recent mountain chains.	Bangladesh, India, Vietnam, China, Cambodia, Hungary	64% of known occurrences of Arsenic is due to this process.
<b>Alkali desorption</b>	Oxic groundwater; pH ~ 8; low levels Fe. Possible elevated levels of other toxic ions such as F <sup>-</sup> , B, Mo, Se.	Alluvium and bedrock aquifers.	Argentina, USA, Spain, China	May affect large areas.

<b>Sulfide oxidation</b>	Oxic groundwater; pH < 7 (Sometimes extremely acidic); high levels of SO <sub>4</sub> <sup>2-</sup>	Areas where mineralization has taken place	Ghana, Thailand, USA	Usually localized, may be associated with lowering of water table
<b>Geothermal</b>	High temperature groundwater; high chloride (Cl <sup>-</sup> )	Areas of geothermal activity, volcanic rocks	Chile, China, Nicaragua	Usually localized

Anthropogenic sources of arsenic contamination in groundwater include industrial spillage, mining wastes, agricultural herbicides, pesticides, etc. [13]. There are several industrial sources of arsenic that elevate the naturally occurring levels. One source is the smelting of ores that contain arsenic trioxide [29]; disposal of fly ash is another one [30]. Moreover, arsenic and its compounds have been used extensively as herbicides and insecticides. Therefore, agricultural drainage waters from treated crop fields may also contribute to higher arsenic levels [31]. Major contribution of arsenic by industry occurs through antifungal wood preservatives. On the other atmospheric arsenic are mainly contributed from mining and metal industries [18, 32].

Surface water is also arsenic contaminated to some extent by human activities (e.g. mining) or natural processes. Natural processes such as soil erosion, mineral leaching and weathering are mainly responsible for introducing arsenic into surface water [33]. In case of arsenic contamination in surface waters, the contribution of arsenic-enriched geothermal water is very significant [34].

There are very few literatures available quantifying the extent of arsenic release to environment due to natural or anthropogenic sources. A table showing population of different countries exposed to arsenic due to natural/anthropogenic sources is shown below-

**Table 1.3** Regionwise population of arsenic affected people vs source of arsenic [29]

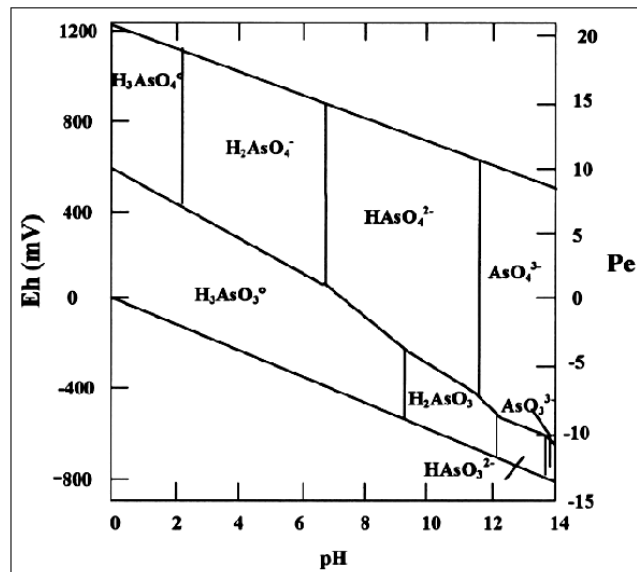
Country	Potential exposed population	Concentration (µg/l)	Source
Bangladesh	30,000,000	<1-2,500	Natural; alluvial/deltaic

			sediments with high phosphate, organics
West Bengal	6,000,000	<10-3,200	Similar to Bangladesh
Vietnam	>1,000,000	1-3.050	Natural; alluvial sediments
Thailand	15,000	1->5,000	Anthropogenic; mining and dredged alluvium
Argentina	2,000,000	<1-9,900	Natural; loess and volcanic rocks, thermal springs; high alkalinity
Brazil	-	0.4-350	Gold mining
Hungary, Romania	400,000	<2-176	Natural; alluvial sediments, organics
Spain	>50,000	<1-100	Natural; alluvial sediments
Greece	150,000	-	Natural and anthropogenic; thermal springs and mining
United Kingdom	-	<1-80	Mining; southwest England

### 1.3.1.3 Arsenic Species at Different pH

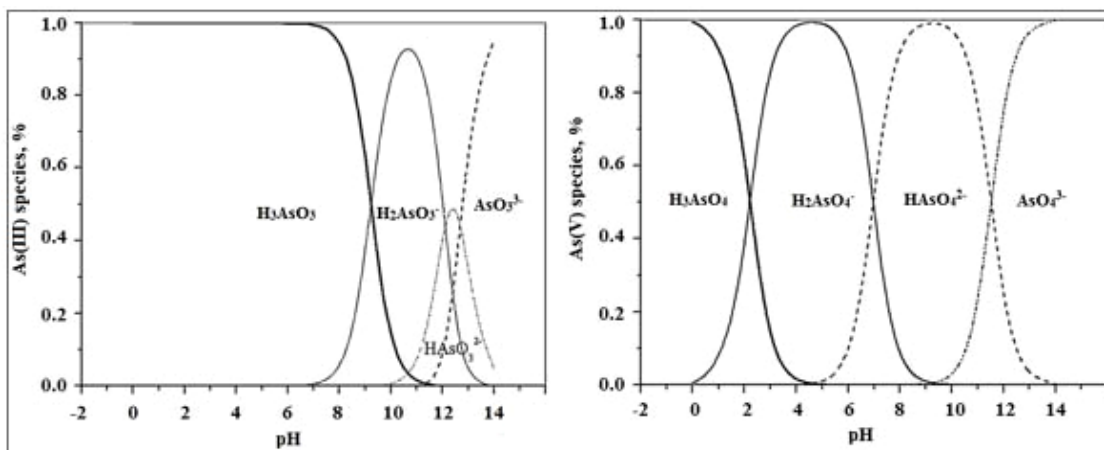
Dominant arsenic species are a function of pH and redox potential (Eh). Several forms of arsenic undergo acid-base equilibrium. Thus, different major and minor arsenic species are present depending on the pH condition. Figure 1.2 shows the availability of arsenic species in different oxidations states on the basis of pH and Eh conditions [35].

At moderate or high redox potential, arsenate is the thermodynamically stable form and is found as a series of pentavalent (arsenate) oxyanions, viz.  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$ . Under oxidizing conditions,  $\text{H}_2\text{AsO}_4^{1-}$  is the dominant species at low pH (between pH 2.2 and 6.9), while at higher pH,  $\text{HAsO}_4^{2-}$  becomes dominant. Arsenic may be present as  $\text{H}_3\text{AsO}_4^0$  and  $\text{AsO}_4^{3-}$  respectively in extremely acidic and alkaline conditions. Under most reducing (acid and mildly alkaline, in anaerobic groundwaters.) conditions and lower redox potential, the trivalent arsenite species ( $\text{H}_3\text{AsO}_3$ ) predominate which is the most common in ground water [15, 36].



