Chapter-1
INTRODUCTION AND OBJECTIVES

1.1 Arsenic: A social mutant and environmental threat

1.1.1 Source and occurrence of arsenic in water

Arsenic is element of Group-15 in latest version of the Periodic Table which is a metalloid and ranked 20th in abundance on the earth’s crust. It is rarely encountered as the free element, but widely distributed in nature among the great variety of rock forming minerals such as igneous rocks, metamorphic rock and sedimentary rocks and soils. It exists mainly as a component of metal arsenide or metal arseno sulphide ores. Arsenic bearing minerals those commonly occurring in nature are arsenopyrite (FeAsS), realger (As₄S₄) and orpiment (As₂S₃) which are being formed under high temperature conditions or microbial precipitation on the earth’s crust [1]. Some iron stone and iron rich rocks are also relatively rich in arsenic almost up to the value of 2900 mg. kg⁻¹ [2]. Although the dominant source of arsenic in soils is geogenic, the additional imputes may be derived locally from the industrial sources, fossil fuel combustion products and agricultural sources such as pesticides and weed killers.

1.1.2. Accumulation, distribution and behavior of arsenic in soil

Sources of arsenic and other trace elements may be anthropogenic or it can naturally occur as minor constituents in soil compartments [3]. Generally, arsenic is deposited on the top soils from burning of fossil fuels, mining and smelting activities, incineration of wastes, cement production, application of arsenic contained fertilizers and pesticides, disposal of sludge containing arsenic etc [4]. Besides, the use of arsenic contaminated groundwater for irrigation
purpose in crop fields elevates arsenic concentration in surface soil and in the plants grown in those areas [5].

Ferric hydroxide plays an important role in controlling the concentration of arsenic in soils and in aqueous media that can be expressed by the following reaction (R-1.1) [6].

\[
\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \quad \text{(R-1.1)}
\]

Arsenic is associated with the primary sulfides, (hydro) oxides of Al, Fe and Mn, clays, sulfates, phosphates and carbonates in the Bengal Delta Plain [7]. It is released in the soil by weathering of arsenopyrite (FeAsS) and sulfide minerals. The grain sizes of soil particles play an important role in controlling the distribution and mobility of arsenic. The surface area of the finely grained particles is large and hence can adsorb more arsenic [4]. For this reason, clay minerals, Fe, Al, and Mn (hydro) oxides are important sinks for arsenic in the aquifers and sedimentary layers in Bengal Delta.

Arsenic in soil normally occurs in pentavalent state under oxidizing conditions while under reducing conditions trivalent As(III) species prevail that is more mobile and bioavailable [8]. Arsenic can also get biomethylated (i.e. addition of CH$_3$ to arsenic through biological activity) in the soil–water, sediment–water interfaces through the activity of bacteria (such as Escherichia coli, Flavobacterium sp, Methanobacterium sp) and fungi (such as Aspergillus glaucus, Candida humicola). In the course of biomethylation, As(III) is oxidized to As(V) following which CH$_3^+$ is reduced to CH$_3^-$ and henceforth, stable arsenic oxy-species is formed [4].
Sorption of arsenic by plants is influenced by the concentration of arsenic in the soil. In Bangladesh, the irrigation is carried out with arsenic contaminated groundwater where the level of arsenic in soil can reach up to 83 mg. kg\(^{-1}\) [9]. Fig. 1.1 represents arsenic cycle in the environment as adapted by Mukhopadhyay et al. in the year 2002 [10].

1.1.3. Mobility of arsenic in ground water

The high concentration of arsenic in ground water occurs due to the presence of arsenical pyrites and iron-oxy-hydroxide in the alluvial sediments of aquifer matrix. Mobility of arsenic depends on interaction with sediments on adsorption/desorption, chemical transformation,
ion-exchange and microbial effects. Desorption and mobilization of arsenic sediments depends on pH, iron and arsenic concentration in the interstitial water. Iron-rich, iron-hydroxide coated elastic grains and antigenic concretion of iron carbonate (siderite) are found to be arsenic carriers and act as sinks for the element. Arsenic occurs in both inorganic and organic forms in natural waters but organic arsenic is of little importance as it goes through biotransformation and detoxifies through methylation [11].

The discussions above strongly suggest that arsenic in groundwater beneath the Ganges Plain is derived from the reductive dissolution of Fe-oxyhydroxide in the sediment [12]. Release of arsenic into the groundwater occurs gradually in successive stages, corresponding to the actual redox state in the aquifer.

Arsenic comes out from these arsenic-rich components through (i) aerial oxidation or water with dissolved oxygen, (ii) ion-exchange with phosphorous derived from phosphate fertilizers and (iii) microbial oxy-hydroxide reduction.

**1.1.3.1. Oxidation**

Oxidation of pyrite is considered to take place by atmospheric oxygen into the aquifer with a concomitant release of arsenic into the ground water. The oxidation process can be shown by the following reaction.

\[
2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2\text{O} = 2 \text{Fe}^{2+} + 4 \text{H}^+ + 4 \text{SO}_4^{2-} \quad \text{------------------------ (R-1.2)}
\]

The ground water so obtained shows enriched acidity. The released iron will be oxidized to ferric oxyhydroxide (FeOOH) which will absorb or co-precipitate dissolved As(V) with consequent decrease of arsenic concentration in the aquifer [13]. Thus, pyrite oxidation is not a very efficient mechanism for releasing arsenic to ground water.
1.13.2. Ion-exchange with phosphorous

Arsenic has a similar chemistry with phosphorus, as a result, the sorbed arsenate into the aquifer is assumed to be released in ground water by competitive exchange with phosphate derived from over application of phosphate fertilizer to surface soils [14]. This proposal was thought initially as ground water in some pockets of Bangladesh was associated with high concentration of phosphate along with arsenic.

1.13.3. Microbial reduction

Arsenic in ground water is actually derived from the reductive dissolution of arsenic-rich iron-oxyhydroxide. This reduction occurs through microbial process that is driven by microbial metabolism of organic matter and is accompanied by reduction of arsenate to arsenite [15] by the following reactions (R-1.3, R-1.4).

\[
8\text{FeOOH} + \text{CH}_3\text{COOH} + 14\text{H}_2\text{CO}_3 \rightleftharpoons 8\text{Fe}^{2+} + 16\text{HCO}_3^- + 12\text{H}_2\text{O} \quad R-1.3
\]

\[
4\text{FeOOH} + \text{HCHO} + 7\text{H}_2\text{CO}_3 \rightleftharpoons 4\text{Fe}^{2+} + 8\text{HCO}_3^- + 6\text{H}_2\text{O} \quad R-1.4
\]

These processes generate dissolved iron, bicarbonate and other sorbed species including arsenic. High iron content is generally found in anoxic ground water of severely arsenic affected areas. During the reduction of FeOOH, arsenate is reduced to arsenite which is less strongly sorbed to FeOOH. As a result, arsenite is the predominant species in ground water under reducing environment. Fig. 1.2 highlights the scheme of arsenic mobilization resulting in the formation of high arsenic contaminated ground water in the Bengal Basin as adapted by Kinniburgh and Smedley in the year 2001 [16].
1.1.4. Aqueous chemistry of arsenic

Arsenic occurs in nature in several oxidation states (-3, 0, +3 and +5), but occurs mostly in inorganic forms as oxyanions of its trivalent and pentavalent state in natural water. However, a detailed study reveals the predominance of a particular state in the medium depends on the redox potential and pH [17].
Fig. 1.3 shows that As(V) remains almost entirely as undissociated H₃AsO₄ in strongly acidic medium (pH ≤ 2.0) at high Eh (pKₐ values of H₃AsO₄ are pK₁ = 2.19, pK₂ = 6.94 and pK₃ = 11.5). In acidic medium (pH = 2.0 to 7.0), pentavalent arsenic mainly exists as H₂AsO₄⁻ where as in neutral or moderately alkaline pH medium (pH = 7.0 to 11.5), the predominant species is HAsO₄²⁻. Arsenate (AsO₄³⁻) only exists in highly alkaline pH (pH > 11.5). Thus, the most common species in natural water is HAsO₄²⁻, which is stable under neutral to mildly alkaline medium at negative Eh values.

Arsenic in trivalent state exists as undissociated H₃AsO₃ over a wide range of pH under reducing environment (pKₐ values of H₃AsO₃ are pK₁ = 9.20, pK₂ = 14.22 and pK₃ = 19.22). Under reducing condition and at pH less than 9.2, the dissociation of H₃AsO₃ is unlikely and it remains mainly in undissociated form. Thus, arsenic is the most problematic element in the environment because of its relative mobility over a wide range of redox conditions.
Percentage of organic form of arsenic is usually minor in surface as well as in ground water. The dominant forms of organic arsenic are mono and dimethyl arsenic acid. In both the cases, arsenic is present in the pentavalent state. Organo arsenic is formed by methylation of inorganic arsenic catalysed by microbial activity.

1.1.5. Speciation of arsenic in ground water

pH and redox potential are the two important factors controlling arsenic speciation. Fig. 1.4 (a, b) shows pH dependent arsenic species in aqueous solution. In groundwater, the ratio of As(III) to As(V) can vary greatly as a result of the variations in the abundance of redox-active solids (especially organic carbon), activity of micro organisms and the extent of convection and diffusion of oxygen from the atmosphere. As(III)/As_Total ratios in anoxic ground water vary between 0.1 and 0.9 [18]. Oxidation of As(III) by dissolved oxygen is a slow reaction and slowest in slightly acidic pH range (pH 5).

![Figure 1.4: (a) Arsenite and (b) arsenate speciation as a function of pH (ionic strength of about 0.01M)](image)

Figure 1.4: (a) Arsenite and (b) arsenate speciation as a function of pH (ionic strength of about 0.01M)
The rate of oxidation is independent on the concentration of dissolved oxygen. It was found that As(III)/As(V) ratio was stable in anoxic solutions for almost 3 weeks lapse of which acidified to pH ~ 5 to preserve their in situ speciation [18].

1.1.6. Distribution of arsenic around the world

1.1.6.1. Distribution of arsenic in West Bengal

Sources of arsenic in Bengal Delta is geogenic and related to the sediments deposited by the rivers Ganges, Brahmaputra, and Meghna along with their tributaries and distributaries [12, 19]. Bengal delta is one of the largest deltas of the world and accommodates an enormous volume of sediments deposited during the Tertiary and Quaternary periods [4].

In groundwater, inorganic arsenic commonly exists as As(V) (arsenate) and As(III) (arsenite), among which the trivalent state is considered to be more mobile and toxic for living organisms [4]. The mobility of arsenic is mainly determined by the adsorption capacity on the mineral surfaces, which is controlled by geochemical parameters such as pH, Eh, ionic composition, and mineral type [20]. However, redox processes in the aquifers trigger the mobility through dissolution of iron oxides that transfer substantial amounts of arsenic into the aqueous phases [21].

The Bengal basin is regarded to be the most acutely arsenic affected geological province in the world [19]. The Bengal arsenic disaster is possibly the worst environmental disaster in the history of human civilization, much more serious than Bhopal Gas Tragedy or Chernobyl Nuclear disaster.

In West Bengal (India), during 1980's, some cases of arsenical dermatosis in the districts of North 24 Parganas, South 24 Parganas, Nadia, Murshidabad and Burdwan were reported. By the end of December 2001, this problem spreads from few villages to two thousand and sixty
five (2065) villages of seventy five (75) blocks in eight (8) districts. Nine (9) districts out of nineteen (19) in West Bengal, seventy eight (78) blocks and around three thousand one hundred and fifty (3150) villages were affected with arsenic-contaminated groundwater [22]. Groundwater is regularly used for agricultural and household purposes in these areas as rainwater is insufficient to support the water demand of the increasing population and intensive agricultural system of West Bengal.

