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# REMOVAL OF ARSENIC AND IRON FROM GROUNDWATER BY OXIDATION-COAGULATION AT OPTIMIZED pH

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**By**

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Dedicated to Maa and Deuta

**(Ms. Minu Bordoloi and Mr. Rajen Bordoloi)**

# REMOVAL OF ARSENIC AND IRON FROM GROUNDWATER BY OXIDATION-COAGULATION AT OPTIMIZED pH

## ABSTRACT

This thesis describes a systematic laboratory and field study of arsenic and iron removal from contaminated groundwater by oxidation-coagulation at optimized pH (OCOP) technique. Sodium bicarbonate ($NaHCO_3$), potassium permanganate ($KMnO_4$) and ferric chloride ($FeCl_3$) were chosen as pH-conditioner, oxidant and coagulant, respectively. The thesis has been organized in four chapters dealing with different aspects of the study as follows:

1. Introduction: Narrates the background, motivation and the scope, objectives and plan of the present work.
2. Experimental: Describes the materials and the general experimental methods.
3. Results and Discussion: Presents the results, their interpretation, explanation and study of the mechanism involved in the removal process.
4. Conclusions: Summarizes the important findings and future scopes of the present investigation.

## Chapter 1

### 1. Introduction

Chapter 1 contains the introduction part of the thesis. A detail analysis of arsenic contamination, its health impacts and mechanism of affect, the existing arsenic removal technologies, their merits and demerits are discussed in this chapter with reference to the literature. Since the removal of arsenic and iron is pH-dependent, different pH-conditioners *viz.*, lime, ash, carbonate and bicarbonate salts of sodium and potassium are used for pH conditioning to facilitate removal of arsenic. Choosing of the suitable pH-conditioner for removal of arsenic with an appropriate dose is necessary to ensure maximum removal of arsenic without adding residual ions arising from the dose and to avoid readjustment of the final pH of the treated water. These facts lead us to think it worthwhile to carry out a systematic study of arsenic removal by oxidation-coagulation by $KMnO_4$ and $FeCl_3$ through optimization of pH.

Iron in ferrous form usually coexists with arsenic in groundwater. The coexisting iron when removed by aerial oxidation also removes a part of the arsenic. We have chosen to carry out a pH-optimization for iron removal alone before taking up the works on pH-optimization for simultaneous removal of iron and arsenic, and the OCOP technique. The lacuna remaining in the area and the scope of the present topic of research has been discussed. The aims and objectives along with the strategy of the present work have been described towards the end of this chapter.

The main points considered for this investigation were to study the efficiency of different pH-conditioners with respect to dose and residence time, quantity of oxidant and coagulant required for the treatment, pH, influence of competing anions on removal rate, analysis of the various water quality parameters before and after treatment, analysis of the precipitate obtained after treatment through different analytical tools and the cost of the treatment per liter of water. The whole work was driven by an instinct to provide a viable solution to the arsenic affected poor rural people.

## Chapter 2

### 2. Experimental

This chapter consists of the description of the materials and the methods applied in this study. The ashes were obtained from banana pseudostem which is still used for cooking as a substitute of edible soda by villagers of Assam, a North-Eastern state in India. All the other required chemicals were analytical grade quality, obtained from Merck and Sigma Aldrich and used as such. The procedure of batch experiments for removal of arsenic and iron has been described here. Also the methods used for physico-chemical analyses of the water were described in details.

Concentration of arsenic, iron and other heavy metal ions were determined by using a Perkin Elmer Atomic Absorption spectrophotometer or an Inductively Coupled Plasma Optical Emission spectrophotometer. The pH of the solutions was measured using a Orion multiparameter kit. The characterization of precipitate obtained after treatment was done by using FTIR, XRD, SEM and EDX analysis. The detailed description of the instruments along with methods has been included in this chapter.

# Chapter 3

## 3. Results and Discussion

This chapter describes the results of the experiments, their interpretation, explanation and study of the mechanism involved in the removal process. For systematic organization, this chapter has been sub-divided into four major sections as follows.

### 3.1 pH-conditioning for removal of iron

As mentioned earlier, we have studied the effects of pH-conditioning on removal of iron from groundwater since iron usually coexists with arsenic and also influences the removal of arsenic. The results on the experiments on removal of iron by using bicarbonate and carbonate salts of sodium and potassium, and banana ash, and their 1:1 binary mixture as pH-conditioner have been discussed in this section. Results of the batch tests have been analysed to assess performance and optimize the process for iron removal by these pH-conditioners. The different parameters considered for this experiment were the quantity of ash or/and salt required, the effect of residence time, the effluent water pH and effect of initial concentration of iron. Both distilled water containing iron and groundwater amended with iron have been used in the study. The bicarbonates, especially, that of potassium, have been found to be the most effective for removal of iron. The pH of the treated water remains in the acceptable range for drinking when the bicarbonates are used. The sludge produced after the treatment were analysed by using various analytical techniques, *viz.*, FTIR, XRD, SEM-EDX and the mechanism involved in the treatment process have been discussed in detail in this section.

### 3.2 pH-conditioning for simultaneous removal of arsenate and iron

In the second section the results of the experiment on simultaneous removal of arsenate and iron by using lime, banana ash, bicarbonate and carbonate salts of sodium and potassium and their 1:1 binary mixture as pH-conditioner have been discussed in this section. The parameters considered for this experiment were similar to that of the previous section. The arsenic removal in presence of the pH conditioners has been found to increase in the order: banana ash < carbonates < bicarbonates < lime. However, only the bicarbonate salts provide the suitable pH condition for simultaneous removal of arsenate and iron ions. The potassium salts are more efficient than the corresponding sodium salts.

However, sodium bicarbonate has also been found to be useful. Lime is disadvantageous because it requires post-treatment correction of highly alkaline pH.

### 3.3 Arsenic and iron removal by oxidation-coagulation at optimized pH (OCOP) method

The results of the batch tests of simultaneous removal of iron and arsenic by OCOP method by using sodium bicarbonate as pH-conditioner, potassium permanganate as oxidant and ferric chloride as coagulant have been discussed in this section. The different parameters considered in this study were the effect of doses of pH-conditioner, oxidant and coagulant, pH of the effluent water, effects of initial concentration of dissolved arsenic and iron, and effect of the presence of coexisting competing anions. Based on these, the doses of the pH-conditioner, oxidant and the coagulant have been optimized. The sludge produced after the treatment were analysed by using various analytical techniques, *viz.*, FTIR, XRD, SEM-EDX and the mechanism involved in the treatment process have been discussed. The sludge has also been examined with respect to leaching of arsenic and sludge-disposal.

### 3.4 Field trial of the OCOP method

User trial of the OCOP method with optimized doses of pH-conditioner, oxidant and coagulant was carried out in different arsenic affected areas in Assam. The doses used for water with arsenic along with iron less than 1 mg/L were: 0.1 g/L of $NaHCO_3$, 0.5 mg/L of $KMnO_4$ and 25 mg/L of $FeCl_3$ as solid powder, 5% and 25% stock solutions, respectively. For the water containing 1-5 mg/L iron ions a higher dose of 4 mg/L of $KMnO_4$ was used. For the water containing above 5 mg/L iron ions, we added $KMnO_4$ solution until it imparts a light pink colour to the water. The colour however disappears after coagulation.

Different types of low-cost units with different capacities were installed at household and small community levels. User trainings were conducted for application of the method as well as for collection of samples of treated water for further analysis. The field trial was conducted at all together 16 spots water sources which included 10 households with 10 L, 5 schools with 25 L and 1 school with 200 L capacity units. The results obtained after treatment of arsenic containing water with the OCOP technique has been described in this section. The initial concentration of arsenic and iron were in the ranges of 196.43-238.12 µg/L and 0.136-16.25 mg/L, respectively. In all cases, the final concentration of arsenic and iron were found to be in the ranges of 3.57-9.21 μg/L and 0.064-0.360 mg/L, respectively. Arsenic removal was found to be better with lower concentration of co-existing iron.

## Chapter 4

### 4. Conclusions and future scope

This is the concluding chapter of the thesis. It delineates the final remarks and future scope of this work. The bicarbonate salts of Na and K provide the best pH condition for removal of arsenate and iron ions. The bicarbonates retain the final pH within the acceptable range for drinking. Though, potassium bicarbonate has been found to be more efficient pH-conditioner than sodium bicarbonate, the later is more preferable due to its easy availability and familiarity among common people.

Removal of arsenic and iron by the OCOP method using $NaHCO_3$, $KMnO_4$ and $FeCl_3$ as pH-conditioner, oxidant and coagulant, respectively, is highly efficient for simultaneous removal of both arsenic and iron from groundwater. The results of the field trial including the potability of the treated water are promising. This together with high efficiency, low-cost, simplicity of operation, safety and environment-friendliness and option of non-requirement of electricity suggest that the OCOP method has a great potential for arsenic removal in rural areas where alternate arsenic-free water is not available.

Finally, the findings of the present work and the proven applicability of the present method of arsenic and iron removal open up scopes for future research and development works, *viz.*, better management and utilization of the solid sludge, developing sophisticated domestic arsenic and iron removal units and field trial of the technique at large community water supply system. The present OCOP method can also be studied for removal of other heavy metals from groundwater.

# DECLARATION BY THE CANDIDATE

The thesis entitled "***Removal of arsenic and iron from groundwater by oxidation-coagulation at optimized pH***" is being submitted to the Tezpur University in partial fulfillment for the award of the degree of Doctor of Philosophy in *Chemical Sciences* is a record of bonafide research work accomplished by me under the supervision of ***Dr. Robin K. Dutta***.

All helps received from various sources have been duly acknowledged.

No part of this thesis has been submitted elsewhere for award of any degree.

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## *CERTIFICATE OF THE SUPERVISOR*

This is to certify that the thesis entitled ***"Removal of arsenic and iron from groundwater by oxidation-coagulation at optimized pH"*** submitted to the ***School of Sciences,*** Tezpur University in partial fulfillment for the award of the degree of Doctor of Philosophy in *Chemical Sciences* is a record of research work carried out by Miss Shreemoyee Bordoloi under my supervision and guidance.

All helps received from various sources have been duly acknowledged.

No part of this thesis has been submitted elsewhere for award of any degree.

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# *Preface*

*Water is considered as "the life line" for every living organism. Arsenic is a carcinogenic, inorganic water pollutant contaminates groundwater as well as surface water originating from some geological and anthropogenic activities. It is creating menace worldwide as a long time exposure of arsenic of drinking water can cause severe health problems including cancer. Therefore, removal to arsenic from groundwater has a prime importance in context of water purification. Various conventional and advanced treatment methods have been proposed for removal of arsenic from groundwater under both laboratory and field conditions. However, still an efficient method of arsenic removal which is economic, with minimized disadvantages and suitable for household and small community scale application in the rural areas is yet to be developed.*

*Coagulation-precipitation is one of the most cost-effective and efficient methods for removal of arsenic. Ferric salts have been found to be quite promising in removing arsenic and effective over a wider range of pH. A coagulant alone cannot give efficient removal of arsenic in +III state. Since, As(V) is easier to remove than As(III), oxidation prior to coagulation to convert As(III) to As(V) species should be considered first. This can be achieved by the addition of efficient oxidizing agents prior to coagulation.* $KMnO_4$ *is a preferred oxidizing agent for the oxidation of As(III) to As(V) as it is cost-effective, easy to preserve and to handle in practice, especially for small systems in rural areas. Although the pH dependence of arsenic and iron removal by coagulation-precipitation is well known, there has been no report of any systematic comparative study of the efficiencies of different pH-conditioners in the simultaneous removal. Therefore, efficiencies of lime, ash, carbonates and bicarbonates of Na and K are studied as pH-conditioners to remove arsenic from water. The aim of the present work is to systematically study (including field trial) simultaneous removal of arsenic and iron based on oxidation-coagulation at optimized pH (OCOP) to develop a simple, efficient, low-cost, user and environment friendly method. We have chosen* $NaHCO_3$ *as pH-conditioner,* $KMnO_4$ *as oxidant and* $FeCl_3$ *as coagulant for the OCOP method.*

*This research was carried out in the Department of Chemical Sciences, Tezpur University with financial assistance from the Department of Science and Technology (DST), Govt. of India, in the form of a project to my supervisor (DST/TSG/WP/2007/14) and latter from the Council of Scientific and Industrial Research (CSIR), Govt. of India, in the form of a Senior Research Fellowship to me.*

*Shreemoyee Bordoloi*

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*Shreemoyee Bordoloi*
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| | |
|---|---|
| UF | Ultrafiltration |
| USA | United States of America |
| USEPA | United State Environmental Protection Agency |
| UV | Ultraviolet |
| UV-vis | Ultraviolet Visible |
| WHO | World Health Organization |
| XRD | X-ray Diffraction |
| ZVI | Zero Valent Iron |

## Symbols used in the thesis

| | |
|---|---|
| °C | degree centigrade |
| cm | centimeter |
| eV | electron volt |
| g | gram |
| L | liter |
| M | mole |
| mg/L | milligram per liter |
| mL | milliliter |
| min | minute |
| ppm | parts per million |
| ppb | parts per billion |
| µM | micromole |
| mM | millimole |
| h | hour |
| S | siemen |
| vol | volume |
| w | weight |
| $\theta$ | theta |
| $\alpha$ | alpha |
| $\lambda$ | lamda |

## Abbreviations used in the thesis

| | |
|---|---|
| AA | Activated Alumina |
| AAS | Atomic Adsorption Spectroscopy |
| ADP | Adenosine Diphosphate |
| ATP | Adenosine Triphosphate |
| BIS | Bureau of Indian Standards |
| DMA | Dimethylarsinic acid |
| ED | Electrodialysis |
| EDS | Energy Dispersive X-ray Spectroscopy |
| FTIR | Fourier Transform Infra Red |
| GFH | Granular Ferric Hydroxide |
| H | Household |
| ICDD | International Centre for Diffraction Data |
| ICP-OES | Inductively Coupled Plasma Optical Emission Spectroscopy |
| IOCS | Iron Oxide Coated Sand |
| IX | Ion Exchange |
| JCPDF | Joint Committee on Powder Diffraction File |
| MCL | Maximum Contaminant Level |
| MF | Microfiltration |
| MMA | Monomethylarsonic acid |
| MPN | Most Probable Number |
| NF | Nanofiltration |
| OCOP | Oxidation-Coagulation at Optimized pH |
| PDH | Pyruvate dehydrogenase |
| PET | Polyethylene Terephthalate |
| RO | Reverse osmosis |
| S | School |
| SD | Standard Deviation |
| SEM | Scanning Electron Microscopy |
| SORAS | Solar Oxidation and Removal of Arsenic |
| TCLP | Toxicity Characteristic Leaching Procedure |
| TDS | Total Dissolved Solid |
| TMA | Trimethylarsine |

## Chapter 1

# Introduction

# 1. Introduction

This thesis describes a systematic laboratory and field study of arsenic and iron removal from contaminated water by a technique based on oxidation-coagulation at optimized pH.

Crisis of drinking water is now a global problem in the urban as well as rural areas of many countries. Millions of people die each year from largely preventable diseases caused by lack of access to clean water and proper sanitation. Access to clean water will become, increasingly, a source of international conflict in the future. Increasing population along with global rise in industrialization is creating environmental problems of massive dimensions. A huge amount of water pollutants like organic, inorganic, bacteriological, etc. entering the aquifer from different sources adds to this crisis. Arsenic, an inorganic pollutant contaminates groundwater as well as surface water originating from some geological and anthropogenic activities. It is a highly toxic element, when dissolved in water it is colorless, odorless and tasteless and cannot be easily detected. Arsenic is creating menace worldwide as a long time exposure to arsenic through drinking water can cause severe health problems including cancer.

## 1.1 Arsenic, the element

Arsenic (As) is a group V heavy metal element with atomic number 33 with a name derived from the Greek word 'arsenikon', meaning yellow orpiment (arsenic trisulphide). Arsenic is a silver-grey brittle crystalline solid with atomic weight 74.9 amu; specific gravity 5.73 g/cm$^3$, melting point 817 °C (at 28 atm), boiling point 613 °C and vapor pressure of 1 mm Hg at 372 °C. Arsenic occurs in both inorganic and organic forms in the environment[1] with different degrees of toxicity[2, 3]. Inorganic arsenic dissolved in groundwater is more harmful than the organic arsenic present in food[2, 4].

### 1.1.1 Natural abundance and distribution of arsenic

Arsenic is a ubiquitous element found in the atmosphere, soils, rocks, natural waters and organisms with serious health effects upon prolonged intake of even with low concentrations. It is the 20th most abundant element in the earth's crust, 14th in sea water and 12th most common in the human body[1]. Arsenic is a major constituent of over 300 minerals and is commonly found in non-ferrous ores such as of copper, lead, zinc, gold and uranium[5]. Arsenic can be mobilized in the environment through the combination of natural processes such as weathering reactions, biological activity and volcanic emissions. Arsenic is released into the aquifer mostly due to the reductive dissolution of arsenic containing iron hydroxides, (FeOOH), stimulated by microbial activity and organic materials. This is regarded as the most important mechanism of releasing arsenic into the aquifer[6-13]. It is also caused by some anthropogenic activities such as metal mining, groundwater abstraction and by use of arsenical pesticides in agriculture and wood preservation. Arsenic is also used in the manufacture of desiccants, glass, alloys, electronic components (semiconductors), pigments, and pharmaceuticals[14].

### 1.1.2 State of arsenic in water

Arsenic can occur in the environment in several oxidation states (-3, 0, +3 and +5) in both inorganic and organic forms. Trivalent arsenic can exist as arsenous oxide ($As_2O_3$), arsenious acid ($HAsO_2$), arsenite ($H_2AsO_3^-$, $HAsO_3^{2-}$, $AsO_3^{3-}$) ions, arsenic trichloride ($AsCl_3$), arsenic sulfide ($AsS_3$) and arsine ($AsH_3$). Pentavalent arsenic commonly exist as arsenic pentoxide ($As_2O_5$), orthoarsenic acid ($H_3AsO_4$), metaarsenic acid ($HAsO_3$) and arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$, $AsO_4^{3-}$) ions. The presence of different forms of organic arsenic, such as monomethylarsonic acid [MMA, $CH_3AsO(OH)_2$], dimethylarsinic acid [DMA, $(CH_3)_2AsO(OH)$], trimethylarsine oxide [$(CH_3)_3AsO$], methylarsine ($CH_3AsH_2$), dimethylarsine [$(CH_3)_2AsH$] and trimethylarsine [TMA, $(CH_3)_3As$], has also been observed in contaminated soil and water[15]. The toxicity of the different arsenic species varies in the order: arsenite [As(III)] > arsenate [As(V)] > MMA > DMA[16, 17]. Toxicity of arsenic in trivalent state [As(III)] is higher than that of its pentavalent [As(V)] species[18]. Thus, different valency states of arsenic play an important role for the behavior of the element in the aqueous system. The valency state of arsenic also determines the sorption behavior and consequently the mobility in the aquatic environment. In 2000, Jain and Ali have reported about the occurrence, toxicity and speciation techniques for arsenic[19]. The toxic effect of arsenic as well as its mobilization in the natural environment was described by Duker et al. in 2005[20].

In natural waters, arsenic is mostly found in inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. In surface waters under oxidizing conditions, the predominant species is pentavalent arsenic, which is mainly present in the protonated oxyanionic forms ($H_2AsO_4^-$, $HAsO_4^{2-}$). However, under mildly reducing conditions and lower redox potential such as in anoxic ground waters, As(III) is the thermodynamically stable form, which at the pH values of most natural waters is present as nonionic arsenious acid ($H_3AsO_3$)[21-26]. $As^0$ and $As^{3-}$ are rare in aquatic environments. Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Organic forms may however occur where water is significantly impacted by industrial pollution. As(III) is more toxic and relatively mobile than As(V) in contaminated soils. Both As(III) and As(V) compounds are highly soluble in water and may change valency states depending on the pH and redox conditions.

### 1.1.3 Arsenic distributions *vs.* pH

Redox potential (Eh) and pH play major roles in the alternation of the oxidation state of arsenic. The Eh *vs.* pH phase diagrams (Figure 1.1) indicate the stability fields and boundary lines of the different arsenic species[25, 27]

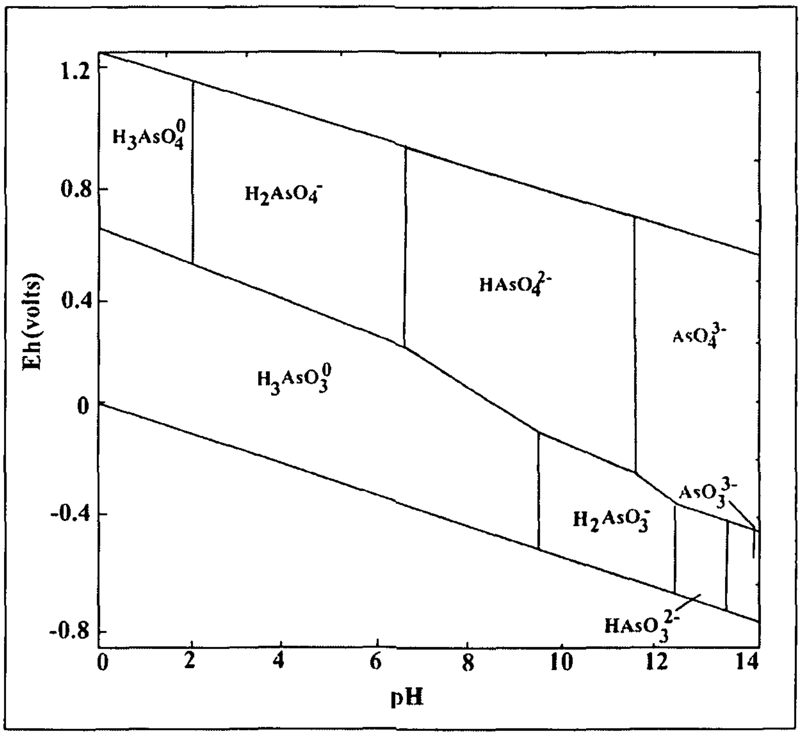


**Figure 1.1.** The Eh–pH diagram for arsenic at 25°C.

Dissolution of arsenic takes place in low acidic pH (<2.0), but it can be dissolved at higher pH (2–11) also, under suitable chemical and physical conditions. Uncharged species of arsenious acid, $H_3AsO_3$ predominates at low pH (<9.2) under mildly reduced conditions and it is easily replaced by $H_2AsO_3^-$ when pH increases. $HAsO_3^{2-}$ is usually formed at very high alkaline pH (>12). In case of As(V), however, a different situation is encountered. $H_2AsO_4^-$ dominates at low pH (less than about 6.9) under oxidizing conditions. At higher pH, $HAsO_4^{2-}$ becomes dominant. $H_3AsO_4$ and $AsO_4^{3-}$ may be present in extremely acidic and alkaline conditions, respectively. It is also apparent from the Figure 1.1 that at a particular Eh and pH value, both As(III) and As(V) species may coexist though under reducing condition As(III) species should prevail over As(V)[28].

### 1.1.4 Drinking water criteria for arsenic

The most important source of arsenic exposure in humans and animals is ingestion of arsenic contaminated drinking water. Presence of inorganic arsenic in drinking water has been recognized as a carcinogen for human even at relatively low concentrations. Long term exposure to arsenic through drinking water causes skin, lung, bladder, liver and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis), anemia, burning sensation of eyes, solid swelling of legs, liver fibrosis, chronic lung disease, gangrene of toes, neuropathy neurological disorders, muscular weakness, loss of appetite, and nausea[29-31]. Therefore, it is very important to document the levels of arsenic in drinking water, and its chemical speciation, and for establishing regulatory standards and guidelines[32].

According to the Bureau of Indian Standards (BIS), arsenic concentration in drinking water should not exceed 50 µg/L[33]. The World Health Organization (WHO) provisional guideline value for arsenic in drinking water is 10 µg/L[34]. However, it is reported that arsenic concentration in drinking water as low as 0.17 µg/L can be toxic[35]. But such low levels are not feasible to determine due to detection limit of analytical techniques. This is why the less protective guideline was adopted[36-38]. Recently, the United State Environmental Protection Agency' (USEPA) has established a health-based, non-enforceable Maximum Contaminant Level Goal (MCLG) of zero As and an enforceable Maximum Contaminant Level (MCL) of 10 µg As/L in drinking water[39, 40]. This would apply to both non-transient, non-community water systems, as well as to the community water systems, as opposed to the previous MCL of 50 µg As/L set by the USEPA in 1975[41]. However, the current drinking water guideline for As adopted by both the WHO and the USEPA is 10 µg/L. This is higher than the proposed Canadian and Australian maximum permissible concentrations of 5 and 7 µg As/L, respectively[42, 43].

## 1.2 Global scenario of arsenic contamination

The arsenic contamination of groundwater of vast areas all over the world and prevalence of arsenic related health problems, *viz.*, arsenicosis due to consumption of such water is a serious worldwide problem[14]. Arsenic is considered as a worldwide recurring pollutant with serious health effects upon prolonged intake of even low concentrations[44-46]. Although trace levels of arsenic is beneficial for plant and animal nutrition[47-49], no comparable data are available for humans[50]. Elevated concentrations of arsenic in the biosphere pose a significant threat to mankind. Arsenic contamination of surface and groundwaters occurs worldwide and has become a sociopolitical issue in several parts of the globe. Thousands of As-contaminated sites have been reported around the world[51, 52]. For example, several million people are at risk from As-contaminated drinking water in India[53, 54] and Bangladesh[55-57]. Natural occurrences of arsenic in groundwater have also been found in many parts of the United States[58-60], China[61-66], Japan[67, 68], Vietnam[69-72], Taiwan[73-78], Chile[79, 80] Canada[81, 82] Argentina[83-85], Southern Thailand[86, 87], Ghana[88, 89], Hungary[90, 91], Finland[92] , Mexico[93-95], Spain[96], Australia[97, 98], Bolivia[95], Cambodia[99-101], Greece[102, 103], Germany[104], Italy[105], Nepal[106-108], Pakistan[109-112], Poland[113] and Romania[114].

### 1.2.1 Indian scenario of arsenic contamination

In India, arsenic contamination in groundwater was first reported in 1983 from 33 affected villages in four districts in West-Bengal. This number of villages has increased to 3417 in 111 blocks in nine districts till 2008 in West Bengal alone[115-118]. Groundwater contamination of arsenic and its health effects of Rajnandgaon district of Chattisgarh state came to light in 1999[119-121]. In 2002, two villages, Barisban and Semaria Ojhapatti, in Bhojpur district, located in the western part of the Bihar state, were reported having arsenic contaminated groundwater[122]. In 2008, it was reported that groundwater of 57 blocks from 15 districts (out of 38 districts) in Bihar having population nearly 10 million is affected by arsenic[123]. During 2003, 25 arsenic affected villages of Ballia district in Uttar Pradesh and people suffering from skin lesions came into limelight[124]. The groundwater arsenic contamination and consequent suffering of hundreds of people were reported from 17 villages of the Sahibgunj district of Jharkhand state, in the middle Ganga plain during 2003-2004[125, 126]. In 2004, a large scale arsenic contamination in groundwater in Assam, Tripura, Arunachal Pradesh, Nagaland and Manipur was also reported[127-129].

### 1.2.2 Arsenic contamination of groundwater in North-East India

Contamination of the groundwater of the entire north-eastern states of India, in general and in the plains on both sides of the Brahmaputra in Assam, in particular, with high level of As has come to light in 2004[127]. As per the available information, arsenic has been detected over 50 μg/L in the groundwater in 23 out of 27 districts of Assam, 6 out of

13 districts of Arunachal Pradesh, 3 out of 4 districts of Tripura, 2 out of 8 districts of Nagaland and 1 out of 9 districts of Manipur. The maximum level of arsenic was found in Midland block of Dibang valley district in Arunachal Pradesh was 618 μg/L. In Manipur, arsenic was found with very high concentration (798-986 μg/L) in Kakching block of Thoubal district[130]. Groundwater of some parts in West Tripura and Dhalai districts contains arsenic in the range of 65-444 μg/L. Arsenic was also found in seven locations in Mokokchung and five locations in Mon district in Nagaland.

### 1.2.3 Arsenic contamination of groundwater in Assam

Groundwater quality of Assam valley is highly ferruginous and among 27 districts, 23 are contaminated with arsenic[127]. Symptoms of arsenicosis have been reported in some residents in Assam in 2010[131]. As per the available report, maximum concentration of arsenic was observed in four districts of Assam *viz.*, Jorhat, Lakhimpur, Nalbari and Nagaon districts in the range of 112-601 μg/L[127]. Other districts where arsenic concentration in groundwater was found in between 100-300 μg/L are Baksa, Barpeta, Darrang, Dhemaji, Dhubri, Golaghat, Sivsagar and Sonitpur. Arsenic concentration in groundwater of remaining 11 districts of Assam was found in between 50-100 μg/L[127].

### 1.2.4 Toxicity and health effects of arsenic exposure

Millions of people are exposed to arsenic containing drinking water worldwide. Long time exposure of arsenic-contaminated drinking water leads to serious health problems including cancer. The toxicology of arsenic is a complex phenomenon and generally classified into acute and chronic arsenic poisoning.

Acute arsenic poisoning usually occurs through ingestion of contaminated food or drink. Symptoms of acute intoxication usually occur within 30 min of ingestion but may be delayed if arsenic is taken with food. Symptoms include burning and dryness of the mouth and throat, dysphasia, colicky abnormal pain, projectile vomiting, profuse diarrhea, and hematuria. The acute arsenic poisoning requires prompt medical attention. The muscular cramps, facial edema and cardiac abnormalities, shock can develop rapidly as a result of dehydration[132]. Following the gastrointestinal phase, multisystem organ damage may occur due to acute arsenic poisoning[133].

Chronic arsenic poisoning is much more insidious in nature. Arsenicosis is a chronic illness resulting from drinking water with high levels of arsenic exposure over a long period of time[134, 135]. In general, there are four recognized stages of arsenicosis[14]:

*Preclinical*: In this case no symptoms can be seen in the patient, but arsenic can be detected in urine or body tissue samples.

*Clinical*: Various symptoms can be seen such as darkening of the skin (melanosis); dark spots on the chest, back, limbs or gums; oedema (swelling of hands and feet); keratosis or hardening of skin into nodules, etc.

*Complications:* In this stage, clinical symptoms become more pronounced and internal organs are affected. Enlargement of liver, kidneys, spleen, conjunctivitis (pink eye), bronchitis, destruction of erythrocytes, high blood pressure, bone marrow depression, diabetes and cardiovascular disease have been reported.

*Malignancy:* Malignant arsenical skin lesions may be tumors or cancers (carcinoma) of skin or other organs, *viz.*, kidney, liver, lung and bladder[136]. Cancer usually takes more than 10 years to develop.

Over 12% of the population in Antofagasta exhibiting dermatological manifestations due to consumption of high arsenic containing drinking water[137]. In Taiwan, intake to arsenic containing drinking water (groundwater) has been reported to cause a severe disease of blood vessels leading to gangrene, known as "blackfoot disease"[138]. According to some estimates in 2000, 35 out of 77 million people in Bangladesh have been chronically exposed to arsenic through their drinking water[139].

### *1.2.4.1 Mechanism of arsenic toxicity*

The detailed mechanisms of arsenic toxicity and carcinogenicity are not well understood. The mechanisms of toxicity of trivalent and pentavalent arsenic are discussed below:

#### ***Mechanism of pentavalent arsenic toxicity***

Arsenate can replace phosphate in many biochemical reactions because they have similar structure and properties[140]. It reacts with glucose and gluconate *in vitro* to form glucose-6-arsenate and 6-arsenogluconate, respectively[141, 142]. These compounds resemble glucose-6-phosphate and 6-phosphogluconate, respectively. Glucose-6-arsenate is a substrate for glucose-6-phosphate dehydrogenase and can inhibit hexokinase[141]. Arsenate can also replace phosphate in the sodium pump and the anion exchange transport system of the human red blood cell[143]. Arsenate damages the formation of adenosine triphosphate (ATP) by a mechanism known as arsenolysis[144, 145]. Arsenolysis occurs during glycolysis which inhibit the generation of ATP during glycolysis in presence of phosphate[146]. Arsenolysis may also occur at the mitochondrial level during oxidative phosphorylation.

Here, in presence of arsenate, adenosine-5-diphosphate (ADP) form ADP–arsenate[142]. ADP–arsenate hydrolyzes easily compared to ADP–phosphate, which is formed during oxidative phosphorylation. Thus, arsenolysis diminishes *in vitro* formation of ATP by the replacement of phosphate with arsenate in the enzymatic reactions. Arsenite is ineffective in depleting ATP in human erythrocytes.

### *B. Mechanism of trivalent arsenic toxicity*

Thiols or vicinal sulfhydryls play a major role in the activity of enzymes, receptors and coenzymes. Trivalent arsenic readily reacts *in vitro* with thiol-containing molecules[147, 148]. The binding of arsenite to critical thiol groups may inhibit important biochemical events which could lead to toxicity. However, binding of arsenite at nonessential sites in proteins may be a detoxication mechanism[149]. Pyruvate dehydrogenase (PDH) is a multi subunit complex that requires the cofactor lipoic acid, a dithiol, for enzymatic activity. Arsenite binds with lipoic acid moiety and thus inhibits PDH[150]. PDH oxidizes pyruvate to acetyl–CoA, a precursor to intermediates of the citric acid cycle. The citric acid cycle degrades the intermediates, and this provides reducing equivalents to the electron transport system for ATP production. Inhibition of PDH may ultimately lead to decreased production of ATP. Also, intermediates of the citric acid cycle can be used in gluconeogenesis. Inhibition of these enzymes may alter cellular redox status and eventually lead to cytotoxicity.

## 1.3 Mitigation of arsenic menace

Arsenic contamination of groundwater is a big threat to human life as well as for plant and other animal life. To overcome the problem of contamination of drinking water by arsenic, there are three possible options.

### 1.3.1 Alternative water sources

Use of alternate arsenic-free water sources is the best solution to get rid of arsenic contamination. This includes surface water and rainwater. Normally, surface water is heavily contaminated with biological and chemical pollutant and it is not possible for the poor communities to use that water, because purification or disinfection becomes costly. Transportation of arsenic-free surface water from other places to arsenic affected areas needs high amount of investments and proper cooperation of government and public. Rainwater is usually a much cleaner water source but its uneven distribution and limited storage capacity in communities or households has made it unsuitable. Moreover, rainwater doesn't contain the required minerals for nutrition, so it cannot be used for drinking purpose. It is unlikely for a developing country to switch the source of water from groundwater to surface water in a short period of time for sparse rural populations. Therefore, one must consider arsenic removal techniques and the economic feasibility and simplicity of the systems in making arsenic remediation strategy[151, 152].

### 1.3.2 Removal of arsenic from groundwater

Arsenic remediation technology in drinking water is almost as old as detection of arsenic in drinking water and knowledge of its toxic effects. Various conventional and advanced treatment methods have been proposed for removal of As from groundwater under both laboratory and field conditions. Most of the existing methods for sequestering As from contaminated water by physicochemical treatment methods are based on one or combinations of the following simple principles: a) Coagulation / co-precipitation, b) adsorption, c) Membrane process, d) Ion exchange[153-157]. The performance and the drawback of the existing techniques are further illustrated specifically in section 1.4.

### 1.3.3 Better nutrition

In Asia, primary food source, rice, is directly contaminated by arsenic accumulation in paddy soil. Thus additional arsenic consumed in rice, cooked in arsenic contaminated water contributes 30-60% of dietary intake of arsenic of polluted regions[158]. Low socioeconomic status and malnourishment enhance the disease conditions because such population has no alternative but to drink the available arsenic-contaminated water[159, 160]. Nutritious diet may be able to inhibit and/or reverse the toxic mechanism of arsenic, whereas a deficient diet can increase the susceptibility to adverse effects of arsenic in drinking water[161-163]. Several epidemiological and experimental studies suggested that nutritious diet reduces the arsenic toxicity by increasing methylation of arsenic[164, 165].

## 1.4 Existing arsenic removal methods

### 1.4.1 Precipitative techniques

### *1.4.1.1 Coagulation/precipitation*

Coagulation/precipitation is the oldest and a widely practiced arsenic remediation technique[166]. Coagulants change surface charge properties of solids to allow agglomeration and/or enmeshment of particles into a flocculated precipitate. In either case, the final products are larger particles, or floc, which more readily filter or settle under the influence of gravity. Coagulation-flocculation processes with alum and iron-containing compounds such as ferric chloride, ferric sulfate etc. as coagulant are most commonly used in arsenic remediation techniques because they are both cheap and effective[167-170]. They are more extensively tested in both laboratory and field studies than other technologies. Other synthetic coagulants, *viz*, lanthanum compounds[171], manganese oxides[172] and granular ferric hydroxide[173, 174] have also proved effective for arsenic removal. Clays and mineral-containing rocks are also used in this purpose[175-181].

Since both alum and ferric salts are more efficient at removing As(V), oxidation of As(III) is required to achieve maximum removal efficiency[182, 183]. On a weight basis, ferric salts are more efficient and preferable to remove arsenic than alum and also because of the suspected ill effect of the later causing Alzheimer's disease[184]. Ferric salts are also effective in removing arsenic over a wider range of pH than alum[185, 186].

In 1997, McNeill and Edwards[187] reported that solubility and stability of the metal hydroxide flocs play an important role in arsenic removal. In case of ferric coagulants, most of the ferric ends up as ferric hydroxide whereas in alum coagulation, a significant portion of the added aluminium salts remains as soluble complexes. Thus particulate metal hydroxide formation decreases which decreases the overall arsenic removal. Removal percentage increases with increased coagulant dosages[188].

The enhanced coagulation process involves modifications to the existing coagulation process such as increasing the coagulant dosage, reducing the pH, or both[189]. Cheng et al.[188] (1994) reported that more than 90% removal of As(V) can be achieved under enhanced coagulation conditions. With ferric salt enhanced coagulation pH does not have a significant effect between 5.5 and 7.0 while lowering pH during enhanced coagulation by alum improved arsenic removal. However, post-treatment for pH adjustment may be required for corrosion control when the process is operated at a low pH.

Lime softening removes hardness caused by calcium and magnesium compounds in solution by creating a shift in the carbonate equilibrium. The addition of lime converts bicarbonate to carbonate as the pH increases, and as a result, calcium is precipitated as calcium carbonate. Lime removes As(III) and As(V) also along with the hardness[190, 191]. Soda ash (sodium carbonate) is added if insufficient bicarbonate is present in the water to remove hardness to the desired level. Softening for calcium removal is typically accomplished at a pH range of 9 to 9.5 while magnesium hydroxide precipitates at pH levels greater than 10.5. Neutralization is required if the pH of the softened water is excessively high (above 9.5) for potable use. The most common form of pH adjustment in softening plants is recarbonation with carbon dioxide. The optimum pH for As(V) removal by lime softening is ≈10.5, and the optimum pH for As(III) removal is ≈11[192].

### *1.4.1.2 Coagulation assisted microfiltration*

Microfiltration is used as a membrane separation process in coagulation techniques to remove particulates, turbidity and microorganism. Microfiltration is used in a similar manner to a conventional gravity filter. The advantages of microfiltration over conventional filtration are outlined below[193]:

- smaller floc sizes can be removed (smaller amounts of coagulants are required); and
- increased total plant capacity

In 1997, Ghurye et al.[194] reported that coagulation assisted microfiltration could reduce arsenic levels to below 2 µg/L in waters with a pH of between 6 and 7, even when the influent concentration of Fe(III) is approximately 2.5 mg/L. With an iron and manganese removal system, it is critical that all of the iron and manganese be fully oxidized before they reach the membrane to prevent fouling[195].

## 1.4.2 Adsorptive techniques

### *1.4.2.1 Activated Alumina*

Activated Alumina (AA) is a physical/chemical process by which ions in the feed water are sorbed to the oxidized AA surface. It is referred to as an adsorption process, although the chemical reactions involved are actually exchanges of ions[196, 197]. Activated alumina is prepared through dehydration of $Al(OH)_3$ at high temperatures, and consists of amorphous and gamma alumina oxide[198]. Feed water is continuously passed through AA packed beds to remove the contaminants. The contaminant anions are exchanged with the surface hydroxides on the alumina. When adsorption sites on the AA surface become filled, the bed must be regenerated. Regeneration is accomplished through a sequence of rinsing with regenerant, flushing with water, and neutralizing with acid. The regenerant is a strong base, typically sodium hydroxide; the neutralizer is a strong acid, typically sulfuric acid.

Several researchers have reported that optimum pH for arsenic removal by AA to be in the range of 5.5 to 6.0 for tests conducted on synthetic waters[199-201]. Field studies involving AA indicate that this technology can remove arsenic to 3 µg/L[202a, b]. But alumina tends to dissolve over successive cycles due to the strong base/strong acid cycling during regeneration. As a result of this, alumina beds may become cemented if close care is not given[203]. Backwashing the AA media may help prevent cementation. When pretreatment is used to reduce the pH to low levels (less than 6.0) to optimize the process, the effluent pH will be less than typically desired in the distribution system. For this reason, post-treatment corrosion control to raise the pH would be necessary for those systems.

#### *1.4.2.2 Granular Ferric Hydroxide*

In 1998, Driehaus et al.[204] reported about a new efficient adsorbent of arsenic granular ferric hydroxide (GFH). Pal et al.[205] concluded that granular ferric hydroxide 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.

#### *1.4.2.3 Nanoadsorbents*

Nanoadsorbents for arsenic removal from water are gaining momentum globally. Although they are mostly still in the laboratory research stage, some have made their way to pilot testing or even commercialization[206]. Some potential nanoadsorbents for arsenic removal are metal oxide nanoparticles (e.g., oxides of iron, titanium, copper, aluminium, zirconium, and manganese) and polymeric nanoadsorbents[207a, b]. Though may be temporary, these nanoadsorbents face certain challenges including technical hurdles, high cost, and potential environmental and human risk[206].

### 1.4.3 Membrane processes

Membranes are selective barriers, allowing some constituents to pass while blocking the passage of others. There is a driving force i.e. a potential difference between the two sides of the membrane which controls the movement of constituents across a membrane. Membrane processes are often classified by the type of driving force, including pressure, concentration, electrical potential, and temperature. Among them pressure driven membrane processes and electrical potential-driven membrane processes are commonly used.

Pressure-driven membrane processes with arsenic removal, are often classified by pore size into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). High-pressure processes (i.e., NF and RO) have a relatively small pore size compared to low-pressure processes (i.e., MF and UF)[208-211]. NF and RO primarily remove constituents through chemical diffusion while MF and UF through physical sieving. An advantage of high-pressure processes is that they tend to remove a broader range of constituents than low-pressure processes. However, the drawback to broader removal is the increase in energy required for high-pressure processes. Electrical potential-driven membrane processes can also be used for arsenic removal e.g. electrodialysis reversal[212, 213].

#### *1.4.3.1 Microfiltration*

This technique is highly dependent on the size distribution of arsenic-bearing particles in the source water. MF pore size is too large to substantially remove dissolved or colloidal arsenic. Although MF can remove particulate forms of arsenic, this alone does not make the process efficient for arsenic removal unless a large percentage of arsenic is present in particulate form. To increase removal efficiency in source waters with a low percentage of particulate arsenic content, MF can be combined with coagulation processes.

