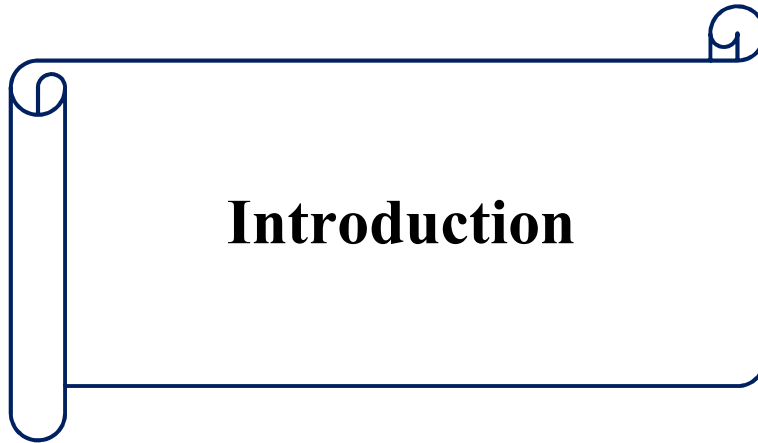


Chapter 1



1. Introduction:

This thesis deliberates the contextual of the problem undertaken in this research work, *i.e.*, the problems associated with contamination of groundwater used for drinking and their remediation by systematically corroborating and applying oxidation-coagulation-adsorption at optimized pH (OCOP) method in removal of arsenic and some heavy metals, *viz.*, *iron, manganese, cadmium, lead, nickel, chromium, copper, and cobalt, etc.*, commonly found in excess in groundwater.

1.1. Contextual:

Currently drinking water crisis is a serious problem in the urban as well as rural areas of many countries all over world [1]. Millions of people face barely preventable diseases caused by consumption of contaminated groundwater [2–4]. The deficiency of safe drinking water is one of the great concerns in front of human beings in the twenty first century [5, 6]. A huge amount of water pollutants like organic, inorganic, bacteriological, *etc.*, enter the aquifers from different sources adding to the drinking water crisis [7–9]. Focusing on the groundwater as a source for drinking it is seen that there are different causes for contamination of it. The major sources of contaminants exposure to groundwater are natural geological activities such as weathering of sedimentary rocks, volcanic emissions, oxidations, leaching from sulphides by carbonates and microbial mobilization, erosion sources, urban discharges, agricultural sources, mining discharges, and combustion/industrial discharges, fertilizations, mining related activities, *etc.* [10–13].

1.2. What is inorganic contaminant?

Inorganic Contaminants (IOC) are elements or compounds such as salt, clays, metals or ions [14, 15] *etc* found in water sources (ground and surface) due to natural cause in the geology or caused by activities of man through mining, industry or agriculture. Because of this it is common to have trace amounts of many IOCs in water supplies. Among the inorganic contaminants found in groundwater, Arsenic (As), Fluoride (F⁻), Nitrate (NO₃⁻) and some heavy metals like Lead (Pb), Mercury (Hg), Copper (Cu), Nickel (Ni), Chromium (Cr), Cadmium (Cd), Cobalt (Co), *etc.*, are most dangerous [16, 17]. Although, to some extent Iron (Fe), Manganese (Mn), Magnesium (Mg), *etc.*, are important for good health, excess of these elements also affect health.

1.3. Origin and mitigation of inorganic contaminants in groundwater:

Earth is covered by a thin “*veneer*” of sediment and the veneer caps igneous and metamorphic “*basement*”. Veneer is converted to sediment and sedimentary rock by several steps. They are *weathering* – breaks pre-existing rock into small fragments or new minerals, transportation of the sediments to a sedimentary basin, deposition of the sediment, burial and lithification to make sedimentary rock [18]. Due to these natural processes sediments and sedimentary rocks containing hazardous elements such as As, Fe, Mn, Pb, Hg, Cu, Ni, Cr, Cd, and Co, etc. comes to the groundwater in excess creating groundwater pollution [19]. Due to volcanic emission highly pressurized lava and volcanic ash containing, heavy metals such as As, Fe, and Mg, *etc.*, coming from the top of volcano flows to the ground contaminating the groundwater sources [20].

Millions of people around the world are anguishing from arsenic contamination [21]. A significant number of reports about the health hazards caused by arsenic poisoning has come from many developing countries such as Bangladesh, China, Myanmar, Vietnam, Nepal, India, Mexico, Argentina, USA and Japan [10]. In Bangladesh alone, more than 75 million people are at risk of arsenic contamination, and 24 million people are exposed to arsenic contamination [22]. In Nepal, in the Terai belt about half million peoples are at high risk of arsenic contamination, and the same problem affects other south Asian and southeast Asian countries [23, 24]. In India, the states of Assam, West Bengal, Bihar, UP and Punjab are highly affected by As contamination of groundwater [25–27]. Most of the districts of Assam are contaminated by perilous Arsenic along with Fe and Mn [28, 29]. **Figure 1.1**, shows As contamination of groundwater of different districts of Assam. All the districts except West Karbi Anglong, East Karbi Anglong, Hojai and Tinsukia are contaminated with arsenic. The districts of Jorhat, Majuli, Lakhimpur, Dhemaji, Nalbari, Golaghat, Baksa and Barpeta are highly contaminated with arsenic [29, 30].

Iron is the 2nd most abundant metal and 4th most abundant element in earth’s crust; present in water in two forms, i.e., the soluble ferrous (Fe^{2+}) iron and the insoluble ferric (Fe^{3+}) iron [32]. Manganese is also one of the most abundant metals on the earth's surface, making up approximately 0.1% of the earth’s crust [32]. Manganese is not found naturally in its pure (elemental) form, but is a component of over 100 minerals [33].

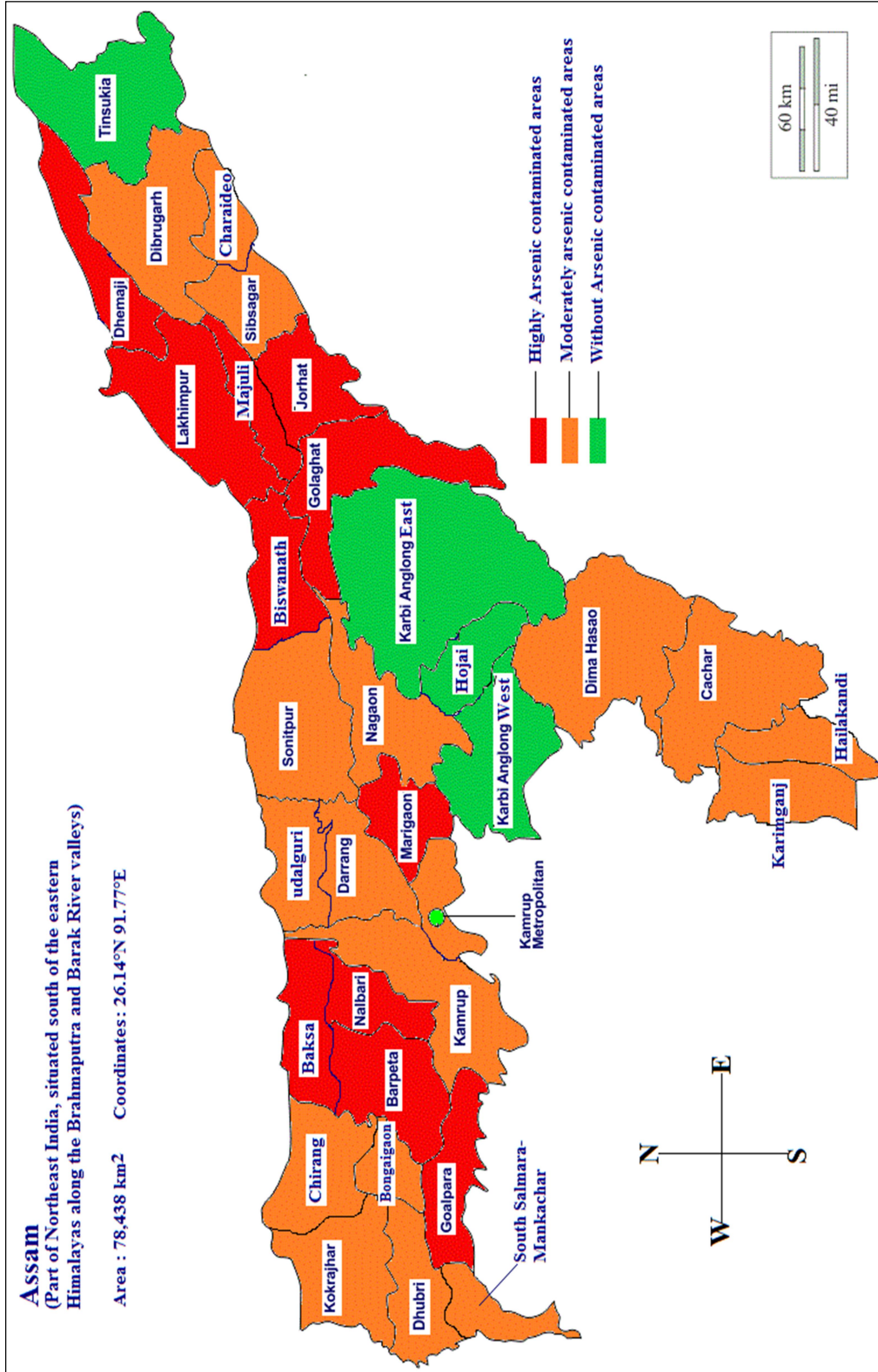


Figure 1.1: Map of state Assam with indication of arsenic contaminated districts [31].

The most common sources of iron and manganese in groundwater are naturally occurring, for example, from weathering of iron and manganese bearing minerals and rocks [34]. Industrial effluent, acid-mine drainage, sewage and landfill leachate may also contribute iron and manganese to local groundwater [35]. Manganese occurs naturally in many surface water and groundwater sources and in soils that may erode into these waters [36]. However, human activities are also responsible for much of the manganese contamination in water in some areas. Iron is the most common element found in groundwater of almost in all over the world. In India, maximum iron concentration in groundwater were found in Assam, Bihar, Gujrat, Haryana, MP, Punjab, Tamil Nadu, UP and West Bengal [36, 37]. Similarly manganese is also found in surface and groundwater of many countries such as USA, Germany, Ghana, England, Wales, Canada, *etc.*[33] In India, manganese ore deposits occur mainly as metamorphosed bedded sedimentary deposits associated with Gondite Series of Madhya Pradesh, Maharashtra, Gujarat, Odisha and with Kodurite Series of Odisha and Andhra Pradesh [38]. So contamination of groundwater by Manganese generally occurs in these states of India.

Other common metals such as Cadmium, Lead, Nickel, Chromium, Copper, Cobalt, *etc.*, are also found in groundwater of some places in excess amount which is very perilous for the human health [39]. Heavy metals, *i.e.*, elements with an atomic density greater than $3.4-7.0 \text{ g/cm}^3$, are one of the most tenacious pollutants found in groundwater [40]. Heavy metals generally exist in nature, as a result of natural phenomenon such as erosion and weathering of parent rocks, spreading the heavy metal concentrations in the groundwater [41]. Releasing the leachates in to groundwater by weak management of disposal of domestic and solid waste is another source of heavy metal contamination in groundwater [41]. Industries like metal plating, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, pharmaceuticals, hospitals *etc.*, directly or indirectly discharge heavy metal waste waters into the environment [42]. Many studies of occurrence and monitoring of heavy metals in ground water have been investigated recently. Groundwater of India, Bangladesh, China, Mexico, USA, Korea, Netherlands, Malaysia, middle Russia, Jordan, Nigeria, *etc.*, are contaminated with heavy metals such as As, Fe, Mn, Hg, Pb, Cr, Cd, Ni, Cu in various concentrations [41, 43]. It has been reported that various heavy metals in the surface water of the river Ganga follows the sequence: $\text{Fe} > \text{Mn} > \text{Ni} > \text{Cr} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Cd}$ [43].

