Fabrication and Monitoring of Single and Double Unit Ceramic Filters for Arsenic Removal

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A Project report submitted to the Department of Civil Engineering of Khulna University of Engineering & Technology, Khulna, Bangladesh in partial fulfillment of the requirements for the degree of

"Master of Science in Civil Engineering"

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Declaration

This is to certify that the Project Work entitled "Fabrication and Monitoring of Single and Double Unit Ceramic Filters for Arsenic Removal" has been carried out by Kumar Fagun Mallick, in the Department of Civil Engineering, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above Project work has not been submitted anywhere for any award of degree or diploma.
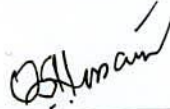

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Dr. Quazi Hamidul Bari
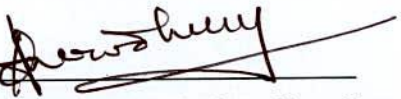
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Approval

This is to certify that the Project Work submitted by Kumar Fagun Mallick entitled as "Fabrication and Monitoring of Single and Double Unit Ceramic Filters for Arsenic Removal" has been approved by the board of examiners for the partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering under Khulna University of Engineering & Technology, Khulna, Bangladesh in November 14, 2011.

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Abstracts

Arsenic contamination of groundwater is one of the vital concerns of human health all over the world, especially in Bangladesh, India, Argentina, Vietnam, Mexico, etc. Among those, Bangladesh and West Bengal of India are most adversely affected. Many technologies have been tried to be induced, but a cheap, easy and more effective technology is yet to come.

The project focused on the development, and also the checking of the performances of that filter unit. The filter unit worked in the biological oxidation process by the cultured iron bacteria for arsenic removal. The treatment unit was composed of a ceramic filter, iron net, iron oxidizing bacteria, clay pot reactor, stand, and bucket for the effluent storage. The ceramic filter was made of locally available cheap materials (i.e. clay soil and rice bran). This filter unit was firstly installed with iron net as the source of the iron. After that, single unit filter systems with different iron options as iron net, scrap iron and iron rod were installed and run for long time. These two attempts were taken to check the suitability of single unit filter systems in case of household tubewells with highly arsenic contaminated water. Double unit filter systems were then developed and installed in the field. Firstly double unit filter systems with both 'W-system' and 'Connect system' were installed and run to compare the performances. There was no big difference found between the performances of these two ways of double unit filtration. Then double unit filter systems with 'Connect system' were being run continuously for the long run.

In case of arsenic removal, the single unit system was not able to reduce the arsenic concentration level to allowable limit, as the raw waters of all the sites were highly contaminated. The average removal efficiency for two single unit filter systems was 65.56% and 67.34% respectively. Average iron removal efficiency was almost 100%.

The comparison among the results of single unit filter systems with iron net, scrap iron and iron rod showed that whatever the iron producing option in the single unit filter system the performances remain almost same. Average arsenic removal efficiency for single unit filter systems with net, scrap and rod ion was 73.63%, 74.42% and 73.73%, respectively during the long run of the filter units in the field. Iron removal was successfully accomplished by every option as iron net, scrap iron or iron rod and average iron concentration was reduced from

7.90 mg/L to almost zero. The color removal efficiency for filter units with iron net, scrap iron and iron rod were as follows 97.15%, 94.70% and 97.11%. Also the turbidity of the raw water samples was reduced significantly by the filtration process. Influent and effluents with iron net, scrap iron and iron rod contained turbidity of average values 98.99, 10.25, 10.65 and 10.79 NTU, respectively.

Prior to the long run of the double unit filter system in field level; a short study was performed in the same household to choose the way of double filtration ('W-system' or 'Connect system'). Arsenic removal efficiency was nearly same in case of double unit filter systems with 'W-system' and 'Connect system'. In 'W-system', the removal efficiency in 1st effluent and 2nd effluent were as 63% and 86.21%, respectively and in 'Connect system', the final removal efficiency was 83.96%. The average values of influent, 1st effluent, 2nd effluent and final effluent were 406 μg/L, 149 μg/L, 57 μg/L and 65 μg/L for 'R1double'; while 421 μg/L, 151 μg/L, 57 μg/L and 62 μg/L for 'R2double' respectively. Also from the performances with respect to other water quality parameters it was found that whatever the way of double unit filtration the performances had a little difference.

Most of the cases, the double unit filter system was proved effective to reduce the arsenic concentration to the allowable standard limit (Bangladesh standard 50 μg/L). Average removal efficiency of 'R1double' and 'R2double' for the long monitoring study was 88.19% and 87.33% respectively. Average influent and final effluent arsenic concentrations were 419 μg/L and 50 μg/L for 'R1double', and 416 μg/L and 53 μg/L for 'R2double'. Iron removal efficiency was 100% for both 'R1double' and 'R2double'. Also the average color and turbidity removal efficiency was above 95%.

Flow rates for different filter options were important factor. It was found that the flow was reduced with time due to the clogging of the filter core. For good filtration rate and removal efficiency, the filter core was cleaned in very 30 days.

The cost of the treatment unit was approximately 150 ~ 200 BDT only and the maintenance was very easy and economic. Thus, the filter unit could be widely used in different arsenic contaminated rural areas of Bangladesh.

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CHAPTER 1

Introduction

1.1 Introduction

Arsenic contamination has become a serious threat to public health challenge almost all over the world, because prolonged exposure to elevated arsenic concentrations (even at quite low concentrations) has been linked to several types of cancer and non-cancer life taking diseases.

Two forms of arsenic are found chemically in ground water: inorganic and organic. Inorganic Arsenic has four main chemical forms having oxidation states, -3, 0, +3, and +5, but in natural water its predominant forms are inorganic oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). As(V) is the predominant species under atmospheric or more oxidizing environment, which exits predominantly as oxyanions, namely, $H_2AsO_4^-$ or $HAsO_4^{2-}$ in the pH range of 6-9. As (III) is thermodynamically stable and exits predominantly as H_3AsO_3 or $HAsO_2$ under mildly reducing conditions (Smedley and Kinniburgh, 2002). The toxicity of different arsenic species varies in the order arsenite> arsenate> monomethylarsonate> dimethylarsinate. As(III) is about 60 times more toxic than arsenic in the oxidized As(V), while inorganic arsenic compounds are about 100 times more toxic than organic arsenic compounds (Jain and Ali, 2000).

Arsenic (As) contamination of groundwater is major concern on a global scale. Arsenic contaminated groundwater has been found in Argentina, Chili, Mexico, China, Hungary, West Bengal, Bangladesh and Vietnam. Of these regions, West Bengal and Bangladesh are most seriously affected in terms of the size of the population at risk and the magnitude of the health problems. A recent survey of shallow groundwater aquifers in Bangladesh showed that 27% of the aquifers have arsenic concentrations >50 µg l⁻¹ (BGS, 1999) and more than 90% of the rural population in Bangladesh gets drinking from 4-5 million tubewells.

A large amount of affected people has been identified in rural area of Bangladesh which is arsenic related disease ranging form melanosis to skin cancer and gangrene. A recent report

maintains that arsenic contaminated tubewells water is contributing to nearly 125,000 cases of skin cancer and killing about 3000 people in Bangladesh each year (Clark, 2003). The mortality rate from arsenic poisoning is expected to rise substantially in the near future as it has a possibility of arsenic contamination in food chain through irrigation water too.

Due to the carcinogenic nature of arsenic, recently EPA as well as WHO revised the maximum concentration limit (MCL) for arsenic in drinking water by decreasing it from 50 to 10 μg l^{-1} (WHO, 1996; EPA, 2002). As a result of this revision, many areas in the world exceeded the new limit of arsenic in drinking water. Moreover, all developing countries affected with contaminated groundwater are still struggling to keep up with the previous WHO guideline value of 50 μg l^{-1}. Chronic exposure to arsenic >50 μg l^{-1} in drinking water can result in serious health problems. Symptoms of chronic exposure include skin, cardiovascular, renal, hematological and respiratory disorders (Marshall et al., 2007; Smith et al., 1998 and Mazumdar et al., 2005).

Therefore, it is urgently needed to find the effective, acceptable and sustainable solution to address the problem of arsenic contamination. Most scientific attention to date has focused mainly on identifying the source and causes of arsenic contamination. Developing of cost effective technology for arsenic removal and possibility of using alternatives water sources also has been tried. The arsenic removal technologies includes the co-precipitation (e.g. with iron or aluminum salts), ion exchange, adsorption by activated carbon and membrane processes. The alternatives water sources are surface water, rain water harvesting, dugwell and deep tubewell.

Quite often it is a very complex task to select a method because of the many difficulties that arise when a particular technology is applied in the field. These difficulties include a wide range of arsenic concentrations, effects of other elements and their variable concentrations in water, the need to adjust pH for optimal removal, optimized dose, proper operation and maintenance, and safe disposal of arsenic waste. Another major issue concerning a technology is that it should not pose risk of bacteriological contamination and should be broadly acceptable to users. Field studies in Bangladesh showed that the main reasons for rejection of some technologies or alternative options are the cost, the amount of operational effort, the level of maintenance, the amount of time until clean water is available, and the volume of water that the technologies can provide on a daily basis.

Developing countries like Bangladesh, India and Vietnam cannot afford expensive and/or large scale treatments. Low-cost, effective technologies that are readily available at the household or community level are needed to solve the present crisis. Large-scale treatments are not appropriate because many people in third-world countries obtain water from wells rather than from large municipal water plants. Appropriate in-home technologies to be implemented in third-world countries should meet certain criteria to be effective. The treatment must be applicable over a wide range of arsenic concentrations and easy to use without running water or electricity, and the materials for the treatment must be cheap, readily available, and/or reusable to reduce costs. Finally, such technology should not introduce any harmful chemicals into drinking water.

Among the arsenic removal technologies, adsorption and subsequent co-precipitation with iron salts is the simplest and convincible arsenic removal technique. Iron salts occur in two forms, Fe (II) and Fe (III), while removal by Fe(III) salts are more commonly used technology (Katsoyiannis and Zouboulis, 2004; Thirunavukkarasu et al., 2003) . Arsenic removal by Fe (III) salts need pre-oxidation of As (III) to As (V) because As (III) is the most common species in anaerobic ground waters (Harvey et al., 2004) and generally is removed less efficiently than the oxidized As (V) (Dixit and Hering, 2003).

Recent studies have been found that As(III) is partially oxidized by reactive intermediates (possibly Fe(IV) species) form during the physicochemical oxidation of Fe(II), results the high efficiency of arsenic removal than those of Fe(III) (Berg et al., 2001; Hug and Leupin, 2003). The removal of As(III) with Fe(II) is thus expected to have advantages over Fe(III) over some reasons: i) Partial oxidation of As(III) to As(V) ii) Higher sorption capacity during Fe(II) oxidation iii) No chemical need to be added in the regions such as Bangladesh and India where an elevated level of dissolved iron (avg.5 mg l^{-1}) with elevated level of dissolved arsenic has been found (Chowdhury et al., 2000). Therefore, the pre-oxidation step of As (III) could be skipped by using Fe (II) salts instead of Fe(III) salts.

Fe (II) can be oxidized by both physicochemically and biologically but the dominant one is depend on the physical and chemical characteristics of the raw water and process conditions. The biological iron oxidation is caused by the presence of several iron oxidizing microorganisms in water. *Gallionella* sp and *Leptrothrix ochracea* cause primary intercellular oxidation by enzymatic action, while secondary extracellular oxidation is caused by the catalytic action of polymer excreted filaments (Czekalla et al., 1985). A biological process of

iron removal has advantages than that of physicochemical process. Mounchet (1992) reported that a biological process could have high filtration rate, high retention capacity, flexibility of operation and reduced the capital cost. On the other hand, the rate of iron oxidation can be increased in the presence of iron oxidizer (Michalakos et al., 1997). In aerobic water slow and continuous release of Fe (II) from Fe (0) and subsequent oxidation to Fe (III) could effectively remove arsenic. Thus the arsenic removal method based on biological iron oxidation would be an ideal option in developing countries such as Bangladesh and India.

In this study, arsenic removal by a process of biological iron oxidation with cultured iron bacteria was conducted by field study in rural arsenic contaminated areas of Bangladesh. The performances were monitored to evaluate the sustainability of the proposed technology.

1.2 Objectives of the Study

The principle objectives of this study are as follows:

- To develop an effective and cheap arsenic removal unit made of locally available materials which will be suitable for the rural people of Bangladesh.
- To study the performance of developed single unit filter system in the field level for not only arsenic removal, but also iron, phosphorus, silica, color, turbidity, TDS etc.
- To study the performance for the systems with the modification of the filter unit. For example, filter units with different sources of iron oxidizing bacteria were compared to find the best option. For that, filter units with iron net, scrap iron and iron rod were run in the field and samples were analyzed.
- To evaluate the performances of double unit filter system in the field level.

1.3 Contents of the Study

Chapter 2: Review of Literature

Detail descriptions about the theories related to the arsenic contamination are stated with arsenic chemistry, present situation of arsenic contamination, arsenic removal technologies etc. are described in this chapter.

↓

Chapter 3: Materials and Methods

The detail methodology of the project work is stated in this chapter. Construction, set up, monitoring of the filter units and sampling, testing etc. of the samples are described in this chapter.

↓

Chapter 4: Results and Discussions: Performance of Single Unit Filter Systems

The whole results of the project work are presented in two chapters. In chapter 4, the performances of the single unit filter system are described. Also, the performances of single unit filter systems with 3 different options of iron are compared in the second portion of the chapter.

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Chapter 5: Results and Discussions: Performance of Double Unit Filter Systems

The performances of double unit filter systems are presented here. Firstly, results of a short study to find the suitable way of double filtration ('W-system' or 'Connect system') are reported. Then, the results of the long run of the double unit filter systems are described.

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Chapter 6: Conclusions and Recommendations

The findings of the project work are stated precisely in this chapter. Also the guidelines for the future works in this sector are mentioned at the end.

Figure 1.1: Contents of the Study

CHAPTER 2

Review of Literature

2.1 Introduction

Arsenic is a well-known toxic metal and is present mainly as oxyanion compounds in groundwater (Smedley and Kinniburgh, 2002). The World Health Organization (WHO) current provisional guideline for arsenic in drinking water is 10 $\mu g l^{-1}$ but all developing countries affected with contaminated groundwater are still struggling to keep up with the previous WHO guideline value of 50 $\mu g l^{-1}$ (Khan et al., 2000). Chronic exposure to arsenic >50 $\mu g l^{-1}$ in drinking water can result in serious health problems. Symptoms of chronic exposure to groundwater contaminated with arsenic at concentrations significantly >50 $\mu g l^{-1}$ include skin, cardiovascular, renal, hematological and respiratory disorders (Smedley and Kinniburgh, 2002). An estimated 300,000 people in West Bengal alone suffer from arsenic-induced skin lesions. Serious illnesses related to arsenic such as melanosis, keratosis, cancer, and gangrene have been reported in West Bengal and Bangladesh. Arsenic contamination of drinking water is presently a worldwide epidemic. Contaminated drinking water has been found in Argentina, Chile, Mexico, China, Hungary, West Bengal, Bangladesh and Vietnam. Of these regions, West Bengal and Bangladesh are most seriously affected in terms of the size of the population at risk and the magnitude of the health problems. A recent survey of shallow groundwater aquifers in Bangladesh showed that 27% of the aquifers have arsenic concentrations >50 $\mu g\ l^{-1}$ (Khan et al., 2000). Although the percentage does not seem remarkably high, it is alarming considering that more than 90% of the rural population in Bangladesh gets drinking from 4-5 million tubewells (Ahmed, 2001). Most of arsenic problems in third-world countries today are caused by natural erosion. One important mechanism through which the groundwater is polluted with arsenic is the reduction of iron oxyhydroxide (FeOOH) by bacteria and subsequent desorption of arsenic from the iron surfaces. In the Bengal Basin (part of Bangladesh and West Bengal), it is the main

mechanism by which groundwater become contaminated with arsenic (BGS, 1999; Fazal, 2001; Smedley and Kinniburgh, 2002).

Arsenic, probably the oldest known human poison, has six characteristics (Nriagu and Azcue, 1990):

- It is a virulent poison on acute ingestion, 76 mg arsenic (III) is considered to be lethal to adults.

- It is extremely toxic on long-term exposure to very low concentrations. The WHO acceptable skin cancer risk is calculated to be 0.17µg arsenic/L of water (WHO, 1996).

- It is not visible in water and food. Even heavy contaminated water may be clear and colorless.

- It has no smell, even at deadly concentrations.

- It has no taste. Even heavy contaminated water may have a pleasant taste.

- It is difficult to analyze, even when occurring in water in concentrations double as high as the WHO guideline.

2.2 History of Arsenic

Arsenic is the 20th most abundant element in the earth's crust and 12th most abundant element in the human body (Abedin et al., 2002; Borgona et al., 1977). It has been used as a homicide since the middle Ages. However, As is also known as a therapeutic agent as early as 400 BC. For example, Fowler solution (arsenite solution containing 7.6 * 106 µg As/l) has been used since the 19th century for the treatment of leukemia, psoriasis, chronic bronchial asthma and also as a tonic. The daily dosage was often as high as 3000 µg. As has also extensively been used as pesticides, herbicides, wood preservatives, and manufacture of dyestuffs, chemical warfare gases, glass industry, electronics, and growth promoting agent (Tseng et al., 2002). The discovery of adverse health effects due to As exposure led to decreased usage of As. For example, the use of As salts in the agriculture went down drastically since 1970's with 70% of the worldwide production As trioxide applied in the agriculture in 1970 to only 45% in 1980 (Mandal and Suzuki, 2002). The usage of As in the glass manufacturing industry is also reduced (Fitzgerald, 1983). The current uses of As

compounds are as clarifier in the glass industry, as wood preservative, in semiconductors, as a desiccant and defoliant in agriculture (Bauer, 1983; Hindmarsh, 2000). One of the present usages of As as therapeutic agent is in Cancer treatment. Recently in 2000 randomized clinical trials in the US led the Food and Drug Administration (FDA) to approve As trioxide for treatment against leukemia (Peters et al., 1996).

2.3 Arsenic in Bengal Delta

2.3.1 Occurrence of Arsenic

The As contamination in the Bengal delta was first discovered in 1980's in West Bengal (India) followed by Bangladesh in 1993 (Guo, 2004). The As contaminated area is mainly situated in the flood plains of the rivers Ganges, Brahmaputra and Meghna emerging from Himalayas. The drinking water in the Bengal delta is mainly extracted using tube wells from 10-150 m depth (also called as shallow tube wells) and elevated As concentrations mainly occur at these depths. The very shallow wells (< 10 m depth), ponds, and river water are basically free from As. Deep tube wells (> 150 m) are also generally free from As, however, some studies show that the As concentration in the deep tube wells increases with age due to reasons like absence of impermeable layer or improper tube well casing (Saha, 2003).

The ground water in shallow tube wells with elevated As is of typically $Ca(Mg)HCO^3$ type and positive correlation exists between As and HCO^{3-}. Dissolved Ca^{2+} follows dissolved As profile. The pH is near neutral with low dissolved oxygen. As is predominantly present as inorganic As(III). High phosphate (P) and silicate (Si) occur along with As. Elevated Fe concentrations also occur and in some areas a positive correlation exists between elevated As and Fe. Although, the Fe and As are not strongly correlated in other areas elevated As concentrations usually occur with elevated Fe concentrations (Vahter, 1994; Stuben et al., 2003).

The recent studies show that the As contaminated area is more widespread than the Bengal delta and occur along the courses of Himalayan Rivers covering Nepal (Wyatt et al., 1998; Ahmed et al., 2004) and other districts of India upstream of the Bengal delta (Maki-Paakkenen et al., 1998; Neku and Tandukar, 2003; Chakroborti et al., 2003), and Pakistan (Chakroborti, 2003; Nickson et al., 2005). Figure 2.1 shows the 4 major rivers along which elevated As concentrations occur, with the Bengal delta being the most studied area for the reasons behind occurrence of As (Sharma, 2006).
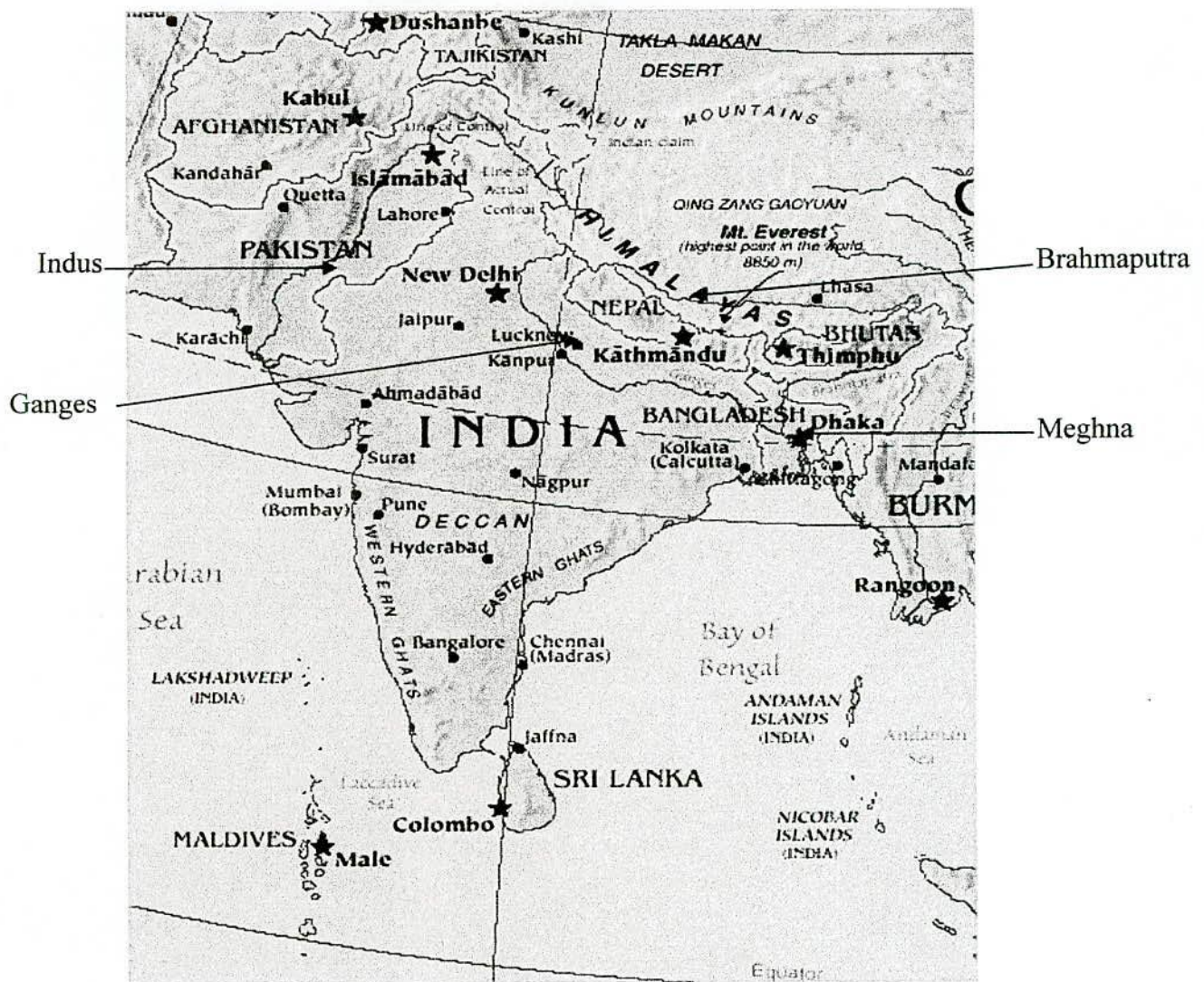
Figure 2.1: Extent of Arsenic contamination in the Indian subcontinent (Sharma, 2006)

2.3.2 Origin of As

At the initial stages of As discovery in the Bengal delta the contamination was thought to be of anthropogenic origin due to reasons like burial of light poles coated with chromate copper arsenates (CCA), application of pesticides and phosphatic fertilizers rich in As, or other industrial contamination (Ahmad et al., 2004). In 1993 a study was also published from Behala, West Bengal on elevated As concentrations in ground water due to discharge from insecticide (Paris Green (copper acetoarsenite)) manufacturing industry (Chatterjee et al., 1993). However, the theory of anthropogenic sources for As contamination in the Bengal delta was later discarded due to the extent and nature of the problem and it was established that the As occurrence is natural in origin. It is believed that the rivers like Ganges, Meghna

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and Brahmaputra carry As bearing primary minerals like pyrite, arsenopyrite and other sulfides from various sources like Himalayas, Subhimalayas (Siwalik mountains), Rajmahal, ChotNagpur, Darjeeling Himalayas, Shillong hills and later deposited along their courses (Saha, 2003; Acharyya et al., 1999; Uddin, 1999; Stanger, 2005).

2.3.2.1 Natural Sources of Arsenic

Arsenic bearing minerals are the primary natural sources of arsenic. There are more than 245 such minerals, mostly ores containing sulfide, along with copper, nickel, lead, cobalt and other metals as well as some oxides. The following table (Table 2.1) provides a list of some important arsenic bearing minerals.

The most important ores of arsenic are Arsenopyrite or Mispickel (FeAsS), Realgar (As_4S_4),Orpimant(As_2S_3), Loellingite (FeAs$_2$), Nicolite (NiAs), Cobalt-glance (CoAsS), Nickel -glance (NiAsS), Smaltite (CoAs$_2$) and Arsenolite (As$_2$O$_3$)). Among these, Arsenopyrite is probably the most common mineral. Arsenic occurs in uncontaminated soil at an average concentration of about 5 to 6 mg/kg, but this varies among geographic regions.

2.3.2.2 Anthropogenic Sources of Arsenic

Recent estimates have placed the ratio of natural to anthropogenic inputs of arsenic at 60:40. The anthropogenic influence on the level of arsenic in soils depends on the human activity, the distance from the pollution sources and the pollution dispersion pattern. Arsenic may accumulate in soil through use of arsenical pesticides, application of fertilizers, irrigation and dust from the burning fuels and disposal of industrial and animal wastes. It is a natural contaminant in lead, zinc, gold and copper ores and can be released during the smelting process.

2.3.2.3 Man-made Sources of Arsenic

Elemental arsenic is produced commercially from arsenic trioxide. Arsenic trioxide is a byproduct of metal smelting operations. About 70% of the world production of arsenic is used in timber treatment, 22% in agricultural chemicals, and the remainder in glass, pharmaceuticals and metallic alloys. Mining, metal smelting and burning of fossil fuels are the major industrial processes that contribute to arsenic contamination of air, water and soil.

Table 2.1: Naturally Occurring Minerals Containing Arsenic (NRCC, 1978)

Mineral	Formula	Mineral	Formula
Arsenite	As	Pearcite	$Ag_{16}As_2S_{12}$
Antimony arsenide	AsSb	Proustite	Ag_2AsS_3
Realger	AsS	Energite	Cu_3AsS_4
Orpiment	As_2S_3	Rathite	Pb_3AsS_4
Arsenopyrite	FeAsS	Aiseiiolite	AS_2O_3
Nicolite	NiAsS	Mutite	$Pbs(PO_4,AsO_4)3CI$
Gersdorffite	CoAsS	Adamite	$Zn_2AsO_4(OH)$
Cobaltite	CoAsS	Erythrite	$CO_3AsO_4.8H_2O$
Smaltite	$(Co,Ni)As_x$	Annabergite	$N_{13}(AsO_4)_2.8H_2O$
Skutteridite	$(Co,Ni)As_x$	Scorodite	$(Fe.Al)AsO_4.2H_2O$
Loellingite	$F eAs_2$	Pharmacosiderite	$Fe_3(AsO_4)OH_4$
Tennantite	$Cu_{12}As_4S_{13}$	Olivenite	$Cu_2(AsO_4)OH$
Jordanite	$(Pb, Ti)_{13}As_7S_{23}$	Beaudanite	$PbFe_3(AsO_4)SO_4$

2.3.3 Causes for release of As

Three different hypotheses on release of naturally occurring As were put forward to explain the mobilization of As into ground water. 1) Desorption due to P from fertilizers 2) Pyrite-oxidation theory 3) Oxi-hydroxide reduction theory. The hypothesis of As release due to displacement with P from phosphatic fertilizers was based on the fact that the ground waters in the Bengal delta contain high concentrations of P along with As (Acharyya et al., 2000; Acharyya et al., 1999). Studies are also available from other parts of the world where elevated As concentrations in groundwater resulted due to application of phosphatic fertilizers (Cherry et al., 1979; Cao et al., 2003; Davenport and Peryea, 1991; Peryea, 1991). However, this theory did not get any support in the Bengal delta context due to inadequate and contradictory evidence. The pyrite oxidation theory also called oxidation theory was put forward due to the discovery of pyrite grains in the sediments both in West Bengal (India) and Bangladesh. The supporters of this theory believe that As is present as pyrite in the

sediments and is released due to heavy withdrawal of groundwater (Das et al., 1995; Acharyya et al., 1999). The lowering of groundwater table due to heavy water withdrawal would result in penetration of oxygen into the deeper sediments resulting in oxidation of pyrites rich in As as shown in equations 2.1 & 2.2.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO^{2-} + 4H^+ \dots\dots\dots \text{ equation (2.1)}$$
$$4FeAsS + 11O_2 + 6H_2O \rightarrow 4\ Fe^{2+} + 4H_3AsO_3 + 4SO_4^- \dots\dots\dots \text{ equation (2.2).}$$

Reported incidences of elevated As concentrations in ground water due to oxidation of pyrite and other arsenic-bearing rocks are available from other parts of the world (Armienta et al., 2001; Saha, 2003). However, in the Bengal delta context, this theory did not either get wider acceptance due to the widespread absence of arsenopyrite in the sediments (Acharyya et al., 1999; Ahmed et al., 2002). There are many other opposing facts to the oxidation theory as the cause of As occurrence. Instead of positive correlation between $SO4^{2-}$ and As concentrations as expected due to pyrite oxidation, negative correlation exists between $SO4^{2-}$ and As concentrations. The presence of pyrite shows that it has not been oxidised, but was formed in situ and hence it is sink and not source for As. The intensity of As problem has no direct relation with groundwater fluctuations. Hence the oxidation theory is not being considered as main mechanism for As release (Nickson et al., 2000; Anawar et al., 2003).