### *1.4.3.2 Ultrafiltration*

UF alone, like MF, may not be a viable technique for arsenic removal for groundwaters, however, UF may be appropriate for surface waters with high colloidal and particulate arsenic concentrations[214, 215].

### *1.4.3.3 Nanofiltration*

Nanofiltration membranes are capable of removing significant portions of the dissolved arsenic compounds in natural waters due to their small pore size. NF will primarily remove divalent ions (e.g., Ca, Mg), but not monovalent salts (e.g., Na, Cl). Through size exclusion, NF can remove both dissolved As(V) and As(III). This makes NF a reliable arsenic removal process for groundwater[216, 217]. The small pore size, however, makes NF membranes more prone to fouling than UF or MF membranes. Therefore, application of NF for surface water treatment is typically not accomplished without extensive pretreatment for particle removal and possibly pretreatment for dissolved constituents to prevent fouling.

Several NF studies have been undertaken for arsenic removal, and the results show that NF processes are effective for the removal of arsenic[218]. Arsenic removal through NF depends on operating parameters, membrane properties, and arsenic speciation[219, 220]. In 1994, Chang et al. [221] 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 arsenic removal efficiency dropped to 65% and when the recovery was increased to 90%, the arsenic removal efficiency dropped down to 16%[220, 222]

### *1.4.3.4 Reverse Osmosis*

Reverse osmosis (RO) is the oldest membrane technology, traditionally used for the desalination of brackish water and sea water. RO is a filtration method that removes molecules and ions from solutions by applying pressure when it is on one side of a selective membrane. The solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. Several bench- and pilot-scale studies reveal RO as capable of removing arsenic to below the WHO guideline value.[223-225]. RO removes As(V) to a greater degree than As(III), so, maintaining oxidative conditions may be important to the process[226, 227]. 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 feed water passes through the membrane; however, the rest is discharged along with the rejected salts as a concentrated stream.

#### *1.4.3.5 Electrodialysis*

Electrodialysis (ED) is a process in which ions are transferred through membranes that are selectively permeable towards cations or anions under the influence of direct electric current. The separation mechanism is actually an ion exchange process. The ions travel from a lesser to a higher concentrated solution. In this process, the membranes are arranged in an array or stack placed between opposite electrodes, with alternating cation and anion exchange membranes. The mobility of the cations or anions is restricted to the direction of the attracting electrodes, and this result in alternating sets of compartments containing water with low and high concentrations of the ions. ED can achieve high removals of total dissolved solid (TDS) from water and typically operates at a recovery of 70 to 80 %[228, 229]. Very few studies have been conducted to exclusively evaluate this process for the removal of arsenic.

### 1.4.4 Ion exchange

Ion exchange (IX) is a physical/chemical process by which ion on the solid phase is exchanged for an ion in the feed water. The solid phase is a synthetic resin which can preferentially adsorb the particular contaminant of concern. In this process feed water containing contaminants is continuously passed through a bed of ion exchange resin beads in a downflow or upflow mode until the resin is exhausted i.e. all sites of the resin beads have been filled by contaminant ions. At this point, the bed is regenerated by rinsing the IX column with a regenerant - a concentrated solution of ions initially exchanged from the resin. The chloride-arsenate exchange chemical reaction typically occurs in the range of pH 8 to 9 when using chloride-form, strong-base resins[230]. Recent studies have also found that sulfate-selective resins tend to be superior to nitrate-selective resins for arsenic removal[231]. The ion exchange method can remove arsenic to below the WHO guideline value but requires high capital cost[232].

### 1.4.5 Other technologies

Besides the methods discussed above several new methods have been studied recently. Some of the interesting methods are briefly described below.

- Iron-manganese oxidation
- Iron oxide coated sand (IOCS)
- Zero-valent iron (ZVI)
- Lanthanum compounds
- Zeolites
- Manganese Greensand
- Goethite
- Manganese coated sand
- In situ (sub-surface) arsenic immobilization
- Biological treatment for arsenic removal
- Solar Oxidation

#### *1.4.5.1 Iron-manganese oxidation*

Conventional iron and manganese removal can result in significant arsenic removal, through coprecipitation and sorption onto ferric or manganic hydroxides[233]. Most of the low-cost methods for arsenic and manganese removal based on aeration and filtration through porous media such as sand and gravel. Any method that effectively removes iron and manganese could be evaluated to see if arsenic is also removed effectively.

#### *1.4.5.2 Iron oxide coated sand*

IOCS sand showed promise as a medium for use in small systems or home-treatment units in developing areas of the world, for removing As(III) and As(V) from ground water[234, 235]. Iron oxide-coated sand is a suitable adsorbent for reducing As(III) concentration to 50 μg/L[236].

#### *1.4.5.3 Zero-valent iron*

Many studies reported ZVI ($Fe^0$) as an effective agent at removing As(III) and As(V), and the predominant mechanistic pathways seems to be surface precipitation or adsorption[237, 238]. $Fe^0$ is nontoxic and inexpensive. From literature, it is found that $Fe^0$ is effective at removing arsenic at low pH and in high-sulfide-containing water[239]. Although the reducing strength of $Fe^0$ decreases significantly at neutral pH, the hydroxide species forming on the surface of $Fe^0$ are effective adsorption sites for both As(V) and As(III) at neutral and basic pH.

### *1.4.5.4 Lanthanum compounds*

Lanthanum is one of the cheapest rare-earth elements. Lanthanum hydroxide, lanthanum carbonate, and basic lanthanum carbonate were investigated for removing As(V) ion from aqueous solutions[240]. The proposed mechanism for arsenic removal by lanthanum compounds is adsorption by exchange of $CO_3^{2-}$ and/or $OH^-$ group with As(V) ions in the neutral-to-basic pH range[241].

### *1.4.5.5 Zeolites*

Zeolites are an important group of minerals due to their catalytic, sieve, and exchange properties. They are naturally abundant and are potentially low-cost materials for arsenic removal[242]. Arsenic removal was also investigated with zeolite modified with iron[243].

### *1.4.5.6 Manganese greensand*

Manganese greensand is a zeolite-type glauconite mineral, artificially coated with a layer of active hydrous manganese dioxide and other high oxides of Mn[244]. In the presence of iron (Fe:As ratio= 20:1), manganese greensand was more effective at removing arsenic than iron-oxide-coated sand and resin[245].

### *1.4.5.7 Goethite*

Goethite is an α-iron(III) hydroxy-oxide mineral [FeO(OH)] and is the most stable form of iron oxide in soil. Many researchers investigated synthetic goethite particles for removal of As(V) from dilute aqueous solutions[246-249]. The small size of the particles necessitated an efficient solid/liquid separation technique.

### *1.4.5.8 Manganese coated sand*

Manganese dioxide can both oxidize As(III) and adsorb As(V). Many studies reveal that manganese dioxide coated sand is efficient in removal As(III) and As(V)[250-252].

### *1.4.5.9 In situ (sub-surface) arsenic immobilization*

It is possible to immobilize the arsenic in groundwater under reducing condition by creating oxidized conditions in the subsurface. In Germany, in order to remediate an aquifer containing high arsenite, high ferrous iron, low-pH groundwater, potassium permanganate was injected directly into contaminated wells, oxidizing arsenite, which coprecipitated with ferric oxides as ferric arsenate. Over 99% (from 13,600 to 60 μg/L) of arsenic removal can be obtained in this process. In another project atmospheric oxygen was used to reduce arsenic concentrations *in situ* from approximately 20 to 5 μg/L, while iron and manganese levels were also lowered[253]. *In situ* immobilization has the great advantage of not producing any wastes that must be disposed of. However, experience is limited, and the technique should be considered with caution.

### *1.4.5.10 Biological treatment*

In microbiological processes employed for arsenic removal, two types of metal-microbe interactions can be potentially used: (a) microbial oxidation of arsenic (III) to arsenic (V) to facilitate its removal by conventional arsenic removal processes, and (b) bioaccumulation of arsenic by microbial biomass[254]. The Biological Activated Carbon system is a biologically active filtration unit developed by the Mainstream BMS Ltd., Vanscoy, Saskatchewan and Davnor Water Treatment Technologies Ltd., Calgary, Alberta[255]. In this system a granular activated carbon filter is used, which are continuously aerated to enhance the growth of biological activity within the filter media. This system has been used in rural Saskatchewan on experimental basis for seven years with consistent arsenic removal exceeding 90%[256]. This system could also remove more than 99% of iron and also dissolved organic material along with arsenic.

### *1.4.5.11 Solar Oxidation*

Solar Oxidation and Removal of Arsenic (SORAS) is a simple method developed by Swiss Federal Institute of Environmental Science and Technology, Switzerland (EAWAG) and Swiss Agency for Development and Cooperation (SDC)[257]. The method is based on photochemical oxidation of As (III) followed by precipitation or filtration of As(V) adsorbed on Fe (III) oxides. It uses irradiation of water with sunlight in Polyethylene Terephthalate (PET) or other Ultraviolet (UV) transparent bottles to reduce arsenic level from drinking water. Arsenic removal efficiency of SORAS was found in between 45-78%. In field tests in Bangladesh, it shows an average of 67% removal efficiency.

## 1.5 A comparison of the existing arsenic removal methods

All the existing technologies described above have their merits and demerits. Though most of the existing methods are efficient, there are many difficulties associated with them such as wide range of initial arsenic concentration in water, other co-existing ions, optimization of right dose for generalization, filtration of the treated water, adjustment of pH in water, post treatment requirement, handling of waste and proper operation and maintenance. Thus selection of an arsenic removal method is really complex. There are many technologies which are successful in the laboratory but they do not work properly in the field condition. A comparison of some existing arsenic removal processes can be seen in Table 1.1.

**Table 1.1.** Advantages and disadvantages of some existing arsenic removal techniques.

| Techniques | Advantages | Disadvantages |
|---|---|---|
| **Coagulation/Coprecipitation** | | |
| Alum coagulation | Low capital costs, available chemicals | Pre-oxidation is must, Low removal of As(III), toxic sludge produced |
| Iron coagulation | Relatively low-cost, efficient, simple operation common chemicals, effective over a wide range of pH | Medium removal of As(III), pre-oxidation may be required to get efficient removal |
| Lime Softening | Common chemicals | Readjustment of pH is required |
| Enhanced coagulation | High removal efficiency, also removes organic matter and metal hydroxides | Emerging technique, not proven in practical scale |
| **Adsorption** | | |
| Activated alumina | Well known, efficient, no daily sludge, commercially available, low maintenance | Readjustment of pH required, produces toxic solid waste, requires monitoring breakthrough and periodical regeneration or medium shift, monitoring is difficult, relatively high cost |
| Iron based sorbent | Well defined technique, no regeneration, comparatively cheap, plenty of possibilities | Requires pH control, requires replacement of media after exhausting, requires regular testing for safe operation |
| Nanoadsorbents | High capacity and efficiency | Technical hurdles and high cost[206] |
| **Membrane technique** | | |
| Microfiltration | Can remove particulate forms of arsenic | Additional removal process is essential |

| | | |
|---|---|---|
| Reverse osmosis | Capable of removing As to below WHO guideline value, easy monitoring, no chemicals required, no toxic solid waste produced | Removal of As(III) is lower than As(V), large reject water with high As, high investment cost, high technical operation and maintenance, pretreatment steps are often required, efficiency is very low with high concentration As contaminated water. |
| Electrodialysis | Capable of removal of other contaminants | Re-adjustment of water quality is required,<br>interference by oxidizing agents, toxic waste water |
| Nanofiltration | Well-defined, high removal efficiency | Very high capital and running cost |
| Ultrafiltration | May be appropriate for surface waters with high colloidal and particulate arsenic concentrations | Not viable for arsenic removal for groundwaters |
| **Ion exchange** | | |
| Anion resin | Capable of removing As to below WHO guideline value, easy monitoring, well defined medium, removal efficiency does not depend on pH | Only removal of As(III) is not possible and prior oxidation necessary,<br>interference from other anions, monitoring is difficult<br>high cost, Produce large volume of toxic brine during regeneration of resins |
| **Oxidation/precipitation** | | |
| Aerial oxidation | Relatively simple, low-cost | Partial removal of arsenic, additional removal process is essential, very slow process |
| Chemical oxidation | Relatively simple, fast<br>oxidizes impurities and kill microbes | Toxic chemicals and carcinogens are produced as by-products, interfering substances decreases the removal efficiency, additional removal process is essential |

To make the methods suitable in rural condition particularly in low income regions, they have to be modified based on their pilot-scale implementation with the objectives to:

- improve effectiveness in arsenic removal
- reduce the capital and operation cost of the systems
- make the technology user friendly
- overcome maintenance problems
- resolve sludge and arsenic concentrates management problems.

A major determinant in the selection of a treatment option by the users is the cost associated with a technique. Arsenic removal from tubewell water is a suitable option for water supply for rural people habituated in drinking tubewell water. In many arsenic affected areas, arsenic removal may be the only option in the absence of an alternative safe source of water supply.

## 1.6 Arsenic removal by oxidation-coagulation

Coagulants such as aluminium sulfate ($Al_2(SO_4)_3.18H_2O$), ferric chloride ($FeCl_3$) and ferric sulfate ($Fe_2(SO_4)_3.7H_2O$) are effective in removing arsenic from water. Ferric salts have been found to be quite promising in removing arsenic than alum on a weight basis and effective over a wider range of pH[258-263]. In alum coagulation, the removal is most effective in the narrow pH range 7.2-7.5 and in iron coagulation, efficient removal is achieved in a wider pH range usually between 6.0 and 8.5[264]. During coagulation and filtration, arsenic is removed through three main mechanisms[265]: (1) precipitation: the formation of the insoluble compounds, $Al(AsO_4)$ or $Fe(AsO_4)$; (2) coprecipitation: the incorporation of soluble arsenic species into a growing metal hydroxide phase; (3) adsorption: the electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide.

Several studies have been reported that arsenic removal from drinking water by coagulation with ferric chloride is more effective than other coagulants[266-268]. Arsenic exists in near neutral reductive groundwater conditions mainly in the +III oxidation state as trihydrogen arsenite ($H_3AsO_3$) which is much less adsorbed on coagulates than the +V species which exists predominantly as anionic dihydrogen arsenate ($H_2AsO_5^-$) ion[269]. A coagulant alone is not capable of lowering arsenic in +III state to below 10 µg/L. Therefore, if As(III) is present, oxidation prior to coagulation to convert As(III) to As(V) species should be considered first. This can be achieved by the addition of efficient oxidizing agents prior to coagulation.

Among the oxidizing agents, oxygen (introduced as air), ozone, hydrogen peroxide, chlorine, sodium hypochlorite, potassium permanganate, solid iron (III) or manganese (IV) compounds and water soluble iron (II) compounds + hydrogen peroxide, also known as Fenton's reagent[270] are commonly used for oxidation in developing countries. Air oxidation of arsenic is very slow and can take weeks for oxidation but chemicals like chlorine and permanganate can rapidly oxidize arsenite to arsenate under wide range of conditions. All these oxidizing agents are associated with some advantages as well as disadvantages which are summarized in Table 1.2.

**Table 1.2.** Comparison of different oxidizing agents.

| Oxidizing agents | Advantages | Disadvantages |
|---|---|---|
| Oxygen (from air) | Readily available everywhere and is not hazardous | Slow and additional equipment requirement to speed it up increases system capital and operating costs |
| Ozone | No chemical storage or handling is required, no by-products left in water, reaction is fast and it is generated at point of use which reduces exposure to ozone | Ozone is a known health hazard and the oxidation system has high operating and maintenance costs |
| Hydrogen Peroxide | It is a safe solution that can be manually or automatically metered in | Reaction may be too slow for practical use and oxidant solution can lose oxidation power |
| Liquid Chlorine | Reaction is very fast and completely removes any potential disease carriers | It is difficult to store or transport safely and system parts can be degraded by corrosion |
| Hypochlorite | Reaction is relatively fast and removes any potential disease carriers | The system parts can be degraded by corrosion and oxidant solution can lose oxidation power with time |
| Permanganate | Reaction is very fast, oxidizes arsenic in less than 1 minute. It is a safe solution that can be manually or automatically metered in, unreactive with membranes | Formation of solid manganese compound that may interfere with system operation |
| Iron (III) or Mn (IV) Compounds | The system design allows oxidation and filtration steps to be combined in one unit | Iron (III) compounds can hydrolyze to form gelatinous solids which may plug up the oxidation/filtration bed |
| Fenton's Reagent | The oxidation rate is faster than hydrogen peroxide and oxidant solution is more stable | Operator error in mixing the iron (II) compound with the hydrogen peroxide can degrade the results, high cost involved |

Borho et al. carried out pilot-scale experiments with a very low initial As(III) concentration varying from 34 to 44 μg/L and revealed that the coupling of manganese dioxide coated quartz sand for As(III) oxidation with iron(II)/oxygen to bind the generated As(V) molecules was very effective for removing As(III)[271]. Potàssium permanganate and potassium ferrate were applied to oxidize As(III) to As(V) and then removed As(V) by

Fe(III) coagulation[272, 273]. Guan et al. evaluated the synergetic performance of permanganate and Fe(II) in removing As(III)[274].

The oxidation of As(III) to As(V) was critical for achieving optimal performance for most processes and former studies demonstrated the feasibility of employing ozone, permanganate, sodium hypochlorite, for As(III) oxidation and subsequent enhanced arsenic removal. Potassium permanganate is a preferred oxidizing agent for the oxidation of As(III) to As(V) as it is cost-effective, easy to preserve and to handle in practice, especially for small systems in rural areas[259, 275].

### 1.6.1 pH-conditioning in arsenic and iron removal by oxidation-coagulation methods

The pH of water is known to play an important role in removal of arsenic and iron from water[276]. Since the removal of arsenic and iron are pH-dependent, different pH-conditioners have been tried for providing favourable pH for removal of these ions by precipitation-coagulation[27, 277]. As(V) exists in anionic forms of $H_2AsO_4^-$, $HAsO_4^{2-}$ or $AsO_4^{3-}$ depending upon the pH of the solution above 3.0[278]. When iron is precipitated at increasing pH, it could facilitate the conversion of soluble arsenic species to insoluble iron-arsenic complex[268, 279]. A pH around 7.3 is required for $Fe(OH)_3$ particles to have a net positive charge. Arsenic removal may also occur at higher pH levels, but not as effectively as at lower pH values[280, 281]. Arsenic removal decreases with increasing pH values above 8.5[168]. On the other hand, at highly alkaline condition, $Fe(OH)_4^-$ ions are formed in water[282, 283], which is also expected to decrease the adsorption of the negatively charged arsenate ions on their precipitate.

Lime, ash, carbonates and bicarbonates of Na and K are used for pH conditioning to facilitate removal of arsenic. While using these pH-conditioners, one not only has to ensure efficient removal of arsenic to desired levels, but sometimes also needs a careful adjustment of the dose of the pH-conditioner for regulating the final pH or readjustment of the pH of treated water, which may be avoided by choosing the appropriate pH-conditioner and its dose.

### 1.6.2 Correlation between arsenic and iron contamination of groundwater

The use of co-existing dissolved iron for removal of arsenic by adsorption is a promising method[284]. Generally, tubewell water contains high concentration of dissolved iron. Geological formations as well as waste effluents of industrial processes are responsible for occurrence of iron in groundwater[285]. In India, groundwater contamination with high concentrations of iron (>15 mg/L) has been reported in several states including Assam, Andhra Pradesh, Chattisgarh, Karnataka and Orissa[286-289]. Iron has been attracting attention of researchers as one of the heavy metals that causes problems especially at high levels of contamination[290]. Presence of iron in water above a certain level makes the water unusable mainly for aesthetic considerations such as discoloration of food and beverage, metallic taste, odor, turbidity, staining of laundry and plumping fixtures, etc.[291]. Ferric hydroxide precipitates formed under an aerobic condition at neutral or alkaline pH[292] can generate toxic derivatives[293] and develop infection, neoplasia, cardiomyopathy, arthropathy, and various endocrine and neurodegenerative disorders[294-296] in human. In addition to that, growth of microorganisms promoted by iron oxide in water inhibits some industrial processes[297, 298]. Since iron in the water is able to induce several problems, it has been regarded as one of the major target materials to be removed. The WHO recommends a guideline value of 0.3 mg/L of iron in drinking water[34]. Among the different technologies of iron removal[299-303], aeration and separation is the most commonly employed method, which works fairly well at lower iron concentrations, however, not so popular at rural and semi-urban communities lacking piped water supply. Other techniques, such as ion-exchange method[304], oxidation with oxidizing agents including chlorine and potassium permanganate[305], filtering with activated carbon and other filtering materials[306, 307], supercritical fluid extraction[308], bioremediation[309] and treatment with limestone[310] have been applied for the removal of high amounts of iron.

Although there is no good correlation between concentrations of iron and arsenic, iron in ferrous form and arsenic in arsenite form have been found to co-exist in ground water. The iron precipitates [$Fe(OH)_3$] formed by oxidation of dissolved iron present in groundwater have the affinity for the adsorption of arsenic. Only aeration and sedimentation of tubewell water rich in dissolved iron has been found to remove arsenic. From literature it has been found that iron removal plants can lower arsenic content of tubewell water to half to one-fifth of the original concentrations[1, 151, 311].

### *1.6.2.1 Iron distribution vs. pH*

Ferrous ($Fe^{2+}$) and ferric ($Fe^{3+}$) ions occur in aqueous solutions in a wide variety of aquatic context. The spontaneous chemical oxidation from ferrous to ferric by oxygen is a complex process involving a variety of partially oxidized ferrous-ferric intermediate species[312]. These intermediates are difficult to characterize and ultimately these iron-intermediates transform into a variety of stable iron oxide end-products such as hematite, magnetite, goethite and lepidocrocite. pH plays an important role in determining the solubility of iron. Iron will be soluble more with lowering the pH. Ranges of concentrations of iron in water can be predicted as a function of Eh and pH together (Figure 1.2)[313].

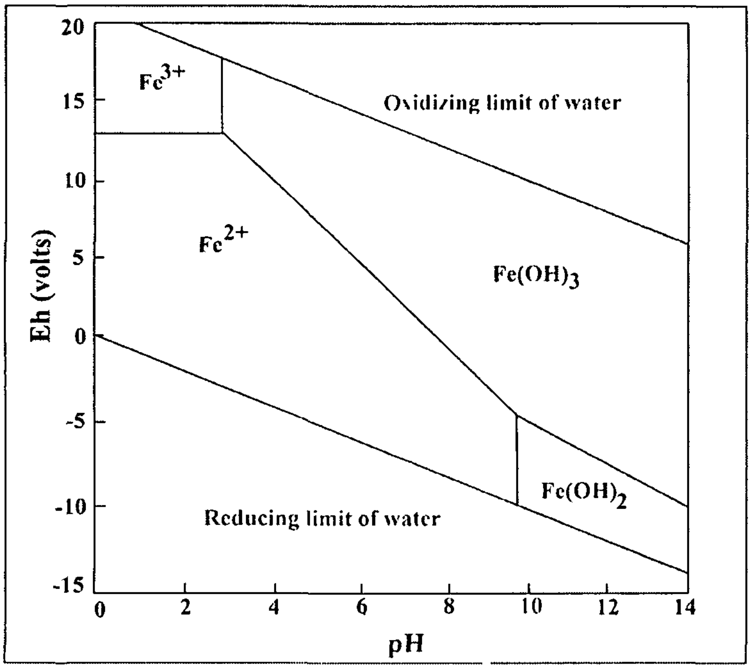


**Figure 1.2.** The Eh–pH diagram for iron at 25°C

## 1.7 The Lacuna

The groundwater of vast areas of Assam, a north-eastern state of India, is contaminated with arsenic much above the WHO guideline value of 10 μg/L. Arsenic contamination of groundwater of Assam came to light in 2004[127], but, till now, no adequate effort has been made to mitigate the problem. During the last few years many small and community scale based arsenic removal technologies have been developed[314, 315]. But, there always arise questions regarding the efficiency and applicability/appropriateness of these technologies. There are many technologies which are successful in the laboratory but they are not popular in the field conditions mainly due to wide range of initial concentration of arsenic, post-treatment requirement, optimization of right dose of chemicals, source water composition etc. Though a number of arsenic removal methods are available, a more cost-effective, environment friendly technology with minimized disadvantages and suitable for household use in rural areas is yet to be developed. A system to become practically successful must be economically viable and socially acceptable.

During a research for evaluation of new method for removal of arsenic from water some factors are to be considered essentially, *viz.*,

a) The method should be simple and can be used by a layman,

b) The method should be low-cost, the overall cost treatment per liter of water should be affordable for the rural area people,

c) The treatment should not produce any hazardous chemical after the treatment,

d) Treatment time should be minimum,

e) The method should be applicable to different ranges of arsenic concentration,

f) The method should work efficiently in the presence of other cations and anions present in the groundwater,

g) The energy requirement of the process should be minimum,

It is not so easy to fulfill all these above mentioned conditions during the evaluation of a method for removal of arsenic. Hence, no such method fulfilling all the above criteria has been possible yet. Research on arsenic removal aiming to get the simplest method to be used in household and community purpose is thus urgently needed.

As it is evident from previous discussions, oxidation-coagulation appears to be one of the most cost effective and efficient arsenic removal methods. Although the pH dependence of arsenic and iron removal by coagulation-precipitation is well known, there has been no report of any systematic comparative study of the efficiencies of different pH conditioners in the simultaneous removal. These pH conditioners produce different concentrations of $OH^-$ ions in water due to hydrolysis of the oxides or salts; thereby affect the pH of water, which consequently affect the removal of iron and arsenate ions. Both As(V) and As(III) have a strong pH dependent sorption affinity for iron hydroxide and oxyhydroxide minerals such as ferrihydrite and goethite[316]. It was therefore worthwhile to carry out a detail systematic study (including field trial) of simultaneous arsenic and iron removal based on oxidation-coagulation at optimized pH (OCOP) to develop a simple, efficient, low-cost, user friendly and environment friendly method executing most of the above criteria. Such a study can be complete with finding out the appropriate pH-conditioner and its adequate use.

## 1.8 Aim of the present work

The aim of the present work is to systematically investigate the pH-conditioning for efficient removal of arsenic and iron and subsequently to study of the OCOP method for removal of arsenic and iron from contaminated water through laboratory experiments and user trial.

### 1.8.1 Selection of the pH-conditioner, the oxidant and the coagulant

Arsenic adsorption onto ferric chloride coagulations or hydrous ferric oxide [27, 317, 318], IOCS[319, 320] or ZVI[321-323], zeolite[324], iron-rich natural adsorbents[325, 326] considering various factors which influence the adsorption have been reported. Among them several studies reported $FeCl_3$ as quite promising coagulant in comparison to other coagulants. As we have discussed earlier that a coagulant alone is not capable of lowering arsenic from +III state to below 0.01 mg/L and oxidation of As(III) to As(V) needs to be considered prior to coagulation. The oxidation of As(III) to As(V) is critical for achieving optimal performance for most arsenic removal processes. The feasibility of employing ozone, potassium permanganate and sodium hypochlorite for As(III) oxidation and subsequent enhanced arsenic removal have been demonstrated[327-329]. Potassium permanganate is preferable over other oxidizing agents for the oxidation of As(III) as it is cost-effective, easy to preserve and to handle in practice, especially for small systems in rural areas[259, 275]. As the removal of arsenic and iron is a pH-dependent process, we planned to study the efficiencies of carbonate and bicarbonate salts of Na and K, banana ash and lime as pH-conditioners and to use the most efficient pH conditioners for simultaneous removal of arsenic and iron.

## 1.9 Objectives:

We proposed to meet this aim with the objectives set as follows:

- Laboratory evaluation of the performance and suitability of different pH conditioners for removal of iron.
- Laboratory evaluation of the performance and suitability of different pH conditioners for simultaneous removal of arsenic and iron.
- Laboratory optimization of the doses of pH conditioner, oxidant and coagulant.
- Examination of the applicability of the method in certain defined range of operational variables.
- Evaluation of the effect of dependent and extraneous variables on the removal characteristics.
- Study of the potability of the purified water.

- Evaluation of effectiveness of the process in the field through user trial at household and small community level.

## 1.10 The strategy

We have studied the removal of arsenic and iron by oxidation-coagulation at optimized pH method. For this purpose we have to choose the appropriate pH-conditioner, the oxidant, the coagulant to obtain efficient removal of arsenic and iron. To meet this, we prepared a plan of work in the order described below:

- Batch tests on removal of iron to evaluate the efficiencies of different pH-conditioners. The pH-conditioners chosen were bicarbonate and carbonate salts of sodium and potassium, banana ash and their binary mixtures.
- Batch tests on simultaneous removal of arsenic and iron to evaluate the efficiencies of bicarbonate and carbonate salts of sodium and potassium, banana ash and their binary mixture as pH-conditioner.
- Comparison of the batch test results to choose the suitable pH-conditioner.
- Batch tests on simultaneous removal of arsenic and iron to obtain the optimum doses of pH-conditioner, oxidant and coagulant.
- To investigate the influence of initial concentration of arsenic on removal rate of arsenic by OCOP method.
- Study of the effects of the coexisting ions on removal of arsenic as the groundwater contains several different anions which may interfere in the adsorption or precipitation of arsenic removal during the OCOP treatment.
- Study of the mechanism of removal of arsenic and iron in the process by using various analytical tools.
- A laboratory bench scale pilot study to examine the performance of the OCOP method in real water purification set-ups with sand-gravel filter.
- Evaluation of the performance of OCOP technique using the optimized doses for removal of arsenic and iron in the field through user trial at domestic and small community levels in various arsenic-affected areas of Assam. The field trial was to involve the following steps:
    - Selection of some suitable arsenic-affected spot sources of groundwater of villages and schools of arsenic-affected areas for the user trial.
    - Conveying the users of the health-hazards of consuming arsenic through drinking water and trained with our method for arsenic removal.

- Arsenic removal and collection of samples of treated water by the users.
- Collection and testing of the samples of treated water for arsenic and other water quality parameters.
- Evaluation of the performance of the arsenic removal method.
- Study of the environmental aspect of the method.

## *Chapter 2*

# Experimental

# 2. Experimental

## 2.1 Materials

### 2.1.1 Banana ash

The ash was obtained from banana pseudostem. Banana pseudostem is used for making 'Kolakhar', a substitute of edible soda by villagers of Assam. The major constituent of banana ash is potassium carbonate[330-333]. The ash was prepared by burning 500 mg of dried banana pseudostem in a porcelain basin at 500°C in muffle furnace for 4 hour[334].

### 2.1.2 Chemicals

Analytical grade potassium carbonate ($K_2CO_3$), sodium carbonate ($Na_2CO_3$), potassium bicarbonate ($KHCO_3$), sodium bicarbonate ($NaHCO_3$), calcium oxide (CaO), potassium permanganate ($KMnO_4$), ferric chloride ($FeCl_3$), ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), sodium sulphate ($Na_2SO_4$), disodium hydrogen phosphate ($Na_2HPO_4$) and sodium meta-silicate ($Na_2SiO_3.9H_2O$) were obtained from Merck, Mumbai and used as such. Sodium meta-arsenite ($NaAsO_2$) and sodium arsenate heptahydrate ($Na_2HAsO_4.7H_2O$) were obtained from Sigma Aldrich and used as such.

### 2.1.3 Water

Doubly distilled water was used for the preparation of arsenic and iron solution for the experiments. The groundwater used during the experiments was drawn from a shallow tube well of depth of approximately 14 m. Some relevant chemical parameters of the groundwater are mentioned in Table 2.1.

**Table 2.1.** Relevant parameters of groundwater used in laboratory experiments.

| Parameter | Concentration in mg/L except pH |
|---|---|
| pH | 7.44 |
| Sodium, $Na^+$ | 5.62 |
| Potassium, $K^+$ | 8.75 |
| Calcium, $Ca^{2+}$ | 0.72 |
| Magnesium, $Mg^{2+}$ | 2.61 |
| Mercury, $Hg^{2+}$ | <0.001 |
| Fluoride, $F^-$ | 0.206 |
| Sulphate, $SO_4^{2-}$ | 200 |
| Phosphate, $PO_4^{3-}$ | <0.003 |
| Silica, $SiO_2$ | 4.35 |
| Total Hardness | 12.6 |
| Total Alkalinity | 69.5 |

### *2.1.3.1 Preparation of synthetic iron-containing water*

The Fe(II) stock solutions of different concentrations were prepared by dissolving the appropriate amount of $FeSO_4.7H_2O$ in distilled water. Synthetic iron-containing groundwater was prepared by amending the iron concentration by addition of the required quantity of iron to freshly withdrawn groundwater.

### *2.1.3.2 Preparation of synthetic arsenic-containing water*

The As(V) and As(III) stock solutions of different concentrations were prepared by dissolving the appropriate amounts of $Na_2HAsO_4.7H_2O$ and $NaAsO_2$, respectively in distilled water. Synthetic arsenic-containing groundwater was prepared by amending the arsenic concentration by addition of the required quantity of arsenic to freshly withdrawn groundwater.

## 2.2 Analytical tools

A Perkin Elmer Atomic Absorption Spectrophotometer (AAS, model Analyst 200 Thermo iCE 3000 series, USA) and an Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES, model Optima 2100 DV, Perkin Elmer, USA) were used for determination of As, Fe, and other heavy metal ion concentration in treated water. Concentration of Fe in the filtrates were sometimes determined also by 1,10-phenanthroline method using a Shimadzu UV-2500 UV-visible Spectrophotometer[335].

The pH of the solutions was measured using a multiparameter kit (model 5 Star pH.ISE.Cond.DO Benchtop, Orion, USA) with temperature compensation. The calibration of the pH was done with standard buffer solutions of pH 7.00 and pH 10.00. The field water samples were preserved in dilute $HNO_3$ (final concentration 0.1% and pH <2) for determination of metal ions[336].

Arsenic and pH were determined in the field using a mobile As detection kit, (Merckoquant 1.17927.0001, Merck, Mumbai) and a pocket-sized pH meter (model HI96107, Hanna instruments, USA), respectively.

The surface micrographs of the precipitate were obtained from a Scanning Electron Microscope (SEM, model JSM-6390LV, Jeol, Japan) with Energy Dispersive X-ray Spectra (EDS) at an accelerating voltage of 15.0 kV. The surface of the sample was platinum coated before SEM analysis. The X-ray Diffraction (XRD) carried out at room temperature (298K) on a X-ray diffractometer (model Miniflex, Rigaku, Japan) with graphite monochromated Cu*Kα* radiation (= 0.15 nm) at 30 kV and 15 mA using a scanning rate of 0.050°/s, over the range of 2θ= (10-90)°. The Fourier Transform Infrared (FTIR) spectra were recorded on an IR spectrophotometer (model Impact 410 FTIR spectrophotometer, Nicolet, Japan).

## 2.3 Methods

The methods used in the study have been presented in four sub-sections (from 2.3.1 to 2.3.4), each corresponding to one of four major parts of the study.

### 2.3.1 Methods of study of pH-conditioning for removal of iron

#### *2.3.1.1 Batch experiments*

Batch experiments were carried out to study the efficiency of different pH-conditioners in removal of iron. The experiments were carried out by adding varying quantities of banana ash and carbonate and bicarbonate salts of Na and K, their 1:1 binary mixture with 50 mL of iron containing water in Erlenmeyer flasks. Then the flasks were shaken manually for 1 minute moderately and allowed to settle. The efficiencies of the ash and the salts in precipitating iron ion were studied in terms of the effects of dose and residence time. The flasks were taken out one by one at predetermined time intervals and the liquid and solid phases were separated immediately by filtration using Whatman 42 filter paper and the residual Fe concentrations in the filtrates were determined.

#### *2.3.1.2 Analysis of iron precipitate*

The precipitates obtained after removal of Fe at different pH were collected. After that, the precipitates were oven-dried before they were subjected to various analytical tools, *viz.*, FTIR, XRD and SEM-EDS to know their characteristics.

### 2.3.2 Methods of study of pH-conditioning for removal of arsenate and iron

#### *2.3.2.1 Batch experiments*

The efficiency of the ash, lime and carbonate and bicarbonate salts of Na and K in precipitating arsenate with iron were studied as a function of dose. The arsenic removal experiments were carried out in batches by mixing varying quantities of the ash or/and the salts with 100 mL of Fe(II) and As(V) containing water in Erlenmeyer flasks. The experiments were performed under open condition to allow natural aerial oxidation. The flasks were shaken moderately in a mechanical shaker for 5 minutes and allowed to settle. The flasks were taken out one by one and the liquid and solid phases were separated after 2 h of residence time by filtration using Whatman 42 filter paper. After that the residual As, Fe concentrations and final pH of the treated water were determined.

#### *2.3.2.2 Analysis of the precipitate*

The precipitates obtained after simultaneous removal of arsenic and iron at different pH were collected. After that, the precipitates were oven-dried before they were subjected to various analytical tools, *viz.*, FTIR, XRD and SEM-EDS to know their characteristics.

### 2.3.3 Methods of study of removal of arsenic and iron by OCOP

#### *2.3.3.1 Batch experiments*

A working solution for experiments was freshly prepared from the stock solution of arsenic and iron. The laboratory batch tests were carried out in Erlenmeyer flasks in triplicate using arsenic containing distilled water and arsenic-amended groundwater. The pH-conditioner, oxidant and coagulant were added in a successive manner with mild stirring after each addition. The mixtures were allowed to settle for 2 h, and then filtered by using Whatman 42 filter paper. The final pH and remaining concentration of As and Fe in the filtrate were determined.

#### *2.3.3.2 Effect of initial concentration of arsenic*

The influence of initial concentration of arsenic on its removal by OCOP method was studied with initial arsenic concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 mg/L.

#### *2.3.3.3 Effect of the presence of co-existing anions in the water*

To investigate the interference of co-existing ions, i.e., $SO_4^{2-}$, $PO_4^{3-}$, and $SiO_3^{2-}$ on arsenic removal, respective sodium salts have been added to the arsenic containing solution before treatment of the water in the concentration ranges of 0-5.20 mM, 0-0.10 mM and 0-0.40 mM, respectively, in which they usually occur in groundwater.

#### *2.3.3.4 Study of the precipitate of arsenic and iron*

The precipitates obtained after removal of arsenic by OCOP method were analysed to know the mechanism of the removal methods of iron and arsenic. The precipitate of iron and arsenic were collected and oven-dried before they were subjected to various analytical tools, *viz.*, FTIR, XRD and SEM-EDS to know their characteristics.

### *2.3.3.5 Leachability test of the precipitate obtained after OCOP treatment*

The sludge generated after treatment of arsenic containing water was collected and tested for leachability of arsenic from the sludge. The leaching behaviour of arsenic in the sludge sample was evaluated with the toxicity characteristic leaching procedure (TCLP)[337]. The extraction fluid according to the TCLP consists of 0.10 M acetic acid and 0.064 M sodium hydroxide. The pH of this fluid should be 4.93. The sludge sample was mixed with the extraction fluid, in a liquid-to-solid weight ratio of 20:1 for 18 h. After 18 h of agitation, the sample was filtered and the concentration of arsenic in the filtrate was measured.

### *2.3.3.6 Pilot study*

For the laboratory bench scale pilot experiments, we have employed a setup as shown in Figure 2.1. It consists of two PET containers as coagulation cum sedimentation chamber and a sand-gravel filter. In the coagulation chamber, calculated quantities of solid $NaHCO_3$, 5% $KMnO_4$ and 25% $FeCl_3$ solutions were added to 1 L of groundwater spiked with arsenic in a stepwise manner with mild intermittent stirring for a while for mixing. For convenient application of the chemicals $KMnO_4$ and $FeCl_3$ were added as 5% and 25% solution, respectively. After 2 h, the precipitates get settled and the clear supernatant water was transferred to the sand-gravel filter. The sand-gravel filter removes the insoluble iron–arsenic complex.

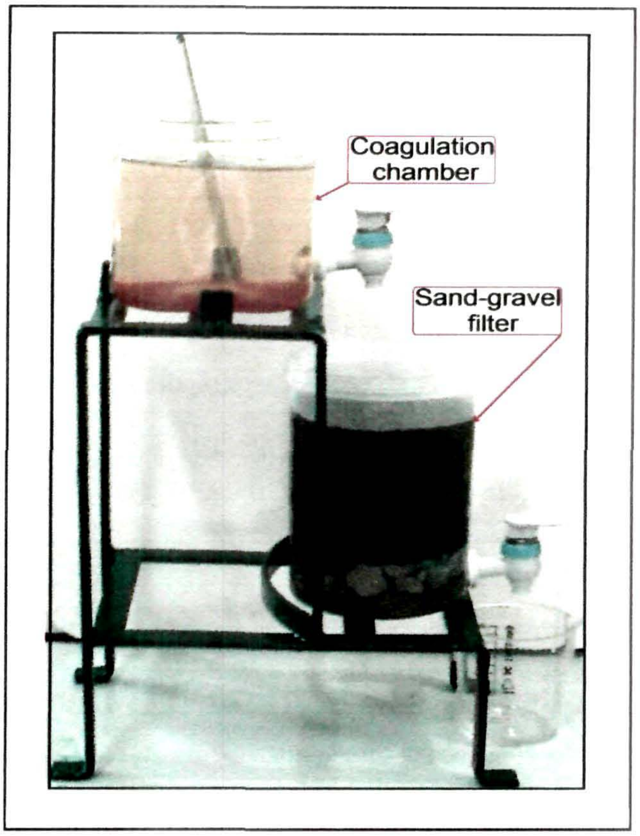


**Figure 2.1.** Picture of the bench scale pilot experimental set up.

### *2.3.3.7 Study of the relevant water quality parameters before and after OCOP treatment*

The relevant water quality parameters *viz.* pH, conductivity, dissolved solids, suspended solids, concentration of other ions such as chloride, fluoride, nitrate, phosphate, sulphate, silica, concentration of heavy metal ions such as cadmium, calcium, chromium, cobalt, copper, lead, magnesium, manganese, mercury, potassium, sodium, zinc of the water samples were measured before and after the OCOP treatment using standard methods. Water purified by the OCOP method using the laboratory scale sand-gravel pilot set-up was used for these studies. The water before and after the treatment were also tested for microbial contamination by using multiple tube method and biochemical assays[338].