**Figure 1.2** Redox potential (Eh)-pH graph for arsenic-water system

Following figure shows the % availability of different As(III) and As(V) species at different pH ranges [37]



**Figure 1.3** As(III) and As(V) species present at different pH conditions

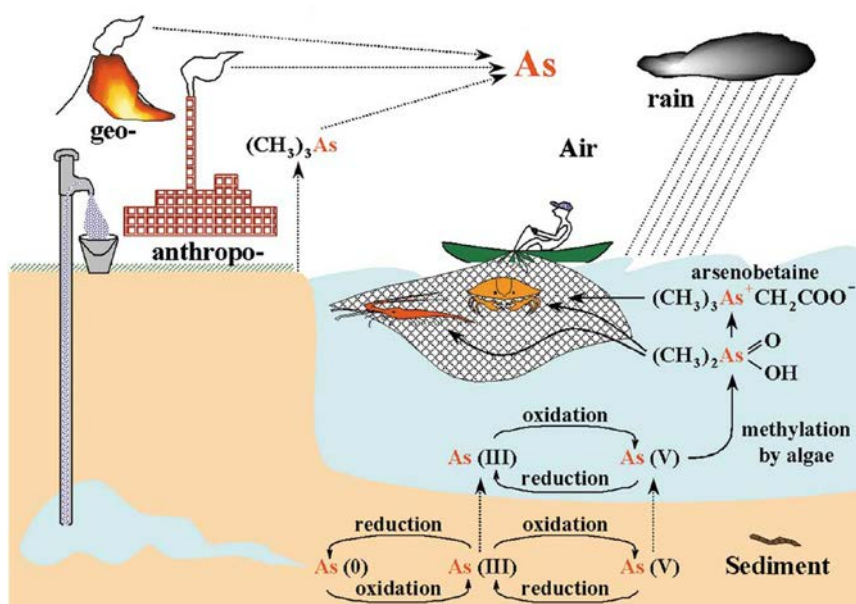
Under anoxic reducing conditions (e.g., subsurface waters, reduced sediments), arsenic primarily exists as arsenite, whereas arsenate is prevalent in aerobic oxidizing environments, such as surface waters. As(III) is more mobile and hence less available to remove by precipitation, sorption or other purification techniques. Moreover, it remains uncharged under normal pH conditions. Hence, it is very difficult to remove As(III) as compared to other oxidation states and often requires pre oxidation step [38, 39].



### 1.3.2 Drinking Water Specifications for Arsenic

Arsenic in drinking water may pose acute as well as chronic toxicity. Acute toxicity includes vomiting, abdominal pain and diarrhoea followed by numbness and tingling of the extremities, muscle cramping and death, in extreme cases [40, 41]. Prolonged Intake of inorganic arsenic causes chronic arsenic poisoning known as arsenicosis. Organic arsenic compounds are less harmful and are rapidly eliminated by the body. The major amount of higher doses of arsenic intake to human occurs through the consumption of groundwater containing naturally high levels of inorganic arsenic, food prepared with this water and food crops irrigated with high-arsenic water sources [42]. Therefore, it is very much necessary to treat the water to reduce the arsenic level in water before using it in drinking purpose, particularly, in areas with naturally high levels of arsenic in groundwater.

Adverse effect of arsenic contamination even in very less amount (50  $\mu\text{g/L}$ ) on intellectual function of children's in Bangladesh was well reported [43]. On the basis of studies on highly exposed populations in Taiwan and elsewhere, the U.S. Environmental Protection Agency (EPA) has reduced the maximum contaminant level (MCL) standard for arsenic in drinking water from 50  $\mu\text{g/L}$  to 10  $\mu\text{g/L}$ . The European union countries also follow the standard of 10  $\mu\text{g/L}$  of arsenic as the maximum concentration limit. Now, WHO provisional guideline of 10  $\mu\text{g/L}$  has been adopted as the drinking water standard.



**Figure 1.4** Geochemical cycle of arsenic

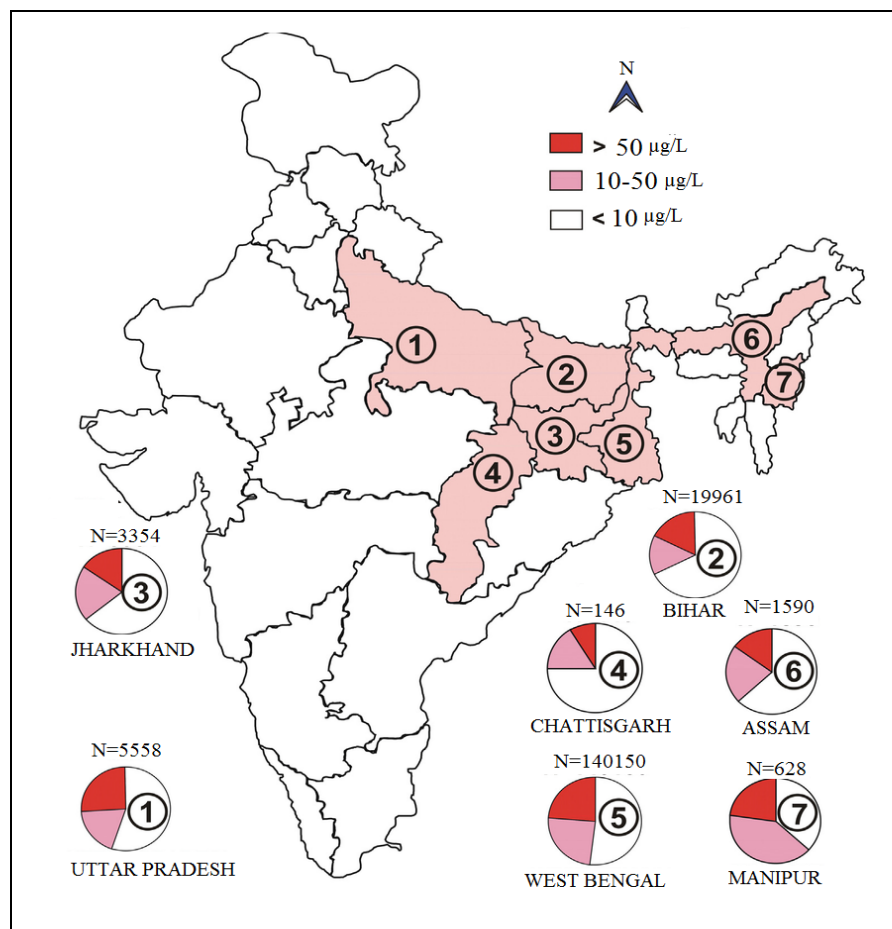
However, the guideline values recommended are not mandatory limits. They are intended to be used in the development of risk management strategies on the basis of national or regional standards in the context of local or national environmental, social, economic and cultural conditions. Countries like Bangladesh and China still follow the earlier WHO guideline of 50 µg/L as their standard. In a study by USEPA on arsenic concentration associated with an excess life-time skin cancer risk in China of  $10^{-5}$  was calculated to be 0.00017 mg/L. But, this value may overestimate the actual risk of skin cancer owing to the possible dose-dependent variations in metabolism that could not be taken into consideration and also it is far below the practical quantification limit. Therefore, the less protective guideline is adopted [44]. The Bureau of Indian Standard (BIS) followed the same limit of arsenic standard as provided by WHO [45].

**1.3.3 Global Overview of Arsenic Contamination in Ground Water**

Millions of people in several countries are exposed to high levels of Arsenic via intake of groundwater. According to Shankar et al. [46] groundwater in 70 countries around the globe is contaminated with arsenic. In a study about 150 million people around the world are estimated as arsenic affected with an increasing prospect of more and more contaminated areas are continuously discovered [47]. Drinking-water poses the greatest threat to public health due to presence of arsenic. Inorganic arsenic is naturally present in groundwater at elevated concentrations in many countries like Argentina, Chile, China, India (West Bengal), Mexico, the United States of America, and Bangladesh [40]. In Bangladesh, approximately half of the total population is at risk of drinking arsenic-contaminated water from tube wells [48].

Chronic As toxicity in humans has been documented in many countries worldwide, particularly in countries of Southeast Asia [49]. The major arsenicosis affected areas have been reported in large deltas and/or along major river basins across the world [26]. An estimated population on arsenic exposure for some countries are: Bangladesh- 35 to 57 million; China- 5.6 million; India- 5 million; Nepal- 550,000 to 3.19 million; Vietnam- >1 million; Chile- 437,000; Mexico- 400,000; Hungary-Romania- 400,000; Argentina- 200,000; and Taiwan- 10,000 [50].