The oxy-hydroxide reduction hypothesis assumes that the As bearing minerals carried by the rivers were oxidized during transportation (as shown in equation 1- 4) and metals and As in solution (mainly as As (V) species) were co-precipitated or adsorbed on the flocculating particulate matter and on the surface of grains coated with Mn- and Feoxyhydroxides (Equation 2.5 & 2.6) and deposited(Nickson et al., 2000; Vahter, 1994).

$$Fe^{2+} + 0.5O + 1.5H_2O \rightarrow FeOOH + 2H^+ \dots\dots\dots\dots \text{Equation (2.3)}$$
$$H_3AsO_3 + O \rightarrow H_2AsO_4^- + H^+ \dots\dots\dots\dots \text{Equation (2.4)}$$
$$MeOOH + H_2AsO_4^- \rightarrow FeOH_2AsO_4 + OH^- \dots\dots\dots \text{Equation (2.5)}$$
$$MeOOH + H_3\ AsO_3 \rightarrow MeOOHH_3\ AsO_3 \dots\dots\dots \text{ Equation (2.6)}$$
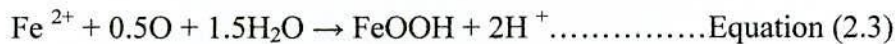
Where, Me denotes metal ions like Mn, Fe.

Adsorbed As and P from metal hydroxides were later released due to reductive dissolution as shown in equations 2.7 and 2.8 leading to ground waters with elevated As (III) and Fe^{2+} concentrations.

$$4FeOOH + CH_2O + 7H_2CO_3 \rightarrow Fe^{2+} + 7HCO_3^- + 6H_2O \ldots\ldots \text{Equation (2.7)}$$

$$2H_2AsO_4^- + CH_2O + H^+ \rightarrow 2H_3AsO_3 + HCO^- \ldots\ldots\text{Equation (2.8)}$$
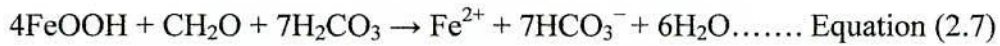
Reported incidences of elevated As concentrations in ground water under reducing conditions are also available from other parts of the world (Saha, 2003; Korte, 1991). Both anthropogenic and natural causes for prevalence of reducing conditions have been suggested (Zheng et al., 2004; Nickson et al., 2000; Harvey et al., 2005). According to Nickson et al. (Nickson et al., 2000) the reducing environments were always there and also when the first tube well was sunk. Nickson et al. (Nickson et al., 2000) and Acharya et al. (Acharyya et al., 2000) explained the origin of organic matter in the sediments based on the changes in the sea level. During the past 18000 years the sea level was both above and below the present level. The As contaminated layer was deposited around 10000 to 7500 years before present (b.p.). Sea level rose rapidly between 7000 to 5500 years b.p. to reach levels higher than present level. This caused flooding of the partly sedimented valleys, resulting in formation of marshes, lagoons and estuaries with organic rich matter. They observed a positive correlation between the location of As-bearing zones with deltaic environment and organic rich deposition during this sea level rise. Another hypothesis for the prevalence of reducing conditions is intensive rice irrigation (Jacks and Bhattacharya, 2000). Cultivation of two crops per year of wetland rice would result in water standing on the fields for about 200-300 days. This would result in reduced diffusion of oxygen into the subsoil. A joint study conducted by Bangladesh University of Engineering and Technology (BUET), Massachusetts Institute of Technology, (MIT) and University of Cincinnati the proposed that release of As is due to introduction of nutrients for the microorganisms (Ahmad et al., 2004). Laboratory investigations also (Akai et al., 2004) showed that addition of nutrients, glucose and polypepton to sediments from Bangladesh resulted in enhanced bacterial activity with rapid drop in Eh values and increase in As concentration. Infiltration of young water rich in organic matter due to heavy withdrawal of ground water was also one of the hypothesis for prevalence of reducing conditions (Harvey et al., 2005). A study (Lawrence et al., 2000) conducted in Hat Yai, Thailand also showed that infiltration of water with highorganic content containing urban recharge caused reducing conditions and release of As to ground water. Though there are many theories explaining the reasons behind prevalence of reducing conditions, the microbial mediated reductive dissolution of As contained Fe-hydroxides is now the most widely accepted hypothesis. However, the possibility of application of other

theories can not be ruled out as a possible cause of As release in some areas of the vast As contaminated Bengal delta.

2.4 Arsenic Chemistry (Shafiquzzaman, 2008)

2.4.1 Acid-Base Chemistry

Apart from elementary arsenic with oxidation state of 0, arsenic is stable in the oxidation states of +5, +3 and —3, but generally found in water only in the trivalent and pentavalent states. The oxidation state is closely related to the arsenic immobilization and hence the release of arsenic from its geological formations into the water bodies and biosphere. Both the oxidation state and the release are determined by the soil and water pH, the redox potential, the in excess occurrence of sulfide, the occurrence of other ions as well as solids of especially iron and manganese. The oxides of both As (III) and As (V) are soluble in water. The dissolution implies direct reaction with the water, hydration, where the oxides behave like non-metals and exhibit acidic character. As (III) forms arsenious acid and As (V) forms the arsenic acid. The two acids dissociate to form respectively arsenite and arsenate ions as shown in the following reactions with their equilibrium constants:

Dissociation of Arsenious Acid

H_3AsO_3 $=$ H^+ + $H_2AsO_3^-$ $\qquad$ pKa = 9.22........Equation (2.9)

H_2AsO_3 $=$ H^+ + $HAsO_3^{2-}$ $\qquad$ pKa = 12.13 ....Equation (2.10)

$HAsO^{2-}$ $=$ H^+ + AsO_3^{3-} $\qquad$ pKa = 13.40 ....Equation (2.11)

Dissociation of Arsenic Acid

H_3AsO_4 $=$ H^+ + $H_2AsO_4^-$ $\qquad$ pKa = 2.20 ......Equation (2.12)

$H_2AsO_4^-$ $=$ H^+ + $HAsO_4^{2-}$ $\qquad$ pKa = 6.97 ......Equation (2.13)

$HAsO_4^{2-}$ $=$ H^+ + AsO_4^{3-} $\qquad$ pKa = 11.53 ....Equation (2.14)
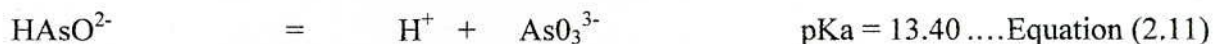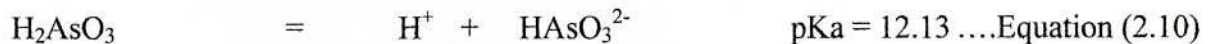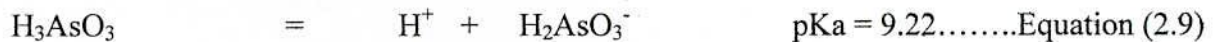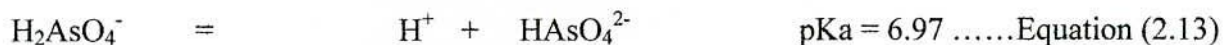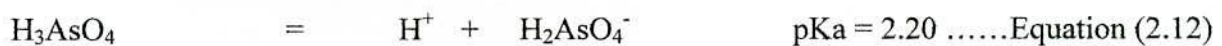
2.4.2 Oxidation Reaction of As (III) to As (V)

Chlorine is widely used for oxidation purpose, but may lead to chlorinated by-products, namely trihalomethenes (THMs), from reactions with natural organic matter. Ozone, widely used in surface water treatment for oxidation and disinfection, is quite effective but is not feasible for a specific application with As (III) oxidation. Permanganate oxidizes As (III),

ferrous and manganese ions specially and quickly. Chlorine and permanganate are able to oxidize arsenic (III) to (V) within a very short time, e.g., half an hour or even few minutes.

$$H_3AsO_3 + 1/2\ O_2 \quad = \quad H_2AsO_4^- \qquad + \quad 2H^+ \dots\dots\dots\text{Equation (2.15)}$$

$$H_3AsO_3 + HClO \quad = \quad H_2AsO_4^- \quad + 2H^+ + Cl^- \dots\dots\text{Equation (2.16)}$$

$$H_3AsO_3 + 2/3\ MnO_4^- = H_2AsO_4^- \quad + \quad 2/3\ MnO_2 + 1/3\ H^+ + 1/3H_2O\dots\text{Equation (2.17)}$$
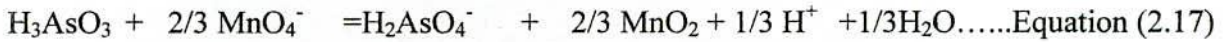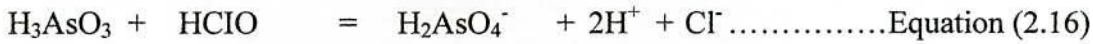
Air oxidation of arsenic is very slow and can take weeks for oxidation but chemicals like chlorine and permanganate can widely oxidize arsenite to arsenate under wide range of conditions.

2.4.3 Analysis Reactions of Arsenic

Determination of arsenic by the "hydride generation" methods involve reduction of arsenic, present in water either as As (III) or As (V), into arsenic hydride or arsine (AsH$_3$). Arsine is insoluble in water making it easy to purge arsenic from the water phase. It is quantitatively captured by organic solvents (e.g., silver diethyldithiocarbamate mercuric bromide), forming coloured complexes. These two properties of arsenic make it unique in the arsenic analytical chemistry and enables its detection in small quantities by the so-called Marsh's test.

In acidic solutions, arsine generation can be carried out by metallic Zinc according to the following reactions:

$$Zn \quad + \quad 2H^+ \qquad = \qquad Zn^{2+} \quad + \quad H \dots\text{Equation (2.18)}$$

$$H_3AsO_3 \ + \quad 6H \qquad = \qquad AsH_3 \quad + \quad 3H_2O \dots\text{Equation (2.19)}$$

$$H_2AsO_4^- + \quad 8H + H^+ \quad = \quad AsH_3 \qquad + \quad 4H_2O \dots\text{Equation (2.20)}$$

$$AsH_3 \quad + \quad \text{diethyldithiocarbamate} = \quad \text{Coloured complex} \dots\text{Equation (2.21)}$$

$$AsH_3 \quad + \quad HgBr_2 \qquad\qquad = \ \text{Coloured complex} \dots\text{Equation (2.22)}$$
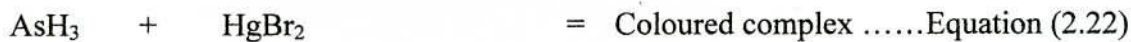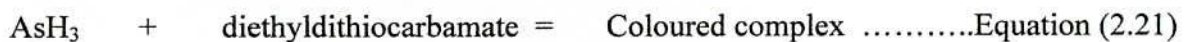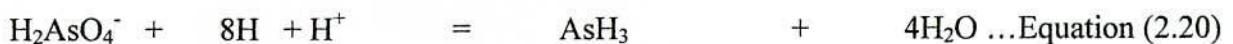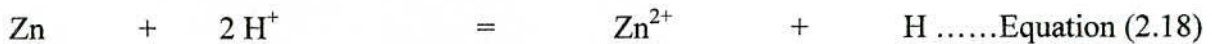
Alternatively, as suggested in the latest Standard Methods, the arsine development can be carried out using sodium borohydride, according to the following reactions:

$$H_3AsO_3 \quad + 3BH_4^- + 6H_2O + 3H^+ = AsH_3 + 3B(OH)_3 + 9H_2 \dots\text{Equation (2.23)}$$

$$H_2AsO_4^- + 5BH_4^- + 11\ H_2O + 6H^+ \ = AsH_3 + 5B(OH)_3 + 16H_2 \dots\text{Equation (2.24)}$$

15
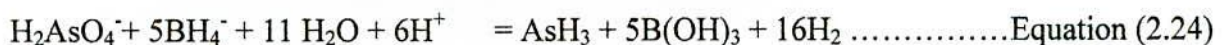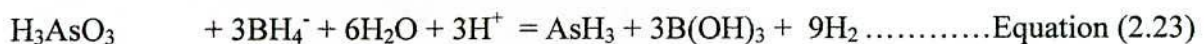
Reaction (Equation 2.23) can be performed at pH=6, whereas reaction (Equation 2.24) demands strong acidification. This very important detail allows for quantitative differentiation between arsenate and arsenite. It should be noted that the methylated arsenic compounds do not take part in this arsenic generation. They therefore escape the standard analytical procedures based on arsenic generation. Sulfide may interfere in coloration of the reagents. It is therefore scrubbed off by gas flow through lead acetate.

2.4.4 Adsorption - Desorption Theory

Adsorption - desorption reactions are very important in determining the mobility of arsenic in nature as well as its removal in many treatment systems. Attachment of arsenic to an iron oxide surface is an example of an adsorption reaction. The reverse of this reaction, arsenic becoming detached from such a surface is an example of desorption. Both arsenate and arsenite adsorb to surfaces of a wide range of solids including iron, aluminium and manganese oxides (e.g., iron oxyhydroxides), and clay minerals.

Unlike many heavy metals (eg, lead, zinc, cadmium) which exist in water primarily as cations, arsenic exists primarily as oxyanions (e.g., HAsO , H and adsorb on hydrous oxide surfaces as anions. Besides arsenic, a number of other ions present in natural water (e.g., phosphate, silicate, sulfate) also have strong affinity for solid surfaces and presence of high concentrations of these ions can reduce removal efficiency of arsenic in adsorption-based treatment system.

Adsorption — desorption of arsenic onto iron oxide surface are important controlling reactions in the subsurface because iron oxides are widespread in the hydro-geologic environment as coating on other solids and because arsenate adsorbs strongly to iron oxide surfaces in acidic and near — neutral pH conditions. The pH dependence of arsenate adsorption desorption appears to be related to the change in net charge on iron-oxide surface with pH. The net charge on iron oxide surface changes from positive to negative as pH increases above the "zero-point-of-charge" (pH at which net surface charge is zero). The zero-point- of-charge" is about 7.7 for goethite (crystalline iron oxide) and about 8.0 for ferrihydrite (amorphous iron oxide). Thus as pH increases above about 8, the net negative surface charge on iron oxides can repel the negatively charged ions such as arsenate. Compared to arsenate, arsenite is less strongly adsorbed by iron oxides.

According to the two-layer model, surface ionization reactions resulting in development of surface charge on iron oxide surfaces can be described by:

$$Fe(OH)_2^+ \quad = \quad Fe(OH)^\circ \quad + \quad H^+ \dots\dots\dots\text{Equation (2.25)}$$

$$Fe(OH)^\circ \quad = \quad FeO^- \quad + \quad H^+ \dots\dots\dots\text{Equation (2.26)}$$
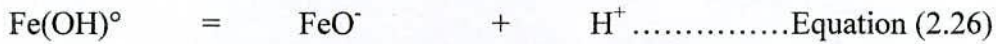
The adsorption-desorption reactions of arsenate and arsenite on hydrous ferric oxide modeled using the generalized two-layer model are shown by the following reactions.

Arsenate Adsorption

$$Ee(OH)^\circ \quad + AsO_4^{3-} \quad + \quad 3H^+ \quad = FeH_2AsO_4^0 \quad +H_2O\dots\dots\text{Equation (2.27)}$$

$$Fe(OH)^\circ \quad + \quad AsO_4^{3-} + \quad 2H^+ \quad =FeHAsO_4^- \quad + \quad H_2\dots\dots\text{Equation (2.28)}$$

$$Fe(OH)^\circ \quad + \quad AsO_4^{3-} + \quad H^+ \quad = FeAsO_4^{2-} \quad + \quad H_2O\dots\dots\text{Equation (2.29)}$$

$$Fe(OH)^\circ \quad + \quad AsO_4^{3-} \quad = Fe(OH)AsO_4^{3-} + \quad H_2O\dots\text{Equation (2.30)}$$

Arsenite Adsorption

$$Fe(OH)^\circ + H_3AsO_3 \quad = \quad FeH_2AsO_3^0 \quad + \quad H_2O \dots\dots\dots\text{Equation (2.31)}$$
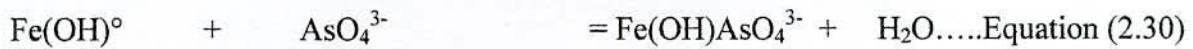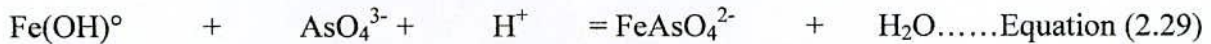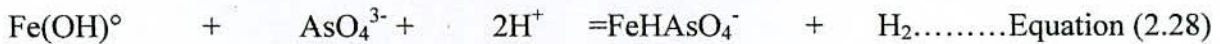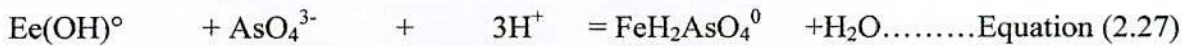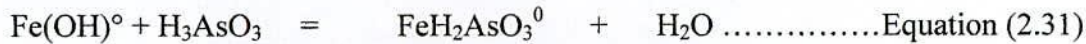
Possible desorption of arsenate in the presence of phosphate ions are shown by the following reactions:

$$FeH_2AsO_4^0 + \quad PO_4^{3-} \quad = FeH_2PO_4^0 + \quad AsO_4^{3-}\dots\dots\text{Equation (2.32)}$$

$$FeHAsO_4^- + \quad PO_4^{3-} \quad = FeHPO_4^- \quad + AsO_4^{3-}\dots\dots\text{Equation (2.33)}$$

$$FeAsO_4^{2-} + \quad PO_4^{3-} \quad = FePO_4^{2-} \quad + \quad AsO_4^{3-}\dots\dots\text{Equation (2.34)}$$
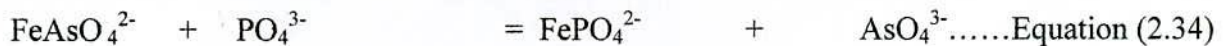
2.4.5 Precipitation and Dissolution

Precipitation- dissolution reactions are important mechanisms controlling mobility of arsenic in the subsurface. As an example, because arsenic often co-precipitates with iron oxide, iron oxide may act as an arsenic source (case of dissolution) or a sink (case of precipitation) for ground water (USGS, 1999). In Bangladesh, reductive dissolution of iron oxyhydroxides and consequent release of adsorbed arsenic could be an important mechanism of arsenic mobilization in the subsurface.

$$4\ FeAsS + 11O_2 + 6\ H_2O = 4\ FeSO_4 + 4\ H_2AsO_3^- + 4H^+ \ldots\ldots\ldots\ldots Equation\ (2.35)$$

$$4\ FeAsS + 13\ O_2 + 6\ H_2O = 4\ FeSO_4 + 4\ H_2AsO_4^- + 4H^+ \ldots\ldots\ldots\ldots Equation\ (2.36)$$
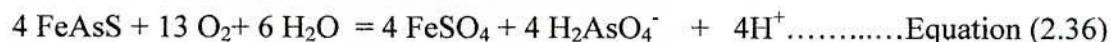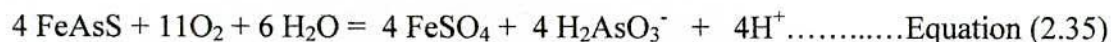
2.4.6 Methylation Reactions

Arsenic taken by mammals is subject to either direct excretion, direct accumulation in some parts of the body (e.g., nails, hair and skin tissue), or to bio-transformation of arsenic contaminated soils. The inorganic forms are more toxic than organic forms. Methylation seems to be the most important pathway of bio-transformation of inorganic arsenic. The inorganic forms are metabolized by consecutive reduction and methylation reactions in humans and mammals to dimethylated arsenic (DMA), which is excreted into urine. The toxicity of arsenite is highly dependent on animal species, which in turn depends on the differences in the metabolism.

2.4.7 Occurrence and Nature of Arsenic

Arsenic (As) is a natural gray or tin white metalloid element. It can't be found in nature as free element and is found as a compound of oxygen, chloride, sulfur, carbon, hydrogen, lead, mercury, gold and iron. There are as many as 150 species of arsenic bearing minerals that exist in nature. Among them three highest arsenic bearing ore are: realgar or Arsenic disulfide (As_2S_2); Orpiment or Arsenic tri-sulfide (As_2S_3); and Arsenopyrite or ferrous arsenic sulfide (FeAsS).

Two forms of Arsenic are found chemically in ground water: inorganic and organic. Inorganic Arsenic has four main chemical forms having oxidation states, -3, 0, +3, and +5, but in natural water its predominant forms are inorganic oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). The toxicity of different arsenic species varies in the order arsenite> arsenate> monomethylarsonate> dimethylarsinate. Trivalent arsenic is about 60 times more toxic than arsenic in the oxidized pentavalent state, and inorganic arsenic compounds are about 100 times more toxic than organic arsenic compounds (Jain and Ali, 2000). The organic forms of arsenic are quantitatively insignificant and are found mostly in surface waters or in areas severely affected by industrial pollution. Unlike other heavy metalloids and oxyanion-forming elements, arsenic can be mobilized under a wide range of

oxidizing and reducing conditions at the pH values typically found in groundwater (pH 6.5-8.5). The relative concentrations of As (III) to As (V) vary widely, depending on the redox conditions in the geological environment (Jain and Ali, 2000).

2.4.8 Effect of pH and Redox Potential

The two most important factors controlling the speciation of arsenic (and, to some extent, solubility) are pH and redox potential. Under oxidizing conditions at pH less than 6.9, $H_2AsO_4^-$ is the dominant species, whereas $HAsO_4^{2-}$ predominates at higher pH. Under reducing conditions at a pH value less than 9.2, the uncharged arsenite species H_3AsO_3 is dominant. In contrast to the pH dependency of As (V), As (III) was found virtually independent of pH in the absence of other specifically adsorbed anions (Smedley and Kinniburgh, 2002). Most often, more trivalent arsenic than pentavalent arsenic is found in reducing groundwater conditions, whereas the converse is true in oxidizing groundwater conditions. The stabilities of arsenic species under different pH and redox conditions are shown in Figure 2.2.
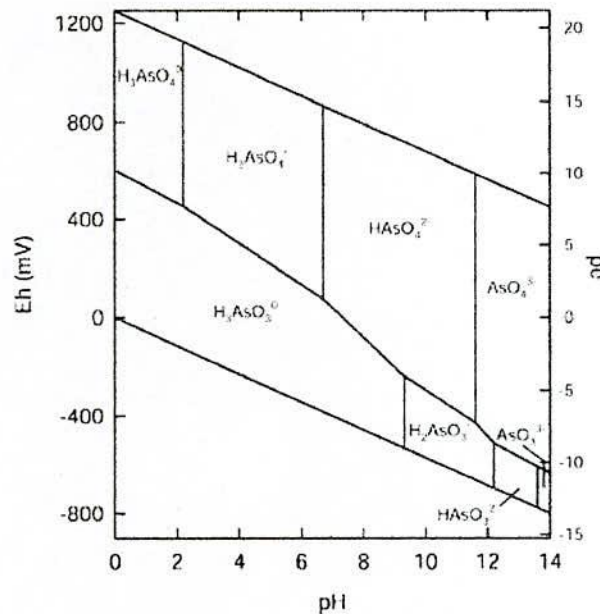
Figure 2.2: Eh-pH diagram for aqueous As species in the system (As–O2–H2O at 25^0C and 1bar total pressure) (Smedley and Kinniburgh, 2002)

2.5 Arsenic in Groundwater (Fuhrman, 2006)

In Bangladesh and the West Bengal area of India, the presence of elevated arsenic concentrations in groundwater is believed to be natural, as no anthropogenic source is likely to cause such a widespread arsenic contamination (Mandal et al., 1998). During the 1970s, in the context of very high occurrences of diarrhoeal diseases, bacteriological quality received priority as a criterion for drinking water supply, and the use of pathogenic microorganism-free groundwater was strongly encouraged by several international institutions, including the World Bank. This led almost 97% of the rural people to use tube wells in Bangladesh. Unfortunately, in recent years the presence of arsenic in excess of acceptable limits has been found in groundwaters in many parts of Bangladesh and West Bengal, and millions of people have shown symptoms of being poisoned by arsenic.

Although it is well established that sorption and desorption are major reaction mechanisms controlling the fate of arsenic in soil and groundwater, there is no general consensus about what mechanisms are responsible for these elevated arsenic concentrations in the Bay of Bengal groundwater (Goldberg and Johnston, 2001). Two principal hypotheses about the natural genesis of arsenic in the groundwater are mentioned in the literature. Previously, it was believed that high arsenic concentrations in the groundwater were related to the oxidative decomposition of arsenopyrite (FeAsS), the most abundant arsenic containing mineral (Francesconi and Kuehnelt, 2002), or other arsenic containing minerals in subsurface sediments due to excessive groundwater withdrawal (Das et al., 1995). Increasing recharge with water containing dissolved oxygen could result in the release of additional dissolved arsenic, as occurs in some acid sulfate soils, (Dhar et al., 1997). The decomposition of arsenic rich pyrite (FeS_2), defined with the following reactions (Mandal et al., 1998), can also release arsenic into groundwater.

$$2FeS_2 + 2H_2O + 7O2 = 2Fe^{2+} + 4HSO_4^- \quad \ldots\ldots\ldots\ldots\text{Equation (2.37)}$$
$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O \quad \ldots\ldots\ldots\ldots\text{Equation (2.38)}$$
$$FeS_2 + 14\ Fe^{3+} + 8H_2O = 15\ Fe^{2+} + 2SO_4^{2-} + 16\ H^+ \quad \ldots\ldots\ldots\ldots\text{Equation (2.39)}$$
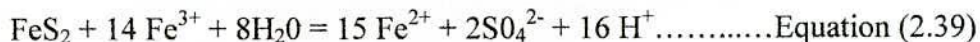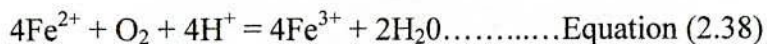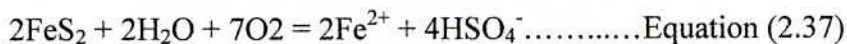
However, present data suggest that when anoxic conditions are dominant the reduction of arseniferous iron hydroxides leads to arsenic release to the groundwater (Nickson et al., 1998, 2000; Chowdhury et al., 1999) and it is postulated that most of the arsenic is released as a result of microbial dissolution of these oxides (Xu et al., 1998; Mandal et al., 1998).

Furthermore, low pH conditions in near-surface waters could also cause dissolution of metal hydroxides that would otherwise bind inorganic arsenic by coprecipitation (Xu et al., 1998). The role of arsenic reducing bacteria on the mobility of arsenic is highlighted by Cummings et al. (1999). They suggest that some organisms, i.e. *Geospirillum barnesii* strain SES-3, may reduce both Fe (III) and arsenate, which in turn promote rapid arsenic solubilization. The reduction process converts precipitated and adsorbed arsenate into more soluble arsenite. Microbiologically induced reduction may be defined in the following pathway (Bhattacharyya et al., 2003):

$$2H_2AsO_4^- + CH_2O + H^+ = 2H_3AsO_3 + HCO3^- \quad \ldots\ldots\ldots\ldots \text{Equation (2.40)}$$
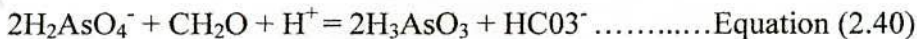
Other studies suggest that neither of the above mentioned mechanisms alone is sufficient to explain the concentration and distribution of arsenic in the groundwater and that both mechanisms are involved (Acharyya et al., 1999).