T. Roychowdhury (2008) reported that thousands of shallow tube-wells were installed for irrigation in last 40-45 years [23]. A vast majority of these tube wells have been installed privately with locally available expertise without any check of the quality and yield of the out flowing treated water. Due to different hydro-chemical behaviors of aquifers in the Bengal delta, the redox potential, pH, temperature, Ca-HCO$_3$ or Ca-Mg-HCO$_3$ water type vary substantially which control the arsenic dynamics in the area. Chakraborti et al. analyzed over 1,25,000 water samples for studying arsenic contamination in the Bengal basin and reported that arsenic levels in the affected areas of the basin vary between <1 and 1300 mg. L$^{-1}$ [22, 24]. Fig. 1.5(a) depicts different areas (marked with different colours) contaminated with varying degree of arsenic concentration in drinking water [16].
Figure 1.5(a): Map of West Bengal showing areas with arsenic contamination in drinking water. (Adapted and modified from Smedley and Kinniburgh, 2002)

1.1.6.2. Distribution of arsenic in India centering around West Bengal

In India, since arsenic contamination in groundwater was first detected from West-Bengal in 1983, following which a number of other states, namely; Jharkhand, Bihar, Uttar Pradesh in flood plain of the Ganga River; Assam and Manipur in flood plain of the Brahmaputra and Imphal rivers, and Rajnandgaon village in Chhattisgarh state have been known to be chronically exposed to arsenic contaminated drinking water from hand tube-well source above previous permissible limit of 50 μg. L⁻¹ [4]. Many more North-Eastern Hill States in the flood plains are also suspected to have the possibility of arsenic contamination in groundwater. Even with every additional survey, new arsenic affected villages and people suffering from arsenic related diseases are being repeatedly reported implying extreme severity of this acute issue. It was predicted and now established that all the arsenic affected river plains have their source origin from the Himalayan region. Over the years, the problem of arsenic
contamination in groundwater had grown complicated and severe leading to a large variability at both local and regional scale, by a number of unknown factors.

Arsenic contamination in groundwater was first reported in the year 1983 from thirty three affected villages in four districts of West Bengal. Since then, the total count of villages reached 3417 in 111 blocks comprising nine districts of West Bengal [4] till 2008. In 1999, arsenic contaminated groundwater along with its health impact was detected in Rajnandgaon district of Chattisgarh state. In 2002, two villages, Barisban and Semaria Ojhapatti in Bhojpur district located in the western part of Bihar were reported for their high arsenic contamination levels much exceeding 50µg. L⁻¹. In the year 2003, twenty five arsenic affected villages of Ballia district in Uttar Pradesh and list of people suffering from skin lesions came into limelight. In 2004, high arsenic concentration in groundwater was also reported in the pockets of two districts from Assam [4]. In 2007, Manipur state, one of the seven North-Eastern Hill States, had come into limelight due to its extreme arsenic contamination in groundwater. Out of 38 districts of Bihar, 57 blocks from 15 districts having total population nearly 10 million have been reported to be affected by arsenic contaminated groundwater above 50µg. L⁻¹ in the year 2008 [4].

Till 2008, West Bengal, Jharkhand, Bihar, Uttar Pradesh in flood plain of Ganga River; Assam and Manipur in flood plain of Brahmaputra and Imphal rivers, and Rajnandgaon village in Chhattisgarh state have so far been exposed to dissolved arsenic present in contaminated hand tube-wells used as potent drinking water [25] source. The area of these states is 529674 km² and approximately 360 million people reside here respectively. Around 88688 km and approximately 50 million people have been projected to be reasonably vulnerable to groundwater arsenic contamination [4]. During 2003-2004, level of arsenic
contaminated groundwater and consequent suffering of thousands of people thereafter were reported from seventeen villages of Sahibgunj district of Jharkhand state, in the middle of Ganga plain [25].

Fig. 1.5(b) shows pictorial representation of arsenic contamination status of groundwater in West Bengal, India (Till September 2006) [25].
1.1.6.3 Distribution of arsenic in Bangladesh

Bangladesh is facing worst arsenic related problem in the whole world. According to estimate, 18% of all wells have level of arsenic above 0.05 mg L$^{-1}$. The affected area has been shown in Fig. 1.5(c).

![Arsenic Contamination in Bangladesh](image)

Figure 1.5(c): Arsenic contamination in Bangladesh.

1.1.6.4 Worldwide distribution of arsenic

Arsenic is derived from various sources, including natural dissolution, desorption reactions, geothermal trigger and mining activity. The worst affected country due to arsenic contamination of groundwater is Bangladesh. Arsenic in groundwater has become a crucial water quality problem in many countries of Asia like India, China, Taiwan, Thailand, Mongolia and Nepal. Arsenic poisoning has also been reported in USA, Chile, Mexico, Argentina, Ghana and Hungary. Fig. 1.5(d) highlights distribution of documented world problems related to arsenic in ground water in major aquifers as well as water and its associated environmental impact related to mining and geothermal sources. A clear understanding of this acute problem can be henceforth concluded from Fig. 1.6 describing
known pockets of ground water around the world with elevated concentrations of geogenic arsenic as compiled in World map (adapted and modified from Nriagu et al. (2007) [26]).

Figure 1.5(d): Distribution of documented world problems related to arsenic contamination in groundwater and environmental problems related to mining and geothermal sources. Areas in blue are lakes. (Adapted and modified from Smedley and Kinniburgh, 2002)
1.1.7 Arsenic toxicity and health effects

Arsenic is recognized as a micronutrient essential to life up to a certain level (10 μg. L\(^{-1}\)). It can lead to physicochemical and toxicological disorder when arsenic level exceeds standard value (10 μg. L\(^{-1}\)) [27]

The carcinogenic effect of arsenic inhibits replication of DNA and interrupts the repair mechanism possibly through linkage with thiol groups of DNA proteins causing headache, nervous disorder, respiratory disorders, loss of nails and hairs. High dose of arsenic cause black-foot disease, caratosis, melanesia, muscular weakness, cardiovascular disease, diabetes, loss of appetite, nausea. Long term exposure to drinking water causes skin, lung, bladder,
kidney cancer. External manifestations of arsenicosis affected patients are shown in Fig. 1.7. Factors that intensify the risk of individuals consuming arsenic contaminated water in rural West Bengal may be due to i) high water consumption, estimated to be 5-6 L. day$^{-1}$, due to tropical heat and high manual labour [27]; ii) poor nutrition, which is very common for poor rural mass, can amplify symptoms. In situ cell carcinoma (or Bowen’s disease), invasive cell carcinoma and multiple basal cell carcinomas, are all known to be associated with chronic arsenic exposure. Other effects are hematopoietic depression, anhydremia (due to loss of fluid from blood into tissue and gastrointestinal tract), liver damage characterized by jaundice, portal cirrhosis and ascites, sensory disturbance and peripheral neuritis, anorexia and loss of weight [28].

Arsenic has phototropic effects on certain plants as it is capable of replacing phosphorous in plant cells causing biological disorders. Looking onto the entire spectrum of arsenic, it becomes apparent that arsenic is extremely hazardous to both plants and animals.
Figure 1.7: Photographs of some arsenic affected patients showing wide range of diseases: Arsenic patient with (a) melanosis, (b) keratosis on hand on palm, (c) squamous carsenoma on hand, (d) non pitting oedema of legs, (e) keratosis and gangrene, (f) skin cancer, (g) multiple Bowens disease in the back in a case of arsenicosis, (h) cancerous growth.
1.1.8 Social issues with arsenic

1.1.8.1 Social problems

Common social problems that an arsenic patient or his/her family members may face are:

➤ People are reluctant to engage in nuptial knots with people from arsenic affected villages.

➤ School children with such symptoms are denied to attend school.

➤ People’s ignorance identifies the person with arsenical disease as leprosy patient and keeps them isolated.

➤ Birth of physically and mentally retarded child.

It may be called as disease of poor because poor people are mostly affected due to malnutrition and less awareness.

1.1.8.2 Economic impact

When one or more member in a family is affected by arsenical diseases, they are economically affected in addition to social problems as well. The main economical problem that an affected family faces can be as follows:

- Due to general weakness caused by arsenical diseases, daily wage earners and farmers loose their earning.

- Increase of medical expenses.

1.1.9 Provision of arsenic-safe water

Provision of safe water is of urgent necessity in the arsenic-prone areas. Surface and dug well water sources cannot be used either for drinking or for cooking purpose because these are not properly preserved and protected. Surface water could be a long term solution but it is capital intensive and requires longer time to implement. Tube-well from safe aquifer is an alternative
for protecting the health of people living in the arsenic prone zone but that too has certain limits. Once known as safe aquifer may not be safe due to subsequent leaching of arsenic from upper layer and migration of aquifer water flow thus, increasing the concentration of arsenic in aquifer beyond maximum concentration limit (MCL).

So, it gets necessary to adopt various strategies and methods (mentioned below) to minimize the content of arsenic in surface and ground water sources for providing arsenic-safe water to mankind.

(i) Treatment of arsenic contaminated groundwater in a centralized facility and supplying through pipe could be made possible for a locality having larger population, but this option is also time-consuming and capital intensive.

(ii) Installation of arsenic removal systems attached to contaminated hand pumps will serve in a huge way to cater safe water to isolated and small habitations.

(iii) A suitable technology which is simple, cost-effective, easy maintenance, no extra electricity should stand appropriate for application in rural areas. Such systems attached to spot sources can be implemented in relatively short time to bring some immediate relief to the agony of the population living in arsenic-prone areas.

1.2 Conventional arsenic removal technologies: A critical overview

Arsenic contamination is mostly observed for groundwater supplies. There are a number of technologies which are in use around the world for arsenic removal from water. The technology adopted is related to the availability of raw materials and requires skill to run the system. The common arsenic removal processes that are mostly used in recent days are:

- Oxidation followed by precipitation,
- Coagulation/ electro-coagulation followed by filtration,
• Ion-exchange,
• Membrane filtration,
• Electro-flocculation,
• Sorption over sorptive media, and
• Sorption over nano-materials.

1.2.1. Oxidation followed by precipitation

This is an in situ arsenic removal process. Oxidation of As(III) to less mobile As(V) and Fe(II) to Fe(III) ion where ferric hydroxide is precipitated with sorbed arsenate reducing arsenic content in water [20]. The oxidizing agents may be oxygen, ozone, free chlorine, hypochlorite, permanganate and Fenton’s reagent. From the thermodynamic consideration, oxygen is the best oxidizing agent but the rate of oxidation is very slow. Catalytic oxidation can be achieved by powdered active carbon and dissolved oxygen.

However, lowering of arsenic level from the contaminated ground water may be problematic due to chemical residue of oxidant, hazardous byproduct from oxidation of other organic and inorganic matter, reagent costs and operational hazards. This method also generates high sludge volume that is difficult to dispose after making it environment friendly.

1.2.2. Coagulation/ electro-coagulation followed by filtration

In this method, the physical or chemical properties of dissolved species (natural organic matter, inorganic matter) are changed by addition of metal salt coagulants. Treatment of contaminated water with coagulants such as alum, ferric salts is effectively used to remove arsenic [20]. Precipitation can be made by ferric chloride, ferric sulphate, ferric hydroxide,
alum or aluminium sulphate. Both ferric and alum are more effective in removing As(V) than As(III) over a wide range of pH.

Removal efficiency is strongly dependent on the solution pH but not on the coagulant dosage or initial As(V) concentration. In case of As(III), removal is independent of solution pH and strongly dependent on the coagulant dosage and As(III) concentration.

Though it is an efficient method for arsenic removal, yet this method suffers from the problem of sludge disposal and dose control in rural condition. Additionally this method enhances total dissolved solid and anions like sulphate etc in treated water.

1.2.3 Ion-exchange

Ion-exchange resins are highly cross-linked polymer matrix to which charged functional groups (carboxylate, sulphonate, tertiary or quaternary amines) are attached by covalent bonding. Ion exchange (IX) is a physico-chemical process by which an ion in the solid phase is exchanged for an ion in the feed water. The solid phase is a synthetic resin on which the contaminant from the bulk liquid is absorbed. In order to facilitate this exchange process, contaminated water is continuously passed through the IX resin bed (either in a down flow or in an up flow mode). In course of time, the bed gets exhausted when all the available sites in the resin bed are filled up with contaminant ions. At this point, the bed is regenerated by rinsing the resin column with a regenerate, a concentrated solution of ions initially exchanged from the resin. The number of bed volumes that can be treated before exhaustion varies with resin type and influent water quality.