**1.3.3.1 Scenario of Arsenic Contamination in India**



**Figure 1.5** Arsenic endemic states in India

In India, the first groundwater arsenic contamination was explored in 33 villages from four districts of West Bengal in 1983. Latter on, the number increased to 3417 in nine districts, in 2008 [51]. Since then several areas in states like Jharkhand, Bihar, Uttar Pradesh, Assam, Manipur, Chhattisgarh, etc. have found to be exposed to drinking arsenic contaminated hand tube-wells water far above the WHO guideline [52].

Ghosh et al. [53] has presented an epidemiological study of arsenocosis in india (Table 1.4). During the study, West Bengal was found to have major brunt of the problem, with almost 12 districts in the grip of deadly disease. Other states in the Ganga/Brahmaputra plains were also reported to be in alarming levels of arsenic in ground water. Following table shows the arsenic contaminations and arsenocosis problems faced in different states of India till 2006.

**Table 1.4** Epidemiological status of arsenicosis in various states of India

Parameters	West Bengal	Bihar	Jharkhand	Assam	Manipur	Uttar Pradesh
Total area (sq. km)	89,193	94,163	1,549	78,438	22,327	2,38,000
Total population (millions)	68	8.2	1	26.6	23.8	166
Total Districts	18	38	22	23	9	70
Water sample analyzed	1,05,000	19,961	3,832	241	584	4,818
Samples (%) > 10 µg/L	51	32.7	32.28	42.3	64.72	45.48
Samples (%) > 50 µg/L	25	17.75	13.44	19.1	41.27	26.51
Districts affected	9	--	--	2	2	3 (out of 3 surveyed)
Population affected (millions)	42.7	--	--	--	--	--
Area affected (sq. km)	38,865	--	--	--	--	--
Blocks affected	74	36	3 (out of 9 surveyed)	2	2	7 (out of 10 surveyed)
Villages affected	2,700	235	68 (out of 115 surveyed)	27	--	9 (out of 122 surveyed)
Number of people drinking contaminated water (millions)	6	--	--	--	--	--
Arsenicosis cases/ People screened	10,134/ 96,000 (10.56 %)	457/ 3,012 (15.13 %)	71/ 562 (12.63 %)	--	--	154/ 989 (15.5 %)

In West Bengal, the majority of registered cases are from the district of Nadia, and the maximum number of deaths due to arsenicosis is from the district of South 24 Paraganas. In a recent survey, out of 10469 participants from Naida, prevalence rate of arsenicosis was found to be 15.43%. Out of 0.84 million people suspected to be

exposed to arsenic, 0.14 million people are estimated to be suffering from arsenicosis in the district. Highest level of arsenic in drinking water sources was found to be 1362  $\mu\text{g/l}$ , and in 23% cases it was above 100  $\mu\text{g/l}$ . Chronic lung disease was found in 207 (12.81%) subjects among cases and 69 (0.78%) in controls. Peripheral neuropathy was found in 257 (15.9%) cases and 136 (1.5%) controls [54]. Mazumder et al. have also critically reviewed different chronic arsenic toxicity occurring in West bengal, India [55].

### *1.3.3.2 Arsenic Contamination in Assam*

In northeastern India, arsenic has been detected in many districts (more than 20) of Assam and in many of them, arsenic concentration exceeds the permissible limit [56]. In Brahmaputra valley, very high concentration of arsenic was observed in Jorhat (Titabor, Dhekorg rah, Selenghat and Mariani Block), Golaghat district (Podumoni Block), Lakhimpur (Boginodi, Lakhimpur Block) Nalbari and Nagaon districts. In Jorhat district, the contamination of arsenic was highest in the range of 194-657  $\mu\text{g/L}$  [57]. In the Barak Valley also, people from Cachar and Karimganj districts are reported of using groundwater with high arsenic-contaminations (max. 350  $\mu\text{g/L}$ ). 66% of tubewells in those two districts have arsenic concentration above 10  $\mu\text{g/L}$  and 26% tubewells have arsenic above 50  $\mu\text{g/L}$  [58]. However, the problem of arsenic in groundwater and related health hazards in Assam is yet to get enough systematic attention [59].

### *1.3.4 Toxicity of Arsenic to Human Health: Signs and Symptoms*

Arsenic is one of the most toxic and carcinogenic element. Dangerous arsenic concentrations in natural waters are now a worldwide problem and often referred to as a 20<sup>th</sup> –21<sup>st</sup> century calamity. Clinical effects of arsenic toxicity depend on the chronicity (acute or chronic) and its state (inorganic, organic, etc.). It causes several acute or chronic hazards to human health, physiology and other biological systems when exposed to high level. Patients frequently exposed to arsenic have a garlic smell to their breath and tissue fluids [60].

The immediate symptoms of acute arsenic poisoning include cholera-like gastrointestinal, symptoms of vomiting (often bloody) and severe diarrhoea (may be rice-watery, often bloody); these patients will experience acute distress, dehydration

(often), and hypovolemic shock. These are followed by numbness and tingling of the extremities, muscle cramping and death, in extreme cases [61]. It also can manifest many other signs and symptoms: Tachycardia, hypotension, and even shock, altered mental status, delirium, coma, seizures (acute encephalopathy) etc. [62].

Exposure to arsenic in drinking water for a long term can lead to a wide range of health problems, collectively known as '*Arsenicosis*' [63]. The risk of arsenic health effect increases with the increase in arsenic concentration and with duration of exposure. High concentration of arsenic in water for human consumption causes cancer of the bladder, lungs, skin, kidney, nasal passages, liver and prostate [64]. Arsenic in inorganic form (iAs) is the most toxic one and has been classified in group 1 as carcinogenic for human being by the International Agency for Research on Cancer. Besides its ability to form carcinogenic tumors, arsenic has been shown to be genotoxic [65].

Non-carcinogenic effects of arsenic include skin lesions, cardiovascular, neurological, pulmonary, endocrine (e.g., diabetes) and immunological disorders. Gastro-intestinal problems are also prevalent [66]. The vascular system may be affected and lead to Gangrene. The pulmonary effects range from mild bronchitis to bronchiectasis and Chronic Obstructive Pulmonary disease [25]. Arsenic exposed children have lower cognitive development. Arsenic exposed populations are always at higher risk of developing hypertension, hepatomegaly (abnormal enlargement of the liver), diabetes, conjunctivitis and heart attacks [25, 67].

#### *1.3.4.1 Mechanism of Arsenic Toxicity*

Toxicity of arsenic species depends greatly on its nature and oxidation state and solubility. Forms of arsenic that are more rapidly absorbed are more toxic while those more rapidly eliminated are less toxic. Arsenite and arsenate are highly soluble in water and are easily absorbed by the intestinal tract and muscle tissues. Hence they are more toxic than the organic counterpart. Arsenite has high affinity to the thiol group as compared to the arsenate. Therefore, arsenite is not easily eliminated from the body. Due to high affinity of the arsenite for thiol groups they can inhibit the thiol dependent enzyme system present in the body tissue proteins like keratin disulfides in hair, nails and skin. Arsenate inhibits ATP synthesis by uncoupling oxidative phosphorylation and replacing the stable phosphoryl groups.