## 2.3.4 Field Trial

### *2.3.4.1 Selection of site*

Based on available reports[127], we have made our first visit to some arsenic affected areas in Assam during June, 2010. We have determined the concentrations of As and pH on the spot using a mobile arsenic detection kit and a pocket-sized pH meter, respectively. Samples were also collected for analysis of As, Fe, etc., in the laboratory by AAS or ICP-

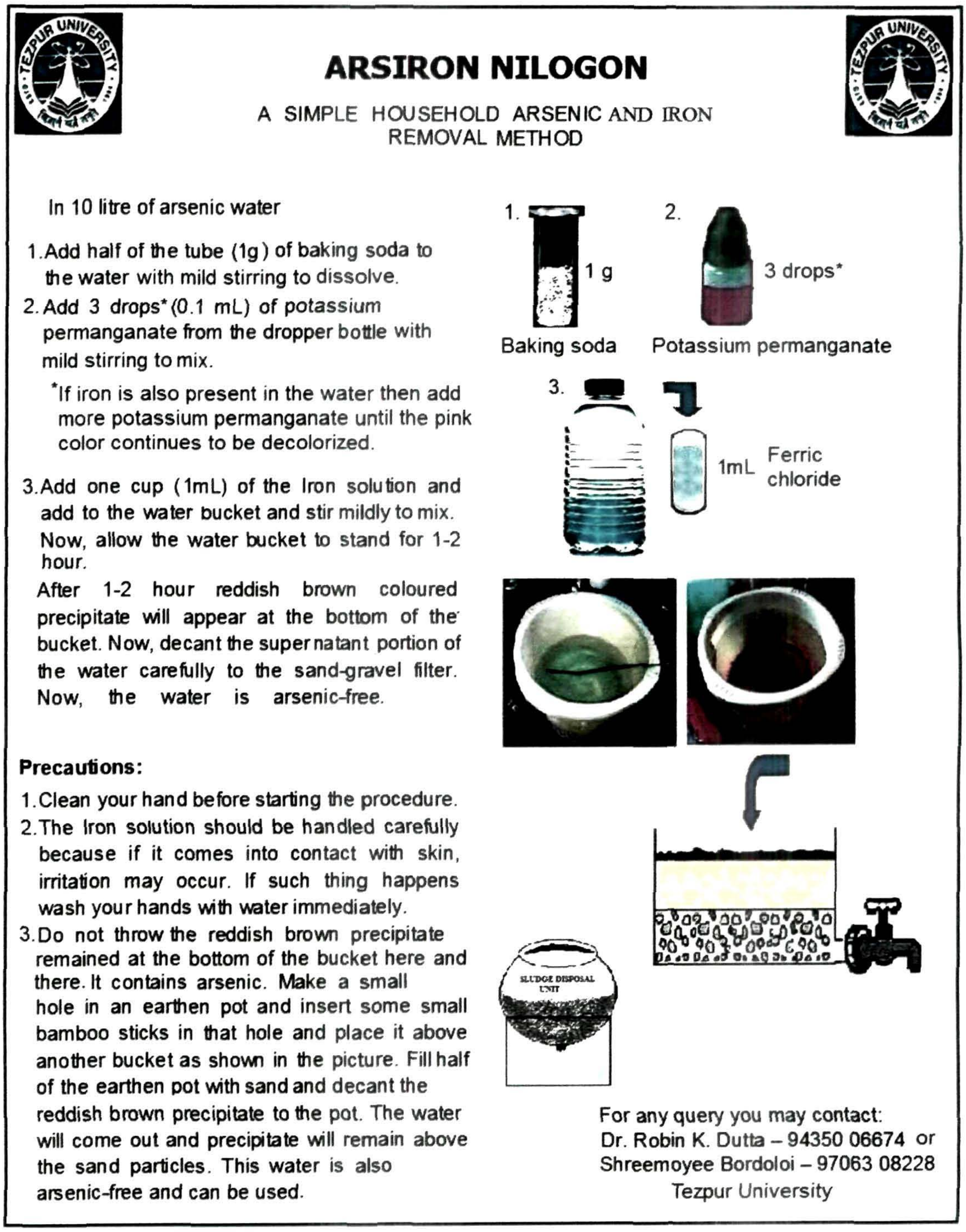
OES. On the basis of the results, we had initially selected two villages, *viz.*, Tatigaon and Kharikotia at Titabor sub-division of Jorhat district of Assam to carry out the user trial.

During our second visit, we have carried out initial field experiments on the selected sites. For this, we have used 15 L tub or bucket to carry out the OCOP treatment with 10 L of arsenic containing groundwater from the arsenic affected sources. The concentration of arsenic and pH of the treated water were determined on the spot. We brought samples of such experiments and again we have analysed for concentrations of As and Fe by AAS or ICP-OES. Later on we had chosen a few more spot sources in other districts for the user trial.

### *2.3.4.2 User training and demonstration*

During the field study we faced some problems mainly due to the lack of awareness of people about arsenic contamination and toxicity. Therefore, we made some attempts for creating awareness about arsenic contamination and the importance of arsenic removal from drinking water among the affected rural people. We demonstrated the method to the villagers and school teachers and taught them how to follow the procedure. We also trained them to set up the systems for removal of arsenic from groundwater at household and small community level. We have also supplied one page instruction manual to the users describing the method in details in English or Assamese language as shown in Figure 2.2 and Figure 2.3, respectively. Some photographs of user training in different arsenic affected areas are shown in Figure 2.4.

We felt the necessity of a suitable name for the method to make the method familiar to the users whose participation in the field trial was vital for the study as well as for popularity of the method. Since the present OCOP method simultaneously removes both arsenic and iron ions, the method was named as '*Arsiron Nilogon*' (আৰ্ছিৰন নিলগন). Here, '*Arsiron*' (আৰ্ছিৰন) stands for '***Ars****enic* and ***iron***. '*Nilogon*' (নিলগন) is the local Assamese equivalent for 'removal'.



ARSIRON NILOGON

A SIMPLE HOUSEHOLD ARSENIC AND IRON REMOVAL METHOD

In 10 litre of arsenic water

1. Add half of the tube (1g) of baking soda to the water with mild stirring to dissolve.
2. Add 3 drops*(0.1 mL) of potassium permanganate from the dropper bottle with mild stirring to mix.

   *If iron is also present in the water then add more potassium permanganate until the pink color continues to be decolorized.
3. Add one cup (1mL) of the Iron solution and add to the water bucket and stir mildly to mix. Now, allow the water bucket to stand for 1-2 hour.

   After 1-2 hour reddish brown coloured precipitate will appear at the bottom of the bucket. Now, decant the supernatant portion of the water carefully to the sand-gravel filter. Now, the water is arsenic-free.

**Precautions:**

1. Clean your hand before starting the procedure.
2. The Iron solution should be handled carefully because if it comes into contact with skin, irritation may occur. If such thing happens wash your hands with water immediately.
3. Do not throw the reddish brown precipitate remained at the bottom of the bucket here and there. It contains arsenic. Make a small hole in an earthen pot and insert some small bamboo sticks in that hole and place it above another bucket as shown in the picture. Fill half of the earthen pot with sand and decant the reddish brown precipitate to the pot. The water will come out and precipitate will remain above the sand particles. This water is also arsenic-free and can be used.

For any query you may contact:
Dr. Robin K. Dutta – 94350 06674 or
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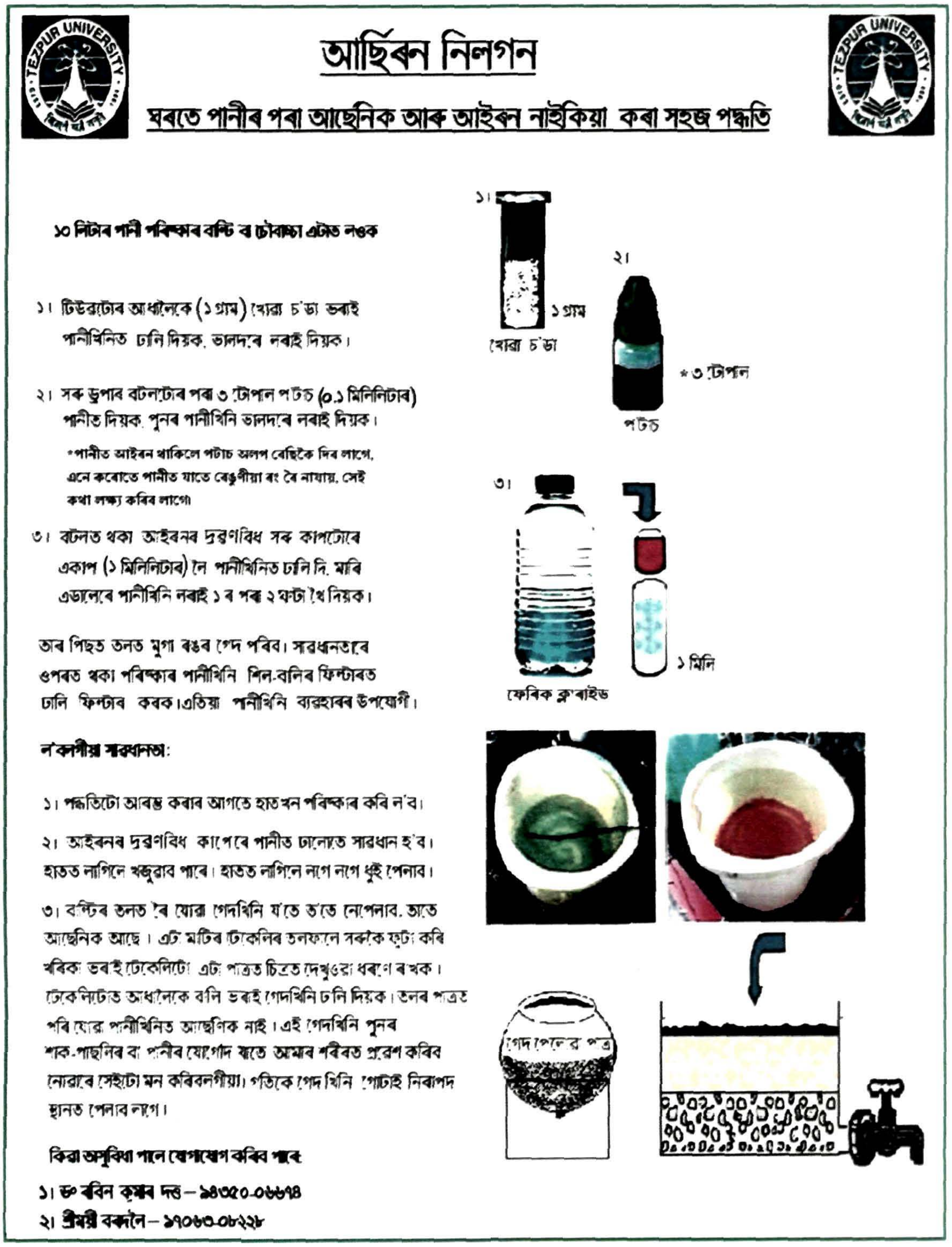
Tezpur University

**Figure 2.2.** Instruction manual that we supplied to the village people and schools in English language.



# আৰ্ছিৰন নিলগন

## ঘৰতে পানীৰ পৰা আৰ্ছেনিক আৰু আইৰন নাইকিয়া কৰা সহজ পদ্ধতি

**১০ লিটাৰ পানী পৰিষ্কাৰ বাল্টি বা চৌবাচ্চা এটাত লওক**

১। টিউবটোৰ আধালৈকে (১ গ্ৰাম) খোৱা চ'ডা ভৰাই পানীখিনিত ঢালি দিয়ক, ভালদৰে লৰাই দিয়ক।

২। সৰু ডুপাৰ বটলটোৰ পৰা ৩ টোপাল পটচ (০.১ মিলিলিটাৰ) পানীত দিয়ক, পুনৰ পানীখিনি ভালদৰে লৰাই দিয়ক।

*পানীত আইৰন থাকিলে পটাচ অলপ বেছিকৈ দিব লাগে, এনে কৰোতে পানীত যাতে বেঙুনীয়া ৰং হৈ নাযায়, সেই কথা লক্ষ্য কৰিব লাগে।

৩। বটলত থকা আইৰনৰ দ্ৰৱণবিধ সৰু কাপটোৰে একাপ (১ মিলিলিটাৰ) লৈ পানীখিনিত ঢালি দি, মাৰি এডালেৰে পানীখিনি লৰাই ১ ৰ পৰা ২ ঘন্টা থৈ দিয়ক।

তাৰ পিছত তলত মুগা ৰঙৰ গেদ পৰিব। সাৱধানতাৰে ওপৰত থকা পৰিষ্কাৰ পানীখিনি শিল-বালিৰ ফিল্টাৰত ঢালি ফিল্টাৰ কৰক।এতিয়া পানীখিনি ব্যৱহাৰৰ উপযোগী।

**ল'বলগীয়া সাৱধানতা:**

১। পদ্ধতিটো আৰম্ভ কৰাৰ আগতে হাতখন পৰিষ্কাৰ কৰি ল'ব।

২। আইৰনৰ দ্ৰৱণবিধ কাপেৰে পানীত ঢালোতে সাৱধান হ'ব। হাতত লাগিলে খজুৱাব পাৰে। হাতত লাগিলে লগে লগে ধুই পেলাব।

৩। বাল্টিৰ তলত হৈ যোৱা গেদখিনি যতে ততে নেপেলাব, তাতে আৰ্ছেনিক আছে। এটা মাটিৰ টেকেলিৰ তলফালে সৰুকৈ ফুটা কৰি বালি ভৰাই টেকেলিটো এটা পাত্ৰত চিত্ৰত দেখুওৱা ধৰণে ৰাখক। টেকেলিটোত আধালৈকে বালি ভৰাই গেদখিনি ঢালি দিয়ক। তলৰ পাত্ৰত পৰি যোৱা পানীখিনিত আৰ্ছেনিক নাই। এই গেদখিনি পুনৰ শাক-পাচলিৰ বা পানীৰ যোগেদি যাতে আমাৰ শৰীৰত প্ৰৱেশ কৰিব নোৱাৰে সেইটো মন কৰিবলগীয়া। গতিকে গেদখিনি গোটাই নিৰাপদ স্থানত পেলাব লাগে।

**কিবা অসুবিধা পালে যোগাযোগ কৰিব পাৰে**

**১। ড° ৰবিন কুমাৰ দত্ত – ৯৪৩৫০-০৬৬৭৪**

**২। শ্ৰীময়ী বৰদলৈ – ৯৭০৬৩-০৮২২৮**

**Figure 2.3.** Instruction manual that we supplied to the village people and schools in local Assamese language.

**Figure 2.4.** Photographs taken during demonstration of *'Arsiron Nilogon'* in different areas in Assam (a) at Kharikotia Lower Primary School, Titabor, Jorhat; (b), (c) at Tatigaon, Titabor, Jorhat; (d) at Bholukaguri Lower Primary School, Gohpur, Sonitpur; (e) at Kakila Chariali Upper Primary School, Gohpur, Sonitpur; (f) at Kakila Chariali Lower Primary School, Gohpur, Sonitpur; (g) at N. N. Saikia College, Titabor, Jorhat; (h) in a workshop in Tezpur University; (i) at Asom Kesori Jatiya Vidyalaya, Kaithalkuchi, Nalbari (The author and her PhD supervisor are in the extreme left of Figure 2.4e and 2.4d, respectively).

### *2.3.4.3 Design and fabrication of Arsiron Nilogon systems of different capacities*

There is no limitation in the technology with respect to quantity of water to be treated. The system can be custom-designed to meet the requirements of a household or a community. Some of the model designed and/fabricated for use in household or small community scales are shown in Figure 2.5.

A household *Arsiron Nilogon* system of 10 L capacity with a sand-gravel filter on a stand has been shown in Figure 2.5a. It requires a bucket (strong enough to withstand the weight of the sand and the gravels) of 25-30 L capacity as a sand-gravel filter. The arsenic containing water is treated in a bucket and poured into the sand-gravel filter after at least one hour when the precipitate is settled down. The filtered arsenic free water is collected in another bucket. This system can provide about 100 L of arsenic-free water a day against a requirement of 20-30 L of drinking water for a family.

**Figure 2.5.** Arsenic removal systems of different capacities (a) 10 L; (b) 25 L;(c) 200 L; (d) 500 L.

A small community scale *Arsiron Nilogon* system shown in Figure 2.5b consists of two treatment tanks of about 30 L drums at the top fitted with a tap each, a sand-gravel filter of a 40 L drum in the middle and a storage tank of a 60 L drum at the bottom fitted with a tap. The water can be treated in the two treatment tanks alternately in order to save time. This system can give 300 L arsenic free water a day. Though any filtration system is found to be useful for the purpose, sand filtration has been found to be a good option. Other small community systems shown in Figure 2.5 (c & d) can have higher capacities. Some household and small community scale *Arsiron Nilogon* units installed at various places are shown with the users in Figure 2.6.

**Figure 2.6.** Various '*Arsiron Nilogon*' units installed at (a) Family no. 1; (b) Family no. 2 at Tatigaon, Titabor, Jorhat; (c) Kharikotia High School, Titabor, Jorhat; (d) Kharikotia Lower Primary School, Titabor, Jorhat; (e) Titabor Tatigaon Child and Women Care Centre, Jorhat; (f) N. N. Saikia College, Titabor, Jorhat.

Initially, we applied the method for removal of arsenic from spot sources which did not have dissolved iron above 1.0 mg/L. After that we tested the method with water containing dissolved iron above 1.0 mg/L.

### *2.3.4.4 Monitoring of the user trial*

The chemicals were distributed in a kit (Figure 2.7) to the families and schools. $NaHCO_3$ is used as white solid powder, $KMnO_4$ and $FeCl_3$ were used as 5% and 25% solution, respectively as shown in Figure 2.7. Filtered water samples were collected from the households and schools periodically and were analyzed for As, Fe and other water quality parameters.

**Figure 2.7.** The chemicals needed for the treatment process in the form of a handy kit supplied to the schools and the families.

### *2.3.4.5 Collection and study of the solid sludge*

Earthen pot (1–3 L) sand filters were used to filter the concentrated sludge, from the coagulation-sedimentation chamber, to collect the sludge in solid form as shown in Figure 2.8. The solid sludge of very small volume deposited in the pot. The nature of the sludge was studied including the TCLP test.

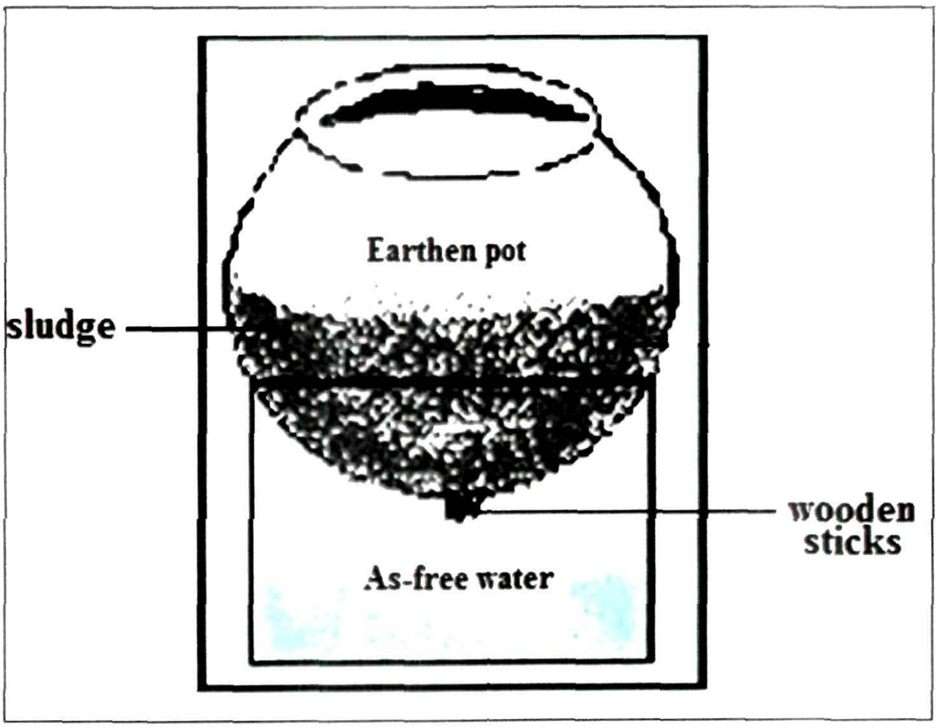


**Figure 2.8.** An earthen pot sand filter for collecting the sludge.

# Results and discussion

# 3. Results and Discussion

## 3.1 pH-conditioning for removal of iron

We have studied the effects of pH-conditioning on removal of iron from groundwater since iron usually coexists with arsenic and also influences the removal of arsenic. The results on the experiments on removal of iron by using bicarbonate and carbonate salts of Na and K, banana ash, and their 1:1 binary mixture as pH-conditioner have been discussed in this section. Results of the batch tests have been analysed to assess performance and optimize the process and dose for iron removal by these pH-conditioners. The different parameters considered for this experiment were the quantity of ash or/and salt required, the effect of residence time, the effluent water pH and the effect of initial concentration of iron.

### 3.1.1 Batch study

Batch tests in Erlenmeyer flasks were performed to determine the efficiency of different pH-conditioners and hence to optimize the doses required to get efficient removal of iron. Different quantities of the pH-conditioners were added to the iron containing water with different residence time. The results of this experiment have been discussed here.

#### *3.1.1.1 Iron ion removal from high initial concentration using banana ash*

Iron ion removal from initial concentrations of 2.2 and 5.2 mg/L by banana ash was reported earlier[286]. As iron ion is found in groundwater also with much higher concentrations than 5.2 mg/L, we have examined its removal from a higher initial iron ion concentration of 20 mg/L by varying quantity of banana ash from 2 mg/L to 500 mg/L at residence time of 1/2 to 2 h. The results of the remaining concentration of iron after treatment against various doses of banana ash added along with the final pH of the treated water for different residence times are shown in Table 3.1 and Figure 3.1.

As can be seen from the Table 3.1, the iron ion concentration comes down from 20 mg/L to about 17 mg/L in the blank experiments performed without addition of the ash. It is well known that groundwater is generally anoxic and iron ion exists in ferrous state, i.e., as $Fe^{2+}$ ion, which when comes into contact with atmospheric oxygen, e.g. during

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* *This work has been published in* ***Desalination****, 281, 190-198, 2011*

aerial oxidation of iron ion practiced in community piped water supply schemes, is oxidized to ferric state. As the present experiments have been carried out in open condition, the observed decrease in the concentration of the iron ion in the blank sample from 20 mg/L to 17 mg/L can be attributed to aerial oxidation of iron ion.

A quantity of 400 mg/L of ash is required to bring down the iron ion concentration from 20 mg/L to 0.3 mg/L as can be seen from Table 3.1. This dose of the ash leaves the pH of the treated water above 9.5. An increase in the residence time to 2 h led to a further increase in the final pH. Such a high final pH can be attributed to the presence of a small amount of $K_2O$ along with $K_2CO_3$ in the ash. High final pH makes banana ash unsuitable to use as pH-conditioner as the pH above 8.5 is not acceptable for drinking water[339]. Thus, to avoid the presence of $K_2O$, iron ion removal abilities of pure carbonates of Na and K have been investigated.

**Table 3.1.** Remaining [Fe] and pH of the water after treatment by banana ash from distilled water containing 20 mg/L of initial [Fe].

| Banana ash/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 17.11 | 17.02 | 16.81 | 5.8 | 5.8 | 5.8 |
| 2 | 15.49 | 12.38 | 10.22 | 5.8 | 5.8 | 5.9 |
| 5 | 12.48 | 11.67 | 9.48 | 5.9 | 5.9 | 5.9 |
| 10 | 10.21 | 9.42 | 7.81 | 5.9 | 6.0 | 6.1 |
| 20 | 10.02 | 8.21 | 7.66 | 6.0 | 6.1 | 6.2 |
| 30 | 8.47 | 7.37 | 7.04 | 6.1 | 6.2 | 6.3 |
| 40 | 8.26 | 6.89 | 5.18 | 6.2 | 6.3 | 6.5 |
| 50 | 6.77 | 4.79 | 3.24 | 6.3 | 6.5 | 6.6 |
| 60 | 6.11 | 3.55 | 2.19 | 6.5 | 6.7 | 6.7 |
| 70 | 5.45 | 3.11 | 2.02 | 6.6 | 6.7 | 7.0 |
| 80 | 4.22 | 3.04 | 1.55 | 7.0 | 7.3 | 7.7 |
| 90 | 3.56 | 2.61 | 1.49 | 8.1 | 8.2 | 8.4 |
| 100 | 3.21 | 2.45 | 1.22 | 8.9 | 9.0 | 9.0 |
| 200 | 2.41 | 1.78 | 1.09 | 9.4 | 9.8 | 9.8 |
| 300 | 1.45 | 1.12 | 1.01 | 9.5 | 9.8 | 9.8 |
| 400 | 1.26 | 1.02 | 0.29 | 9.6 | 9.9 | 9.9 |
| 500 | 1.04 | 0.89 | 0.21 | 9.6 | 9.9 | 9.9 |

Error limits: $\Delta$[Fe] = ±0.05 mg/L and $\Delta$pH= ±0.1

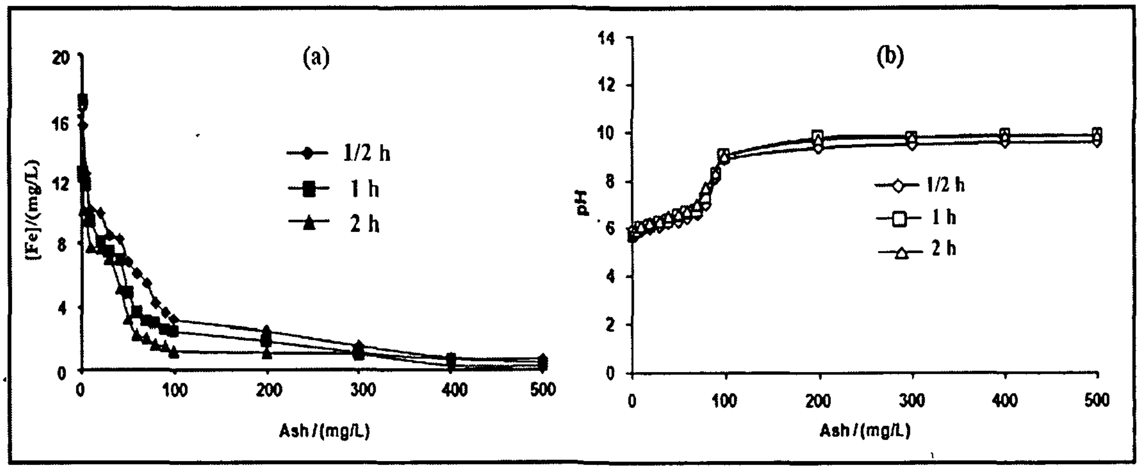

**Figure 3.1.** Remaining [Fe] in mg/L and pH after treatment *vs.* amount of added ash in mg/L at varying residence time with initial [Fe] of 20 mg/L.

### *3.1.1.2 Iron ion removal with $K_2CO_3$ and $Na_2CO_3$*

The results of the iron ion removal with carbonate salts of Na and K have been shown in Table 3.2 (a & b) and Figure 3.2.

**Table 3.2a.** Remaining [Fe] and pH of the water after treatment by potassium carbonate from distilled water containing 20 mg/L of initial [Fe].

| Potassium carbonate/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 17.04 | 16.91 | 16.78 | 5.6 | 5.7 | 5.7 |
| 2 | 15.45 | 12.37 | 10.18 | 5.7 | 5.8 | 5.8 |
| 5 | 12.51 | 10.11 | 8.38 | 5.7 | 5.8 | 5.9 |
| 10 | 8.49 | 7.36 | 6.92 | 5.8 | 5.9 | 6.0 |
| 20 | 8.27 | 6.87 | 5.18 | 5.9 | 6.0 | 6.2 |
| 30 | 6.81 | 4.76 | 3.17 | 6.1 | 6.3 | 6.3 |
| 40 | 6.04 | 4.11 | 3.02 | 6.2 | 6.4 | 6.6 |
| 50 | 5.11 | 3.78 | 2.68 | 6.2 | 6.4 | 6.7 |
| 60 | 4.55 | 3.21 | 2.17 | 6.3 | 6.6 | 7.0 |
| 70 | 3.11 | 2.59 | 1.78 | 6.5 | 6.9 | 7.1 |
| 80 | 2.89 | 2.38 | 1.58 | 7.0 | 7.3 | 7.5 |
| 90 | 2.48 | 1.88 | 1.16 | 7.3 | 7.8 | 8.0 |
| 100 | 1.56 | 1.46 | 0.99 | 7.5 | 7.9 | 8.2 |
| 200 | 1.38 | 1.21 | 0.69 | 7.9 | 8.2 | 8.5 |
| 300 | 1.18 | 1.01 | 0.28 | 8.2 | 8.5 | 8 9 |
| 400 | 1.11 | 0.89 | 0.18 | 9.1 | 9.2 | 9.4 |
| 500 | 1.02 | 0.58 | 0.12 | 9.2 | 9.4 | 9.6 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

**Table 3.2b.** Remaining [Fe] and pH of the water after treatment by sodium carbonate from distilled water containing 20 mg/L of initial [Fe].

| Sodium carbonate/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 16.79 | 16.78 | 16.77 | 5.6 | 5.7 | 5.7 |
| 2 | 13.96 | 12.67 | 10.09 | 5.6 | 5.7 | 5.9 |
| 5 | 12.48 | 10.21 | 8.67 | 5.7 | 5.8 | 6.1 |
| 10 | 10.11 | 8.77 | 7.01 | 5.8 | 5.9 | 6.2 |
| 20 | 8.91 | 8.28 | 6.56 | 5.9 | 6.0 | 6.3 |
| 30 | 8.48 | 8.04 | 5.89 | 6.1 | 6.2 | 6.3 |
| 40 | 8.18 | 6.56 | 5.09 | 6.2 | 6.3 | 6.4 |
| 50 | 6.21 | 5.77 | 4.78 | 6.3 | 6.4 | 6.5 |
| 60 | 5.29 | 4.78 | 4.01 | 6.4 | 6.6 | 6.7 |
| 70 | 4.09 | 3.18 | 2.45 | 6.5 | 6.6 | 6.9 |
| 80 | 3.28 | 2.87 | 2.22 | 6.7 | 6.8 | 7.0 |
| 90 | 2.78 | 1.89 | 1.36 | 6.9 | 7.2 | 7.8 |
| 100 | 2.16 | 1.78 | 1.09 | 7.0 | 7.3 | 8.0 |
| 200 | 1.28 | 1.28 | 0.98 | 7.5 | 8.0 | 8.5 |
| 300 | 1.57 | 1.09 | 0.76 | 8.0 | 8.2 | 8.7 |
| 400 | 1.29 | 0.97 | 0.31 | 8.2 | 8.4 | 8.9 |
| 500 | 1.09 | 0.88 | 0.28 | 9.0 | 9.3 | 9.4 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

In the plots in Figure 3.2 (a-d), remaining concentration in mg/L of iron ion after treatment along with the final pH against various doses of carbonate salts of Na and K as pH-conditioner in the range of 0-500 mg/L at residence times of ½ h to 2 h have been shown. The iron removal by the carbonate salts of Na and K has been found to be slightly better than that by the banana ash. The iron removal again showed improvement on increase in the residence time from ½ h to 2 h. A residual Fe of 0.3 mg/L was achieved with 300 mg/L of $K_2CO_3$ at residence time of 2 h. From Table 3.2a, it is clear that the remaining Fe concentration can be further reduced to below 0.3 mg/L on increasing the quantity of potassium carbonate.

In case of $Na_2CO_3$, the quantity required to achieve the removal of iron to 0.3 mg/L was 400 mg/L. Thus, the removal of iron in case of potassium salt is slightly better than the sodium salt of carbonate. The pHs of the treated water with the carbonates have been found to be within 9.5 up to the salt concentrations of 500 mg/L, which is slightly lower than that observed with the ash but still above the acceptable limit of 8.5. This led us to investigate the iron ion removal using the bicarbonate salts of Na and K in an attempt to further reduce the final pH to below 8.5.

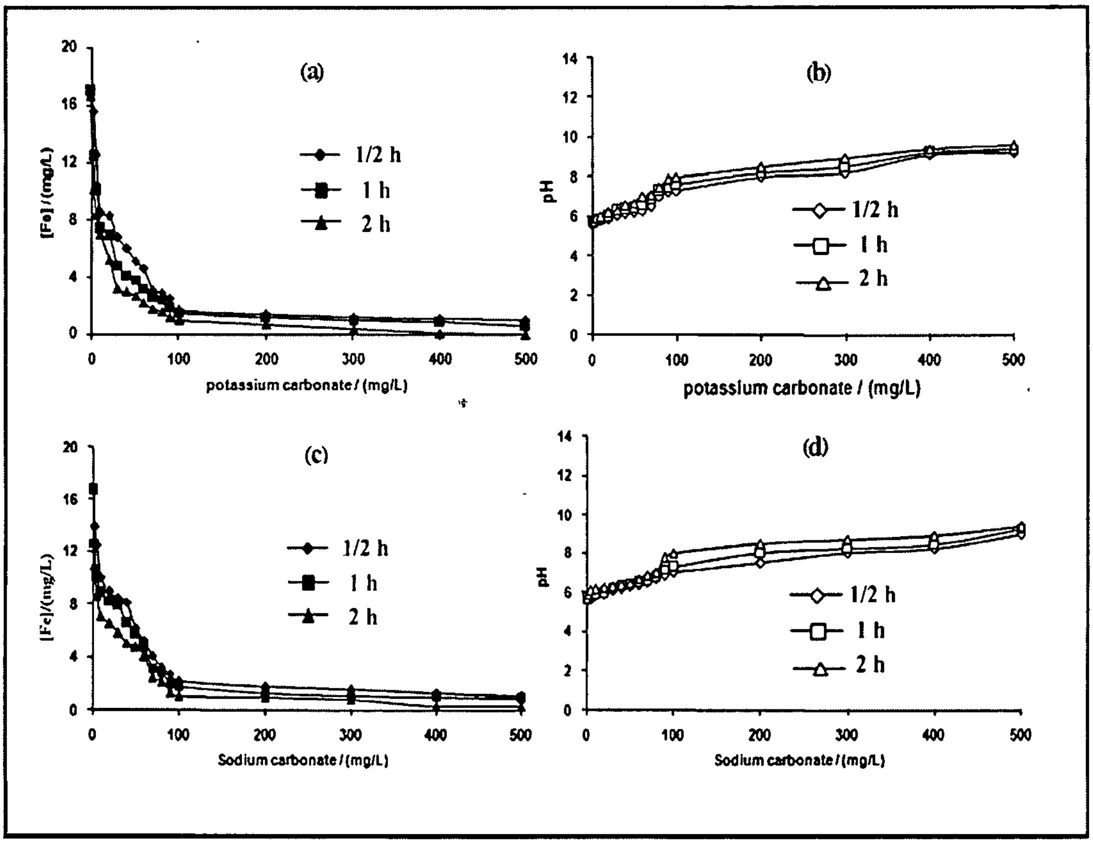

**Figure 3.2.** Remaining [Fe] in mg/L and pH after treatment *vs.* amount of added carbonate salts of Na and K in mg/L of water at varying residence time with initial [Fe] of 20 mg/L.

### *3.1.1.3 Iron ion removal with $KHCO_3$ and $NaHCO_3$*

The results of iron ion removal by Na and K bicarbonates have been shown in Table 3.3 (a & b) and Figure 3.3. The observed curves for the residual iron ion and the final pH *vs.* quantity of the bicarbonate salts reveal an interesting fact that the iron ion removal is far better with both of the bicarbonates than the corresponding carbonate salts. On the other hand, the final pH obtained with the bicarbonates were lower than that with the carbonate salts. In case of $NaHCO_3$, less than 200 mg/L of the salt can reduce the iron ion concentration from 20 mg/L to 0.3 mg/L at residence time of 2 h. Again, a dose more than 200 mg/L of $NaHCO_3$ can further reduce the concentration of iron ion to below 0.3 mg/L (Table 3.3b).

**Table 3.3a.** Remaining [Fe] and pH of the water after treatment by potassium bicarbonate from distilled water containing 20 mg/L of initial [Fe].

| Potassium bicarbonate/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 17.18 | 16.89 | 16.91 | 5.7 | 5.7 | 5.7 |
| 2 | 12.47 | 11.67 | 6.17 | 5.9 | 5.9 | 6.2 |
| 5 | 10.17 | 9.38 | 3.11 | 6.0 | 6.1 | 6.2 |
| 10 | 8.89 | 8.09 | 2.46 | 6.1 | 6.2 | 6.3 |
| 20 | 8.21 | 7.51 | 2.27 | 6.2 | 6.3 | 6.4 |
| 30 | 7.67 | 7.46 | 1.78 | 6.2 | 6.4 | 6.6 |
| 40 | 6.97 | 6.45 | 1.35 | 6.3 | 6.6 | 6.8 |
| 50 | 6.89 | 5.77 | 1.08 | 6.5 | 6.8 | 7.3 |
| 60 | 5.48 | 4.78 | 0.94 | 6.8 | 7.0 | 7.4 |
| 70 | 4.85 | 4.37 | 0.27 | 6.9 | 7.2 | 7.4 |
| 80 | 3.76 | 3.18 | 0.21 | 7.1 | 7.3 | 7.5 |
| 90 | 2.77 | 2.21 | 0.14 | 7.3 | 7.5 | 7.6 |
| 100 | 2.45 | 1.78 | 0.08 | 7.5 | 7.6 | 7.9 |
| 200 | 2.09 | 1.27 | 0.06 | 7.6 | 7.8 | 8.2 |
| 300 | 1.67 | 1.11 | 0.05 | 7.8 | 8.0 | 8.5 |
| 400 | 1.37 | 0.88 | 0.04 | 8.1 | 8.3 | 8.6 |
| 500 | 1.16 | 0.51 | 0.04 | 8.3 | 8.5 | 8.7 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

**Table 3.3b.** Remaining [Fe] and pH of the water after treatment by sodium bicarbonate from distilled water containing 20 mg/L of initial [Fe].

| Sodium bicarbonate/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 17.18 | 16.95 | 16.92 | 5.6 | 5.7 | 5.7 |
| 2 | 12.45 | 11.66 | 9.46 | 5.9 | 6.4 | 6.3 |
| 5 | 10.18 | 9.41 | 7.78 | 6.1 | 6.5 | 6.6 |
| 10 | 8.89 | 8.05 | 5.22 | 6.4 | 6.6 | 6.7 |
| 20 | 8.17 | 7.53 | 4.51 | 6.5 | 6.6 | 6.9 |
| 30 | 7.67 | 7.45 | 3.94 | 6.5 | 6.7 | 7.2 |
| 40 | 6.99 | 6.48 | 3.82 | 6.6 | 6.9 | 7.4 |
| 50 | 6.91 | 5.78 | 3.18 | 6.8 | 7.2 | 7.4 |
| 60 | 5.46 | 4.78 | 2.19 | 7.0 | 7.3 | 7.6 |
| 70 | 4.89 | 4.36 | 1.82 | 7.2 | 7.5 | 7.8 |
| 80 | 3.78 | 3.21 | 1.47 | 7.4 | 7.6 | 7.8 |
| 90 | 2.77 | 2.17 | 1.11 | 7.7 | 7.7 | 7.9 |
| 100 | 2.45 | 1.76 | 0.82 | 7.9 | 7.8 | 8.2 |
| 200 | 2.07 | 1.29 | 0.28 | 8.0 | 8.2 | 8.6 |
| 300 | 1.67 | 1.06 | 0.14 | 8.3 | 8.4 | 8.8 |
| 400 | 1.38 | 0.92 | 0.12 | 8.6 | 8.7 | 8.9 |
| 500 | 1.17 | 0.54 | 0.09 | 8.7 | 8.8 | 9.1 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

The removal effeciency of Fe by $KHCO_3$ is found to be better than that of $NaHCO_3$, analogous to that observed with the carbonate salts of Na and K. A quantity of 70 mg/L of $KHCO_3$ can remove iron ion to below 0.3 mg/L (Table 3.3a). Again, a quantity of 100 mg/L of $KHCO_3$ removed iron ion almost to an undetectable level. It is also interesting to note that in case of $KHCO_3$, the final pH remains within the acceptable range for drinking, *i.e.*, within 6.5 to 8.5 up to 300 mg/L of $KHCO_3$ dose.

Thus, in case of $KHCO_3$ the dose required to bring iron concentration to 0.3 mg/L from an initial concentration of 20 mg/L is the minimum among all other salts and ash. The final pH also remains within the acceptable range for drinking water unlike the carbonate salts of Na and K and banana ash. Hence, $KHCO_3$ is the most suitable candidate among all four salts and the banana ash from the consideration of dose of salt/ash and the final pH of water.

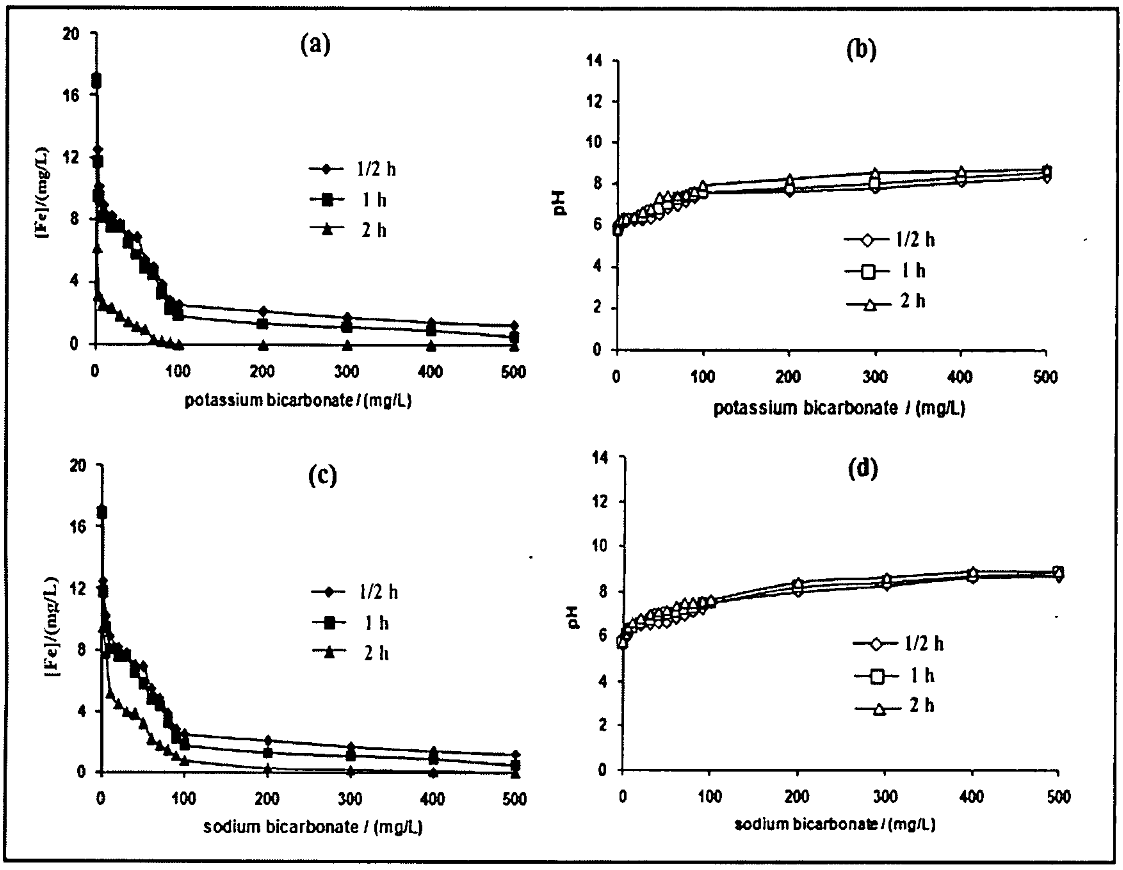

**Figure 3.3.** Remaining [Fe] in mg/L and pH after treatment *vs.* amount of added bicarbonate salts of Na and K in mg/L of water at varying residence time with initial [Fe] of 20 mg/L.