2.6 Effects and Risk Assessment

2.6.1 Health Effects

Drinking water is known to be closely linked to chronic arsenic-related health problems, the sometimes poor relationship observed between arsenic intake from water and health symptoms poses the possibility that other pathways of arsenic exposure may also occur. Food is one potential source. Crops irrigated with high-arsenic groundwater are potentially vulnerable to arsenic take-up, particularly following long-term groundwater use and soil arsenic accumulation.

Ingestion of arsenic through highly contaminated groundwater can cause multi-site cancers in the human body. For people who are exposed to arsenic level > 50 µg l^{-1} in drinking water, the cancer risk could be as high as 1 in 1000 (Morales et al., 2000). Population with ingestion of arsenic in drinking water more than 200 µg l^{-1} or higher, reported to have increased risk of skin, bladder and lung cancers (Chen et al., 1985; Marshall et al., 2007; Mazumder et al., 2005; Smith et al., 1998). The current evidence also suggests the risk of liver and kidney cancer may also be increased following the exposure of high arsenic water.

The data collected by the governmental bodies, NGOs and private organizations reveal that a large number of populations in Bangladesh are suffering from melanosis, leuco-melanosis, keratosis hyperkeratosis, dorsum, non-petting oedema, gangrene and skin cancer, melanosis (93.5%) and keratosis (68.3%) are the most common presentations among the affected

people. Patients of Leucomelanosis (39.1%) and hyper-keratosis (37.6%) have been found in many cases. Few cases of skin cancer (0.8%) have also been identified among the patients seriously affected by the arsenicals (arsenite and arsenate). The occurrence of arsenic diseases depends on the ingestion of arsenic compounds and their excretion from the body. It has been reported at 40% to 60% arsenic can be retained by the human body. It indicates that the level of hazards will be higher with the greater consumption of arsenic contaminated water. The daily consumption of arsenic contaminated water is very high in Bangladesh, especially in villages. There are several factors may have been responsible for triggering off the arsenic related diseases in Bangladesh. The primary reason appears to be the malnutrition, a state that describes 80% percent of the population of Bangladesh. Having less immunity, a huge number of people are suffering from the chronic arsenic poisoning. Many People have died, many are dying and many will die of arsenic diseases. In brief, the majority of the people in Bangladesh are grappling with the massive health crisis caused by the arsenic diseases. Some symptoms of arsenicosis in Bangladesh rural area are shown in Fig. 2.2.

Figure 2.3: Various diseases due to excessive Arsenic intake in drinking water

Table 2.2: Arsenic Poisoning from Drinking Water

Sl. No.	Main Organ	Effects
1	Nervosas system	Ataxia, Paralysis, Peripheral neuropathy
2	Respiratory system	Nasal septum perforation, Bronchitis, Cancer
3	Skin	Melanosis, Dermatitis, Hyperkeratosis, Cancer
4	Heart	Heart and occlusive arterial disease
5	Liver	Liver cirrhoses and cancer

2.6.2 Social Effects (Safiuddin and Karim, 2001)

Although what is causing arsenic contamination in groundwater is not clear indisputably, its effect on people is well known. The sudden increase in arsenic related diseases has panicked the local people. The native people consider the arsenic diseases contagious. In many instances, the people suffering from arsenic diseases have been ostracized by neighbors, friends and relatives. The affected people are either avoided or discouraged to appear in public places. The affected children are often barred from attending schools and the adults are discouraged from attending offices and any public meetings. Qualified persons are refused jobs when found suffering from arsenicosis. Those affected with a higher level of contamination are considered incapable of working and hence victimized by the growing poverty. The situation is worse for women. The women suffering from arsenic diseases are increasingly facing ostracization and discrimination. Young women suffering from arsenicosis are often compelled to stay unmarried. Married women affected by arsenic are no longer considered acceptable as wives due to skin lesions and sent back to their parents with children. Thus, the unaffected parents and children are also suffering socially with the affected females. Above all, the affected people are losing their as usual social relation with the neighbors and relatives.

2.7 Worldwide Groundwater Arsenic Contamination

2.7.1 Reducing Environment: Bangladesh, India, Vietnam, China and Taiwan

Approximately 30-35 million people in Bangladesh and 7 million people in West Bengal are exposed to elevated levels of arsenic in drinking water. Arsenic concentrations were found from >0.5 μg l^{-1} to 3200 μg l^{-1}, with As (III) present as the dominant species. The relative ratio of dissolved As (III) to As(V) is often greater than 1 because As(III) is more mobile under reducing conditions. The groundwaters in these regions usually have high iron content, as well. High concentrations of arsenic are more often found in shallow wells (100-150 m deep). About 27% of shallow wells less than 150 m deep have arsenic concentrations >50 μg l^{-1}, whereas wells greater than 150-200 m deep usually have arsenic concentration <5 μg l^{-1} (Smedley and Kinniburgh, 2002).

The Bengal Delta and North Vietnam have similar reducing geological features, with relatively young alluvial sediments and anoxic groundwater (Berg et al., 2006). Many Vietnamese depend on aquifers of the large deltas of the Mekong and Red Rivers for drinking

water. More than 10 million people are exposed to harmful arsenic concentrations from drinking well water (Smedley and Kinniburgh, 2002). The groundwater usually has high concentrations of Fe, Mn, and NH4. Shallow tubewells in Hanoi have been found to have significant concentrations of As, ranging from 1 to 3050 μg l^{-1} (mean = 159). Investigations of tube wells indicated that arsenic concentrations in 48% of them were >50 μg l^{-1} (20% were >150 μg l^{-1}). In highly affected areas, the groundwater had an average arsenic concentration of 430 μg l^{-1} (Berg et al., 2001). Arsenic contamination in Vietnam was not well understood until recently, and the work is ongoing to better understand the problem (Smedley and Kinniburgh, 2002).

China faces similar contamination, with more than 5 million people exposed to arsenic from drinking contaminated groundwater. Inner Mongolia and the Xinjiang and Shanxi Provinces in Northern China were found to have high arsenic concentrations in groundwater. Concentrations of arsenic ranged from 40 to 750 μg l^{-1} in deep artesian groundwater from Dzungaria Basin on the north side of the Tianshan Mountains. High arsenic concentrations were found less frequently in non-artesian groundwater. However, In inner Mongolia, aquifers were found to have arsenic concentrations >50 μg l^{-1}, with As(III) present as the dominant species (60- 90% of the total) (Smedley and Kinniburgh, 2002).

2.7.2 Arid Oxidizing Environment: Argentina, Mexico and Chili

Oxidizing groundwater environments favor mobilization of As (V) at above-neutral pH. Below pH 8.5, arsenate strongly adsorbs to the mineral oxides or becomes part of the mineral structure. Some large areas in Argentina, Mexico, and Chile were found to have arsenic contaminated groundwater under oxidizing conditions (Smedley and Kinniburgh, 2002). The primary factor in their mobilization was believed to be arsenic-bound metal oxides, especially Fe and Mn oxides under high pH conditions.

Problems due to arsenic contamination have also affected Central America. Significant chronic arsenic-related health problems have arisen in the Lagunera Region in Northern Mexico. Groundwater is an important source of drinking water there because the region is arid. The groundwater environment is predominantly oxidizing, with neutral-to-high pH (6.3- 8.9). The main form of arsenic present in the region is As(V), and total arsenic concentrations

are 8 to 624 μg l^{-1} (mean = 100 μg l^{-1}) with 50% of the groundwater samples investigated having arsenic concentrations >50 μg l^{-1}.

Table 2.3: Major Countries Facing Serious Arsenic Contamination in Drinking Water

(Smedley and Kinniburgh, 2002)

Country /Region	Population exposed (million)	Concentration range (μg l^{-1})	Groundwater properties	Other dissolved ions
Bangladesh	30	<0.5-2500	Strongly reducing conditions, neutral pH, high alkalinity	High Fe
West Bengal (India)	6	<10-3200	As for Bangladesh (27% >50 μg l^{-1})	High Fe
China	5.7	10-1820	Strongly reducing artesian conditions	-
Argentina	2	<1-5300	Oxidizing conditions, neutral-to-high pH, high alkalinity; arsenic present mainly as As(V)	-
Mexico	0.4	8-620	Oxidizing conditions, neutral-to-high pH; arsenic present mainly as As(V)	Low concentrations of dissolved Fe and Mn
Chili	0.5	100-1000	Oxidizing conditions, high pH; arsenic present mainly as As(V)	-
Red river delta Vietnam	>10	1-3050	Reducing conditions, high alkalinity	High concentrations of Fe, Mn and NH$_4$
USA	-	2.1	-	-

Exposed population was estimated at more than 400,000 in the Lagunera Region (Smedley and Kinniburgh, 2002). In South America, Chili's Administrative Region II was seriously affected by high concentrations of arsenic in both surface and groundwater. Water resources in the region are limited because of arid conditions. Arsenic concentrations in both surface and groundwater are usually >100 µg l^{-1}, with arsenate anion present as the main species. Although arsenic treatment plants were installed in the towns several decades ago, rural populations still rely largely on groundwater for drinking (Smedley and Kinniburgh, 2002).

2.7.3 Standards for Arsenic Concentrations in Water

Due to carcinogenic nature of arsenic, WHO has issued provisional guideline for maximum permissible concentration of arsenic in drinking water of 10 µg l^{-1}. WHO guidelines are intended as a basis for setting national standards to ensure the safety of public water supplies, and the guideline values recommended are not mandatory limits. Limits are meant to be set by national authorities, considering local environmental, social, economic, and cultural conditions.

Table 2.4: Current National Standards of Selected Countries for Arsenic in Drinking Water

(World Bank, 2005)

Country/ Region	Standard (µg l^{-1})	Country/ Region	Standard (µg l^{-1})
Australia (1997)	7	Bangladesh (1997)	50
EU (1998)	10	India	50
Japan (1993)	10	Nepal	50
USA(2002)	10	Pakistan	50
Vietnam	10	Cambodia	50
Canada	25	Myanmar	50

Most developing countries still use the former WHO-recommended concentration of 50 μg l^{-1} as their national standard for arsenic in drinking water, due to economic considerations and the lack of tools and techniques to measure accurately at such low concentrations (Table 2.5).

2.8 Arsenic in Bangladesh

2.8.1 Scale of the Problem

Approximately 20 incidents of ground water arsenic contamination have been reported from all over the world. Of these, two major incidents were in Bangladesh and West Bengal, India (Chowdhury et al., 2000; Dhar et al., 1997). In terms of population exposed, As problem in groundwater from the alluvial and deltaic aquifers of Bangladesh and west Bengal represent the most serious occurrence identified globally. Arsenic concentration in groundwater in these two affected regions has a very large range from < 5 μg l^{-1} to 3200 μg l^{-1}. Over 70 million people in Bangladesh and in their regions of India subcontinent are routinely exposed arsenic poisoning through drinking water (Dhar et al., 1997). In Bangladesh, arsenic contamination of water in tubewells was confirmed in 1993 in the Nawabganj district. Further testing and investigation was done by the several institute and organization. These includes, School of environmental studies, Jaydevpur University Calcutta (Dhar et al., 1997) , National Institute for Preventive and Social Medicine, Bangladesh (Ahmad et al., 1997), the Bangladesh Atomic Energy Commission, The Department of Public Health Engineering, Dhaka Community Hospital (Choudhury et al., 2000) , British Geological Survey (BGS, 1999).

A study in the Rajarampur village of the Nawabganj district, conducted by National Institute of Preventive and Social Medicine and the School of Environmental Studies, found that 29% of the 294 tube-wells water had arsenic concentrations greater than 50 μg l^{-1} (Ahmad et al., 1997). Another survey in Samta village Jessore was conducted jointly by Dhaka Community Hospital and School of Environmental Studies in between 1996 and 1997. About 91% of the 265 tubewells had the arsenic concentration higher than 50 μg l^{-1}.

In 1998, British Geological Survey collected 2022 water samples from 41 districts (Smith et al., 2000). 35% have arsenic concentrations above 50 μg l^{-1} and 8.4% were above 300 μg l^{-1} (BGS, 1999). Based on population density measured in 1998, this group estimated the number of people exposed to arsenic concentrations above 50 μg l^{-1} was about 21 million. This number would be approximately doubled if WHO's Standard (WHO, 1996) of 10 μg l^{-1}

were adopted. Further studies conducted by the Dhaka Community Hospital and School of Environmental Studies found that 59% of the 7800 groundwater samples had arsenic concentrations greater than 50 μg l^{-1} (Chowdhury et al., 1999).

Table 2.5: Percentage of Groundwater Surveyed in 1998 by British Geological Survey with Arsenic Levels above 0.05 mg/l (BGS, 1999)

District	Percentage of Ground water surveyed	District	Percentage of Ground water surveyed
Bagerhat	66	Madaripur	93
Barisal	63	Magura	19
Brahmanbaria	38	Manikganj	15
Chandpur	96	Meherpur	60
Chittagong	20	Moulvibazar	12
Chuadanga	44	Munshiganj	83
Comilla	65	Narail	43
Cox's Bazar	3	Narayanganj	24
Dhaka	37	Nawabganj	4
Faridpur	66	Noakhali	75
Feni	39	Pabna	17
Gopalganj	94	Pirojpur	24
Jessore	51	Rajbari	24
Jhalakati	14	Rajshahi	6
Jhenaidah	26	Satkhira	73
Khulna	32	Shariatpur	80
Kushtia	28	Syllhet	19
Lakshmipur	68		

2.8.2 Source and Causes of the Problem

Figure 2.3 shows the arsenic contamination map of Bangladesh. For arsenic contamination in Bangladesh the several sources were considered, such as 1) Use of fertilizers, pesticides, insecticides and herbicides containing arsenic; 2) Industrial waste disposal and 3) Enhanced leaching beneath irrigated land (BGS, 1999). But gradually all this sources were rejected based on the field observation. Finally, it is believed that the source of arsenic in Bangladesh ground water is the geological deposits. The arsenic affected groundwater in the Bengal basin are associated with sediments of Holocene age and comprise micaceous sand, silts and clays having total arsenic concentrations in the range $<2\text{-}20$ mg kg^{-1}. These sediments are derived from the drainage systems of 3 major rivers (Ganges, Brahamaputra and Meghna) which are they sourced from a wide area of the Himalaya. Two common and strong hypotheses are prevailing to describe the cause (mobilization) of arsenic into ground water in Bangladesh. They are: a) Pyrite oxidation and b) Oxy-hydroxide reduction

Pyrite Oxidation Hypothesis:

Arsenic exists with the certain Sulphide minerals (pyrites) which are deposited within the aquifer sediments. These arsenopyrites oxidized in the vadose zone due to lowering the water table and release arsenic as arsenic adsorbed on iron hydroxide. During the subsequent recharge period arsenic hydroxide releases arsenic into ground water (Fazal, 2001). According to this hypothesis the origin of arsenic rich groundwater is man made. The intensive irrigation development in the country supports this hypothesis. Irrigation development in Bangladesh using Deep tubewells (DTWs) started in the early 1960s and rapidly expanded in the early 1980s when a low cost shallow tubewells (STWs) were introduced in the country. As results the water table becomes lower.
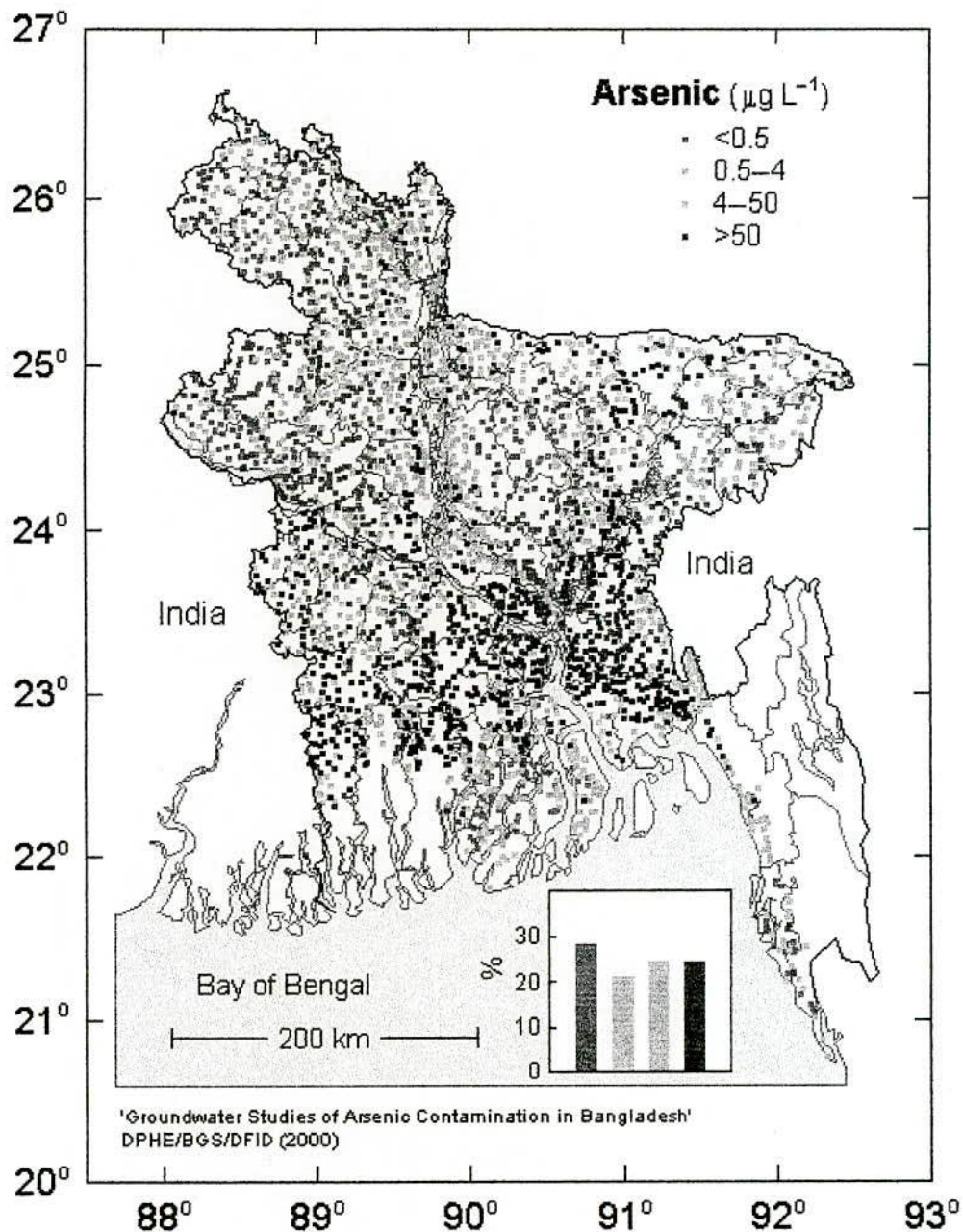
Figure 2.4: Arsenic Contamination Map of Bangladesh (DPHE/BGS/DFID, 2000)

Oxy-Hydroxide Reduction Hypothesis:

Arsenic is assumed to be present in alluvial sediments with high concentrations in sand grains as coating of iron hydroxides. The organic matter also deposited with the sediments. These aquifer sediments are capped by a layer of clay or silt which effectively restricts entry of air

to the aquifers. This, together with presence of solid organic matter, has resulted in the development of highly reducing conditions which favor the metabolism of arsenic. The metabolism has probably occurred by a complex combination of redox changes brought on by rapid burial of the alluvial and deltalic sediments, including reduction of the solid phase As to As (III), desorption of As from Fe oxides, reductive dissolution of the oxides themselves and likely changes in Fe oxide structure and surface properties following the on set reducing condition (BGS, 2000; Smedley and Kinniburgh, 2002)

2.9 Arsenic Treatment Technologies

This section provides an overview for the most commonly used arsenic removal methods and presents some basic criteria to consider when comparing these methods; the main advantages and disadvantages of each method are also listed. Various treatment technologies have been proposed in the literature for the removal of arsenic from water. Readily available literature on arsenic removal methods includes conservative treatment processes (e.g. coagulation), softening and iron-manganese oxidation, co-precipitation, membrane processes, ion exchange and adsorption processes, in-situ immobilization, and biological oxidation of iron and manganese.

2.9.1 Oxidation

In water, the most common valence states of arsenic are As (III), or arsenite and As (V), or arsenate. As (III) is more likely to occur in anaerobic groundwater. Whereas As (V) is more prevalent in aerobic surface waters and, which in the pH range of 4 to 10, the predominant As (III) compound is neutral in charge, while the As (V) species are negatively charged. Removal efficiencies for As (III) are poor compared to removal As (V) due to the negative charge. Therefore, As (III) may be converted through pre-oxidation to As (V) to treat the water containing both As (III) and As (V). As (III) can be oxidized by Oxygen, Ozone chlorine, potassium permanganate, hydrogen peroxide, hypochloride. All oxidants have their advantages and disadvantages that should be taken into account when choosing the one to be used. For instance, although high oxidation efficiency is obtained using chlorine, the possibility of producing elevated concentrations of unwanted disinfection by-products with organic matter, and the release of taste and odor compounds from algal cells should be considered (Gregor, 2001). Potassium permanganate, on the other hand, produces no harmful

by-products, but may produce colour in the water and cause filtration problems later in the treatment plant (Borho and Wilderer, 1996). It should be noted that oxidation alone cannot serve as a sufficient technology for arsenic removal, though it may well be employed as a pre-treatment step to increase the efficiency of the main removal method. Biological oxidation of iron and manganese may be inexpensive, but is not yet fully established.

2.9.2 Chemical Precipitation through Coagulation-Filtration

Chemical precipitation through coagulation filtration includes alum coagulation, iron coagulation and lime softening. Coagulants are those substances that are capable of removing colloidal impurities from water, and coagulation is the process by which such removal is brought about (Pande et al., 1997). Entrapment during coagulation removes the particulate arsenic (Gregor, 2001), but mechanisms other than entrapment are required to remove soluble arsenic. Co-precipitation occurs when an inorganic contaminant (e.g. arsenic) forms an insoluble complex (e.g. metal hydroxide flocs) with the coagulant. This may occur via adsorption, inclusion or occlusion. Aluminum or ferric chlorides/sulfates can be added as coagulants, and following their addition the relevant amorphous aluminum hydroxide $(Al(OH)3(am))$ or ferric hydroxide $(Fe(OH)3(am))$ is precipitated (Cheng et al., 1994; Hering et al., 1997). Moreover, the addition of aluminum or iron coagulants facilitates the conversion of soluble inorganic arsenic species into insoluble products by precipitation, coprecipitation or adsorption. The formation of these insoluble products facilitates their subsequent removal from the water by means of sedimentation and filtration processes.

Previous studies have concluded that arsenate is more effectively removed than arsenite when using coagulation, thus a pre-oxidation step to oxidise arsenite to arsenate is beneficial (Hering et al., 1997). In addition, coagulation also has other limitations. In particular, coagulation has the disadvantage of high daily toxic sludge production. The flocs are usually dominated by fine colloidal particles and it can be very difficult to dewater them, resulting in large volumes of residual wet sludge that are difficult to manage (Xu et al., 1998). Furthermore, if the water contains large amounts of phosphate and fluoride along with the arsenic, optimum conditions for arsenic removal may not be compatible with conditions favouring the removal of these other anions (Johnston and Heijnen, 2001). The costs associated with this method include coagulation chemicals, pH adjustment before and after

treatment, and sludge residue management. The following reactions illustrate the arsenic adsorption process:

Ferric salts:

As(III) and Fe^{2+} are oxidized to As(V) and Fe^{3+} respectively. Ferric chloride reacts with water and form $Fe(OH)_3$, which strongly adsorbs As(V) (Ahmed et al., 2001).

Fe^{2+} (II) + NaClO → Fe^{3+} Oxidation ------------ (Equation 2.41)

As(III) + NaClO → As(V)   Oxidation------- (Equation 2.42)

$FeCl_3$ + H_2O → $Fe(OH)_3$ Iron precipitation---- (Equation 2.43)

$Fe(OH)_3(s)$ + H_3AsO_4 → $FeAsO_4.2H_2O$ + H_2O Iron complex----- (Equation 2.44)
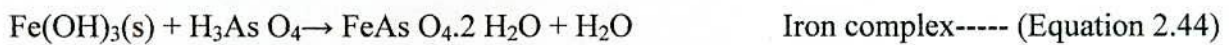
Aluminum co-precipitation:

Alum dissociates in water and forms aluminum hydroxide, which co-precipitates with arsenic (Ahmed et al., 2001).

$Al_2(SO_4)_3.18H_2O$ → $2Al_3^+$ Alum dissolution------------ (Equation 2.45)

$2Al_3^+$ + $6H_2O$ → $2Al(OH_3)_3$ + $6H^+$ Aluminum precipitation------------ (Equation 2.46)

$H_2AsO_4^-$ + $Al(OH)_3$ → Al-As   Complex Co-precipitation----------- (Equation 2.47)
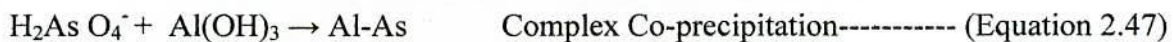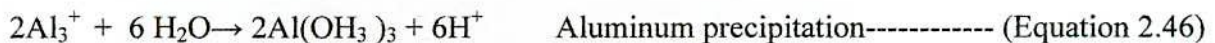
2.9.3 Naturally Occurring Iron

The use of naturally occurring iron precipitates in ground water in Bangladesh is a promising method of removing arsenic by adsorption. It has been found that hand tubewell water in 65% of the area in Bangladesh contains iron in excess of 2 mg l^{-1} and in many acute iron problem areas; the concentration of dissolved iron is higher than 15 mg l^{-1}. Although no good correlation between concentrations of iron and arsenic has been derived, iron and arsenic

have been found to co-exist in ground water. Most of the tubewell water samples satisfying Bangladesh Drinking Water Standard for Iron (1 mg l⁻¹) also satisfy the standard for Arsenic (50 mg l⁻¹). Only about 50% of the samples having iron content 1 - 5 mg l⁻¹ satisfy the standard for arsenic while 75% of the samples having iron content > 5 µg l⁻¹ are unsafe for having high concentration of arsenic The iron precipitates $(Fe(OH)_3)$ formed by oxidation of dissolved iron $(Fe(OH)_2)$ present in groundwater, as discussed above, 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. The Iron Removal Plants (IRPs) in Bangladesh constructed on the principles of aeration, sedimentation and filtration in a small unit have been found to remove arsenic without any added chemicals.

2.9.4 Iron Filings

Zero valent iron (Fe(0)) has many important applications in environmental chemistry. It has been used to destroy chlorinated hydrocarbons and to remove inorganic contaminants, such as CrO_4^{2-}, via reductive precipitation. Fe (0)has also proved effective at removing As (III) and As (V), and the predominant mechanistic pathways seems to be surface precipitation or adsorption (Su and Puls, 2001). Fe (0) is a strong reducer and thus is an effective agent for removing both inorganic and organic arsenic. Another advantage of using Fe^0 is that it is nontoxic and inexpensive.

Ramaswami et al. investigated for arsenic removal using a batch-mixed iron treatment with zerovalent iron. High removal efficiency (93%) was achieved for a short contact time (0.5-3 hours). Only As (III) species were tested, however. The highest rate of removal was found in headspace-free systems when sulfates were present in solution. Four types of zerovalent iron filings (Fisher, Peerless, Master Builders, and Aldrich) were investigated for removal of As(III) and As(V) from drinking water (Su and Puls, 2001). The metals were allowed to react with arsenic, and relative removal efficiencies were achieved in the following order: Fisher> Peerless, Master >Aldrich. With the exception of Aldrich Fe^0, arsenic concentrations decreased exponentially with time in other Fe^0 solutions and were <10 µg l⁻¹ in four days.

The Sono 3- kolshi is one of the prominent As filter that use zero valent iron fillings and had been extensively distributed in Bangladesh rural area. The most important advantage of this filter is that it doesn't need to add any chemical either for pre-oxidation or adsorption. Top

kolshi contain iron fillings and coarse sand. Middle kolshi contain fine sand and bottom kolshi is the water collector (Khan et al., 2000). The sono 3-kolshi unit has been found to be very effective in removing arsenic but the media favor the growth of microorganism (BAMWSP, DFID and Water Aid, 2001). The filters was further modified to two buckets system and named as sono arsenic filter. The upper buckets contain a 4-5 cm thick composite iron (mixed of metal iron and iron hydroxides) layer at the middle of the bucket where majority of arsenic (As (III) and As (V)) is adsorbed. The lower bucket contain sand and charcoal layer to remove the iron hydroxides and organic matter release for the upper bucket. The final water is collected at the bottom of the lower bucket.