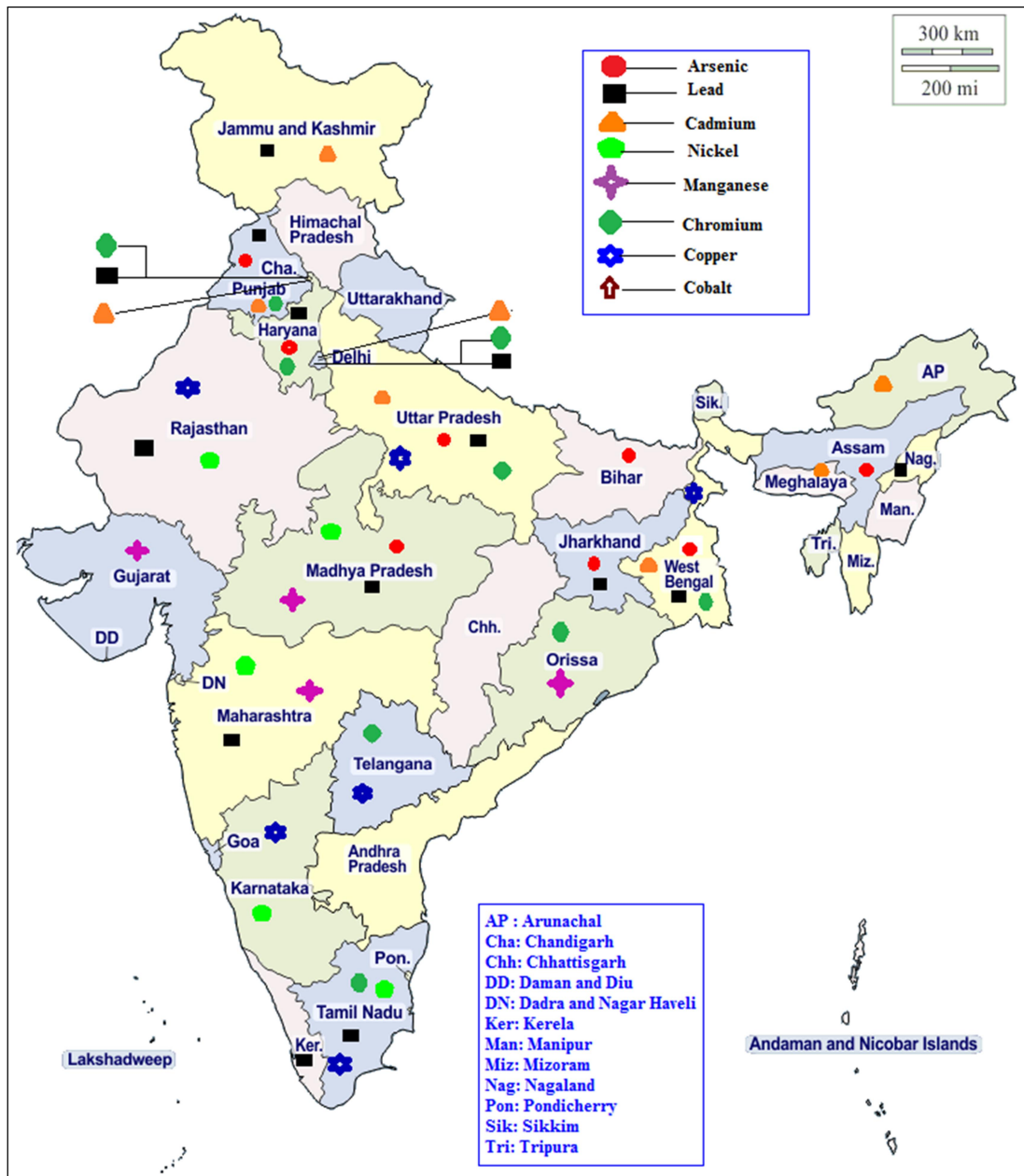


Figure 1.2: Map of India showing heavy metal contaminations found in groundwater in different states [44].

The spread of heavy metals such as As, Fe, Mn, Hg, Pb, Cr, Cd, Ni, Cu, etc., in groundwater of different states of India map are shown in **Figure 1.2**. State-wise details of ground water contamination by different heavy metals in India are shown in **Table 1.1**.

Table 1.1: State-wise details of ground water contamination in India [45]

Sl No	Name of the State	Arsenic (> 0.01 mg/L)	Iron (>1.0 mg/L)	Heavy metals		
				Lead (> 0.01 mg/L)	Cadmium (> 0.003 mg/L)	Chromium (> 0.05 mg/L)
1	Andhra Pradesh	3	7	-	-	-
2	Arunachal Pradesh	-	4	-	-	-
3	Assam	19	18	-	-	-
4	Bihar	23	19	-	-	-
5	Chhattisgarh	1	4	1	1	1
6	Delhi	2	-	3	1	4
7	Goa	-	-	-	-	-
8	Gujarat	12	6	-	-	-
9	Haryana	15	17	17	7	1
10	Himachal Pradesh	1	-	-	-	-
11	Jammu & Kashmir	3	6	3	1	-
12	Jharkhand	1	6	1	-	-
13	Karnataka	2	22	-	-	-
14	Kerala	-	15	2	-	1
15	Madhya Pradesh	8	42	16	-	-
16	Maharashtra	-	20	19	-	-
17	Manipur	2	1	-	-	-
18	Meghalaya	-	3	-	-	-
19	Nagaland	-	1	-	-	-
20	Odisha	1	21	-	-	1
21	Punjab	10	9	6	8	10
22	Rajasthan	1	33	4	-	-
23	Tamil Nadu	9	2	3	1	5

24	Telangana	1	8	2	1	1
25	Tripura	-	4	-	-	-
26	Uttar Pradesh	29	15	10	2	4
27	Uttarakhand	-	-	-	-	-
28	West Bengal	9	15	6	2	2
29	Andaman & Nicobar	-	1	-	-	-
30	Chandigarh	-	-	-	-	-
31	Dadra & Nagar Haveli	-	-	-	-	-
32	Daman & Diu	1	-	-	-	-
33	Pondicherry	-	-	-	-	-

1.4. Consequences of metal contamination of groundwater:

Contamination of groundwater by hazardous metal causes various problems such as chronic diseases in human health, lower and damaged agricultural production, washing problems in laundries, etc. Among the heavy metals arsenic is the most dangerous element found in groundwater [33]. Long-term consumption of As through drinking water causes various chronic diseases (Arsenicosis) in human body including hyperkeratosis; cancer of various organs and tissues; and adverse cardiovascular, neurological, haematological, renal and respiratory problems [46–52]. In India and Bangladesh alone, a population over 450 million are at a risk of arsenic poisoning [53]. The World Health Organization (WHO) is prescribing 10 µg/L as a provisional guideline value for As in drinking water [54, 55]. In India, the Bureau of Indian Standard (BIS) also has recently set a permissible limit of 10 µg/L for As in drinking water [56].

Symptoms of Arsenicosis found on the body of some people of arsenic effected areas at Sariyotli in Nagaon district and Titabar of Jorhat district in Assam, India are presented in **Figure 1.3**. Manganese and iron are essential elements to a certain level only but above this level they also become toxic [33, 54]. Although Fe is essential for human health, excessive amount of consumption causes hemochromatosis, change or mutation in a gene [54, 57]. Iron accumulation in organs within the body causes liver, heart, and pancreatic damage; stomach problems; nausea and vomiting [58, 59]. Early

symptoms include fatigue, weight loss and joint pain. Iron also imparts a bitter astringent taste to water and a brownish colour to laundered clothing and plumbing fixtures.



Figure 1.3: Symptoms of Arsenicosis found at Sariyohali in Nagaon district and Titabar of Jorhat district in Assam, India.

The syndrome known as “manganism” [33] is caused by exposure to very high levels of manganese consumption and is characterized by a “Parkinson-like syndrome”, including weakness, anorexia, muscles pain, apathy and slow speech, monotonous tone of voice, emotionless “masklike” facial expression and slow, clumsy movement of the limbs. In general, these effects are irreversible [60]. From animal experiments, it is known that inhaled manganese (even the insoluble manganese dioxide) is transported in a retrograde direction from the olfactory epithelium to the striatum of the brain [33]. During its uptake through the olfactory nerve endings, it may damage the astrocytes. Manganese existence in groundwater causes aesthetic and economic damage, and imparts brownish stains to laundry. Manganese affects taste of water and causes dark brown or black stains on plumbing fixtures. It is relatively non-toxic to animals but toxic to plants at high levels [61]. Differences in valence state play an important role in the level of bioavailability hence in the degree of potential risk. The Eh-pH diagram [62] indicates that the dominant dissolved species of manganese in natural waters is Mn^{2+} .

Epidemiological studies indicated neurological effects of manganese exposures from untreated anaerobic groundwater where the majority of the manganese was in solution, i.e., Mn^{2+} [63].

Excessive concentrations of lead, cobalt, cadmium and nickel can cause variety of harmful health effects even sometime cause death [64]. Cd^{2+} is a potent neurotoxic metal and is known to cause kidney damage, renal dysfunction, bone degeneration, lung inefficiency, liver damage and hypertension in humans [65]. Though Co is a key constituent of cobalamin (vitamin B12); the excess intake of Co results in toxic, carcinogenic and mutagenic effects on human health [64]. Excess concentration of Cr^{6+} found in groundwater is acutely toxic, carcinogenic, mutagenic and teratogenic [66–69]. Ingestion of copper at high dose causes health effect on human body such as lesions in the central nervous system, and liver and kidney damage or Wilson's disease [70]. Lead poisoning through drinking water in human body causes damage of kidney, liver and brain, nervous system, reproductive system, and causes anaemia, sickness or death [72]. Severe exposure to lead has been associated with sterility, abortion, stillbirth and neonatal deaths [68]. Ni exposure to drinking water causes allergic skin reaction, weight gain, weakness, and damage to lungs, the nervous system and mucous membranes [73]. So it is necessary to remove heavy metals stated above from groundwater sources before drinking. The WHO sets guideline values of the heavy metals of Pb, Cr, Ni, Cu and Cd as 0.01 mg/L, 0.05 mg/L, 0.07 mg/L, 2.0 mg/L, 0.003 mg/L, respectively, [55, 74–77] for drinking water.

1.5. Occurrence of inorganic contaminants in groundwater:

Arsenic exists generally in four oxidation states (-3, 0, +3, +5) and the most common species of arsenic in water are Arsenite (As^{3+}) and Arsenate (As^{5+}). Redox potential (Eh) and pH are the most important factors controlling arsenic speciation [78]. Arsenite is the dominant species in anoxic conditions and found to be as H_3AsO_3^0 (pKa1 = 9.1), H_2AsO_3^- (pKa2 = 12.1), HAsO_3^{2-} (pKa3 = 13.4), and AsO_3^{3-} , whereas arsenate exists under oxic conditions and it is found to be as H_3AsO_4^0 (pKa1 = 2.1), H_2AsO_4^- (pKa2 = 6.7), HAsO_4^{2-} (pKa3 = 11.2), and AsO_4^{3-} depending upon the pH of the water [79]. In groundwater systems, iron occurs in one of two oxidation states: reduced soluble divalent ferrous iron (Fe^{2+}) or oxidized insoluble trivalent ferric iron (Fe^{3+}) depending upon the

pH of the water. Eh-pH diagram of As, Fe, and Mn is presented in **Figure 1.4**, **1.5**, and **1.6**, respectively.