### *3.1.1.4 The reason for better performance of bicarbonate salts than carbonate salts of Na and K*

It is well known that iron ion is precipitated as ferric oxide ($Fe_2O_3$) from neutral water, as goethite (FeOOH) from mild alkaline water and as ferric hydroxide (ferrihydrite, $Fe(OH)_3$) from highly alkaline water in presence of sufficient oxygen[340]. The reactions of formation of goethite and ferrihydrite can be represented as[246, 341-344]:

$$2Fe^{2+} + O_2 + 2OH^- \rightarrow 2FeOOH\downarrow \qquad \text{Eq. (3.1)}$$

$$4Fe^{2+} + O_2 + 8OH^- + 2H_2O \rightarrow 4Fe(OH)_3\downarrow \qquad \text{Eq. (3.2)}$$

The solubility of these compounds decreases in the order $Fe_2O_3 > FeOOH > Fe(OH)_3$ due to increasing $OH^-$ groups in the same order. Iron ion is precipitated as goethite and ferrihydrite in the alkaline pH range of 7.0 to 9.8. The bicarbonates of Na and K produce milder alkaline solution than the corresponding carbonates. Therefore, it is likely that the goethite: ferrihydrite ratio in the precipitate is higher in the case of the bicarbonates than that in the case of equivalent quantity of the corresponding carbonate salt or banana ash, lime or NaOH. This is supported also by the fact that the removal of iron ion is slower with the bicarbonates than with the corresponding carbonates, which can be seen in Figure 3.2a and c and Figure 3.3a and c, since the precipitation of goethite is expected to be slower compared to that of ferrihydrite[345]. Although the overall iron ion removal was much better with the bicarbonates than the corresponding carbonates after residence time of ½ h, the reverse was however observed after residence time of ½ h and 1 h.

### *3.1.1.5 The reason for better performance of K-salts than the corresponding Na-salt*

The equivalent concentration of potassium is less than that of sodium with equal concentrations in mg/L of their salts having the same anion. On the other hand, potassium is more basic than sodium. These mutually opposing factors may cancel each other, as reflected in the plots of pH *vs.* salt concentrations shown in Figure 3.2 and 3.3. Thus, the observed slightly higher iron removal by the K-salts than the corresponding Na-salts can be attributed to the slightly lower pH produced by the K-salts than that by the corresponding Na-salts.

### *3.1.1.6 Iron ion removal with 1:1 binary mixtures of the bicarbonate salts with the ash*

The effect of 1:1 weight by weight mixture of ash with the bicarbonate salts of Na and K on removal of iron ion was investigated. The results were shown in Table 3.4 and Figure 3.4.

**Table 3.4a.** Remaining [Fe] and pH of the water after treatment by 1:1 potassium bicarbonate & ash from distilled water containing 20 mg/L of initial [Fe].

| 1:1 Potassium bicarbonate & ash/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 17.28 | 17.17 | 16.91 | 5.5 | 5.5 | 5.6 |
| 2 | 12.67 | 11.89 | 9.99 | 5.6 | 5.6 | 5.7 |
| 5 | 11.89 | 10.09 | 9.11 | 5.6 | 5.7 | 5.9 |
| 10 | 9.98 | 9.58 | 7.97 | 5.7 | 5.9 | 6.0 |
| 20 | 9.57 | 7.78 | 7.47 | 5.9 | 6.0 | 6.3 |
| 30 | 8.43 | 6.88 | 5.33 | 6.1 | 6.3 | 6.6 |
| 40 | 5.68 | 5.17 | 3.97 | 6.2 | 6.4 | 6.8 |
| 50 | 3.77 | 2.98 | 2.37 | 6.5 | 6.7 | 7.0 |
| 60 | 2.98 | 2.58 | 2.12 | 6.6 | 6.8 | 7.1 |
| 70 | 2.48 | 2.04 | 1.76 | 6.9 | 7.1 | 7.3 |
| 80 | 1.87 | 1.89 | 1.17 | 7.1 | 7.2 | 7.3 |
| 90 | 2.11 | 1.77 | 1.07 | 7.3 | 7.4 | 7.6 |
| 100 | 1.77 | 1.38 | 0.99 | 7.5 | 7.7 | 8.0 |
| 200 | 1.56 | 1.18 | 0.77 | 8.1 | 8.2 | 8.4 |
| 300 | 1.38 | 0.92 | 0.32 | 8.5 | 8.6 | 8.9 |
| 400 | 1.17 | 0.64 | 0.28 | 8.9 | 9.0 | 9.1 |
| 500 | 0.92 | 0.12 | 0.09 | 9.0 | 9.1 | 9.2 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

**Table 3.4b.** Remaining [Fe] and pH of the water after treatment by 1:1 sodium bicarbonate & ash from distilled water containing 20 mg/L of initial [Fe].

| 1:1 Sodium bicarbonate & ash/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 17.17 | 17.02 | 16.78 | 5.5 | 5.5 | 5.6 |
| 2 | 12.87 | 11.97 | 10.11 | 5.6 | 5.6 | 5.7 |
| 5 | 11.77 | 11.12 | 9.91 | 5.6 | 5.7 | 5.9 |
| 10 | 10.27 | 9.78 | 8.56 | 5.7 | 5.9 | 6.1 |
| 20 | 9.56 | 7.84 | 7.48 | 5.9 | 6.0 | 6.2 |
| 30 | 8.56 | 6.89 | 5.26 | 6.2 | 6.3 | 6.5 |
| 40 | 6.17 | 5.47 | 4.12 | 6.3 | 6.3 | 6.7 |
| 50 | 5.12 | 4.26 | 3.09 | 6.4 | 6.5 | 6.9 |
| 60 | 3.27 | 2.96 | 2.37 | 6.6 | 6.7 | 7.0 |
| 70 | 2.89 | 2.28 | 1.89 | 7.2 | 7.3 | 7.3 |
| 80 | 2.48 | 2.09 | 1.37 | 7.3 | 7.4 | 7.5 |
| 90 | 1.98 | 1.89 | 1.17 | 7.4 | 7.6 | 7.7 |
| 100 | 1.89 | 1.47 | 1.09 | 7.5 | 7.8 | 8.2 |
| 200 | 1 67 | 0.98 | 0.56 | 8.3 | 8.5 | 8.7 |
| 300 | 1.37 | 0.92 | 0.27 | 8.9 | 9.1 | 9.2 |
| 400 | 1.04 | 0.74 | 0.12 | 9.0 | 9.2 | 9.3 |
| 500 | 0.92 | 0.18 | 0.09 | 9.1 | 9.3 | 9.5 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

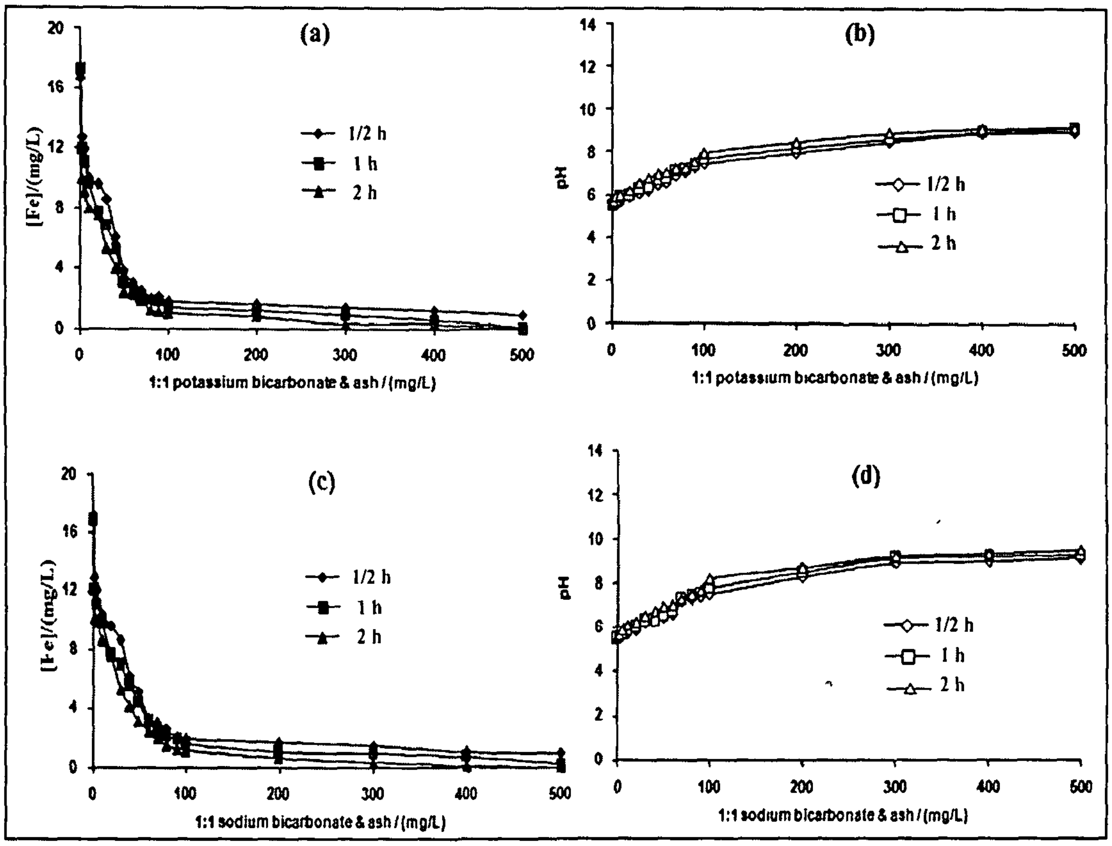

**Figure 3.4.** Remaining [Fe] in mg/L and pH after treatment *vs.* amount of 1:1 mixture of added bicarbonate salts of Na and K and ash in mg/L at varying residence time with initial [Fe] of 20 mg/L.

It has been found that the mixtures of $NaHCO_3$ and $KHCO_3$ with the ash showed lower iron ion removal abilities than the corresponding bicarbonate salts alone. The final pHs of the water treated with the mixtures were higher than that with the corresponding bicarbonate salts alone and were found to surpass 9.0, which is above the acceptable maximum limit for drinking water. The poor iron ion removal by the mixtures of bicarbonate and carbonate salts compared to the corresponding bicarbonates alone can be attributed to lower goethite: ferrihydrite ratio in the precipitate obtained with the mixtures than that obtained with the corresponding bicarbonate salts alone.

### *3.1.1.7 Iron ion removal with 1:1 binary mixtures of the potassium bicarbonate and carbonate salts of Na and K*

Removal of iron ion with 1:1 binary mixture of potassium bicarbonate and carbonate salts of Na and K with the final pH of the treated water has also been studied. The results were shown in Table 3.5 and Figure 3.5.

**Table 3.5a.** Remaining [Fe] and pH of the water after treatment by 1:1 potassium bicarbonate & potassium carbonate from distilled water containing 20 mg/L of initial [Fe].

| 1:1 potassium bicarbonate &, potassium carbonate/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 17.21 | 17.14 | 17.12 | 5.6 | 5.6 | 5.5 |
| 2 | 12.67 | 11.89 | 9.98 | 5.6 | 5.6 | 5.8 |
| 5 | 11.89 | 10.96 | 9.08 | 5.8 | 5.9 | 5.9 |
| 10 | 10.14 | 9.56 | 7.95 | 5.9 | 6.0 | 6.1 |
| 20 | 9.39 | 9.18 | 7.78 | 5.9 | 6.1 | 6.3 |
| 30 | 8.67 | 8.49 | 6.17 | 6.1 | 6.3 | 6.5 |
| 40 | 6.54 | 5.52 | 3.21 | 6.2 | 6.4 | 6.7 |
| 50 | 5.68 | 3.19 | 2.17 | 6.5 | 6.7 | 6.8 |
| 60 | 4.09 | 3.29 | 1.89 | 6.7 | 6.8 | 7.0 |
| 70 | 2.78 | 2.46 | 1.38 | 7.0 | 7.1 | 7.2 |
| 80 | 2.09 | 1.78 | 1.14 | 7.2 | 7.3 | 7.8 |
| 90 | 1.88 | 1.51 | 0.78 | 7.3 | 7.5 | 8.0 |
| 100 | 1.16 | 1.27 | 0.72 | 7.4 | 7.7 | 8.1 |
| 200 | 1.14 | 0.98 | 0.31 | 8.0 | 8.2 | 8.6 |
| 300 | 0.91 | 0.48 | 0.27 | 8.2 | 8.4 | 8.9 |
| 400 | 0.58 | 0.32 | 0.12 | 8.7 | 8.9 | 9.0 |
| 500 | 0.31 | 0.11 | 0.09 | 9.2 | 9.4 | 9.5 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

**Table 3.5b.** Remaining [Fe] and pH of the water after treatment by 1:1 potassium bicarbonate & sodium carbonate from distilled water containing 20 mg/L of initial [Fe].

| 1:1 potassium bicarbonate & sodium carbonate/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 17.09 | 17.21 | 16.94 | 5.5 | 5.5 | 5.6 |
| 2 | 12.99 | 12.21 | 10.31 | 5.6 | 5.7 | 5.7 |
| 5 | 12.12 | 11.38 | 9.29 | 5.7 | 5.8 | 5.9 |
| 10 | 10.18 | 10.04 | 9.78 | 5.8 | 6.0 | 6.1 |
| 20 | 9.89 | 9.45 | 8.94 | 6.0 | 6.2 | 6.3 |
| 30 | 8.91 | 9.12 | 7.12 | 6.1 | 6.4 | 6.5 |
| 40 | 8.66 | 8.46 | 6.18 | 6.2 | 6.3 | 6.5 |
| 50 | 7.46 | 7.19 | 6.48 | 6.4 | 6.5 | 6.7 |
| 60 | 5.11 | 4.81 | 4.17 | 6.6 | 6.7 | 6.9 |
| 70 | 4.29 | 3.94 | 2.19 | 6.7 | 6.8 | 7.2 |
| 80 | 3.38 | 3.09 | 1.52 | 6.9 | 7.0 | 7.7 |
| 90 | 2.67 | 2.47 | 1.22 | 7.3 | 7.5 | 7.9 |
| 100 | 1.89 | 1.67 | 0.98 | 7.4 | 7.6 | 8.1 |
| 200 | 1.38 | 1.14 | 0.77 | 8.0 | 8.1 | 8.8 |
| 300 | 1.18 | 0.94 | 0.39 | 8.1 | 8.3 | 9.1 |
| 400 | 1.04 | 0.42 | 0.24 | 8.4 | 8.8 | 9.2 |
| 500 | 0.67 | 0.12 | 0.08 | 8.9 | 9.2 | 9.4 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

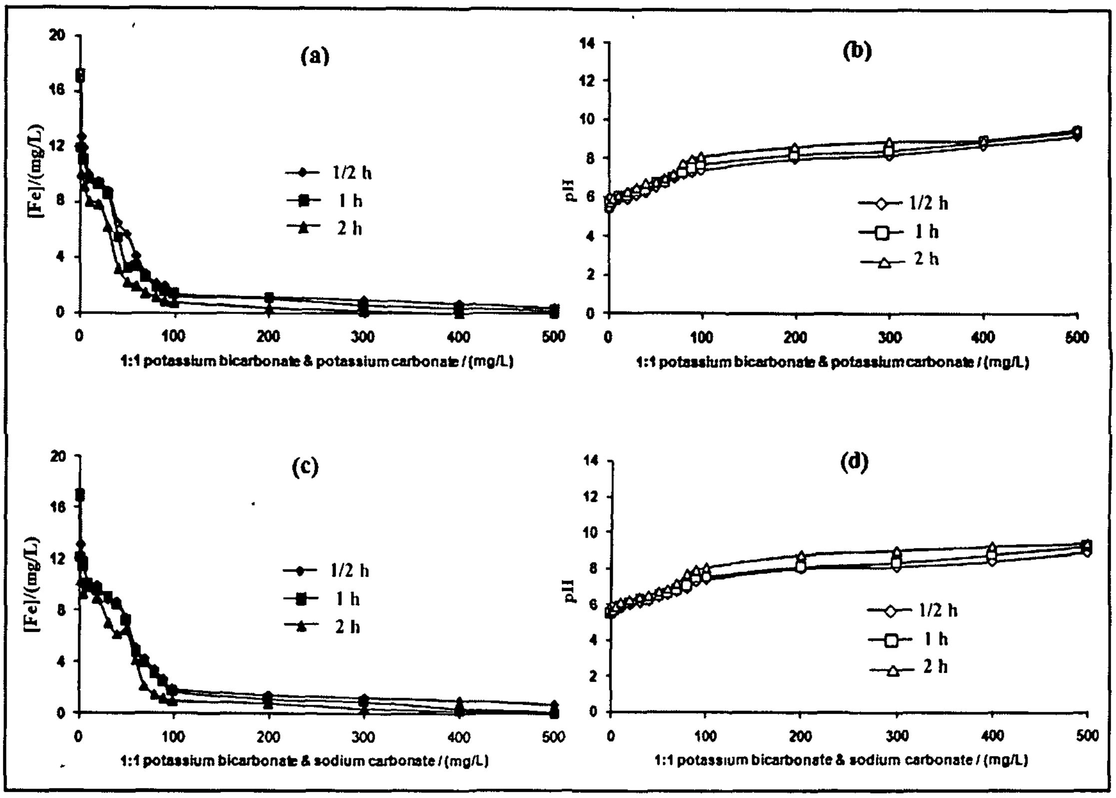

**Figure 3.5.** Remaining [Fe] in mg/L and pH after treatment *vs.* amount of 1:1 mixture of added potassium bicarbonate and carbonate salts of Na and K in mg/L of water at varying residence time with initial [Fe] of 20 mg/L.

The results obtained with the 1:1 mixture of carbonate and bicarbonate salts of potassium were found to be poor than that obtained with potassium bicarbonate alone but showed slight better performance than that with potassium carbonate. That means presence of more basic carbonate salts along with potassium bicarbonate lowers the ability of the later to remove iron by increasing the final pH of the water.

Again, 1:1 binary mixture of potassium bicarbonate and sodium carbonate showed similar trend as shown in Table 3.5b and Figure 3.5 (c & d). Thus, potassium bicarbonate alone is found to be far better than the 1:1 mixture of potassium bicarbonate with sodium carbonate.

### *3.1.1.8 Iron ion removal with 1:1 binary mixtures of the sodium bicarbonate and carbonate salts of Na and K*

·Table 3.6 and Figure 3.6 show the results of removal of iron ion and pH of the water after treatment by 1:1 binary mixtures of sodium bicarbonate and carbonate salts of Na and K. In this case also, iron removal becomes lesser than that obtained with sodium bicarbonate alone but slightly better than that with carbonate salts alone.

**Table 3.6a:** Remaining [Fe] and pH of the water after treatment by 1:1 sodium bicarbonate & potassium carbonate from distilled water containing 20 mg/L of initial [Fe].

| 1:1 sodium bicarbonate & potassium carbonate/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 17.09 | 17.11 | 16.79 | 5.6 | 5.6 | 5.5 |
| 2 | 12.54 | 12.04 | 10.38 | 5.6 | 5.7 | 5.7 |
| 5 | 12.09 | 11.56 | 10.09 | 5.8 | 5.9 | 6.0 |
| 10 | 10.48 | 10.17 | 9.31 | 5.8 | 5.9 | 6.1 |
| 20 | 9.56 | 9.38 | 8.17 | 5.9 | 6.0 | 6.3 |
| 30 | 8.89 | 8.67 | 6.97 | 6.0 | 6.3 | 6.6 |
| 40 | 6.8 | 6.11 | 4.47 | 6.3 | 6.5 | 6.8 |
| 50 | 6.09 | 4.78 | 3.08 | 6.6 | 6.7 | 6.9 |
| 60 | 4.48 | 4.28 | 2.35 | 6.7 | 6.9 | 7.0 |
| 70 | 2.96 | 2.89 | 1.47 | 7.0 | 7.2 | 7.2 |
| 80 | 2.17 | 1.97 | 1.16 | 7.2 | 7.3 | 7.3 |
| 90 | 1.97 | 1.57 | 0.97 | 7.5 | 7.2 | 7.5 |
| 100 | 1.57 | 1.38 | 0.91 | 7.6 | 7.5 | 8.0 |
| 200 | 1.28 | 1.03 | 0.57 | 8.0 | 8.4 | 8.8 |
| 300 | 0.97 | 0.67 | 0.28 | 8.3 | 8.5 | 9.2 |
| 400 | 0.67 | 0.32 | 0.17 | 8.7 | 9.2 | 9.6 |
| 500 | 0.37 | 0.28 | 0.09 | 9.3 | 9.4 | 9.8 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

**Table 3.6b.** Remaining [Fe] and pH of the water after treatment by 1:1 sodium bicarbonate & sodium carbonate from distilled water containing 20 mg/L of initial [Fe].

| 1:1 sodium bicarbonate & sodium carbonate/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 16 89 | 16.86 | 17.02 | 5.5 | 5.5 | 5.6 |
| 2 | 13.37 | 12.67 | 10.98 | 5.6 | 5.7 | 5.8 |
| 5 | 12.17 | 11.48 | 10.02 | 5.7 | 5.8 | 6.0 |
| 10 | 11.19 | 11.04 | 10.78 | 5.8 | 6.0 | 6.1 |
| 20 | 10.42 | 10.22 | 9.82 | 5.9 | 6.2 | 6.3 |
| 30 | 9.94 | 9.18 | 7.67 | 6.0 | 6.2 | 6.5 |
| 40 | 9.12 | 8.62 | 6.98 | 6.2 | 6.3 | 6.5 |
| 50 | 8.06 | 7.31 | 6.38 | 6.4 | 6.5 | 6.7 |
| 60 | 6.94 | 6.57 | 6.17 | 6.5 | 6.6 | 6.9 |
| 70 | 5.52 | 5.12 | 3.18 | 6.6 | 6.8 | 7.2 |
| 80 | 4.56 | 4.27 | 2.19 | 6.9 | 7.0 | 7.3 |
| 90 | 3.62 | 3.35 | 1.89 | 7.3 | 7.3 | 7.4 |
| 100 | 2.98 | 2.67 | 1.38 | 7.3 | 7.5 | 8.2 |
| 200 | 2.21 | 1.89 | 0.97 | 7.6 | 7.8 | 8.5 |
| 300 | 1.78 | 1.38 | 0.56 | 8.1 | 8.3 | 8.8 |
| 400 | 1.22 | 1.12 | 0.12 | 8.3 | 8.7 | 9.0 |
| 500 | 1.04 | 0.21 | 0.09 | 8.8 | 9.1 | 9.3 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

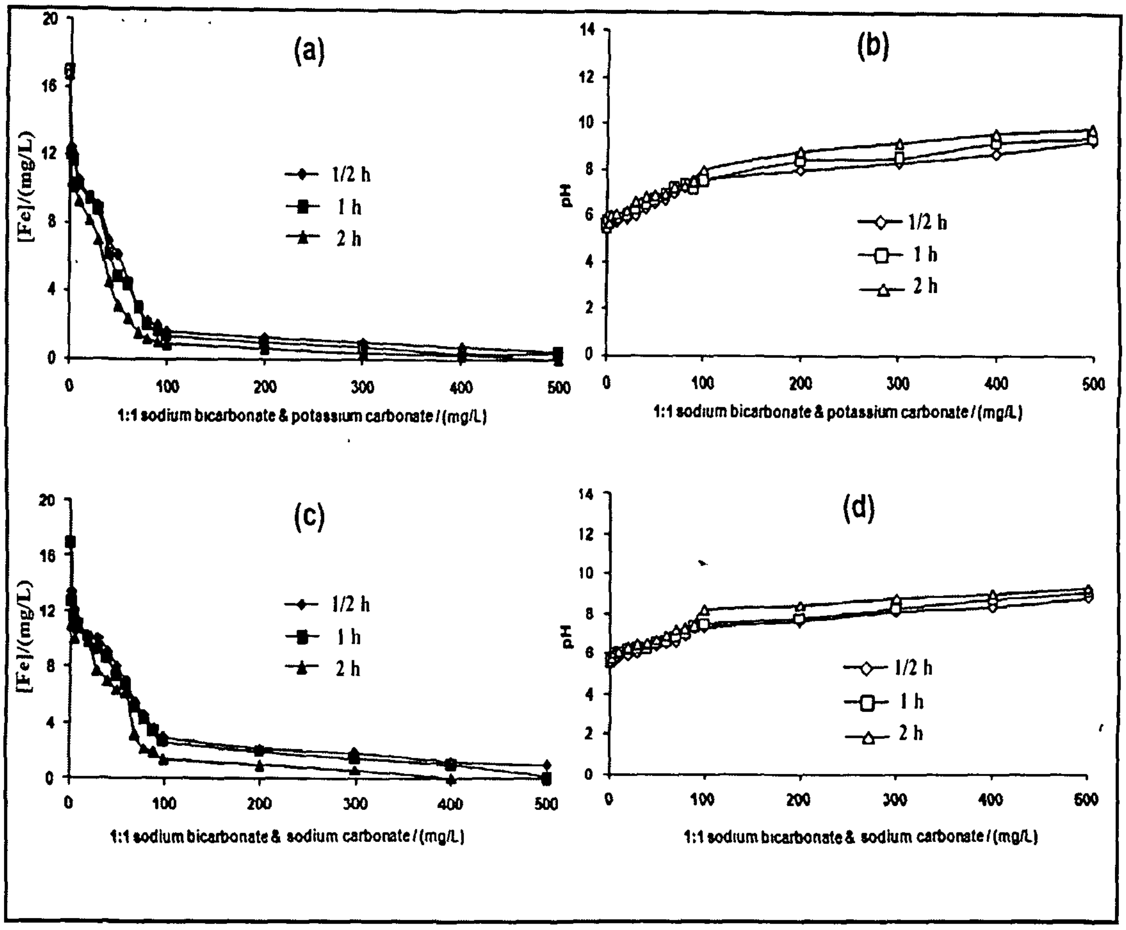

Figure 3.6. Remaining [Fe] in mg/L and pH after treatment *vs.* amount of 1:1 mixture of sodium bicarbonate and carbonate salts of Na and K in mg/L at varying residence time from initial [Fe] of 20 mg/L.

### *3.1.1.9 Iron ion removal with 1:1 binary mixtures of the bicarbonate salts of Na and K*

Table 3.7 and Figure 3.7 show the results of removal of iron ion and final pH by 1:1 binary mixtures of the bicarbonate salts of Na and K. Among all the mixtures of salts, $NaHCO_3$ and $KHCO_3$ mixture showed the highest ability to remove iron ion, of which, 100 mg/L can remove iron ion almost completely. The removal of iron ion by the binary mixtures of the carbonate and bicarbonate salts of Na and K, after a constant residence time of 2 h, was found to increase in the order ($NaHCO_3$+$Na_2CO_3$) < ($NaHCO_3$+$K_2CO_3$) < ($KHCO_3$+$Na_2CO_3$) < ($KHCO_3$+$K_2CO_3$) < ($NaHCO_3$+$KHCO_3$). In terms of the final pH of the treated water also the combination of $NaHCO_3$ and $KHCO_3$ has been the best, for which the pH remained within 8.5 up to the concentrations of the salts of 500 mg/L.

**Table 3.7.** Remaining [Fe] and pH of the water after treatment by 1:1 mixture of bicarbonate salts of Na and K from distilled water containing 20 mg/L of initial [Fe].

| 1:1 potassium bicarbonate & sodium bicarbonate/ (mg/L) | Remaining [Fe] after treatment from different residence time / (mg/L) | | | pH of the treated water | | |
|---|---|---|---|---|---|---|
| | ½ h | 1 h | 2 h | ½ h | 1 h | 2 h |
| 0 | 17.28 | 17.11 | 16.79 | 5.7 | 5.7 | 5.7 |
| 2 | 12.31 | 10.96 | 6.11 | 5.9 | 5.9 | 6.2 |
| 5 | 10.05 | 9.21 | 2.96 | 6.1 | 6.2 | 6.2 |
| 10 | 8.78 | 7.98 | 2.67 | 6.1 | 6.2 | 6.3 |
| 20 | 8.39 | 7.29 | 2.11 | 6.2 | 6.4 | 6.5 |
| 30 | 7.98 | 7.12 | 1.88 | 6.3 | 6.4 | 6.8 |
| 40 | 7.12 | 6.38 | 1.36 | 6.4 | 6.5 | 6.9 |
| 50 | 6.67 | 5.27 | 1.28 | 6.6 | 6.8 | 7.1 |
| 60 | 5.16 | 4.26 | 1.09 | 6.9 | 7.0 | 7.3 |
| 70 | 3.09 | 1.78 | 0.34 | 7.0 | 7.1 | 7.5 |
| 80 | 3.14 | 1.18 | 0.31 | 7.2 | 7.3 | 7.7 |
| 90 | 2.67 | 1.04 | 0.18 | 7.3 | 7.6 | 7.8 |
| 100 | 2.19 | 1.08 | 0.14 | 7.4 | 7.8 | 7.9 |
| 200 | 1.66 | 0.94 | 0.09 | 8.0 | 8.3 | 8.5 |
| 300 | 1.39 | 0.89 | 0.08 | 8.1 | 8.4 | 8.6 |
| 400 | 1.11 | 0.34 | 0.06 | 8.2 | 8.4 | 8.6 |
| 500 | 1.02 | 0.31 | 0.06 | 8.4 | 8.5 | 8.7 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

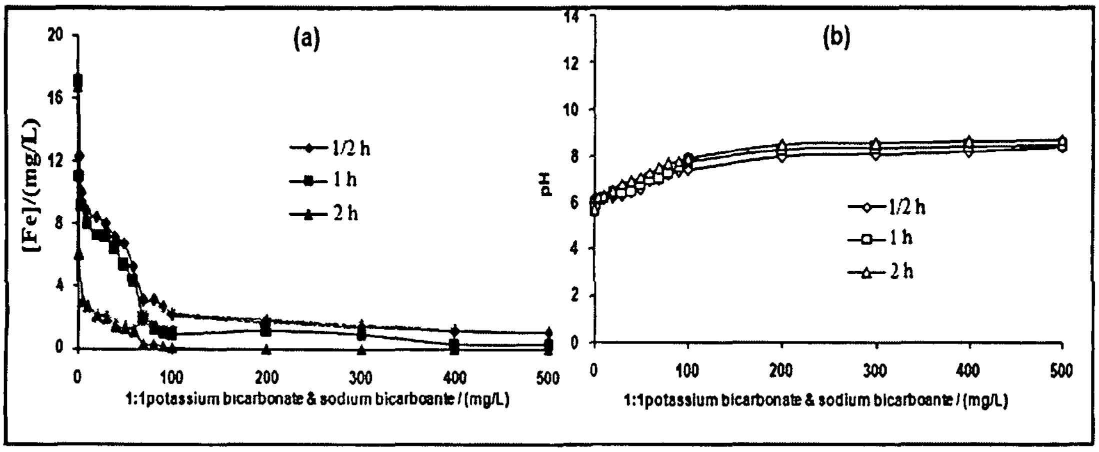

**Figure 3.7.** Remaining [Fe] in mg/L and pH after treatment *vs.* amount of 1:1 mixture of added bicarbonate salts of Na and K in mg/L at varying residence time with initial [Fe]of 20 mg/L.

### *3.1.1.10 The shapes of the curves of remaining iron and final pH vs. dose*

The following common characteristics can be noticed in the shapes of the curves of the remaining iron and the final pH *vs.* dose of ash/salts in Figure 3.1-3.7:

a. There are three distinct regions in the curves – a steep fall in the concentration of remaining iron up to a dose of about 5 mg/L (limit A), then a moderate fall between about 5 mg/L and about 90 mg/L (limit B) of the dose and finally a very blunted decrease in the concentration of remaining iron above the dose of about 90 mg/L.
b. The limits A and B also correspond to distinct changes in trend in the pH variation. There is a moderate increase in the pH upto the limit A, then a relatively blunted increase till the dose approaches the limit B followed by a sharp increase in the pH around the limit B and finally a more blunted or an almost leveled off curve beyond that.

The three regions of the curves may be attributted to removal of iron in three different forms, *viz.*, as iron oxide at pH lower than 6.5 within limit A, as goethite at moderate pH between the limits A and B and as ferrihydrite at high pH above the limit B.

### *3.1.1.11 $KHCO_3$ alone is the best choice*

The best iron removals have been achieved with $KHCO_3$ alone and 1:1 mixture of $KHCO_3$ and $NaHCO_3$. Only 70 mg/L of the $KHCO_3$ is sufficient to reduce the Fe from initial concentration of 20 mg/L to 0.3 mg/L, the WHO guideline value. A dose of 100 mg/L of the salt can remove iron almost completely. Moreover, with $KHCO_3$ alone as well as with the 1:1 mixture of $KHCO_3$ and $NaHCO_3$, the pH of the treated water does not exceed 8.5. However, the presence of $NaHCO_3$ did not improve the performance of $KHCO_3$ in removal of iron. Hence, given equal efficiency of $KHCO_3$ alone with its 1:1 mixture with $NaHCO_3$ having double total salt concentration, the former alone has a practical advantage in addition to the advantage of less cost. Thus, it has been found that $KHCO_3$ is the best candidate for iron precipitation compared to banana ash and other carbonates and bicarbonates of Na and K and their binary mixtures. Having known this fact, the further investigation of removal of iron from fabricated iron containing distilled water and groundwater having different initial Fe concentrations has been restricted only to the treatment with $KHCO_3$.

### *3.1.1.12 Effect of initial iron ion concentration on removal with $KHCO_3$ from distilled water and groundwater*

The iron removal ability of $KHCO_3$ with initial iron ion concentrations of 2, 5, 10, 15 and 20 mg/L has been investigated with iron containing distilled water as well as synthetically prepared iron containing groundwater with residence time of 2 h and the results have been summarized in Table 3.8 and Figure 3.8. It can be seen from the figure that the quantity of $KHCO_3$ required to bring down the iron ion concentration to 0.3 mg/L increased with increase in the initial concentration of iron ion in distilled water as well as groundwater.

Interestingly, the iron removal by $KHCO_3$ from groundwater has been found to be considerably better than that from distilled water at all initial concentrations of iron ion. While 30 mg/L of $KHCO_3$ is required to bring down the iron ion concentration from 2 mg/L to 0.3 mg/L in distilled water, the required quantity of the salt is only 10 mg/L in the case of groundwater. Similarly, while 70 mg/L of $KHCO_3$ is required to bring down the iron ion concentration from 20 mg/L to 0.3 mg/L in distilled water, the required quantity of the salt is only 50 mg/L in the case of groundwater.

**Table 3.8a.** Remaining [Fe] and pH of the water after treatment by $KHCO_3$ from distilled water containing different initial [Fe] in mg/L.

| $KHCO_3$ dose / (mg/L) | Remaining [Fe] after treatment from different initial [Fe] / (ppm) | | | | | pH of the treated water | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | 5 | 10 | 15 | 20 | 2 | 5 | 10 | 15 | 20 |
| 0 | 1.78 | 3.28 | 8.56 | 11.11 | 16.94 | 5.8 | 5.8 | 5.8 | 5.8 | 5.8 |
| 2 | 1.29 | 2.11 | 2.94 | 5.07 | 6.21 | 6.4 | 6.4 | 6.3 | 6.3 | 6.2 |
| 5 | 1.11 | 1.89 | 2.18 | 2.98 | 3.11 | 6.5 | 6.4 | 6.4 | 6.3 | 6.2 |
| 10 | 0.78 | 1.68 | 1.99 | 2.51 | 2.48 | 6.6 | 6.5 | 6.5 | 6.4 | 6.3 |
| 20 | 0.48 | 1.09 | 1.78 | 2.18 | 2.27 | 6.8 | 6.7 | 6.6 | 6.5 | 6.4 |
| 30 | 0.28 | 0.91 | 1.45 | 1.97 | 1.78 | 6.9 | 6.8 | 6.7 | 6.7 | 6.6 |
| 40 | 0.12 | 0.69 | 1.09 | 1.28 | 1.36 | 7.0 | 6.9 | 6.9 | 6.9 | 6.8 |
| 50 | 0.09 | 0.48 | 0.89 | 1.08 | 1.09 | 7.6 | 7.5 | 7.5 | 7.4 | 7.3 |
| 60 | 0.09 | 0.28 | 0.78 | 0.79 | 0.89 | 7.7 | 7.6 | 7.5 | 7.5 | 7.4 |
| 70 | 0.08 | 0.13 | 0.31 | 0.29 | 0.28 | 7.9 | 7.8 | 7.6 | 7.5 | 7.4 |
| 80 | 0.07 | 0.09 | 0.23 | 0.14 | 0.22 | 8.0 | 7.9 | 7.7 | 7.6 | 7.5 |
| 90 | 0.06 | 0.08 | 0.09 | 0.12 | 0.13 | 8.2 | 8.1 | 7.9 | 7.7 | 7.6 |
| 100 | 0.06 | 0.07 | 0.09 | 0.08 | 0.09 | 8.4 | 8.2 | 8.0 | 7.7 | 7.9 |

Error limits: $\Delta$[Fe] = ±0.05 mg/L and $\Delta$pH= ±0.1

**Table 3.8b.** Remaining [Fe] and pH of the water after treatment by $KHCO_3$ from groundwater water prefabricated with different initial [Fe] in mg/L.

| $KHCO_3$ dose / (mg/L) | Remaining [Fe] after treatment from different initial [Fe] / (ppm) | | | | | pH of the treated water | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | 5 | 10 | 15 | 20 | 2 | 5 | 10 | 15 | 20 |
| 0 | 1.48 | 3.12 | 5.09 | 8.19 | 10.88 | 7.1 | 7.1 | 7.1 | 7.1 | 7.1 |
| 2 | 0.91 | 1.09 | 2.96 | 3.31 | 5.12 | 7.5 | 7. 5 | 7.4 | 7.4 | 7.3 |
| 5 | 0.47 | 0.92 | 1.79 | 2.99 | 3.19 | 7.6 | 7.5 | 7.5 | 7.4 | 7.4 |
| 10 | 0.32 | 0.68 | 1.48 | 2.04 | 2.18 | 7.7 | 7.6 | 7.6 | 7.5 | 7.4 |
| 20 | 0.14 | 0.24 | 0.79 | 1.29 | 1.28 | 7.8 | 7.7 | 7.6 | 7.5 | 7.4 |
| 30 | 0.09 | 0.12 | 0.36 | 0.37 | 1.09 | 7.8 | 7.7 | 7.7 | 7.6 | 7.5 |
| 40 | 0.09 | 0.09 | 0.18 | 0.28 | 0.89 | 7.9 | 7.8 | 7.7 | 7.7 | 7.5 |
| 50 | 0.07 | 0.08 | 0.13 | 0.12 | 0.29 | 7.9 | 7.8 | 7.8 | 7.7 | 7.6 |
| 60 | 0.06 | 0.08 | 0.08 | 0.11 | 0.22 | 8.0 | 7.9 | 7.9 | 7.8 | 7.7 |
| 70 | 0.05 | 0.07 | 0.08 | 0.09 | 0.12 | 8.1 | 8.0 | 7.9 | 7.8 | 7.7 |
| 80 | 0.05 | 0.06 | 0.07 | 0.09 | 0.09 | 8.2 | 8.12 | 8.0 | 7.9 | 7.8 |
| 90 | 0.03 | 0.06 | 0.05 | 0.07 | 0 .08 | 8.3 | 8.3 | 8.2 | 8.0 | 7.9 |
| 100 | 0.03 | 0.05 | 0.05 | 0.06 | 0.08 | 8.5 | 8.4 | 8.3 | 8.1 | 8.0 |

Error limits: Δ[Fe] = ±0.05 mg/L and ΔpH= ±0.1

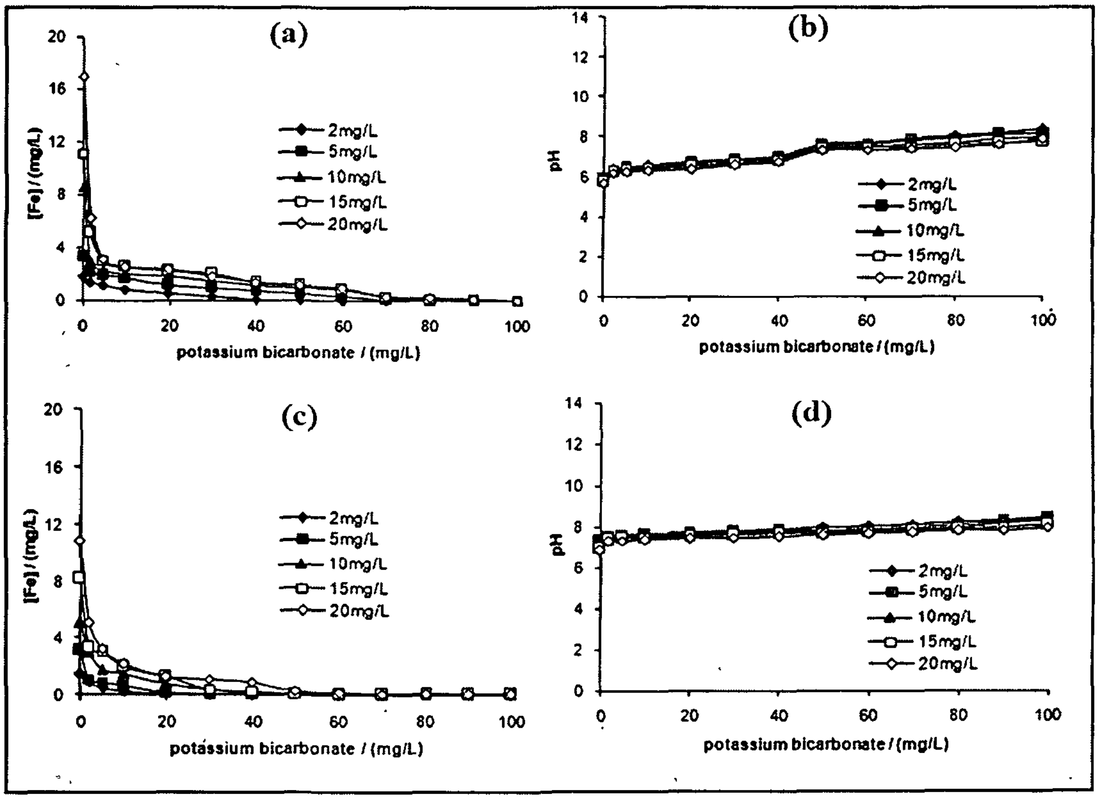

**Figure 3.8.** Remaining [Fe] in mg/L after treatment and pH *vs.* amount of potassium bicarbonate in mg/L of water from varying initial concentration of iron 2, 5, 10, 15 and 20 mg/L (a, b) in distilled water and (c, d) in groundwater with residence time of 2 h.

The better iron ion removal from groundwater than distilled water can be attributted to an optimum pH required for the formation of ferrihydrite which has prevailed in the groundwater in the presence of iron ion and $KHCO_3$, whereas, the pH of distilled water up to $KHCO_3$ dose of 40 mg/L remained below 7.00, which may be lower than the optimum range of pH that is required for the formation of ferrihydrite. Some relevant chemical parameters of the groundwater were mentioned in Table 2.1. It has been seen that the presence of the other ions in the groundwater did not have any negative effect on the removal of the iron.