2.9.5 Membrane Technologies

Membrane units include coagulation/microfiltration, reverse osmosis (e.g. nanofiltration and hyperfiltration) and electrodialysis and uses special filter media that physically retain the impurities present in water. When arsenic contaminated water passes through the media, all kinds of impurities, including As, are removed from the water. The process is expected to have high arsenic removal efficiency as a result of the small molecular weight of dissolved arsenic species (<150 Daltons). Furthermore, when the membrane is slightly negatively charged, it is advantageous for the removal of As from water (Brandhuber and Amy, 2001). Source water quality and the effluent concentration to be reached are important design parameters. If the water is free of suspended solids before the membrane treatment, then the process can be very effective, but high capital and operational costs are major concerns. The costs associated of these methods include the cost of membrane unit construction (e.g. pumps, etc.) as well as additional treatment costs (especially at high initial arsenic concentrations).

2.9.6 Biological Arsenic and Iron Removal

Biological arsenic removal has been received a lot of attention because of its several advantages over the conventional chemically arsenic treatment technologies. The mechanism of As removal is, that iron in the contaminated water was oxidized by some iron oxidizing bacteria such as *Gallionella ferruginea* and *Leptothrix Ochracea*. *Leptothrix spp.* would grow autotrophically or mixotrophically, utilizing the energy liberated upon the oxidation of Fe

(II). The letothrix group of iron bacteria is also well known as sheath format bacteria. They can deposit a large amount of ferric iron on their sheaths. The optimal tempuratures at which these organisms grow are between 10-35°C and at pH range of 6.0-8.0 (Veen et al., 1978).

The main product of biological oxidation of iron is usually a mixture of poorly ordered iron oxides often containing significant amounts of organic matter. The intermixing of iron oxides, organic material and bacterial presence, produces complex multiple sorbing solids, which exhibit unique metal retention properties. Arsenic can be removed by direct adsorption or co-precipitation on the preformed biogenic iron oxides. A partial oxidation of As (III) also has been simultaneously occurred during the biological iron oxidation processes, which improve overall As removal efficiency (Katsoyiannis and Zouboulis, 2004).

Katsoyiannis and Zouboulis reported that highest arsenic removal efficiency (80-84%) was achieved at an initial arsenic concentration range of 35-80 μg l^{-1} under a linear velocity range of 7-14 m h^{-1}. The removal efficiency slightly decreased when the initial arsenic concentration was >80 μg l^{-1}. The field results of biological technology have not been reported yet. Therefore the field implication and compare the results with laboratory results are crucial.

2.9.7 Alternative Arsenic-free Water Sources

Possible alternative sources include deep tubewells, dugwells, rainwater harvesting systems and surface water facilities, which are currently being promoted under mitigation programs in Bangladesh. Groundwater in deeper aquifers (below 150 to 200 meters) is generally free of arsenic and can be used as an alternative source of water. Surface water from ponds or river can be boiled and filtered at home to remove biological contamination. Rain water can also be a source of arsenic free water. At tin roof or a plastic sheet can be used to collect rainwater, which is then stored in a large tank made of cement / brick. Dugwells are ultra shallow aquifers (5 to 10 meter deep) generally have low concentration of arsenic.

However, these technologies have their limitations. It may be difficult to ensure that the water is free from bacterial contamination, particularly when using surface water sources. Water from dugwells is also susceptible to bacteriological contamination. Method such as rain water harvesting may not provide an adequate quantity of water to meet the annual water demand due to the prolonged dry season in Bangladesh. Moreover, possibility of the growth of

bacteria or insects inside the stored tank needs further treatment before using. Deep tubewells are a promising safe water option in Bangladesh, but they have following three drawbacks:

- Installation cost is too high.
- It may be difficult to drill up aquifers in some areas because of unfavorable geological conditions.
- The water may be unsustainable for drinking because of salinity, for example, in costal belt, south Bangladesh.

The deep tubewells are currently safe for arsenic, however there is a growing concern that these deep aquifers may get across- contaminated by arsenic seeping from shallow aquifers.

2.10 Mechanism of Arsenic Removal in This Study (by Biological Oxidation)

This removal of arsenic occurred due to the oxidation of iron and arsenic followed by their subsequent adsorption and precipitation on and with biologically produced iron hydroxides. Biological oxidation of iron by iron bacteria is the main mechanism in respect to the removal of arsenic in this study.

Both forms of inorganic arsenic (AS (III) and As (V)) could be removed more efficiently during iron oxidation than formed iron precipitation. This might be because a very fine iron hydroxide floc is produced which had the high adsorptive surface area and high binding energy resulting in the effective removal of both forms of arsenic at the beginning of biological iron oxidation.

Firstly Fe (II) oxidation is catalyzed by the iron bacteria and transformed to Fe (III). Secondly a part of As (III) is oxidized to As (V) in the presence of Fe (II) and the iron bacteria. Finally adsorption of As (V) on iron hydroxides occurred. These processes are schematically shown in the equations 2.48 to 2.50. The mechanism is presented in Figure 2.4.

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe\,(OH)_3 + 8H^+ \qquad \text{------------ (Equation 2.48)}$$

$$H_3AsO_3 + (O_2,\ OH^-,\ Fe\,(II)) \rightarrow H_3AsO_4 \qquad \text{------------ (Equation 2.49)}$$

$$Fe\,(OH)_3 + H_3AsO_4 \rightarrow FeAsO_4 \cdot 2H_2O + H_2O \qquad \text{------------ (Equation 2.50)}$$
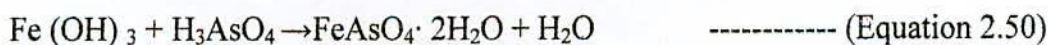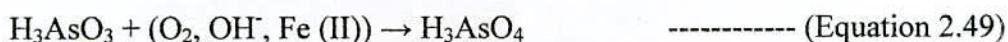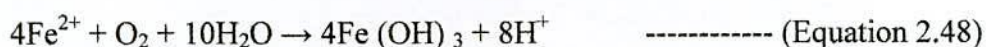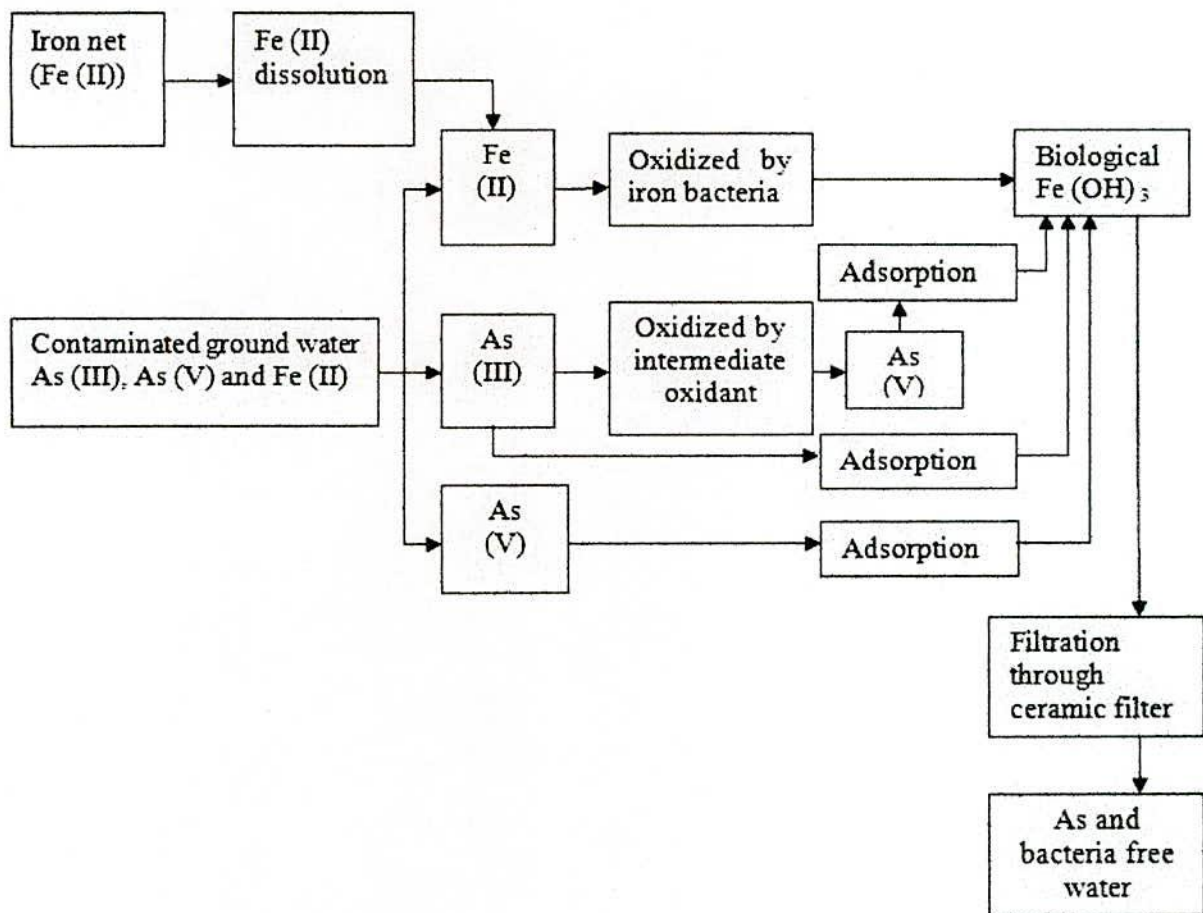
Figure 2.5: Conceptual Mechanism of Arsenic Removal by Iron Oxidation

2.11 Arsenic Waste Disposal

Arsenic waste can be disposed of by converting it into volatile organic forms through the activities of the microbes in soil or sediments. One such disposal method was used in Bangladesh where arsenic waste was disposed in soil in the backyard with cow dung added. Das et al. (1995) claim that the microbes residing in the cow dung helped convert arsenic into volatile arsenic species since analyses of the soil failed to produce concentrated As values. This result appears dubious and it is worth noting that disposal of arsenic-rich residues is rarely addressed in the literature.

2.12 Requirements for Appropriate Treatment Technology

Developing countries like Bangladesh, India cannot afford expensive and/or large scale treatments. Low-cost, effective technologies that are readily available at the household or community level are needed to solve the present crisis. Large-scale treatments are not

appropriate because many people in third-world countries obtain water from wells rather than from large municipal water plants. Appropriate in-home technologies to be implemented in third-world countries should meet certain criteria to be effective. The treatment must be applicable over a wide range of arsenic concentrations and easy to use without running water or electricity, and the materials for the treatment must be cheap, readily available, and/or reusable to reduce costs. Finally, such technology should not introduce any harmful chemicals into drinking water. Field studies in Bangladesh showed that the main reasons for rejection of some technologies are the amount of operational effort, the level of maintenance, the amount of time until clean water is available, and the volume of water that the technologies can provide on a daily basis. Hence, it is proposed that for an appropriate arsenic removal technique the following requirements should be fulfilled:

i) Water Quality

- The selected method must be effective enough to meet the required water quality standards for arsenic.

- The necessity of meeting other water quality standards besides arsenic is highlighted. If the applied method is not capable of meeting the standards for other water contaminants or if the technology itself is a source of unwanted contaminants to the water, a secondary treatment may be needed, hence increasing the overall cost.

- The selected method must perform well in the combined presence of potentially competing ions such as phosphate, silicate, sulfate and bicarbonate, and the method should be tested using natural water samples.

ii) Economy

- The expected cost of the method in terms of set-up, operation and maintenance should be affordable to poor people.

iii) Operation & Maintenance

- Simple operational and maintenance requirements should be preferred in addition to minimal energy requirements.

- Optimum pH range for the removal needs to be taken into account, as changing the pH during, before or after the treatment may not be practical. Moreover, if the method is effective within a small range of pH it may be difficult to maintain this pH throughout the removal.

iv) Safety & Reliability

- Operation of the process should be safe, reliable and robust.
- Storage and handling of any required chemicals should be addressed, including the associated costs.
- The method should preferably be effective in removing both arsenite and arsenate species.

v) Social Acceptance

- The likely acceptance of the method by local residents should be evaluated.

vi) Environmental Effects

- If other pollutants are produced as a result of the treatment such as wastewater and toxic sludge, their treatment should be addressed.
- Occupational health (hazard potential of the utilized chemicals) should be considered.

This review of arsenic removal technologies indicates that iron filings, ferric salts, granular and ferric hydroxide are potentially low-cost sorbents that can remove arsenic after simple mixing in a relatively short time. The most well known treatment makes use of a ferric salt (such as ferric chloride and ferric sulfate). Ferric salts are cheap and very effective at removing arsenic. Ion exchange resins can remove As (V) very well, but competing anions such as nitrate and sulfate strongly reduce arsenic removal potential. Therefore, this sorbent is not practical to use in groundwater where anions such as nitrate and sulfate are present in high concentrations. The next-most-effective very common arsenic technology consists of a fixed column of sorbents that can remove arsenic simply by passing groundwater through the column. The most well known fixed-bed columns make use of activated alumina and iron-coated sands. These fixed bed columns often do not work well with groundwater having high concentrations of iron because iron precipitates in the presence of air, which could clog and foul the column. Many synthetic sorbents have also recently been developed that have many advantages over other sorbents. These synthetic sorbents are highly selective and effective and do not often pose much waste disposal concern since they are usually non-hazardous.

Alternative water sources such as deep tubewells, surface water facilities, rainwater harvesting also another promising option, but all of them have some drawbacks. Therefore, it may be difficult to promote those technologies in the field level of Bangladesh rural area.

Most of the technologies discussed have slow reaction rates and are not very simple to use. The quest for a simple, low-cost, effective technology that can remove arsenic is still ongoing. Another highly innovative treatment makes use of biological oxidation. Certain bacteria are cultured to oxidize iron, which are often present in high concentrations in groundwater. Arsenic was removed through adsorption to the iron solids. Our current research on biological and hybrid technology may provide a viable, low-cost option. The process consists of a simple mechanism of arsenic removal. In the biological method iron oxidizing bacteria would oxidized the naturally occurring Fe (II) in groundwater while As could be removed by oxidation and co-precipitation. On the other hand, if natural Fe (II) is not sufficient to remove As from ground water below standard level, additional Fe (II) can supply in the biological method by introducing zero valent iron (Hybrid method). These processes would a sustainable as the technology is simple, low-cost and no additional chemical is needed in the process.

However, successful implementation of any technology is needed to be considering the social and economic condition of the region. Furthermore, it is necessary to make a frame work for implementation strategy for the long-term sustainability of the technology (Shafiquzzaman, 2008).

CHAPTER 3

Methods and Materials

3.1 Introduction

Developing countries like Bangladesh, India cannot afford expensive and/or large scale treatments. Low-cost, effective technologies that are readily available at the household or community level are needed to solve the present crisis. Large-scale treatments are not appropriate because many people in third-world countries obtain water from wells rather than from large municipal water plants. Appropriate in-home technologies to be implemented in third-world countries should meet certain criteria to be effective. The treatment must be applicable over a wide range of arsenic concentrations and easy to use without running water or electricity, and the materials for the treatment must be cheap, readily available, and/or reusable to reduce costs. Finally, such technology should not introduce any harmful chemicals into drinking water.

Quite often it is a very complex task to select a method because of the many difficulties that arise when a particular technology is applied in the field. These difficulties include a wide range of arsenic concentrations, effects of other elements and their variable concentrations in water, the need to adjust pH for optimal removal, optimized dose, proper operation and maintenance, and safe disposal of arsenic waste. Another major issue concerning a technology is that it should not pose risk of bacteriological contamination and should be broadly acceptable to users. In Bangladesh, the main reasons for rejection of some technologies are the amount of operational effort, the level of maintenance, the amount of time until clean water is available, and the volume of water that the technologies can provide on a daily basis.

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The review of arsenic removal technologies indicates that iron filings, ferric salts, granular and ferric hydroxide are potentially low-cost sorbents that can remove arsenic after simple mixing in a relatively short time. The most well known treatment makes use of a ferric salt (such as ferric chloride and ferric sulfate). Ferric salts are cheap and very effective at removing arsenic. Ion exchange resins can remove As(V) very well, but competing anions such as nitrate and sulfate strongly reduce arsenic removal potential. Therefore, this sorbent is not practical to use in groundwater where anions such as nitrate and sulfate are present in high concentrations. The next-most-effective very common arsenic technology consists of a fixed column of sorbents that can remove arsenic simply by passing groundwater through the column. The most well known fixed-bed columns make use of activated alumina and iron-coated sands. These fixed bed columns often do not work well with groundwater having high concentrations of iron because iron precipitates in the presence of air, which could clog and foul the column. Many synthetic sorbents have also recently been developed that have many advantages over other sorbents. These synthetic sorbents are highly selective and effective and do not often pose much waste disposal concern since they are usually non-hazardous (Ahmed and Rahman, 2000).

Alternative water sources such as deep tubewells, surface water facilities, rainwater harvesting also another promising option, but all of them have some drawbacks. Therefore, it may be difficult to promote those technologies in the field level of Bangladesh rural area.

Most of the technologies discussed have slow reaction rates and are not very simple to use. The quest for a simple, low-cost, effective technology that can remove arsenic is still ongoing.

In this study, biological oxidation process was tried with simple process and procedures. Certain bacteria were cultured to oxidize iron, which are often present in high concentrations in groundwater. Arsenic was removed through adsorption to the iron solids. In the biological method iron oxidizing bacteria would oxidized the naturally occurring $Fe(II)$ in groundwater while As could be removed by oxidation and co-precipitation. On the other hand, if natural $Fe(II)$ is not sufficient to remove As from ground water below standard level, additional $Fe(II)$ can supply in the biological method by introducing zero valent iron. These processes would a sustainable as the technology is simple, low-cost and no additional chemical is nodded in the process.

3.2 Preparation of Filter Unit

The main components of the filter are:

- Ceramic filter

- Iron net / Iron scrap / Iron bar

- Iron bacteria sludge

- Reactor (14-16 L Clay pot was used)

- Effluent storage bucket

- Wooden stand etc.

3.2.1 Preparation of Ceramic Filter

The filter was made with locally available and cheap materials as rice bran, clay soil and water.

Fixing the Ratio of the Ingredients

Firstly dry clay soil and rice bran was mixed homogeneously in a specific ratio. The mixing ratio of the ingredients was selected after testing the filtration flux and flexural strength of several ceramic bars prepared with different ratios of soil and rice bran. Rice bran content in soil varied from 0 to 30% (by weight) in various specimen ceramic bars. The mixer was homogenized and molded to form 160 mm (L) × 40 mm (W) × 40 mm (H) bars. The molded specimens were air dried at room temperature for 24 h, and then oven dried at 105 ^{0}C for another 24 h to remove water content. The dried specimens were then heated at 900 ^{0}C in electric furnace. The specimens sample were then underwent a series of tests including hardness test, filtration rate, firing shrinkage, pore volume, to determine the optimum percentage of soil and rice bran for actual filter.

The filtration fluxes of ceramic bars made with 0%, 15%, 20% and 25% rice bran at 28.5 cm of water head were 0.11 ± 0.02, 0.16 ± 0.01, 0.53 ± 0.08 and 1.92 ± 0.39 ml/cm^2/min,

respectively. The flexural strengths of the bars were 0.75 ± 0.19, 0.48 ± 0.15, 0.27 ± 0.14 and 0.08 ± 0.01 KPa, respectively. The results indicated that fired ceramic bars with a higher percentage of rice bran (25%) were low in strength and easily broken, while those with lower percentages (10% and 15%) produced a relatively low filtration flux. On the basis of these results, a mixture of 80% soil and 20% rice bran was selected for ceramic filters in this study.

Filter Manufacture Procedures

- The soil was collected from the Khulna region of Bangladesh. After collecting the soil was oven dried at 105 ^{0}C for 24 h. The oven dried soil was then ground with hammer and screened through 0.5mm sieve (Figure 3.1).

- Rice bran was collected from local rice mill in Khulna. Dry bran was screened through 1 mm sieve (Figure 3.1).

- 80% soil and 20% bran was taken and mixed homogeneously. For example, 640 gm of soil and 160 gm of rice bran was needed for 1 filter. This dry mixture (800 gm) was combined with water to make dough (Figure 3.2).

- A special type of dice made of wooden board (20cm×20cm), wooden bar (Height 9cm and Diameter 6cm) and Polyvinylchloride (PVC) pipe (Height 11cm and Diameter 11cm) was used to make the filter from the dough of soil, rice bran and water (Figure 3.3).
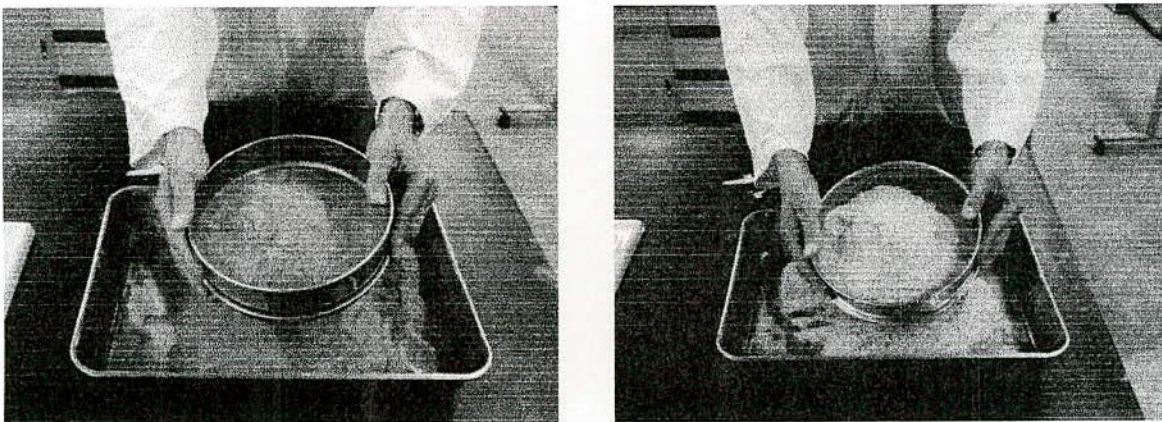

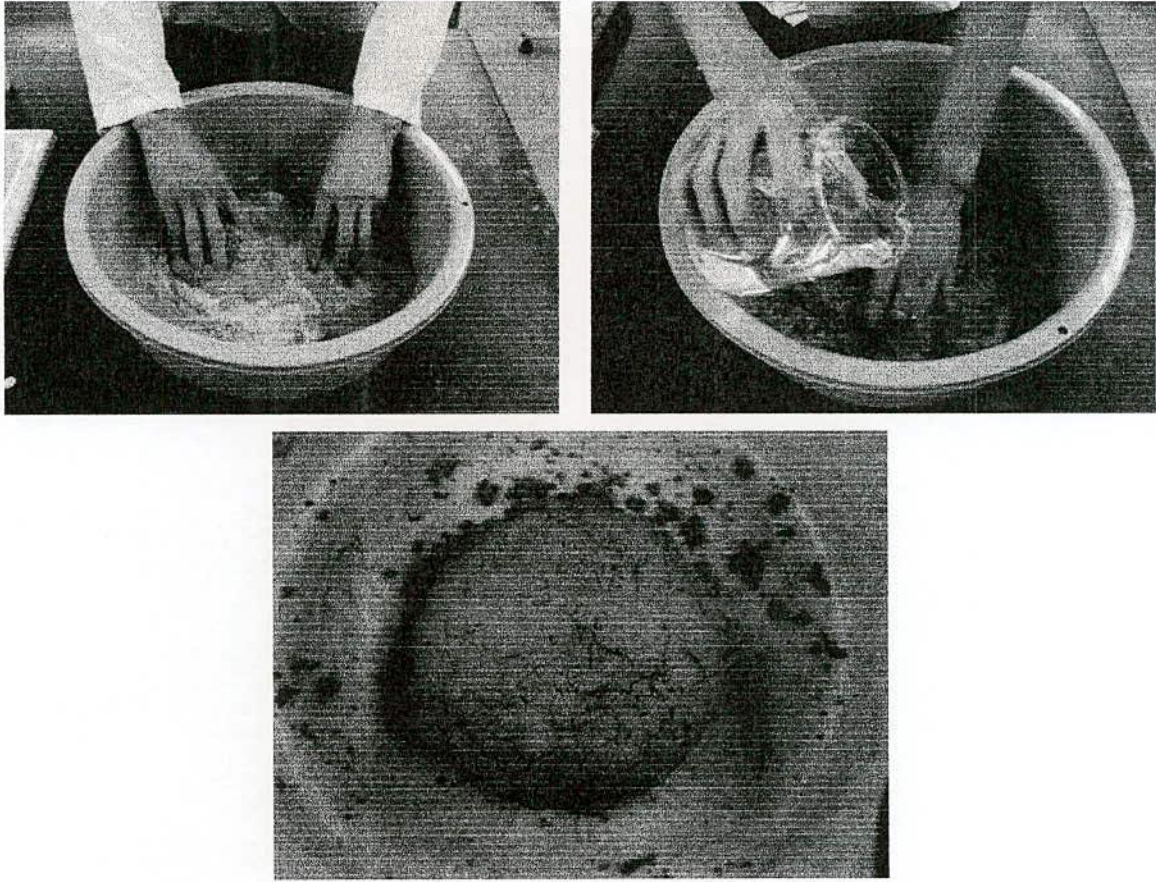Figure 3.1: Sieve analysis of soil and rice bran

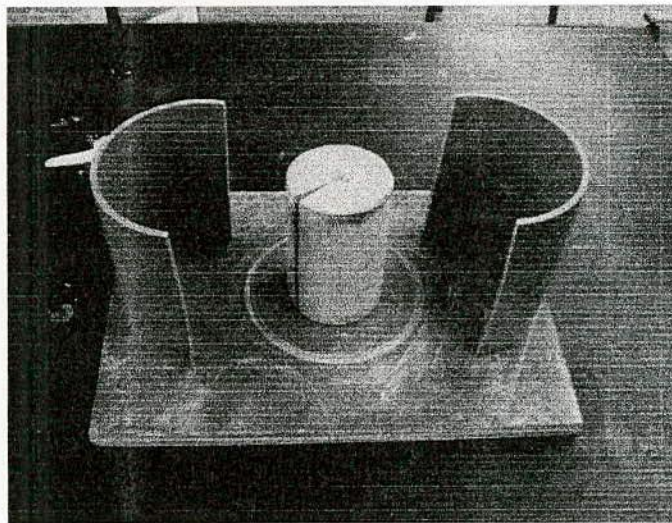Figure 3.2: Mixing of soil and rice bran and making of dough with water
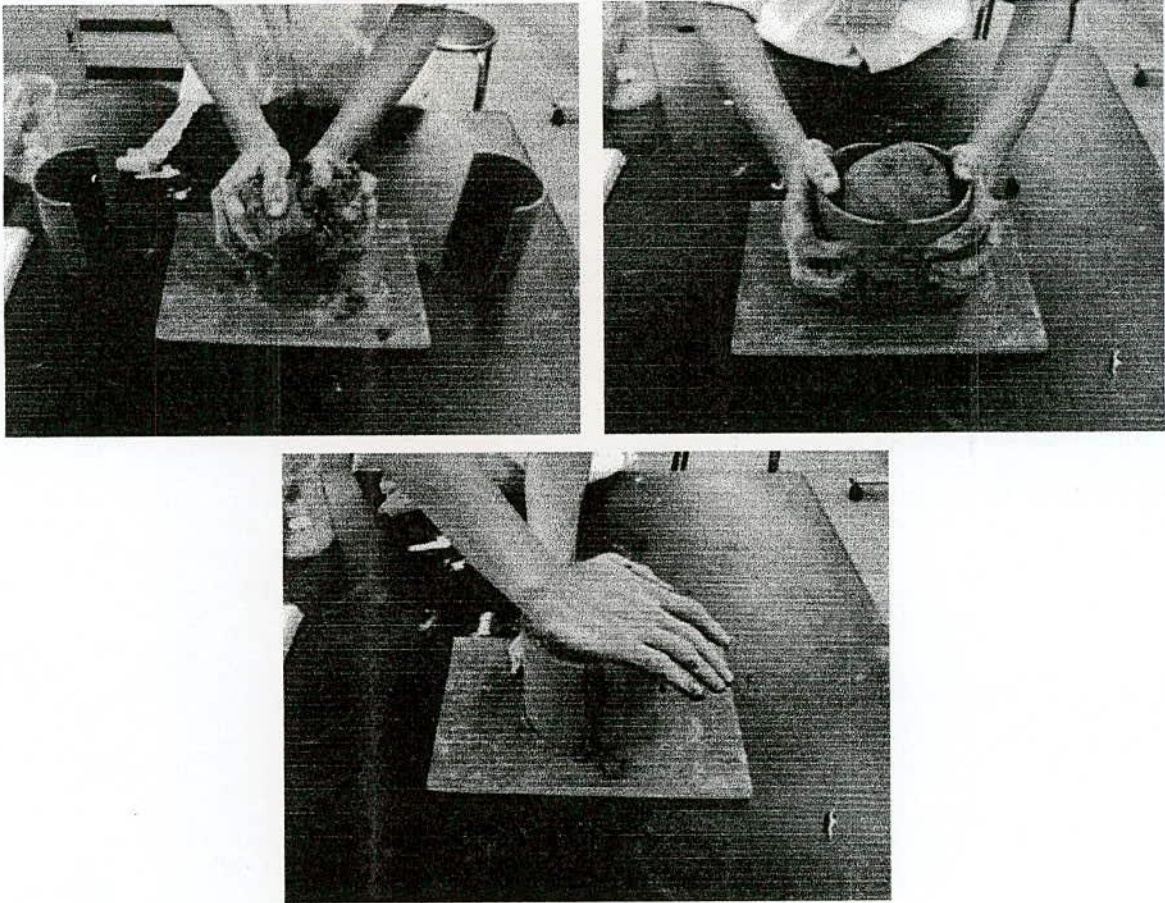

Figure 3.3: Filter dice

Figure 3.4: Shaping of filter from dough using dice

- The wooden bar of the dice was wrapped with newspaper. Then dough was placed around the bar of the dice and two pieces of PVC pipe were pushed by hand from both sides to make cylindrical shape. Extra soil mix was removed and the upper side was flattened (Figure 3.4).