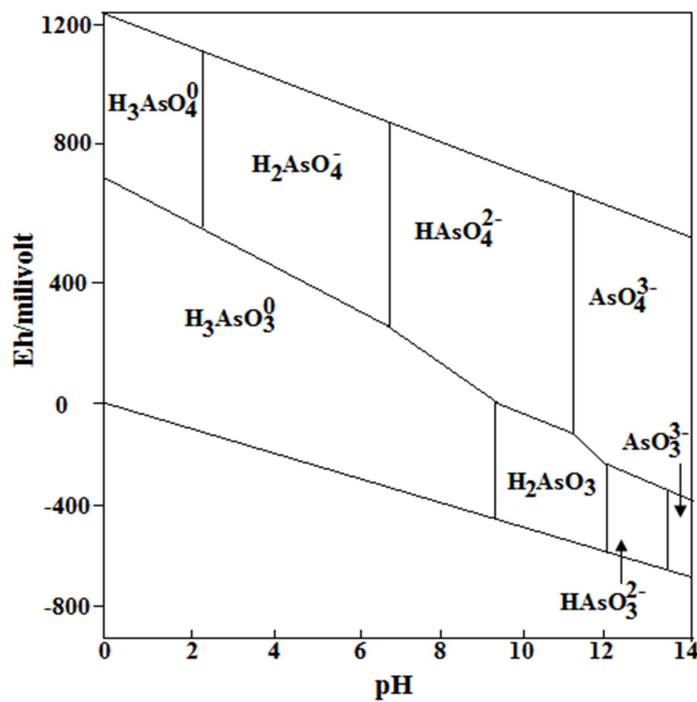


Figure 1.4: Eh-pH diagram for arsenic [80] in water at 25°C.

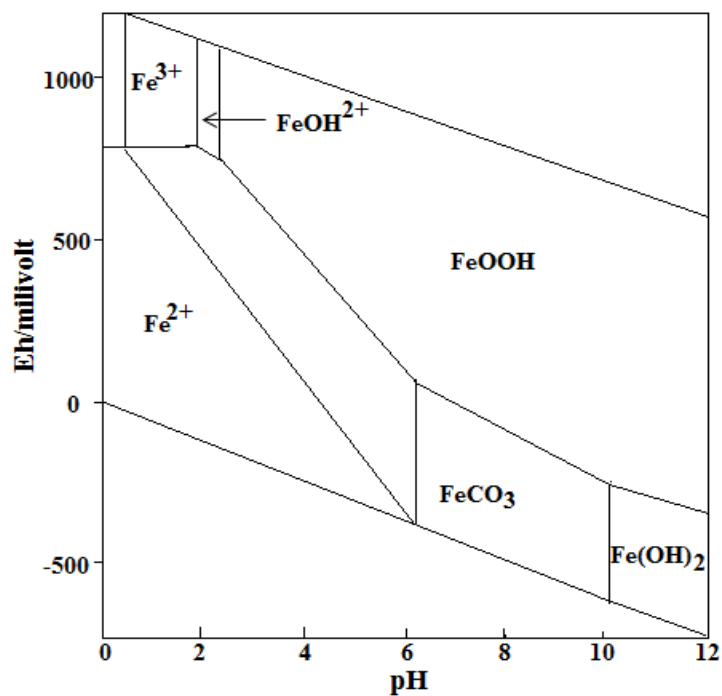


Figure 1.5: Eh-pH diagram for iron [62] in water at 25°C.

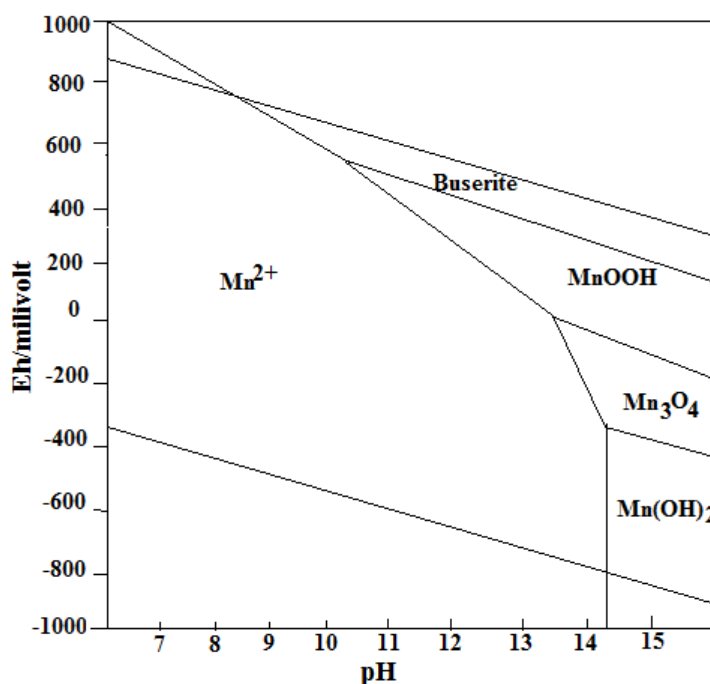


Figure 1.6: Eh-pH diagram of Manganese [62] in water at 25°C.

Besides As, Fe and Mn in groundwater other heavy metals such as Hg, Pb, Cd, Ni, and Cu, etc., get stable in bivalent state, [81, 82] except Cr, which is found in both trivalent and hexavalent states [67]. Lead exists in three oxidation states: Pb^0 , the metal; Pb^{2+} ; and Pb^{4+} [83]. In the environment, lead primarily exists as Pb^{2+} . Pb^{4+} is only formed under extremely oxidizing conditions and inorganic Pb^{4+} compounds are not found under ordinary environmental conditions. When both oxygen and water are present, metallic lead is converted to lead hydroxide ($\text{Pb}(\text{OH})_2$) [83]. Elementary lead does not dissolve in water under normal conditions (20°C, and pressure = 1 bar). It may however occur dissolved in water as PbCO_3 or $\text{Pb}(\text{CO}_3)_2^{2-}$. In environment and water bivalent cadmium, Cd^{2+} exists as CdS and CdCl_2 [84]. Ni is a silver-white metal found in several oxidation states ranging from -1 to +4, however, the +2 oxidation state, Ni^{2+} [85] is the most common state in biological systems. In water, Cr^{3+} is a positive ion that forms hydroxides and complexes, and is adsorbed at relatively high pH values [75]. In surface waters, the ratio of Cr^{3+} to Cr^{6+} varies widely, and relatively high concentrations of the latter can be found locally [75]. In general, Cr^{6+} salts are more soluble than those of Cr^{3+} , making Cr^{6+} relatively mobile. In pure water, the Cu^{2+} ion is the more common oxidation state [86] (USEPA, 1995) and will form complexes with hydroxide and carbonate ions. The formation of insoluble malachite [$\text{Cu}_2(\text{OH})_2\text{CO}_3$] is a major factor in controlling the

level of free Cu^{2+} ion in aqueous solution [86]. Cu^{2+} ion is the major species in water up to pH 6; at pH 6–9.3, aqueous CuCO_3 is prevalent; and at pH 9.3–10.7, the aqueous $[\text{Cu}(\text{CO}_3)_2]^{2-}$ ion predominates [86].

1.6. Remediation of inorganic contaminants from groundwater:

Fresh water occurs in two main sections as surface water and groundwater. Though groundwater contributes only 0.6 % of the total water resources on earth [87] it is the preferred source for drinking water collection particularly in under developing countries because treatment of the groundwater including disinfection is generally not required for these sources. However, groundwater of all parts of the world is not suitable for drinking purposes [87]. So, it is necessary to pre-treat groundwater before using as drinking water. In recent years, brisk research activities have been reported on development of low cost methods based on reverse osmosis, electro-dialysis, adsorption, oxidation, coagulation, nano-filtration, aeration, etc., [88, 89] for removal of As and other hazardous heavy or light metals (Fe, Mn, Hg, Pb, Cr, Cd, Ni, Cu, Co, etc.) from groundwater.

1.6.1. Coagulation/precipitation:

Coagulation/precipitation is the oldest and a widely used inorganic contaminants remediation technique [90]. Coagulation is the clumping together of particles in solution [91]. This process transforms dissolved contaminants into insoluble solids and allows them to form agglomeration and/or enmeshment of particles into a flocculated precipitate with the coagulant, facilitating the contaminant's subsequent removal from the liquid phase by sedimentation or filtration [90, 91]. The process usually uses pH adjustment, addition of a chemical coagulant/precipitant, and flocculation [92, 93]. In both coagulation and precipitation the final products are larger particles or floc, which more readily filter or settle under the influence of gravity. Coagulation/precipitation processes with alum, $\text{XAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, AlCl_3 and iron containing compounds such as FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, FeClSO_4 , etc., as coagulant are most commonly used in arsenic, iron and other heavy metal removal techniques because they are both cheap and effective [94–96]. Granular ferric hydroxide ($\alpha\text{-FeOOH}$) obtained from neutralised FeCl_3 solution, lanthanum compounds, and manganese oxides also have effective arsenic removal capacity [97–99]. Both Al and Fe salts are efficient at removing As^{5+} from water. Pre-oxidation of As^{3+} is required to achieve maximum removal efficiency of dissolved As

[100, 101]. On a mass basis, Fe^{3+} salts are more efficient and preferable to remove arsenic than alum and other Al compounds because of the suspected causing of Alzheimer's disease by Al [102]. The enhanced coagulation process involves some changes to the existing coagulation process such as increasing the coagulant dosage, reducing the pH, or both, and addition of polymer or any supporting material with the coagulant [103]. Cheng, et al., reported that more than 90% removal of As^{5+} could be achieved under enhanced coagulation process. Coagulation process is traditionally realized by adding Fe^{3+} or Al^{3+} ions [104]. Hering, et al., observed that at low pH minimum dose of coagulant for As^{5+} removal is higher for alum than for FeCl_3 [104]. As^{3+} removal from source water by FeCl_3 was found to be much less efficient than As^{5+} and highly influenced by water compositions and neutral pH range. So, peroxidation is urgent for coagulation process for removal of hazardous As from groundwater source. Baskan, et al. used the coagulation and flocculation method for As^{5+} removal from drinking water using ferric chloride, ferric sulphate, and ferrous sulfate as coagulant [105]. He found that residual As^{5+} concentrations decreased to below, 10 $\mu\text{g/L}$ with the dosage of 30 and 80 mg/L of Ferric chloride and Ferrous sulphate, respectively.

Removal efficiency of heavy metals is often different in diverse raw water and coagulation conditions [106]. Metal salts, such as alum, aluminum chloride, ferric sulfate, and ferric chloride, are traditional coagulants for heavy metals removal and polymerized species that are generally acknowledged the active ingredients for the removal of turbidity and contaminants are gradually formed during these processes [106]. Along with the development of the research, prehydrolyzed coagulants, such as polyaluminum chloride and polymeric ferric sulfate, produced by the forced hydrolysis are believed to have an excellent performance in water treatment [91, 106].