The initial pH of the double distilled water was 6.02 which was due to dissolved $CO_2$. The pH of iron ion solutions in the distilled water in the presence of iron ion was found to be lower than 6 which can be attributted to hydrolysis of $FeSO_4$. Similarly, the initial pH of the groundwater was 7.44, which also decreased slightly on addition of iron ion. As expected, the pH increased with increasing the dose of $KHCO_3$ and decreased with increase in the initial iron concentration. The final pH with initial iron concentrations from 2 to 100 mg/L was in the ranges of 6.20 to 8.40 and 7.30 to 8.50 for distilled water and the groundwater, respectively. The increments in the pH after treatment from its initial value slightly decreased with increase in the initial iron ion concentration. This is because, more hydroxide ions are used up in precipitating iron ion as goethite or ferrihydrite with higher initial iron ion concentration[286]. The results indicate that a dose of 10-50 mg/L of $KHCO_3$ and a residence time of 2 h seem to be quite sufficient for removal of iron from a level 2 to 20 mg/L from groundwater retaining the pH within acceptable range for drinking water.

### *3.1.1.13 Minimum dose of $KHCO_3$ required for removal of iron to 0.3 mg/L from different initial concentration of iron*

It can be seen from the Figure 3.8 that there is a correlation between the iron ion removal and the final pH. The minimum required doses for achieving an iron ion removal from distilled water and groundwater, from 2 to 20 mg/L initial iron ion to 0.3 mg/L, corresponded to final pH ranges of 6.88 to 7.62 and 7.61 to 7.72, respectively.

The minimum dose required to bring iron ion to below 0.3 mg/L increased with the initial iron ion concentration in both disttilled water as well as in groundwater as can be seen from Figure 3.9. The figure also shows that the final pH showed a slight nearly linear decrease with increase in the initial iron ion in the case of groundwater. The same trend was observed in case of distilled water except that the final pH corresponding to 2 mg/L of initial iron ion was considerably low.

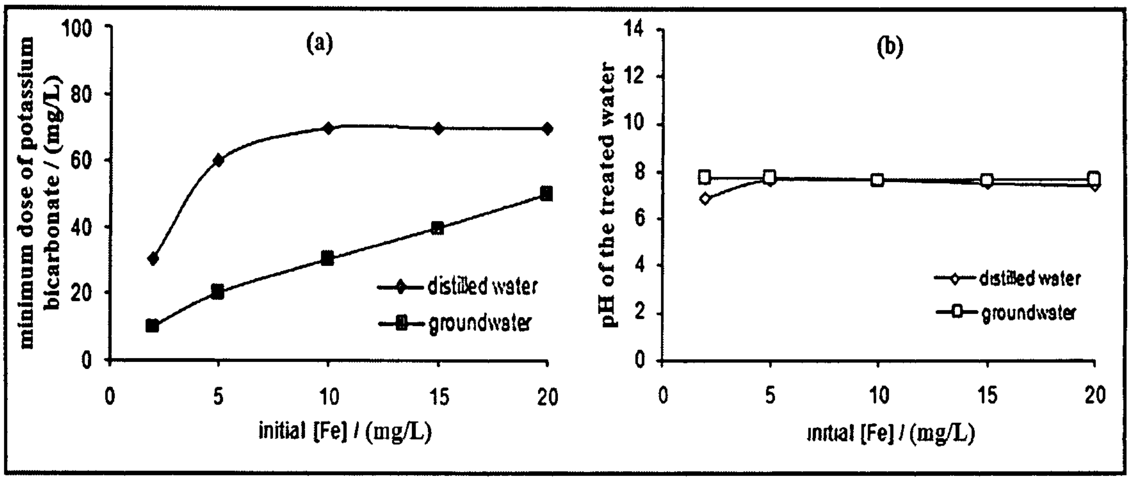

**Figure 3.9.** The minimum dose of potassium bicarbonate in mg/L required to bring iron to below 0.3mg/L from initial iron concentration of 2-20 mg/L and pH of the treated water in both distilled as well as in groundwater.

### *3.1.1.14 General remarks on effect of residence time and dose*

The effects of residence time on removal of iron by bicarbonate and carbonate salts of Na and K and banana ash and their binary mixtures can be seen in Figure 3.1-3.7. It has been observed that the most of the iron removal takes place within first half an hour and then the removal continued to increase slowly thereafter. Though the removal appears to improve a little more beyond 2 h, we have confined our study to a maximum residence time of 2 h considering practicality of the technique.

The effect of varying the dose of banana ash, carbonate and bicarbonate salts of Na and K and also their 1:1 mixtures on iron removal and final pH of the water can be seen in Figure 3.1-3.7. The doses of ash and salts were varied between 2 and 500 mg/L. One can see from the figures that even without addition of ash or/and salts the concentration of Fe decreased from 20 mg/L to about 17 mg/L, which can be attributed to removal of iron due to aerial oxidation alone. The dose of salts and ash has an influence on the extent of iron precipitation. The final pH of water has been found to increase with the increase in the quantity of the material or salts added. Although no health-based guideline value was proposed for pH in the guideline of WHO[34], it is one of the most important operational water quality parameters, the acceptable maximum pH limit for public water supply is considered as 8.5[339]. The recommended upper pH limit in India is also 8.5[346]. The results indicate that a dose of 10-50 mg/L of $KHCO_3$ and a residence time of 2 h is sufficient for removal of iron from a level 2-20 mg/L of groundwater retaining the pH within acceptable range for drinking water.

### *3.1.2 Analysis of iron ion precipitate*

A characterization of the precipitate of iron ion formed after treatment using different tools, presented below, will help in understanding the observed iron ion removal in the present experiments.

#### *3.1.2.1 XRD analysis*

From the XRD analysis (Figure 3.10a, b), distinct difference has been observed between the precipitants obtained by using bicarbonate salts and carbonate salts.

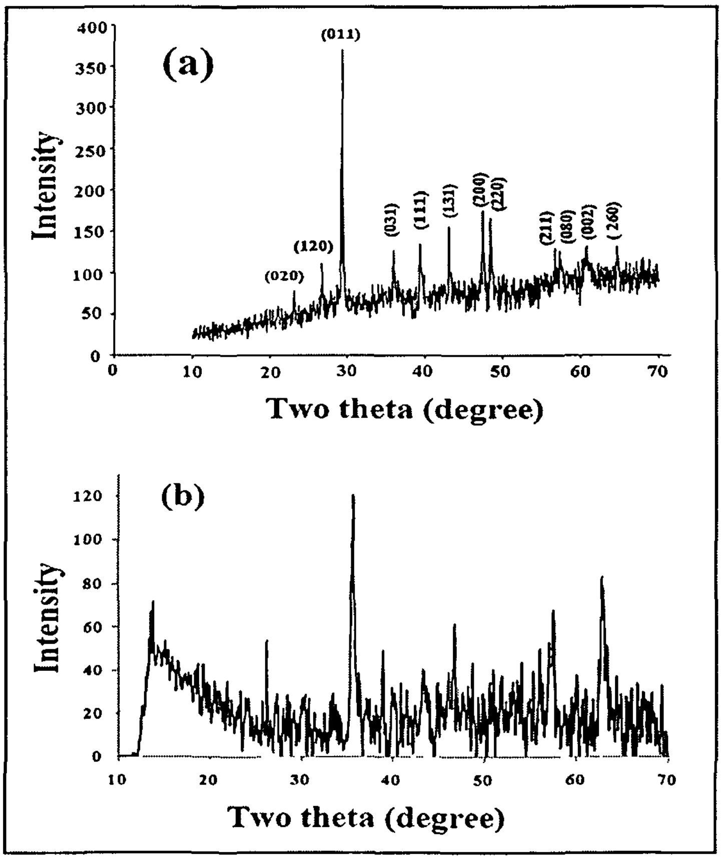

**Figure 3.10.** XRD of the precipitate formed after treatment with (a) bicarbonate salts in the pH range 7-8 (b) carbonate salts in the pH range 9-10.

The precipitate obtained with bicarbonate salts (Figure 3.10a) has the characteristic peaks at 23°, 26.7°, 29.4°, 36°, 39.4°, 43.1°, 47.5°, 48.45°, 56.7°, 58°, 60° and 65° matching the planes (020), (120), (011), (031), (111), (131), (200), (220), (211), (080), (002) and (260), respectively. This resembles of orthorhombic crystal structure of iron oxyhydroxide or goethite [FeO(OH)] [Ref. no- PCPDFWIN -74-1877, Calculated from ICSD using

POWD-12++, (1997)][347]. This clearly indicates a dominant presence of goethite in the precipitate.

On the other hand, the precipitate obtained after the treatment with carbonate salts (Figure 3.10b) has the characteristic 2θ values of 13.9°, 26.3°, 36.1°, 38°, 47°, 58°, 64° matching the corresponding peaks of ferric hydroxide [$Fe(OH)_3$] [Ref. no- PCPDFWIN - 38-0032][348]. This indicates dominant presence of $Fe(OH)_3$ in the precipitate after the treatment with the carbonate salts.

### *3.1.2.2 FTIR analysis*

Figure 3.11 (a & b) shows the FTIR spectrum of the precipitates obtained with bicarbonate salts (pH= 7-8) and carbonate salts (pH= 9-10), respectively.

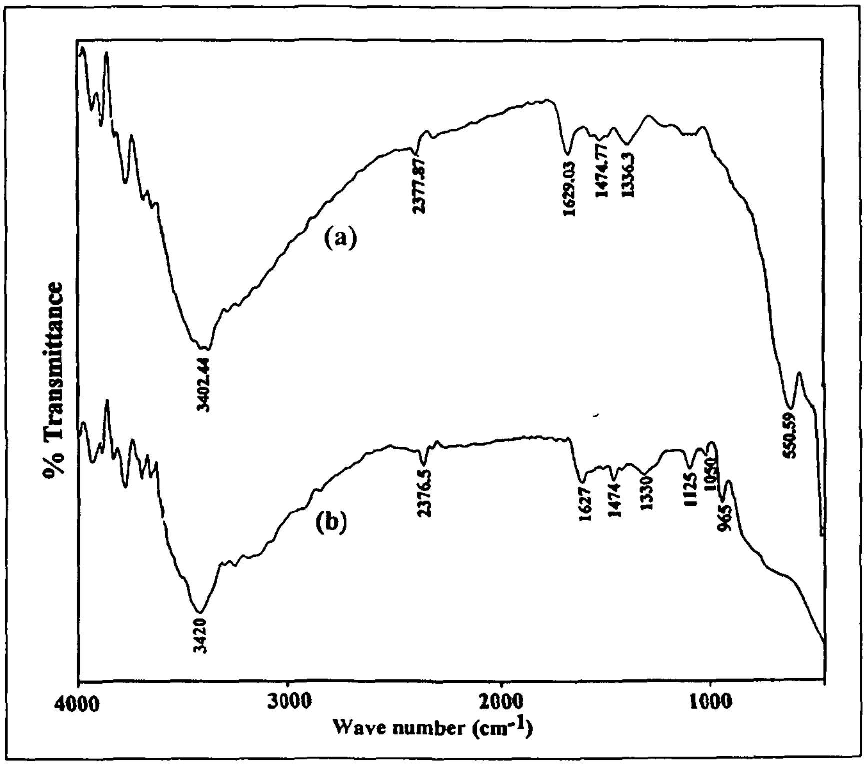

**Figure 3.11.** FTIR spectra of the precipitate formed after treatment by (a) bicarbonate salts in the pH range 7-8 (b) carbonate salts in the pH range 9-10.

In Figure 3.11a, the absorption band at 3418 $cm^{-1}$ indicates O-H stretching. The band at 1629 $cm^{-1}$ may be attributed to bending of HOH [349, 350]. The absorption band for δ (OH) was obtained at 1474 $cm^{-1}$ & 1336 $cm^{-1}$. These bands together with an absorption band at 550 $cm^{-1}$, indicating the presence of Fe-O bond, confirm the formation of goethite [351, 352]

On the other hand, with the carbonate salts, three peaks at 1125, 1050, and 976 $cm^{-1}$ corresponding to the bending vibration of the (Fe-OH) group have been found in the precipitate (Figure 3.11b). These peaks indicate the presence of ferric hydroxide in the precipitate obtained with the carbonate salt[352, 353].

### *3.1.2.3 SEM-EDS analysis*

The SEM-EDS images of the precipitate obtained with $KHCO_3$ are presented in Figure 3.12. From the SEM micrograph (Figure 3.12a) the larger-sized fraction of these precipitates showed irregularly shaped crystallized particles. The particles were randomly aggregated, and rough surfaces were observed. The EDS analysis showed the presence of K and significant quantities of Fe in the precipitant (Figure 3.12b).

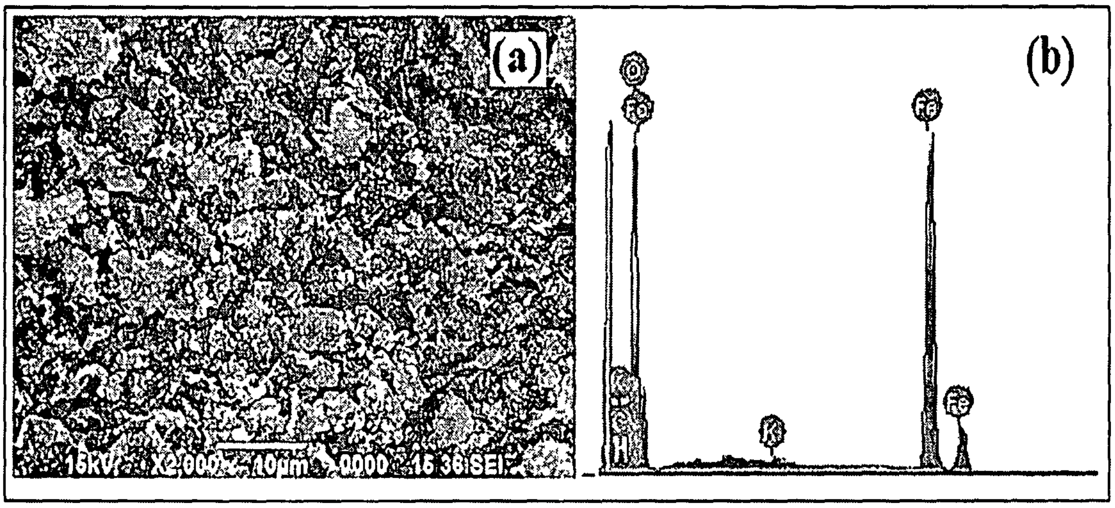

Figure 3.12. SEM-EDS of the precipitate formed after treatment by bicarbonate salts.

### *3.1.2.4 About slower iron ion removal by bicarbonates*

The analysis of the precipitate in case of bicarbonate salt reveals it to be predominantly goethite. Precipitation of iron ion as ferrihydrite to a greater extent in the presence of the carbonates and banana ash than that in the presence of bicarbonates may be responsible for comparatively faster but lower iron ion removal in the cases of the carbonates and the ash than that in the case of the bicarbonates.

## 3.1.3 Cost-benefit and suitability analysis

The recurring cost of $KHCO_3$ per liter of water has been estimated on the basis of the minimum quantity of $KHCO_3$ required for bringing down the iron ion concentration to below 0.3 mg/L taking the retail price of $KHCO_3$ as US$ 2 per kg. The recurring costs per liter for initial iron ion concentrations of 2 and 20 mg/L have estimated to be approximately US$ 0.00001 and 0.0001 (or INR 0.00045 and 0.0045), respectively. The recurring cost of the present method of iron ion removal using $KHCO_3$ is quite competitive compared to that of other existing methods such as ion-exchange method, electrocoagulation, oxidation with oxidizing agents including chlorine and potassium permanganate, supercritical fluid extractions, etc.

The treatment with bicarbonate salts of Na and K does not affect colour, odor, and taste of the water. The process does not need electrical and thermal power or pressure except for plumbing. The process can give satisfactory iron ion removal within 1-2 h without needing any post-treatment including pH correction as the materials used are common and nontoxic.

### 3.1.4 Summary

The following conclusions have been drawn from the present study:

- The carbonate and bicarbonate salts of sodium and potassium, banana ash and their binary mixtures are effective in the removal of iron ion from water.
- The bicarbonate salts especially that of potassium, have been found to be very effective for removal of iron ion, which also retains the pH of water in the acceptable range for drinking.
- Upto 99-100% removal of iron ion from initial 2-20 mg/L can be achieved with a quantity of $KHCO_3$ as low as 70-100 mg/L within 1-2 h retaining the pH between 6.8 and 7.7.
- The removal rate has been found to improve with increase in the amount of the dose and residence time.
- The bicarbonates remove iron ion mostly as goethite.
- The removal becomes poor in presence of the carbonate salts and the ash because of formation of ferrihydrite.
- Given the high efficiency, low-cost and simplicity of application, the bicarbonate salts of Na and K have potential for application in removal of iron ion from groundwater.

## 3.2 pH-conditioning for simultaneous removal of arsenate and iron

We have described in the previous section 3.1 about iron ion removal efficiency of bicarbonate and carbonate salts of sodium and potassium, banana ash and found that the bicarbonate salts are more efficient than the carbonate salts and the ash. While the iron ion removal efficiency was found to increase in the order: banana ash < $CO_3^{2-}$ < $HCO_3^-$, the K-salts were found to be slightly more efficient than the corresponding Na- salts. The better iron ion removal by the bicarbonate salts was attributed to lower pH of the water and the resulting lower solubility of the iron oxyhydroxide prevailing in the presence of the bicarbonate salts. Since arsenic is removed along with removal of iron ions, we intended to carry out a systematic study on simultaneous removal of arsenate and ferrous ion from water in the presence of different pH conditioners, *viz.*, banana ash, lime, the carbonates and the bicarbonates of sodium and potassium and their binary mixtures. Banana ash has been included in the study because it is used in the removal of arsenic and iron[286, 354].

### 3.2.1 Batch experiments

The batch tests for simultaneous removal of arsenic and iron from water were carried out by following a similar procedure as in case of iron removal. Different amount of pH-conditioners were added to the arsenic and iron containing water in Erlenmeyer flasks. The efficiency of the pH conditioners in precipitating arsenate with iron ions were studied as a function of the dose. The results of the batch experiments are discussed here.

#### *3.2.1.1 Removal with individual pH conditioners*

Each of the pH conditioners enhanced the simultaneous removal of both iron and arsenate ions to different extents. The results of addition of lime, banana ash, carbonate and bicarbonate salts of Na and K and their 1:1 binary mixtures as pH-conditioner on arsenate and iron ion removal from initial concentrations of 0.25 mg/L for arsenic and 20 mg/L for iron are shown in Table 3.9-3.16 and Figure 3.13-3.19. Though the iron ions are removed to some extents even in the absence of any pH conditioner, the removal is significantly improved on addition of the pH conditioners. On the other hand, the arsenate ions are hardly removed in the absence of the pH conditioners due to predominance of the

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*This work has been published in **Process Saf. Environ. Prot.** 91,405-414, 2013* less adsorbed $H_2AsO_4^-$ forms at the prevailing low pH (≈5.72) caused by the slightly acidic ferrous salt[25]. Arsenate is removed well even at very low concentrations (≈2 mg/L) of the pH conditioners due to increase in the easily adsorbed $HAsO_4^{2-}$ ions with increase in the pH to a favourable range. The removal of iron ion increases on increasing the dose of the pH conditioners but the higher doses lowered the arsenate removal. The higher doses also increased the pH of the water to different extents. The precipitates of iron subsequently remove the arsenate ions also. It appears from the figures that a competition of the $OH^-$ ions with the arsenate ion for adsorption on iron precipitate plays a major role in the arsenate removal in the present method. Thus, the simultaneous removal of iron and arsenate ions is facilitated by the pH conditioners in a complex manner. Interestingly, the arsenic removal to below the guideline value of WHO can be achieved with the final pH of the water below 8.5, the upper acceptable limit. The bicarbonate salts leave the water pH within the acceptable range of drinking water at all concentrations but an excess of the carbonate salts and the ash makes the water pH higher than the acceptable range for drinking. The effects of these materials on the removal of iron and arsenate ions are discussed in details below.

### *3.2.1.2 Simultaneous removal of arsenic and iron with lime and banana ash*

The results of removal of arsenate along with residual iron and final pH after treatment with lime are shown in Table 3.9 and Figure 3.13.

**Table 3.9.** Remaining [As], [Fe] and pH of the water after treatment by lime and banana ash from distilled water containing 0.25 mg/L and 20 mg/L of initial [As] and [Fe] respectively.

| Wt. of salt / (mg/L) | Remaining [Fe], [As] in mg/L & pH with CaO | | | Remaining [Fe], [As] in mg/L & pH with banana ash | | |
|---|---|---|---|---|---|---|
| | [Fe] | [As] | pH | [Fe] | [As] | pH |
| 0 | 17.18 | 0.249 | 5.7 | 16.78 | 0.249 | 5.7 |
| 2 | 15.48 | 0.006 | 5.9 | 8.82 | 0.001 | 6.4 |
| 10 | 14.67 | 0.005 | 6.1 | 7.67 | 0.002 | 6.7 |
| 40 | 6.18 | 0.005 | 10.1 | 4.51 | 0.005 | 7.5 |
| 80 | 2.09 | 0.005 | 11.8 | 2.19 | 0.019 | 8.8 |
| 100 | 1.48 | 0.005 | 12.1 | 1.78 | 0.025 | 9.3 |
| 200 | 0.56 | 0.004 | 12.3 | 1.28 | 0.043 | 9.8 |
| 300 | 0.29 | 0.004 | 12.4 | 0.91 | 0.048 | 9.8 |
| 400 | 0.14 | 0.004 | 12.7 | 0.28 | 0.052 | 9.9 |
| 500 | 0.11 | 0.004 | 12.8 | 0.11 | 0.089 | 9.9 |

Error limits: Δ[As] = ±0.0004 mg/L, Δ[Fe] = ±0.05 mg/L and ΔpH = ±0.1

Arsenate is removed to below 0.01 mg/L from water containing 0.25 mg/L of arsenate and 20 mg/L ferrous ion by adding lime of very small quantities, i.e., 2 mg/L and above (Table 3.9)[38].

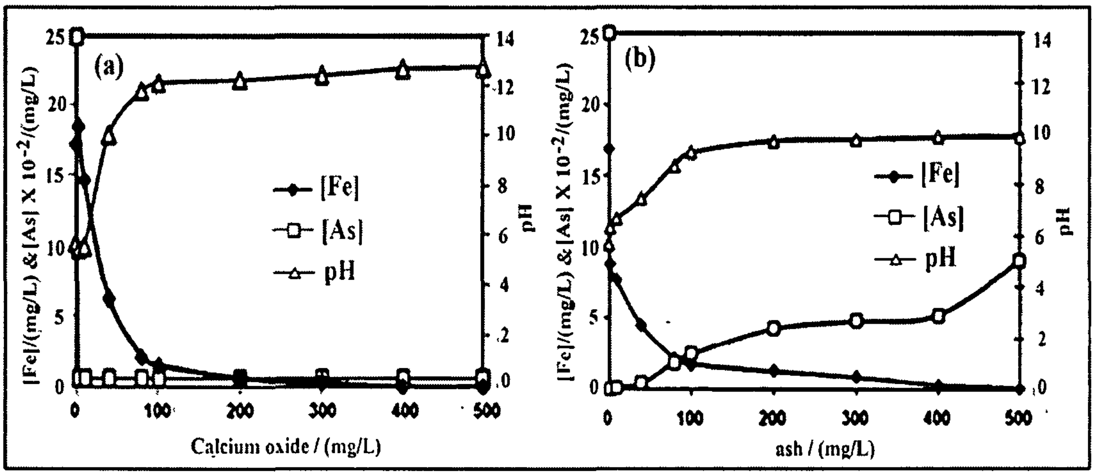

**Figure 3.13.** Remaining [Fe], [As] in mg/L and pH *vs.* amount of pH-conditioners in mg/L lime (a), banana ash (b) of distilled water at residence time of 2 h with initial [Fe(II)]= 20 mg/L and [As(V)]= 0.25 mg/L.

However, the removal of iron was poor at low dosage of lime which improved to 0.3 mg/L above 200 mg/L of lime. Though higher dose of lime shows satisfactory simultaneous removal of arsenate and iron ion, it makes the pH greater than 12 which is far above the acceptable range of pH (pH 6.5-8.5) for drinking water[14, 34]. The method for controlling increased pH after removal of iron and arsenic using lime may not cost much but this will add one more step in the treatment. Moreover, one has to add more chemicals for the pH correction. Thus, the requirement of post-treatment pH correction of the strongly alkaline water makes use of lime less preferable even though lime costs the minimum among all pH conditioners.

From the Figure 3.13b, it can be seen that on addition of banana ash, both the iron and arsenate are removed considerably from initial concentrations of 20 mg/L and 0.25 mg/L, respectively. We have examined the effect of dose of banana ash from 2 mg/L to 500 mg/L on the removal of arsenate and iron ion. A small dose of 2 mg/L of banana ash removed arsenate ion from an initial 0.25 mg/L to an undetectable level, but removed iron ion to 9 mg/L only. With the doses of banana ash between 2-40 mg/L the final pH was in the range of 6.0-8.0 and the arsenate ion was removed to undetectable level with a residual iron concentration of about 4.5 mg/L. The removal of iron ion improved with the increase in the dose of banana ash and with about 400 mg/L of the ash the iron ions were removed to 0.3 mg/L. However, higher doses of the ash increased the pH of the treated water to above 9.5 which is above the acceptable limit for drinking [333]. On the other hand, as reported earlier[339], the removal of arsenate ion decreased when the pH increased over 8.5. The high final pH observed with high dose of the ash can be attributed to the presence of a small amount of $K_2O$ along with $K_2CO_3$ in the ash. In order to avoid the presence of $K_2O$, the arsenic and iron ion removal abilities of pure carbonates of Na and K have been investigated.

### *3.2.1.3 Simultaneous removal of arsenic and iron with carbonate salts of Na and K*

Table 3.10 and Figure 3.14 show the results of arsenate and iron ion removal with 2 to 500 mg/L of the carbonate salts of Na and K with residence time of 2 h. There were only slight improvements in simultaneous removal of arsenate and iron ions with the carbonate salts, which is indicated by a decrease in the common areas under the curves for remaining arsenate and iron ions *vs.* the quantity of the pH-conditioner.

**Table 3.10.** Remaining [As], [Fe] and pH of the water after treatment by carbonate salts of K and Na from distilled water containing 0.25 mg/L and 20 mg/L of initial [As] and [Fe] respectively.

| Wt. of salt / (mg/L) | Remaining [Fe], [As] in mg/L & pH with $K_2CO_3$ | | | Remaining [Fe], [As] in mg/L & pH with $Na_2CO_3$ | | |
|---|---|---|---|---|---|---|
| | [Fe] | [As] | pH | [Fe] | [As] | pH |
| 0 | 16.78 | 0.249 | 5.7 | 16.18 | 0.249 | 5.7 |
| 2 | 7.56 | 0.001 | 6.3 | 7.38 | 0.001 | 6.3 |
| 10 | 5.11 | 0.001 | 6.5 | 5.48 | 0.004 | 6.6 |
| 40 | 3.47 | 0.002 | 7.0 | 3.78 | 0.005 | 7.2 |
| 80 | 1.48 | 0.009 | 8.5 | 1.81 | 0.025 | 8.6 |
| 100 | 0.92 | 0.019 | 8.7 | 0.98 | 0.042 | 8.7 |
| 200 | 0.68 | 0.022 | 8.7 | 0.92 | 0.051 | 8.8 |
| 300 | 0.28 | 0.025 | 8.9 | 0.48 | 0.068 | 9.0 |
| 400 | 0.14 | 0.048 | 9.2 | 0.21 | 0.091 | 9.2 |
| 500 | 0.11 | 0.051 | 9.7 | 0.12 | 0.101 | 9.6 |

Error limits: $\Delta[As] = \pm 0.0004$ mg/L, $\Delta[Fe] = \pm 0.05$ mg/L and $\Delta pH = \pm 0.1$

Though an arsenate removal to less than 0.01 mg/L could be achieved in the ranges of 2 to 60 mg/L of $K_2CO_3$ and 2 to 50 mg/L of $Na_2CO_3$, the simultaneous removal of iron ion is still unsatisfactory. With 60 mg/L of $K_2CO_3$ and 50 mg/L of $Na_2CO_3$, residual iron ions of 2.2 mg/L and 3.2 mg/L remained with the two salts, respectively. So, one needs to increase dose of salts to remove iron to <0.3 mg/L which increases the pH of the water resulting in poor removal of arsenate ion. Increase in the dose of carbonate salts however increases the pH of the water which results in the poor removal of arsenate ion. This prompted us to investigate the arsenate and iron ion removal with the bicarbonate salts of Na and K in an attempt to maintain the final pH in the acceptable range for drinking water.

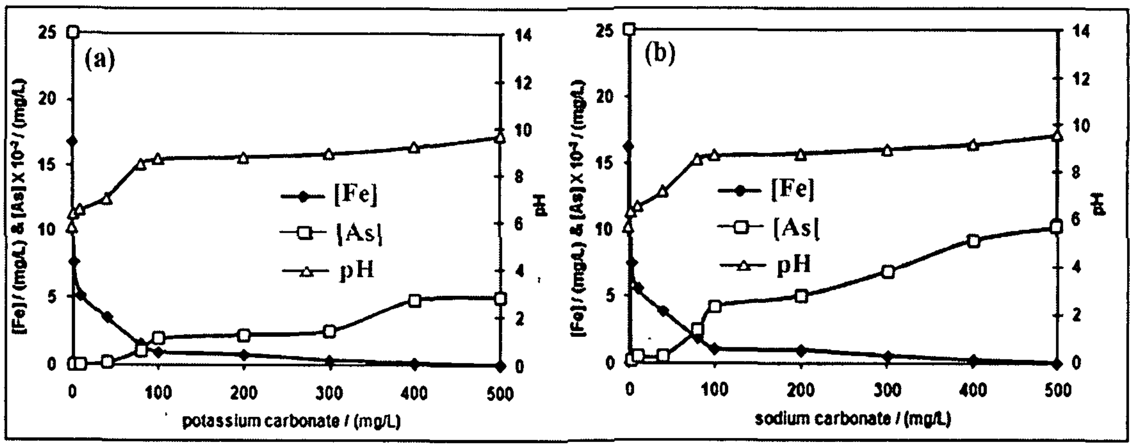

**Figure 3.14.** Plots of remaining [Fe] and [As] in mg/L *vs.* amount of carbonate salts of K (a) and Na (b) in mg/L of distilled water at residence time of 2h with initial [Fe(II)] = 20 mg/L and initial [As(V)] = 0.25 mg/L.

### *3.2.1.4 Simultaneous removal of arsenic and iron with bicarbonate salts of Na and K*

The results of arsenate and iron ion removal by $NaHCO_3$ and $KHCO_3$ are shown in Table 3.11 and Figure 3.15. The observed curves for the bicarbonate salts reveal that the arsenate as well as iron ion removal is far better with both of the bicarbonates than their corresponding carbonate salts. On the other hand, the final pHs obtained with the bicarbonate salts were lower than that of the carbonate salts of Na and K. In the case of $NaHCO_3$, 200 mg/L of the salt can remove arsenate and iron ion to <0.01 mg/L and <0.3 mg/L, respectively with a final pH ≈8.0. Whereas, in the case of $KHCO_3$, 80 mg/L of the salt can remove both the arsenate and iron ion to <0.01 mg/L and <0.3 mg/L, respectively, with final pH ≈7.5. Interestingly, with a dose of 100 mg/L of $KHCO_3$, both the ions are removed to undetectable levels with the final pH too remaining within the acceptable upper limit of 8.5. Thus, in terms of the dosage, $KHCO_3$ is the most efficient pH conditioner for simultaneous removal of iron and arsenate ion. It may also be noted that the cost of 80 mg/L of $KHCO_3$ is just US$ 0.16 per 1000 L of water. Moreover, 80 mg/L of $KHCO_3$ increases $[K^+]$ by only ≈31 mg/L which is not a matter of concern.

**Table 3.11.** Remaining [Fe], [As] and pH of the water after treatment by bicarbonate salts of Na and K from distilled water containing 0.25 mg/L and 20 mg/L of initial [As] and [Fe] respectively.

| Wt. of salt / (mg/L) | Remaining [Fe], [As] in mg/L & pH with $KHCO_3$ | | | Remaining [Fe], [As] in mg/L & pH with $NaHCO_3$ | | |
|---|---|---|---|---|---|---|
| | [Fe] | [As] | pH | [Fe] | [As] | pH |
| 0 | 16.81 | 0.249 | 5.7 | 16.47 | 0.249 | 5.7 |
| 2 | 10.19 | 0.001 | 6.2 | 12.21 | 0.001 | 6.3 |
| 10 | 9.67 | 0.001 | 6.4 | 10.78 | 0.002 | 6.7 |
| 40 | 4.09 | 0.005 | 6.8 | 4.47 | 0.005 | 7.1 |
| 80 | 0.29 | 0.005 | 7.5 | 2.97 | 0.005 | 7.6 |
| 100 | 0.11 | 0.005 | 7.9 | 1.45 | 0.005 | 7.8 |
| 200 | 0.09 | 0.005 | 8.1 | 0.27 | 0.009 | 8.4 |
| 300 | 0.08 | 0.009 | 8.5 | 0.11 | 0.009 | 8.6 |
| 400 | 0.06 | 0.011 | 8.6 | 0.07 | 0.023 | 8.9 |
| 500 | 0.06 | 0.013 | 8.7 | 0.07 | 0.024 | 8.9 |

Error limits: Δ[As]= ±0.0004 mg/L, Δ[Fe]= ±0.05 mg/L and ΔpH= ±0.1

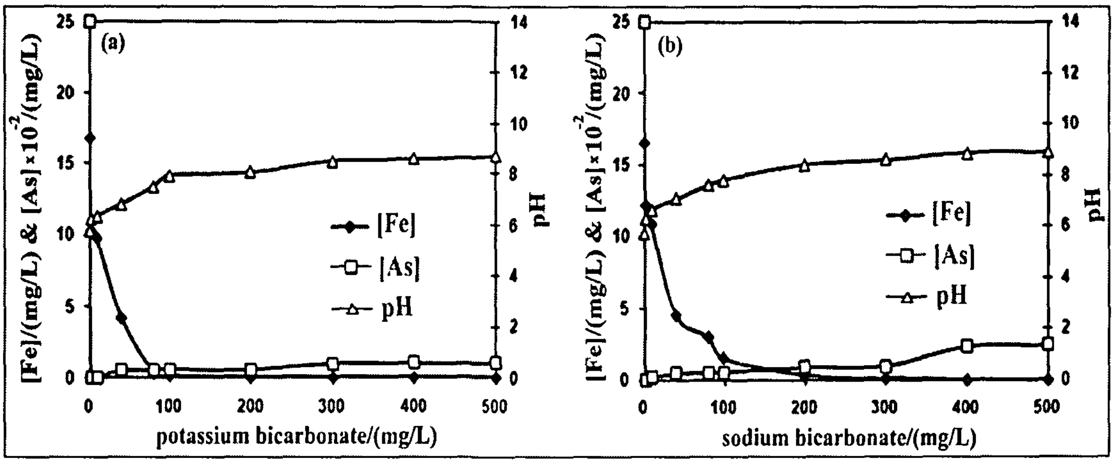

**Figure 3.15.** Plots of remaining [Fe] and [As] in mg/L *vs.* amount of bicarbonate salts of K (a) and Na (b) in mg/L of distilled water at residence time of 2 h with initial [Fe(II)] = 20 mg/L and initial [As(V)] = 0.25 mg/L.

The iron removal in the presence of arsenate ion has been found to be exactly similar with that in absence of arsenate ions also at high doses of the bicarbonate salts alone under otherwise similar conditions. However, at low doses of the bicarbonate salts, the iron removal in the presence of arsenate ion is less than that observed earlier in the absence of arsenate ion. The observed lower iron removal at low dosages of the bicarbonate salts in the presence of arsenate ions may be due to ionization of hydrogen arsenate releasing hydrogen ions which should slow down the iron removal. This effect is insignificant in the presence of more strongly basic materials like the ash, lime or the carbonate salts.

### *3.2.1.5 pH of the treated water*

pH is one of the most important parameters controlling the metal ion sorption process[355]. The initial pH of our experimental double distilled water was ≈6.00 due to dissolved $CO_2$. This pH is decreased on the addition of iron ion to ≈5.72 due to hydrolysis of $FeSO_4$. The final pH of the water after treatment with various pH-conditioners and their 1:1 binary mixtures are shown in Table 3.12 (a & b) and Figure 3.16.

In the present cases, the removal of As(V) increases with increase in the pH initially and then decreased markedly above pH of ≈7.5 as expected. While the initial increase, up to pH 7.5, is due to increase in ionization of the arsenate[356], the decrease in the arsenate removal at high dose, above pH 7.5, is due to increase in the concentration of $OH^-$, $HCO_3^-$ and $CO_3^{2-}$ ions which compete with arsenate ion for adsorption on iron precipitate[276]. The very good removal of arsenate with lime, which is independent of the pH, has been attributed to precipitation of calcium arsenate, $Ca_3(AsO_4)_2$[357].

**Table 3.12a.** pH of the water after treatment by bicarbonate and carbonate salts of K and Na, lime and ash alone.

| Wt. of salt / (mg/L) | pH of the treated water with bicarbonate and carbonate salts of sodium and potassium, ash and lime alone | | | | | |
|---|---|---|---|---|---|---|
| | CaO | Ash | $K_2CO_3$ | $Na_2CO_3$ | $KHCO_3$ | $NaHCO_3$ |
| 0 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 |
| 2 | 5.9 | 6.4 | 6.3 | 6.3 | 6.2 | 6.3 |
| 10 | 6.0 | 6.7 | 6.5 | 6.6 | 6.4 | 6.6 |
| 40 | 10.0 | 7.5 | 7.0 | 7.2 | 6.8 | 7.1 |
| 80 | 11.8 | 8.8 | 8.5 | 8.6 | 7.5 | 7.6 |
| 100 | 12.1 | 9.3 | 8.7 | 8.7 | 7.9 | 7.8 |
| 200 | 12.3 | 9.8 | 8.7 | 8.8 | 8.1 | 8.4 |
| 300 | 12.4 | 9.8 | 8.9 | 9.0 | 8.5 | 8.6 |
| 400 | 12.7 | 9.9 | 9.2 | 9.2 | 8.6 | 8.9 |
| 500 | 12.8 | 9.9 | 9.7 | 9.6 | 8.7 | 8.9 |

Error limit: ΔpH= ±0.1

**Table 3.12b.** pH of the water after treatment by 1:1 binary mixture of bicarbonate and carbonate salts of K and Na, and ash.

| Wt. of 1:1 salt mixture / (mg/L) | pH of the treated water with bicarbonate and carbonate salts of sodium and potassium, ash and lime alone | | | | | | |
|---|---|---|---|---|---|---|---|
| | $KHCO_3$: Ash | $NaHCO_3$: Ash | $KHCO_3$: $NaHCO_3$ | $KHCO_3$: $K_2CO_3$ | $NaHCO_3$: $Na_2CO_3$ | $NaHCO_3$: $K_2CO_3$ | $KHCO_3$: $Na_2CO_3$ |
| 0 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 |
| 2 | 6.4 | 6.4 | 6.2 | 6.3 | 6.4 | 6.3 | 6.3 |
| 10 | 6.6 | 6.6 | 6.3 | 6.5 | 6.6 | 6.5 | 6.5 |
| 40 | 6.9 | 7.0 | 6.9 | 7.1 | 7.2 | 7.2 | 7.1 |
| 80 | 7.9 | 8.3 | 7.7 | 8.3 | 8.4 | 8.2 | 8.3 |
| 100 | 8.6 | 8.5 | 7.9 | 8.6 | 8.7 | 8.5 | 8.6 |
| 200 | 8.7 | 8.8 | 8.5 | 8.8 | 8.9 | 8.6 | 8.8 |
| 300 | 9.1 | 9.1 | 8.6 | 8.9 | 9.1 | 9.0 | 8.9 |
| 400 | 9.3 | 9.3 | 8.6 | 9.2 | 9.3 | 9.2 | 9.2 |
| 500 | 9.4 | 9.5 | 8.7 | 9.5 | 9.6 | 9.6 | 9.5 |

Error limit: ΔpH= ±0.1

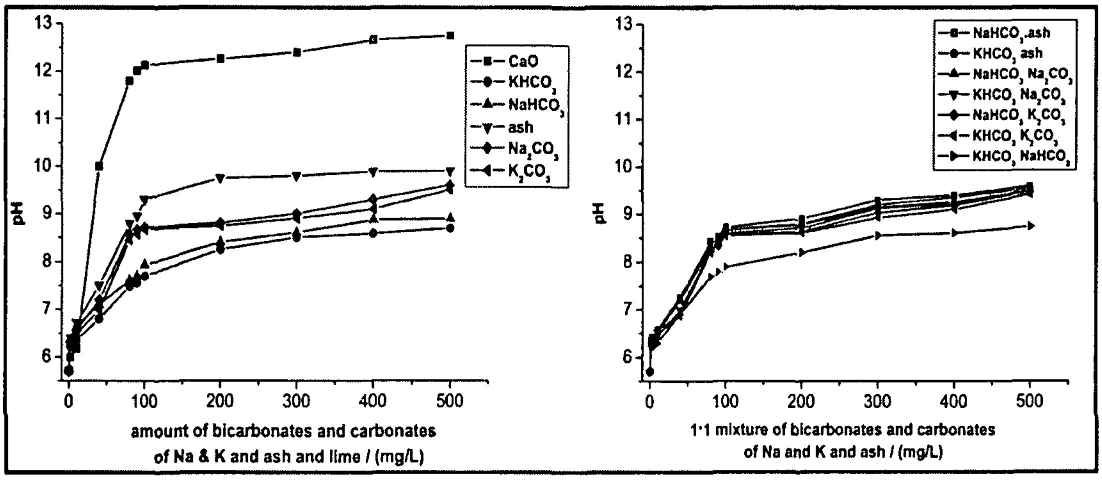

**Figure 3.16.** pH of the filtered water after treatment (a) with bicarbonate and carbonate salts of Na and K, ash and lime alone (b) with their 1:1 mixture.

### *3.2.1.6 Simultaneous removal of arsenate and iron with 1:1 binary mixtures of bicarbonate salts with the ash*

The effect of 1:1 weight by weight mixture of ash with bicarbonate salts of Na and K on removal of iron and arsenate ion was shown in Table 3.13 and Figure 3.17. It can be seen that the mixtures of $NaHCO_3$ and $KHCO_3$ with the ash showed lower iron ion removal as well as arsenate removal than that of the individual bicarbonate salts alone.

This can be attributed to higher pH in presence of the mixtures than that in presence of the individual bicarbonate salts. Almost similar iron removal was observed in the presence of the mixtures of the binary mixtures of the bicarbonate salts with the ash in the presence and the absence of the arsenate ions under otherwise similar conditions as discussed earlier in section 3.1.