This IX technology is effective in removing arsenic from drinking water when it is in +5 oxidation state. The resins are not effective for arsenic removal when the total dissolved solids (> 500 mg. L⁻¹), sulphate (> 25 mg. L⁻¹), nitrate (> 10 mg. L⁻¹) and bicarbonate (> 200 mg. L⁻¹) levels are high.
enough in the feed water [29-30]. Additionally, IX materials are also inefficient to remove As(III) as it exists as As(OH)$_3$ at pH below 9.0.

Moreover, the IX technology has some more limitations such as high cost of resin, high-tech operation and maintenance. The regeneration also creates a sludge disposal problem.

1.2.4 Membrane filtration

Membranes are selective barriers, allowing some constituents to pass while blocking the passage of others. Membrane techniques like reverse osmosis, ultra filtration, nano-filtration and electro dialysis are capable of removing dissolved solids including arsenic [31]. In all cases, As(V) removal is more effective than As(III). No toxic solid wastes are produced and all other contaminants present in water can be removed by this process.

Removal depends on the chemical characteristics, particularly charge and hydro-phobicity of both the membrane material and feed water constituents [32].

However this technique is very much costly, time consuming for precondition and large amount of toxic water is produced.

1.2.5. Electro-flocculation

Electro-flocculation is the technique involving electrolytic addition of coagulating metal ions directly from sacrificial electrodes. These ions coagulate with the pollutants (here, arsenic) present in water, in a similar manner as like the addition of coagulating chemicals such as alum and ferric chloride, allowing easy removal of the pollutants. The electrolytic addition of these ions has a number of advantages over their addition chemically. There is no addition of anions which means that there is no increase in salinity of the treated water. For removal of arsenic from groundwater, iron electrodes are used taking advantage of dissolved iron in
water that separates out arsenic by co-precipitation. Iron from anode dissolves to accelerate precipitation [33].

However, large scale application must be associated with too cost and hence, unusable in third world countries like India, Bangladesh etc.

1.2.6. Adsorption on to sorptive media

Arsenic removal technologies already discussed suffer from one or more drawbacks, limitations and scope of application. Adsorption is evolving as a front line defense that is defined as the process of transferring material from a fluid phase to a solid phase. It is a separation process in which the pollutant material (adsorbate) is concentrated from the bulk liquid phase on to the surface of a porous (micro/ macro) solid (adsorbent). It reacts in the following way:

\[
A + S \rightleftharpoons A \cdot S \quad \text{(R-1.5)}
\]

where 'A' denotes adsorbate and 'S' denote the solid with active sites which functions as adsorbent. The reversible reaction indicates a forward reaction in adsorption can be changed to desorption with change in state of solid-solution temperature, pH and input of any external additive. Adsorption is a mass transfer process in which a substance is transferred from the liquid phase to the surface of a solid where it becomes bound by chemical or physical forces. Surface sorption has been found to be an alternative option for the treatment of high arsenic content surface and ground water and is well accepted by rural people of under developed countries due to its following advantages and considerable effectiveness.

- Simple operation
- Low recurring cost
- No trained personnel

25
A filter can be designed and developed with these sorbents for household purpose.

Henceforth, we discuss the following reported sorptive media used for arsenic mitigation purpose.

1.2.6.1. Commercial and synthetic activated carbons

Commercial activated carbons are extensively used for As(III) and As(V) adsorption from water [34]. Capacity of As(III) sorption on carbon derived from activated charcoal [35] was constant at pH 0.16–3.5. However, As(V) exhibited a maximum adsorption at pH 2.35 over the pH range 0.86–6.33.

Gu et al. [36] developed iron-containing granular activated carbon adsorbents (Fe-GAC) for arsenic removal from drinking water. As(V) and As(III) removal from water was studied using a char carbon (CC) derived from fly ash. The maximum uptakes of As(V) were 34.5 mg g⁻¹ [As(V) concentration: 490 mg L⁻¹, pH 2.2] for CC versus 30.5 mg g⁻¹ [As(V) concentration: 159 mg L⁻¹, pH 7.5] for AC. Those of As(III) were 89.2 mg g⁻¹ [As(III) concentration: 709 mg L⁻¹ and pH 2.2] for CC and 29.9 mg g⁻¹ [As(III) concentration: 992 mg L⁻¹ and pH 7.0] for AC.

1.2.6.2. Low-cost adsorbent

1.2.6.2.1. Agricultural products and by-products

Both As(III) and As(V) removal were cent percent from aqueous arsenic solution [37] of initial arsenic concentration 100 μg L⁻¹ between pH range 6.0 to 6.5 and rice husk dose 6.0 g L⁻¹.
1.2.6.2.2. Industrial by-products/wastes

1.2.6.2.2.1. Red mud

Red mud is a waste material formed during the production of alumina when bauxite ore is subjected to caustic leaching. Red mud has been explored as adsorbent for arsenic [38]. Effective removal of As(III) had occurred at alkaline pH, while that of As(V) had been noted at acidic pH. The capacities reported were 4.31 μmol. g\(^{-1}\) at pH 9.5 for As(III) and 5.07 μmol. g\(^{-1}\) at pH 3.2 for As(V).

1.2.6.2.2.2. Miscellaneous

Singh et al. [39] employed hematite and feldspar to As(V) removal from aqueous systems at different pHs, temperatures, and adsorbent particle size. Maximum removal was 100% with hematite (pH 4.2) and 97% with feldspar (pH 6.2) at an arsenic concentration of 13.35 μmol. L\(^{-1}\).

1.2.6.2.3. Soils and Constituents

1.2.6.2.3.1. Sand

Iron oxide-coated sand (IOCS) exhibited a high adsorption capacity (136 μg. L\(^{-1}\)). Another study [40] achieved 285 μg. g\(^{-1}\) of arsenic removal on iron oxide-coated sand. Sulfate modified iron oxide coated sand (SMIOCS) was also used for As(V) and As(III) removal [41-42]. Maximum As(V) removal was obtained in acidic pHs [41] while maximum As(III) removal was obtained at pH 7–9 [42]. Gupta et al. [43-44] utilized both iron oxide-coated and uncoated sands for As(III) removal. Maximum Langmuir adsorption capacity for As(III) onto coated sand was five times higher (28.57 μg. g\(^{-1}\)) than that achieved for uncoated sand (5.63
µg. g\(^{-1}\) at pH 7.5 in 2 h. Rapid oxidation of As(III) to As(V) followed by As(V) sorption onto
biogenic manganese oxide surfaces was also examined [45]

1.2.6.2.3.2. Clay minerals

Distinct As(V) adsorption maxima of 0.15–0.22, 6.0 and 6.5 mmol As(V) kg\(^{-1}\) was achieved
for kaolinite, montmorillonite and illite respectively at approximate pH 5.0. When both
As(V) and phosphate were present at equimolar concentrations (6.7×10\(^{-7}\) M), As(V)
adsorption decreased slightly. In contrast, As(V) adsorption decreased substantially in binary
As(V)/phosphate systems when the phosphate concentration was 10 times greater than As(V)
(e.g., 6.7×10\(^{-6}\) M).

Goethite (surface area 103 m\(^2\). g\(^{-1}\)) prepared from the oxidation of ferrous carbonate from
double decomposition of ferrous sulfate doped with sodium lauryl sulfate and sodium
carbonate was also used for arsenate removal [46]. Adsorption capacity of ~5 mg. g\(^{-1}\) (pH 5.0)
was achieved in this case.

1.2.6.2.3.3. Zeolites

Zeolites are crystalline, hydrated alumino-silicates of alkali and alkaline earth cations, having
infinite, three-dimensional structure [47]. They can loose and gain water reversibly and
exchange constituent cations without change in structure. Adsorption of As(V) from drinking
water by an aluminum-loaded Shirasu- zeolite (AI-SZP1) was slightly dependent on initial pH
over a wide range (3–10) [48]. Competing arsenite, chloride, nitrate, sulfate, chromate, and
acetate ions had little effect but phosphate greatly interfered with the adsorption process. A
ligand-exchange mechanism between As(V) ions and surface hydroxyl groups on AI-SZP1
was presumed. An iron-conditioned zeolite was prepared and used for arsenic removal from
groundwater at pH 7.8 and temperature 145° C [49].
1.2.6.2.4. Oxides

Oxides are widespread and abundant in aquatic and terrestrial environments. Synthetic single and mixed metal oxides had been studied extensively for removal of arsenic since they usually possess very strong arsenic scavenging power due to their surface nature. Manganese oxide and its mineral were reported as effective adsorbent for both As(V) and As(III) [45, 50-58]. As(III) is oxidized on manganese oxide surface during sorption process.

1.2.6.2.4.1. Single oxides

Single oxides that show promising results in the removal of arsenic have been extensively used as sorptive media [59-63].

1.2.6.2.4.1.1. Activated alumina

Arsenic adsorption on activated alumina (AA) has received substantial attention [64-73, 75]. As(V) sorption occurs best mostly between pH 6.0 and 8.0 where AA surfaces are positively charged. The surface modified AA had also been studied for arsenic removal. The modification was done either by manganese oxide support [71] or by ferric hydroxide [70, 73, 75]. In both cases, better adsorption capacity was reported than that for pure AA. Singh and Pant [64, 70, 74] investigated arsenite removal from water with AA [64] and iron oxide-impregnated AA [70]. Adsorption capacity of iron oxide impregnated AA (12 mg. g⁻¹) [70] was much higher than AA (7.6 mg. g⁻¹) [64]. Conventional AA has ill-defined pore structures, low adsorption capacities and exhibits slow kinetics [64]. An ideal adsorbent should have uniformly accessible pores, three-dimensional pore system, high surface area, fast adsorption kinetics and good physical and/or chemical stability. To achieve these features, mesoporous alumina (MA) with a large surface area (307 m². g⁻¹) and uniform pore
size (3.5 nm) was prepared and tested for arsenic removal [67]. A sponge-like interlinked pore system was developed through the process of post-hydrolysis. The resulting MA was insoluble and stable at pH 3 to 7 and its adsorption kinetics were rapid. Maximum As(V) uptake by MA was seven times higher [121 mg As(V). g\(^{-1}\) and 47 mg As(III). g\(^{-1}\)] than that of conventional AA. This adsorbent’s surface area did not greatly influence the adsorption capacity. The key factor is the uniform pore size.

Hlavay and Polyak [73] precipitated Fe(OH\(_3\)) on the surface of activated Al\(_2\)O\(_3\) supports in situ. The iron content of AA was 0.31% m/m (56.1 mmol. g\(^{-1}\)) having pHzpc = 6.9. The total capacity was 0.12 mmol. g\(^{-1}\).

1.2.6.2.4.1.2. **Titanium dioxide**

Both synthetic and commercially available titanium dioxide had been thoroughly investigated for arsenic removal [60-62, 76].

The ability of nano-crystalline titanium dioxide's (TiO\(_2\)) to remove arsenate and arsenite and to photocatalytically oxidize As(III) was evaluated [60]. Bang et al. [62] studied a novel granular titanium dioxide (TiO\(_2\)) for the removal of groundwater arsenic. More arsenate was adsorbed than arsenite on TiO\(_2\) at pH 7.0. Adsorption capacities for As(V) and As(III) were 41.4 and 32.4 mg. g\(^{-1}\) on the surface of TiO\(_2\), respectively.

1.2.6.2.4.1.3. **Ferrihydrite/iron hydroxide/iron oxides/Surface modified iron(III) oxide.**

Iron oxide is the most studied single oxide for the purpose of arsenic remediation from contaminated water since iron has a natural tendency to bind to arsenic species. Different forms of iron oxides like oxyhydroxide, hydroxide, goethite, and hematite are promising for
removing both As(III) and As(V) from water [59, 63, 77-89]. Among these amorphous FeO(OH) has the highest adsorption capacity since it has the highest surface area.

Granular ferric hydroxide (GFH) was investigated for arsenic removal from natural water [80] and the sorption capacity obtained was found to be 8.5 g kg⁻¹.