#### 1.3.4.1.1 Trivalent Arsenic

Arsenite interferes with cellular longevity by allosteric inhibition of an essential metabolic enzyme pyruvate dehydrogenase (PDH) complex, which catalyzes the oxidation of pyruvate to acetyl-CoA by  $\text{NAD}^+$  [68]. With the enzyme inhibited, the energy system of the cell is disrupted resulting in cellular apoptosis. Low potassium levels in the cells increase the risk of experiencing a life-threatening heart rhythm problem from arsenic trioxide [69]. Arsenic in cells clearly stimulates the production of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). When the  $\text{H}_2\text{O}_2$  reacts with certain metals such as iron or manganese it produces highly reactive hydroxyl radicals [70]. Inorganic arsenic trioxide found in groundwater particularly affects voltage-gated potassium channels disrupting cellular electrolytic function resulting in neurological disturbances, cardiovascular episodes such as prolonged QT interval, neutropenia, high blood pressure, central nervous system dysfunction, anaemia, and death. At the level of the citric acid cycle, arsenic inhibits pyruvate dehydrogenase and by competing with phosphate, it uncouples oxidative phosphorylation, thus inhibiting energy-linked reduction of  $\text{NAD}^+$ , mitochondrial respiration, and ATP synthesis [71,72]. These metabolic interferences lead to death from multi-system organ failure, probably from necrotic cell death.

#### 1.3.4.1.2 Pentavalent Arsenic

Arsenate being similar in chemical behavior to that of phosphate, replaces the later in many reactions. It is able to form Glc-6-Arsenate and 6-arsenogluconate in vitro replacing phosphate; therefore, it has been argued that hexokinase can be inhibited leading to muscle weakness in chronic arsenic poisoning [72, 73]. In the glyceraldehyde 3-phosphate dehydrogenase reaction arsenate attacks the enzyme-bound thioester [72]. The formed 1-arseno-3-phosphoglycerate is unstable and hydrolyzes spontaneously. Thus, ATP formation in Glycolysis is inhibited while bypassing the phosphoglycerate kinase reaction. Moreover, the formation of 2,3-bisphosphoglycerate in erythrocytes might be affected, followed by a higher oxygen affinity of hemoglobin and subsequently enhanced cyanosis. Thus, by a variety of mechanisms, arsenate leads to an impairment of cell respiration and subsequently diminishes ATP formation [73].

### 1.4 Alleviation of Arsenic Toxicity by Conventional Techniques

Several conventional techniques have been adopted to mitigate the toxicity of arsenic occurring via ground water. Those include chemical and physical agents, boiling, distillation, reverse osmosis, water sediment filters (fiber and ceramic), activated carbon, pitcher and faucet-mount filters, solid block, ion exchange activated alumina altered water etc. Many oxidants or oxidant generating systems, including

manganese oxides, ozone, UV irradiation with (TiO<sub>2</sub>/UV) and many others have been tested for the oxidation of As(III). Driehau et al. has presented the oxidation and co-precipitation of As(III) into As(V) with the help MnO<sub>2</sub> [74]. Maliyekka et al. has immobilized manganese oxide over alumina to made stable oxidizing as well as removal system for As(III) [75]. Iron in different oxidation states is also well known to oxidize As(III) to As(V) followed by precipitation. Lee et al. [76] oxidized As(III) by ferrate [Fe(VI)] and performed arsenic removal tests using Fe(VI) as both an oxidant and a coagulant.

Biological oxidation is also reported to be advantageous in many respects over the conventional physicochemical treatment. Zouboulis et al. has presented biological processes for the oxidation and removal of dissolved ferrous cations and arsenic oxyanions in long-term experiments for different ground water sources and demanded it more economical and safer for the environment. The oxidation process was proved to be accelerated by the presence of certain indigenous bacteria [77]. Oxidation of ammonium, manganese and arsenic, followed by coagulation with FeClSO<sub>4</sub> was performed. During the process iron(II) and Mn(II) were biologically oxidized to corresponding insoluble oxides, NH<sub>4</sub><sup>+</sup> to nitrates while, As(III) is oxidized only and removed during subsequent coagulation and filtration treatment stage [78]. Another study analyzed the oxidization efficiency of As(III) in a mature biological manganese removal filtration. As(III) oxidation was found to accompany the removal of Mn<sup>2+</sup> in the filtration system [79].

Commercially available arsenic removal techniques include aeration, pre-chlorination, sedimentation etc. But they do not comply with the proposed maximum contaminant level for arsenic. However, chemically, energetically and operationally, these methods are often highly intensive. They are focused on large systems and therefore, require large investments in the form of capital, infrastructure and engineering expertise. Even, in the developed countries, it becomes very hard to establish state-of-the-art large conventional water and wastewater purification facilities due to the time and cost involved. Moreover, intensive chemical treatments and residuals resulting from treatment can further add to the problems of contamination and salting of fresh water sources. Thus, all those conventionally adopted methods have their own advantages and disadvantages which may also depend on the arsenic speciation in water. A comparison of the merits and demerits of those existing methods is listed in table 1.5.

**Table 1.5** Merits and demerits of the existing arsenic remediation techniques [80, 81]

Techniques	Merits	Demerits
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<b>Ion exchange</b>	high efficiency, high removal capacity and fast kinetics	low selectivity in the presence of other competing ions contact time and spent regenerate disposal
<b>Coagulation/Co precipitation</b>		
Alum precipitation	Low cost, simple to use, available chemical	Toxic sludge, low removal, pre oxidation may be required
Iron coagulation	Low cost, available chemical, effective in varying pH	Medium removal efficiency, pre oxidation may be required
Lime softening	Common chemicals	pH adjustment is required
Chemical precipitation	Highly efficient	Requires large amount of chemicals and produces toxic sludge
<b>Membrane separation</b>		
Ultra filtration	Good for large particles	Not suitable for arsenic removal
Reverse osmosis	No chemical additives, no toxic sludge, easy to monitor,	Power consumption and the restoration of the membranes
Microfiltration	Well defined and high removal efficiency	Very high capital and running cost
Nanofiltration	No toxic solid wastes produced	High tech operation and maintenance
Electrolysis	Capable of removal of other contaminants	Toxic wastewater produced
<b>Oxidation/precipitation</b>		
Aerial oxidation	Simple, low cost	Slow process, efficiency less, additional removal process is required
Chemical oxidation	Rapid process, removes other impurities like microbes as well	Toxic chemical/carcinogens are produced, additional process is required

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<b>Adsorption</b>	Well defined technique, highly efficient, plenty of possibilities on proper modification, regeneration	May be associated with high cost and technical hurdles which can be overcome by taking proper steps
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#### ***1.4.1 Water Purification by Adsorption Technique***

Adsorption has many advantages as compared to other existing conventional techniques, especially at low concentrations of contaminants. This is because of its low cost, easy operation, better efficiency and minor use of chemical additives, as well as the possibility of reusing the adsorbent materials. It is less expensive than membrane separation, safer and easier to handle as compared to the contaminated sludge produced by chemical precipitation and more versatile than ion exchange [82]. So, removal of arsenic by adsorption has become a new interest in research. Different materials have been used as adsorbents currently which include polymer resins, activated carbon, carbon nanotubes (CNTs), metal-loaded coral limestone, hydrous metal oxides such as activated alumina, hematite, ion exchange resins, sandy soils, lanthanum-loaded silica gel, ferric hydroxides etc. [83, 84]. New adsorbents such as activated red mud, kaolinite acid complexes, ferruginous manganese, biosorbents, clay and porous resin loaded with crystalline hydrous zirconium oxide have been developed and evaluated [85-87].

Metal oxides are excellent material for adsorption of arsenic. Different metal oxides like Mn-oxides, Fe-oxides, TiO<sub>2</sub>,  $\gamma$ -AlOOH,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> etc. are efficient as adsorbents [88-90]. Since, the adsorption is a surface phenomenon, the surface area of the adsorbent is of great interest for studying the extent of adsorption and therefore is a key quality parameter.

Sorption has acquired global importance for minimization of the problem of contamination of water and air, and these processes have become a significant addition to Green Chemistry endeavors [52, 91]. The different adsorption mechanisms and the factors affecting the uptake of metals have been reviewed with respect to the effects of selected anions, competition among metals, pH, metal concentration, loading, variable metal adsorption capacity, ionic strength, etc. [92-94]. A variety of adsorption models have been briefly introduced with a view to extend the laboratory studies to field.