Lime softening [107] is also used for remediation of arsenic, iron and other heavy metals by reducing the hardness of water in coagulation processes in which calcium hydroxide, $\text{Ca}(\text{OH})_2$ and soda ash, Na_2CO_3 mixture is used. Lime softening increases the removal efficiencies of the arsenic and other heavy metals in coagulation processes [107]. Amuda, et al., found that addition of ferric chloride alone results significant removal of the metals reaching up to 91%, 72% and 54% of total chromium, zinc and total iron respectively while addition of polymer achieved 95%, 87% and 88% of total chromium, zinc and total iron respectively [108]. In hydroxide precipitation process, the

incorporation of coagulants like iron salts, alum, and some polymers may improve heavy metal separation from wastewater and groundwater. Ayoub, et al., investigated seawater liquid bittern (LB), [109] as an inexpensive source of magnesium, added to wastewater alkalized with lime or caustic soda as a possible coagulant. The lime-LB process showed high removals (>90%) of Cd, Cr, Pb, Hg, and Zn and reasonably good, 71, 82 and 75% removals for arsenic, copper and nickel, respectively [109]. Aziz, et al., reported that more than 80% of Cd, Pb, Zn, Ni, Cu and Cr with an initial concentration of 2 mg/L could be removed by limestone at a final pH of 8.5 [110]. Hydroxide precipitation process using $\text{Ca}(\text{OH})_2$ and NaOH in removing Cu^{2+} and Cr^{3+} ions from wastewater was evaluated by Mirbagheri and Hosseini [111]. Maximum precipitation of Cr^{3+} occurred at pH 8.7 with the addition of $\text{Ca}(\text{OH})_2$ and the concentration of Cr^{6+} was reduced from 30 mg/L to 0.01 mg/L. The Cu^{2+} was removed by aeration and at an optimum pH of about 12.0 by $\text{Ca}(\text{OH})_2$ and NaOH from 48.51 mg/L to 0.694 mg/L [111]. Using chemically enhanced primary treatment with 40 mg/L of FeCl_3 and 0.5 mg/L of anionic polymer stretches the best removal of Cr, Cu, Ni, Pb, and Zn. This study by Johnson, et al., [112] also showed ferric chloride to be more effective than alum for metal ion capture from wastewater.

1.6.2. Electrocoagulation:

Electrocoagulation technology is a waste water treatment process applying electrical current to coagulate/flocculate contaminants without adding coagulants. Electrocoagulation occurs when the direct current applied is capable of removing small particles setting them into motion [113]. Electrocoagulation consists of a pair of metal sheets called electrodes, one as anode and the other as cathode [114]. Using the principles of electrochemistry, the cathode is oxidized (loses electrons), while the water is reduced (gains electrons) [113, 114]. When the cathode makes contact with the wastewater, the metal is emitted into the apparatus. When this happens, the particulates are neutralized by the formation of hydroxide complexes for the purpose of forming agglomerates. These agglomerates begin to form at the bottom of the tank and can be siphon out through filtration. Parga, et al. investigated that electrocoagulation with or without air injection process for removal of As from the contaminated water and found 95.5% and 99.77% removal efficiency with and without injection of air, respectively [115]. Kumar, et al. used electrocoagulation to bring down aqueous phase arsenic

concentration to less than $10 \mu\text{gL}^{-1}$ with iron electrodes and current density varied from 0.65 to 1.53 mAcm^{-2} and it was observed that higher current density led to rapid As removal [116]. They also observed that As removal efficiencies with different electrode materials follow the sequence: $\text{Fe} > \text{Ti} > \text{Al}$. Kamaraj, et al., observed that electrocoagulation using magnesium and galvanized iron as anode and cathode, respectively, with a current density 0.8 A/dm^2 with an energy consumption of 0.72 kWh/m^3 gives 99.3 % removal of Pb from aqueous solution [117]. Azimi, et al., reviewed various electrocoagulation methods developed earlier. Different electrocoagulation methods with different electrode types and removal efficiencies reviewed are given in **Table 1.2** [118].

Table 1.2: Various electrocoagulation methods with removal efficiencies of different heavy metals [118]

Metal	Type of electrode	pH	Contact time(min)	Removal efficiency %	Current density
Cd	Zn	7	NA	94.1-99.6	$0.1-0.5 \text{ Adm}^{-2}(\text{AC})$
Pb	Fe-Fe	NA	40	96.7	6 mAcm^{-2}
Ni	Fe	6.9	30	98	50 Am^{-2}
Ni	Al-Fe	NA	180	52	NA
Ni	Fe-Fe	9.6	45	98	$4 \text{ mAcm}^{-2} (\text{DC})$
Cu, Ni, Zn	Fe	5.7	50	96	$15 \text{ mAcm}^{-2} (\text{DC})$
Cu, Ni, Zn	Fe-Al	3	20	99	10 mAcm^{-2}
Cu, Zn	Fe-Fe	9.5	45	96	$4 \text{ mAcm}^{-2} (\text{DC})$
Cu, Ni, Zn	Al-Fe	NA	60	>95	NA
Cu, Zn	Al-Al	7	5	99	NA
Cr, Cu	Al-Al-Al	4	15	99.9	0.8 A
Cu	Al-Fe	NA	180	90	NA
Cr	Fe-S	6.9	30	97	$50 \text{ Am}^{-2} (\text{DC})$
Cr	Al-Al-AL	8	15	58	0.8 A
Cr	Al-Al	5	24	90.4	
Mn	Fe	5.5	50	72.6	$15 \text{ mAcm}^{-2} (\text{DC})$

1.6.3. Membrane processes:

Membranes are selective porous walls, allowing some constituents particles or ions to pass while blocking the passage of others [90]. There is a driving force, i.e., a potential difference between the two sides of the membrane which controls the movement of constituents across the membrane. Membrane processes are often classified on the basis of driving force, including concentration, electrical potential, pressure, and temperature. Among them pressure driven membrane processes and electrical potential-driven membrane processes are commonly used in wastewater treatment process or any purification process. Pressure-driven membrane processes with removal of inorganic contaminants such as arsenic, iron, manganese and some other heavy metals (Cd, Pb, Ni, Cu, Cr, Co, etc.) are often classified on the basis of pore size into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) [119]. High-pressure processes (i.e., NF and RO) have a membrane with relatively small pore size, primarily remove constituents through chemical diffusion compared to low-pressure processes (i.e., MF and UF) [120–122] which have comparatively large pore size remove constituents through physical sieving. Drawback of membrane process is to remove broader ions or particles require increase in energy.

1.6.3.1 Microfiltration:

Microfiltration is a type of physical filtration process where a contaminated fluid is passed through a special pore-sized membrane to separate microorganisms, heavy metals and suspended particles from process liquid [123]. MF can remove particulate forms of As, but this process alone cannot provide an efficient arsenic removal unless a considerable percentage of As is in particulate form since MF performance is primarily dependent on the size distribution of As-bearing particles and pore size [124]. MF pore size is too large to substantially remove dissolved or colloidal As [124]. Although MF can remove particulate forms of As [121], this alone does not make the process efficient for arsenic removal unless a large percentage of As is present in particulate form. To increase removal efficiency in source waters with a low percentage of particulate As content, MF can be combined with coagulation processes [125]. Due to high recovery up to 99% and low energy requirement, microfiltration process has been used widely in water treatment. MF membranes have the largest pore size, ranging from 0.1 μm to 10

μm . The smallest pore sizes correspond to the size of suspended solids, colloids and bacteria. The sieving mechanism of microfiltration process is illustrated in **Figure 1.7**.

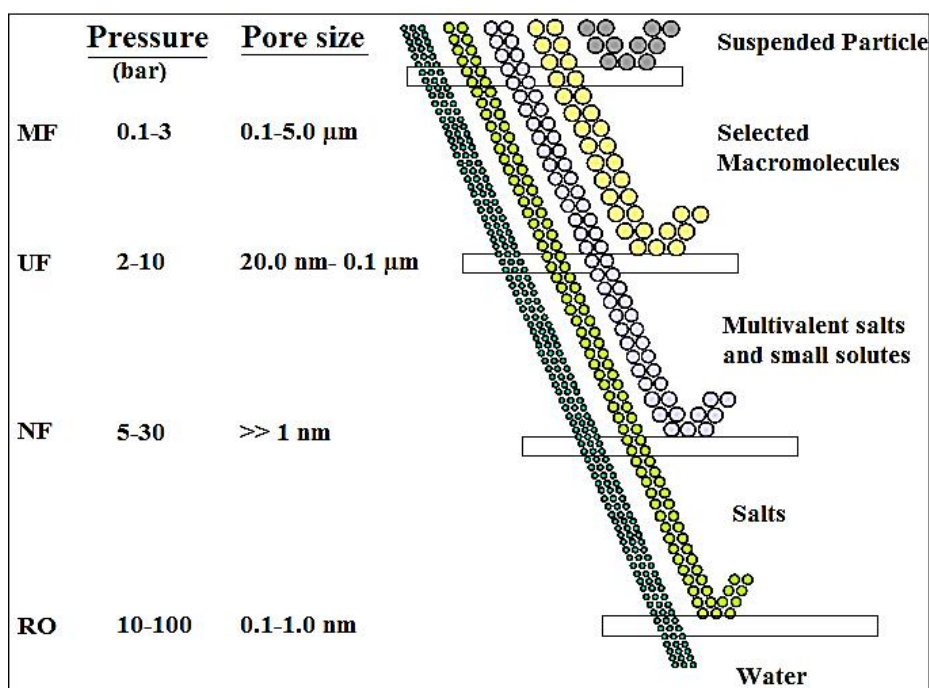


Figure 1.7: The sieving mechanism of membrane processes [126].

USEPA recognized coagulation/microfiltration (C/ME) process as an emerging technology for As removal [127]. Chen, et al., reported that more than half of the total As could be removed by a filter with a pore size of 0.45 μm [128]. Furthermore, in extreme cases, as much as 90 percent of the As present in groundwater could be removed by microfiltration or ultrafiltration [128]. Joseph, et al., showed that the coagulation/microfiltration process consisting of addition of an iron-based coagulant, such as FeCl_3 to As-contaminated water followed by the MF process achieved good As removal efficiencies to below 2 $\mu\text{g/L}$ [129]. Bayhan, et al., investigated removal of heavy metal ions, viz., Ni^{2+} , Cu^{2+} and Pb^{2+} using yeast (*Saccharomyces cerevisiae*) as carriers in a crossflow microfiltration [130]. The binding affinity of the metals to yeast cell was found to be in the order: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$ [130], which was also reflected in the metal ion rejection under identical process conditions. Keerthi, et al., [123] combined EC with microfiltration to remove heavy metals in a synthetic waste water containing salts of Ni, Zn and Cd. The EC process was optimized with respect to initial concentration, current density and pH, and percentage of metal removal at the optimized condition was found to be 95% for Cd and 98% for Ni and Zn.

1.6.3.2 Ultrafiltration:

Ultrafiltration is similar to microfiltration in configuration and construction and used similarly. But when it comes to understanding the difference between MF and UF the main difference is simply about the pore size, which affects which particles can get through. While pores in microfiltration membranes range from 0.1 to 10 μm that in ultrafiltration membranes range from 0.01 to 0.1 μm . UF alone, like MF, may not be a viable technique for arsenic and other heavy metal removal for groundwater, however, UF may be appropriate for surface waters with high colloidal and particulate sizes. Complexation-assisted ultrafiltration is a promising process for the removal of heavy metal ions from aqueous solutions which involves bonding the metals to a bonding agent, and then separating the agents from wastewater by ultrafiltration [131]. Polyethylene glycol is found to more efficient complexing agent, but highest retention coefficient was achieved using Diethylaminoethyl cellulose for Cd (95%) and Zn (99%) [131]. The removal of Zn^{2+} was more efficient than of Cd^{2+} which was attributed to higher coordination ability of Zn with macro-ligands. Huang, et al., [132] investigated the removal of heavy metals, viz., Co^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Fe^{3+} , Cd^{2+} , Zn^{2+} and Mn^{2+} from water with polymer enhanced ultrafiltration using polyvinylamine (PVAm) as a complexing agent and found that at a PVAm dosage of 0.1wt%, metal rejections were achieved over 99% for Pb^{2+} , Cu^{2+} , and Fe^{3+} . A polymer-enhanced ultrafiltration process was investigated for removal of toxic heavy metals such as Cu^{2+} , Ni^{2+} , and Cr^{3+} from synthetic wastewater solutions by Barakat, et al [133]. Poly-ether sulfone (FUS 0181) was used as ultrafiltration membrane, while carboxy methyl cellulose was used as a metal bonding agent. It was shown that the metal rejection was more efficient at neutral and alkaline conditions than at acidic one. The metal rejection efficiency values, with initial metal ion concentration of 10 mg/L, were 97.6, 99.5 and 99.1% for Cu^{2+} , Cr^{3+} , and Ni^{2+} , ions, respectively, at pH 7 [133].