- Next the pipes were taken off and the surface of the filter was polished with water (Figure 3.5).

- The total frame was then toppled down to remove the dice (Figure 3.6).

- The resulting cylindrical ceramic filters were hollow with one side open (Figure 3.7). The final ceramic filters had a height of 10 cm and a thickness of 2 cm. This soft filter

was then dried in the sun for at least 3 days. Finally, the filters needed to be burnt in a muffle furnace in the laboratory or in a small-scale pottery kiln in the field at 900°C.
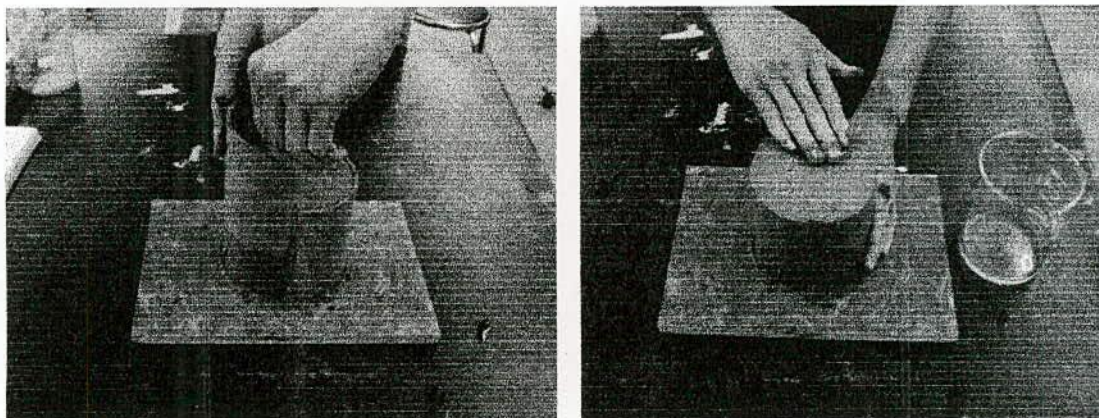

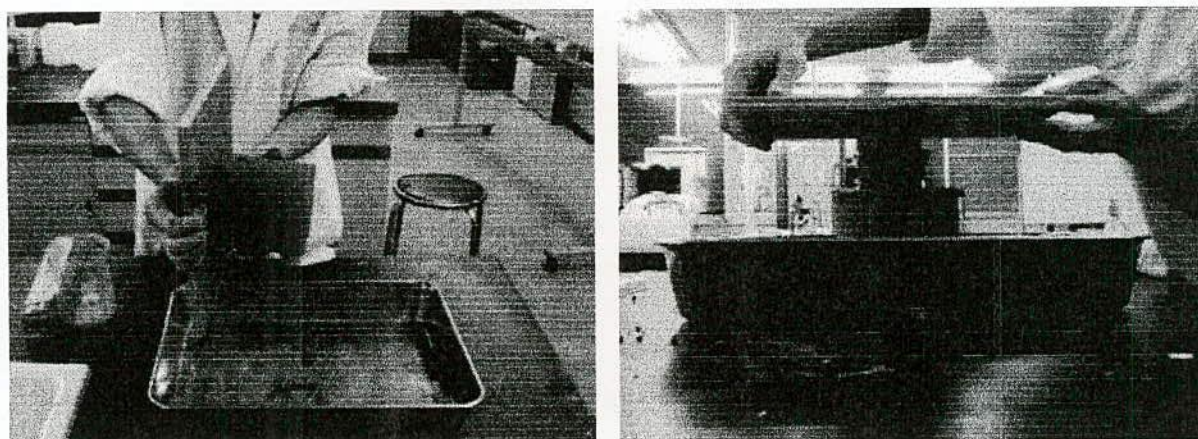Figure 3.5: Shaping of filter from dough using dice (Cont.).

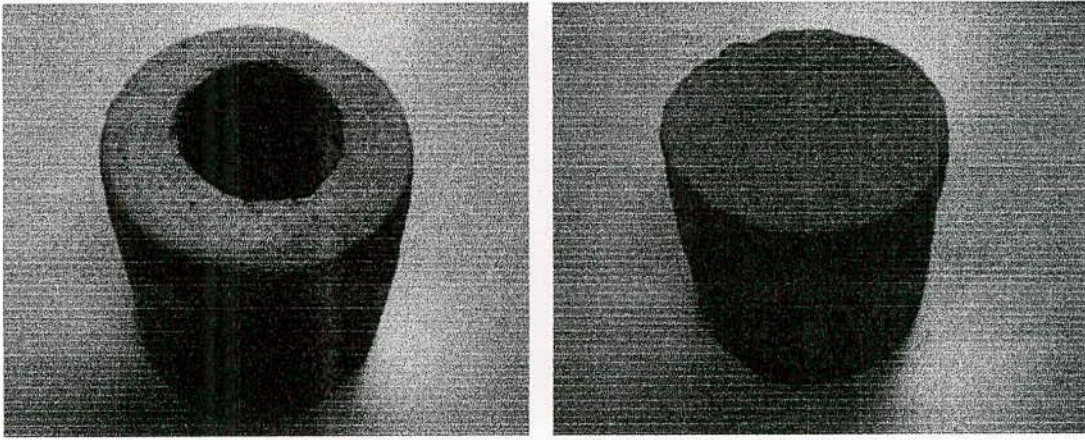Figure 3.6: Final step to get raw ceramic filter

Figure 3.7: Final ceramic filter before burning

Field-level Burning of Filter

The air dried filters may be easily burnt in potter kiln. The potters of Bangladesh use small-scale kiln for the burning of their staffs. The temperature inside the kiln is almost 900 to 1000°C. So these kilns may be easily used to burn the filters cheaply.

In this study, the filters were burnt in a potter kiln in Dighalia, Daulatpur, Khulna.

- The filters were arranged with the potteries with wood and other fuels.

- Then the outside of the kiln was sealed with mud and straw.

- The burning was continued with wood, rice husk etc.

- The temperature of the inside of the kiln was checked occasionally.

- After continuous burning for 6 to 8 hours, the kiln was kept to cool down. After some more hours the filters were taken out from the kiln and the quality of the burnt filters was checked. The over-burnt and cracked filters were abandoned for using in the field level arsenic removal unit.

The burning process of filters is shown in Figure 3.8.
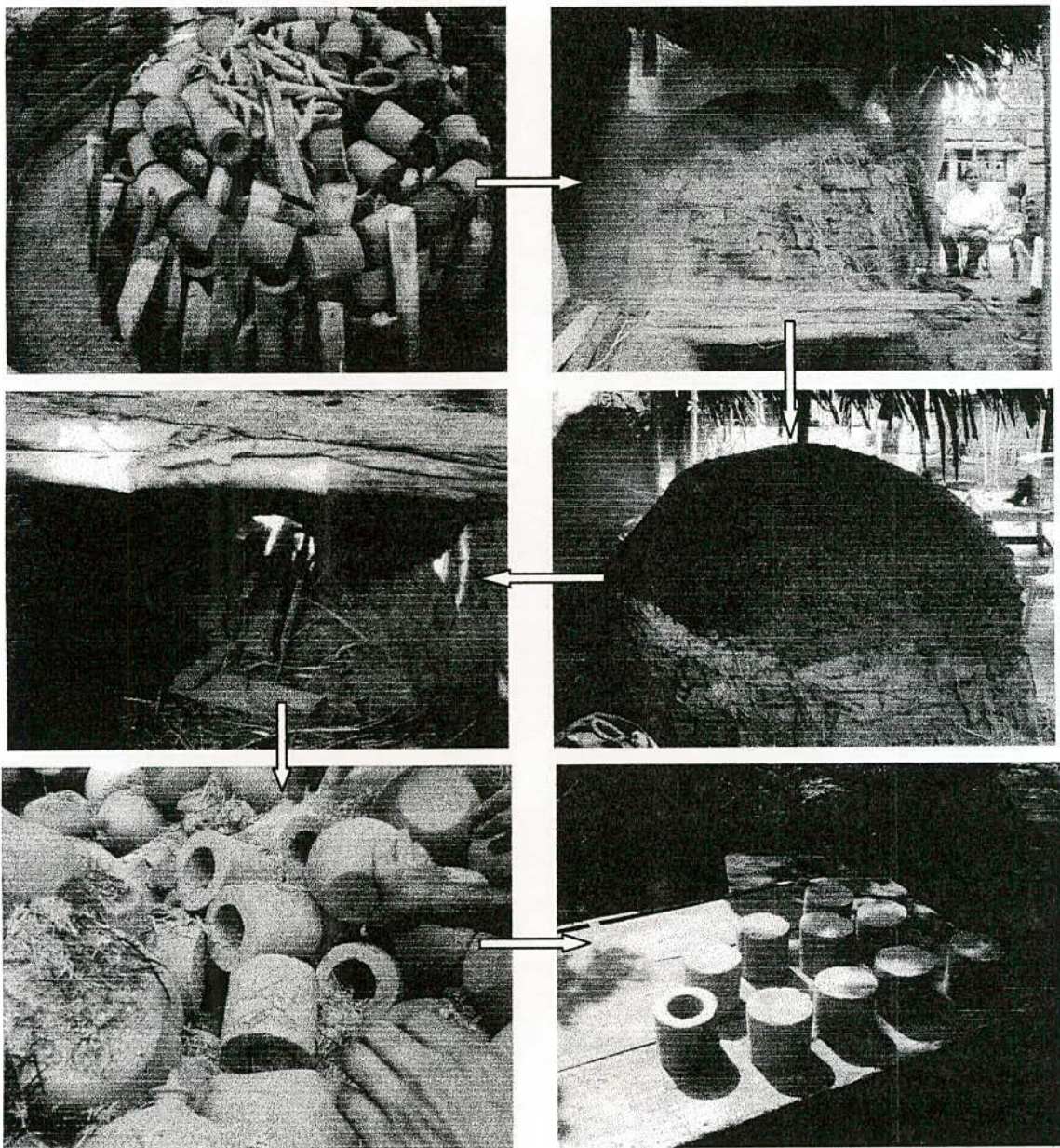
Figure 3.8: Filter burning in Potter kiln

3.2.2 Preparation of Iron Net

Metal oxides such as Fe, Al and Mn oxides have been found to be major sorbents for As because of their high reactivity and high surface area (Fenford et al., 1997; Himemstra and Van Riemsdijk, 1999). Among the species, As (V) binds more strongly with the metal oxides of Fe compared to As (III) species. But, the dissolved Fe present in the Bangladesh groundwater was not enough to remove the As present in the water suggesting to introduce of

another method with the filter (Shafiquzzaman, 2008). Therefore, Fe (0) net was added to the filter unit.

In this study, commercially available iron net without coating was used. It was bought from local market of Fulbarigate, Daulatpur, Khulna. At first, 600 gm iron net was taken. Then 11cm×11cm×11cm cube with one side open by the iron net was made.
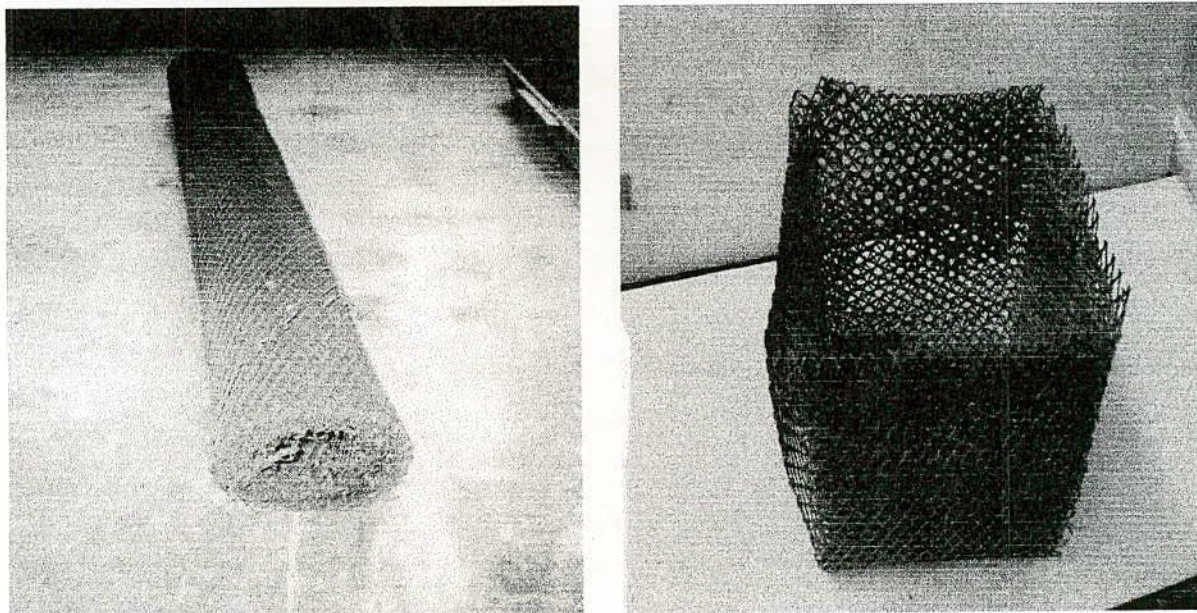
Figure 3.9: Preparation of iron net cube from locally available iron net

3.2.3 Preparation of Iron Bacteria

The biological iron oxidation is caused by the presence of several iron oxidizing microorganisms in water. So, iron bacteria sludge was added to the filter unit to accomplish the arsenic removal easily and readily. Iron bacteria may either be found in nature or a cultured.

Searching Iron Bacteria

Iron bacteria may be found some places having solution of water with ironware, rusty staffs etc.

Usually, iron bacteria is available at the places such as near iron factory drain, iron rich tubewell drain etc. If the water color in these drains is found reddish then it contain iron bacteria.

Iron Bacteria Culturing

Iron bacteria sludge may be easily cultured. In our study, this sludge was produced in the laboratory of Khulna University of Engineering and Technology, Khulna.

- Water was filled in a big drum of capacity 100 L.
- Some iron net, iron bar and other iron materials was added in the drum.
- This was aerated with a stick for 5 minutes daily.
- Iron bacteria layer will be deposited at the bottom of the drum after 10-15 days. This sludge solution was collected and used in the filter unit.

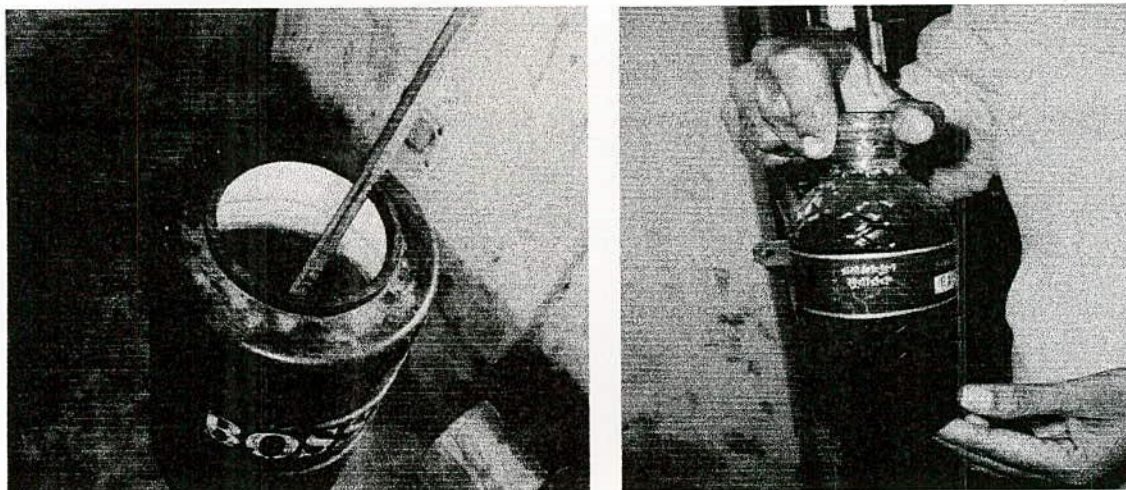Or the sludge from the previous operated filter may be used as the iron bacteria sludge for new one.

Figure 3.10: Iron bacteria culturing and collected iron bacteria sludge

Amount of Iron Bacteria per Filter

About 5 g (dry weight basis) iron bacteria is necessary in our proposed filter. Therefore, approximately 1 mug (0.5 L) of iron bacteria sludge was added to each filter.

3.2.4 Set up of Filter Unit

The set up process of the filter unit very simple and even non-technical people may able to install and run it.

- The opening side of the ceramic filter was attached at the bottom of the reactor using cement paste as shown in the figure below. Then it was kept 1 day for drying.
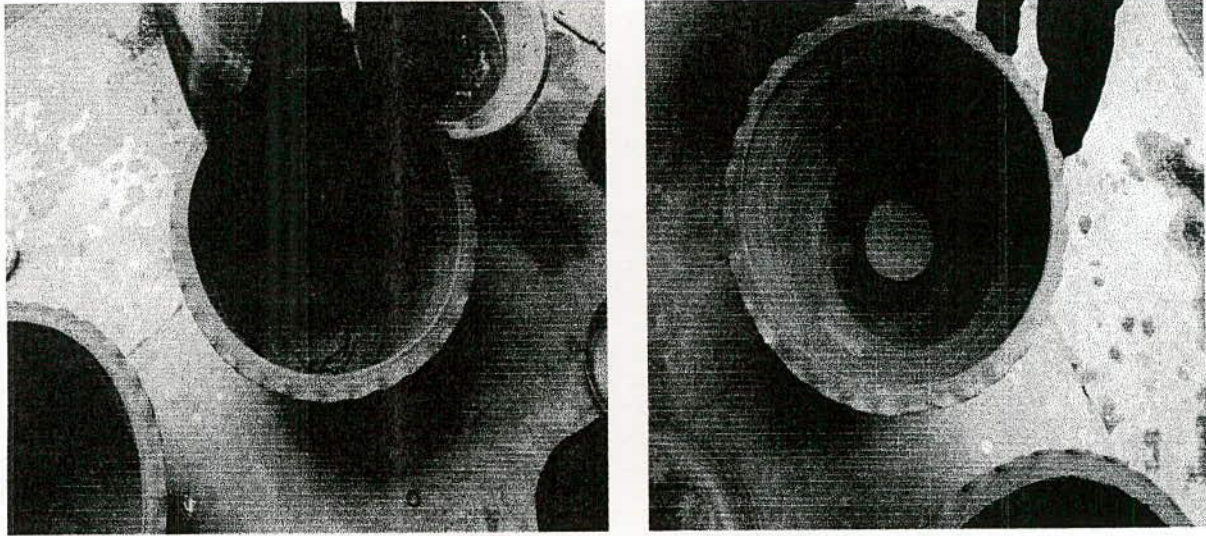
Figure 3.11: Pasting of ceramic filter with reactor (clay pot)

- After drying, a 2 cm hole was made at the middle of the bottom of the reactor (clay pot) to make the path of flow of filtrated water during the running of the filter unit (Figure 3.12).

- The filter was then covered by square shape iron net box. The reactor was placed on the wooden stand and the effluent storage bucket was placed under it.

- Then about 500 ml iron bacteria sludge was added in the reactor. The filter unit was then ready to be used with the addition of influent raw water.

Figure 3.12: Making of flow path for filtrated water

Figure 3.13: Placing of iron net box in the filter unit

Figure 3.14: Addition of iron bacteria sludge in filter
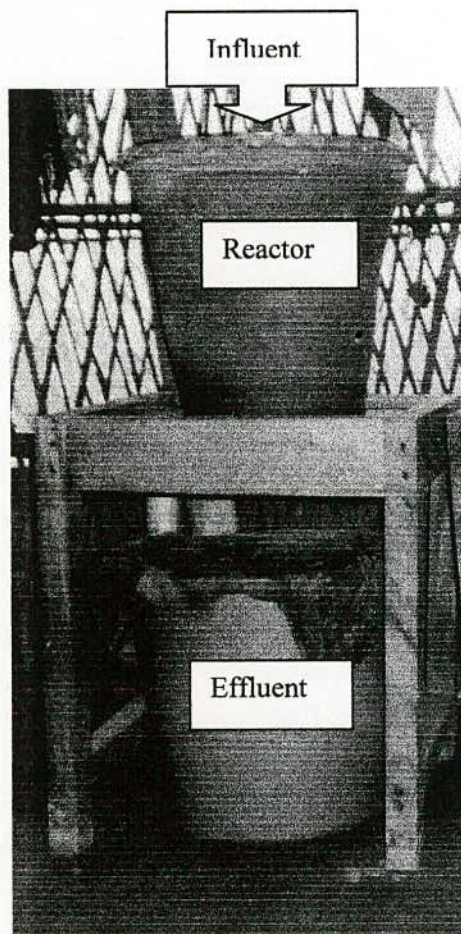
Figure 3.15: Single unit filter system continuing

3.3 Site Selection

My field study was conducted in two villages of two upazilas (Sub-district) Dighalia and Rupsha of Khulna district (Figure 3.16a and Figure 3.16b). The household tubewells of both upazilas contained very highly arsenic contaminated water.
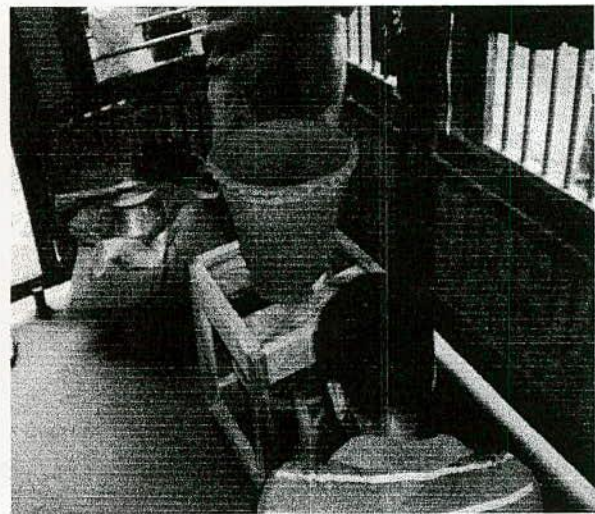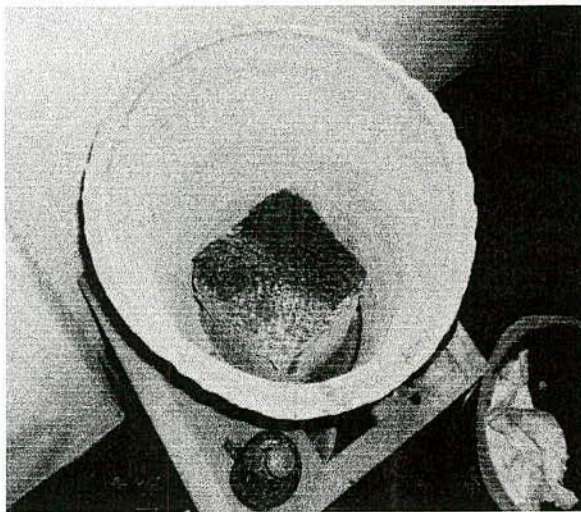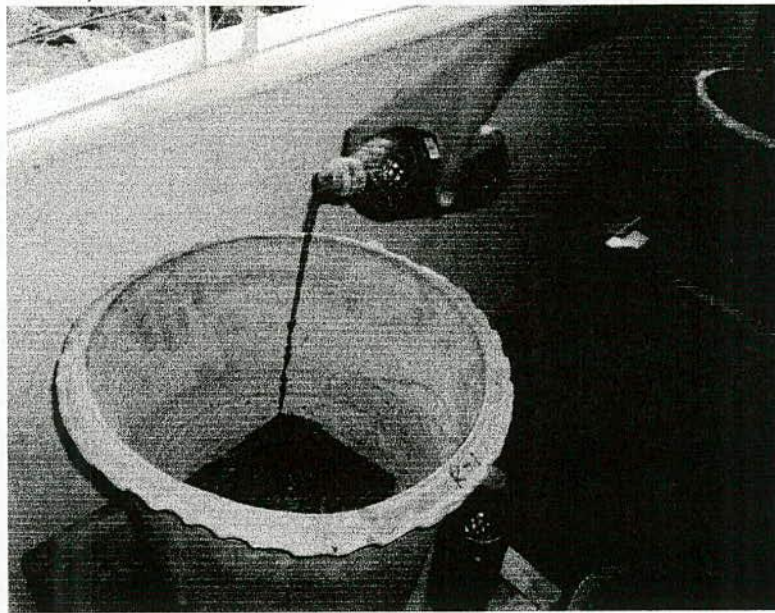
In Dighalia, Khulna, three filters were installed in a household having tubewell with elevated level of arsenic. These three filters were named as 'K1net', 'K1scrap' and 'K1rod'. 'K1net' represented single unit filter system with iron net. Similarly, 'K1scrap' represented single unit filter system with scrap iron and 'K1net' represented single unit filter system with iron rod.

In Rupsha,firstly, two single unit filter systems with iron net were installed in two different households with tubewells of highly arsenic contaminated water. They were named as 'R1single' and 'R2single'. Secondly, in these two households, two double unit filter systems with iron net were installed replacing the previous single unit filter systems. These double unit filter systems were named as 'R1double' and 'R2double'.

The investigated household tubewells represent a broad and representative range of groundwater composition in Bangladesh, with the variation of values of As, Fe, P, pH, Color, Turbidity etc.