Technical feasibility of using various low-cost adsorbents for heavy metal removal from contaminated water has also been reviewed earlier.

#### *1.4.1.1 Use of Polymers for Arsenic remediation*

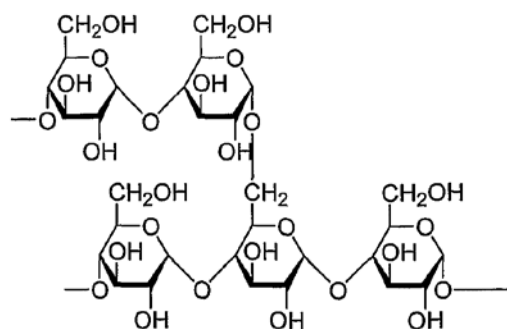
Polymers (especially functional polymers) can play a significant role in arsenic remediation. They usually work through chelation (Polychelators) or ion exchange method (Polyelectrolytes) [95, 96]. A number of benefits arise from the use of polymers: the capacity of a treatment facility may be more than doubled because the rate of solid and water phase separation is dramatically increased. Also, the range of waters which can be treated is greatly widened [97, 98].

In the process of elimination of heavy metals from waste water, natural polymers, principally polysaccharides, for example, starch and its subordinates, chitosan, cyclodextrin have gained much attention because of their physical and chemical properties, minimal effort, accessibility and the existence of different reactive groups on their chemical structure. Moreover, they are available in nature, bio-compatible, non-toxic and bio-degradable.

They can also be re-used several times, which makes them a cost-effective solution for water purification [99]. Their particular structure, chemical stability, physico-chemical characteristics, high reactivity and excellent selectivity towards aromatic compounds and metals can be utilized for better adsorption efficiency. It is due to the presence of chemically reactive functional groups like hydroxyl, acetamido, amino groups etc.

##### *1.4.1.1.1 Starch in Water Purification*

Starch is one of the most promising renewable biopolymers because of its low cost, biodegradability, versatility and applicability for developing new biomaterials. Starch is produced during photosynthesis and functions as the main polysaccharide reserve source in the plants. It is homopolymer of  $\alpha$ -D-glucose where glucose units are joined by glycosidic linkages. It consists of two types of polysaccharides, namely the linear and helical amylose and the branched amylopectin [100].



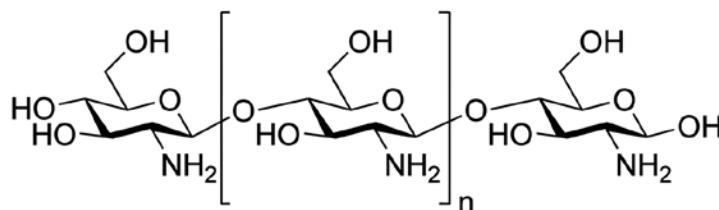
**Figure 1.6** Chemical structure of Starch

Starch and its derivatives represent a low cost and environmentally safe source of material for the preparation of better, cost-effective adsorbents that may be useful for the removal of heavy metal ions and other contaminants from water [101]. The special properties of starch such as chemical stability, high reactivity and re-usability make it a suitable sorbent.

The application of starch polymer in water treatment can be further expanded by proper modifications [102, 103]. Starch in its modified forms—either by grafting or functionalization with different functional groups have been cited to be very good flocculating material for the treatment of contaminated water [104, 105]. Polyacrylamide grafted starch/modified starch as an efficient flocculent for wastewater treatment is also well explored [106]. Along with the removal ability of contaminants from water, starch and its modified forms are widely used in immobilization of different nanomaterials which further enhances the treatment efficiency [107,108].

#### 1.4.1.1.2 Chitosan in Water Purification

Chitosan is a linear polysaccharide composed of randomly distributed  $\beta$ -linked D-glucosamine and N-acetyl-D-glucosamine. It is extracted from chitin shells of shrimp and other crustaceans using an alkaline deacetylation procedure that yields a heteropolymer [109]. Chitosan bio polymer represents an attractive alternative as adsorbents. It is largely available in nature, bio-compatible, non-toxic and biodegradable as compared to the synthetic polymers. These excellent properties are attributed to the chemically reactive functional groups like hydroxyl, acetamido, amino groups etc. which makes chitosan an edge over others [110-112].



**Figure 1.7** Chemical structure of chitosan

Chitosan in its native form is used in number of applications for adsorption of different metals/ metal ions and other contaminants. Bhatnagar and Sillanpää have reviewed the use of numbers of chitin and chitosan derivatives in detoxification of water [114]. Efficient, fast, and convenient material of magnetic chitosan nanoparticle for removal of arsenic from water were well reported [115].

Since chitosan has different and large number of binding sites on its skeleton and it can be modified easily to numerous derivatives, hence it has been selected as a suitable polymer to make composite of it with other polymers and nanomaterials to get better performance in arsenic remediation.

#### 1.4.1.2 Biosorption of Arsenic

'Biosorption' is defined as the property of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules from aqueous solutions. It is a passive immobilization of metals by biomass. The mechanism involves chemisorption, complexation, adsorption on surface and pores, ion exchange, chelation, adsorption by physical forces, entrapment in inter and intra fibrillar capillaries and spaces of the structural polysaccharides network as a result of the concentration gradient and diffusion through cell wall and membrane [116].

Advantages of biosorption over conventional ones include its availability, low cost, high efficiency, minimisation of chemical or biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery following adsorption.[117] Agricultural materials which shows potential metal biosorption capacity contain mainly cellulose, hemicellulose, lignin, hydrocarbons, starch etc. containing variety of functional groups that facilitates metal complexation which helps for the sequestering of heavy metals [118, 119].

##### 1.4.1.2.1 Dried Biomass of Water hyacinth (*E. crassipes*) Root Powder

Water hyacinth is a wild fern belonging to the family of pontederiaceae, found abundantly in various tropical and sub-tropical countries. The possible utilization of the weed includes as a phytoremediation agent, as a biosorbent for toxic metals, for power alcohol and biogas production, as compost, and for animal fodder/ fish feed.



**Figure 1.8** Different parts of water hyacinth

Water hyacinth possesses a great potential to remove pollutants when being used as a biological filtration system. It contains many polyfunctional metal-binding sites for both cationic and anionic metal complexes. The weed could remove several heavy metals including arsenic and other pollutants. It is reported that heavy metals are uptaken by the roots of the plant, translocated to the shoots and other plant tissues, where they are concentrated and harvesting the plant can permanently remove these contaminants [120].

The use of living biomass may not be a viable option for the continuous treatment of highly toxic contaminants as the bioaccumulation of these heavy metals is closely connected with their toxicity, affecting plant and its growth. After the accumulation of certain amount of toxicant during remediation the plant metabolism may get interrupted. The use of biomaterial derived from non-living dried water hyacinth roots may be a more convenient and effective method for the removal of toxic metal/metalloids [121]. Non-living, dried roots of *E. crassipes* can remove As(III), As(V) or both species from contaminated water efficiently [122, 123]. Batch and column experiments have been reported in successful performance of *E. crassipes* for sorption of arsenic and different kinetic and isotherm models have also been applied to understand the sorption mechanism [124, 125].

#### 1.4.1.3 Nanomaterials and Adsorption

In recent years, the development of nanoscience and nanotechnology has provided many exciting opportunities to develop more cost effective and environmentally acceptable water purification techniques. Nanomaterials are those materials which have at least one of their dimensions in the range 1-100 nm. Sorption being a surface phenomenon, so nanomaterials provide a far better option as adsorbents compared with traditional materials because of their very high surface to volume ratio. It provides ample opportunity for creating new materials and devices, taking advantage of those properties.