Badruzzaman et al. [81] evaluated porous granular ferric hydroxide for arsenic removal in potable water systems. Granular ferric hydroxide (GFH) is a highly porous (micropore volume: ~ 0.0394 cm³ g⁻¹, mesopore volume: 0.10 cm³ g⁻¹) adsorbent with a BET surface area ~235 m² g⁻¹. The pseudo-equilibrium (18 days of contact) arsenate adsorption capacity at pH 7.0 was 8 μg As mg⁻¹ dry GFH at a liquid phase arsenate concentration of 10 μg As L⁻¹.

Raven et al. [79] compared the adsorption behavior of arsenite and arsenate on ferrihydrite. At relatively high arsenic concentrations, adsorption was almost complete in a few hours and arsenite reacted faster than arsenate with ferrihydrite. However, arsenate adsorption was faster at low arsenic concentrations and low pH. Maximum adsorption capacities of 8.5 and 14.7 mg g⁻¹ were reported for As(V) and As(III), respectively, at pH 3.0 in 100 μg L⁻¹ to 100 mg L⁻¹ concentration range [82].

Abundant iron (III) oxide occurring in various mineralogical forms in the earth crust is a well-known natural water purifier that has good arsenic adsorption capacity in a wide pH range. Consequently, a number of surface modified iron(III) oxide had been investigated for the adsorptive removal of arsenic [40-43, 70, 73, 75, 86-89].

1.2.6.2.5. Phosphates

As(III) and As(V) were removed using amorphous or crystalline iron(III) phosphate [90]. As(III) oxidation by iron(III) and phosphate substitution by As(V) occur during arsenic sorption. Solid dissolution and phosphate/arsenate exchange led to the presence of Fe³⁺ and
PO$_4^{3-}$ in solution. Fe$^{3+}$ in solution can oxidize As(III) to As(V). Crystalline and amorphous FePO$_4$ exhibited a maximum phosphate release at the highest arsenic adsorption, pointing out the probable exchange between arsenate and phosphate due to their similar ionic radii (AsO$_4^{3-}$: 248 nm; PO$_4^{3-}$: 238 nm). As(III) was present as H$_3$AsO$_3$; therefore these results suggest As(III) oxidation to As(V) occurs, followed by an arsenate/phosphate exchange.

1.2.6.2.6. Metal-based methods

1.2.6.2.6.1. Zero-valent iron.

Zero-valent iron (ZVI) was synthesized and worked upon by different workers [91-105] from time to time and showed interesting results. Kanel et al. [104-105] synthesized nano-scale (1–120 nm diameter) zero-valent iron (NZVI) for rapid, first order As(III) and As(V) removal ($k_{obs} = 0.07–1.3 \text{ min}^{-1}$) This rate was about 1000 times faster than that of micron-sized iron. Maximum As(III) adsorption Freundlich capacity was 3.5 mg of As(III). g$^{-1}$ for NZVI.

1.2.6.2.6.2. Bimetallic adsorbent

Among the oxide classification, mixed oxides of iron(III) with some other metal ions [106-113] showed higher arsenic removal efficiency than many of the single metal oxides because incorporation of other metal with iron(III) oxide changes some physical properties such as surface area, surface charge and crystallinity etc.

1.2.6.2.7. Biosorbents

Biosorption is capable of removing traces of heavy metals and other elements from dilute aqueous solutions. Algae, fungi and bacteria are examples of biomass-derived sorbents for several metals Biosorption (or bioadsorption) is a passive immobilization of metals by biomass. Bioaccumulation can also be regarded as a second part of the metal sequestering.
process by living biomass. Since it depends on cell metabolism, it can be inhibited by metabolic inhibitors such as low temperature and lack of energy sources.

**Biomass**

*Lessonia nigrescens*, an algae, was utilized for As(V) removal with maximum adsorption capacities of 45.2 mg. g⁻¹ (pH 2.5); 33.3 mg. g⁻¹ (pH 4.5); and 28.2 mg. g⁻¹ (pH 6.5) in the concentration range of 50–600 mg As(V). L⁻¹ [114].

### 1.2.7. Adsorptive removal of arsenic by column method of analysis

Nano materials of different metal oxide had been utilized in fixed bed column for arsenic removal from ground water by Hristovski et al. [115]. All the nano materials studied showed very high As(V) uptake capacity. Equilibrium data described Freundlich isotherm best. Short bed adsorber (SBA) study with TiO₂ nano aggregates showed that rapid mass transport of arsenate occurred and it was controlled by rapid intra-particle diffusion rather than external film diffusion.

In this study, the use of iron oxide nano-particles (19.3 nm magnetite and 37.0 nm hematite) were examined by Shipley et al. [116] to remove arsenate and arsenite through column studies. The columns contained 1.5 or 15 wt% iron oxide nano-particles and soil. A long-term study was conducted with 15 wt% magnetite nano-particles in soil at 0.3 mL. h⁻¹ with an initial arsenate concentration of 100 µg. L⁻¹. A retardation factor of about 6742 was calculated indicating strong adsorption of arsenic to the magnetite nano-particles in the column.

A new zirconium oxide-based media for arsenate removal from water was fabricated by Hristovsk et al. [117] and evaluated in batch and continuous flow experiments. Highly porous (P ≈ 0.9) nano-structured zirconium oxide spheres were fabricated by the impregnation of macroporous ion-exchange media with zirconium salt. The spheres generally ranged from 200
to 800 μm in diameter, and consisted of ZrO₂ nano-structures generally ranging between 20
and 100 nm. For a packed bed adsorbent operating at a loading rate of 11.5 m³. m⁻². hr⁻¹ in a
realistic continuous flow experiment, the external mass transport coefficient was estimated to
be \( k_f \approx 6.3 \times 10^{-3} \text{ cm. s}^{-1} \). The pore diffusion and the external mass transport coefficient were
used along with the pore surface diffusion model (PSDM) to predict the arsenate
breakthrough curve. A short bed adsorbent (SBA) test was conducted under the same
conditions to validate the model. In this study, surface diffusion was ignored because the
particles had a very high porosity.

Gupta et al. [118] developed a novel granular media by coating iron, barium and sulfur on
quartz sand surface that has been demonstrated as an effective sorbent for removal of As(V)
from a 0.01 M NaNO₃-spiked distilled water system in laboratory-scale tests. The results of
the fixed bed studies indicated that As(V) removal is dependent on pH, size of sorbent and
influent arsenic concentrations. Removal of As(V) may be explained using the surface
complexation theory. The presence of alkalinity (250–260 mg. L⁻¹ as CaCO₃) and hardness
(200 mg. L⁻¹ as CaCO₃) slightly increase the reactor breakthrough time for similar
experimental conditions.

Continuous fixed bed studies were undertaken by Gupta et al. [119] to evaluate the efficiency
of iron oxide-coated cement (IOCC) as an adsorbent for the removal of As(III) from aqueous
solution under the effect of various process parameters like bed depth (10-20 cm), flow rate
(4.3-12 ml. min⁻¹) and initial As(III) concentration (0.5-2.7 mg. L⁻¹). Also, the total As(III)
removal percentage increased with the increase in bed depth. Thomas model predictions were
in very good agreement with the experimental results studied indicating that they were very
suitable for IOCC column design. The apparent mechanism of As(III) removal in the IOCC column were ion exchange and physisorption on the adsorbent surface.

1.2.8. Sorption by nano-materials

Nano-structured materials have gained special attention in the field of sorption science since they show very interesting and exciting results. Nano-structured materials usually possess very high surface/volume ratio and so, the surface of such materials are highly reactive than the bulk materials due to quantum confinement. As a result, not only the sorption capacity of such materials is high but also, the rate of sorption. The materials need few minutes to few hours for reaching equilibrium in case of both As(V) and As(III) sorption reactions.

Iron oxide nano particles (IONPs) were synthesized from a precursor of Fe$^{3+}$ species dispersed in PVA molecules by De et al. [120]. In the pH range 4.5 to 7.5 and initial As(III) concentration 0.25 mg. L$^{-1}$, almost 96% As(III) adsorption took place within first 60 minutes. As(III) adsorption process onto IONPs occurs most efficiently at a critical dose of 2.0 g. L$^{-1}$ and the corresponding isotherm analysis shows Langmuir model fit.

Deliyanni et al. [121] reported As(V) sorption behavior on akaganeite-type nano crystal. Akaganeite is β-FeO(OH) and was synthesized using aqueous solution of ferric chloride and ammonium carbonate. Amount of arsenate adsorption increased by lowering initial pH of the system, thereby, increasing the amount of the sorbent with the change in ionic strength of the system. Regeneration of the adsorbent up to 75% could be carried out with NaOH at pH 12. Akaganeite looses about 25–30% of its capacity with each regeneration cycle so that it must be replaced after three or four regenerations.

Three dimensional flowers like iron oxide nanostructures were synthesized by Liang et al. [122]. The synthetic method was simple and the self assembled different phases of iron oxide
thus, obtained were highly crystalline in nature. These iron oxide nanostructures were very much effective for As(V) removal. Almost 100% As(V) adsorption took place at pH 4 and 2.0 g. L\(^{-1}\) of adsorbent dose in a short period of time at 20°C.

Nano crystalline titanium dioxide had been found to be effective for the removal of arsenic [60-61, 123-125]. Both As(III) and As(V) sorption capacity were very much pH dependent. TiO\(_2\) caused rapid photo catalytic oxidation of As(III) to As(V) in the presence of oxygen and sunlight. This material could effectively remove As(V) in the pH range less than 8.0, and had maximum adsorption affinity for As(III) at pH approximately 7.5. A surface complexation model of As(III) and As(V) sorption on TiO\(_2\) had been suggested by Pena et al. [125].

Arsenate adsorption by nano structured ZrO\(_2\) spheres had been reported by Kiril et al. [126]. ZrO\(_2\) spheres (diameter: ~200-800 \(\mu\)m) consisted of ZrO\(_2\) nano structures that ranged between 20 to 100 nm. Arsenate sorption equilibrium on this material obeyed Freundlich isotherm model. The external mass transport co-efficient was estimated to be \(k_f \approx 6.3 \times 10^3\) cm. s\(^{-1}\). The high porosity of this media provides improved pore diffusion and faster overall mass transport.

\(\alpha\) and \(\delta\)-phase manganese dioxide nano adsorbents were synthesized by Singh et al.[127] and studied for their arsenate adsorption behavior. Birnessite (\(\delta\)-phase MnO\(_2\)) showed clumps (ball like aggregates) of the two- dimensional nano platelet structures in the size range 50 to100 nm where as \(\alpha\)-MnO\(_2\) consisted of needle shaped nano rods having length 50–100 nm with a width of 5 nm. Isotherm study showed that Langmuir model was the best fit model for both the materials and the monolayer sorption capacity of \(\alpha\)-MnO\(_2\) was 19.41 mg. g\(^{-1}\) and that of \(\delta\)- MnO\(_2\) was 15.33 mg. g\(^{-1}\).
Hierarchical nanostructure CuO was synthesized by CaO et al. [128] and studied for arsenic adsorption behaviour. CuO particles consisted of interconnected crystallites of less than 10 nm size. The mono layer As(III) sorption capacity was 5.7 mg. g$^{-1}$. CuO adsorbent could be regenerated by rinsing the material with arsenic free water and could be reused for arsenic sorption purpose.

Peng et al. [129] reported ceria nano-particles supported on carbon nanotubes for adsorptive removal of As(V) from aqueous solution. The sorption process was pH dependent and As(V) sorption capacity gradually decreased from pH 3.0 to pH 11.0. Isotherm study showed that Freundlich model was the best fit model. Sorption capacity of the material increased in the presence of Ca$^{2+}$ and Mg$^{2+}$ ions. As(V)-loaded adsorbent can be efficiently regenerated by dilute NaOH, and a high regeneration efficiency of 94% was achieved using 0.1 mol. L$^{-1}$ NaOH.