1.6.3.3 Nanofiltration:

Nanofiltration is a membrane filtration-based method where nanometre size particles pass through pores of the membrane. NF membranes have pore sizes from 1 nm to 10 nm, smaller than that used in MF and UF, but just larger than that in reverse osmosis (RO). Nanofiltration is a relatively recent membrane filtration process used most often with low total dissolved solids (TDS) water such as surface water and groundwater, with

the purpose of softening and removal heavy metal ions with organic matter; both natural and synthetic. NF predominantly removes divalent ions, e.g., Ca, Mg, but not monovalent salts, e.g., Na, Cl. Through size exclusion, NF can remove both dissolved As^{5+} and As^{3+} . This makes NF a reliable arsenic removal process from groundwater sources [134, 135]. Due to the small pore size NF membranes are more prone to fouling than UF or MF membranes. Therefore, NF for surface water treatment is typically not proficient without far-reaching pre-treatment for particle removal and for dissolved constituents to prevent fouling.

Several NF studies have been reported for As removal, and the results show that NF processes are effective for the removal of As in both form As^{3+} and As^{5+} . Arsenic removal through NF depends on operating parameters, membrane properties, and As speciation [136, 137]. Chang, et al. [138] revealed that the removal efficiency dropped significantly during pilot-scale tests where the process was operated at more realistic recoveries. When the membrane unit was operated at a recovery of 65%, the As removal efficiency dropped to 65% and when the recovery was increased to 90%, the arsenic removal efficiency dropped down to 16% [137, 139]. Al-Rashdi, et al, observed that removal of some heavy metals Cu^{2+} , Cd^{2+} , Mn^{2+} , Pb^{2+} , As^{3+} , and As^{5+} from water solution using absorption and NF membrane techniques [137]. For NF membrane, research showed removal efficiencies around 97% for Cd, 99.9% for Cu, 84% Pb, 93% As^{5+} , 89% As^{3+} and 98% for Mn [140]. Niaki, et al., examined NF technology in removal efficiency of Ni, Zn, and Cu as the index of heavy metals in plating sewages and evaluated the effects of pressure, concentration and filtration time [141]. Results of this experiment showed that increasing of pressure increases rejection. At 8 bars of pressure Cu was more rejected (100%) than Zn and Ni.

1.6.3.4. Reverse Osmosis:

Reverse Osmosis is a process by which a solvent passes through a porous membrane in the direction opposite to that for natural osmosis when subjected to a hydrostatic pressure greater than the osmotic pressure. The solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. RO is the firstborn membrane process, traditionally used for the desalination of sea water and brackish water. Several bench- and pilot-scale studies reveal RO as capable of removing As to below the WHO guideline value [142–144]. RO removes As^{5+} better than As^{3+} , so,

preserving oxidative conditions may be necessary to the process [145, 146]. Compared to other membrane techniques, osmotic pressure becomes great in RO due to the concentration of salts on the feed side of the membrane. The majority of the treated water passes through the membrane; however, the rest is discharged along with the rejected salts as a concentrated brook. Pawlak, et al., studied As removal from groundwater at Spiro Tunnel on pilot scale, by two RO membrane filtration systems and showed the potential of this technology for water purification [147]. Total As concentrations were reduced by RO from an average 60 $\mu\text{g/L}$ in the source water to less than 1 $\mu\text{g/L}$ (99%) where soluble As^{3+} and As^{5+} were reduced by 93% and 98%, respectively [147].

George, et al., achieved 79% reductions in As concentrations after filtration [148]. Abejón, et al. demonstrated the economic and technical viability of removing As^{5+} using an optimized RO process [149]. The optimized results showed that the total costs of a two-stage membrane cascade used for the removal of As^{5+} from drinking water for a population of 20,000 inhabitants were 1041 $\$/\text{d}$ and 0.52 $\$/\text{m}^3$ of drinking water produced [149]. Energy consumption was the most relevant cost, amounting to 35% of the total cost. Sensitivity analysis was performed to determine the total costs of the installation for different scenarios in terms of drinking water production: (i) 0.44–0.56 $\$/\text{m}^3$ for electricity prices of 0.05–0.10 $\$/\text{KWh}$; (ii) 0.88–0.45 $\$/\text{m}^3$ for populations ranging from 5000 to 50,000 inhabitants; and (iii) 0.52–0.61 $\$/\text{m}^3$ when the membrane lifetime was reduced from 3 to 1.5 years [149]. Ning, et al., showed that As in the common high oxidation states of 5+ is very effectively removed by RO and removal efficiency was found better in if the RO operation is done in high pH condition [150]. Algureiri, et al., showed that synthetic industrial wastewater containing Ni^{2+} , Pb^{2+} , and Cu^{2+} ions at various concentrations (50 to 200 mg/L), pressures (1 to 4 bar), temperatures (10°C to 40°C), pH (2.0 to 5.5), and flow rates (10 to 40 L/h), when subjected to treatment by RO system in the laboratory results in high removal efficiency of the heavy metals, i.e., 98.5%, 97.5% and 96.0% for Ni^{2+} , Pb^{2+} , and Cu^{2+} ions, respectively [151]. The application of both RO and NF technologies for the treatment of wastewater containing Cu^{2+} and Cd^{2+} ions was also investigated. The results showed that high removal efficiency of the heavy metals could be achieved by RO process (98% and 99% for Cu^{2+} and Cd^{2+} , respectively. NF, however, was capable of removing more than 90% of Cu^{2+} existing in the feed water [151].

1.6.4. Adsorptive techniques:

1.6.4.1. Activated Alumina:

Adsorbent is a physicochemical process by which ions in the contaminated water are sorbed to solid surface. It is referred to as an adsorption process, although the chemical reactions involved in water purification are actually exchanges of ions [152]. Activated alumina (AA) is produced by de-hydroxylating aluminium hydroxide at high temperatures in a way that results in a highly porous material, viz., amorphous and gamma alumina oxide, Al_2O_3 [153]. Contaminated water is continuously passed through AA packed beds and ions are exchanged with the surface hydroxides on the alumina. The AA packed bed must be regenerated when adsorption sites on the AA surface become filled. Regeneration is accomplished through a sequence of rinsing with regenerating agent (e.g., NaOH, etc.), flushing with water and neutralizing with acid. Several researchers have reported that optimum pH for As removal by AA to be the range of 5.5 to 6.0 [154–156]. Johnston, et al., stated that As removal efficiency by AA is excellent (typically > 95%), for both As^{3+} and As^{5+} , but As removal capacity varies significantly, and is controlled primarily by pH, and influent As concentration and speciation [157]. As^{5+} removal capacity is best in the narrow range from pH 5.5 to 6.0, where the alumina surfaces are protonated but acid anions are not yet concentrated enough to compete with As for sorption sites [154].

Kim, et al., developed a mesoporous alumina (MA) with a wide surface area (307 m^2/g) and uniform pore size (3.5 nm), and a sponge like interlinked pore system through a post-hydrolysis method [158]. The maximum adsorption of As^{5+} by MA was found to be 7 times higher than that of conventional AA, and complete the adsorption in less than 5 h as compared to the conventional AA (about 2 days to reach half of the equilibrium value). Badalians, et al., in his work stated that AA, viz., ALCAN AAFS-50 can adsorb As^{3+} about 40% of its capacity for As^{5+} [159]. Oxidation is recommended to assist with for better As^{3+} removal, when possible. Modified AA has high efficiency for removal of As and can reduce As concentration to below WHO guidelines. Removal efficiency increases as a result of increasing dose and reaches to 98% for As^{5+} during 2 hours of treatment time. Park, et al., observed [160] that efficiency of removing As using the activated alumina gel more than 80% of As in an aqueous solution within 24 h and more than 95% when the aqueous solution was continuously observed for about one week.

Cervera, et al., found that a 0.4 g of AA can retain 0.6 mg of Cr^{3+} and 0.2 mg of Cd^{2+} from 20 mL sample adjusted at pH 4 and stirred for 30 min [158]. It is therefore possible to totally decontaminate 500 mL of a waste containing 5 mg/L Cd^{2+} and Cr^{3+} with 10 g AA. Szatyłowicz, et al., [160] verified the granular AA sorption properties, during the process of removal of Cd, Pb and Cu from water, and monitored the impact of magnetic field (MF) on the effectiveness of removing these heavy metals. Pilot tests for removal of Cd, Pb, and Cu showed that the use of AA with MF increases efficiency of removal the Cd, Pb, and Cu content in the model water than the conventional AA [161].

1.6.4.2. Granular Ferric Hydroxide, $\beta\text{-FeOOH}$:

Granular ferric hydroxide (GFH) is a poorly crystallised $\beta\text{-FeOOH}$ prepared from a ferric chloride solution by neutralisation and precipitation with sodium hydroxide. GFH has a high adsorption capacity for heavy metals in model systems and in natural waters. Driehaus, et al., [163] reported about GFH as a new efficient adsorbent of As. Pal, et al., [161] showed that GFH is a superior adsorbent because it meets four important criteria: high removal efficiency, safety, simple operation, and minimum residual mass. The most significant weakness of this technology appears to be its cost. Currently, GFH media costs approximately \$4,000 per ton [164]. GFH can be applied in simple fixed bed reactors, similar to those for activated alumina or activated carbon to remove As from natural water [163]. GFH has a high adsorption capacity in model systems and in natural waters. Saha, et al., [165] observed that the adsorptive capacity of GFH is high for As^{5+} . According to his experiment the adsorption of As^{5+} was found to decrease as the pH of the solution was increased, thus giving the optimal adsorption of As^{5+} onto GFH in the pH range of 4 with an initial As^{5+} concentration of 400 $\mu\text{g/L}$. Guan, et al., investigated the As^{5+} adsorption on GFH and found a broad adsorption maximum at sorbent concentration of 10 g/L when the initial As^{5+} concentration was less than 500 $\mu\text{g/L}$ [98].

1.6.4.3. Laterite:

‘Laterite’ is a soil and rock type rich in iron and aluminium, and is commonly found in hot and wet tropical areas. Due to the high iron oxide content nearly all laterites are rusty-red coloured and developed by intensive and prolonged weathering of the underlying parent rock. Rahman, et al., investigated As removal by heat treated laterite from contaminated water through batch adsorption experiments and it was found that

laterite can be effectively used for the removal of As from contaminated groundwater (CGW) [166]. Maiti, et al., [167] prepared a porous and efficient As adsorbent from raw laterite by acid treatment followed by alkali treatment. They have studied adsorption of As on treated laterite (TL) using CGW in the batch and fixed-bed column modes and found that 6.5 cm TL bed is proficient to produce ~3000 times the bed volume of treated water with an effluent As concentration $<10 \mu\text{g/L}$ using CGW as an influent. The As adsorption capacity of TL is found to be 30 to 40 times higher compared to that of raw laterite with exhaust time of 74 days. Maji, et al., [168] also used laterite soil for removal of As from contaminated water through both batch and continuous mode and found that under optimized conditions the laterite soil could remove up to 98% of total As. In this study the optimum adsorbent dose and equilibrium time were found to be 20 g/l and 30min, respectively, with exhaust period of 19 h [168]. TL was successfully utilized for removal of Pb from water by Chatterjee, et al., recently [169]. At optimized conditions of 1 g/L adsorbent concentration, 0.26 mm size and a pH of $7.0(\pm 0.2)$ the adsorption capacity of Pb on TL was found to be 15 mg/g, 14.5 mg/g and 13 mg/g at temperatures of 303 K, 313 K and 323 K, respectively [169]. Mitra, et al., observed that laterite soil gave the removal efficiency of Pb^{2+} and Cr^{6+} metal ions from aqueous solution as 95% and 74%, respectively [170]. Optimum condition for both metals were found as pH 6, contact time 240 min, adsorbent dose 10 g/L, and initial concentration 20 mg/L for single component adsorption [170].