**Table 3.13.** Remaining [As], [Fe] and pH of the water after treatment by 1:1 binary mixture of bicarbonate salts of K and Na and banana ash from distilled water containing 0.25 mg/L and 20 mg/L of initial [As] and [Fe] respectively.

| Wt. of 1:1 binary salt mixture/ (mg/L) | Remaining [Fe], [As] in mg/L & pH with $KHCO_3$:ash | | | Remaining [Fe], [As] in mg/L & pH with $NaHCO_3$:ash | | |
|---|---|---|---|---|---|---|
| | [Fe] | [As] | pH | [Fe] | [As] | pH |
| 0 | 16.78 | 0.249 | 5.7 | 17.16 | 0.249 | 5.7 |
| 2 | 11.81 | 0.001 | 6.4 | 11.56 | 0.001 | 6.4 |
| 10 | 10.39 | 0.001 | 6.6 | 10.78 | 0.002 | 6.6 |
| 40 | 2.11 | 0.003 | 6.9 | 3.67 | 0.005 | 7.0 |
| 80 | 1.17 | 0.005 | 7.9 | 2.08 | 0.009 | 8.3 |
| 100 | 0.78 | 0.009 | 8.6 | 1.17 | 0.011 | 8.5 |
| 200 | 0.68 | 0.011 | 8.7 | 0.89 | 0.019 | 8.8 |
| 300 | 0.45 | 0.012 | 9.1 | 0.38 | 0.025 | 9.1 |
| 400 | 0.14 | 0.012 | 9.3 | 0.14 | 0.033 | 9.3 |
| 500 | 0.11 | 0.013 | 9.4 | 0.11 | 0.049 | 9.5 |

Error limits: Δ[As]= ±0.0004 mg/L, Δ[Fe]= ±0.05 mg/L and ΔpH= ±0.1

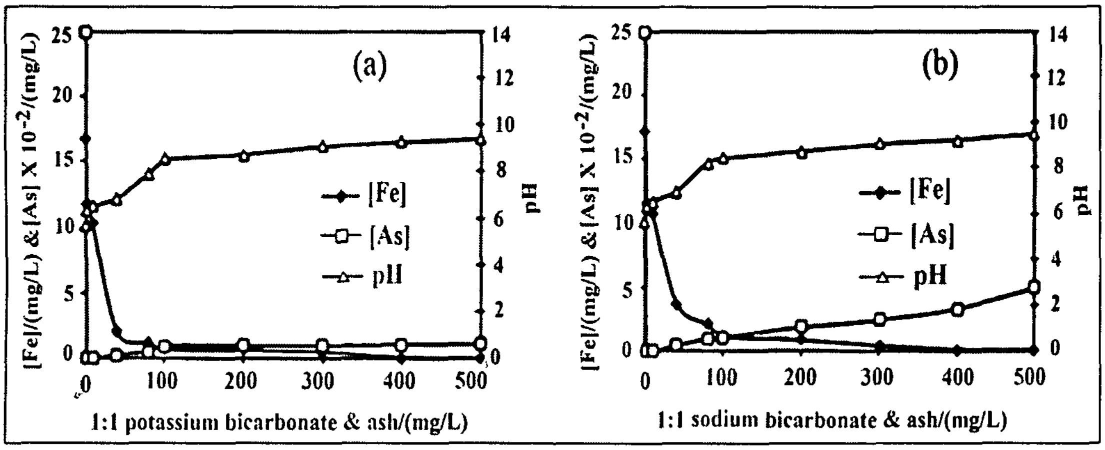

**Figure 3.17.** Plots of remaining [Fe] and [As] in mg/L *vs.* amount of 1:1 mixture of bicarbonates of K and Na with ash in mg/L of distilled water at residence time of 2 h with initial [Fe(II)] = 20 mg/L and [As(V)] = 0.25 mg/L.

### *3.2.1.7 Simultaneous removal of arsenate and iron using 1:1 binary mixtures of bicarbonates and carbonates of Na and K*

Removal of iron and arsenate ion by 1:1 mixtures of the bicarbonate salts and carbonate salts of Na and K has also been studied. The results were summarized in Table 3.14 and 3.15. The plots of remaining [Fe], [As] and final pH of the water after treatment with these mixtures is shown in Figure 3.18.

**Table 3.14.** Remaining [Fe], [As] and pH of the water after treatment by 1:1 binary mixture of potassium bicarbonate and carbonates of K and Na from distilled water containing 0.25 mg/L and 20 mg/L of initial [As] and [Fe] respectively.

| Wt. of 1:1 binary salt mixture/ (mg/L) | Remaining [Fe], [As] in mg/L & pH with $KHCO_3$:$K_2CO_3$ | | | Remaining [Fe], [As] in mg/L & pH with $KHCO_3$:$Na_2CO_3$ | | |
|---|---|---|---|---|---|---|
| | [Fe] | [As] | pH | [Fe] | [As] | pH |
| 0 | 16.89 | 0.249 | 5.7 | 16.89 | 0.249 | 5.7 |
| 2 | 10.21 | 0.001 | 6.3 | 10.38 | 0.001 | 6.3 |
| 10 | 6.12 | 0.001 | 6.5 | 7.99 | 0.002 | 6.5 |
| 40 | 1.97 | 0.005 | 7.1 | 3.11 | 0.005 | 7.1 |
| 80 | 0.94 | 0.011 | 8.2 | 1.08 | 0.011 | 8.3 |
| 100 | 0.48 | 0.024 | 8.5 | 0.58 | 0.024 | 8.6 |
| 200 | 0.21 | 0.025 | 8.6 | 0.38 | 0.025 | 8.8 |
| 300 | 0.14 | 0.032 | 8.9 | 0.22 | 0.032 | 8.9 |
| 400 | 0.11 | 0.046 | 9.0 | 0.14 | 0.046 | 9.2 |
| 500 | 0.09 | 0.049 | 9.5 | 0.10 | 0.049 | 9.5 |

Error limits: Δ[As]= ±0.0004 mg/L, Δ[Fe]= ±0.05 mg/L and ΔpH= ±0.1

**Table 3.15.** Remaining [Fe], [As] and pH of the water after treatment by 1:1 binary mixture of sodium bicarbonate and carbonates of Na and K from distilled water containing 0.25 mg/L and 20 mg/L of initial [As] and [Fe] respectively.

| Wt. of 1:1 binary salt mixture/ (mg/L) | Remaining [Fe], [As] in mg/L & pH with $NaHCO_3$:$Na_2CO_3$ | | | Remaining [Fe], [As] in mg/L & pH with $NaHCO_3$:$K_2CO_3$ | | |
|---|---|---|---|---|---|---|
| | [Fe] | [As] | pH | [Fe] | [As] | pH |
| 0 | 16.88 | 0.249 | 5.7 | 16.89 | 0.249 | 5.7 |
| 2 | 10.45 | 0.001 | 6.3 | 10.46 | 0.001 | 6.4 |
| 10 | 8.25 | 0.001 | 6.5 | 8.21 | 0.002 | 6.6 |
| 40 | 3.21 | 0.008 | 7.2 | 3.36 | 0.005 | 7.2 |
| 80 | 1.92 | 0.015 | 8.2 | 1.78 | 0.015 | 8.4 |
| 100 | 1.08 | 0.022 | 8.5 | 0.89 | 0.028 | 8.7 |
| 200 | 0.92 | 0.024 | 8.6 | 0.69 | 0.031 | 8.9 |
| 300 | 0.71 | 0.035 | 9.0 | 0.28 | 0.045 | 9.1 |
| 400 | 0.14 | 0.044 | 9.2 | 0.14 | 0.048 | 9.3 |
| 500 | 0.09 | 0.051 | 9.6 | 0.11 | 0. 048 | 9.6 |

Error limits: Δ[As]= ±0.0004 mg/L, Δ[Fe]= ±0.05 mg/L and ΔpH= ±0.1

Here also, the removal of both arsenate and iron ions were found to be lesser than that of bicarbonate salts alone due to higher pH in presence of the mixtures than that in presence of the individual bicarbonate salts.

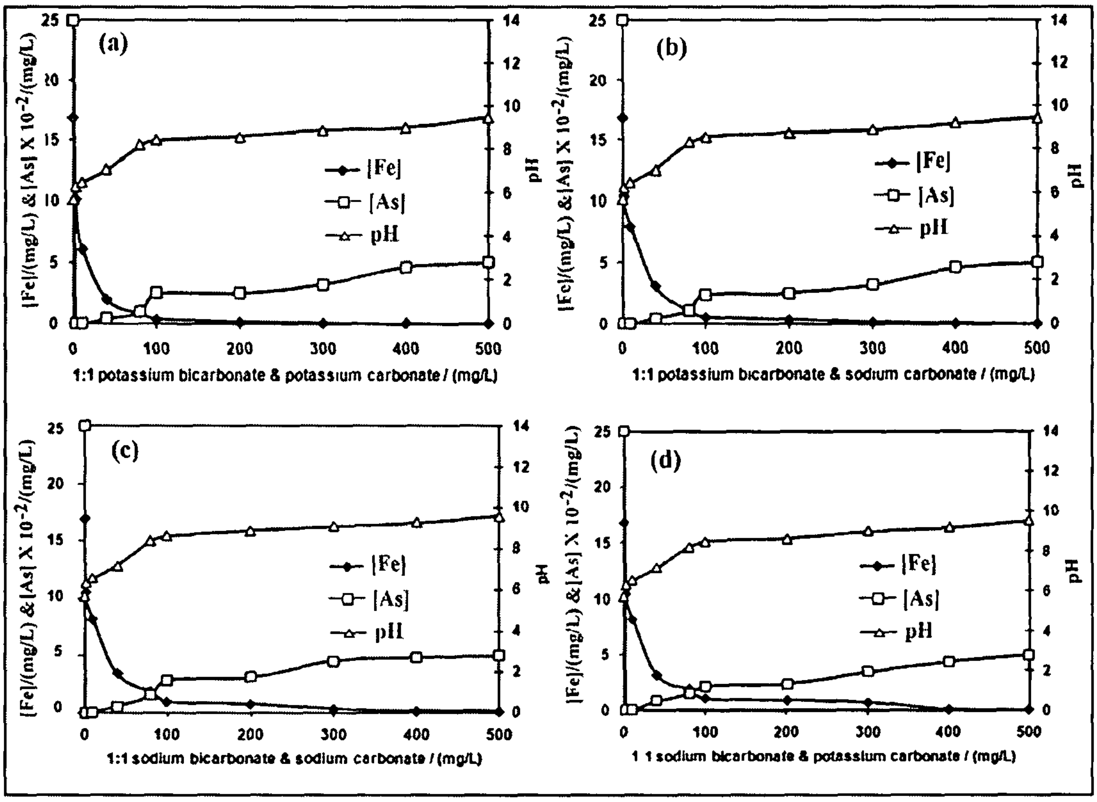

**Figure 3.18.** Remaining [As], [Fe] in mg/L and pH of the water after treatment by 1:1 binary mixture of bicarbonates and carbonates of Na and K of distilled water containing 0.25 mg/L and 20 mg/L of initial [As] and [Fe] respectively.

### *3.2.1.8 Simultaneous removal of arsenate and iron using 1:1 binary mixtures of bicarbonates of Na and K*

The results obtained after treatment of arsenic and iron with 1:1 binary mixture of bicarbonate salts of Na and K have been shown in Table 3.16 as well as Figure 3.19. Among all the combinations, the mixture of the bicarbonate salts of Na and K showed the best performance, 70 mg/L of which removed both iron and arsenate ion to undetectable levels with a fine final pH of 7.5.

The simultaneous removal of iron and arsenate ion by the binary mixtures of the carbonate and bicarbonate salts of Na and K, after a constant residence time of 2 h was found to improve in the order: ($NaHCO_3$+$Na_2CO_3$) < ($NaHCO_3$+$K_2CO_3$) < ($KHCO_3$+$Na_2CO_3$) < ($KHCO_3$+$K_2CO_3$) < ($NaHCO_3$+$KHCO_3$). The 1:1 weight by weight mixture of the bicarbonates of Na and K is also best in terms of final pH of the treated water, in which, the pH remained within 8.5 upto 400 mg/L of the mixture. Thus, the presence of more basic salts has been found to reduce the arsenate removal effeciveness of the less basic salt in a binary mixture. For example, the presence of $Na_2CO_3$ reduces the effectiveness of $NaHCO_3$, $NaHCO_3$ reduces the effeciveness of $KHCO_3$, etc.

**Table 3.16.** Remaining [Fe], [As] and pH of the water after treatment by 1:1 binary mixture of bicarbonates of Na and K from distilled water containing 0.25 mg/L and 20 mg/L of initial [As] and [Fe] respectively.

| Wt. of 1:1 binary salt mixture/ (mg/L) | Remaining [Fe], [As] in mg/L & pH with $KHCO_3$:$NaHCO_3$ | | |
|---|---|---|---|
| | [Fe] | [As] | pH |
| 0 | 17.18 | 0.249 | 5.7 |
| 2 | 9.48 | 0.001 | 6.2 |
| 10 | 8.98 | 0.001 | 6.3 |
| 40 | 3.89 | 0.003 | 6.9 |
| 80 | 0.14 | 0.005 | 7.7 |
| 100 | 0.11 | 0.005 | 7.9 |
| 200 | 0.09 | 0.015 | 8.5 |
| 300 | 0.07 | 0.021 | 8.6 |
| 400 | 0.06 | 0.024 | 8.6 |
| 500 | 0.04 | 0.025 | 8.7 |

Error limits: Δ[As]= ±0.0004 mg/L, Δ[Fe]= ±0.05 mg/L and ΔpH= ±0.1

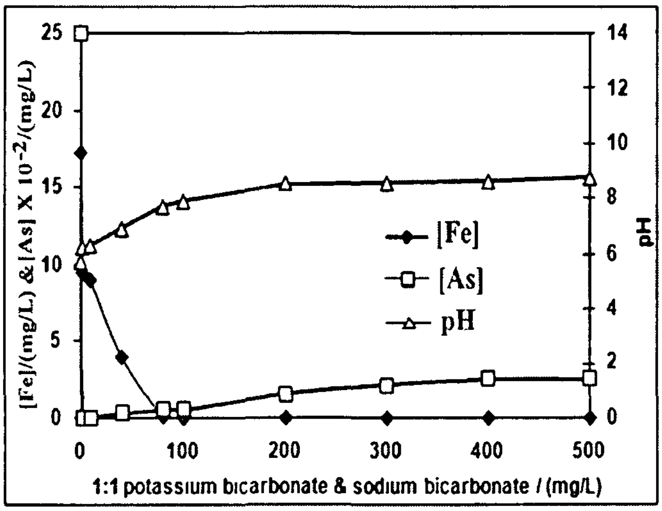

**Figure 3.19.** Remaining [Fe], [As] in mg/L and pH after treatment *vs* amount of 1:1 mixture of bicarbonates of Na and K of distilled water at residence time of 2 h with initial [Fe(II)] = 20 mg/L.

It has been observed that $KHCO_3$ alone is the most effective candidate for arsenic removal, followed by the 1:1 mixture of the bicarbonate salts and then $NaHCO_3$ alone, when the individual materials alone and their binary mixures are considered together. Hence, the further investigation of integrated removal of iron and arsenate ions has been restricted to the use of only $KHCO_3$.

### *3.2.1.9 The optimum dosage*

It has been seen that there is a maximum amount of a particular pH conditioner dose that can remove the arsenate to the guideline value ($D_{As,max}$) and a minimum amount the pH conditioner required to remove the iron ions to the guideline value ($D_{Fe,min}$). Table 3.17 shows these maximum and minimum quantities along with the corresponding pH values. The difference between these two quantities, $\Delta W = (D_{As,max} - D_{Fe,min})$, indicates the range within which a pH conditioner can remove both arsenate and the iron ions to the respective guideline values.

It can be seen from Table 3.17 that only $KHCO_3$, ($KHCO_3$+$NaHCO_3$) and $NaHCO_3$ have a positive $\Delta W$, i.e., the minimum concentration of the material required for removal of iron ion to its guideline value is smaller than the maximum concentration of the material required for removal of arsenate to its guideline value. The $\Delta W$ is a measure of the flexibility for variation in the concentration of the pH conditioner for simultaneous removal of arsenate and the iron ion to their respective guideline values. The $\Delta W$ values for $KHCO_3$, ($KHCO_3$+$NaHCO_3$) and $NaHCO_3$ were found to be 220, 130 and 100 mg/L indicating a decrease in the flexibility in the concentration of the materials to be added in the same order.

The ranges between the final pH values, $pH_{As,max}$ and $pH_{Fe,min}$ corresponding to $D_{As,max}$ and $D_{Fe,min}$, respectively, i.e., $\Delta pH = (pH_{As,max} - pH_{Fe,min})$, are also included in Table 3.17. It is interesting to note that the $\Delta pH$ obtained for both bicarbonate salts and their binary mixture are within the acceptable range for drinking water and increases in the order: $NaHCO_3 < (KHCO_3+NaHCO_3) < KHCO_3$. Thus, $KHCO_3$ not only has the maximum flexibility in the concentration, for satisfactory simultaneous removal of arsenate and iron ions, but also needs the least care in adjustment of its dose for regulating the initial and the final pH. Therefore, $KHCO_3$ is more suitable pH conditioner than other basic substances including $NaHCO_3$ for simultaneous removal of arsenate and ferrous ions from groundwater.

**Table 3.17.** $D_{As,max}$ and $D_{Fe,min}$ of the pH conditioners that can simultaneously remove the arsenate and iron ions to the respective guideline values at fixed initial concentrations of iron and arsenate ions of 20 mg/L and 0.25 mg/L, respectively, along with ΔW and ΔpH for distilled water.

| Material | Arsenate removal | | Iron ion removal | | ΔW /(mg/L) | ΔpH |
|---|---|---|---|---|---|---|
| | $D_{As,max}$ /(mg/L) | pH | $D_{Fe,min}$ /(mg/L) | pH | | |
| Lime | >500 | 12.8 | 300 | 12.4 | >200 | 0.35* |
| Banana ash | 70 | 8.7 | 400 | 9.9 | – 330 | – ive |
| $K_2CO_3$ | 70 | 8.3 | 300 | 8.9 | – 230 | – ive |
| $Na_2CO_3$ | 60 | 8.2 | 400 | 9.2 | – 340 | – ive |
| $KHCO_3$ | 400 | 8.5 | 80 | 7.5 | 220 | 1.05 |
| $NaHCO_3$ | 300 | 8.5 | 200 | 8.4 | 100 | 0.12 |
| 1:1 $KHCO_3$ : ash | 100 | 8.6 | 400 | 9.3 | – 300 | – ive |
| 1:1 $NaHCO_3$ : ash | 90 | 8.4 | 400 | 9.3 | – 310 | – ive |
| 1:1 $KHCO_3$ : $K_2CO_3$ | 80 | 8.2 | 200 | 8.6 | – 120 | – ive |
| 1:1 $NaHCO_3$ : $K_2CO_3$ | 60 | 8.1 | 400 | 9.2 | – 340 | – ive |
| 1:1 $KHCO_3$ : $Na_2CO_3$ | 70 | 8.2 | 300 | 8.9 | – 230 | – ive |
| 1:1 $NaHCO_3$ : $Na_2CO_3$ | 60 | 8.1 | 300 | 9.1 | – 240 | – ive |
| 1:1 $KHCO_3$ : $NaHCO_3$ | 200 | 8 5 | 70 | 7.5 | 130 | 1.20 |

*Unacceptable for drinking

**Table 3.18.** $D_{As,max}$ and $D_{Fe,min}$ of $KHCO_3$ that can simultaneously remove arsenate and iron ions to the respective guideline values from different initial concentrations of iron ion and a fixed initial arsenate concentration of 0.25 mg/L along with ΔW and ΔpH with distilled water and groundwater.

| Initial iron ion /(mg/L) | Type of water | Arsenate removal | | Iron ion removal | | ΔW /(mg/L) | ΔpH |
|---|---|---|---|---|---|---|---|
| | | $D_{As,max}$ /(mg/L) | pH | $D_{Fe,min}$ /(mg/L) | pH | | |
| 2 | Distilled water | 20 | 6.5 | 60 | 7.4 | – 40 | – 0.96 |
| | Groundwater | 30 | 6.5 | 20 | 6.4 | 10 | 0.09 |
| 5 | Distilled water | 30 | 6.6 | 70 | 7.5 | – 40 | – 0.84 |
| | Groundwater | 40 | 6.7 | 20 | 6.4 | 20 | 0.32 |
| 10 | Distilled water | 60 | 7.4 | 80 | 7.5 | – 20 | – 0.13 |
| | Groundwater | 60 | 7.4 | 40 | 6.7 | 20 | 0.66 |
| 15 | Distilled water | 300 | 8.5 | 80 | 7.5 | 220 | 1.01 |
| | Groundwater | 300 | 8.4 | 40 | 6.7 | 260 | 1.70 |
| 20 | Distilled water | 400 | 8.5 | 80 | 7.5 | 320 | 1.05 |
| | Groundwater | 400 | 8.5 | 80 | 7.5 | 320 | 1.03 |

Table 3.18 shows that the ΔW and the ΔpH increased with increase in the initial iron ion concentration. The tables again show better simultaneous removal of arsenate and iron ion from groundwater than that from distilled water. While at least 15 mg/L of initial iron ion is required for simultaneous removal of both arsenate and iron ions satisfactorily with $KHCO_3$ from distilled water, a concentration of just 2 mg/L is enough for the purpose in the case of groundwater. The requirement of the much lower initial iron ion concentration in the case of groundwater than that in the case of distilled water owes mainly to the better iron removal in the former.

### *3.2.1.10 Effect of initial concentrations of iron ion on arsenate removal*

The removal of arsenate ion on addition of varying concentrations of $KHCO_3$, from arsenate ion containing distilled as well as fabricated groundwater, has been studied at different initial ferrous ion concentartions of 2, 5, 10, 15 and 20 mg/L and at fixed initial arsenate ion concentration of 0.25 mg/L with a residence time of 2 h. It can be seen from the Table 3.19 & 3.20 and Figure 3.20 that the arsenate could be removed to below 0.01 mg/L in the presence of iron ion concentration of as low as 2 mg/L with $KHCO_3$ doses of 20 mg/L and 30 mg/L, for distilled water and groundwater. The observed slightly less arsenate removal from groundwater than from distilled water can be attributted to competition by the other anions present in groundwater with arsenate for adsorption [151, 274, 358].

The simultaneous removal of iron ion by $KHCO_3$ from the fabricated groundwater (Figure 3.20c) has been found to be considerably better than that from distilled water (Figure 3.20a) at all initial concentrations of iron ion as was observed in the presence of arsenate. The minimum dose of the bicarbonate salt required to simultaneously bring down iron concentrations also to below 0.3 mg/L decreased with decrease in the initial concentration of iron. The initial pH of the groundwater was ≈7.44 which decreased slightly on addition of iron ion. The higher initial pH of the groundwater than that of the distilled water and the presence of other ions may be the reasons for the observed better iron removal from the groundwater than from distilled water in the presence of arsenate (Table 3.20).

**Table 3.19.** Remaining [Fe] and [As] of the water after treatment by $KHCO_3$ from distilled water containing different initial [Fe] in mg/L and fixed initial [As] of 0.25 mg/L.

| $KHCO_3$ dose / (mg/L) | Remaining [Fe] after treatment from different initial [Fe] and fixed initial [As] / (mg/L) | | | | | Remaining [As] after treatment from different initial [Fe] and fixed initial [As] / (mg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | 5 | 10 | 15 | 20 | 2 | 5 | 10 | 15 | 20 |
| 0 | 1.78 | 3.78 | 8.21 | 11.18 | 16.78 | 0.249 | 0.249 | 0.249 | 0.249 | 0.248 |
| 2 | 1.56 | 2.57 | 4.38 | 6.21 | 10.22 | 0.011 | 0.011 | 0.005 | 0.006 | 0.001 |
| 5 | 1.38 | 2.17 | 3.98 | 4.89 | 10.04 | 0.012 | 0.013 | 0.005 | 0.006 | 0.002 |
| 10 | 1.18 | 1.89 | 3.56 | 4.18 | 9.67 | 0.013 | 0.012 | 0.005 | 0.006 | 0.003 |
| 20 | 0.99 | 1.56 | 2.78 | 3.48 | 8.99 | 0.012 | 0.012 | 0.005 | 0.005 | 0.005 |
| 30 | 0.91 | 1.41 | 2.28 | 2.96 | 6.46 | 0.011 | 0.012 | 0.005 | 0.005 | 0.005 |
| 40 | 0.56 | 1.09 | 1.89 | 2.19 | 4.09 | 0.012 | 0.011 | 0.005 | 0.005 | 0.004 |
| 50 | 0.42 | 0.91 | 1.52 | 1.78 | 2.96 | 0.021 | 0.012 | 0.005 | 0.005 | 0.005 |
| 60 | 0.29 | 0.48 | 1.09 | 1.18 | 2.21 | 0.022 | 0.011 | 0.012 | 0.005 | 0.005 |
| 70 | 0.11 | 0.37 | 0.56 | 0.89 | 1.11 | 0.024 | 0.022 | 0.021 | 0.005 | 0.005 |
| 80 | 0.09 | 0.36 | 0.35 | 0.34 | 0.32 | 0.025 | 0.023 | 0.021 | 0.005 | 0.005 |
| 90 | 0.08 | 0.11 | 0.14 | 0.14 | 0.28 | 0.042 | 0.025 | 0.025 | 0.005 | 0.005 |
| 100 | 0.08 | 0.09 | 0.11 | 0.12 | 0.11 | 0.049 | 0.031 | 0.031 | 0.005 | 0.005 |

Error limits: Δ[As]= ±0.0004 mg/L and Δ[Fe]= ±0.05 mg/L

**Table 3.20.** Remaining [Fe] and [As] of the water after treatment by $KHCO_3$ from ground water containing different initial [Fe] in mg/L and fixed initial [As] of 0.25 mg/L.

| $KHCO_3$ dose / (mg/L) | Remaining [Fe] after treatment from different initial [Fe] and fixed initial [As] / (mg/L) | | | | | Remaining [As] after treatment from different initial [Fe] and fixed initial [As] / (mg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | 5 | 10 | 15 | 20 | 2 | 5 | 10 | 15 | 20 |
| 0 | 1.51 | 3.18 | 5.19 | 7.98 | 10.89 | 0.249 | 0.249 | 0.249 | 0.248 | 0.247 |
| 2 | 0.98 | 1.31 | 3.48 | 3.96 | 8.12 | 0.009 | 0.013 | 0.005 | 0.001 | 0.001 |
| 5 | 0.78 | 0.99 | 2.21 | 3.48 | 5.45 | 0.009 | 0.012 | 0.005 | 0.001 | 0.001 |
| 10 | 0.48 | 0.82 | 2.81 | 2.28 | 4.56 | 0.008 | 0.011 | 0.005 | 0.001 | 0.002 |
| 20 | 0.31 | 0.31 | 0.98 | 1.48 | 3.78 | 0.009 | 0.009 | 0.005 | 0.004 | 0.003 |
| 30 | 0.11 | 0.13 | 0.81 | 0.48 | 3.18 | 0.009 | 0.008 | 0.005 | 0.004 | 0.005 |
| 40 | 0.09 | 0.11 | 0.34 | 0.3 | 2.16 | 0.009 | 0.009 | 0.005 | 0.004 | 0.005 |
| 50 | 0.09 | 0.09 | 0.16 | 0.15 | 1.67 | 0.018 | 0.009 | 0.005 | 0.005 | 0.005 |
| 60 | 0.08 | 0.08 | 0.12 | 0.14 | 1.08 | 0.021 | 0.016 | 0.009 | 0.005 | 0.005 |
| 70 | 0.06 | 0.08 | 0.11 | 0.11 | 0.81 | 0.025 | 0.022 | 0.018 | 0.005 | 0.005 |
| 80 | 0.06 | 0.07 | 0.08 | 0.09 | 0.28 | 0.025 | 0.021 | 0.025 | 0.005 | 0.005 |
| 90 | 0.06 | 0.07 | 0.07 | 0.08 | 0.14 | 0.046 | 0.025 | 0.025 | 0.005 | 0.005 |
| 100 | 0.04 | 0.07 | 0.07 | 0.08 | 0.11 | 0.051 | 0.032 | 0.031 | 0.005 | 0.005 |

Error limits: Δ[As]= ±0.0004 mg/L and Δ[Fe]= ±0.05 mg/L

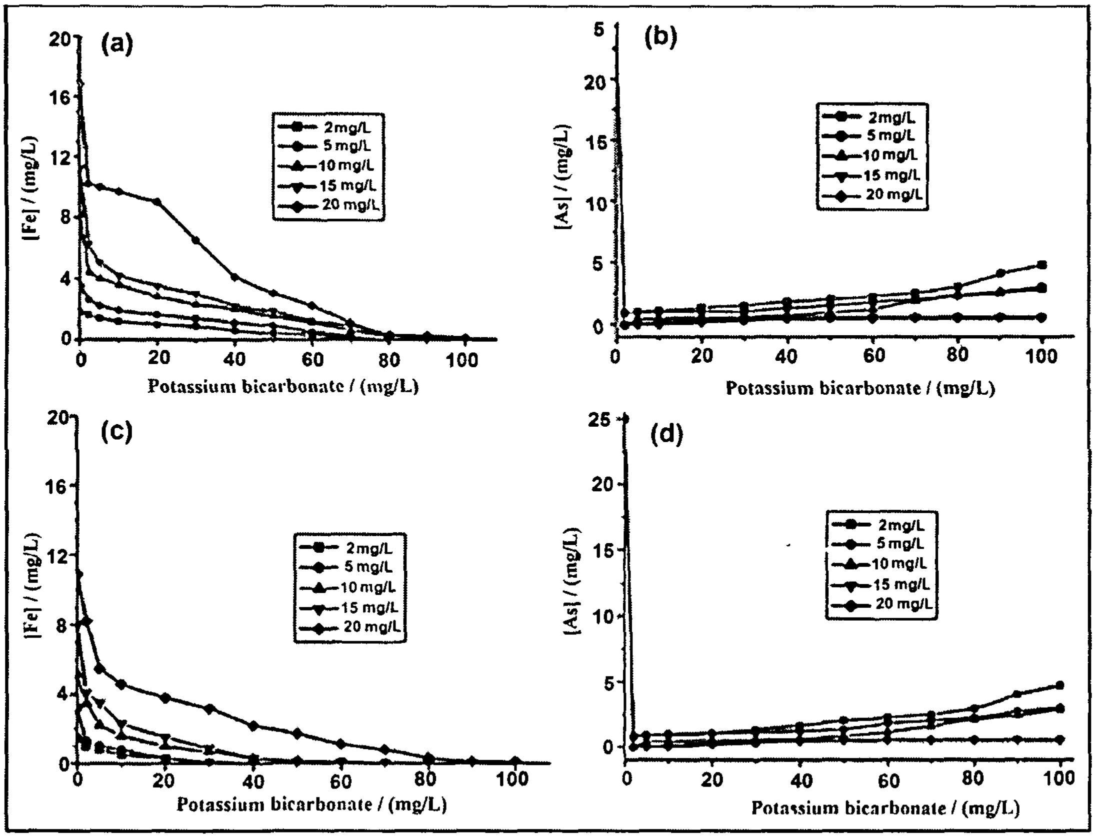

**Figure 3.20.** Plots of remaining [Fe] and [As] in mg/L *vs.* amount of potassium bicarbonate in mg/L of water from fixed initial arsenic concentration of 0.25 mg/L and varying initial iron ion concentration of 2, 5, 10, 15 and 20 mg/L with residence time of 2 h: (a, b) in distilled water and (c, d) in groundwater.

### 3.2.2 Mechanism of removal

The observed order of increasing simultaneous removal of arsenate and iron ions with various pH conditioners excluding lime: bicarbonates > carbonates > banana ash is in agreement with that observed earlier for iron ion removal. The bicarbonates of Na and K produce milder alkaline solution than the corresponding carbonates. An observed better iron ion removal ability of bicarbonate salts than the corresponding carbonate salts of Na and K was attributed to lower solubility of iron oxide/hydroxide in the presence of the bicarbonates than in the carbonates. Fe(II) is precipitated as ferric oxide ($Fe_2O_3$) from neutral water, as goethite (FeOOH) from mild alkaline water and as ferric hydroxide (ferrihydrite, $Fe(OH)_3$) from highly alkaline water in presence of sufficient oxygen[340]. The solubility of these compounds decreases in the order $Fe(OH)_3$ > FeOOH > $Fe_2O_3$ due to decreasing $OH^-$ groups which is the reason for the observed order of efficiency of the pH conditioners for simultaneous removal of iron ion and arsenate. The adsorption of arsenate ions is expected to be more with greater precipitation. However, it can be seen from the Figure 3.13-3.15 that with a particular material, although the iron ion removal increased considerably with increase in the quantity of the material, the arsenate ion removal showed an opposite trend. The decrease in arsenate removal with increase in the amount of a pH conditioner may be attributed to increase in the pH, *i.e.*, $OH^-$ ions, which compete with the arsenate ions for adsorption on iron precipitate[168, 194, 280, 282, 359].

As(V) exists in anionic forms of $H_2AsO_4^-$, $HAsO_4^{2-}$ or $AsO_4^{3-}$ depending upon the pH of the solution above 3.0[278]. Thus, when added iron salt is precipitated with the pH conditioners by increasing pH, it could facilitate the conversion of soluble arsenic species to insoluble reaction products[278]. These products might form through three major steps: (i) precipitation in forms of $Fe(AsO_4)$ solid; (ii) coprecipitation where soluble arsenic species were incorporated into a growing hydroxide phase via inclusion, occlusion, or adsorption; and (iii) adsorption involving the formation of surface complexes between soluble arsenic and the solid hydroxide surface site[360]. A pH around 7.3 is required for $Fe(OH)_3$ particles to have a net positive charge. Since arsenate is an anion and will adsorb onto positively charged $Fe(OH)_3$ particles by surface complexation, arsenic removal should be optimized at a pH of 7.3 or less. Arsenic removal may also occur at higher pH levels, but not as effectively as at lower pH values[280]. Arsenate removal decrease with increasing pH values above 8.0[168]. On the other hand, at highly alkaline condition, $Fe(OH)_4^-$ ions are formed in water[282], which is also expected to decrease the adsorption of the negatively charged arsenate ions on their precipitate. As(V) ions present in the water are more highly charged at pH 9.0[1]. So, both of these two factors tend to suggest that arsenate should be more readily removed from solution by both co-precipitation and adsorption at higher pH. However at pH 9, the high concentration of $OH^-$ tends to make the surface of iron precipitates and dissolved iron complexes more negatively charged, so hindering the approach of arsenate anions to the surface[358]. The better arsenic removal at low pH values is attributted also to decreased concentration of hydroxide anion, which is an excellent ligand that strongly competes with arsenic for adsorption sites[194]. Thus, the charges on the iron precipitate and the arsenate ions play a greater role in arsenate removal than the quantity of the iron precipitate available for arsenate adsorption. In the present case, arsenate is probably removed mainly through co-precipitation with iron ion and adsorption on goethite at slightly alkaline pH and ferrihydrite at alkaline pH as shown in the following equations:

$xFeOOH\downarrow + yHAsO_4^{2-} \rightarrow (FeOOH)_x.(HAsO_4^{2-})_y\downarrow$ Eq. (3.3)

$pFe(OH)_3\downarrow + qHAsO_4^{2-} \rightarrow (Fe(OH)_3)p.(HAsO_4^{2-})_q\downarrow$ Eq. (3.4)

The observed slightly higher arsenate ion removal by the K-salts than the corresponding Na-salts can also be attributed in a similar way to the slightly lower pH produced by the K-salts than that by the corresponding Na-salts.

## 3.2.3 Precipitate study

### *3.2.3.1 FTIR analysis*

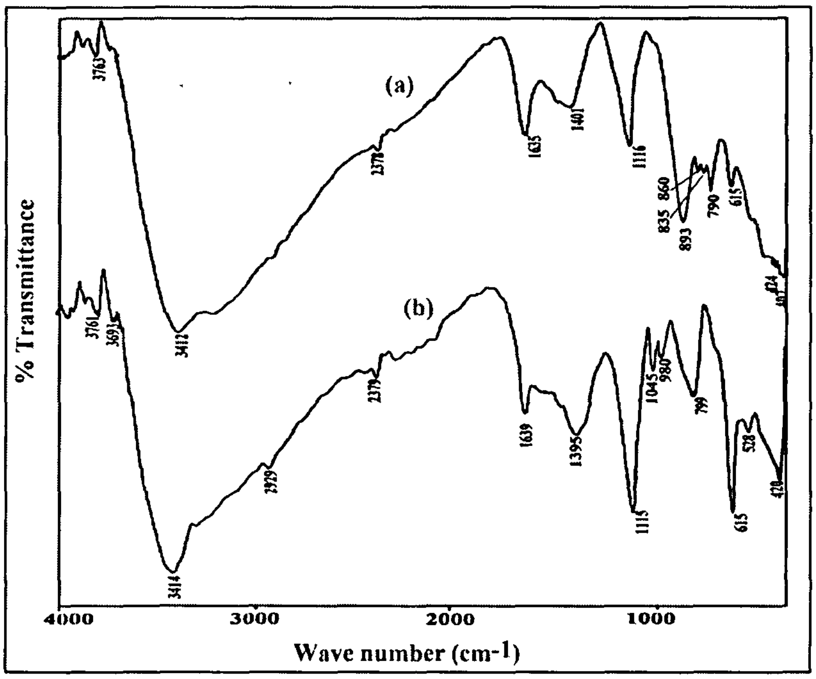

**Fig. 3.21.** FTIR spectra of the precipitate formed after treatment by (a) bicarbonate salts in the pH range 7-8 (b) carbonate salts in the pH range 9-10.

The FTIR spectra of the precipitates obtained at pH 7-8 with bicarbonate (Figure 3.21a) showed absorption bands at 3412 cm$^{-1}$, 1635 cm$^{-1}$ and 1401 cm$^{-1}$ due to OH stretching, bending of HOH[349, 350] and δ (OH), respectively. Intense peaks, characteristic of goethite, corresponding to γ and δ -OH bending modes of out and in plane modes were seen at 790 and 893 cm$^{-1}$[361]. Symmetric stretching of Fe-O is indicated by a band at 615 cm$^{-1}$[247]. Small absorption peaks at 860 cm$^{-1}$ and 835 cm$^{-1}$ could be assigned to the presence of $HAsO_4^{2-}$ ion and As-O-Fe groups[362, 363]. The IR spectrum of the precipitate obtained at pH 9-10 with the carbonate salts (Figure 3.21b) is quite similar with the spectrum obtained with the bicarbonates except the peaks at 1045 and 980 cm$^{-1}$ corresponding to the bending vibration of (Fe-OH) groups suggesting formation of ferric hydroxide, Fe(OH)$_3$[352, 353].

### *3.2.3.2 XRD analysis*

The XRD patterns of the precipitates obtained by using carbonate and bicarbonate salts are shown in Figue 3.22.

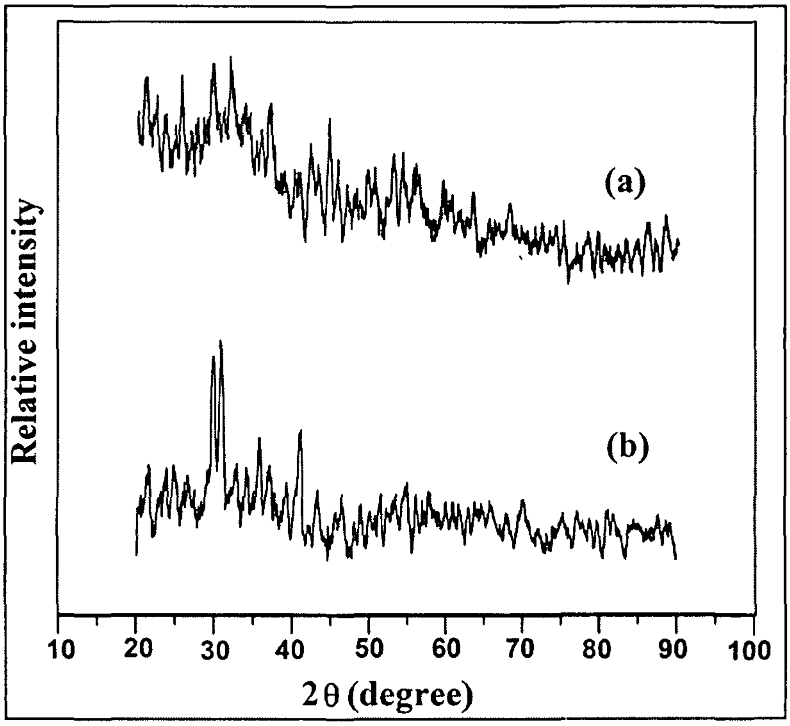

**Figure 3.22.** XRD of the precipitate formed after treatment with (a) bicarbonate salts in the pH range 7-8 (b) carbonate salts in the pH range 9-10.

As the XRD patterns show the poorly crystaline nature of the precipitate, it was difficult to differenciate between arsenate and ferric oxide phase using simple powder XRD analysis[362, 364]. A comparison of the XRD pattern of the precipitate obtained at both the pH with JCPDF-ICDD database[365] and with literature indicated that the XRD pattern showed similarity with that of ferric arsenate[366]. Two characteristic broad XRD bands were observed at ~29° and ~57° 2θ for poorly crystalline ferric arsenate in the both cases.

### *3.2.3.3 SEM-EDS analysis*

The SEM-EDS image of the precipitate obtained by using bicarbonate salts is shown in Figure 3.23. SEM image showed randomly aggregated large and irregularly shaped particles suggestive of poor crystallinity of the precipitate. The poor crystallinity may be attributted to incorporation of arsenate. From the EDS analysis the presence of significant quantities of Fe and As in the precipitate obtained by using potassium bicarboante salt can be seen clearly (Figure 3.23b).

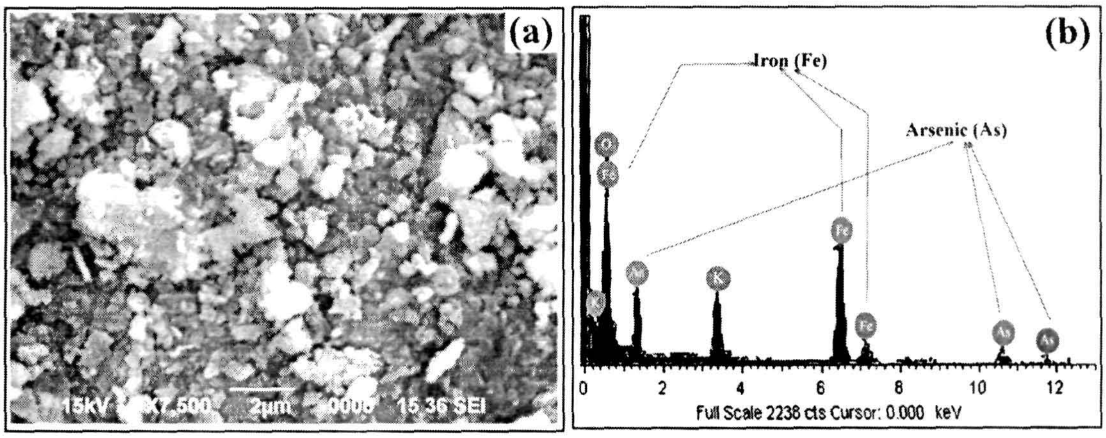

**Figure 3.23:** SEM-EDS of the precipitate formed after treatment by bicarbonate salts.

### 3.2.4 Summary

The following conclusions have been drawn from the present study:

The arsenic removal in presence of the pH conditioners increases in the order: banana ash < carbonates < bicarbonates < lime. However, the bicarbonate salts provide the best pH condition for simultaneous removal of arsenate and iron ions.

- The potassium salts are more efficient than the corresponding sodium salts. Lime is disadvantageous because it requires post-treatment correction of highly alkaline pH. The bicarbonates retain the final pH within the acceptable range for drinking.
- Arsenate and iron ions can be removed simultaneously to below 0.01 mg/L and 0.3 mg/L, respectively, retaining the pH of water within the acceptable range for drinking, using only the bicarbonate salts alone or their mixture as the pH conditioner.