Bimetal oxide nano materials had also been studied for arsenic remediation. Zhang et al. [109] reported the use of magnetic nano material MnFe$_2$O$_4$ and CoFe$_2$O$_4$ for arsenic removal behavior. It was found that As(III) sorption was independent of the solution pH. But As(V) sorption was very much pH dependent and high uptake capacity was shown under acidic pH condition. Isotherm data showed that both As(III) and As(V) sorption obeyed Freundlich isotherm model under the reaction condition. Phosphate and silicate were powerful competitors with arsenic for adsorptive sites on the adsorbent. Adsorbed As(V) could be desorbed easily from adsorbents with NaOH solution. An inner-sphere surface complexation model had been suggested for arsenic sorption on these materials.

Magnetite supported on multi walled carbon nano tube (a super capacitor) had been used for the removal of As(III) and As(V) from the contaminated water by a super capacitor based
The isotherm data fits were equally well for both Langmuir and Freundlich model. Sorption kinetics followed Elovich model indicating chemisorption nature of the sorption process.

Magnetite-reduced graphene oxide composite was synthesized and used for As(V) and As(III) treatment from aqueous solution [131]. The magnetite particle size was ~10 nm. The composite was superparamagnetic at room temperature and could be separated by the application of external magnetic field. The material showed higher binding affinity for As(III) and As(V) than pure magnetite. Adsorption data fit was equally well with both Langmuir and Freundlich models. Arsenic removal capacity of the material decreased with increase of temperature as As(V) sorption capacity gradually decreased with increase of initial pH, but in case of As(III) the sorption capacity increased up to pH 7 and then, gradually decreased. The composites showed nearly complete (over 99.9%) arsenic removal within 1 ppb. Thus, they were practically usable for arsenic separation from water.

Li et al. [132] synthesized ultrafine iron oxide (α-Fe₂O₃) nano-particles by a solvo thermal process and used to remove arsenic ions from both laboratory prepared and natural water samples. Nano-particles of α-Fe₂O₃ assumed a near-sphere shape with an average size of about 5 nm. They aggregated into a highly porous structure with a high specific surface area of ~162 m².g⁻¹, while their surface was covered by high-affinity hydroxyl groups. Near the neutral pH, the adsorption capacities of laboratory prepared α-Fe₂O₃ nano-particles on As(III) and As(V) were found to be no less than 95 mg.g⁻¹ and 47 mg.g⁻¹, respectively. In the presence of most competing ions, these α-Fe₂O₃ nano-particles maintained their arsenic adsorption capacity even at very high concentrations of competing anion.
Ghosh et al. [133] synthesized Goethite nano-particles using hydrazine sulfate as a modifying agent and evaluated As(V) adsorption capacity. The precipitated goethite particles were spherical with particle size less than 10 nm. Batch adsorption study was carried out systematically with varying parameters such as pH, contact time, initial As(V) concentration and adsorbent doses. Langmuir isotherm represented the equilibrium data well and the estimated monolayer adsorption capacity at ambient temperature was 76 mg.g⁻¹.

Jean et al. [134] discussed the adsorption kinetics of As(V) onto nano-sized iron oxide-coated perlite. Perlite is cheap and naturally occurring volcanic silicates. Perlite is mainly composed of silica, aluminum, potassium and sodium that has been extensively used for the adsorption of heavy metals including Cd, Cu(II), Cr(III) etc. Furthermore, nano-sized iron oxide-coated perlite (IOCP) has been shown to be an effective adsorbent for the removal of arsenate from aqueous solution. Moreover, it suggests that the Langmuir isotherm is more adequate than Freundlich isotherm in simulating the adsorption isotherm of As(V). The adsorption rate constant was 44.84 L.mg⁻¹ min⁻¹ and the maximum adsorption capacity was 0.39 mg.g⁻¹.

In this batch experimental study, a commercial grade nano-size ‘magnetite’ was used by Chowdhury et al. [135] for the uptake of arsenic and chromium from different water samples. The results of this study showed 96-99% arsenic and chromium uptake under controlled pH conditions. Maximum arsenic adsorption occurred at pH 2 with values of 3.69 mg.g⁻¹ for As(III) and 3.71 mg.g⁻¹ for As(V) when the initial concentration was kept at 1.5 mg.L⁻¹ for both arsenic species. The results also showed the limitation of arsenic uptake by nano-size magnetite maghemite mixture in the presence of a competing anion such as phosphate. At a fixed adsorbent concentration of 0.4 g.L⁻¹, arsenic and chromium uptake decreased with
increasing phosphate concentration. In natural groundwater containing more than 5 mg. L$^{-1}$ phosphate and 1.13 mg. L$^{-1}$ of arsenic, less than 60% arsenic uptake was achieved.

In this study, zirconium nano-particle sorbent was synthesized by Chen et al. [136] for significant enhanced adsorption of As(V). HRTEM micrographs showed that the sorbent was nano-scale with particle size ranging from 60 to 90 nm. The optimal pH for As(V) adsorption was between 2.5 and 3.5. Langmuir equation described the adsorption isotherm well. Maximum adsorption capacity of 256.4 mg As. g$^{-1}$ was obtained at optimal pH, better than most of the sorbents available in the market.

Chen et al. [137] evaluated the effectiveness of a readily prepared zirconia nano-particle in removing arsenite [As(III)] from aqueous solution. It was demonstrated that the sorbent was highly effective for As(III) removal with a maximum adsorption capacity of 1.85 mmol As. g$^{-1}$ without undergoing pre-oxidation. The sorbent had a high adsorption capacity towards As(III) at pH 5–10, and the optimal pH was around 8.0. Equilibrium adsorption isotherm data were well described by Langmuir model. The adsorption was independent on ionic strength, implying As(III) may form inner-sphere complexes on the sorbent. The presence of humic acid or typical anions (e.g., fluoride, silicate, phosphate, and sulphate) did not greatly pose negative effects on As(III) adsorption. However, the uptake of As(III) was hindered by the existence of bicarbonate.

Reddy et al. [138] synthesized CuO nano-particles and evaluated it as an adsorbent to remove As(III) and As(V) from groundwater. CuO nano-particles had a surface area of 85 m$^2$. g$^{-1}$ and were 12–18 nm in diameter. Maximum adsorption capacity was 26.9 mg. g$^{-1}$ for As(III) and 22.6 mg. g$^{-1}$ for As(V). Presence of sulphate and silicate in water did not inhibit adsorption of As(V) but only slightly inhibited adsorption of As(III). High concentrations of phosphate
 (>0.2 mM) reduced the adsorption of arsenic onto CuO nano-particles. X-ray photoelectron spectroscopy (XPS) indicated that As(III) was oxidized and adsorbed in the form of As(V) on the surface of CuO.

Ramaprabhu and Mishra [139] had synthesized the graphene sheets by hydrogen induced exfoliation of graphitic oxide followed by functionalization. These functionalized graphene sheets were used for simultaneous removal of high concentration of arsenic (both trivalent and pentavalent) from aqueous solution using super capacitor based water filter. Sodium arsenate and sodium arsenite containing aqueous solutions with the initial arsenic concentrations varying from 50 mg. L\(^{-1}\) to 300 mg. L\(^{-1}\) were used for the above purpose. Maximum adsorption capacities, using Langmuir isotherm, for arsenate and arsenite were found to be nearly 142 and 139 mg. g\(^{-1}\), respectively.

Bimetal oxide magnetic nano-materials (MnFe\(_2\)O\(_4\) and CoFe\(_2\)O\(_4\)) were synthesized by Cai et al. [109] and studied as a function of pH, initial arsenic concentration, contact time and coexisting anions. Langmuir and Freundlich isotherm models were applied to fit the adsorption data, and the maximum adsorption capacities of As(III) and As(V) on MnFe\(_2\)O\(_4\) were 94 and 90 mg. g\(^{-1}\), and on CoFe\(_2\)O\(_4\) were 100 and 74 mg. g\(^{-1}\), respectively.

Multiwalled boron nitride nanotubes (BNNTs) functionalized with Fe\(_3\)O\(_4\) nanoparticles (NPs) were synthesized by Zhi et al. [140] and used for arsenic removal from aqueous solutions. Sonication followed by a heating process was adopted to functionalize Fe\(_3\)O\(_4\) nano-particles in situ onto a tube surface. A batch of adsorption experiments were conducted at neutral pH (6.9) and room temperature (25°C), using developed nano-composites that revealed effective As(V) removal. Langmuir, Freundlich, and Dubinin- Radushkevich adsorption isotherms were measured for a range of initial concentrations of As(V) from 1 to 40 mg. L\(^{-1}\) under the
same conditions. Equilibrium data fit was good for all the isotherms, indicating that the mechanism of As(V) adsorption was a combination of chemical complexation and physical electrostatic attraction with a slight preference for chemisorption. The applicability of the two isotherms to arsenic sorption showed the possibility of both monolayer sorption and heterogeneous energetic distribution of active sites on the surface of the sorbent. The adsorption capacity, estimated by Langmuir isotherm model was 32.2 mg. g\textsuperscript{-1}.

Shang et al. [141] synthesized hydrous cerium oxide (HCO) nano-particles by a simple precipitation process, and further investigated their arsenic adsorption performances. Due to their high specific surface area (198 m\textsuperscript{2}. g\textsuperscript{-1}) and the presence of high affinity surface hydroxyl groups, HCO nano-particles demonstrated exceptional adsorption properties in terms of adsorption capacity on both As(III) and As(V). At neutral pH, arsenic adsorption capacity of HCO reached over 170 mg. g\textsuperscript{-1} for As(III) and 107 mg. g\textsuperscript{-1} for As(V). Over a wide pH range from 3 to 11, HCO nano-particles could readily remove As(III) by adsorption. Such exceptional arsenic adsorption properties by HCO nano-particles were shown to derive from strong inner-sphere complexion.

1.3. Previous investigations on the sorptive removal of arsenic from the present laboratory

Synthesis of crystalline hydrous ferric oxide (CHFO), a modified iron-based adsorbent, and its arsenic sorption behaviour had been reported by Manna et al. [142]. Sorption of As(V) is highly dependent on the concentration and pH of the experimental system, while that for As(III) is pH insensitive. Equilibrium data confirmed to the Langmuir isotherm. Evaluated Langmuir constants indicated that CHFO is a better As(III) adsorber under experimental conditions. Sulphate, phosphate and bicarbonate compete poorly with As(III) sorption. A field
test using CHFO-packed fixed-bed column was also reported. Regeneration of the exhausted column was achieved up to 80 to 85% efficiency using 3 BV of 5 M NaOH solution recycled through the column five times. Arsenic was recovered as \( \text{As}_2\text{S}_3 \) from the regenerates, to avoid recycling of arsenic into the environment.

A systematic report on As(III) removal using synthetic crystalline hydrous titanium(IV) oxide (CHTO) was made by Manna et al. [143]. Absolute As(III) sorption capacity was 72 to 75 g. kg\(^{-1}\) at a pH of 7.0. CHTO has nearly the same sorption density in the pH range of 6.0 to 9.0. Interfering effect studies of some ions showed poor effect on the sorption process except for \( \text{HCO}_3^- \). Sorption data fit Freundlich and Langmuir isotherms well. Batch and column methods for regeneration of arsenic rich CHTO with 1.0 M NaOH solution showed 90% and 75 to 80% regain of its initial efficiency, respectively. Lab-bench mini-pilot scale application of a fixed-bed (bed volume=30.0 cm\(^3\)) CHTO column was reported at a down flow-rate of 33 to 34 B.V. (bed volume) h\(^{-1}\) using As(III) spiked (320 µg l\(^{-1}\)) natural tap water sample from Presidency College, Kolkata. Reuse of the bed after regeneration showed a decrease in As(III) removal efficiency to the extent of 20–25% to that of a fresh column. Arsenic recovery (99.25%) from the regenerate was also reported.