Figure 3.16a: Sites of the field study (http://98.131.7.106/lged/images/Bangladesh.jpg)

Figure 3.16b: Sites of the field study (Cont.)
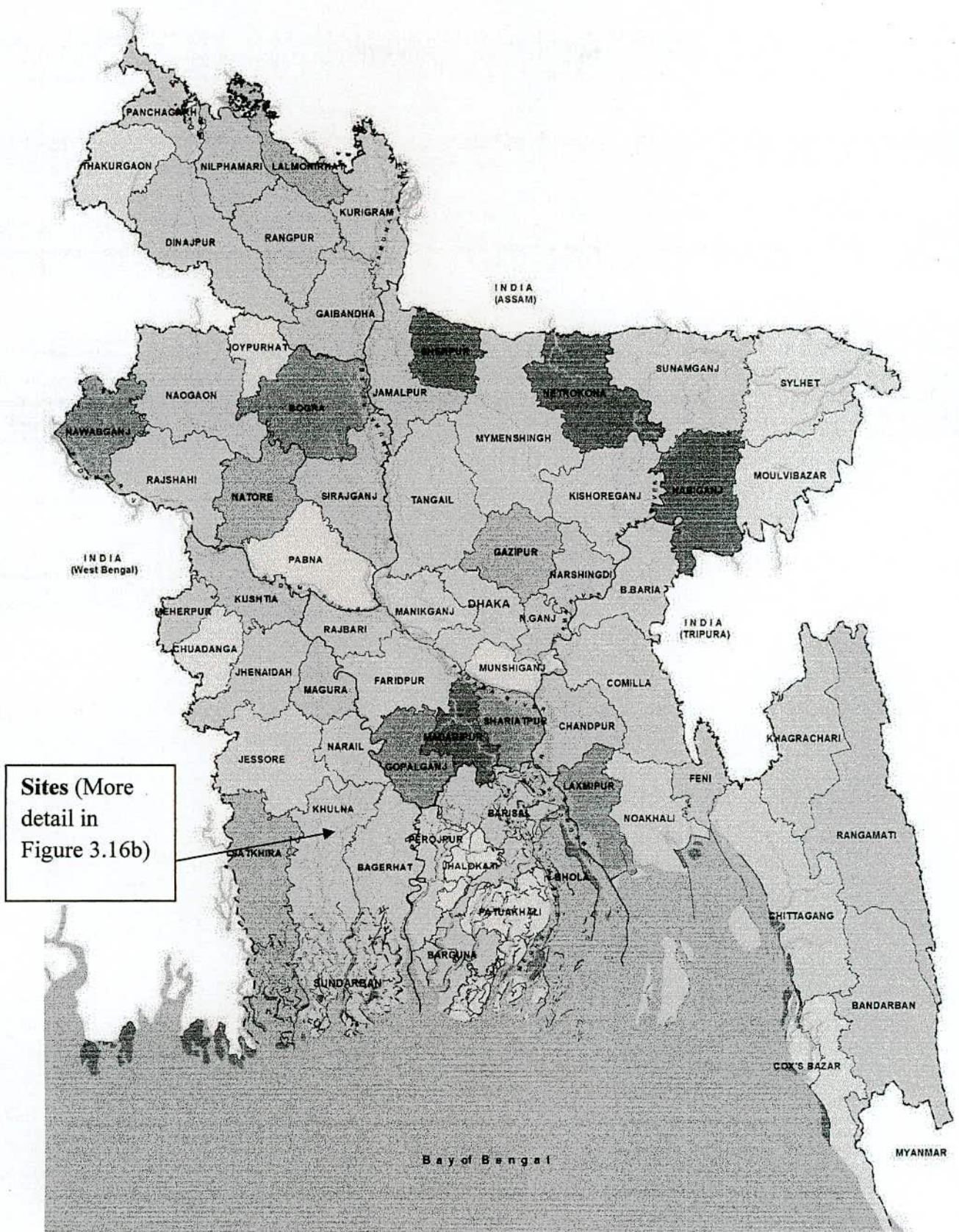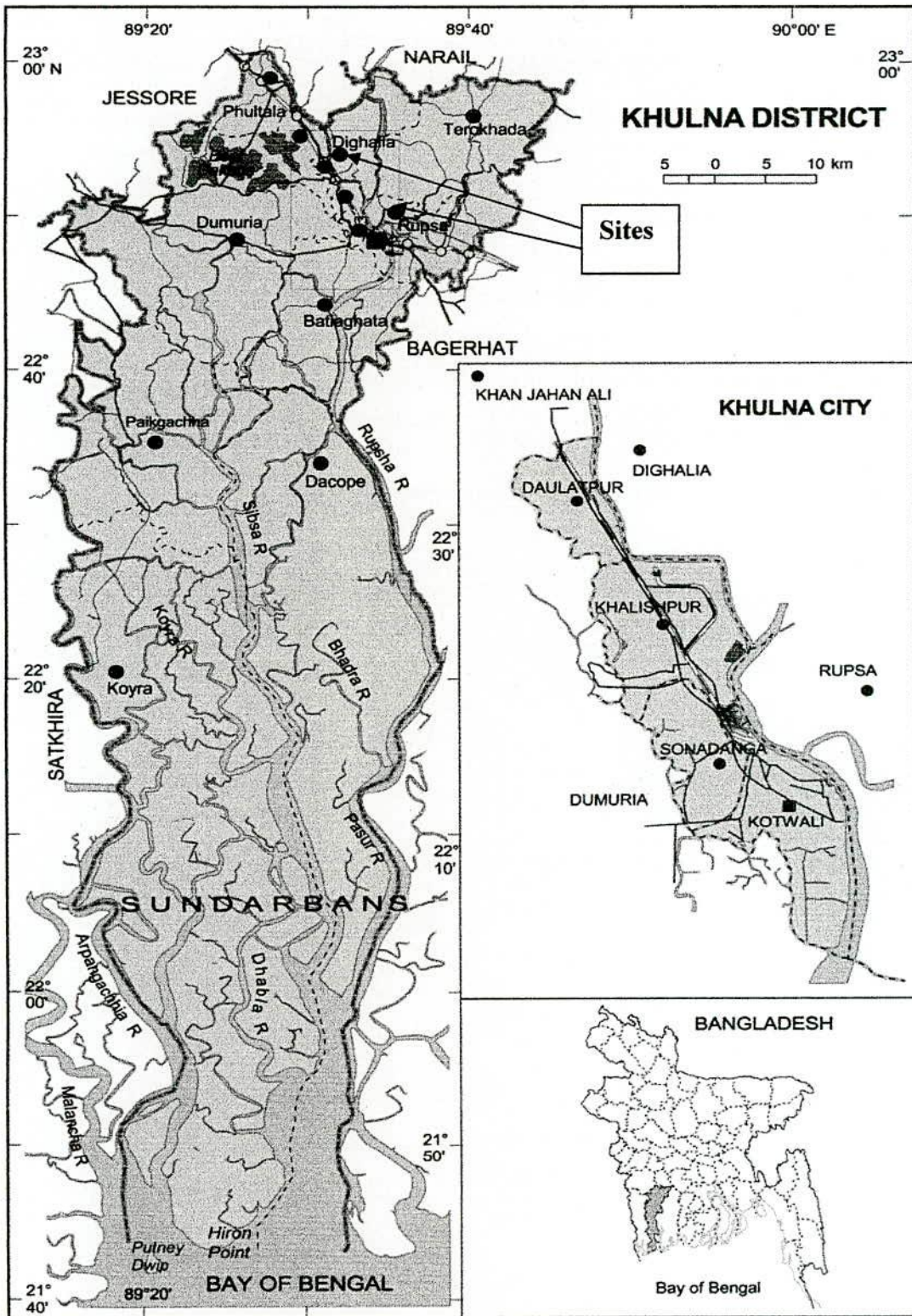
(http://1.bp.blogspot.com/_Xh4MstvdVIw/TL9OqR4LzgI/AAAAAAAAALc/aFMSNxwQhr

k/s1600/District+Map+of+Khulna.gif)

3.4 Filter Installation and Operation

Each filter, both from Dighalia and Rupsha, was operated with groundwater from the tubewell from each household. Freshly withdrawn groundwater from tubewll was collected in a bucket and increases the dissolved oxygen (DO) level to 5-6 mg/L by performing aeration. Because, DO level of groundwater was found to be <2 mg/L in most cases and was thought to be inadequate to complete biological oxidation procedure in the reactor. The aeration was simply performed by changing the groundwater from one bucket to another bucket and repeated for a minimum 5 times.

Groundwater DO level was increased from 2-3 mg/L to 5-6 mg/L in this way. All filters were filled with 14-18 L (Maximum capacity) of groundwater once a day. The water was come out through the bottom hole of the reactor within 2-3 min and it took about 2-6 hours to filters all water depending on the flow rate.

Filter Cleaning Process

In most cases, the filtrated water was used by the people of the households for the purpose of drinking. So, the filters were in the stage of continuous operation. The flow rate was decreased below desirable limit due to the accumulation of the sludge on the ceramic filter. Then the filters were needed to be cleaned.

- The iron net from the reactor was taken out as shown in the figure below.

- After that the accumulated iron sludge on the ceramic filter was removed with a soft cloth or brush as shown in the next figure.

- After cleaning, the iron net was put in the filter again.

- The filter was started using again as previous.

This process is shown in the next figure (Figure 3.17).
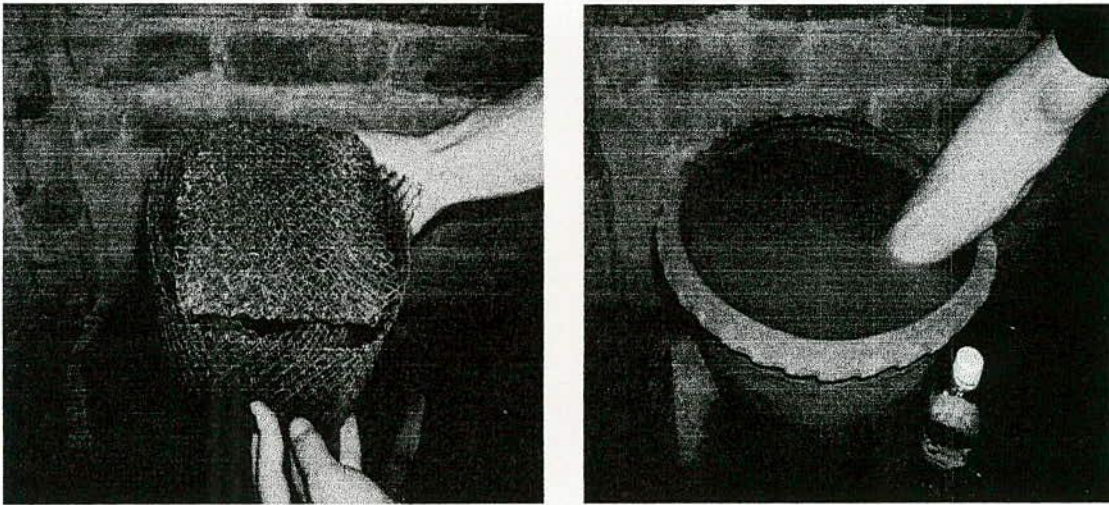
Figure 3.17: Filter cleaning process

Change of Iron Net and Filter

Iron net was needed to be changed after 1 year of continuous using.

In case of filters, even if after cleaning and disposing the sludge, no filtration is happened then filter has to be changed.

Sludge Disposal Guidance

Shafiquzzaman (2008) examined the release of arsenic from the biological sludge that had been accumulated in arsenic contaminated groundwater treatment column & conducted the TCLP & TCLP kinetic tests. According to result of the study, the sludge would not be classified as 'Hazardous Waste Material' under the Australian Hazardous Waste Act. 1989 or US Resource Conservation Act. 1976, respectively, when based on the leachibility of arsenic (Shafiquzzaman, 2008). So, it can be assumed that the sludge produced in my filter system is not hazardous. However, for safety measure, disposable sludge has to be kept in a clay pot with some cow dung and kept away from children.

3.5 Filter Monitoring

The corresponding tubewell of our Khulna (Zogipol, Dighalia) site contained very high value of arsenic and salinity. Even after using the filter system it did not come below the guideline level for drinking purpose. But the filter systems the household with the single unit filter systems 'K1net', 'K1scrap' and 'K1rod' were run continuously and the samples were collected in every week to the Environmental Engineering Laboratory, Department of Civil Engineering, KUET for the laboratory tests. Flow rates were taken every day.

On the other hand, the households with the filter systems were very kin to use the filtrated water. For safety, they were not allowed to drink the water from single unit systems. In case of double unit filter systems they were permitted to drink after testing the effluent water in the lab. However, the performance of single unit filter systems 'R1single' and 'R2single' were monitored for 1 month in August, 2009. Then in March, 2010 these systems were again monitored. The double unit systems were started in August, 2010 and monitored for a week daily, initially. Then these systems were monitored in every 2 weeks and samples were collected to the Environmental Engineering Laboratory, Department of Civil Engineering, Khulna University of Engineering and Technology (KUET) for the laboratory tests.

Some tests were performed in fields also. Some selected samples were also taken to Environmental Engineering Laboratory of Ritsumeikan University, Japan for further analysis and cross checking of arsenic and other metals in the groundwater and treated water. Samples of tubewell water were acidified with 1% HNO_3 to a pH <2 in order to prevent precipitation of solid phases.

3.6 Filter Unit with Scrap Iron and Iron Rod

In Khulna site, the performance of filter unit with other options than iron net were installed and run. The set up of these filter units were same as the filter unit with iron net except 600 gm of scrap iron or iron rod was used in the place of iron net as the source of zero-valent iron.
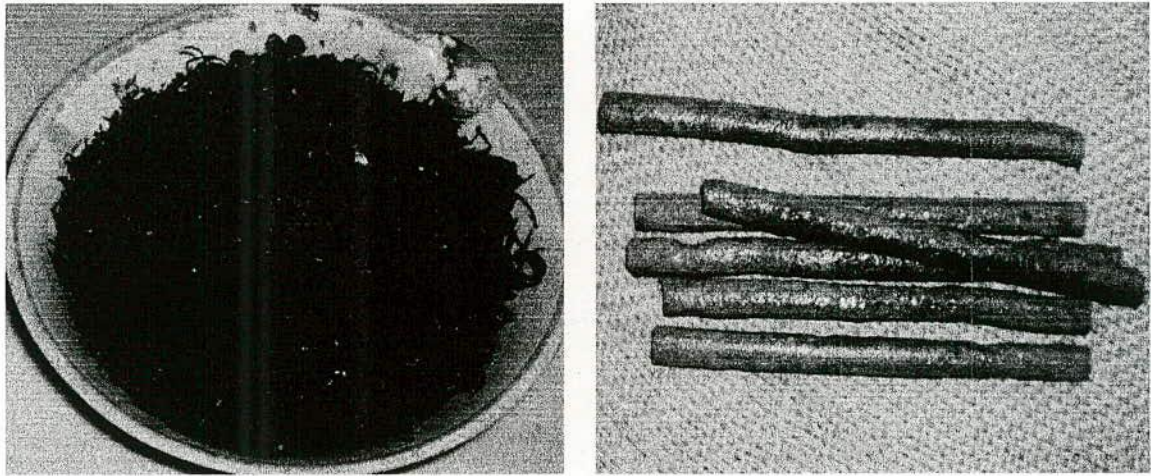
Figure 3.18: Scrap iron and Iron rod

3.7 Double Unit Filter System

When the raw influent water contained highly arsenic contamination then single unit filter system was unable to reduce the arsenic level to allowable limit. Then, in this study, double unit system was tried to induce. This double unit system may be arranged in two ways-

- W- system: In this double unit filter system two single unit systems were used in series where the effluent of first unit was poured in to the second unit reactor as influent and final effluent was found in the storage bucket of second unit.
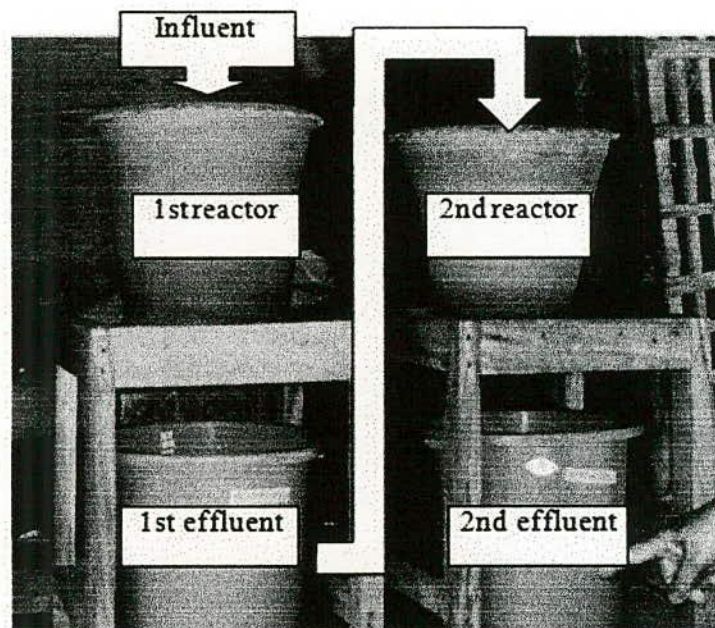
Figure 3.19: W-system double unit filter system

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- Connect system: In this double unit filter system raw influent was poured into the first reactor and the filtrated effluent was automatically poured into the second reactor and final effluent was found in the storage bucket.
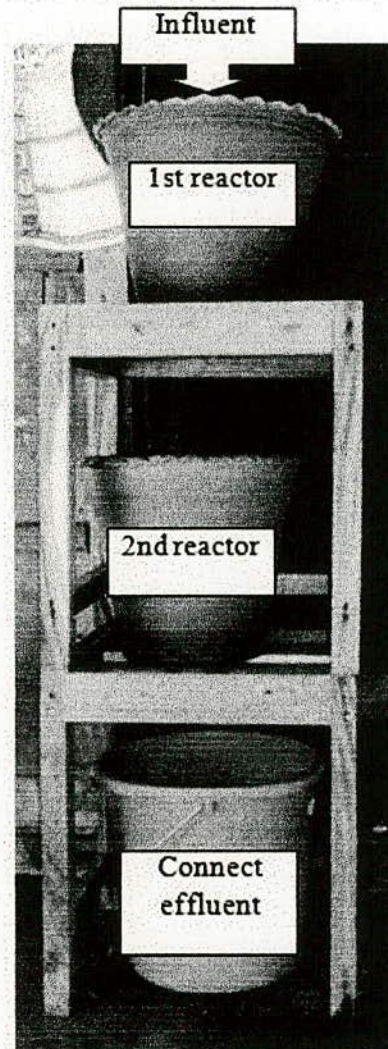
Figure 3.20: Connect system double unit filter system

3.8 Field and Laboratory Tests

Among tests some were conducted in field and some were completed in laboratory. The data were determined by various standard and dependable methods. Table 3.1 shows the detail about the tests.

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Table 3.1: Applied Methods for Water Quality Analysis

Parameter	Method/ Meter
pH	pH meter (HACH SensIon2, USA)
DO	DO meter (HACH HQ 40d, USA)
TDS	Filter Paper Method (Whatman 15.0 cm)
Turbidity	Turbidity meter (HACH 2100p Turbidity meter, USA)
Color	HACH Spectrometer (DR/2500)
Salinity (Chloride)	Titration
Nitrate, Nitrite, Hardness, Alkalinity	Aqua Check Method, ECO
Fe (Fe^{2+})	Pack Test Method (O-Phenanthroline Color Comparison Method)
P (PO_4), Si (SiO_2)	Pack Test Method (Molybodenum Blue Color Comparison Method)
Arsenic	DDTC Method

CHAPTER 4

Performance of Single Unit Filter Systems

4.1 Introduction

The main objective was to find out the reasonable and effective arsenic removal solution for the rural Bangladesh. Firstly, the performances of two single unit filter systems set and run continuously in Rupsha will be presented.

Next, the single unit filter system with iron net will be compared with the filter units with other options than iron net. Scrap iron and iron bar may be the other good options. So, in another study, three filter systems were set and run continuously. The performances of these three single unit filter systems will be presented in the next segment of this chapter (Section 4.3).

Then, the performance of double unit filter system will be presented to find out the final and suitable solution to solve the arsenic removal problem in rural Bangladesh in easy and cheap way. Hence, the detail performances of two double unit filter systems with iron net will be presented in next chapter.

4.2 Performance of Single Unit Filter System with Iron Net

In August 2009, two single unit filter systems with iron net were set in two different households in Rupsha. After installation, these filters ('R1single' and 'R2single') were monitored and samples were collected everyday for one month. Along with arsenic and iron, some other water quality parameters like pH, Dissolved Oxygen (DO), Electro conductivity (EC), Nitrate, Nitrite, Hardness, Alkalinity, Phosphorus, Silica, Temperature, Flow rate etc. were checked.

4.2.1 pH

The pH of a solution is a measure of hydrogen (H+) ion concentration, which is, in turn, a measure of acidity. Pure water dissociates slightly into equal concentrations of hydrogen and hydroxyl (OH⁻) ions. Low pH is associated with high acidity, high pH with caustic alkalinity. pH is important in the control of a number of water treatment processes. It is expressed on a scale ranging from 0 to 14. The recommended pH range for treated drinking water is 6.5 to 8.5.
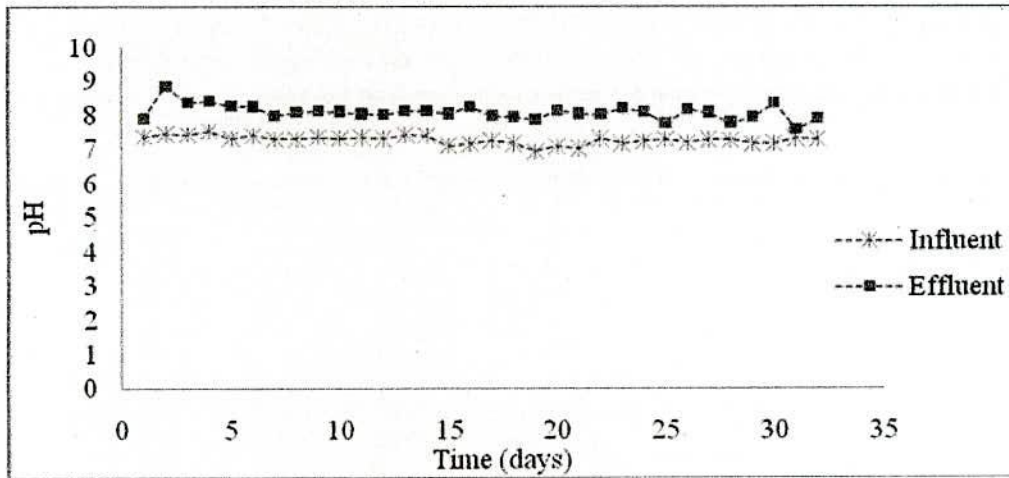

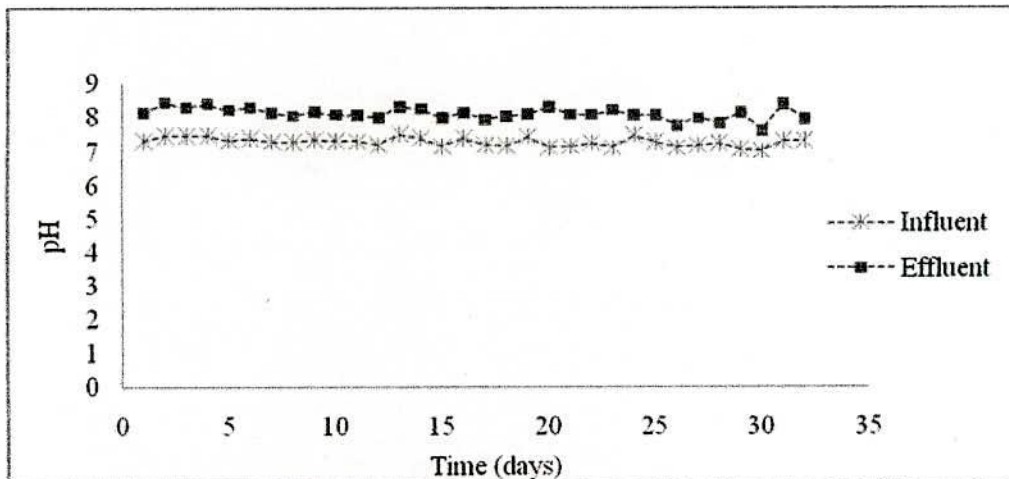Figure 4.1: pH of Influent and Effluent of 'R1single'

Figure 4.2: pH of Influent and Effluent of 'R2single'

The pH values of influent and effluent for the filter unit 'R1single' starting from day 1 to day 32 is shown Figure 4.1. The average pH value of influent was 7.26 with highest and lowest value 7.53 and 6.92 respectively. The average effluent pH value was 8.07 with highest and lowest value 8.84 and 7.56 respectively. Similarly, Figure 4.2 represents the pH values of influent and effluent of the filter unit 'R2single'. The average influent pH value was 7.28 with highest and lowest value 7.51 and 7.01 respectively. The average effluent pH value was 8.11 with highest and lowest value 8.44 and 7.61 respectively. The Standard Deviation (S.D.) of influent data and effluent data are 0.13 and 0.23 for 'R1single' and 0.13 and 0.19 for 'R2single'.

pH values increased after filtration. pH increase was attributed to water decomposition by the iron net and to the sorption reaction of arsenic, which released OH⁻ groups from sorbents.

4.2.2 Dissolved Oxygen (DO)

Dissolved oxygen analysis measures the amount of gaseous oxygen (O_2) dissolved in an aqueous solution. This DO in water affects oxidation-reduction reactions involving arsenic, iron, manganese, copper, and compounds containing Nitrogen and Sulphur. A high DO level in a community water supply is good because it enhances the taste of drinking water.
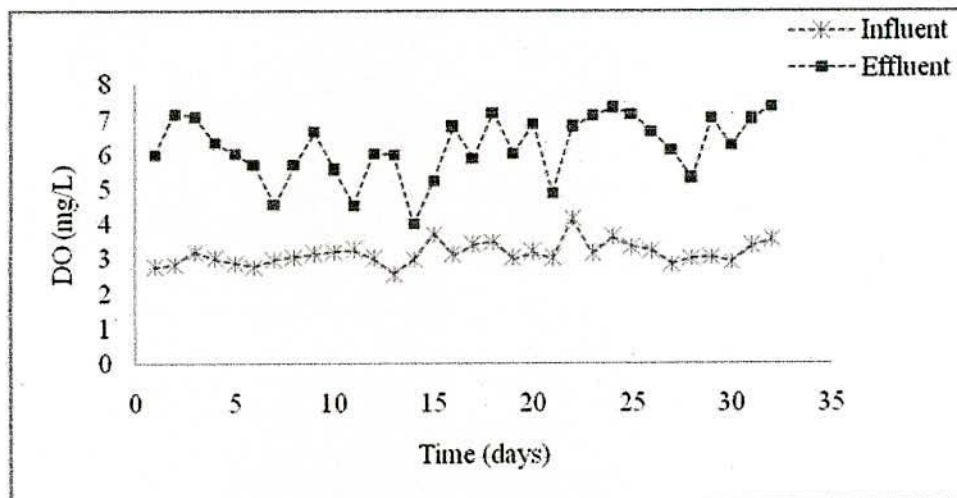

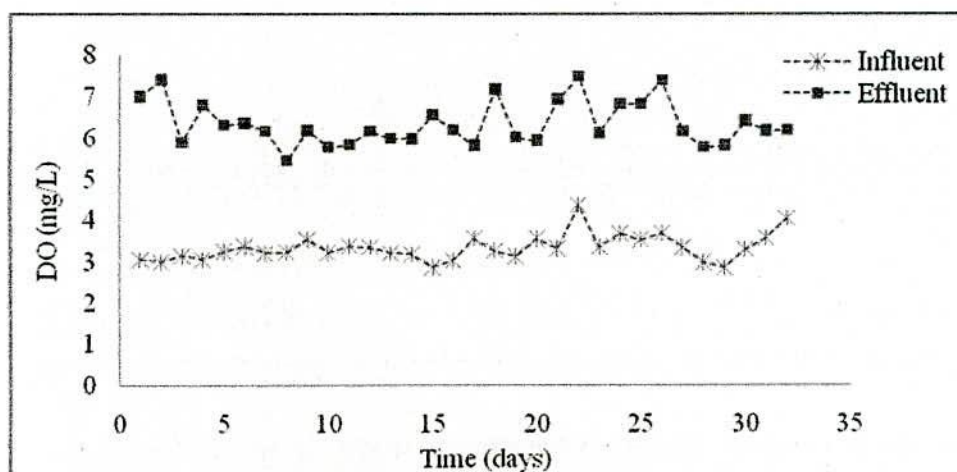Figure 4.3: DO of Influent and Effluent of 'R1single'

Figure 4.4: DO of Influent and Effluent of 'R2single'

In this study, arsenic removal was mainly attributed to the adsorption on iron hydroxides, and which was produced through the oxidation of zero-valent iron (iron net). The oxidation was accomplished by the dissolved oxygen in the solution. So, high level of DO value was required for the removal of arsenic by this filter system.

Figure 4.3 and 4.4 shows the graphical presentation of values of DO value in influent and effluent of 'R1single' and 'R2single'. For 'R1single', the average value of influent was 3.13 with highest and lowest value of 2.54 and 4.12. The average value of effluent was 6.20 with highest and lowest value 3.99 and 7.37, respectively. For 'R2single', the average value of influent was 3.31 with highest and lowest value of 2.83 and 4.35, respectfully. The average value of effluent was 6.35 with highest and lowest value 5.46 and 7.48, respectively. In the figures, DO level increased, because before pouring in the reactor, manual aeration was performed for influent water.

4.2.3 Electrconductivity (EC)

Solids can be found in nature in a dissolved form. Salts that dissolve in water break into positively and negatively charged ions. Conductivity is the ability of water to conduct an electrical current, and the dissolved ions are the conductors. The major positively charged ions are sodium (Na^+) calcium (Ca^{+2}), potassium (K^+) and magnesium (Mg^{+2}). The major negatively

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charged ions are chloride (Cl^-), sulfate (SO_4^{-2}), carbonate (CO_3^{-2}), and bicarbonate (HCO_3^-). Nitrates (NO_3^{-2}) and phosphates (PO_4^{-3}) are minor contributors to conductivity, although they are very important biologically.

Figure 4.5 and 4.6 show the EC values of influent and effluent for the filter unit 'R1single' and 'R2single', respectively. For 'R1single', the average EC value of influent was 0.702 with highest and lowest value 0.745 and 0.612, respectively. The average effluent EC value was 0.652 with highest and lowest value 0.740 and 0.549, respectively. Similarly, for 'R1single', the average EC value for influent samples was 0.696 with highest and lowest value 0.743 and 0.617, respectively. The average effluent value was 0.662 with highest and lowest value 0.729 and 0.585, respectively. The Standard Deviation (S.D.) of influent data and effluent data are 0.029 and 0.042 for 'R1single' and 0.032 and 0.036 for 'R2single', respectively.