- The use of $KHCO_3$ is more advantageous over the use of the more basic substances including $NaHCO_3$ because, with it, one not only needs the smallest dose but also can avoid careful adjustment of the dose for regulating the initial and the final pH.
- The arsenate ion is removed predominantly through goethite or ferrihydrite in the presence of the bicarbonates and through ferric hydroxide in the presence of the more alkaline pH-conditioners.

From the present study, $KHCO_3$ is expected to be the most effective pH-conditioner for application along with other precipitating/coagulating agents for simultaneous removal of arsenate and iron ions.

## 3.3 Arsenic and Iron Removal by Oxidation-Coagulation at Optimized pH (OCOP) method

The efficiencies of bicarbonate and carbonate salts of Na and K, ash and lime have been studied in removal of arsenic and iron ions as pH-conditioners for precipitation-coagulation as discussed in section 3.1 and 3.2. It was found that $KHCO_3$ and $NaHCO_3$ are the most efficient pH conditioners for simultaneous removal of arsenic and iron. Though $KHCO_3$ is more efficient than $NaHCO_3$, the later may be more suitable because of easier availability and its familiarity as baking soda among common people. Moreover, $NaHCO_3$ does not impart any unpleasant taste to water unlike $KHCO_3$.

Since arsenic is present in groundwater mainly as difficult-to-remove arsenite ions, different oxidants have been used for oxidizing the arsenite to easy-to-remove arsenate ions. $KMnO_4$, a popular oxidizing agent used in water treatment, has another edge over its competitors because of its stable solid form with high solubility[275]. The oxidation potential and reduction products of $KMnO_4$ are also pH-dependent. Under weak acidic, neutral and weak alkaline conditions, the half-reaction is[367]:

$$MnO_4^- + 2H_2O + 3e^- = MnO_2\,(S) + 4OH^- \qquad E^\circ = +0.588\ V \qquad \text{Eq. (3.5)}$$

In the presence of 1.19 mM (0.1 g/L) $NaHCO_3$, the possible reaction through which $KMnO_4$ would oxidize As(III) to As(V) at the prevailing mild alkaline pH is[274]:

$$3H_3AsO_3 + 2KMnO_4 + 4OH^- = 3HAsO_4^{2-} + 2MnO_2 + 5H_2O + 2K^+ \qquad \text{Eq. (3.6)}$$

Therefore, after oxidising others in the presence of $NaHCO_3$, manganese separates as insoluble $MnO_2$ without leaving any dissolved manganous ions in the treated water[259]. The As(III) oxidation efficiencies obtained under basic conditions for Mn(VII)-As(III) system is also reported to be higher than those under acidic conditions[329]. Thus, we thought it worthwhile to carry out a detail systematic study of simultaneous removal of arsenic and iron ion from groundwater by oxidation-coagulation at optimized pH using $NaHCO_3$, $KMnO_4$ and $FeCl_3$ as the pH-conditioner, oxidant and coagulant, respectively. We have studied the effects of dosage of the oxidant, the coagulant and the pH-conditioner on the simultaneous removal of arsenic and iron ions.

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### 3.3.1 Batch experiments

Batch tests were carried out to optimize the doses of $NaHCO_3$ as pH-conditioner, $KMnO_4$ as oxidant and $FeCl_3$ as coagulant in the OCOP method for simultaneous removal of arsenic and iron. The effect of dissolved Fe(II), sulfate, phosphate and silicate on removal of arsenic and iron were also studied through batch experiments. The results of the batch experiments are discussed here.

#### *3.3.1.1 Effect of coagulant dose on As and Fe removal*

Water having initial arsenite concentrations, $[As]_0$ in the range of 1.33-6.67 μM (0.1-0.5 mg/L) was treated with varying doses of $FeCl_3$ in the range of 0-191.1 μM (0-31 mg/L) in presence of fixed concentrations of 1.19 mM (0.1 g/L) of $NaHCO_3$ and 3.16 μM (0.5 mg/L) of $KMnO_4$. The variations in the remaining arsenic concentrations after the treatment along with the residual iron ion concentrations originating from the added $FeCl_3$ are shown in Table 3.21-3.22 and Figure 3.24.

**Table 3.21.** Remaining [As] in μM from different initial $[As]_0$ in the range of 1.33-6.67 μM (0.1-0.5 mg/L) after treatment with varying dose of $FeCl_3$ with fixed doses of $NaHCO_3$ (1.19 mM) and $KMnO_4$ (3.16 μM).

| Dose of $FeCl_3$/ μM | Remaining [As] from different initial concentrations of arsenic | | | | |
|---|---|---|---|---|---|
| | 6.67 | 5.34 | 4.00 | 2.60 | 1.33 |
| 0 | 6.54 | 5.08 | 3.74 | 2.54 | 1.20 |
| 6.2 | 3.60 | 2.53 | 1.29 | 1.01 | 0.67 |
| 12.3 | 2.24 | 1.73 | 0.76 | 0.53 | 0.33 |
| 18.5 | 1.88 | 1.33 | 0.54 | 0.32 | 0.23 |
| 24.6 | 1.60 | 1.07 | 0.34 | 0.24 | 0.13 |
| 30.8 | 1.28 | 0.80 | 0.29 | 0.20 | 0.13 |
| 36.9 | 1.12 | 0.64 | 0.21 | 0.17 | 0.12 |
| 43.2 | 0.98 | 0.51 | 0.15 | 0.13 | 0.12 |
| 49.3 | 0.80 | 0.40 | 0.14 | 0.12 | 0.11 |
| 55.5 | 0.64 | 0.31 | 0.13 | 0.12 | 0.10 |
| 61.6 | 0.51 | 0.24 | 0.13 | 0.12 | 0.10 |
| 67.8 | 0.47 | 0.15 | 0.13 | 0.11 | 0.09 |
| 73.9 | 0.38 | 0.13 | 0.12 | 0.10 | 0.09 |
| 80.1 | 0.33 | 0.12 | 0.12 | 0.10 | 0.09 |
| 86.3 | 0.26 | 0.11 | 0.12 | 0.10 | 0.08 |
| 92.5 | 0.22 | 0.11 | 0.11 | 0.09 | 0.08 |
| 98.6 | 0.20 | 0.11 | 0.11 | 0.09 | 0.08 |
| 104.8 | 0.19 | 0.10 | 0.10 | 0.09 | 0.07 |
| 110.9 | 0.18 | 0.10 | 0.10 | 0.08 | 0.07 |
| 117.1 | 0.17 | 0.09 | 0.09 | 0.08 | 0.07 |

| | | | | | |
|---|---|---|---|---|---|
| 123.3 | 0.15 | 0.09 | 0.09 | 0.08 | 0.07 |
| 129.5 | 0.14 | 0.09 | 0.08 | 0.07 | 0.06 |
| 135.6 | 0.14 | 0.09 | 0.08 | 0.07 | 0.06 |
| 141.8 | 0.13 | 0.08 | 0.07 | 0.06 | 0.05 |
| 147.9 | 0.12 | 0.08 | 0.06 | 0.06 | 0.04 |
| 154.1 | 0.11 | 0.08 | 0.06 | 0.05 | 0.04 |
| 160.3 | 0.11 | 0.08 | 0.05 | 0.05 | 0.03 |
| 166.4 | 0.10 | 0.07 | 0.04 | 0.03 | 0.02 |
| 172.6 | 0.08 | 0.06 | 0.04 | 0.02 | 0.02 |
| 178.8 | 0.08 | 0.06 | 0.03 | 0.02 | 0.01 |
| 184.9 | 0.07 | 0.05 | 0.03 | 0.02 | 0.01 |
| 191.1 | 0.06 | 0.04 | 0.02 | 0.01 | 0.01 |

**Table 3.22.** Residual [Fe] in μM after treatment of arsenic from different initial $[As]_0$ in the range of 1.33-6.67 μM (0.1-0.5 mg/L) with varying dose of $FeCl_3$ with fixed doses of $NaHCO_3$ (1.19 mM) and $KMnO_4$ (3.16 μM).

| Dose of $FeCl_3$/ μM | Residual [Fe] with different dose of $FeCl_3$ after treatment of arsenic from different initial concentrations of arsenic | | | | |
|---|---|---|---|---|---|
| | 6.67 | 5.34 | 4.00 | 2.60 | 1.33 |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 6.2 | 4.65 | 4.65 | 4.48 | 4.47 | 4.12 |
| 12.3 | 6.08 | 6.09 | 6.27 | 6.09 | 6.27 |
| 18.5 | 7.16 | 7.16 | 7.34 | 7.52 | 7.16 |
| 24.6 | 7.70 | 7.88 | 8.06 | 8.24 | 8.24 |
| 30.8 | 8.42 | 8.59 | 8.59 | 8.77 | 8.77 |
| 36.9 | 9.85 | 9.49 | 9.49 | 9.85 | 9.67 |
| 43.2 | 10.74 | 10.38 | 10.2 | 10.74 | 10.56 |
| 49.3 | 11.64 | 10.74 | 11.10 | 11.46 | 11.64 |
| 55.5 | 11.99 | 11.46 | 11.82 | 12.17 | 12.53 |
| 61.6 | 13.07 | 12.53 | 12.89 | 12.71 | 13.43 |
| 67.8 | 13.61 | 13.25 | 13.43 | 13.43 | 14.32 |
| 73.9 | 14.32 | 14.32 | 14.14 | 14.32 | 15.04 |
| 80.1 | 15.04 | 15.22 | 15.22 | 15.04 | 15.93 |
| 86.3 | 15.93 | 16.11 | 16.29 | 15.94 | 16.65 |
| 92.5 | 16.47 | 16.65 | 16.83 | 16.65 | 17.73 |
| 98.6 | 17.55 | 17.73 | 17.70 | 17.73 | 18.80 |
| 104.8 | 18.80 | 19.16 | 18.60 | 18.98 | 19.52 |
| 110.9 | 19.69 | 20.59 | 19.87 | 20.05 | 20.23 |
| 117.1 | 20.59 | 21.49 | 20.76 | 21.30 | 21.49 |
| 123.3 | 21.48 | 23.27 | 22.38 | 22.20 | 22.56 |
| 129.5 | 23.27 | 24.35 | 23.28 | 23.28 | 23.28 |
| 135.6 | 24.17 | 25.43 | 25.07 | 24.35 | 23.99 |
| 141.8 | 25.78 | 26.86 | 26.32 | 25.78 | 24.89 |
| 147.9 | 27.75 | 28.65 | 27.93 | 27.04 | 25.78 |
| 154.1 | 30.44 | 30.08 | 29.54 | 28.65 | 27.21 |

| | | | | | |
|---|---|---|---|---|---|
| 160.3 | 32.23 | 31.87 | 30.97 | 29.54 | 28.65 |
| 166.4 | 35.81 | 34.02 | 32.77 | 30.97 | 30.08 |
| 172.6 | 41.18 | 39.39 | 35.81 | 32.59 | 31.87 |
| 178.8 | 46.55 | 42.97 | 39.39 | 35.81 | 34.38 |
| 184.9 | 53.71 | 50.13 | 46.55 | 42.97 | 39.39 |
| 191.1 | 59.08 | 57.3 | 51.92 | 50.13 | 46.55 |

From the Figure 3.24a we see that removal of arsenic increased on increase the coagulant dose as expected.

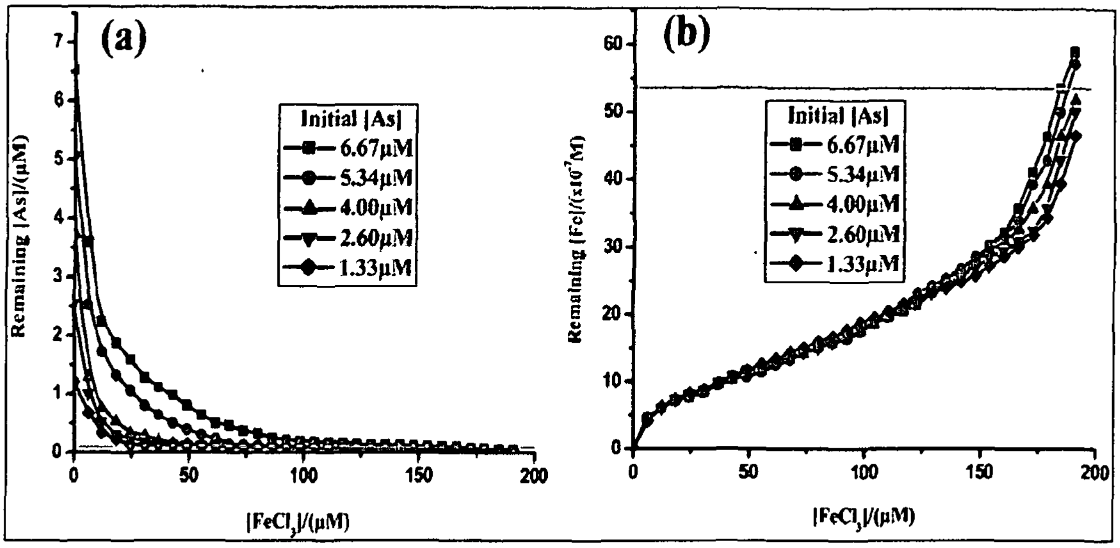

**Figure 3.24.** Remaining [As] (a) and residual [Fe] in μM (b) from different $[As]_0$ *vs.* varying dose of $FeCl_3$ at fixed doses of $NaHCO_3$ (1.19 mM) and $KMnO_4$ (3.16 μM) at residence time of 2 h in distilled water. The horizontal yellow lines represent the respective WHO guideline values.

It can further be seen that the $FeCl_3$ dose required to remove arsenic to a particular concentration increases also with $[As]_0$. The minimum dose of $FeCl_3$, $[FeCl_3]_{min}$ required for lowering the arsenic concentration to below the WHO guideline value has been found to increase linearly with $[As]_0$ until the $[As]_0$ exceeded the stoichiometric equivalent i.e., 2/3rd of the molar concentration (4.45 μM) of the $KMn0_4$ dose. The $[FeCl_3]_{min}$ increased more rapidly beyond that As-Mn equivalence point in alkaline condition (Figure 3.25). Thus, the excess arsenic over the stoichiometric equivalent of $KMn0_4$ remains in the arsenite form which requires a larger quantity of $FeCl_3$[27, 268]. This explanation is supported by the fact that the plot of $[FeCl_3]_{min}$ *vs.* $[As]_0$ is linear in the entire range of 1.33-6.67 μM (0.1-0.5 mg/L) of $[As]_0$ when the highest $[As]_0$ was less than the Mn equivalent at the

$KMnO_4$ dose of 4.45 μM in alkaline condition (Figure 3.25). The linear relation between $[FeCl_3]_{min}$ *vs.* $[As]_0$ at 4.45 μM $KMnO_4$ has been found to be

$$[FeCl_3]_{min} = 12.39[As]_0 + 2.316;\ R^2 = 0.994 \qquad \text{Eq. (3.7)}$$

The linear relation between $[FeCl_3]_{min}$ and $[As]_0$ suggests a minimum molar stoichiometric ratio of approximately 12.39:1 between them for efficient sorption of arsenic under the experimental conditions.

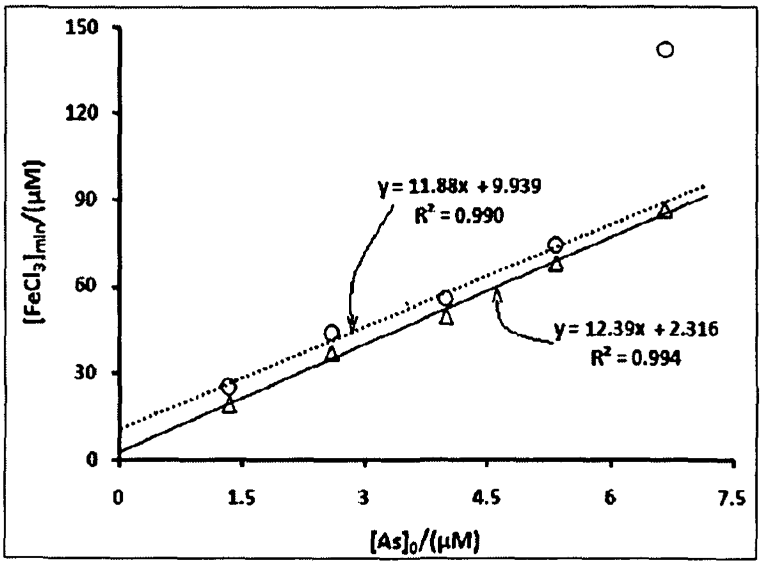

**Figure 3.25.** Plots of $[FeCl_3]_{min}$ *vs.* $[As]_0$ at 3.16 μM (dotted line) and at 4.45 μM (solid line) of $KMnO_4$ at fixed dose of $NaHCO_3$ (1.19 mM).

The residual iron ion concentration increases on increasing the dose of $FeCl_3$ for fixed $[As]_0$ as can be seen in Figure 24(b) and Table 22. The residual iron increases also with the increase in $[As]_0$ for a fixed dose of $FeCl_3$, particularly, at higher doses of $FeCl_3$. However, the residual iron ion remains within the WHO guideline value of 0.3 mg/L for drinking water at the $[As]_0$ range of 1.33-6.67 μM (0.1-0.5 mg/L) when the dose of $FeCl_3$ was less than 184.9 μM (30 mg/L).

Thus, both of the remaining arsenic and residual iron ions remain below their respective WHO guideline values within a range of the $FeCl_3$ dose of 123.3-184.9 μM (20-30 mg/L). It may also be mentioned here that the concentration of arsenic in the groundwater sources in Assam is normally below 0.4 mg/L (5.34 μM). Therefore, we have chosen 154.1 μM (25 mg/L) as the optimum dose of $FeCl_3$ and used the same in the remaining studies.

### *3.3.1.2 Effect of oxidant dose on As and Fe removal*

The effect of variation of the $KMnO_4$ dose at fixed doses of $FeCl_3$ (154.1 μM) and of $NaHCO_3$ (1.19 mM) on removal of As(III) from different $[As]_0$ is shown in Figure 3.26. As expected, the arsenic removal increased with increase in the concentration of $KMnO_4$ which can be seen clearly from Table 3.23.

**Table 3.23.** Remaining [As] in μM from different initial $[As]_0$ in the range of 1.33-6.67 μM (0.1-0.5 mg/L) after treatment with varying dose of $KMnO_4$ with fixed doses of $FeCl_3$ (154.1 μM) and $NaHCO_3$ (1.19 mM).

| $[KMnO_4]$ / μM | Remaining [As] from different initial $[As]_0$ with varying dose of $KMnO_4$ | | | | |
|---|---|---|---|---|---|
| | 6.67 | 5.34 | 4.00 | 2.60 | 1.33 |
| 0 | 3.58 | 3.27 | 2.80 | 1.99 | 0.95 |
| 0.63 | 2.01 | 1.73 | 1.29 | 1.05 | 0.39 |
| 1.26 | 1.04 | 0.77 | 0.51 | 0.32 | 0.16 |
| 1.89 | 0.51 | 0.31 | 0.12 | 0.09 | 0.07 |
| 2.53 | 0.24 | 0.09 | 0.07 | 0.05 | 0.04 |
| 3.16 | 0.07 | 0.06 | 0.05 | 0.04 | 0.03 |
| 3.79 | 0.05 | 0.05 | 0.02 | 0.02 | 0.02 |
| 4.43 | 0.04 | 0.03 | 0.02 | 0.01 | 0.01 |
| 5.06 | 0.04 | 0.02 | 0.01 | 0.009 | 0.007 |
| 5.69 | 0.02 | 0.01 | 0.01 | 0.006 | 0.005 |
| 6.32 | 0.02 | 0.01 | 0.006 | 0.005 | 0.001 |

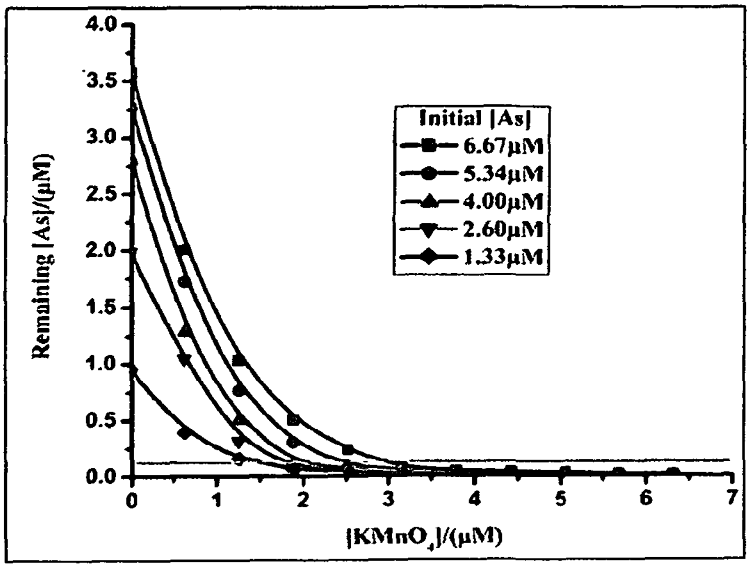

**Figure 3.26.** Remaining [As] from different $[As]_0$ *vs.* varying dose of $KMnO_4$ with fixed doses of $NaHCO_3$ (1.19 mM) and $FeCl_3$ (154.1 μM) at residence time of 2 h in distilled water. The horizontal yellow line represent the WHO guideline value for arsenic in drinking water.

The minimum amount of $KMnO_4$ required to remove arsenic to below the WHO guideline value, $[KMnO_4]_{min}$ also increased with increase in the $[As]_0$. The plots of $[KMnO_4]_{min}$ *vs.* $[As]_0$ is also linear in the experimental range of $[As]_0$ (Figure 3.27):

$$[KMnO_4]_{min} = 0.31[As]_0 + 1.037;\ R^2 = 0.993 \qquad \text{Eq. (3.8)}$$

A zero intercept and a slope of 2/3 are expected from the redox reaction between $KMnO_4$ and arsenite. The observed deviations from the expected intercept and slope can be attributed to the contribution of $MnO_2$ to arsenic removal by adsorption in addition to the oxidation of arsenite[268]. A zero intercept is possible at the limit of $[As]_0 \rightarrow 0$. It can be mentioned here that the pH of 8.3 observed after addition of $NaHCO_3$ decreases to ≈7.49 after addition of $FeCl_3$. The final pH of ≈7.49 is a result of the hydrolysis of FeCl3 and the oxidation of As(III) by $KMnO_4$. In this pH range, $KMnO_4$ oxidizes arsenite to more easily removable arsenate form while itself is reduced from Mn(VII) to Mn(IV), i.e., to insoluble $MnO_2$ and not to soluble Mn(II). Dissolved Mn(II) is unwanted in drinking water. The solid hydrous $MnO_2$, which also adsorbs ionic As(V) species is reported to be coprecipitated through complex surface reactions[172].

It can be seen from Figure 3.26 that 3.16 μM (0.5 mg/L) of $KMnO_4$ is sufficient to remove arsenic to below the WHO guideline value from the $[As]_0$ range of 1.33-6.67 μM (0.1-0.5 mg/L) under the experimental conditions. Therefore, 3.16 μM (0.5 mg/L) of $KMnO_4$ has been chosen as the optimum dose of $KMnO_4$ for arsenic removal from water in the absence of initial iron contaminant.

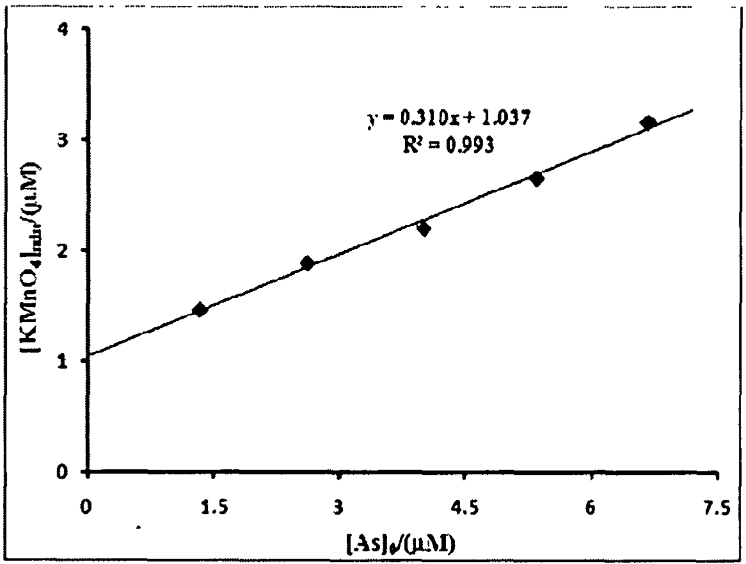

Figure 3.27. Plot of $[KMnO_4]_{min}$ *vs.* $[As]_0$ at fixed doses of $FeCl_3$ (154.1 μM) and of $NaHCO_3$ (1.19 mM).

### *3.3.1.3 Effect of pH-conditioner dose on As and Fe removal*

The effect of the dose of NaHCO$_3$ on arsenic removal from different [As]$_0$ at fixed concentrations of KMn0$_4$ (3.16 μM) and FeCl$_3$ (154.1 μM) is shown in Table 3.24 and Figure 3.28.

**Table 3.24.** Remaining [As] in μM from different initial [As]$_0$ in the range of 1.33-6.67 μM (0.1-0.5 mg/L) after treatment with varying dose of NaHCO$_3$ with fixed doses of FeCl$_3$ (154.1 μM) and KMn0$_4$ (3.16 μM).

| [NaHCO$_3$] / mM | Remaining [As] from different initial [As]$_0$ with varying dose of KMn0$_4$ | | | | |
|---|---|---|---|---|---|
| | 6.67 | 5.34 | 4.00 | 2.60 | 1.33 |
| 0 | 3.47 | 3.07 | 2.4 | 1.73 | 0.67 |
| 0.059 | 1.73 | 1.45 | 1.30 | 1.04 | 0.60 |
| 0.119 | 1.30 | 1.07 | 0.96 | 0.83 | 0.53 |
| 0.24 | 1.07 | 0.84 | 0.75 | 0.61 | 0.43 |
| 0.36 | 0.89 | 0.72 | 0.63 | 0.51 | 0.31 |
| 0.48 | 0.75 | 0.57 | 0.52 | 0.37 | 0.23 |
| 0.59 | 0.61 | 0.47 | 0.40 | 0.31 | 0.15 |
| 0.71 | 0.44 | 0.35 | 0.27 | 0.21 | 0.11 |
| 0.83 | 0.27 | 0.20 | 0.16 | 0.12 | 0.09 |
| 0.95 | 0.15 | 0.11 | 0.09 | 0.08 | 0.08 |
| 1.07 | 0.09 | 0.08 | 0.06 | 0.06 | 0.05 |
| 1.19 | 0.05 | 0.04 | 0.04 | 0.03 | 0.02 |

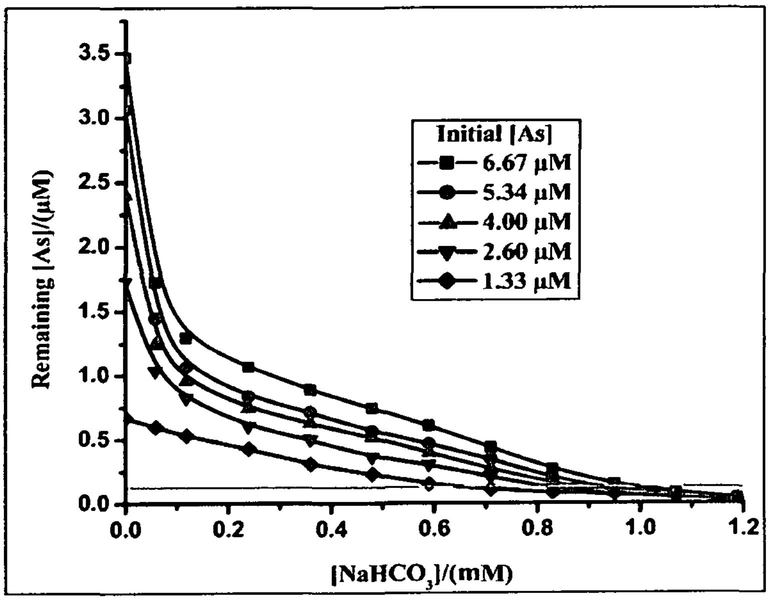

**Figure 3.28.** Remaining [As] from different [As]$_0$ *vs.* varying dose of NaHCO$_3$ with fixed doses of KMn0$_4$ (3.16 μM) and FeCl$_3$ (154.1 μM), at residence time of 2 h in distilled water. The horizontal yellow line represent the WHO guideline value for arsenic in drinking water.

The arsenic removal increased with increase in the concentration of $NaHCO_3$. The quantity of $NaHCO_3$ required to bring down the arsenic concentration to a particular concentration also increased with increase in $[As]_0$. It can be seen from the figure that the arsenic concentration from $[As]_0$ in the range of 1.33-6.67 μM (0.1-0.5 mg/L) is lowered to below the WHO guideline value with a minimum dose of ≈1.19 mM (0.1 g/L) of $NaHCO_3$. Therefore, 1.19 mM (0.1 g/L) was considered as the optimum concentration of the pH-conditioner for the remaining study.

The plots of the minimum amount of $NaHCO_3$ required to remove arsenic to below the WHO guideline value, $[NaHCO_3]_{min}$ *vs.* $[As]_0$ is also linear in the experimental conditions (Figure 3.29):

$$[NaHCO_3]_{min} = 0.064[As]_0 + 0.628;\ R^2 = 0.990 \qquad \text{Eq. (3.9)}$$

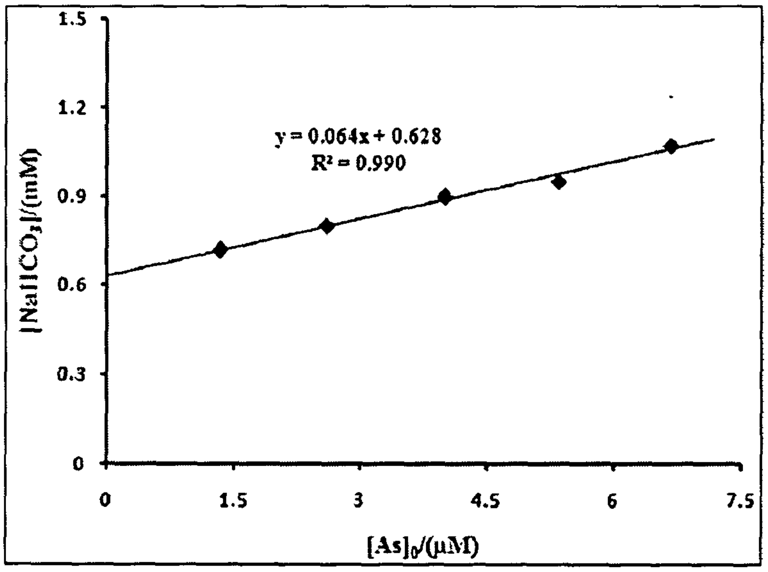

**Figure 3.29.** Plot of $[NaHCO_3]_{min}$ *vs.* $[As]_0$ at fixed doses of $KMnO_4$ (3.16 μM) and $FeCl_3$ (154.1 μM).

The observed increase in $[NaHCO_3]_{min}$ with increase in $[As]_0$ may be attributed to sorption of $OH^-$ ions in the coagulates and consumption of $OH^-$ ions in the oxidation of arsenite. As $OH^-$ ions are removed by these mechanisms, more $NaHCO_3$ is required to maintain the optimal pH for sorption of $H_2AsO_4^-$ ions by coagulates (Eq. 3.6).

### *3.3.1.4 Effect of initial dissolved iron ions*

In the presence of appreciable concentration of dissolved Fe(II) ions along with arsenic, the ferrous ions consume $KMnO_4$ for the oxidation to ferric ions before $KMnO_4$

can oxidize arsenite to arsenate[274]. Therefore, in such cases, an additional amount of $KMnO_4$ is necessary to oxidize the ferrous ions. Under mild alkaline condition, the oxidation reaction of Fe(II) and As(III) by permanganate can be represented as[274]:

$$3Fe^{2+} + MnO_4^- + 5H_2O = 3Fe(OH)_3 + MnO_2 + H^+ \qquad \text{Eq. (3.10)}$$

According to eqs. (3.6) and (3.10), 2.2 μM and 29.8 μM permanganate are required for complete oxidation of 3.34 μM As(III) and 89.5 μM Fe(II), respectively, under mild alkaline condition. The dose of $KMnO_4$ was varied in a range of 2-35 μM in water containing 3.34 μM As(III) and ferrous sulfate in a range of 17.9-89.5 μM (1-5 mg/L) to study the effect of permanganate dose in arsenic removal in the presence of soluble Fe(II) by the present OCOP method. It was found that, in the presence of ferrous iron up to 89.5 μM, a $KMnO_4$ dose of 25.3 μM is enough for removal of arsenic from 1.33-6.67 μM (0.1-0.5 mg/L) to below the WHO guideline value.

### 3.3.2 Effect of competing ions

Anions, particularly, the di-anions and tri-anions directly compete for available surface binding sites and indirectly influence adsorption by alteration of the electrostatic charge at the solid surface[368]. Therefore, the effects of such ions, *viz.*, sulphate, phosphate and silicate in the OCOP process were examined through batch laboratory experiments. The concentrations of these ions were taken in selected ranges in which they normally occur in groundwater[276].

In the present OCOP method, the optimized doses of the pH-conditioner at 1.19 mM (0.1 g/L), the oxidant at 3.16 μM (0.5 mg/L) and the coagulant at 154.1 μM (25 mg/L) was added successively with mixing by mild stirring with a glass rod after each addition. The removals of arsenic from $[As]_0$ of 3.34 μM (0.25 mg/L) by the present method in the presence of sulphate, phosphate and silicate ions separately in their concentrations in the ranges of 0-5.20 mM (0-500 mg/L as sulphate), 0-0.10 mM (0-3 mg/L phosphate as P) and 0-0.40 mM (0-10 mg/L silicate as Si), respectively, in distilled water are shown in Figure 3.30.

Sulfate has been reported to influence the adsorption of both arsenate and arsenite in many surface and subsurface aquatic systems. In the present case, Figure 3.30a shows that the presence of sulfate had negligible effect on As(III) removal at low concentration of sulfate, while As(III) removal was decreased by 5-16% the presence of 100-500 mg/L $SO_4^{2-}$. However, the results of our study and those in the literature suggested that sulfate can compete with arsenate and occupy surface sites for which the arsenate has weak affinity[276].

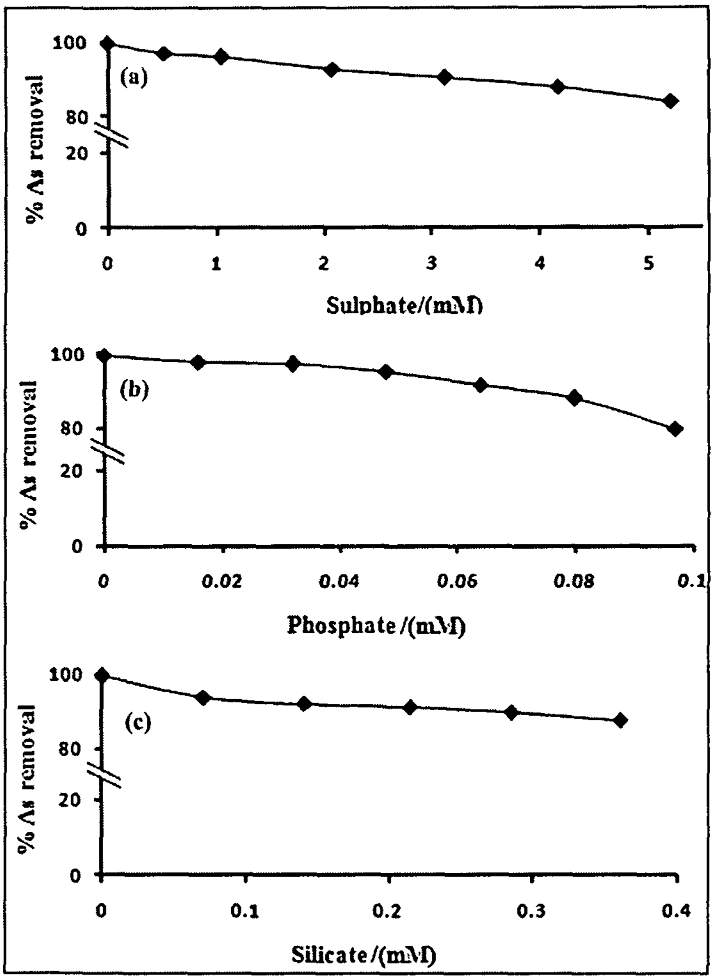

**Figure 3.30.** Effects of the competing ions on arsenic removal from $[As]_0$ of 3.34 μM (0.25 mg/L) by the present OCOP method: (a) sulphate, (b) phosphate, (c) silicate in distilled water.

Phosphate has a similar structure and deprotonation constants as arsenate in solution and these similarities between phosphate and arsenate complexes make it a possible competing ion for arsenate. Therefore, the effects of phosphate on As(III) removal in the present method were examined at various phosphate concentrations as demonstrated in Figure 3.30b. Presence of low phosphate concentration showed negligible effect on As(III) removal while 0.08-0.1 mM (2.5-3 mg/L) phosphate as P reduced As(III) removal by 12-20%.

Silicate species are common oxyanions in natural water, with concentration ranging from 0.45 to 14 mg/L Si (0.016-0.5 mM)[151]. Figure 3.30c shows the effect of silicate ion of different concentrations on As(III) removal and it was revealed that silicate ion at low concentration as Si had no effect on arsenic removal under this condition. With the presence of 0.35 mM (10 mg/L) of soluble silicate as Si, the removal percentage of arsenic decreased by 12%. When silica is dissociated under alkaline conditions, its affinity for iron hydroxide surface increases significantly, resulting in a stronger competition with arsenic.

Thus we see that the presence of each of these ions has been found to inhibit the arsenic removal indicating that these ions compete for the surface adsorption sites as was reported earlier[358]. The removal of arsenic gradually decreases with increase in the concentrations of each of the competing ions. The removal of arsenic at the highest experimental concentrations of the ions have been found to be 84%, 80% and 88% in the presence of sulphate, phosphate and silicate ions, respectively, compared to >99% in their absence.

The inhibitory effect of phosphate has been found to be nonlinear and has been found to increase more rapidly above 0.048 mM (1.5 mg/L of phosphate as P). The inhibitory effect of sulphate and silicate were linear. Phosphate has a similar structure and deprotonation constants as arsenate in solution unlike sulphate and silicate. The different inhibitory behaviour of phosphate may be attributed to suppression of the 1st acid dissociation of $H_3AsO_4$ by high concentration of phosphate which is not there in the cases of sulphate and silicate in the experimental conditions. The inhibitory effects of these competing anions on arsenic removal by ferric chloride coagulation with permanganate oxidation at optimized pH is associated with the affinity of the competing anions for the surface and degree of these anions influencing the arsenic removal increases in the order: sulphate < silicate < phosphate.

As the inhibitory effects of these ions are mainly due to competition for the adsorption sites of coagulates, one may have to increase the coagulant dose if they are present in significant concentrations. To investigate the effect of $FeCl_3$ dose on arsenic removal in the presence of these co-existing anions, we have varied the dose of $FeCl_3$ in the range of 154.1-308.2 μM (25-50 mg/L) in presence of fixed concentrations of sulphate at 3.12 mM (300 mg/L), phosphate at 0.064 mM (2 mg/L as P) and silicate at 0.214 mM (6 mg/L as Si), separately. The results are shown in Figure 3.31. It can be seen from the figure that with the increase of $FeCl_3$ dose from 154.1 μM (25 mg/L) to 184.9 μM (30 mg/L), the removal of arsenic increased from 90% to more than 96% and increasing the dose of $FeCl_3$ upto 308.2 μM (50 mg/L) more than 98% removal has been achieved even in presence of the significant concentrations of sulphate, phosphate and silicate. Thus, the effects of the competing ions can be offset by appropriately increasing the coagulant dose.

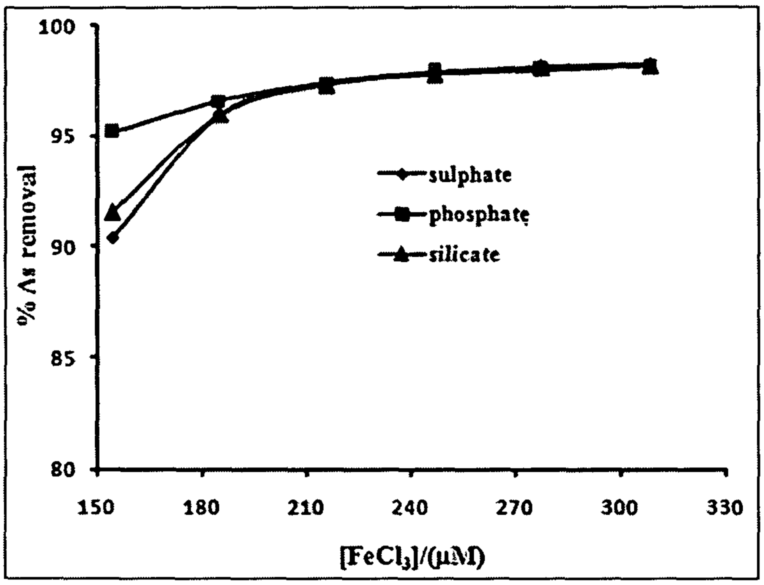

**Figure 3.31.** Effect of the coagulant dose on arsenic removal from distilled water in presence sulphate (3.12 mM), phosphate (0.064 mM) and silicate (0.214 mM) in the OCOP method.

## 3.3.3 Analysis of the precipitate

### *3.3.3.1 FTIR analysis*

The IR adsorption patterns of the precipitate obtained after the OCOP treatment in presence and the precipitate of only iron obtained in the absence of arsenic in distilled water are shown in Figure 3.32. The vibrational band observed at 3443 $cm^{-1}$ in presence of arsenic (3395 $cm^{-1}$ in absence) is supposed to be the OH stretching band[349]. The adsorption bands at 1637 and 1466 $cm^{-1}$ (1619 and 1466 $cm^{-1}$ in absence) may be ascribed to HOH bending[350] and $\partial$ (OH), respectively. Symmetric stretching of Fe–O is indicated by a band observed at 599 $cm^{-1}$ (a small shoulder in absence)[247]. The peak at 778 $cm^{-1}$ observed in the presence of arsenic, which is absent in the absence of arsenic, can be assigned to the As–OH stretching[363, 369]. It may be due to sorption of $HAsO_4^{2-}$ on iron precipitate.