Pilot-scale performance in reducing excess iron and arsenic from contaminated groundwater has been systematically reported by Manna et al. [144]. Here, a double column unit, the first packed with \( \beta \)-MnO\(_2\) and the second with crystalline FeOOH (goethite variety) with filters attached to the outlet of hand-pump tube-wells had been used in the field. Results showed that the filters generate 10,000 to 15,000 BV and 19,000 to 35,000 BV water with iron ≤ 0.3 mg. L\(^{-1}\) and arsenic ≤ 10 µg. L\(^{-1}\) from groundwater having influent iron and arsenic levels around 3.75 to 7.25 mg. L\(^{-1}\) and 70 to 220 µg. L\(^{-1}\) respectively. The down flow rate of effluent water
was 237.6 to 305.5L m⁻² min⁻¹. Cost evaluation showed $US 0.50 to 0.70 per 1000 gallons of treated water and, hence, the technology is cost-effective for countries such as India and Bangladesh.

In the pH range of 3.0 to 9.0, adsorption of As(III) was found to be nearly the same while that of As(V) decreased with increasing pH for the studied arsenic concentrations (5.0 to 20.0 mg. L⁻¹) as established by Manna et al. [145]. The rate of adsorption of As(III) was faster than that of As(V) at equilibrium pH ~7.0 and temperature 30 (± 2)°C. Analysis of adsorption data for As(III) and As(V), respectively, at equilibrium pH 6.8 (±0.1) and 7.3 (±0.1) with three different two-parameter isotherm model equations showed the fitting order: Langmuir > Freundlich > Temkin. The monolayer adsorption capacity \( \theta_0 \) (mg g⁻¹) values evaluated from Langmuir isotherm for As(III) and As(V) were 43.86 and 27.55, respectively.

Hydrated stannic oxide (HSO) was synthesized by Manna et al. [146] and arsenic adsorption behaviour on it was reported. HSO was found to be amorphous, and stable thermally up to 700 °C. Analysis of isotherm adsorption data by two parameter isotherm model equations showed the order to obey: Langmuir > Freundlich > Temkin for As(III), and Langmuir > Temkin > Freundlich for As(V) respectively. Monolayer adsorption capacities (mg. g⁻¹) obtained for As(III) and As(V) were 15.85 and 4.30, respectively. Excepting phosphate, other anions studied show no adverse effect on adsorption of As(III) onto HSO. A fixed bed HSO packed column (internal diameter- 0.70 cm, bed height- 3.7 cm) with particle size (0.14–0.29 mm) generated 2400 and 450BV of potable water (As < 0.01 mg. L⁻¹), respectively, for As(III) and As(V) from spiked (1.0 mg. L⁻¹) water samples at pH 7.0 (±0.1).

Characterization of synthetic Fe(III)-Zr(IV) mixed oxide (NHIZO) by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM)
analysis confirmed the material to be agglomerated nanocrystallite particles (16-21 nm). Equilibrium data described Langmuir as well as Redlich-Peterson isotherm models very well as established by Gupta et al. [147]. Langmuir capacity was 65.5 mg g⁻¹ at 303 K, that increased with increasing temperature. Positive enthalpy (ΔH⁰) and negative free energy (ΔG⁰) changes indicated the endothermic and spontaneous nature of the reaction, respectively. Sorbed arsenic could be desorbed (~80%) by 2.0 M alkali.

Synthesis of nanostructure hydrous iron–titanium binary mixed oxide (NHITBMO) had been reported by Gupta et al. [148]. The synthetic oxide was hydrated and microcrystalline with 77.8 m² g⁻¹ BET surface area. Preliminary investigation of NHITBMO showed good pH dependent arsenic sorption affinity from aqueous solution reflected from Langmuir monolayer capacity (mg. g⁻¹) 80.0 and 14.6, for As(III) and As(V) respectively. Minimum dose required was 1.6 g NHITBMO per L of water (As total = 0.24 mg. L⁻¹) to reduce the arsenic level below 0.01 mg. L⁻¹ in batch treatment process.

Gupta et al. [149] had investigated the above material for arsenic removal systematically and found that Langmuir isotherm model described the equilibrium data (303 ±1.6 K) very well. Langmuir adsorption capacity (qₘ, mg. g⁻¹) obtained for the material was 85.0 (+ 4.0) and 14.0 (+ 0.5), respectively, for the reduced and oxidized species. Sorption percentage reduction of As(V) was significant while that of As(III) was insignificant in the presence of phosphate and sulfate. Fixed bed material column (5.1cm x 1.0cm) sorption tests gave 3.0, 0.7 and 4.5 L treated water (As content ≤ 0.01mg. L⁻¹) from separate As(III) and As(V) spiked (0.35 ± 0.02 mg. L⁻¹) natural ground water sample, respectively when inflow rate was (0.06 L. h⁻¹).

Langmuir monolayer capacity estimated was 9.3582 mg·g⁻¹ for As(V) sorption on to nanostructured hydrous iron(III)-zirconium(IV) bimetal mixed oxide (NHIZO) as established by
Gupta et al. [150] performed thermodynamic analysis of the equilibrium sorption data, suggesting the endothermic and spontaneous nature of the sorption reaction that took place with an increase of entropy ($\Delta S_0 = 96.6087 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

Gupta et al. [151] synthesized three samples of manganese associated hydrous iron(III) oxide (MNHFO), prepared by incinerating metal hydroxide precipitate at $T (\pm 5) = 90, 300$ and $600 \degree C$, showing an increase of crystalline nature in XRD patterns with decreasing As(III) removal percentages. Optimization of pH indicated that MNHFO heat treated at $90\degree C$ (MNHFO-1) could remove aqueous As(III) efficiently at pH between 3.0 and 7.0. Langmuir capacity ($q_m$) estimated was $691.04 \text{ mmol. kg}^{-1}$. Values of enthalpy, Gibb's free energy, and entropy changes ($\Delta H^0 = +23.23 \text{ kJ. mol}^{-1}$, $\Delta G^0 = -3.43$ to $-7.20 \text{ kJ. mol}^{-1}$ at $T = 283-323 \text{ K}$, $\Delta S^0 = +0.094 \text{ kJ mol}^{-1} \cdot \text{K}^{-1}$) suggested that the reaction was endothermic and spontaneous. As(III) sorbed by MNHFO-1 underwent surface oxidation to As(V) as evident from XPS and FTIR investigations. MNHFO-1 packed column (internal diameter: 1.0 cm, height: 3.7 cm) filtered $11.5 \text{ dm}^3$ groundwater ($105 \mu\text{g. As dm}^{-3}$) with a reduction in arsenic concentration to $< 10 \mu\text{g. dm}^{-3}$.

Gupta et al. [152] also prepared four samples of ceria incorporated manganese oxide (NCMO) by co-precipitation, calcination, and sol–gel methods. The synthetic samples were nanoparticle agglomerates with irregular surface morphology ($\text{Ce:Mn} = 1:1$). NCMO-1b sample, prepared by calcinations of metal hydroxide at $573 \text{ K}$ for $3.0 \text{ h}$, was nano-crystalline (70–90 nm) and that this hydrated material had a high BET surface area ($116.96 \text{ m}^2 \cdot \text{g}^{-1}$). Optimum pH range for As(V) sorption was 3.0–7.0 at $303 (\pm 1.0) \text{ K}$. Estimation of the sorption energy ($E = 17.15 \text{ kJ. mol}^{-1}$) indicated that As(V) was chemisorbed on NCMO-1b. Phosphate only reduced As(V) removal efficiency over NCMO-1b.
As(III) sorption was investigated with cerium incorporated manganese oxide (NCMO) nanoparticles as synthesized by Gupta et al. [153]. Kinetics and equilibrium data (pH = 7.0 ± 0.2, T = 303 ± 1.6 K, and I = 0.01 M) of As(III) sorption by NCMO described, respectively, pseudo-second order and Freundlich isotherm equations well. The sorption process was somewhat complicated in nature and divided into two different segments, initially very fast sorption followed by slow intra-particle diffusion process. Energy of As(III) sorption estimated by analyzing the equilibrium data using D–R isotherm model was 15.4 kJ. mol⁻¹, indicating ion-exchange type mechanism. Raman, FT-IR, pH effect, desorption, etc. studies indicated that As(III) was oxidized to As(V) during the sorption process.

1.4. Effect of ground water co-occurring ions in effective arsenic removal

Our objectives lie in the preparation of agglomerated mixed oxide nano-particles to be used in fixed-bed column for designing arsenic removal filter (ARF). However, the installation of ARFs based on adsorption, and ion-exchange techniques began at the end of 1998 in West Bengal (India) [154-155].

Again, the ARFs installed by various commercial companies at the Technological Park (Baruipore, S-24 Parganas) of West Bengal (India) when assessed regularly by a group of researchers showed that the assessment performances of those filters at field were not up to the level of specification given by the manufacturers [154-155].

Effectiveness of the arsenic removal plants (ARPs) to provide safe water was evaluated based on a study of five hundred and seventy seven (577) ARPs out of 1900 installed in five (5) arsenic-affected districts of West Bengal, India [155]. Out of five hundred and seventy seven (577), one forty five (145) (comprising 25.1%) were found in defunct condition. Both raw and filtered water from three hundred and five (305) ARPs were analyzed for total arsenic.
concentration. Forty-eight (48) ARPs were installed despite the concentration of arsenic in raw water below the Indian standard (50 μg. L⁻¹) and in twenty two (22) cases, even below WHO guideline value (10 μg. L⁻¹). Among two sixty four (264) ARPs, that have arsenic concentration in raw water above 50 μg. L⁻¹, one hundred and forty (140) (comprising 53.1%) and seventy three (73) (comprising 27.7%) failed to remove arsenic below WHO guideline value and Indian standard, respectively.

Highest arsenic concentration in treated water was 705 μg. L⁻¹. Analysis of two hundred and seventeen (217) treated water samples for iron showed that one hundred and seventy five (175) (comprising 80.6%) failed to remove iron below 300 μg. L⁻¹. The treated water became coloured on standing 6 to 8 h, for one hundred ninty one (191) (comprising 44.2%) ARPs, out of which twenty five (25) (comprising 5.8%) produced bad-odoured water.

Overall, the study showed that four hundred and seventy five (475) (comprising 82.3%) of the ARPs were not useful. Reasons for ineffectiveness and poor performance of these ARPs include improper maintenance, sand gushing problems, lack of user-friendliness and absence of community participation. Proper watershed management with active participation from the villagers is urgently required for successful mitigation.

The ineffectiveness and poor reliability of those ARFs are presumably due to the adverse influence of the dissolved ions (sulfate, phosphate, chloride, bicarbonate, silicate etc.) on arsenic adsorption reaction usually co-occurring in groundwater [154-155]. The interaction of dissolved ions (like sulfate, phosphate, bicarbonate, silicate etc.) with arsenic is manifested by the decrease in removal efficiency of arsenic as confirmed from Raman and ATR-FTIR spectroscopy.
Batch experiments were conducted by Meng et al. [156] to investigate the combined effects of phosphate, silicate, and bicarbonate on the removal of arsenic from Bangladesh groundwater (BGW) and simulated groundwater by iron hydroxides. The apparent adsorption constants indicated that the affinity of the anions for iron hydroxide sites decreased in the following order arsenate > phosphate > arsenite > silicate > bicarbonate. Phosphate, silicate and bicarbonate decreased the removal of As(III) even at relatively low concentrations and low surface site coverage. In the presence of bicarbonate and silicate, the adverse effect of phosphate on As(V) adsorption was magnified. The results suggested the combined effects of phosphate, silicate, and bicarbonate in promoting high mobility of arsenic in Bangladesh water.