Nanomaterials used as sorbents for removing heavy metal ions in wastewater, should satisfy the following criteria:

- The nanosorbents themselves should be nontoxic.
- Should have high sorption capacities and selectivity to even very low concentration of contaminant.
- The adsorbed contaminant should be easily removable from the sorbent surface.
- The sorbents should be infinitely recyclable.

Nanosorbents such as nanotubes, magnetic nanoparticles, metal particles, supramolecular assembly's oxides of Mn, Fe, Al, Ti etc. have wide applicability in the field of water purification. They have two key properties that make them very attractive as sorbents viz. large surface area and ease of functionalization with various chemical groups to increase their affinity towards target compounds. They show unique adsorption properties due to the different distributions of reactive surface sites and disordered surface regions. Researches are going on around the world on exploiting these unique properties of nanoparticles to develop high capacity and selective sorbents for heavy metal ions and anions and also for other contaminants. The removal of arsenic by nanoparticles like nanocrystalline titanium dioxide, different forms of clay, nanoscale zero valent iron and modified zero and magnetic iron nanoparticles and many others are reported to exhibit promising results.

#### 1.4.1.3.1 Clay Minerals as Adsorbent

Clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction ( $> 2 \mu$ ) of soils, sediments, rocks and water and may be

composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. Clays play an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both [126]. Advantages of clay-based sorbents are as follows: it is environmentally friendly and relatively cheap sorbent, it has a comparatively low cost and can be treated for secondary use.

Clays and their modified forms have received wide attention recently for use as adsorbents of metal ions from aqueous medium. This is due to their unique properties such as high ion exchange capacity, swelling property, micro and meso-porosity and also their surface properties. Clay materials have dimensions in the nanometer range. Kaolinite, montmorillonite and illite are typical clay minerals often used for As adsorption. Mahapatra et al. [127] have demonstrated the sorption of the sorption of As(V) over these mentioned cases as due to inner sphere complex formation. All of them showed significant adsorption capacity with kaolinite the highest efficiency (0.86mg/g). Goldberg had performed similar experiments with those clay minerals at different pH for the competitive sorption between As(III) and As(V). As(V) sorption was better in acidic pH and for As(III) a pH=8.5 was found to be optimum. The competitive effect of equimolar arsenate on arsenite adsorption was small and apparent only on kaolinite and illite in the pH range 6.5 to 9 [128]. But in their study regeneration experiment was missing and also the probable leaching of sorbent materials was not systematically performed, limiting the practical applicability of the materials. Clay materials are usually characterized by features like having a 2:1 phyllosilicate layered structure with a dimension in the nano scale, where the thickness of the 2:1 layer is about 0.7nm. Because of high water absorption by clay, and the infeasibility of separation of heavy metals, the surface properties of clay minerals can be changed by replacing the exchangeable interlayer cations with organic cationic surfactants, as the nature of the surface can be altered from hydrophilic to hydrophobic.

#### 1.4.1.3.1.1 Montmorillonite Clay (MMT)

It is a clay mineral with substantial isomorphous substitution [127]. Exchangeable cations in the 2:1 layers balance the negative charges generated by isomorphous substitution. The uptake kinetics of cation exchange is fast and the cations such as  $\text{Na}^+$  and  $\text{Ca}^{2+}$  form outer-sphere surface complexes, which are easily exchanged with solute



ions by varying the cationic composition of the solution. In addition to cation exchange there is a pH-dependent uptake of metals on montmorillonite. In this adsorption process, adsorbate ions are bound to the clay surface by sharing one or several ligands (generally oxygen) with adsorbent cations as isolated complexes. With increasing pH or adsorbate cation concentration, metal precipitation can occur. In the montmorillonite structure, interlayer swelling occurs when it is exposed to water. The swelling procedure depends on valences and atomic radii of the exchangeable cations. Al and Si atoms exposed to the crystallite edges are partially hydrolyzed to silanol (SiOH) and aluminol (AlOH) groups. These unsaturated edge sites are much more reactive than the saturated basal sites [129]. In montmorillonite, adsorption can occur both at the edge sites, which leads to inner-sphere metal complexes, and at the planar (internal) sites of the clay mineral, which results in outer sphere metal complexes.

#### 1.4.1.3.1.2 Organically Modified Montmorillonite Clay (OMMT)

The rate of reaction and the efficiency of adsorption of Arsenic on clay is comparably low and therefore less suitable for the remediation process in their native forms. In order to improve the adsorption of arsenic on clay, certain modifications such as surface functionalization, exfoliation of layer within certain matrix, surfactant modifications etc. are required. Surfactant modification converted clay surface from negatively charged to a positively charged one, and thus organoclay became a potential sorbent of Arsenics from aqueous solution. Sorption of arsenate, and other anionic species like nitrate, chromate etc, on organo-kaolinite were reported two fold greater than their sorption on unmodified kaolinite [130].

Organic surfactants are usually used to create organophilic (hydrophobic) surfaces in clay materials. Organically modified nanoclays are widely used as adsorbents for the removal of organic pollutants and metal ions. The suitability of these organically modified nanoclays as adsorbent is because of their nano-size and specific surface area and also their great tendency to absorb ions and organic compounds. Therefore, organically modified nanoclays may be suitable for the removal of organic and inorganic pollutants from wastewater.

#### 1.4.1.3.2 Iron Based Nanoparticles in Arsenic Remediation

Among all sorbents, iron based ones are most widely used for arsenic remediation. In the last decade, investigations with several types of iron and iron oxides nanoparticles were carried out in this field. Natural iron containing minerals, such as magnetite, siderite and hematite, have been studied as sorption agents [99, 131-132]. Metallic iron, a zero valent iron, has been used in past for the treatment of groundwater in permeable reactive barrier systems [133, 134]. There, zero valent iron forms spontaneously Fe(II) and Fe(III) oxides and hydroxides and As(III) and As(V) are forming complexes with the resulting corrosion products [135, 136].

#### 1.4.1.3.2.1 Iron oxyhydroxide in water purification

Fe(III) based sorbents have received particular attention because of their strong affinity towards arsenic species and selectivity during the adsorption process. Ferrihydrite is a common Fe(III) (hydro) oxide in soils and sediments and exhibits high sorption affinity towards both As(III) and As(V) species. Recent studies have revealed that both As(III) and As(V) species may undergo inner-sphere surface complex with ferrihydrite, and their relative affinity depends on solution chemistry and characteristics of iron oxide. Previous studies have shown that As(V) and As(III) form relatively strong inner sphere complexes on the ferrihydrite surface, which acts as sorption surface [137, 138]. Iron oxyhydroxide was also reported to improve the sorption capacity of clay mineral by six fold, tested for As(V) remediation. [133]. Banerjee et al. have extensively studied the impacts of pH, temperature on the adsorption kinetics and equilibrium capacities of granular ferric hydroxide (GFH) for arsenic (V) and arsenic (III) in an aqueous solution [139]. In a study Tresintsi et al. have established the significant role played by ion exchange due to  $\text{SO}_4^{2-}$  ions present at the surface of iron oxyhydroxide (prepared from  $\text{FeSO}_4$ ), in acidic medium along with formation of monodentate and bidentate inner sphere complexes for sorption of As(V). On the other hand Sorption of As(III) was explained as due to Lewis acid-base ligand-exchange reaction preferably onto non-ionized surface functional groups on basis of performance of the material with different arsenic concentrations. Along with very high adsorption capacity it could bring down the residual arsenic below 10 mg/L and also maintaining its superiority in column tests compared to number of commercial granular materials [140].