1.6.4.4. Activated Carbon:

Activated carbon (AC), also known as *activated charcoal*, is a form of *carbon* processed to have small, low-volume pores that increases the surface area available for adsorption or chemical reactions. So, it is widely used as adsorbent for As, Fe and other heavy metal removal from water. The As^{5+} adsorbing efficiency of AC produced from oat hulls in was tested in a batch reactor by Chuang, et al., [171]. They found that adsorption capacity of AC was decreasing from 3.09 to 1.57 mg As per g of AC when the initial pH values increased from 5 to 8. AC does not remove As efficiently alone [171]. Therefore, Gallios used iron modified AC as alternative sorbents for the removal of As^{5+} from aqueous solutions [172]. In his study, he prepared magnetic $\text{Fe}^3(\text{Mn}^{2+})\text{O}_4$ (M:Fe and/or Mn) AC and impregnated with magnetic precursor solutions and then calcined at 400°C . The iron impregnation presented an increase in As^{5+} maximum adsorption capacity

(Q_{\max}) from about 4 mg/g for the raw carbon to 11.05 mg/g, while Mn incorporation further increased the adsorption capacity at 19.35 mg/g. Jahan, et al., [173] studied the As removal in both As^{3+} and As^{5+} forms using AC obtained from jute stick using H_3PO_4 . Removal of As in continuous method was found to be better than the bed feeding system. In this work As^{5+} was removed more, i.e., 80% than the As^{3+} , which needed peroxidation with small amount of $KMnO_4$ [173]. In 2014 Rahman, et al., prepared acid AC obtained from oil palm and coconut shells using H_3PO_4 and modified by dispersing hydrated iron oxide to remove as Ni^{2+} , Pb^{2+} , and Cr^{6+} [174]. They showed that prepared AC had significantly higher adsorption capacity in removing heavy metal cations such as Ni^{2+} (19.6 mg/g) and Pb^{2+} (74.6 mg/g) [174]. Bernard, et al., used AC produced from coconut shell as adsorbent to remove Cu^{2+} , Fe^{2+} , Zn^{2+} , and Pb^{2+} ions from electroplating industrial wastewater [81]. The optimum adsorbent dosage, stirring rate and pH, were found to be at 1 g, 350 rpm and pH 6, respectively. For As^{3+} and As^{5+} removal from water commercial ACs has been widely used [175]. Coal-derived commercial AC has a huge As sorption capacity of 2860 mg/g [176]. Some ACs, impregnated with metallic Ag and Cu were also used for As remediation [177].

1.6.4.5. Nano-adsorbents:

Removal of As by nano-adsorbents from water is gaining impetus globally. Although they are typically in the laboratory research stage, some researcher had made their way to pilot testing or even commercialization [178]. Some potential nano-adsorbents for As removal are metal oxide nanoparticles such as oxides of Fe, Ti, Cu, Al, Zr, and Mn and polymeric nano-adsorbents [178, 179]. These nano-adsorbents face certain challenges including technical obstacles, high cost, and environmental and human risk [178]. Silica/AC (2:3) composite was found to be most operative micro particle for Ni^{2+} removal and it is highly recommended to be used in water treatment for its high adsorptive capacity followed by AC and silica nanoparticles [180]. The AC was modified with carbon nanotubes (CNT) by chemical vapour deposition [181]. The CNTs were synthesized in the presence of a metal-oxide catalyst prepared using a citrate sol gel method. Experimental results showed that the nano-modification of ACs increased their adsorption capacity of heavy metals, viz., Ni^{2+} and Co^{2+} by 10–30% [182]. Li, et al., achieved 74.8% removal efficiency of Cu by using CNTs and 83.3% by using CNTs/AC from initial Cu^{2+} concentration of 20 mg/L at pH 5.0 and adsorbent dose of 0.05 g [182].

1.6.4.6. Zero-valent Iron (ZVI):

Zero-valent iron (ZVI), usually granular iron, is the bulk reducing agent has a variety of applications ranging from filters to electrodes to trenches. Nanoparticles of zero-valent iron (nZVI) and carbon-encapsulated nanoparticles of zero-valent iron (CE-nZVI) represent a promising agent for heavy metal remediation from environment and water [183]. Nikolaidis, et al, [184] performed a large-scale pilot experiment and found that iron filing filters can remove efficiently As^{3+} from aqueous solutions (mixed matrix) to levels less than 10 mg/L, without maintenance for more than 8 months. Lien, et al, determined As removal capacity of ZVI approximately as 7.5 mg As per g of Fe [185]. They also identified carbonate green rust from the analysis of surface precipitates; As^{3+} uptake by green rust may be a major mechanism responsible for As remediation by ZVI [185]. Bang, et al., conducted batch and column experiments to investigate the effect of dissolved oxygen (DO) and pH on As removal with ZVI [186]. Under oxic conditions, As^{5+} removal by ZVI was faster than As^{3+} with percentage of removal of 99.8% and 82.6% at pH 6 after 9 h of mixing, respectively [186]. Fan, et al., designed a magnetic propeller agitator and a magnetic reactor to enhance the removal of heavy metals by ZVI [187]. The weak magnetic field (WMF) applied in the magnetic propeller agitator or the magnetic reactor significantly improved the Cu(II)-EDTA removal by ZVI from 10% to 98% within 2.5 h and at pH 6.0 [187]. Chen, et al., [188] investigated for removal of heavy metals from synthetic wastewater by ZVI under various operational conditions. They showed that decrease in initial pH results in the increase in the removal with maximum efficiency of metal removal obtained at initial pH of 2 [188]. The removal efficiency of heavy metal was higher than 80% when 2.0 g/L of ZVI was added in the wastewater.

1.6.5. Electro dialysis:

Electro dialysis (ED) is a process in which movement of ions is aided by an electric field applied across the semipermeable membrane [189]. The mechanism of separation is actually an ion exchange process in which ions travel from a lesser to a higher concentrated solution [189]. In this process, the membranes are arranged in an array or stack placed between two electrodes, with alternating cation and anion exchange membranes [190]. The mobility of the cations or anions is controlled to the direction of the attracting electrodes resulting alternating sets of chambers containing water with low

and high concentrations of the ions. Very few studies have been conducted to exclusively evaluate this process for the removal of As.

The effectiveness of electro-dialysis (ED) in removing As from aqueous solution was investigated by Mendoza, et al., [191]. They used a tailor-made ED stack to achieve current-voltage and optimization experiments in a batch mode. 100% of As^{3+} to As^{5+} transformation of samples was done with the help of oxidant NaClO using 1:2 samples to oxidant weight ratio in 180 seconds. Optimum conditions that provided maximum As removal were obtained at potential of 12 V, feed flow rate of 0.033 L/s, feed concentration of 662.0 $\mu\text{g/L}$ and operating time of 45 min [191]. Removal of heavy metals Cu^{2+} , Zn^{2+} , Fe^{3+} , and Cr^{3+} from water rinsing of plating baths by ED results the order of removal as $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Fe}^{3+}$ [192]. Choi, et al., [193] studied removal of heavy metals and nitrate nitrogen by an ED and evaluated the removal of As, Pb, Mn and nitrate nitrogen was 73.9, 89.9, 98.8 and 95.1%, respectively, when the conductivity reached 100 $\mu\text{s/cm}$.

1.6.6. Ion exchange:

Ion exchange (IE) is a physicochemical process by which ion in the feed water is exchanged for an ion on the solid phase [194]. The solid phase is a synthetic resin which can preferentially adsorb the particular contaminant of the feed water [195]. In this process feed water containing contaminants is continuously passed through a bed of IE resin in a down flow or up flow mode until the resin is exhausted [14]. At the point of exhaust, the bed is regenerated by rinsing column with a regenerant; a concentrated solution of ions initially exchanged from the resin [195]. Chloride-form of strong-base resins are used for the chloride-arsenate exchange reaction occurs in the range of pH 8 to 9 [196]. Recent studies have also found that sulphate selective resins tend to be superior to nitrate-selective resins for As removal [197]. The IE method can remove As to below the WHO guideline value but requires high capital cost [198]. Oehmen, et al., developed a hybrid process for As removal from drinking water consisting of As^{5+} transport through an anion exchange membrane followed by coagulation [199]. Use of AlCl_3 in this case as coagulant was reported to be more advantageous over FeCl_3 in terms of reduced membrane scaling, and results in an increased As flux at high feed water flow rate per membrane area ratios [198]. Two strong acid cation exchanger resins, Amberlite 252 and Amberjet 1200 can be used for the removal of Cu^{2+} and Zn^{2+} from synthetic rinse water

[200]. Beker, et al., [201] used IE resin based on hydroxyethyl cellulose to remove the heavy metals, such as Fe, Co, Cu, and Zn from aqueous solutions. The resin having an average swelling percentage of 75.94 and an exchange capacity of 2.57 meq/g of resin were used as new IE resin [201].

1.6.7. Oxidation processes:

Loss of electrons from any atom or ion in presence of an oxidising agent to gain higher oxidation state of the atom or ion is called oxidation. In oxidation the oxidising agent itself is reduced to help the oxidation of others. There are various types of oxidation processes used to oxidise the hazardous heavy metal atom or ion in water which will help for removal of them from the water. Some heavy metals are difficult to remove in their lower oxidation state from water so before removal of them by any coagulation, adsorption or any membrane process, oxidation of heavy metal ion in water is important [202]. Arsenic (As) is difficult to remove in its dominant species, As^{3+} from groundwater [202]. So it is necessary to oxidise As^{3+} by using an oxidising agent to As^{5+} , which is easy to remove from water [95]. Accordingly, an oxidant such as pure oxygen, chlorine, hydrogen peroxide, potassium permanganate, ozone, ferrate, fenton's reagent, and photochemical oxidation, *etc.*, can be added to oxidize As^{3+} to As^{5+} [3].

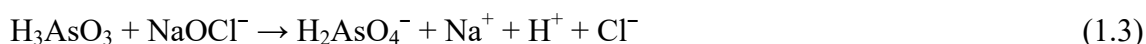
Lee, et al., (2003) investigated the stoichiometry, kinetics, and mechanism of oxidation of As^{3+} to As^{5+} by ferrate (Fe^{6+} , FeO_4^{2-}) and achieved As removal by using Fe^{6+} as both an oxidant and a coagulant [203]. Fe^{6+} is found to be highly efficient in oxidation and coagulation-adsorption of As from water [203–205]. However, it is difficult to handle and transport requiring in situ preparation of Fe^{6+} which is impractical for As removal plants in a rural set up.

Jasudkar, et al., observed good As removal by pre-oxidation using Fenton's reagent (H_2O_2 in the presence of Fe^{2+} catalyst) followed by filtration [205]. The dose of Fenton's reagent used consisted of 50 μ L of H_2O_2 plus 50 mg of $FeSO_4 \cdot 7H_2O$ per 500 mL of As spiked water [205]. In case of Fenton reagent Fe^{2+} is oxidised to Fe^{3+} in the form of iron oxides in water adsorbs As^{5+} on their surface while H_2O_2 also oxidises As^{3+} to easily removable As^{5+} as shown in **Equation (1.1) and (1.2)** [207, 208]:



Oxidation using Fenton's reagent is an attractive oxidant for the oxidation of As^{3+} because of the absence of toxicity of the reagents and residual matters [208].