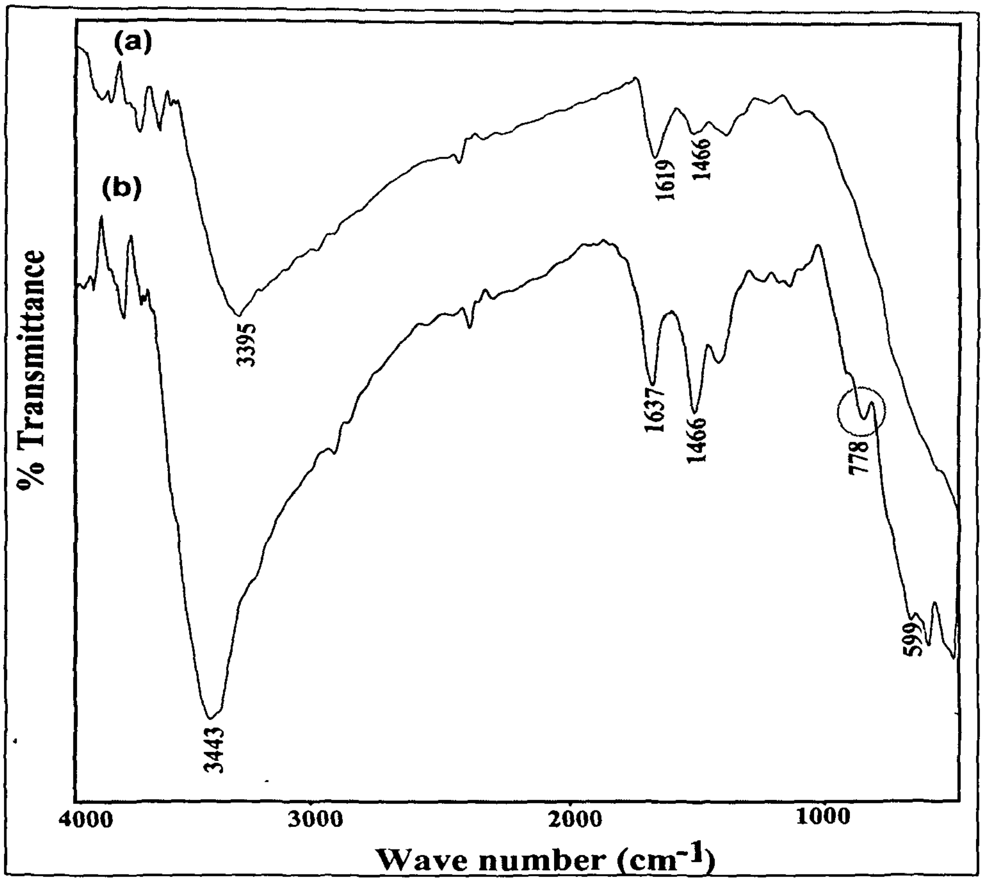

**Figure 3.32.** FTIR spectrum of precipitate obtained after treatment (a) in absence of arsenic (b) in presence of 3.34 μM (0.25 mg/L) arsenic from distilled water with 1.19 mM $NaHCO_3$ (100 mg/L), 3.16 μM $KMnO_4$ (0.5 mg/L) and 154.1 μM $FeCl_3$ (25 mg/L).

### *3.3.3.2 XRD analysis*

The XRD of the precipitates (Figure 3.33) obtained in presence of arsenic shows only two major peaks with overall poor crystallinity. A strong peak at 2θ of 31.75 which may correspond to iron oxide[365, 370], formed due to dehydration of water from ferric hydroxide. Another peak at 2θ of 45.55 may correspond to ferric hydroxide[365, 371]. Thus, the mostly amorphous precipitate contains some crystalline iron oxides and hydroxides in it. The appearance of some crystallinity in the present XRD spectra which were not seen in the XRD spectra of the precipitate of section 3.2.3.2 may be attributed to the presence of additional ferric ions from ferric chloride and $MnO_2$ in the present case. The XRD pattern does not show similarity with that corresponding to $FeAsO_4 \cdot xH_2O$ in the literature[372]. This may be due to very small As:Fe ratio in the water and due to the presence of Mn. The dominant arsenic removal mechanism involved in the OCOP method is supposed to be the sorption of arsenic onto the surface of poorly crystalline precipitate of ferric hydroxide instead of the precipitation of arsenic as insoluble crystalline iron-arsenic compound such as $FeAsO_4 \cdot xH_2O$[317, 372].

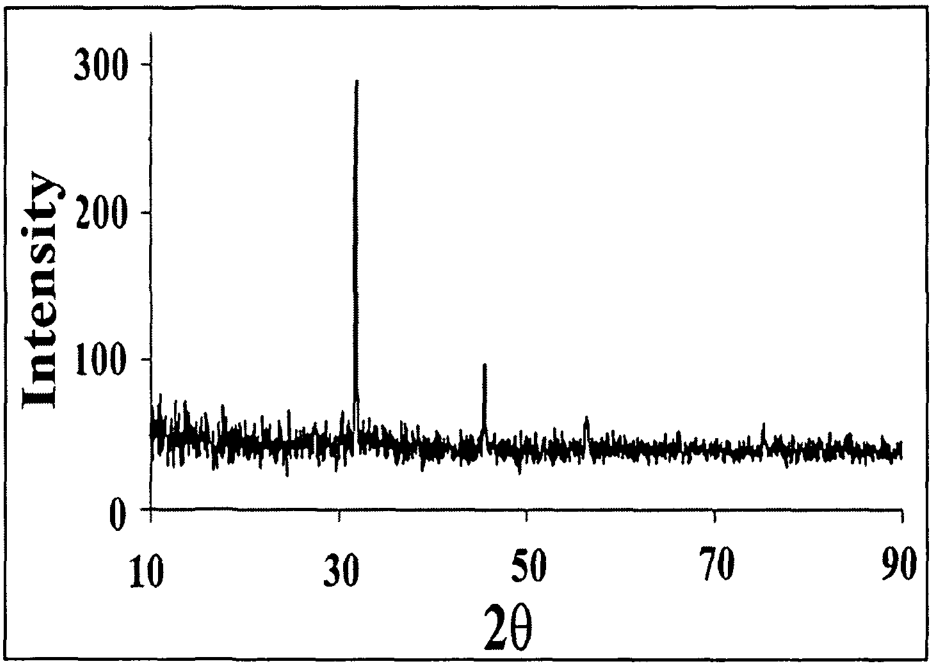

**Figure 3.33.** XRD pattern of the precipitate obtained after the OCOP treatment of arsenic (3.34 μM) containing distilled water with 1.19 mM $NaHCO_3$ (100 mg/L), 3.16 μM $KMnO_4$ (0.5 mg/L) and 154.1 μM $FeCl_3$ (25 mg/L).

### *3.3.3.3 SEM-EDS analysis*

The morphology and surface elements distribution of the precipitate obtained after treatment were studied by a SEM combined to an EDS. The SEM image of the precipitate reveals a 1-3 μm platelike morphology with smooth surfaces (Figure 3.34a).

The EDS analysis (Figure 3.34b) of the precipitate shows the presence of a small amount of arsenic in addition to iron and manganese. EDS analysis provided direct evidence that arsenic was adsorbed on a complex iron oxide precipitate. The observed manganese is from $MnO_2$. Other elements detected such as Na, K, Cl come from the chemicals used in the treatment.

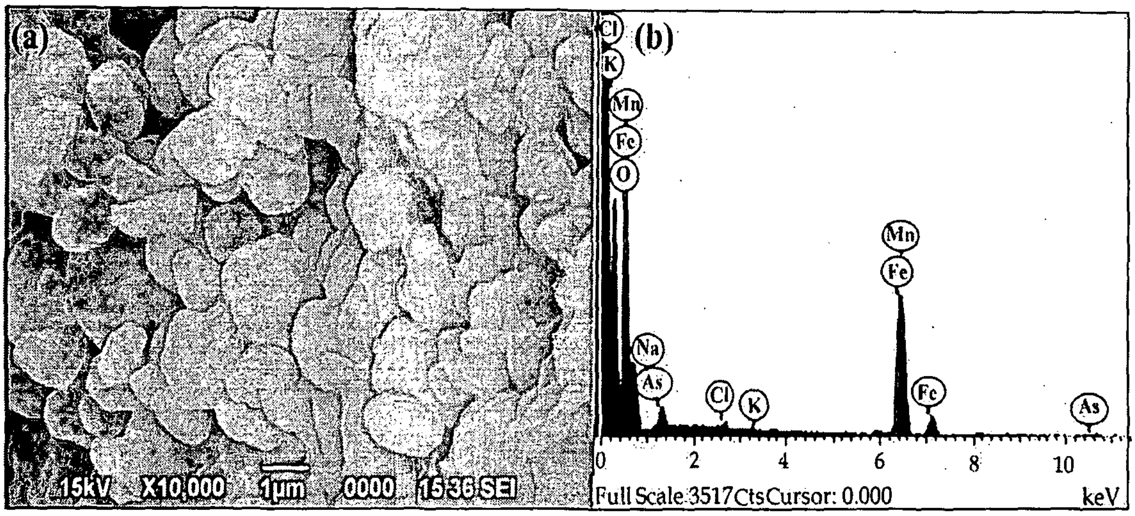

**Figure 3.34.** SEM-EDS image of the precipitate obtained after the OCOP treatment of arsenic (3.34 µM) containing distilled water with 1.19 mM $NaHCO_3$ (100 mg/L), 3.16 µM $KMnO_4$ (0.5 mg/L) and 154.1 µM $FeCl_3$ (25 mg/L).

### 3.3.4 Potability of the treated water

#### *3.3.4.1 Relevant water quality parameters before and after treatment*

The relevant water quality parameters of the water samples before and after the OCOP treatment determined using standard methods[336] are given in Table 3.25a and 3.25b. The final pH of the treated water is also well within the acceptable range for drinking water. All the water quality parameters determined after treatment were within the respective WHO guideline values for drinking water[34]. The concentrations of Fe, Mn, Na, K and Cl, which are present in the materials used, also remain within the WHO guideline values. The conductivity, total dissolved solids and total alkalinity showed marginal increase but within the respective WHO guideline values. It may be noted that anions, *viz.*, fluoride and silicate showed a decrease after the treatment. Also from Table 3.25b, one can see that final concentrations of some metal ions, *viz.*, Ca, Mg, Zn, Cd, Co, Mn and Cu decreased from their initial values after OCOP treatment.

**Table 3.25a.** Physicochemical water quality parameters and anion concentrations in water before and after arsenic removal by the OCOP treatment.

| Physicochemical property | WHO guideline value | Before | After |
|---|---|---|---|
| pH | 6.5-8.5 | 7.44 | 7.49 |
| Conductivity (μS/cm) | NS | 199 | 248 |
| Dissolved Solids (mg/L) | 600 | 130 | 166 |
| Suspended Solids (mg/L) | NS | 10 | 12 |
| Total Alkalinity as $CaCO_3$ (mg/L) | 200 | 84.0 | 92.0 |
| Total Hardness as $CaCO_3$ (mg/L) | 200 | 82.0 | 82.0 |
| Chloride (mg/L) | 250 | 6.0 | 12.0 |
| Fluoride (mg/L) | 1.50 | 0.33 | 0.31 |
| Nitrate (mg/L) | 50 | <1.0 | <1.0 |
| Phosphate as P (mg/L) | NS | <0.003 | <0.003 |
| Silica (mg/L) | NS | 4.35 | 2.51 |
| Sulphate (mg/L) | 500 | 6.2 | 6.2 |

**Table 3.25b.** Concentration of the metal ions in water before and after arsenic removal by the OCOP treatment.

| Metals / (mg/L) | WHO guideline values | Before | After |
|---|---|---|---|
| Cadmium | 0.003 | 0.001 | ND |
| Calcium | 75 | 0.72 | 0.64 |
| Chromium | 0.05 | ND | ND |
| Cobalt | NS | 0.001 | ND |
| Copper | 2 | 0.009 | 0.003 |
| Lead | 0.01 | ND | ND |
| Magnesium | NS | 2.61 | 1.1 |
| Manganese | 0.5 | 0.092 | ND |
| Mercury | 0.006 | <0.001 | <0.001 |
| Potassium | NS | 8.75 | 7.5 |
| Sodium | 50 | 5.62 | 18.9 |
| Zinc | 3.0 | 0.58 | 0.13 |

Ns: Not specified; ND: Not detectable

### *3.3.4.2 Bacteriological quality of the water*

The water before and after treatment by the OCOP method was tested for microbial contamination by using multiple tube method and biochemical assays[338]. Analysis was done to determine most probable number (MPN) of coliform organisms per milliliter of water as well as to determine the presence of pathogenic bacteria such as Escherichia coli. The results were recorded as MPN of coliform per 100 ml of water (Table 3.26). The MPN value for the water samples before and after treatment of arsenic was found to be <1.8 and thus acceptable for drinking with respect to bacteriological contamination[34]. The observed low MPN value may be attributed to disinfection property of potassium permanganate which is used as the oxidant in the present method[338].

**Table 3.26.** Bacteriological quality of the As-containing water before and after treatment.

| Type of water | Total Coliform bacteria | | | Escherichia coli or thermotolerant Coliform bacteria | | | Bacterio-logical quality |
|---|---|---|---|---|---|---|---|
| | MPN/ 100ml | Low Conf. limit | High Conf. limit | MPN/ 100ml | Low Conf. limit | High Conf. limit | |
| Before treatment | <1.8 | - | 6.8 | <1.8 | - | 6.8 | Acceptable |
| After treatment | <1.8 | - | 6.8 | <1.8 | - | 6.8 | Acceptable |

### 3.3.5 Environmental Impact

#### *3.3.5.1 Leachability test for arsenic in the sludge after water treatment*

The sludge generated after treatment of arsenic containing water was collected and tested for leachability of arsenic from the sludge. The leaching behaviour of arsenic in the sludge sample was evaluated with the toxicity characteristic leaching procedure (TCLP)[337]. Arsenic concentration in the TCLP leachate of the sludge sample was only <10 μg/L against the maximum permissible TCLP limit of the US-EPA of 5 mg/L. Thus, the arsenic concentration in the TCLP extract of the solid sludge of the present OCOP method is very low and more than 500 times lower than the US-EPA TCLP limit for disposing in land-fill[317]. The solid sludge can therefore be disposed in land-fill safely.

### 3.3.6 Suitability assessment

Arsenic removal technologies have to compete with the other technologies in which cost is a major determinant in the selection of a treatment option by the users. Considering the Indian retail prices of $NaHCO_3$, $KMnO_4$ and $FeCl_3$ as INR 13.50, 134.00 and 26.00 per kg, respectively, the recurring cost of treatment in the present method has been estimated as INR 0.0079 (USD 0.000158) per liter. The method can efficiently remove both arsenic and iron to below the respective WHO guideline values.

### 3.3.7 Summary

The laboratory batch studies have revealed that the present OCOP method using $NaHCO_3$, $KMnO_4$ and $FeCl_3$ as the pH-conditioner, oxidant and coagulant, respectively, is highly efficient for removal of both arsenic and iron from groundwater. The following conclusions have also been drawn from the present study:

- Arsenic can be removed from an initial concentration range of 1.33-6.67 μM (0.1-0.5 mg/L) to below 0.067 μM (0.005 mg/L) by OCOP method by using $NaHCO_3$ as buffering agent, $KMnO_4$ as oxidant and $FeCl_3$ as coagulant.
- The optimized dose of $NaHCO_3$ is 1.19 mM (0.1 g/L), $KMnO_4$ is 3.16 μM (0.5 mg/L) and $FeCl_3$ is 154.1 μM (25 mg/L) for removal of arsenic from an initial concentration range of 1.33-6.67 μM (0.1-0.5 mg/L) when there is no initial soluble iron in the water.
- The minimum dose of each of $NaHCO_3$, $KMnO_4$ and $FeCl_3$, required to bring arsenic to below 10 μg/L (0.133 μM), when plot individually against initial arsenic concentration at fixed chosen doses of the others, have been found to be linear in all three cases.
- In presence of soluble Fe(II), $KMnO_4$ dose should be increased to achieve the efficient removal of arsenic. About 25.3 μM (4 mg/L) of $KMnO_4$ is required for the complete oxidation of As(III) in presence Fe(II) up to 89.5 μM (5 mg/L).
- The inhibitory effects of competing ions on the arsenic removal by the present method increases in the order sulphate < silicate < phosphate.
- The inhibitory effects of the competing ions on the arsenic removal can be taken care of by increasing the dose of coagulant if they are present in significant concentration.
- Arsenic is removed through adsorption on a solid consisting of ferric hydroxide and Mn probably as $MnO_2$.
- Other relevant water quality parameters after treatment showed that the treated water is safe for drinking purpose.
- The OCOP process does not add any bacteriological contamination to the water.

- The recurring cost of treatment in the present method has been estimated as INR 0.0079 (USD 0.000158) per liter, which is competitive.
- The method is safe, environment friendly and has potential for rural application.

## 3.4 Field trial of the OCOP method

The field trial of the OCOP method was started in a phased manner at all together 16 spot water sources which included 10 households with 10 L, 5 schools with 25 L and 1 school with 200 L capacity systems. Though started in a phased manner, the trials later on continued simultaneously. An initial survey of use of household water and public tube well water was undertaken at the start of the field trial. These households were using groundwater for drinking and washing purpose. The tube well water in the schools was particularly used for drinking purpose. Arsenic levels in the water source of the household and schools were measured using Merck field test kits.

### 3.4.1 Field trial of the OCOP method with < 1.0 mg/L dissolved iron

In the first phase, the field trial was started on 9th of June, 2010 at the village of Tatigaon, in Titabor sub-division of Jorhat district of Assam, where the dissolved iron in the water was less than 1.0 mg/L. Water did not have dissolved iron but had about 200 µg/L of arsenic. Groundwater from 4 such hand tube wells, *viz.*, H1a, H2a, H3a and S1 were treated by the OCOP method with doses as mentioned in Table 3.27. The removal of arsenic was done at three households with water from each of the sources H1a, H2a and H3a. The arsenic removal from water from the source S1 was done at a child and woman care centre. The doses used for water with arsenic along with iron less than 1.0 mg/L were: 0.1 g/L of $NaHCO_3$, 0.5 mg/L of $KMnO_4$ and 25 mg/L of $FeCl_3$ as solid powder, 5% and 25% stock solutions, respectively. The procedure of application of the method has been described below:

#### 3.4.1.1 Procedure of the OCOP method

The three steps involved in the procedure are as follows:

***Step 1.*** A specified quantity of $NaHCO_3$ (baking soda or cooking soda) is added to the arsenic containing water in a bucket or a container and thoroughly mixed by stirring with a stick. It controls the pH of the water in an optimum range where the chemicals added in the subsequent steps work as desired. It dissolves and mixes immediately.

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***Step 2.*** A specified quantity of $KMnO_4$ is added to the water with thorough mixing by stirring. At the prevailing pH, $KMnO_4$ oxidizes arsenite to more easily removable arsenate form while reducing manganese from Mn(VII) to Mn(IV) state, i.e., to $MnO_2$ and not to Mn(II) state. Mn(II) is soluble in water and is unwanted in drinking water whereas $MnO_2$ is an insoluble solid and is removed in the process. The presence of bicarbonate also accelerates oxidation of arsenite to easily adsorbed arsenate.

***Step 3.*** After mixing of the $KMnO_4$ solution, a specified quantity of $FeCl_3$ is added to the water with thorough mixing by stirring for at least a minute. $FeCl_3$ is the most popular coagulating agent used in water treatment worldwide which is highly acidic and corrosive in aqueous solution but is safe in alkaline solution, e.g., in the presence of the specified quantity of baking soda. Ferric chloride coagulates sufficiently in the presence of baking soda.

**Table 3.27.** Doses of the chemicals for iron-free and iron containing water with arsenic concentration in the range of 100-500 μg/L.

| **Groundwater type** | **$NaHCO_3$** | **$KMnO_4$** | | **$FeCl_3$** | |
|---|---|---|---|---|---|
| | in mg/L | in mg/L | in ml (of 5% aqueous solution) per 10L of water | in mg/L | in ml (of 25% aqueous solution) per 10L of water |
| Having < 1.0 mg/L dissolved iron | 100 | 0.5 | 0.1 | 25 | 1 |
| Having 1.0 – 5.0 mg/L dissolved iron | 100 | 4 | 0.8 | 25 | 1 |
| Having > 5.0 mg/L dissolved iron | 100 | less than that imparts a light purple colour* | | 25 | 1 |

*For the water containing iron concentration above 5 mg/L, $KMnO_4$ was added until it imparts a light purple colour to the water. The colour, however, disappears after coagulation.

Coagulation in the form of reddish brown particles will be visible within minutes as shown in Figure 3.35. The water is then allowed to settle for at least an hour. The supernatant clear water can be decanted and filtered through sand-gravel filters.

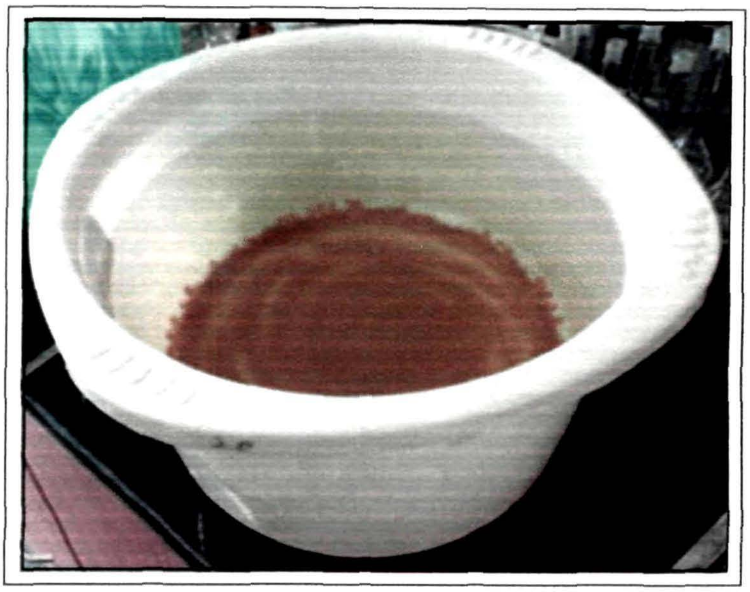

**Figure 3.35.** The settling of the precipitate after treatment.

### *3.4.1.2 Performance of the OCOP method with <1.0 mg/L dissolved iron*

The results of the field trial with groundwater having less than 1.0 mg/L dissolved iron are shown in Table 3.28a&b. The water samples after treatment were collected from the households and schools for one month and analysed for remaining [As] and [Fe] in the sample after arsenic removal. The average value of 15 samples from each source for remaining [As] and [Fe] with standard deviations are included in the table. From the results, it can be seen that arsenic was removed to below 5 µg/L when the initial iron ion concentration in the water was less than 1.0 mg/L. Concentrations of Fe were also reduced to below 0.1 mg/L in all cases of initial iron of less than 1.0 mg/L. Small standard deviations indicate close agreements among the results (Table 3.28a). The pH of the treated water remained within 7.4 to 8.2, which is within the acceptable range for drinking, i.e., 6.5-8.5. In addition to the results of the arsenic removal from the sources H1a, H2a and H3a, presented in Table 3.28a, results of arsenic removal at some more households with the same sources of water are also shown in Table 3.28b. This table includes one more groundwater source H4. The results shown in this table are averages of at least three. The results of Table 3.28b are similar to those of Table 3.28a. These results can be compared with the results available in the literature[373]. Thus, the results show that over 95% arsenic removal can be achieved with the used doses of the pH conditioner, oxidant and coagulants from arsenic-containing water with low dissolved iron. The process also lowers the iron concentrations and retains the pH within the acceptable range for drinking.

**Table 3.28a.** [As] (in μg/L) and [Fe] (in mg/L) before and after treatment by the present OCOP method in some field water from tube wells at schools (S) and households (H) in Jorhat district along with standard deviations (SD). The sample number was 15 from each source.

| Source[Ψ] | Capacity /L | [As]/(μg/L)* | | | [Fe]/(mg/L)* | | | pH* | |
|---|---|---|---|---|---|---|---|---|---|
| | | Before | After | SD[#] | Before | After | SD[#] | Before | After |
| H1a | 10 | 196.4 | 3.7 | 1.0 | 0.19 | 0.06 | 0.01 | 7.5 | 7.7 |
| H2a | | 208.5 | 4.1 | 1.1 | 0.28 | 0.08 | 0.01 | 7.8 | 8.1 |
| H3a | | 211.2 | 3.9 | 1.4 | 0.14 | 0.08 | 0.02 | 7.6 | 7.9 |
| S1 | 25 | 204.7 | 3.9 | 1.4 | 0.41 | 0.08 | 0.01 | 7.5 | 7.8 |
| S2 | | 238.1 | 7.6 | 0.7 | 2.61 | 0.14 | 0.60 | 7.3 | 7.5 |
| S3 | | 229.1 | 7.4 | 1.2 | 3.15 | 0.17 | 0.73 | 7.0 | 7.4 |

[Ψ]H1a, H2a, H3a and S1 were at Tatigaon village. S2 and S3 were at Kharikotia village. *Error limits: Δ[As]= ±0.4 μg/L, Δ[Fe]= ±0.05 mg/L and ΔpH= ±0.03. [#]SD's are for water samples after treatment. Other data are averages of at least three.

**Table 3.28b.** [As] (in μg/L) and [Fe] (in mg/L) before and after treatment by the present OCOP method in some field sample at schools (S) and households (H).

| Source | Capacity /L | [As]/(μg/L)* | | [Fe]/(mg/L)* | | pH* | |
|---|---|---|---|---|---|---|---|
| | | Before | After | Before | After | Before | After |
| H1b[#] | 10 | 196.4 | 5.3 | 0.19 | 0.06 | 7.5 | 7.7 |
| H1c[#] | | 196.4 | 4.5 | 0.19 | 0.06 | 7.5 | 7.7 |
| H2b[#] | | 208.5 | 5.2 | 0.28 | 0.08 | 7.8 | 8.2 |
| H2c[#] | | 208.5 | 6.1 | 0.28 | 0.08 | 7.8 | 8.1 |
| H3b[#] | | 211.2 | 3.6 | 0.14 | 0.08 | 7.6 | 7.9 |
| H3c[#] | | 211.2 | 5.2 | 0.14 | 0.08 | 7.6 | 7.8 |
| H4 | | 220.2 | 4.3 | 0.25 | 0.07 | 7.7 | 7.9 |
| S4 | 25 | 127.4 | 6.6 | 2.35 | 0.15 | 7.6 | 7.9 |
| S5 | | 185.4 | 8.2 | 5.73 | 0.20 | 7.5 | 7.7 |
| S6 | 200 | 106.5 | 9.2 | 16.25[Ψ] | 0.36 | 7.4 | 7.8 |

*Error limits: Δ[As] = ±0.4 μg/L, Δ[Fe] = ±0.05 mg/L and ΔpH = ±0.03. The data presented here are averages of at least three.

[#]Indicates same source as in Table 3.28a but As removal done at different households or schools. H4 was at Tatigaon village in Jorhat district. S4 and S5 were at Kakila and Kutumgaon villages in Sonitpur district and S6 was Kaithalkuchi village in Nalbari district.

[Ψ]$KMnO_4$ was added until it imparted a light pink colour to the water to oxidize ferrous iron. The colour disappeared after coagulation.

### 3.4.2 Field trial of the OCOP method with 1-5 mg/L dissolved iron

The second phase of the field trial was started a fortnight latter on 9th of September, 2010 at 2 schools (Sources S2 and S3 in Table 3.28a), *viz.*, Kharikatia High School and Kharikatia Lower Primary School with about 500 and 50 students, respectively, at Kharikatia in Titabor sub-division, Jorhat district. The water here had initially about 235 μg/L of arsenic and about 3 mg/L of iron. Latter, we started a field trial of arsenic and iron removal at one more school (Source S4 in Table 3.28b), *viz.*, Kakila Chariali Lower Primary School, Kakila, in Gohpur subdivision of Sonitpur district of Assam where the arsenic and iron concentrations were 127 μg/L and 2.4 mg/L, respectively.

An arsenic removal to 25 μg/L only was achieved with a $KMnO_4$ dose of 0.5 mg/L from the groundwater of S2 and S3 which had about 3 mg/L dissolved iron. The lower arsenic removal in presence of dissolved iron indicates oxidation of ferrous ions before oxidation of arsenite ions. However, we noticed better arsenic removal on increasing the dose of the oxidant. We had chosen a $KMnO_4$ dose of 4 mg/L, which is at least equivalent to the total initial arsenic and iron ions, assuming the entire initial arsenic and iron to be in arsenite and ferrous forms, respectively, for removing arsenic to below the WHO guideline value for arsenic affected groundwater containing dissolved iron in the range of 1-5 mg/L (Table 3.28). It can be mentioned here that the colour of $KMnO_4$ was not noticed in the treated water as any excess $KMnO_4$ was removed during the coagulation.

The results of the arsenic and iron removal of the groundwater sources, S2, S3 and S4, which had dissolved iron in the range of 1-5 mg/L are included in Table 3.28a&b. With this dose, both arsenic and iron were removed to below their respective WHO guideline values. It can be seen from the tables that despite addition of higher dose of $KMnO_4$, arsenic was lowered only to below 8 μg/L when the water contained iron >1.0 mg/L, which is slightly poorer than that in the presence of lower dissolved iron concentrations. This indicates that though initially present iron can remove arsenic to some extent[238], there is a negative effect of initially present iron on the arsenic removal to below 5 μg/L, even if the initial ferrous ions are oxidized in the process. However, with the chosen dose of $KMnO_4$, the OCOP process could remove both arsenic and iron to below their respective WHO guideline values.

### 3.4.3 Field trial of the OCOP method with > 5 mg/L dissolved iron

In the third phase, the field trial was conducted at 2 arsenic affected water spot sources, *viz.*, S5 and S6 at Bholukaguri Lower Primary School, Kutumgaon, in Chaiduwar sub-division of Sonitpur district and at Asom Kesori Jatiya Vidyalaya (a high school) at Kaithalkuchi village in Nalbari district of Assam, respectively. The groundwater of the tube wells of S5 and S6 had arsenic concentrations of 185 and 106 μg/L, respectively; whereas, they had dissolved iron concentrations of 5.73 and 16.25 mg/L, respectively. A 25 L *Arsiron Nilogon* unit for S5 and a 200 L *Arsiron Nilogon* unit for S6 (Figure 2.5c) were installed on 12 April, 2011 and on 15th of November, 2012, respectively. The difference in the timing was due to the time taken for choosing an appropriate and convenient site for the studies.

Arsenic from groundwater from S5 and S6 could be lowered only to 25 μg/L using 0.5 mg/L of $KMnO_4$. In these cases, rather than using a fixed dose of $KMnO_4$, we had chosen to determine the optimum doses for the individual groundwater sources. For this, we add $KMnO_4$ solutions slowly with stirring until a light pink colour remains in the water. A dose of $KMnO_4$, slightly little less than that imparts colour to the water was chosen and used in the OCOP process for the groundwater sources S5 and S6 in order to achieve removal of arsenic to below the WHO guideline values. The results are included in Table 3.28). Iron is also removed from 5.73 mg/L to 0.2 mg/L in case of S5 and from 16.25 mg/L to 0.36 mg/L in case of source S6. Thus, removal of arsenic to below the WHO guideline value and iron upto 97% have been achieved with this method retaining the final pH within the acceptable limit for drinking.

### 3.4.4 Post field-trial status

The State public health engineering department of Assam has, on 28 May 2013, started supplying river water to most of the arsenic-affected areas of Titabor sub-division. Therefore, the users there have stopped arsenic removal by the OCOP method. Two of the household users, however discontinued the arsenic removal after a few months. We attributted their discontinuation too their lack of awareness about the ill effects of arsenic because a large number of villagers from that area came forward and used the method with our help for removal of arsenic from their drinking water. We of course did not include these households (about 20) in the user trial study. Overall, the responses of the villagers and schools during the field-trial in the Titabor sub-division were encouraging.

The other schools, *viz.*, S4, S5 and S6, are continuing the method for arsenic and iron removal. All of them have time to time expressed their happiness with the *Arsiron*

*Nilogon* method. Moreover, to our knowledge at least one more school and 5-6 households in other areas have been using *Arsiron Nilogon* for removal of arsenic and iron from water.

In addition to the above, we receive enquiries and advice about application of the method every now and then from different people. Based on these we can conclude that the present OCOP method, *Arsiron Nilogon* has acceptability among rural arsenic affected people. Provided that the people are aware of the groundwater arsenic toxicity and provided that adequate measures are taken to popularize the present OCOP method in rural arsenic as well as iron affected areas where alternate source of arsenic-free or iron-free water is not available.

### 3.4.5 Summary

From the field trial, we found that the present OCOP technique has shown a good performance in arsenic removal in the field with real arsenic and iron containing groundwater. The following conclusions have also been drawn from the present study:

- The *Arsiron Nilogon* units can remove arsenic and iron simultaneously from contaminated groundwater to below their respective WHO guideline values for drinking.
- The procedure is simple to be practised by a layman within about 3 min for a household application.
- This method is a promising way of providing arsenic free drinking water in the areas where there is no alternative to removal of arsenic from contaminated groundwater in the state of Assam as well as elsewhere.
- From the experience during the field study, it can be said that awareness amongst the people and their whole hearted participation is very much essential to achieve success at field level.
- The high efficiency, simplicity of operation and the option of non-requirement of electricity make the present OCOP method highly competitive with other existing arsenic removal methods, *viz.*, ion exchange, nanofiltration, reverse osmosis and electrodialysis.

# Conclusions and future scope

# 4. Conclusions and Future scope

## 4.1 Conclusions

In the present work, we have chosen banana ash, lime, bicarbonate and carbonate salts of sodium and potassium as pH-conditioners and studied their efficiencies in arsenic and iron removal. After finding the best pH-conditioner to be used for arsenic removal, we have developed a method for simultaneous removal of arsenic and iron by pre-oxidation and coagulation in presence of the pH-conditioner in the prospect of field application. The method is named oxidation coagulation at optimized pH (OCOP). The conclusions of the study carried out in four stages, *viz.*, pH-conditioning for removal of iron, pH-conditioning for simultaneous removal of arsenic and iron, a laboratory study of the OCOP method and a field trial of the OCOP method, have been summarized here.

### 4.1.1 pH-conditioning for removal of iron

- The iron removal efficiencies of various pH-conditioners, *viz.*, the carbonate and bicarbonate salts of sodium and potassium, banana ash and their binary mixtures have been studied. Among them, potassium bicarbonate alone has been found to be the most effective pH-conditioner in the removal of iron from water followed by sodium bicarbonate.
- The pH of the treated water remains within the acceptable range for drinking when potassium bicarbonate or sodium bicarbonate is used.
- The removal rate has been found to improve with increase in the amount of the dose and residence time.
- The bicarbonates remove iron ion mostly as goethite, whereas, carbonates and ash precipitate iron mostly as ferrihydrite.
- Thus, the sodium or potassium bicarbonates may be the most potential pH-conditioners for simultaneous removal of iron and arsenic.

### 4.1.2 pH-conditioning for simultaneous removal of arsenic and iron

- For the simultaneous removal of arsenic and iron, the removal efficiency of different pH-conditioner has been found to be in the order: banana ash < carbonates < bicarbonates < lime.

- With the bicarbonate salts the final pH remains within the acceptable range for drinking, whereas, with lime the final pH is too high requiring a post treatment pH-adjustment.
- Among all the pH-conditioners $KHCO_3$ is the most effective, followed by $NaHCO_3$, for application along with other precipitating/coagulating agents for simultaneous removal of arsenate and iron ions.

### 4.1.3 Arsenic and Iron Removal by the OCOP method

- The present OCOP method using $NaHCO_3$, $KMnO_4$ and $FeCl_3$ as the pH-conditioner, oxidant and coagulant, respectively, is highly efficient for removal of both arsenic and iron ions simultaneously from groundwater.
- Arsenic can be removed from an initial concentration range of 100-500 μg/L to about 1-2 μg/L with the OCOP method.
- The doses of $NaHCO_3$, $KMnO_4$ and $FeCl_3$ have been optimized at 0.1 g/L, 0.5 mg/L and at 25 mg/L, respectively, for removal of arsenic from an initial concentration range of 100-500 μg/L in the absence of dissolved initial iron contamination in the water.
- The results of the analysis of the water quality parameters of treated water suggest that the treated water is suitable for drinking.
- In presence of dissolved Fe(II), $KMnO_4$ dose should be increased to get the efficient removal of arsenic.
- The inhibitory effects of competing ions on the arsenic removal by the present method can be taken care of by increasing the dose of coagulant.
- The method is low-cost, safe and environment friendly and is a potential method for rural application.

### 4.1.4 Field trial of the OCOP method

- The field trial of the OCOP method showed good performance.
- Arsenic removal to below the WHO guideline value from an initial concentration range of As of about 100-240 μg/L for drinking can be achieved with the present method in practical field along with lowering of the iron concentrations and retaining the pH within the acceptable range for drinking.

- The method is simple to be easily used by rural people.

Finally, from the systematic study that we have carried out with laboratory experiments and field trial, we have been able to present a simple, low-cost, safe, environment friendly and user friendly method, *viz.*, *Arsiron Nilogon*, based on oxidation-coagulation at optimized pH, for simultaneous removal of arsenic and iron ions from contaminated groundwater by the affected rural people.

## 4.2 Future scope

The findings of the present work and the proven applicability of the present OCOP method open up scopes for future research and development works in the following areas:

- Better management and utilization of the solid sludge may be explored.
- Sophisticated domestic arsenic and iron removal units based on the present method may be developed.
- Field trial of the technique at large community water supply system may be carried out.
- The present OCOP method can also be studied for removal of other heavy metals from groundwater.

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# Appendices

## Papers in Journals

1. **S. Bordoloi,** S.K Nath, R.K. Dutta, Iron ion removal from groundwater using banana ash, carbonates and bicarbonates of Na and K, and their mixtures, *Desalination* **281,** 190-198 (2011).
2. **S. Bordoloi,** M. Nath, R.K. Dutta, pH-conditioning for Simultaneous Removal of Arsenic and Iron Ions from Groundwater, *Process Saf. Environ. Prot.* **91,** 405-414 (2013).
3. **S. Bordoloi,** S.K. Nath, S. Gogoi, R.K. Dutta, Arsenic and iron removal from groundwater by oxidation-coagulation at optimized pH: laboratory and field studies, *J. Hazard. Mater.* **260,** 618-626 (2013).
4. S.K. Nath, **S. Bordoloi,** R.K. Dutta, Effect of acid on morphology of calcite during acid enhanced defluoridation, *J. Fluorine Chem.* **132,** 19-26 (2011).
5. S. Gogoi, S.K. Nath, **S. Bordoloi**, R.K. Dutta, Fluoride removal from groundwater by limestone treatment in presence of phosphoric acid. (Communicated)

## Patents applied/published

1. R.K. Dutta, S.K. Nath, **S. Bordoloi,** *Iron Removal From Water using* $HCO_3^-$ *or* $CO_3^{2-}$ *salts of* $K^+$ *or* $Na^+$ *Retaining the pH within the Acceptable Limit For drinking* (**Application No.2132/KOL/2008; Publication Date : 25/12/2009**).
2. R.K. Dutta, **S. Bordoloi,** S.K. Nath, *Arsenic Removal from Groundwater by Oxidation-Coagulation at Controlled pH for Domestic and Community Applications* (**Application No. 704/KOL/2010; Publication Date: 29/07/2011**).
3. R.K. Dutta, S.K. Nath, **S. Bordoloi,** Arsenic removal from water using $NaHCO_3$ or $KHCO_3$ or plant ash or their mixtures (**Application No. 508/KOL/2009 dated 23/03/2009 12:54:55**).

## Presentation in conferences

1. **Bordoloi, S.**, Nath, S.K., & Dutta, R.K. *Removal of iron from contaminated groundwater by carbonate or bicarbonate salts of Na and K with banana ash,* **National Seminar on Crisis of Fresh Water, A Challenge to Humanity and Life Processes, What is the Solution?** August 17-18, 2010. Dept. of Chemistry, D.R. College, Golaghat, Assam, India (**Oral Presentation**).

2. **Bordoloi, S.**, & Dutta, R.K. *Iron Removal from Groundwater using Banana Ash, Carbonates and Bicarbonates of Na and K, and their Mixtures,* **National Seminar on Green Chemistry for Sustainable World** on 4-5 February, 2011 at Gargaon College, Assam (**Oral presentation**).
3. **Bordoloi, S.**, & Dutta, R.K. *Integrated removal of arsenic and iron from contaminated groundwater by carbonate or bicarbonate salts and banana ash,* **UGC sponsored National Seminar on Sustainable soil & water resources management and environmental challenges** of the 21st Century, on 19th & 20th November, 2011, Chaiduar College, Gohpur, Sonitpur, Assam (**Oral presentation**).
4. **Bordoloi, S.**, & Dutta, R.K. *Removal of Arsenic and Iron by banana ash, carbonate and bicarbonate salts of sodium and potassium as pH-conditioner,* **International Seminar and workshop on Energy, sustainability and development** on 12-14 October, 2012 at Sibsagar College, Joysagar, Assam, India. (**best poster awarded**)
5. **Bordoloi, S.**, Nath, S.K., & Dutta, R.K. *Removal of Arsenic from groundwater by Oxidation-coagulation at Optimum pH,* **National conference on Chemistry, Chemical technology and Society** on 11th-12th November, 2011at Department of Chemical Sciences, Tezpur University (**Poster presentation**).
6. **Bordoloi, S.**, & Dutta, R.K. *pH-conditioning in Simultaneous Removal of Arsenic and Iron from Groundwater by Coprecipitation-adsorption,* **National Conference on Hydrology and water quality management** on 20-22 September, 2012 at Morigaon College, Morigaon, Assam (**Oral presentation**).
7. **Bordoloi, S.**, & Dutta, R.K. *A laboratory study on Removal of Arsenic from Contaminated Groundwater by Oxidation-Coagulation Process at optimized pH,* **2nd International Science Congress** on 8th-9th December, 2012 held at Bon Maharaj Engineering College, Vrindavan, Mathura, UP, India (**Oral presentation**).

**Conferences and school/workshops participated**

1. **Summer School on Green Chemistry**, 2-22nd June 2009, Sponsored by Department of Science and Technology (DST), New Delhi, India and organized by Dept. of Chemical Sciences, Tezpur University, Tezpur, Assam, India.

2. **Frontier Lecture Series**, 20-22 Nov 2009, Organized by Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) Bangalore, India in collaboration with Dept. of Chemical Sciences, Tezpur University, Tezpur, Assam, India.
3. **Workshop on Integrated Arsenic and Iron removal from Ground Water, "Arsiron Nilogon"**, 25th June, 2011, Sponsored by Department of Science and Technology (DST), New Delhi, India and organized by Dept. of Chemical Sciences, Tezpur University, Tezpur, Assam, India.
4. **Workshop on Arsenic and iron removal from groundwater** on 18th July, 2011 at Sonari College, Sonari, Sivsagar, Assam, India.
5. **Workshop on Groundwater Arsenic: Its Effects and Removal** on 22nd March, 2013 at Majuli College, Jorhat, Assam.
6. **Workshop on Groundwater Arsenic: Its Effects and Removal,** on 23rd March, 2013 at Uttar Majuli College, Jorhat, Assam.
7. **Workshop on Spectroscopic tools and their applications** on 6th April, 2013 at Department of Chemical Sciences, Tezpur University
8. **Workshop on Intellectual Property rights Sensitization**: IPRSW-2010 on 23rd December, 2010 at Tezpur University, Tezpur, Assam.
9. **International Congress on renewable energy** on 2-4th November, 2011 at Tezpur University, Tezpur, Assam.
10. **DST Workshop on Water Purification Possibility and Prospects**, 2011, Dept. of Chemistry, J.N.V. University, Jodhpur, India.