#### 1.4.1.3.2.2 Magnetite Nanoparticles in Water Purification

Magnetite is a common magnetic iron oxide which has an inverse spinel structure with oxygen and forms a fcc lattice system. It has high affinity to bind with different heavy metal ions, non metals and other pollutants in water. The surface properties of iron oxides are key factors governing the sorption ability of this material [141]. Yavuz et al. [142] has reported that the sorption of arsenic over magnetite particles occurred due to electrostatic interaction between the adsorbate and arsenic. Khodabakhshi et al. [115] has studied the efficacy of magnetic iron oxide nanoparticles ( $\text{Fe}_3\text{O}_4$ ) in the removal of As (III) from industrial waste water. Wang et al. have presented magnetic nanoparticle showing  $Q_{\text{max}}$  value as high as 35 mg/g for both As(III) and (V) [143]. Separation of the material was also very easy (magnetic separation) and showed high efficiency up to 5th cycle. Another efficient sorbent of magnetic composite of cellulose and iron oxide nanoparticles for arsenic removal was reported with very high efficiency. But in all these cases very high amount of initial arsenic concentrations were taken. Moreover, in many cases, regeneration of the material was not done [144, 145]. Lenoble et al. cited the disadvantage of using iron hydroxide in arsenic remediation as they were damaged during cyclic run and not useful for long term applicability [146]. Magnetic nanoparticles have the specific advantage of separation by magnetic field. But it is also associated with leaching as well as degradation during recycle. Numbers of iron based materials including magnetic nanoparticles, iron oxyhydroxide etc. have been reported to show very high adsorption capacity of arsenic. Wang et al. have presented magnetic nano particle based material with high  $Q_{\text{max}}$  (35 mg/g) for both As(III) and (V) and good recyclability. Another composite of cellulose and iron oxide nanoparticles for arsenic removal was reported with very high efficiency [147, 148]. Composite system of magnetite with chitosan biopolymer is reported to be an excellent tool for remediation of different heavy metals from aqueous medium along with recyclability of the materials [115, 116].

#### 1.4.1.3.3 Titanium Dioxide Nanoparticles in Arsenic Treatment

In recent times, researchers from around the globe have given special interest in the use of  $\text{TiO}_2$  for the removal of heavy metal ions from water. It is because of its high adsorption capacity, low cost, biocompatibility, photostability in solution, redox selectivity and strong oxidizing power of holes. The application of  $\text{TiO}_2$  in the

nanoscale further improves the efficiency due to their high surface area, large pore volume and presence of high affinity surface hydroxyl groups.

Titanium Dioxide occurs in nature in four polymorphs viz. anatase, rutile, brookite and  $\text{TiO}_2$ .  $\text{TiO}_2$  is found as a mineral in magmatic rocks and hydrothermal veins and in weathering rims on perovskite. The photocatalytic activity of  $\text{TiO}_2$  nanoparticles is used for degradation of wastewater pollutants. It shows great potential in removal of heavy metal ions from water due to high surface area, adsorption sites density, particle size, surface energy, crystallinity and crystalline structure [149].

$\text{TiO}_2$  is capable of removing Arsenite and Arsenate from contaminated water [150,151]. Xu and O'shea have studied the photocatalytic degradation of organic arsenic to inorganic form by  $\text{TiO}_2$  and successful sorption on its surface [152]. In its hydrous form, it is excellent adsorber Arsenic and many other heavy metal ions [153, 154]. The influence of different experimental conditions on sorption of arsenic is also well reported. Moreover,  $\text{TiO}_2$  has been found to be very effective against a lot of bacteria. Hence,  $\text{TiO}_2$  can be an excellent material for arsenic remediation along with other contaminants from water.  $\text{TiO}_2$  in different forms like in suspension or hydrous titanium dioxide nanoparticle are found to be very efficient adsorbent for arsenic with very high adsorption capacity. Some of them are also successfully utilized in treatment of naturally contaminated arsenic water [155, 156]. But, those studies were lacking the reusability or probable leaching from sorbent material, thus, limiting the practical applicability of the material.

#### *1.4.1.4 Nanocomposite in Arsenic Remediation*

Nanocomposites are hybrid nanostructured materials. According to Cammarata, nanocomposites are “multiphase materials where one or more of the phases have at least one dimension  $\leq 100$  nm” [157]. Properties of nanocomposites can display synergistic improvements over those of the component phases individually. In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high aspect ratio of the reinforcing phase. The area of the interface between the matrix and reinforcement phase(s) is typically in order of magnitude greater than for conventional composite materials [127].

As discussed earlier, the nanomaterials have high capacity for removal of pollutant including arsenic from aqueous solution but their application could be limited because of their tendency to agglomerate due to their high surface energy. Moreover, reusability, leaching of material during the treatment etc. are the major concerns of using the nanomaterials in water treatment process. Therefore, it is necessary to stabilize them on host materials such as granular activated carbon, cellulose, and polymeric materials. When incorporated into polymer matrix, these nano materials not only help in enhancing the removal rate but in certain cases also facilitate crosslinking of the polymer.

A widely studied type of nanocomposite is a class of hybrid materials composed of organic polymer matrices and nanoclay fillers. Due to the hydrophilic nature of clay minerals, sometime it becomes necessary to modify them organically to make compatible with the organic polymers. The presence of nanoclay in polymer formulations increases the tortuosity of the diffusive path for a penetrating molecule, and decreases the molecular mobility, which reduces the solvent absorption along with many other properties. The incorporation of MMT in proportions below 5% also offers benefits such as low density, transparency, good flow, better surface properties and recyclability [158].

Nanocomposite of iron with different polymer is widely studied for water purification as the former is an excellent material for adsorption of contaminants from water. Immobilization of different iron nanoparticles (magnetite, hematite, zerovalent iron nanoparticle etc.) on starch, chitosan and many other polymeric matrix for arsenic removal is well known [159]. Oxyhydroxide nanoparticles can also be used in nanocomposite preparation where it serves two functions– as a crosslinker for the polymer matrix and adsorbent of arsenic from water [160 a]. Since these particles get trapped in the polymer matrix during the preparation, therefore, their agglomeration into larger particles can be prevented, and thus their removal efficiency can be enhanced.

### **1.5 Some commercially available low cost adsorbent**

A few commercially available low cost adsorbent and methods are mentioned below [160 b]-

Littleton, Colorado-based ADA technologies developed an amended silicate sorbents which could remove arsenic from high concentration of 1000  $\mu\text{g/L}$  to 10  $\mu\text{g/L}$  in just 30 min.

Purolite has presented iron-impregnated ion-exchange resin which has equal or better capacity than competitive iron-based media. The material was claimed to be regenerable, disposable, and cost effective. Moreover, frequent backwashes are not needed.

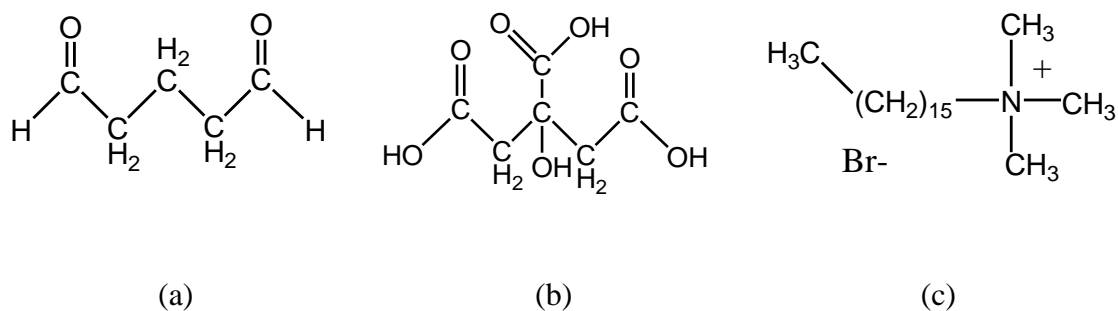
A ferric/lanthanum hydroxide compound based nanocrystalline media developed by Eagle Picher Filtration & Minerals. The media doesn't require any chemical treatment for As(III) and As(V) sorption.