Iron oxide and aluminum oxide were used by Maohong et al. [157] for studying the competing effects of solutes on the adsorption of As(V). These oxides, Fe$_2$O$_3$ and Al$_2$O$_3$, are nonporous adsorbents with low specific surface areas (5.05 and 0.55 m$^2$. g$^{-1}$) and focused on the effect of several typical competing solutes on removal of arsenic. The test results indicate that chloride, nitrate and sulfate did not have detectable effects, and that Se(IV) and V(V) showed slight effects on the adsorption of As(V) with Fe$_2$O$_3$. The results also showed that adsorption of As(V) on Al$_2$O$_3$ was not affected by chloride and nitrate anions, but slightly by Se(IV) and V(V) ions. Both phosphate and silica have significant adverse effects on the adsorption of As(V) over Fe$_2$O$_3$ and Al$_2$O$_3$. Compared to the other tested anions, phosphate anion was found to be the most prominent solute affecting As(V) adsorption with Fe$_2$O$_3$ and Al$_2$O$_3$. In general, Fe$_2$O$_3$ has a better performance than Al$_2$O$_3$ in the removal of As(V) within a water environment where multi competing solutes are present.
Meng et al. [158] studied the effects of silicate, sulfate, and carbonate on the removal of As(III) and As(V) by co-precipitation with ferric chloride. Silicate significantly decreased As(III) removal when silicate concentration was higher than 1.0 mg. L\(^{-1}\) and pH greater than 5. Removal of As(V) was decreased moderately by silicate in 0.04 M KNO\(_3\) solution. Addition of Ca\(^{2+}\) and Mg\(^{2+}\) to KNO\(_3\) solution reduced the adverse affect of silicate on As(V) removal. In the pH range 6.8, the adsorption capacity of ferric hydroxide for As(V) and As(III) was reduced from 864 and 116 mg. g\(^{-1}\) to 274 and 23 mg. g\(^{-1}\) Fe, respectively. Sulfate and carbonate had a negligible effect on the removal of As(III) and As(V). The triple layer model was used with site binding reactions to describe As(III) and As(V) removal by ferric hydroxide in the presence of silicate. The results obtained in the present study suggest that silicate in natural water can significantly decrease the efficiency of As(III) removal by coagulation treatment with ferric chloride.

The strong interaction of HCO\(_3\)^- at lower pH is related to the pH dependency of the carbonate adsorption.

Effects of sulphate, phosphate, silicate and humic acid (HA) on the removal of As(III) in KMnO\(_4\)-Fe(II) process were investigated by Guan et al. [159] in the pH range of 4.0–9.0 with permanganate and ferrous sulphate applied at selected dosage. Sulphate decreased the removal of arsenic by 6.5-36.0% at pH 6.0-9.0 and this decrease in adsorption did not increase with increasing concentration of sulphate from 50 to 100 mg. L\(^{-1}\). In the presence of 1.0 mg. L\(^{-1}\) phosphate, arsenic removal decreased gradually as pH increased from 4.0 to 6.0, and a sharp drop occurred at pH 7.0-9.0. The presence of 10 mg. L\(^{-1}\) silicate had negligible effect on arsenic removal at pH 4.0-5.0 but had reverse effect at pH 6.0-9.0 and this decrease was more significant at higher pH. The presence of HA dramatically decreased arsenic removal over the
pH range 6.0-9.0 and HA of higher concentration resulted in greater drop of arsenic removal. The effects of the competing anions on arsenic removal in KMnO₄- Fe(II) process were highly dependent on pH and the degree of these four anions influencing As(III) removal decreased in the following order, phosphate > humic acid > silicate > sulphate. Sulphate differed from the other three anions because sulphate decreased the removal of arsenic mainly by competitive adsorption while phosphate, silicate and HA decreased the removal of As(III) by competitive adsorption and also sequestering the formation of ferric hydroxide derived from Fe(II).

Thus, the objectives of this present work was to synthesize and characterize some bimetal mixed metal oxides and their evaluation for arsenic adsorption behavior with the prediction of fixed-bed column performances in the presence of ions occurring at high level in groundwater.

A summarized review of most of the sorbents along with their brief specification, discussed here have been presented in tabular form (Table-1)

**Table-1.1: Comparative assessment of naturally occurring, synthetic and low-cost sorbent for effective arsenic removal**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH Concentration range (mg. L⁻¹)</th>
<th>Capacity (mg. g⁻¹)</th>
<th>As(III)</th>
<th>As(V)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated red</td>
<td>5.8-7.5 for As(III) and 133.5 μmol</td>
<td>87.54%</td>
<td>96.52%</td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>mud</td>
<td>1.8-3.5 for As(V)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfate</td>
<td>7.2 for As(III) and 0.5-3.5 μmol</td>
<td>0.14</td>
<td>0.13 (pH-4)</td>
<td></td>
<td>41, 42</td>
</tr>
<tr>
<td>modified iron-</td>
<td>4-10 for As(V)</td>
<td></td>
<td></td>
<td></td>
<td>51</td>
</tr>
<tr>
<td>Material</td>
<td>pH</td>
<td>Size</td>
<td>Density</td>
<td>Stability</td>
<td>Sorption Capacity</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----</td>
<td>------------</td>
<td>---------</td>
<td>-----------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Iron oxide-coated sand (SMIOCS)</td>
<td>7.6</td>
<td>100 μL⁻¹</td>
<td>0.041</td>
<td>0.043</td>
<td>43</td>
</tr>
<tr>
<td>Synthetic goethite</td>
<td>9.0</td>
<td>0–60</td>
<td>22.0</td>
<td>4.0</td>
<td>46</td>
</tr>
<tr>
<td>Aluminum-loaded shirasu-zeolite</td>
<td>3–10</td>
<td>1.3 Mm</td>
<td>10.49</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>Manganese dioxide</td>
<td>7.9</td>
<td>&lt;1</td>
<td>-</td>
<td>0.172</td>
<td>54</td>
</tr>
<tr>
<td>Nano crystalline titanium dioxide</td>
<td>7.5 for As(III) &lt;8 for As(V)</td>
<td>59.93</td>
<td>37.46</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Granular titanium dioxide</td>
<td>7.0</td>
<td>for As(III) and As(V)</td>
<td>32.4</td>
<td>41.4</td>
<td>62</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>7.6</td>
<td>1</td>
<td>0.180</td>
<td>-</td>
<td>64</td>
</tr>
<tr>
<td>Mesoporous activated alumina</td>
<td>3–7</td>
<td>-</td>
<td>47</td>
<td>121</td>
<td>67</td>
</tr>
<tr>
<td>Activated for As(III)</td>
<td>7.00</td>
<td>0.79–4.90</td>
<td>3.48</td>
<td>11.9</td>
<td>69</td>
</tr>
</tbody>
</table>

52
<table>
<thead>
<tr>
<th>Material</th>
<th>As(V)</th>
<th>As(III)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina grains</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium oxide suspension</td>
<td>7.0</td>
<td>59.93</td>
<td>37.46</td>
</tr>
<tr>
<td>Ferricydrite</td>
<td>0.267-26.7 mmol. L⁻¹</td>
<td>266.5</td>
<td>111.02</td>
</tr>
<tr>
<td>Granular ferric hydroxide (GFH)</td>
<td>7</td>
<td>10 µg. L⁻¹</td>
<td>8 µg As g⁻¹</td>
</tr>
<tr>
<td>Natural Fe and Mn enriched sample</td>
<td>3</td>
<td>100 µg. L⁻¹</td>
<td>8.5</td>
</tr>
<tr>
<td>Iron oxide coated cement (IOCC)</td>
<td>7.0</td>
<td>0.5- 10.0 0.7- 13.5 mg. L⁻¹</td>
<td>0.67</td>
</tr>
<tr>
<td>Zero-valent iron</td>
<td>7.0</td>
<td>1 g. L⁻¹</td>
<td>1.80</td>
</tr>
<tr>
<td>Fe–Ce bimetal oxide</td>
<td></td>
<td>13.3 mmol. L⁻¹</td>
<td>2.0 mmol. g⁻¹</td>
</tr>
<tr>
<td>Fe(III)-Si(IV)</td>
<td>3-9</td>
<td>0-23</td>
<td>14.9</td>
</tr>
<tr>
<td>MnFe₂O₄ and CoFe₂O₄</td>
<td>3.0</td>
<td>0.2 g. L⁻¹</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>7.0 for As(V)</td>
<td>(MnFe₂O₄)</td>
<td>(MnFe₂O₄)</td>
</tr>
<tr>
<td>bimetal oxide</td>
<td>ω</td>
<td>𝑂₄</td>
<td>O₄)</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>magnetic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nanomaterials</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Al binary oxide</td>
<td>6</td>
<td>0.2</td>
<td>26.6</td>
</tr>
<tr>
<td>oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron–zirconium binary oxide</td>
<td>7.0</td>
<td>120</td>
<td>46.1</td>
</tr>
<tr>
<td>binary oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce-Ti oxide</td>
<td>&lt;7.0</td>
<td>50</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>µg. L⁻¹</td>
<td></td>
</tr>
<tr>
<td>Nano-structured ZrO₂</td>
<td>7.3</td>
<td>120</td>
<td>115-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>µg. L⁻¹</td>
<td>400</td>
</tr>
<tr>
<td>Spheres</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Akaganeite-type</td>
<td>7.5</td>
<td>10-100</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>mmol. g⁻¹</td>
</tr>
<tr>
<td>nanocrystals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nano-porous titania</td>
<td>4-7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>for As(III) and near 4.0 for As(V)</td>
<td></td>
</tr>
<tr>
<td>Ultrafine α-Fe₂O₃ nanoparticles</td>
<td>7.0</td>
<td>Upto 200</td>
<td>95.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>47.0</td>
</tr>
<tr>
<td>Nano-sized iron oxide-coated perlite</td>
<td>6.5-7.0</td>
<td>1.5</td>
<td>0.043</td>
</tr>
<tr>
<td>Zirconium based nano-</td>
<td>2.5-3.5</td>
<td>256.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle</td>
<td>Concentration (mmol g(^{-1}))</td>
<td>Solubility (mg L(^{-1}))</td>
<td>pH</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>----------------------------------</td>
<td>-----------------------------</td>
<td>----</td>
</tr>
<tr>
<td>Zirconia nanoparticle</td>
<td>8.0</td>
<td>1.85</td>
<td>-</td>
</tr>
<tr>
<td>Cupric oxide nano-particles</td>
<td>8.0</td>
<td>0.1 - 100</td>
<td>26.9</td>
</tr>
<tr>
<td>Hydrous cerium oxide nanoparticles</td>
<td>7.0</td>
<td>As(III, V, µg, L(^{-1})): 10 and 50</td>
<td>13.0</td>
</tr>
<tr>
<td>Crystalline hydrous ferric oxide (CHFO)</td>
<td>7.0</td>
<td>50.0</td>
<td>33.0</td>
</tr>
<tr>
<td>Crystalline hydrous titanium (IV) oxide (CHTO)</td>
<td>7.0</td>
<td>25.0</td>
<td>31.74</td>
</tr>
<tr>
<td>Hydrous iron(III)- Tin(IV) Binary Mixed Oxide</td>
<td>6.8 for As(III) and 7.3 for As(V)</td>
<td>43.86</td>
<td>27.55</td>
</tr>
<tr>
<td>Synthetic hydrous stannic oxide</td>
<td>7.0</td>
<td>20.0</td>
<td>6.44</td>
</tr>
<tr>
<td>Nanostructure iron(III)-</td>
<td>7.0 and 6.4</td>
<td>5-350</td>
<td>66.5</td>
</tr>
</tbody>
</table>
### 1.5. Summary of the present work

In the first phase, synthetic iron(III)-chromium(III) mixed oxide (NHICO) was synthesized in accordance with environment friendly green chemistry and characterized as agglomerated nanoparticles (40 to 50 nm). It was investigated for arsenic sorption behavior from aqueous...
media in the presence of ground water co-occurring ions at optimized pH, range for As(III) = 6.8 - 7.0 and that for As(V) = 6.2 - 6.4.

Time required to attain dynamic equilibrium was 40 minutes and two hours, respectively for As(V) and As(III) reaction. Sorption kinetics of As(V) and As(III), respectively, could well be described by the pseudo-second order kinetic model.

Good agreement of the equilibrium data of As(V) with the Freundlich isotherm suggested that NHICO surface was heterogeneous and not equally accessible to all As(V) species. Modeling of the equilibrium As(III) data showed that the goodness of the data fit with the Langmuir model was comparatively better than that of the Freundlich model. Well fits of the equilibrium data with the Langmuir model indicated that the sorption sites on NHICO surface were homogeneous and equally accessed by all As(III) species.

It was found that the reactions of arsenic in the presence or the absence of ions at background were endothermic (ΔH° = positive), which took place with increasing entropy (ΔS° = positive) at the solid-liquid interface. Values of ΔG° were found to be increasingly negative with increasing temperature on the reactions in the absence or presence of background ions, indicating increase of spontaneity (ΔG° = negative) of the reactions.