Sodium hypochlorite (liquid chlorine) is also an efficient oxidant used by several researchers to oxidise As^{3+} to As^{5+} [209, 210]. The oxidation reaction equation of sodium hypochlorite and As^{5+} is given by **Equation 1.3**:



Pettine, M., et al. (1999) [211] restrained the oxidation of As^{3+} to As^{5+} by H_2O_2 in NaCl solutions as a function of pH and temperature ranging from 7.5-10.3 and 10-50°C, respectively, and found that oxidation was rapid at higher pH range and sluggish at lower pH of range. Voegelin, A. and Hug, S. (2003) studied catalysed oxidation of As^{3+} by H_2O_2 on the surface of iron hydroxides (ferrihydrite surface) [212]. Hug and Leupin, used H_2O_2 in presence of OH^- radical scavenger to oxidise As^{3+} to As^{5+} [213]. Good As^{3+} oxidation yields can also be reached in presence of H_2O_2 combined with a high UV radiation dose [214].

KMnO_4 is one of the prominent oxidant which is widely used in removal of inorganic contaminants such as As. Though theoretical redox analyses suggest that KMnO_4 should have better performance in oxidization of As^{3+} within lower pH ranges, the experimental results show similar oxidation efficiencies of As^{3+} under basic and acidic conditions; which was attributed by Na, et al., to adsorption of As^{3+} on $\text{Mn}(\text{OH})_2$ and MnO_2 surface resulting from the oxidation of KMnO_4 [215, 216]. Reactions involved in oxidations of As^{3+} by KMnO_4 in water are given below [215, 216]:



Li, et al., found a promotional effect of KMnO_4 on the oxidation of As by air and attributed that to a catalytic effect of Mn species, probably the nascent MnO_2 [216]. They reported that oxidation of As^{3+} sharply increased with the increase of initial pH of feed from 12 to 14. Another method based on sequential addition of permanganate and ferric iron reported by Ahmad, et al., [217] showed higher removal of As. A low cost method of removal of As based on oxidation-coagulation at optimized pH (OCOP), reported by our research group, removes As along with Fe using small doses of NaHCO_3 , KMnO_4

and FeCl_3 to the contaminated water as pH conditioner, oxidant and coagulant, respectively [218].

1.6.8. Other technology:

Furthermore there are some more existing technologies and processes for removal of As, Fe and other heavy metals found in water. Microbial oxidation of As, bio-accumulation of As by microbial biomass, etc., are biological treatment processes used to remove As from drinking water [218]. Swiss Federal Institute of Environmental Science and Technology, Switzerland and Swiss Agency for Development and Cooperation developed a simple method, viz., Solar Oxidation and Removal of Arsenic, based on photochemical oxidation of As^{3+} followed by precipitation or filtration of As^{5+} adsorbed on Fe^{3+} oxides, for removal of As from water [219]. It uses irradiation of water with sunlight in polyethylene terephthalate or other ultraviolet transparent bottles to reduce As level from drinking water with 67 % removal efficiency.

1.7. Comparison of technologies:

All the existing technologies described above have their advantages and disadvantages to some extent. Though many of the standing methods are competent, there are many hitches associated with them such as effectiveness in wide range of initial concentration of inorganic contaminants in water, influence of other co-existing ions in removal efficiency, optimization of right dose for generalization, filtration of the treated water, adjustment of pH in water, pre-treatment requirement, handling of waste and proper operation and maintenance. Thus, selection of an arsenic removal method is really complex job. There are many technologies which are successful in the laboratory experiments, but practically they are not able to work properly in the variety of field conditions. Removal efficiencies of some existing arsenic removal technologies can be seen in **Table 1.2** and that of heavy metals such as Fe, Mn, Pb, Cd, Ni, Cu, Cr, Co, etc., can be seen in **Table 1.3** [106, 107, 118, 220]. A comparison of the existing methods for removal of inorganic contaminants from water are summarised in **Table 1.4**. Advantages and disadvantages of some existing As and other heavy metal removal techniques are summarised in **Table 1.5** [106, 107, 118].

Table 1.3: Table of efficiencies of removal of As³⁺ and As⁵⁺ by conventional techniques

Technology	Chemical/Material used	As(III) removal Efficiency (%)	As(V) removal Efficiency (%)	Ideal conditions	References
Coagulation-filtration	FeCl ₃	<30	90-95	pH 6-8	[220] [222]
	Sulphates of (Al, Cu, ammonia)	<30	80-90	pH 6-6.5	[223] [224]
Adsorption	Activated Carbon/activated alumina	30-60	>95	pH 5.5-6	[220] [106] [107] [225]
	Iron hydroxides (Granular)	30-60	>95	pH ≈ 8	
Ion exchange	Anionic resins	<30	80-90	[SO ₄ ²⁻] <20mg/L [TDS]<500 mg/L	[220] [222] [226]
Membrane filtration	Nano filtration	60-90	>95	-	[220] [224]
	Reverse Osmosis	80-95	>95	-	
Oxidation-coagulation	KMnO ₄ /FeCl ₃	95-99	100	pH 6.5-7.5	[220] [222]
	Ferrate/FeCl ₃ or FeSO ₄	85-90	95-98	pH 5.5-6.5	[227] [228]
	Cl ₂ or NaOCl/FeCl ₃	80-85	85-90	pH 6.5-8.5	

Table 1.4: Table of efficiencies of removal of heavy metals by conventional removal techniques

Technology	Heavy Metal	Chemical/ material used	Removal efficiency %	Optimized Conditions	References	
Coagulation	Pb	Iron hydroxides	85-90	pH 5.5, Dose 4g/L	[106] [229]	
	Pb	Alum	90-95	pH6.5-7.0, Dose100 mg/L	[106] [230]	
Precipitation	Pb	Ferric sulphate	85-90	pH 9-10, Dose 0.2M/L	[106] [231]	
	Cd	Iron hydroxides	>95	pH 5.5, Dose 4g/L	[106] [229]	
	Cd	Ferric sulphate	98	pH 9-10, Dose 0.2mol/L	[106] [232]	
	Ni	Alum	-	pH6.5-7.0, Dose100 mg/L	[106] [230]	
	Ni	Ferric sulphate	98	pH, Dose 0.2 mol/L	[106] [231]	
	Cr	Ferric chloride	90	pH 7, Dose 0.7 g/L	[106] [233]	
	Cr	Alum	98	pH6.5-7.0, Dose100 mg/L	[106] [230]	
	Co	Alum	-	pH6.5-7.0, Dose100 mg/L	[106] [230]	
	Electrocoagulation	Cd	Zn electrode	94-99	pH 7, Current 0.1-0.5Adm ⁻²	[118] [234]
Pb		Fe-Fe electrode	96.7	Current 6 mAcm ⁻²	[118] [235]	
Ni		Fe, Al-Fe, Fe-Fe electrode	98, 52, 98	Current 50Am ⁻² , 4mAcm ⁻²	[118][236] [237] [238]	
Cu		Fe, Fe-Al, Fe-Fe, Al-Fe, Al-Al-Al	95-99	Current 4-15 mAcm ⁻²	[118][239] [240] [237]	
Adsorption	Ni, Pb	Activated carbon	32(Ni), 53(Pb)		[118][241] [118] [174]	
	Cd, Cr	Activated alumina	90-100(Cd),40-95 (Cr)	pH 4, Dose 0.4 g/L	[153, 155, 156, 160]	
	Ni, Co	Nano-adsorbent	10-30	Dose 1.75 g	[118][241] [178]	
	Membrane processes	Pb, Cu, Ni, Cd	EC with micro filtration, Cross flow Microfiltration	99(EC/MF),31-98 (Cross flow MF)	pH 6-7, External energy for pumping	[117,118-120, 150, 151]
Ion exchange		Fe, Co, Cu	anionic resin	75.94	pH 3.5-4.0	[200, 201]

Table 1.5: Advantages and disadvantages of some existing As and other heavy metal removal techniques [107, 118].

Technology	Advantage	Disadvantage
Coagulation/ Co-precipitation [107, 242, 243]	Low capital costs, efficient, available chemicals, effective over a wide range of pH	Compulsory pre-oxidation, low removal of As ³⁺ , toxic sludge Produced
Electrocoagulation [107, 242, 243]	Emerging technology, high removal efficiency, also removes organic matter and metal hydroxides	Not proven in practical scale, application of current increases the cost of the process
Lime softening Adsorption [107, 244, 245]	Common chemicals Well known and well defined technique, efficient, no daily sludge, commercially available, low maintenance, comparatively cheap, sufficient application	Readjustment of pH is required Controlling of pH required, produces toxic solid waste, requires periodical regeneration or medium change is difficult, relatively high cost, requires regular testing for safe operation
Membrane process [107, 119-122]	Easy monitoring, no chemicals required, no toxic solid sludge produced	Additional process is required to get the complete removal of arsenic and some heavy metals, large rejection of water, investment cost is high, high technical operation and maintenance
Ion exchange [107, 194-201]	Capable of removing metal ions below WHO guideline value, easy monitoring, well known, favourite for industrial use, removal efficiency does not depend on pH	Removal of As ³⁺ is not possible and pre-oxidation is necessary, interference from other anions, monitoring is high cost, large volume of toxic waste of brine, acid and base is produced during regeneration of resins
Oxidation-precipitation [107, 202-218, 246, 247]	Relatively simple operation, low cost, highly efficient	Toxic chemicals and carcinogens are produced as by-products
Oxidation by UV ray and sun light in presence of iron [222]	No use of chemicals; The residues with or without solidification passed the standard of USEPA leach test for disposal.	pH of treated water is low
Oxidation by iron oxidizing bacteria in presence of iron and Mn [222]	No use of chemical; cheaper and eco-friendly; indigenous microbes	Not well-established.
Nano adsorptions/ filtration [241]	High adsorption power	Costly and extra synthesis process for nano adsorbent is necessary. Moreover, nano adsorbents are sometimes toxic copounds.

For existing methods to be suitable in rural condition especially in low income regions, have to be modified based on their laboratory as well as pilot-scale application with the objectives to:

- improve effectiveness in removal of As and other heavy metals
- reduce the capital and operation cost of the systems
- find the optimum conditions
- make the process user friendly
- minimize maintenance problems and
- resolve hazardous sludge management problems formed during the process

Selection of a treatment option by the users on the basis of cost associated with a technique is major determinant. ‘As’ and other heavy metal removal from tube well water is a suitable option for water supply for rural people habituated in drinking tube well water. In many contaminated areas removal may be the only option in the absence of an alternative safe source of drinking water. Among all the processes ‘oxidation assisted coagulation/precipitation’ is considered to be preferable in majority concerns. Oxidation-coagulation is practical and advantageous because of simple operational procedure, low-cost, green and easy handling. One such oxidation-coagulation-adsorption method, viz., oxidation-coagulation at optimized pH (OCOP), developed by our research group has been gaining popularity in domestic, small community as well as large scale community applications as “Arsiron Nilogon” (Arsenic + iron removal) [218, 248, 249]. In the OCOP method NaHCO_3 , KMnO_4 and FeCl_3 are used as pH conditioner, oxidant and coagulant, respectively. KMnO_4 oxidises of As^{3+} to easily removable As^{5+} . In the presence of the pH conditioner, manganese is separated out as insoluble MnO_2 , which also adsorbs ‘As’. The recommended doses of NaHCO_3 , KMnO_4 and FeCl_3 in OCOP in the absence of coexisting iron are 100 mg/L, 4 mg/L, and 25 mg/L, respectively [218]. In presence of coexisting iron, however, more KMnO_4 is added until the water gives light purple colouration to completely oxidise the dissolved Fe^{2+} to Fe^{3+} along with oxidising As^{3+} to As^{5+} .