In the graph it can be easily observed that the influent and effluent values were nearly same. Because, the proposed simple filter system was not appropriate to filtrate the contributor ions for Electroconductivity.
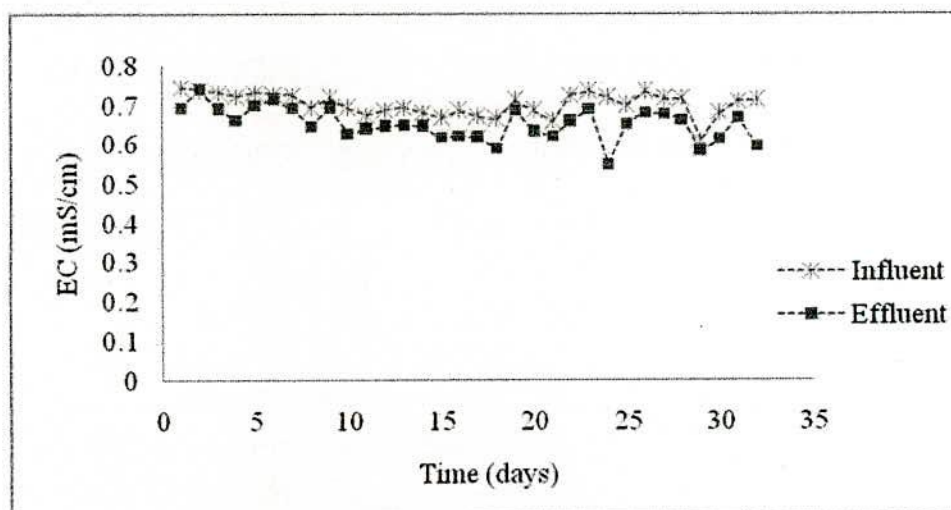

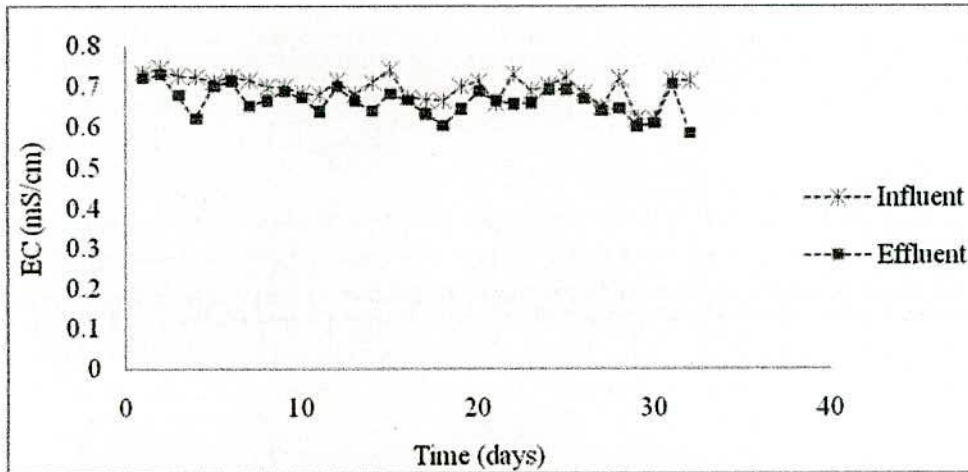Figure 4.5: EC of Influent and Effluent of 'R1single'

Figure 4.6: EC of Influent and Effluent of 'R2single'

4.2.4 Nitrate and Nitrite

Nitrate is toxic when present in excessive amounts in drinking water and may cause 'Methamoglobinaemia' in infants. The Nitrates are reduced in the body of Nitrite which reacts with the oxygen receptor sites on the hemoglobin fraction of the blood and impairs the oxygen carrying capacity. There is a possibility that certain forms of cancer might be associated with very high concentration. For this reason, a value of less than 10mg/L is recommended for Nitrate concentration (Ahmed and Rahman, 2000).

From the Aqua Check, it was found that in the influent samples of 'R1single' and 'R2single' had a very small amount of Nitrate and Nitrite (tends to zero). So, there was no chance for the removal.

4.2.5 Hardness

Hard waters are generally considered to be those waters that require considerable amount of soap to produce to produce a foam or lather. The principle hardness causing cations are the divalent Calcium and Magnesium, Strontium, Ferrous ion and Manganous ion. A hardness level of about 100 mg/L of $CaCO_3$/L provides an acceptable balance between corrosion and the problem of encrustation. The Bangladesh Drinking Water Quality Standards recommend hardness between 200 to 500 mg/L based on taste and household use considerations (Ahmed and Rahman, 2000).

In this study, it was found that the tubewell waters of the households in Rupsha contained high amount of hardness. From the Aqua Check test the influent water hardness was determined as around 400 to 500 mg/L in most cases. It was also found that the filter system was not able to reduce the hardness significantly.

4.2.6 Alkalinity

Alkalinity is defined as the quantity of ions in water that will react to neutralize hydrogen ions. Alkalinity is thus a measure of the ability of water to neutralize acids. In large quantities, alkalinity imparts a bitter taste to water. The principle objection to alkaline water, however, is the reactions that can occur between alkalinity and certain cations in the water. The resultant precipitate can foul pipes and other water system appurtenances.

In this study, it was found that the tubewell waters in the field contained high amount of alkalinity. The values were around 180 mg/L. So it can be assumed that this water contained high amount of Calcium carbonate. There was no big change in the amount of alkalinity in influent and effluent samples.

The inability of removing nitrate, nitrite and alkalinity was conducted as the inability to removing Nitrogen, Calcium or Magnesium contents.

4.2.7 Iron (Fe)

Iron is found on earth mainly as insoluble ferric oxide. When it comes in contact with water, it dissolves to form ferrous bicarbonate under favorable conditions. This ferrous bicarbonate is oxidized into ferric hydroxide, which is precipitate. Under anaerobic conditions, ferric ion is reduced to soluble ferrous ion. Iron can impart bed taste to the water, causes discoloration in clothes and incrustations in water mains. Bangladesh standard for iron concentration in drinking water is 0.3 to 1 mg/L.

Iron concentration in raw influent has a significant role in the removal of arsenic in Biological iron oxidation process. Because, the oxidation of iron and arsenic followed by their subsequent

adsorption and precipitation on and with biologically produced iron hydroxides is the main basic process in the arsenic removal by this filter system (Shafiquzzaman, 20008).

The influent water contained very high amount of iron. By using Pack Test, the influent and effluent Fe (2+) concentrations were determined. For 'R1single', the average Fe (2+) concentration was 8.52 mg/L with highest and lowest value 10 mg/L and 6 mg/L respectively. Similarly, for 'R2single', the average Fe (2+) concentration was 9.16 mg/L with highest and lowest value 10 mg/L and 7 mg/L respectively. The single unit filter system was able to reduce this high level of Fe (2+) almost fully. This is shown in Figure 4.7 and Figure 4.8.
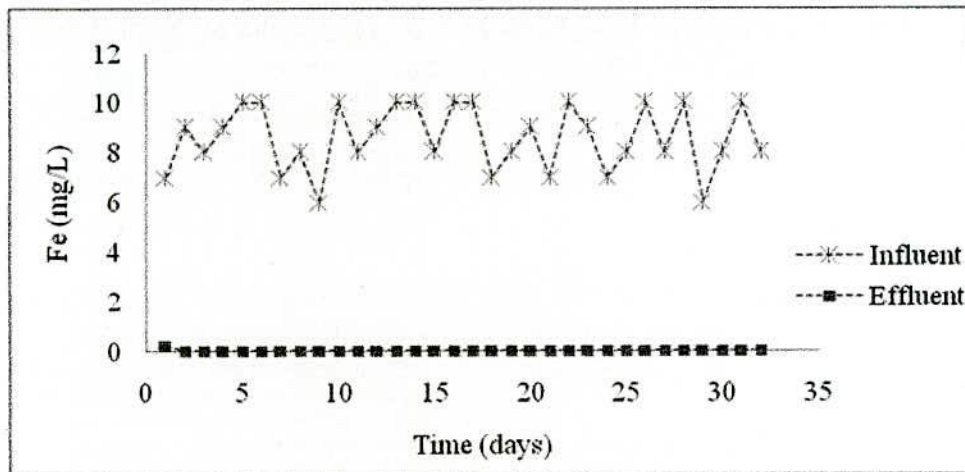

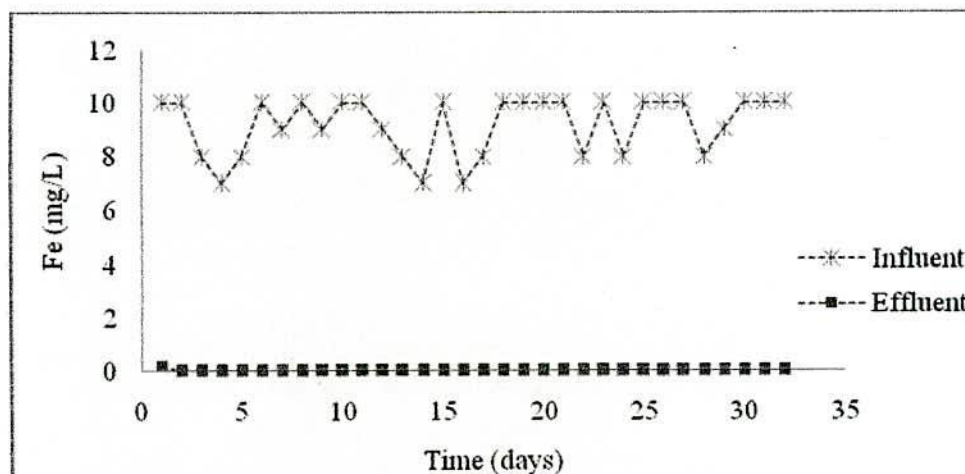Figure 4.7: Fe (2+) concentration of Influent and Effluent of 'R1single'

Figure 4.8: Fe (2+) concentration of Influent and Effluent of 'R2single'

In this study, aeration of influent water was conducted before pouring in to the reactor. As a result, soluble ferrous ions present in water were oxidized to insoluble ferric ions and then precipitated. High iron removal efficiency in this filtration system can be explained this way.

4.2.8 Phosphorus (P)

Phosphorus (P) appears exclusively as Phosphate (PO_4^{3-}) in aquatic environments. While Phosphates are not toxic and do not represent a direct health threat to human or other organisms, they do represent a serious indirect threat to water quality. Bangladesh standard for drinking water for Phosphate is 6 mg/L. In case of arsenic removal in Biological iron oxidation process, the P concentrations in influent and effluent were needed to be determined. This was accomplished by Pack Test.

Figure 4.9 shows the P values of influent and effluent for the filter unit 'R1single'. The average P value of influent was 1.72 with highest and lowest value 2.5 and 0.8, respectively. The average effluent P value was 0.45 with highest and lowest value 0.8 and 0.1, respectively. Similarly, Figure 4.10 represents the P values of influent and effluent of the filter unit 'R2single'. The average influent P value was 1.3 with highest and lowest value 2 and 0.6, respectively. The average effluent value was 0.36 with highest and lowest value 0.6 and 0.1, respectively.
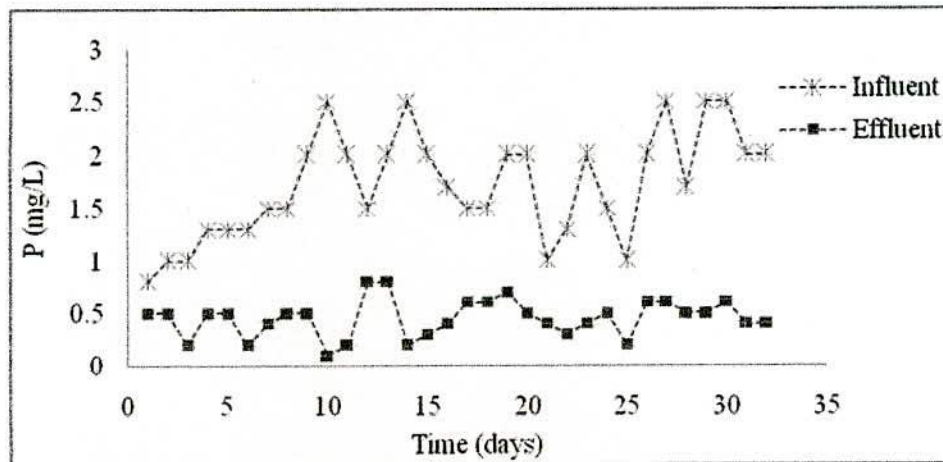

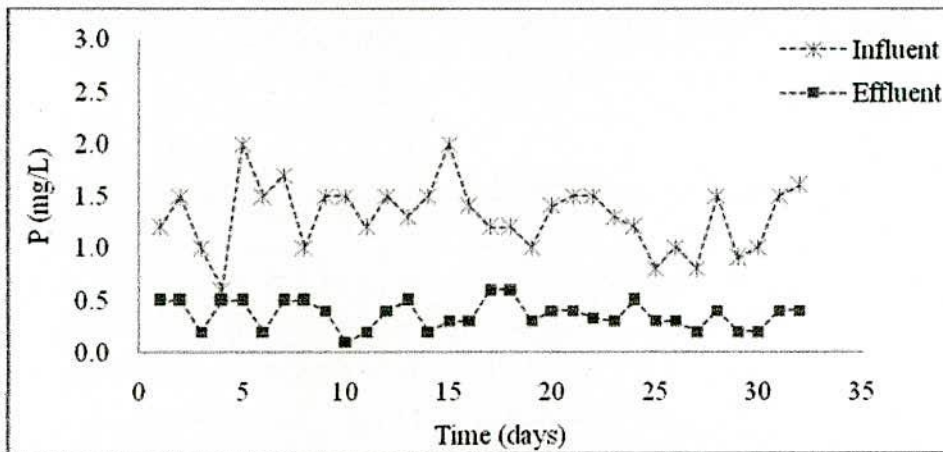Figure 4.9: P concentration of Influent and Effluent of 'R1single'

Figure 4.10: P concentration of Influent and Effluent of 'R2single'

Arsenate and phosphate have similar chemical and biological properties and they are the competitors each other in iron hydroxides adsorption. As a result of this adsorption the P removal shown in Figure 4.9 and 4.10 occurred.

4.2.9 Silica (Si)

Silica (silicon dioxide) is compound of silicon and oxygen (SiO_2). This is not surprising since silicon is the second most abundant chemical element in the earth. It is a hard, glassy mineral substance which occurs in a variety of forms such as sand, quartz, sandstone, and granite. It also is found in the skeletal parts of various animals and plants. The silica content of water ranges from a few parts per million in surface supplies to well over 100 mg/L in certain well waters.

By the Pack Test method, the Silica concentration of raw influent and treated effluent samples were tested. It was found that the filter was not significantly able to reduce the silica concentration. Figure 4.10 shows the Silica values of influent and effluent for the filter unit 'R1single'. The average Silica value of influent was 44.53 mg/L with highest and lowest value 60 mg/L and 25 mg/L, respectively. The average effluent Silica value was 34.84 mg/L with highest and lowest value 50 mg/L and 25 mg/L, respectively.

Similarly, Figure 4.11 represents the Silica values of influent and effluent of the filter unit 'R2single'. The average influent Silica value was 40.63 mg/L with highest and lowest value 55

mg/L and 30 mg/L, respectively. The average effluent value was 34.22 mg/L with highest and lowest value 40 mg/L and 30 mg/L, respectively.
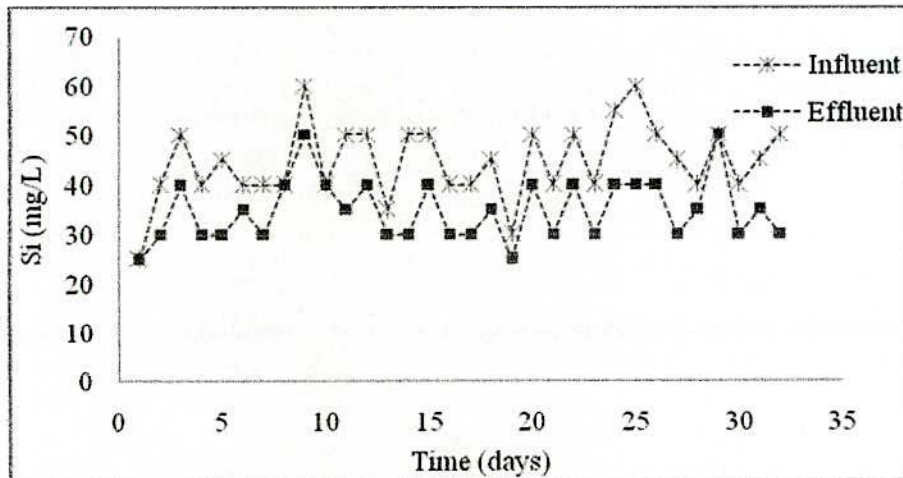
Figure 4.11: Silica concentration of Influent and Effluent of 'R1single'
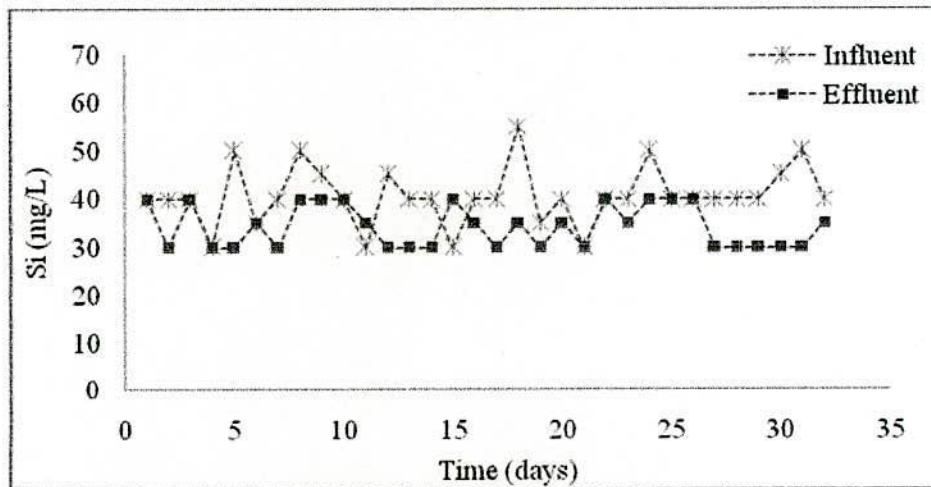
Figure 4.12: Silica concentration of Influent and Effluent of 'R2single'

4.2.10 Arsenic (As)

Arsenic removal was the main objective of the filter unit. Tubewell water of the households of this study was highly arsenic contaminated. For 'R1single' filter, average influent arsenic value was 361 µg/L with highest and lowest value as 448 µg/L and 256 µg/L, respectively. So, the tubewell water may be very much harmful and dangerous if used for drinking purpose. The

average effluent arsenic concentration was found as 128 µg/L with highest and lowest 295 µg/L and 55 µg/L, respectively.
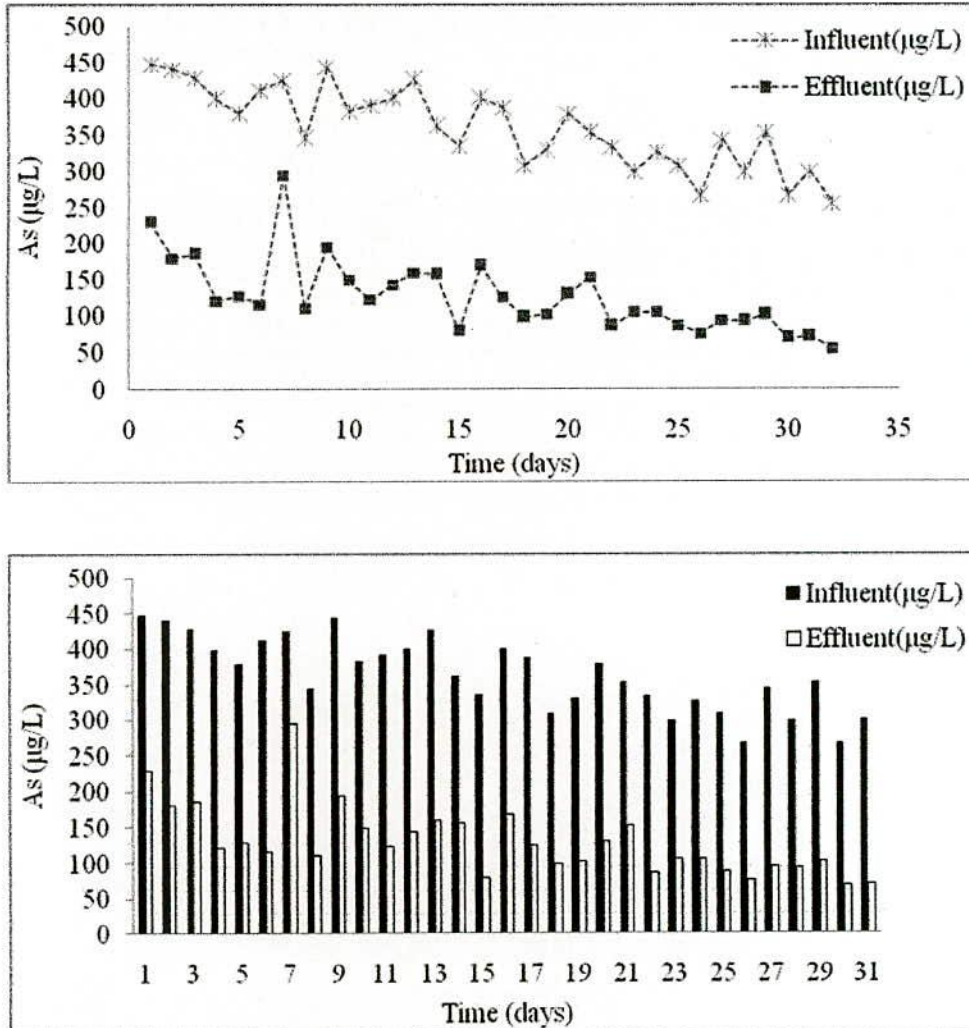
Figure 4.13: Arsenic concentration of influent and effluent of 'R1single'

The average removal efficiency was found as 65.56% with highest and lowest as 79% and 31%, respectively. The removal efficiency with time is graphically presented in Figure 4.14. It may be observed from the graph that the removal efficiency for the whole period was quite same except for the seventh day as it decreased suddenly from 72% in sixth day to 31%. It may be caused due to inadequate adsorption or any other unexpected act during the operation.
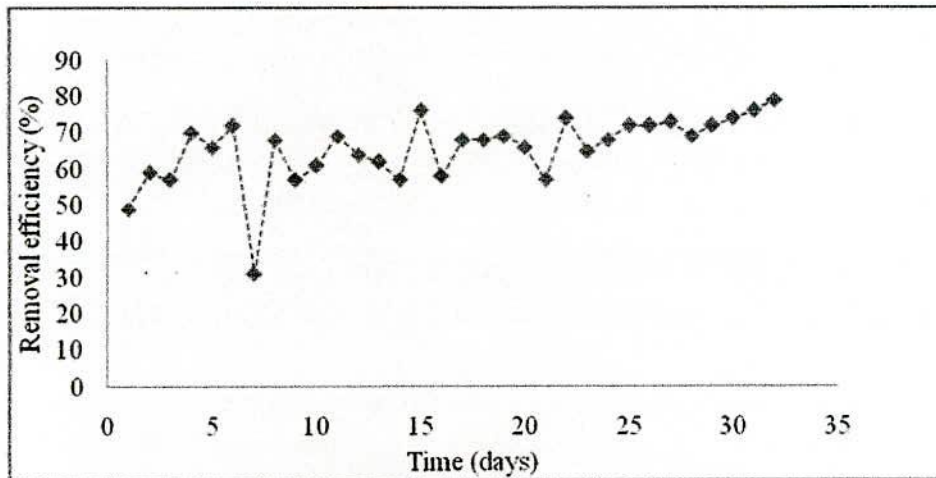
Figure 4.14: Arsenic removal efficiency (%) of 'R1single'

The tubewell water of household having 'R2single' filter unit was also highly arsenic contaminated. The average influent arsenic value was 396 µg/L with highest and lowest value as 476 µg/L and 312 µg/L. After the filtration the concentration of arsenic was significantly reduced. The average effluent arsenic concentration was found as 130.47 µg/L with highest and lowest 233 µg/L and 55 µg/L, respectively.

The average removal efficiency was found as 67.34% with highest and lowest as 82% and 51%, respectively. The Standard Deviation for 'R2single' filter data of influent, effluent and removal efficiency was 41.85, 40.24 and 8.31, respectively.

The arsenic concentration patterns shown in the graphs were quite same. This removal of arsenic occurred due to the oxidation of iron and arsenic followed by their subsequent adsorption and precipitation on and with biologically produced iron hydroxides.
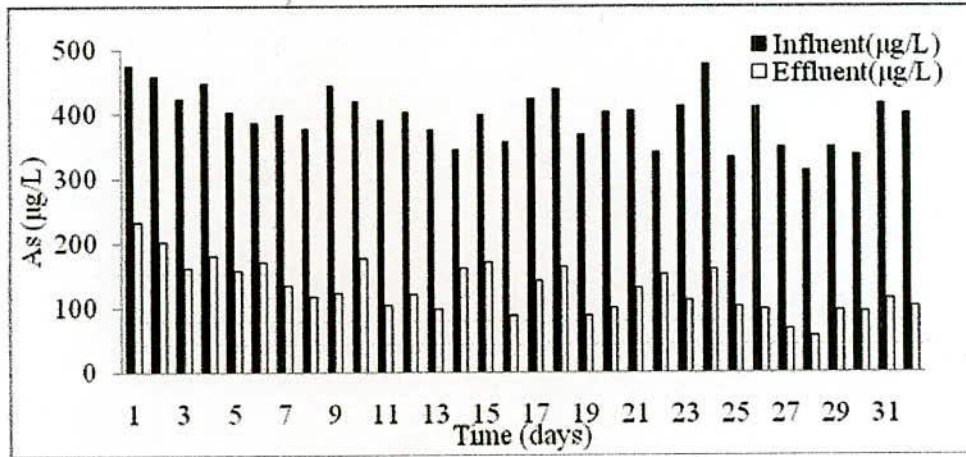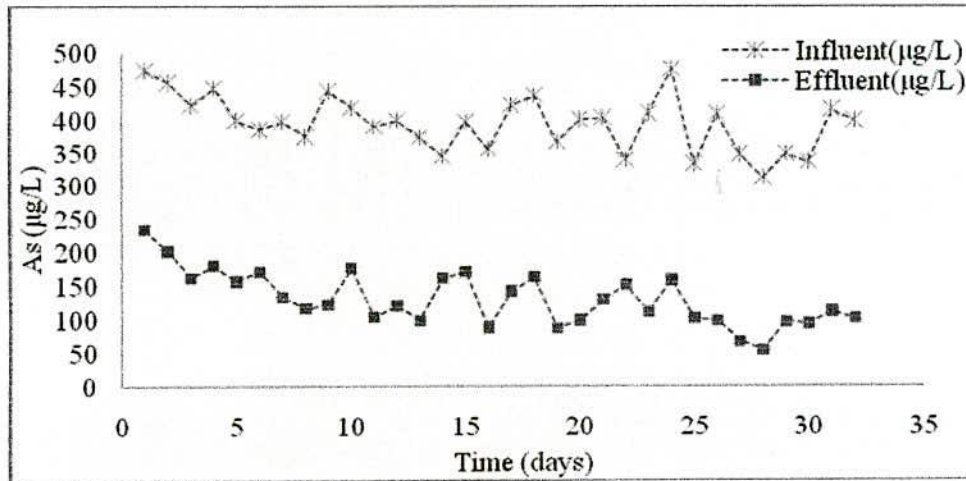
Figure 4.15: Arsenic concentration of influent and effluent of 'R2single'
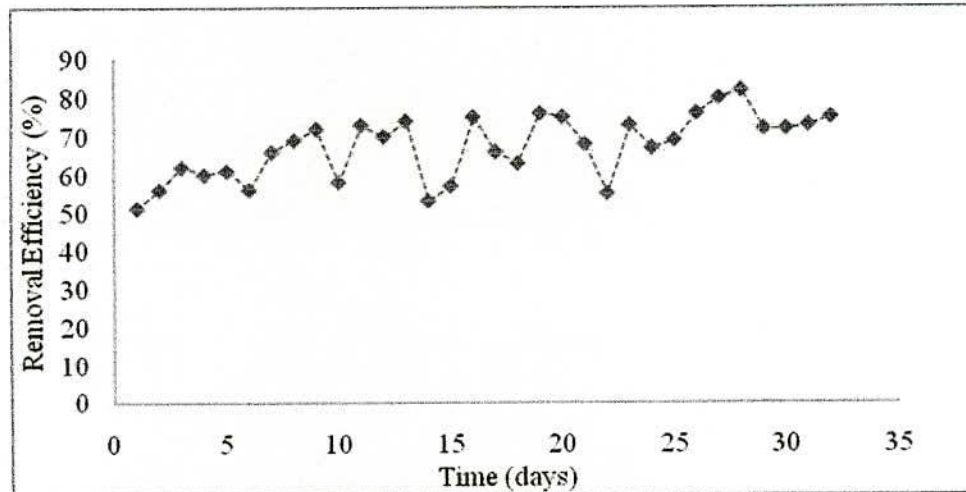
Figure 4.16: Arsenic removal efficiency (%) of 'R2single'

4.2.11 Flow Rate

Flow rate is one of the main factors for the sustainability of a water treatment system or water purification system. The user will not be inspired to use the system if it is unable to produce treated water according to their requirement. In the rural Bangladesh, the water requirement for drinking purpose is 2 to 3 lpcd (Ahmed and Rahman, 2000). That means for a 5-member rural family, around 10 mL/min flow rate is enough for drinking purpose. Here, the flow rate with time (32 days) of filters 'R1single' and 'R2single' is shown graphically in Figure 4.17 and Figure 4.18.
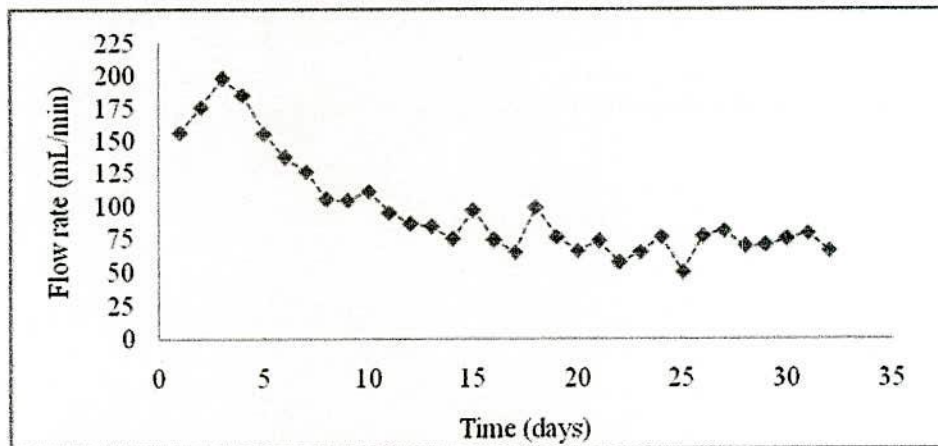
Figure 4.17: Flow rates with time of 'R1single'
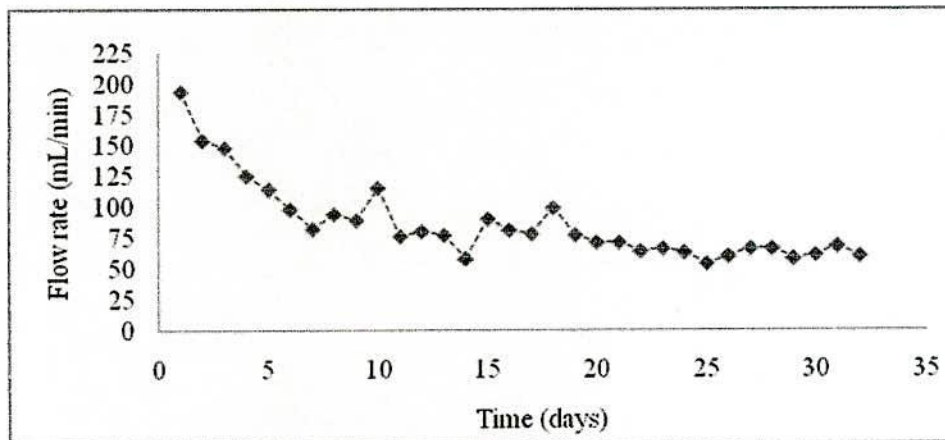
Figure 4.18: Flow rates with time of 'R2single'

The patterns of the curves showing flow rates with time were descending. Because, with the continuous running of the filters, little clogging was occurred and flow of treated water decreased everyday.