Microscopic images served a long way in qualitatively and quantitatively establishing the sorption mechanism of arsenic over the given synthetic material. Magnitudes of the mean sorption energy (E_{DR}) of As(V) and As(III), respectively ranged between 8.0 to 16.0 kJ. mol^{-1}, indicating ion/ligand exchange mechanism for the sorption reaction involving surface M—OH groups that was further supported by the FTIR analysis.
Application of NHICO was highlighted through its column performance in filtering ground water contaminated samples either by its kinetic modeling of stationary, fixed bed column or through analyzing its decontamination technique via idealized curve.

NHICO packed column upto a bed height 6.0 cm (internal diameter, i.d.: 1 cm, length of glass tube: 25.0 cm) when used for the filtration of high arsenic ground water (As concentration: 0.101 mg L\(^{-1}\)), yielded 4.7 L water with arsenic concentration ≤ 0.01 mg L\(^{-1}\). Fixed stationary bed after use was regenerated up to a level of 90 (± 1.5) % with 0.35 L of optimized 0.25 M NaOH solution.

Kinetic modeling of the break through curves (bed height 5.0 cm, i.d.: 0.7 cm) of the fixed-bed column experiments were conducted using uniformly packed NHICO using the same ground water field sample for their variation in bed depth, effluent flow rate and arsenic concentration in input solution.

In the next phase, performances of As(V) and As(III) sorption, respectively, over agglomerated nano-particles of calcined (250°C) iron(III)–aluminum(III)bimetal mixed oxide (NIAO-250°C) were investigated at 30°C and pH 7.0 in the absence/presence of background ions occurring in groundwater.

Value of sorption amount was maximum for both As(V) and As(III), respectively in the absence of any externally added ion that significantly decreased amplifying varying degree of competitive influence of the ions present in the system under investigation.

Langmuir monolayer capacity of As(V) and As(III) sorption over NIAO-250, respectively estimated in the absence of any other ion was about 15–35% higher than that in the presence of tested ions occurring in groundwater, implying adverse influence on the removal reaction.
Microscopic images, x-ray diffraction pattern and FTIR analysis prove to be quite handy in qualitative and quantitative estimation of the real state of the actual sorbate on the surface as well its distribution in the inner core. Difficulty of desorption of sorbed arsenic indicated strong binding of As(V) as well as As(III) onto the given sorbent (NIAO-250) surface.

Kinetic modeling of the fixed bed column experiments was also performed here with column specification (bed height 6.0 cm, i.d.: 0.7 cm) using ground water sample of a different source compared to the field chosen for NHICO.

Arsenic saturated NIAO-250 bed was regenerated with 2.5 L of 1.0 M NaOH [effluent rate: 1.0 (± 0.1) mL. min\(^{-1}\), EBCT ~ 2.31 min] and washed with pH 7.0 water to make it free from alkali.

Reuse of the fixed bed column (BV 2.31 cm\(^3\)) of NIAO-250 after intermediate reactivation twice yielded 10.90 L (~ 4719 times of column BV) filtered water with arsenic level ≤ 10 µg. L\(^{-1}\) from a sample of groundwater (130 µg As(III). L\(^{-1}\)).

Idealized fixed-bed column experiments were also conducted using uniformly packed NIAO-250 up to a bed height of 6.0 cm in glass tubes of internal diameter (i. d.) 2.1 cm and length of the column 25.0 cm. It was found that the stationary fixed-bed column of NIAO-250 filtered 6.5 L water with outlet water volume (V\(_b\)) at breakthrough point (As concentration = 10 µg. L\(^{-1}\)) to be 4.2 L and EBCT value 20 minute.

In the final phase, synthetic cerium(IV) associated iron(III) bimetal mixed oxide (NICMO) was characterized to be agglomerated nano-particles (10-20 nm) with zero-point surface charge pH (pH\(_{zpc}\)) at 7.13 (± 0.05) and crystallite size 10-20 nm (TEM image analysis) under crystal packing force.
The observations established that the kinetics of As (V) as well as As(III) sorption reaction with NICMO in the presence of tested ions at background was pseudo-second order type. Equilibrium data for the sorption reactions of As(V) as well as As(III) in the absence/presence of background ions described the Langmuir and the D-R isotherm model relatively better than the Freundlich model.

Range of values of standard enthalpy (ΔH°) in case of As(V) indicated physio-sorption to be the actual nature of the reactions and the negative values of Gibb’s free energy (ΔG°) confirmed the overall spontaneity of the reactions in the given direction. Contrary to which is chemo-sorption, the actual nature of the reaction taking place for As(III) with the sorption process getting more favorable with the increase of temperature. Different percentage of desorption supported by energy of sorption values established the varying degree of interaction of As(V) and As(III) over the given oxide surface.

Microscopic images and XRD analysis prove to be quite handy in quantifying the degree of change of morphology and composition of the sorbent surface after arsenic binding.

Interpretation of experimental evidences of As(III) sorption over NICMO surface confirmed oxidation of surface adsorbed As(III) to As(V) in a thermodynamically controlled sorption reaction. Break-through curves obtained for As(III) removal from the spiked groundwater were described well by the Thomas model better than that of Adam-Bohart model.

Kinetic modeling of the fixed bed column experiments was performed here with column specification (bed height 5.0 cm, i.d.: 0.7 cm) to get an insight of the sorptive behaviour of arsenic used in this study.
It was found that the stationary fixed-bed column of NICMO filtered 3.2 L water with outlet water volume \( (V_b) \) at breakthrough point (As concentration = 10 \( \mu g.L^{-1} \)) to be 2.0 L and EBCT value 9.24 minute.

Natural ground water filtration efficiency can be estimated from the fixed bed column (bed height: 6.0 cm, i.d.: 1.4 cm) saturation at exhaustion point that was found to be 70.34 %.

This extensive study of all the laboratory prepared sorbents established those synthetic bimetal mixed oxides as good arsenic scavenger that could be used as an effective media for sorptive removal of arsenic from naturally occurring, contaminated ground water through different experimental modes.

1.6 Aims and objective of the present work

Naturally occurring high arsenic (>10 \( \mu g. L^{-1} \)) containing groundwater is a worldwide serious threat to public health and is endemic in the third world countries like India and Bangladesh etc. To overcome this problem and reinforce its remedial measures, various treatment methods have been adopted under both laboratory and field conditions. Technologies frequently used so far have already been detailed discussed in this chapter. Among them, the sorption process is the most promising and user-friendly technology because it is simple, effective, low cost and no involvement of trained personnel.

Consequently, a good number of materials (both natural and synthetic) had been investigated for the treatment of arsenic contaminated water. Recently, nano-structured materials have gained special attention for the removal purpose since they possess very high removal capacity compared to the bulk materials. Thus, a numerous nano-structured materials have been reported in the literature which had been applied for the treatment of high arsenic (>10 \( \mu g. L^{-1} \)) contaminated groundwater. Mixed metal oxides of nano dimension usually show
abnormally high sorption capacity not only for its high surface/volume ratio but also for its high surface energy that is attributed to the crystallographic changes like lattice contraction or deformation, appearance of lattice defects, rearrangements of surface atoms, or changes in morphology.

To mitigate arsenic problem locally in West Bengal, various arsenic removal filters (ARFs) had been developed based on sorption and ion-exchange techniques that began at the end of 1998 in West Bengal (India). With this objective, a number of filters had been developed in the commercial scale and professionally brought to lime light by several companies under different trade names. Before installation for the public welfare, various commercial companies were asked to evaluate the assessment performance of ARFs at Bengal basin of river “The Ganga” under the supervision of the Government of West Bengal (India). Surprisingly, performances of those ARFs were not up to the level of specification given by the manufacturers when assessed regularly by a group of researchers. The ineffectiveness and poor reliability of those ARFs are presumably due to the adverse influence of the dissolved ions (sulfate, phosphate, chloride, bicarbonate, silicate etc.) on arsenic sorption reaction usually co-occurring in groundwater.

Objectives of the present work undertaken are

❖ Preparation and characterization of agglomerated bimetal mixed oxide nano-particles,
❖ Use of such materials for As(III) and As(V) sorption behavior in the presence of ions occurring in groundwater with arsenic, and
❖ Evaluation of the removal efficiency of the materials in packed fixed-bed columns for designing arsenic removal filters (ARF).
Thus, arsenic removal technology based on the development and application of upgraded nano-structured material in adversant with the real life natural ground water system for the purification of contaminated water is the main objective of this present work. Despite the wide spectrum of the plan of work, the points that can be highlighted for the present work are given below:

❖ Synthesis of some nano-structured bimetal mixed oxides by simple environmental friendly chemical routes for their use in arsenic sorption from aqueous phases.

❖ Characterization of the synthesized oxide by some modern instrumental techniques such as x-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR), thermal analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), BET surface analysis, Raman spectroscopy to account for its actual physical and chemical nature.

❖ A detailed study of its physio-chemical aspects like the effect of calcinations temperature, pH, kinetics, isotherm, thermodynamic parameters etc of arsenic sorption reaction on these oxides to evaluate its reaction behavior and uptake capacity.

❖ Study of the effect of ground water co-occurring ions on arsenic removal capacity by the sorbents and its experimental interpretation.

❖ Development of a simple mechanistic path way to account for the nature of arsenic sorption and its binding onto the oxide surface.

❖ Column application followed by modeling using these sorbents in natural as well as spiked water sample. A close look at the improvement of the water quality parameters of the ground water sample was also a part of this present work.

It had been mentioned previously that the nano-structured bimetal mixed metal oxides could be synthesized by a number of methods. But the materials obtained by all the routes might not
have the same solute scavenging power from its aqueous solutions due to the absence of surface hydroxyl groups. Thus, the synthetic strategies pertaining to the synthesis of nano-structured bimetal mixed metal oxides are to be so adopted that the materials should retain the surface hydroxyl groups for scavenging arsenic from aqueous solution. In order to keep our objectives unperturbed, the following strategic points were taken into consideration before undergoing the following synthesis:

❖ Synthetic routes should be as simple as possible.
❖ The synthesis process should hold on to large scale i.e., large amount of product must be obtained from a single set of reaction.
❖ Starting materials should be cheap and easily available.
❖ Step-wise reactions, reaction conditions applied and waste disposal management involved in this synthetic route should be environment friendly.
❖ The reaction should occur at low temperature such that the surface hydroxyl groups must be retained to serve the purpose of surface binding to arsenic species.
❖ The binary oxide should not be a physical mixture of the pure individual oxides.

In accordance to these synthetic strategies undertaken in the adsorbent synthesis, we have finally adopted a chemical route. Despite a number of chemical routes available, co-precipitation is the simplest one encapsulating all the strategic points highlighted above. Thus, the present work emphasizes on the synthesis and characterization of some nano-structured binary mixed metal oxides and their evaluation for arsenic sorption behavior with the prediction of fixed-bed column performances in presence of ions occurring at high level in groundwater.
Literature Cited


[8] Bhattacharya, S., Gupta, K., Debnath, S., Ghosh, U.C., Chattopadhyay, D., Mukhopadhyay, A. Arsenic bioaccumulation in rice and edible plants and subsequent


cerium incorporated manganese oxide (NCMO): A physical insight into the mechanistic

Das, B., Nayak, B., Roy, B.K., Mukherjee, A., Chakraborti, D. Ineffectivenesss and poor
reliability of arsenic removal plants in West Bengal, India, Environ. Sci. Technol. 39 (11)

A., Rahman, M.M., Chakraborti, D. Million dollar arsenic removal plants in West Bengal,


[157] Jeong, Y., Maohong, F., Leeuwen, J.V., Belczyk, J.K. Effect of competing solutes on

[158] Meng, X., Bang, S., Korfiatis, G.P. Effects of silicate, sulfate, and carbonate on arsenic

[159] Guan, X., Dong, H., Ma, J., Jiang, L. Removal of arsenic from water: Effects of
competing anions on As(III) removal in KMnO₄- Fe(II) process. Water Res. 43 (2009) 3891-
3899.