To get more pluses from OCOP method the following factors may be noted. ₹ 0.5 per 100 L of recurring cost of chemicals in OCOP is far cheaper than the other chemical-based processes [222]. With 95%-98% removal power the OCOP is equivalent or better than some conventional processes [218, 220, 222]. The OCOP is advantageous because it

uses common chemicals [218]. The OCOP has no fixed conditions of external power, temperature and pressure. However, it depends on dosing of the chemicals and better works at moderately basic condition with pH changing from initial 8.3 to final 7.3. The OCOP being simpler and easier as compared to other processes it is gaining rapid popularity especially in Assam and also in some other states of India at present, gave me curiosity for doing further research.

1.7.1. Design and procedure of OCOP method:

OCOP method requires a three chambered system arranged as shown in **Figure 1.8**. The upper chamber is known as treatment chamber containing the contaminated water to which the doses of NaHCO_3 , KMnO_4 and FeCl_3 are added successively [218]. After addition of each dose a mild stirring is necessary by a glass rod or wooden stick for quick mixing. The outlet tap of the treatment chamber is fitted about 3-4 cm from the bottom so that the arsenic and iron containing coagulates can settle down and remain within the chamber. The water is then allowed a residence time in this chamber for 1-2 h to coagulate and then settle down at the bottom of the chamber. The dissolved arsenic are adsorbed by the coagulates of FeOOH , Fe_2O_3 and MnO_2 . Then the supernatant clear water is transferred to the middle chamber, usually simple sand gravel filter to filter out any arsenic containing coagulates coming along with the water. The filtrate water does not contain arsenic and iron and is suitable for drinking purposes.

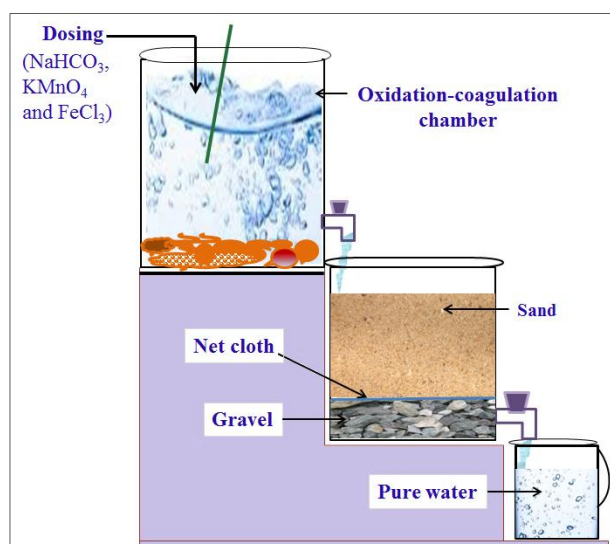


Figure 1.8: Schematic diagram of OCOP set up for arsenic and iron removal.

1.8. Motivation for the present work:

The OCOP process is highly efficient and it can remove groundwater arsenic from initial concentration of about 500 $\mu\text{g/L}$ to less than 5 $\mu\text{g/L}$ and iron from initial concentration up to 25 mg/L to below 0.003 mg/L , which are below the respective WHO guideline values [55]. The OCOP method is gaining popularity in India [218]. Literature shows positive effect in As^{5+} removal in presence of coexisting ferrous iron [250, 253]. So it was expected to be beneficial for the treatment of As contaminated groundwater that usually contains large amount of dissolved ferrous iron. It was also felt that there was scope for further modification of the OCOP method by utilizing the co-existing iron in ground water reducing the dose of FeCl_3 in the OCOP. Therefore it was decided to explore the possibility of reducing the dose of FeCl_3 as coagulant through optimization of the doses of NaHCO_3 , KMnO_4 , and FeCl_3 at varying concentrations of coexisting Fe^{2+} in order to reduce the cost of the process.

The OCOP method is known to remove only arsenic and iron from groundwater. Since groundwater often contains excessive amount of manganese also along with arsenic and iron, it was also thought worthwhile to systematically investigate removal Mn also along with As and Fe.

Use of various oxidants for oxidizing As^{3+} have been reported in the literature including potassium permanganate, ozone, hydrogen peroxide, chlorine, ferrate, Fenton's reagent, hypochlorite, etc., [252–254]. However, a comparative study of the most potential oxidants for the purpose was lacking. Therefore, it was decided to carry out a comparative study of the performances of the commonly used oxidants in the OCOP method.

Though the OCOP method was reported to remove commonly found hazardous metals such as Cd, Pb, Ni, Cr, Cu, Co, etc., from groundwater no systematic study was done on the removal of the heavy metals by the method. It has also been noted that rarely all these heavy metals are removed by a single process. So, it was thought that OCOP method could be used to remove all these heavy metals along with As, Fe and Mn using the same pH conditioner, oxidant and coagulant. Therefore, a systematic study was planned to evaluate removal of the heavy metals by the OCOP method. The proposed

works were expected to complement the OCOP method of As removal in removing heavy metals including Fe and Mn in a more efficient way.

1.9. Aim and Objectives of the research work:

Aim of the present work is to systematically investigate the effect of coexisting Fe on simultaneous removal of As, Fe and Mn by the OCOP method and to optimize the doses of NaHCO_3 , KMnO_4 and FeCl_3 for the purpose; to carry out a comparative study of different oxidants for the OCOP method; and to study removal of heavy metals by the OCOP method. The detail objectives set to meet the aim have been narrated separately for each section below:

1.9.1. Utilization of co-existing Fe for simultaneous removal of As and Fe by OCOP:

In OCOP method the recommended doses of NaHCO_3 , KMnO_4 and FeCl_3 in the absence of coexisting iron are 100 mg/L, 4 mg/L, and 25 mg/L, respectively [218]. It is already reported that coexisting iron has a capability to increase the removal efficiency of As [255, 256]. Therefore, it is possible to reduce the dose of FeCl_3 by utilizing the coexisting iron for coagulation and thereby to reduce the cost in the OCOP method when applied to groundwater having coexisting iron. So in this work it was proposed to use the FeCl_3 dose as equal to the difference between the coagulant dose of the OCOP method and the coexisting iron concentration, $[\text{Fe}^{2+}]_0$ in mg/L, i.e., as $(25 - [\text{Fe}^{2+}]_0)$ mg/L. The dose of pH conditioner NaHCO_3 and oxidant KMnO_4 will be added by varying the doses of NaHCO_3 in mg/L and KMnO_4 as percentage equivalent of coexisting iron in OCOP.

The possibility of reducing the cost of OCOP method by using coexisting iron was examined through a strategy involving a series of laboratory experiments and modelling for optimising the doses of KMnO_4 and NaHCO_3 , using response surface methodology (RSM). RSM is one of the methods to determine the optimum conditions in a limited number of experiments [257-260].

Finally, the optimized doses by RSM was planned to verify through a series of field trial experiments in 32 households and 8 schools with 20 L and 200 L batch capacity, respectively, in some arsenic affected areas in Assam, India.

1.9.2. Simultaneous removal of As, Fe and Mn by OCOP:

Since sometimes groundwater sources contains excess Mn along with As and Fe [55] it is necessary to remove Mn also along with As and Fe for drinking purpose. Considering the coexistence of Fe and Mn ions along with As in groundwater and the roles of Fe ions, KMnO_4 and MnO_2 in simultaneous removal of As, Fe and Mn; it was thought worthwhile to investigate the simultaneous removal of these contaminants by the OCOP method. For this it was planned to optimise doses of NaHCO_3 , KMnO_4 and FeCl_3 for OCOP through RSM [257] and to examine the performance of the method with the optimized doses.

It was also planned to examine the performance of the OCOP method with the optimized doses for simultaneous removal of arsenic, iron and manganese from the groundwater in some selected contaminated field areas of Assam.

1.9.3. Evaluation of performance of different oxidizing agents in OCOP:

KMnO_4 is a prominent oxidant [215, 219] used in various As removal methods as pre-treatment process to oxidise difficult-to-remove As^{3+} to As^{5+} . In OCOP method also it is used as a pre-oxidant showing remarkable result. There are several other oxidants such as ozone, hydrogen peroxide, chlorine, ferrate, Fenton's reagent, hypochlorite which have been tried for oxidising As^{3+} to As^{5+} [253, 254]. However, the efficacy of the oxidants, viz., Fenton's reagent, NaOCl and H_2O_2 , and KMnO_4 , in OCOP method has not yet been studied systematically. Moreover there is hardly any clear report available in the literature on adsorption of arsenic by MnO_2 generated from KMnO_4 in neutral or alkaline water [215, 216]. So it was thought to study of the performances of the most potential other oxidants namely hydrogen peroxide, Ferrate, Fenton's reagent, and hypochlorite in comparison to the performance of KMnO_4 by OCOP method. In that tenacity OCOP method was intended to apply to remove As using KMnO_4 , H_2O_2 , Fenton's reagent, and NaOCl as oxidant separately in equivalent concentration of KMnO_4 using the doses of NaHCO_3 and FeCl_3 as 100 mg/L and 25 mg/L, respectively, as is used in OCOP.

It was also thought worthwhile to investigate the contribution of adsorption of arsenic by MnO_2 in arsenic removal by OCOP method to find out the advantage of KMnO_4 as oxidant in removal of As than the other selected oxidants.

We also planned to study the nature of adsorption of arsenic by the in situ produced adsorbent, *viz.*, FeOOH and MnO₂ in order to understand the nature of adsorption taking place in OCOP.

Effect of pH, temperature, and initial arsenite concentration on oxidation by KMnO₄ was intended to examine to complement the study as these are important parameter influencing redox reactions.

1.9.4. Removal of some metals: Cd, Pb, Ni, Cr, Cu and Co by OCOP:

Seeing the effectiveness and increasing popularity of the OCOP method in removing As, Fe, and Mn together, it was thought worthwhile to carry out a detail study of the removal of other heavy metals also by the method. Because the removal of the other commonly found heavy metals by the OCOP method was not studied in detail. Accordingly in this study it was planned to investigate the removal of six common metals, *viz.*, Pb, Cd, Cu, Cr, Ni, and Co from contaminated water by OCOP method considering the relevance of a low-cost and simple method.

A set of experiments with variation of initial concentration of the metals *viz.*, Pb, Cd, Cu, Cr, Ni, and Co was planned to verify to see the capacity of removal of them by OCOP with same dosing of NaHCO₃, KMnO₄ and FeCl₃ in each experiment and same time.

Another set of experiment was also planned with variation of residence time and with a fixed initial concentrations of each of metal *viz.*, Cu²⁺, Cr⁶⁺, Ni²⁺, Cd²⁺, Pb²⁺, and Co²⁺, respectively, to see the influence of residence time on removal of heavy metals by OCOP method.

1.10. Novelty of the work:

Optimization of the doses of OCOP method will help us to get better removal efficiency of As and Fe with lower cost than the existing OCOP method. Newly used RSM for optimization of doses will definitely give us finer optimization and perfection to get better removal efficiency and lowering of cost. Not only for fixed use of OCOP in removal of As and Fe simultaneously from groundwater, this work may also help us to remove Mn. Comparative study of oxidants for oxidation of As³⁺ to As⁵⁺ in OCOP method is new and it will give us preference of oxidant as well as effectiveness of it to remove arsenic. A study of OCOP in removal of Cu²⁺, Cr⁶⁺, Ni²⁺, Cd²⁺, Pb²⁺ and Co²⁺ from the water is also expected to have potential new scopes for practical application.