Another arsenic remediation method widely used in Bangladesh is the three-kolshi method of which requires only clay pots, iron filings, and charcoal.

## 1.6 Role of Crosslinkers and Other Materials

### 1.6.1 Glutaraldehyde

It is a linear dialdehyde with the chemical formula  $\text{OCH}(\text{CH}_2)_3\text{CHO}$  (Figure 1.9). At room temperature, it is a pungent, colorless, oily liquid. It is mainly available as an aqueous solution where the aldehydic groups remain hydrated [161]. It is used as a crosslinking agent in many applications such as controlled drug delivery, leather industry, pharmaceutical industry etc.



**Figure 1.9** Chemical structure of (a) Glutaraldehyde, (b) Citric acid and (c) CTAB

In water purification technique, it is used to stabilize polymeric nanocomposite systems which enhances its applicability in diverse experimental conditions, entrapment and immobilization of nanoparticles within polymer matrix, controlling

particle size etc. Suguna et al. has [162] reported an improvement in metal sorption capacity of glutaraldehyde crosslinked chitosan. In many scientific studies related to water purification, glutaraldehyde has been explored as a significant component which enhances the efficiency of the materials used in that purpose [163, 164].

### **1.6.2 Citric acid**

Citric acid (2-Hydroxypropane-1,2,3-tricarboxylic acid) is a tricarboxylic acid represented by the chemical formula  $C_6H_8O_7$ . It is naturally found in citrus fruits and can be used as a crosslinker due to the polyfunctional groups. Citric acid has been used in numerous applications in material chemistry which includes cell delivery, polymeric film preparations, adsorption by polymeric system and many others [165,166]. Demitri et al. has [167] used citric acid in the preparation of cellulose based supersorbent owing to its non toxicity and low cost compared to other crosslinking reagents. In many literatures, it is reported to enhance the sorption of heavy metals and provide antimicrobial activities due to incorporation of citric acid to polymeric system [168].

### **1.6.3 N-cetyl-N,N,N-trimethylammoniumbromide (CTAB)**

In order to enhance the dispersion as well as processing, sometimes it is required to modify the nanoparticles. Use of surfactants is a good alternative in this purpose.  $TiO_2$  nanoparticles can be modified by using surfactants like CTAB. It has an organic end which is hydrophobic [Figure 1. 9 (C)], non-polar and an inorganic end which is hydrophilic, polar. The hydrophobic, non-polar end can interact with  $TiO_2$  and the hydrophilic, polar end can interact with water, forming micelles. This facilitates the dispersion of  $TiO_2$  properly. The efficacy of magnetic nano particles has been found to increase significantly on modification with CTAB [169, 170].

## **1.7 Treatment of leachets produced after arsenic treatment.**

Mixing arsenic wastes with cow dung is reported to be useful where, microbial arsenic methylation to produce gaseous methylarsines takes place [171]. Those are less toxic than inorganic forms. Mixing with concrete in a controlled ratio or Mixing with clay for brick manufacturing are some other simple process for the sludge disposal.

## **1.8 Objective of the Work**

Numbers of techniques are adopted for removal of arsenic from water. All of them have certain merits and demerits as discussed earlier (table 1.4). Adsorption is

considered as one of the most suitable techniques in terms of efficiency, cost, environmental friendliness and regeneration. A wide variety of materials can be used as adsorbent for the sorption of arsenic, but few of them satisfy all the requirements for a good adsorbent. The criteria for selection of a good adsorbent for arsenic are-

- Cost effective and ease of separation and handling
- Use of minimum chemical additives and production of less/negligible hazardous materials during preparation and use
- Achievement of good result using minimum power
- Minimum or negligible interference of other contaminants, if any, on its efficacy
- Reusability without losing efficiency

No such material is developed so far which can fulfill all those criteria at a time. Polymeric materials, either synthetic or natural are good choice for this. But the efficiency for arsenic removal needed to be compromised. Synthetic polymers are also associated with high cost during processing, and disposal of leachates may pose another problem. Use of biopolymer/biomass may be helpful to overcome such difficulty although sometime they may generate unwanted turbidity. They are biodegradable and most importantly, biocompatible. Large numbers of surface functionality in the backbone of the chitosan, starch and cellulosic material of water hyacinth, greatly impressed and motivated to work with those biomaterials in arsenic treatment. They are naturally widely available and water hyacinth plant in many a time is considered as waste materials in tropical countries. Starch and chitosan have wide scopes for modifications which make them tunable towards desired requisite qualities. Again, attracting correlation between metal concentration in water hyacinth plant and the respective water body showed good prospect of using it in arsenic treatment also. However, during desorption of arsenic (acid or alkali treatment) from the surface of the material for reuse, the polymeric materials may degrade when used in their pristine form. Hence, it is most important to stabilize them prior to use. Nanosorbents on the other hand are highly efficient and specific in arsenic removal. Use of clay minerals like kaolinite and montmorillonite are well established for sorption purpose. They are found to be least toxic to human and the beauty lies behind the availability for



exchanging ions and ability to control the inter laminar distances. On the other hand, the ease of preparation/modifications and availability of raw materials of iron and titanium based nanoparticles and their high efficiency to adsorb different heavy metals/ions from water drew a lot attention for their use in arsenic treatment. But the main problem of using them are agglomeration and separation from liquid phase after the treatment. Hence, it is necessary to modify surface of the nanoparticles for better selectivity, aqueous stability, leaching prevention and reusability. These are the most important concern for using these materials effectively in water treatment process. Most of the reports addressed the use of very high initial arsenic concentrations which limits their practical applicability. Moreover, in many cases, regeneration of the material were not done systematically and many are associated with complicated synthesis/preparation steps. Hence, there are wide scopes to do further work in these areas.

Keeping these things in mind the main objectives of present investigations were set as below-

- a. Development of some nanocomposite systems of polymer by using different nanomaterials like clay, metal oxide nanoparticles etc.
- b. Characterization of these nanocomposites with different analytical techniques like FT-IR, SEM, XRD, TEM etc.
- c. Study the efficacy of the prepared nanocomposite systems in the removal of water contaminants (special emphasis to be given on arsenic species only).
- d. Study the influence of different parameters like temperature, pH, amount of nanomaterial, their nature, amount and types of crosslinker on removal efficiency of the nanocomposites.
- e. Optimization of the experimental conditions for obtaining best performance.

### **1.9 The Strategy**

Present investigation is aimed at stabilizing few nanomaterials by immobilizing over different polymeric moieties and apply those systems in remediation of arsenic from contaminated water. In order to achieve best overall performance of the composites, the optimization of experimental conditions is necessary and accordingly the plan of work has been set up as per the following-

- a. Selection of different functional polymers (either naturally occurring like starch, chitosan, cellulose etc or synthesised)
- b. Preparation of nanocomposites of these polymers or mixture of polymers with different nano materials like nanoclay, metal oxide nanoparticle etc.
- c. Characterization of the prepared nanocomposites by using different analytical techniques like fourier Infrared spectroscopy (FT-IR), X-ray diffractometry (XRD), Scanning Elctron Microscopy (SEM), Transmission Electron Microscopy (TEM), etc.
- d. Analysis of the treated water samples by Atomic absorption spectrophotometer (AAS), ion meter and Inductively Coupled Plasma Spectrophotometer (ICPS).
- e. Optimization of the nanocomposites for removal of water contaminants by varying different reaction parameters like ratio of polymer to crosslinker or nanomaterials, their nature, pH, temperature etc.
- f. Optimization of reusability and efficacy of nanocomposites towards removal of contaminants.

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