4.3 Comparison among Single Unit Filter Systems with Iron Net, Scrap Iron and Iron Rod

It was found that single unit filter system with iron net was not able to reduce the arsenic level below guideline value (Bangladesh standard 50 µg/L, WHO standard 10 µg/L). So, filter units with other options as scrap iron and iron net were tried. In Khulna site, 3 filter units were installed as 'K1net', 'K1scrap' and 'K1rod'. Along with arsenic and iron, water quality parameters like pH, Dissolved Oxygen (DO), Electro conductivity (EC), Total Dissolved Solids (TDS), Color, Turbidity, Salinity, Nitrate, Nitrite, Hardness, Alkalinity, Phosphorus, Silica, Flow rate etc. were evaluated in the whole testing period.

4.3.1 pH

pH of influent and effluent samples with iron net, scrap iron and iron rod are shown in Figure 4.19.

Figure 4.19: pH of influent and various effluent options

The graph shows that pH increased in small amount due to filtration. Average, highest and lowest pH and standard deviation for influent and effluent options are shown in Table 4.1. In Figure 4.20, the average values of various samples are presented.

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pH increase was occurred because of the water decomposition by various iron sources present in the system and also by the sorption reaction of arsenic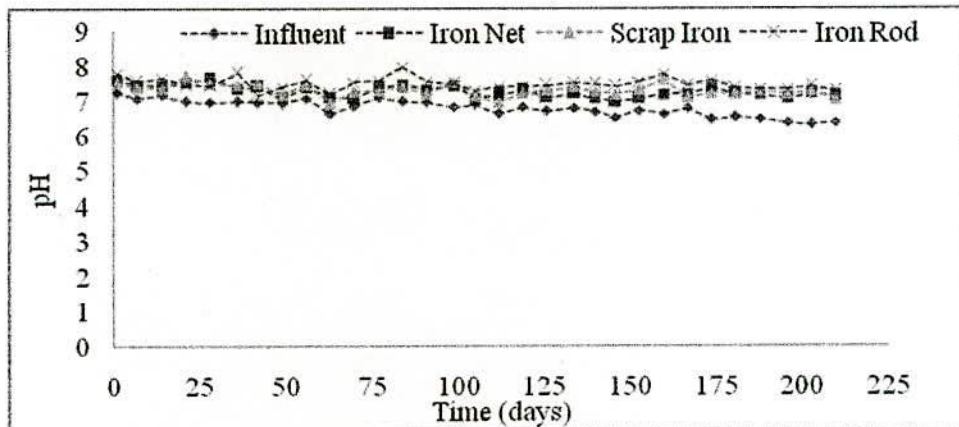, which released OH⁻ groups from sorbents. As a result, slight high pH was found in effluent samples. The pH in different effluent samples were nearly same. May be the production rate of OH⁻ by different options were same.

Table 4.1: Variation of pH of Influent and Effluent

	Average pH	Highest pH	Lowest pH	Standard Deviation
Influent	6.82	7.26	6.35	0.25
Effluent (Net)	7.29	7.69	7.00	0.18
Effluent (Scrap)	7.33	7.72	6.96	0.18
Effluent (Rod)	7.51	7.98	7.19	0.17
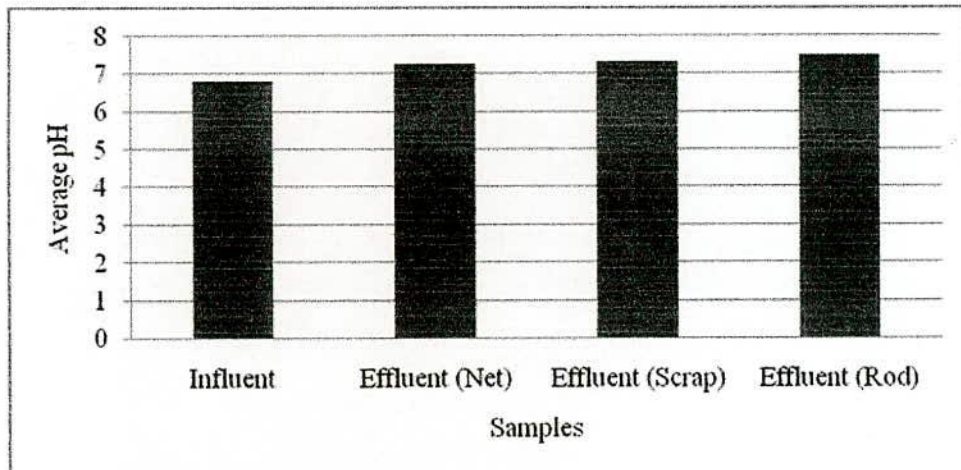
Figure 4.20: Average value of pH of Influent and Effluent options

4.3.2 Dissolved Oxygen (DO)

The Dissolved Oxygen (DO) values of influent and effluents with iron net, scrap iron and iron rod are shown graphically in Figure 4.21.

It was found that the DO level increased when influent water was filtered. Average, highest and lowest DO and standard deviation (S.D.) for influent and effluent options are shown in Table 4.2. In Figure 4.21, the average values of various samples are presented. Figure 4.21 and 4.22 depict that DO values of the effluent water from filters with iron net, scrap iron and iron rod have

nearly the same values. It also clarifies that there is no big deal with the iron source in the system. The detail of the results of DO is shown in the Appendix section (B.2).

Table 4.2: Variation of DO of Influent and Effluent

	Average DO (mg/L)	Highest DO(mg/L)	Lowest DO(mg/L)	Standard Deviation
Influent	2.87	3.56	2.31	0.33
Effluent (Net)	4.64	6.01	3.42	0.82
Effluent (Scrap)	4.65	5.99	3.33	0.81
Effluent (Rod)	4.44	5.73	3.41	0.74

Figure 4.21: DO of influent and various effluent options
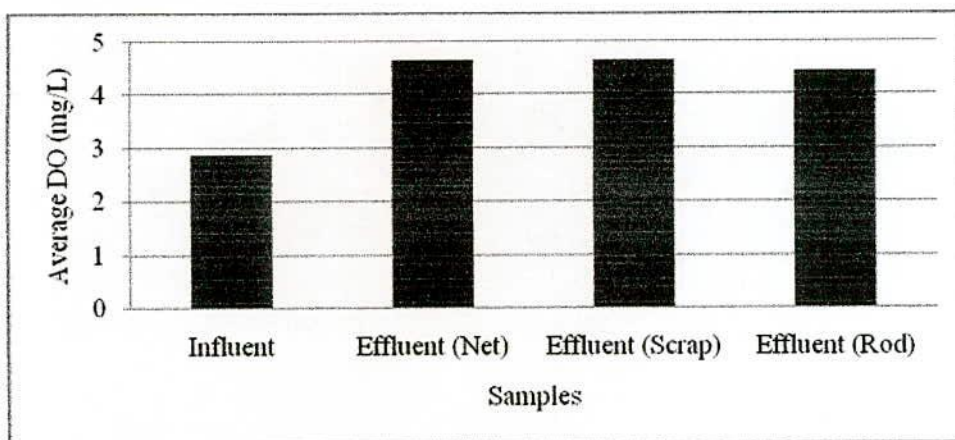
Figure 4.22: Average value of DO of Influent and Effluent options

4.3.3 Electroconductivity (EC)

In case of Electroconductivity (EC), there is no big effect on the influent and effluent samples. Table 4.3 represents the EC values of the influent and different effluents.

Table 4.3: Variation of EC of Influent and Effluent

	Average EC (mS/cm)	Highest EC (mS/cm)	Lowest EC (mS/cm)	Standard Deviation
Influent	0.707	0.812	0.593	0.060
Effluent (Net)	0.668	0.782	0.534	0.063
Effluent (Scrap)	0.665	0.796	0.517	0.065
Effluent (Rod)	0.661	0.792	0.518	0.064

There is almost no change in the average values of EC. Also the following figures exhibit the inability of the filter systems to reduce the EC.

The filter systems with none of the iron options showed ability to filtrate the contributing ions for electroconductivity. That's why there is no change visible in the data of influent and effluent options in Figure 4.23 and 4.24.
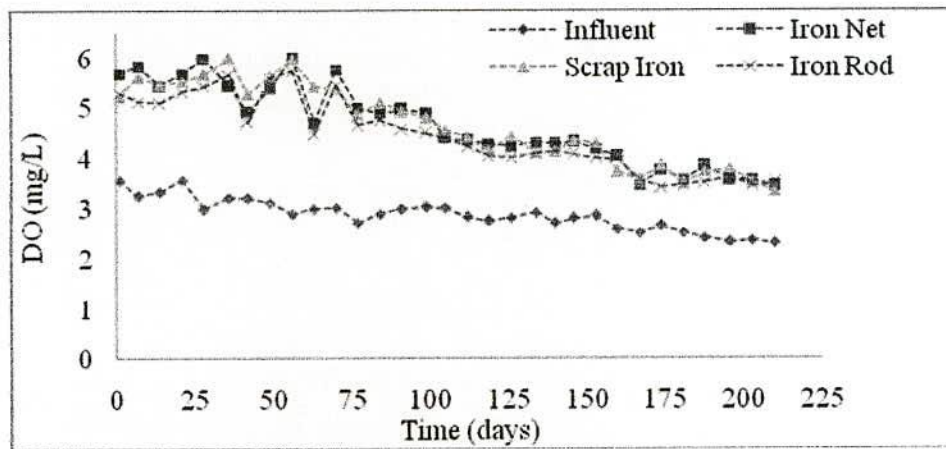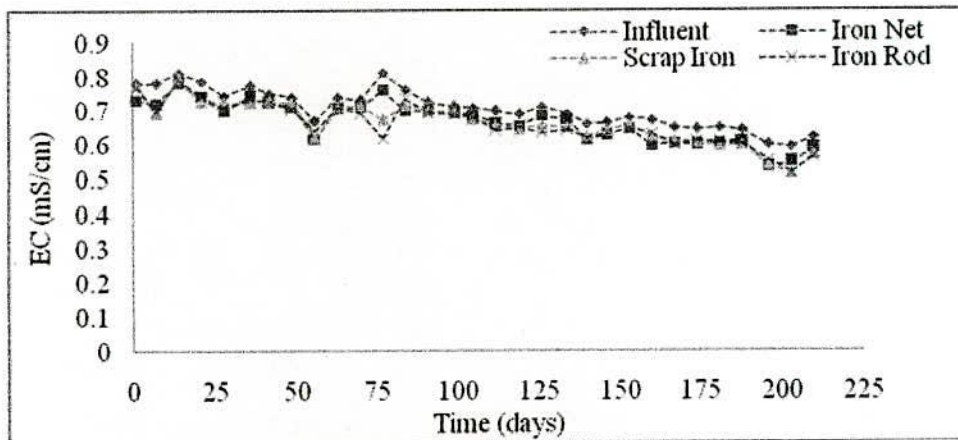

Figure 4.23: EC of influent and various effluent options
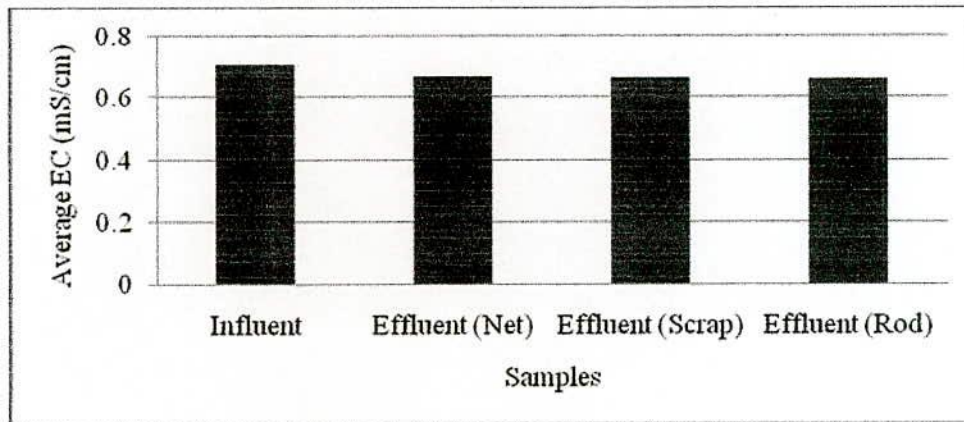
Figure 4.24: Average value of EC of Influent and Effluent options

4.3.4 Total Dissolved Solids (TDS)

Total Dissolved Solids (TDS) comprise inorganic salts and small amount of organic matter. The guideline value for drinking water is 1000 mg/L. Though there is no evidence of deleterious physiological reactions occurring in persons consuming drinking water supplies that have TDS level in excess of 1000 mg/L. Dissolved minerals, gases, and organic constituents may produce aesthetically displeasing color, tastes and odors. TDS less than 300 mg/L is excellent, 300 to 600 mg/L is good, 600 to 900 is fair, 900 to 1200 mg/L is poor and greater than 1200 mg/L is unacceptable.
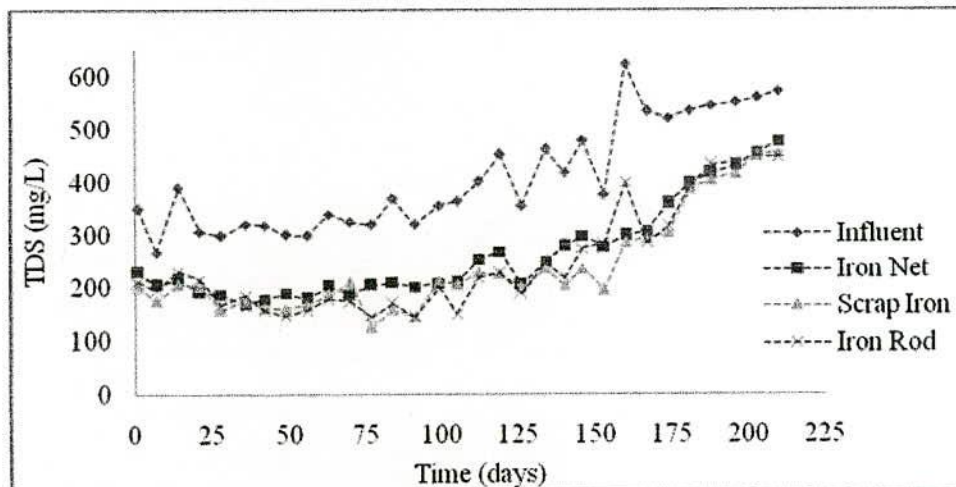
Figure 4.25: TDS of influent and various effluent options

Total Dissolved Solids (TDS) values of influent and effluents with iron net, scrap iron and iron rod are shown graphically in Figure 4.25. It was found that the TDS level decreased when influent water was filtered. In Figure 4.26, the average values of various samples are presented. It is seen from this figure that for TDS, the effluent water from filters with iron net, scrap iron and iron rod have nearly the same values.

Table 4.4: Variation of TDS of Influent and Effluent

|	Average TDS (mg/L)	Highest TDS (mg/L)	Lowest TDS (mg/L)	Standard Deviation
Influent	407.23	621	268	101.42
Effluent (Net)	261.93	476	167	90.27
Effluent (Scrap)	237.16	456	125	92.81
Effluent (Rod)	246.10	450	144	100.49
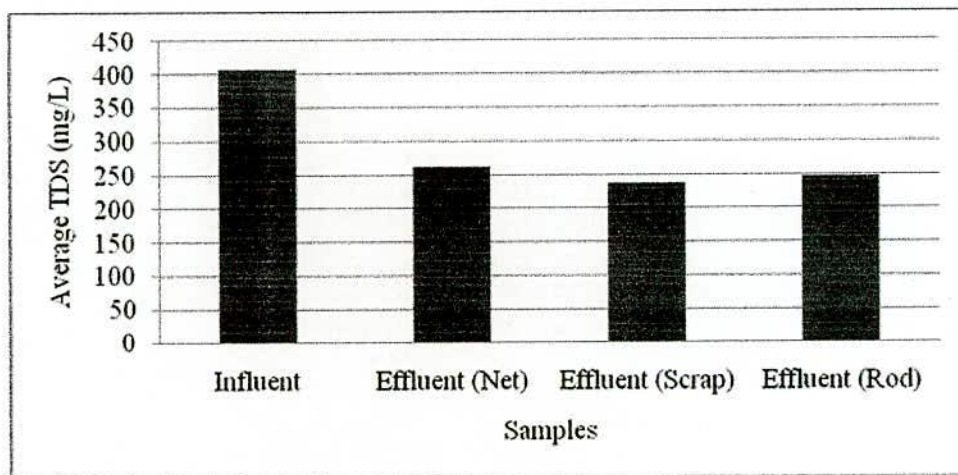
Figure 4.26: Average value of TDS of Influent and Effluent options

As dissolved solids can not be removed easily by filtration processes, TDS removal was not satisfactory in this proposed technology.

4.3.5 Color

Color in water is primarily due to the presence of colored organic substances (primarily humic substances), metals such as Fe, Mn or highly colored industrial wastes. The supply of visibly colored water to consumers may not be acceptable for aesthetic reason. Most consumers can

Chapter 4: Performance of Single Unit Filter Systems

detect a color of 15 unit (WHO guideline value and Bangladesh standard for drinking water) in a glass of water (Ahmed and Rahman, 2000).

Table 4.5: Variation of Color of Influent and Effluent

	Average Color (Pt-Co)	Highest Color (Pt-Co)	Lowest Color (Pt-Co)	Standard Deviation
Influent	473.42	620	359	76.15
Effluent (Net)	14.26	49	5	9.29
Effluent (Scrap)	25.90	93	12	14.96
Effluent (Rod)	14.16	41	5	7.69

In this study, it was found that the influent raw water contains high level of color. The filter unit reduced the color level significantly. The color values of influent and effluents with iron net, scrap iron and iron rod are shown graphically in Table 4.5. Figure 4.27 and 4.28 show the color concentrations of influent and effluent samples with respect to time.
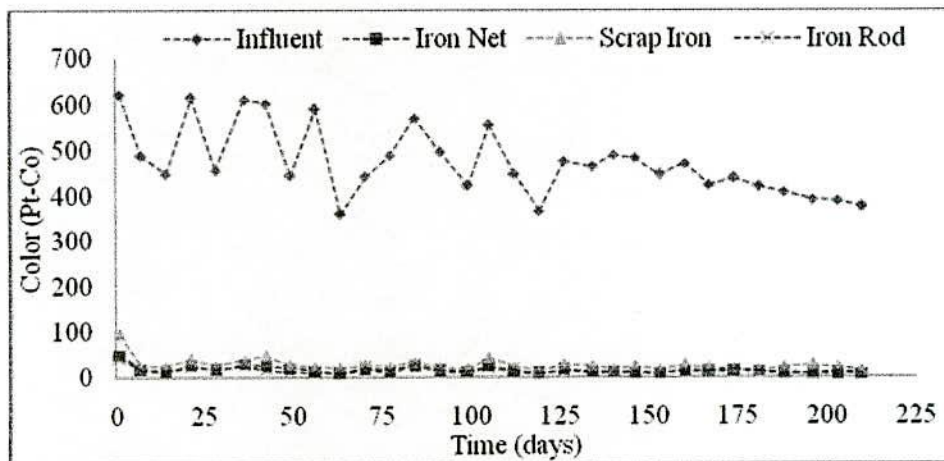
Figure 4.27: Color of influent and various effluent options
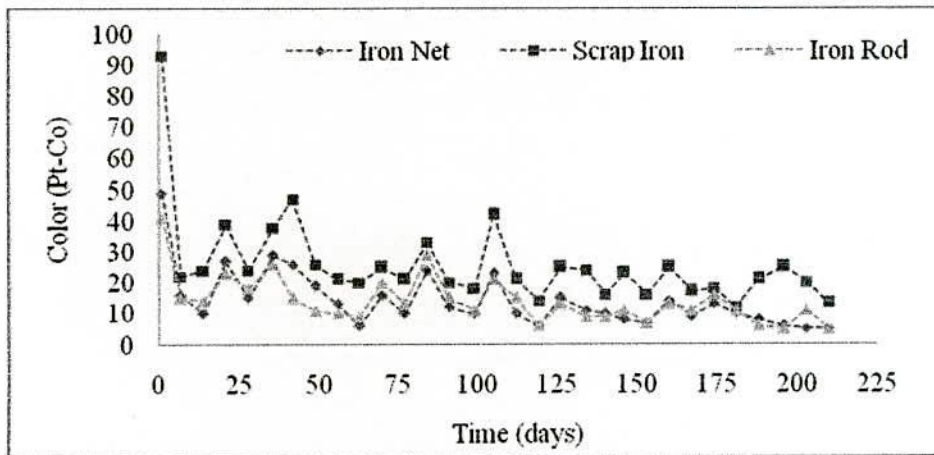
Figure 4.28: Color concentration of various effluent options

From the figures above, it is clear that effluent from the filters with iron net and iron rod had almost same values. The effluent from the filter unit with scrap iron had higher values. It may be occurred because of the possibility of higher amount emission of zero-valent iron from the more surface area of scrap iron.

Various suspended solids causing color in water can easily removed by filtration process. Therefore, color removal efficiency was found satisfactory. Figure 4.29 represents average values of various samples.
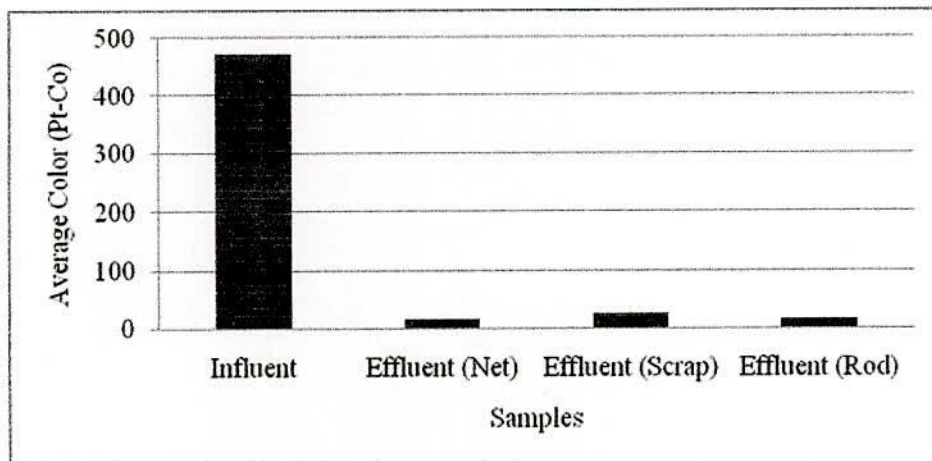
Figure 4.29: Average value of Color of Influent and Effluent options

4.3.6 Turbidity

A direct measure of suspended solids is not usually performed on samples from natural bodies of water or on potable (drinkable) water supplies. The nature of the solids in these waters and the secondary effects they produce are more important than the actual quantity. For such waters a test for turbidity is commonly used. Turbidity is a measure of the extent to which light is either absorbed or scattered by suspended material in water (Peavy et al., 1985). If a large amount of suspended solids are present in water, it will appear turbid in appearance. Turbidity in excess of 5 NTU is generally objectionable to consumers.

Influent raw water was highly turbid containing average of about 99 NTU of turbidity. Proposed filter unit reduced the turbidity level of raw water significantly. Average, highest and lowest Turbidity and standard deviation (S.D.) for influent and effluent options are shown in Table 4.6. Turbidity values of influent and effluents with iron net, scrap iron and iron rod are shown graphically in Figure 4.30. To have a clear view, the effluent values are presented in Figure 4.31.

Table 4.6: Variation of Turbidity of Influent and Effluent

|	Average Turbidity (NTU)	Highest Turbidity (NTU)	Lowest Turbidity (NTU)	Standard Deviation
Influent	99	211.2	61.1	31.76
Effluent (Net)	10.25	25.2	5.8	4.03
Effluent (Scrap)	10.65	20.5	5.8	3.57
Effluent (Rod)	10.79	27.6	4.5	4.51
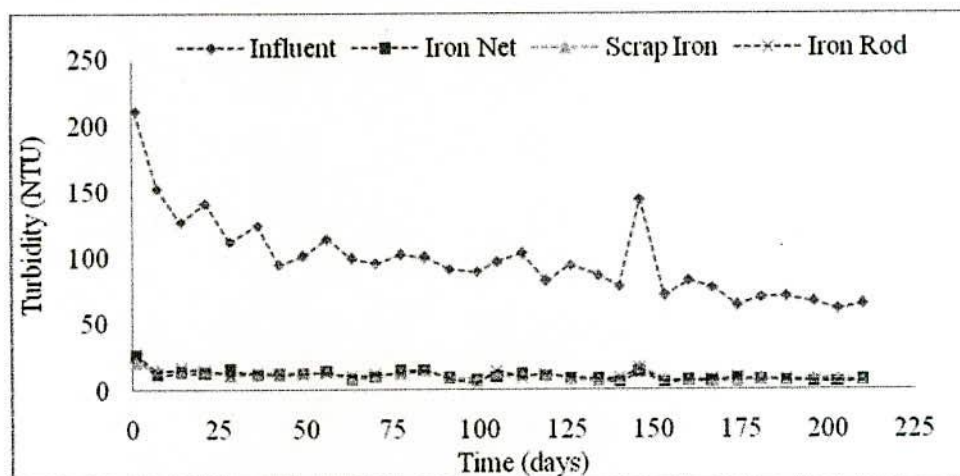
Figure 4.30: Turbidity of influent and various effluent options
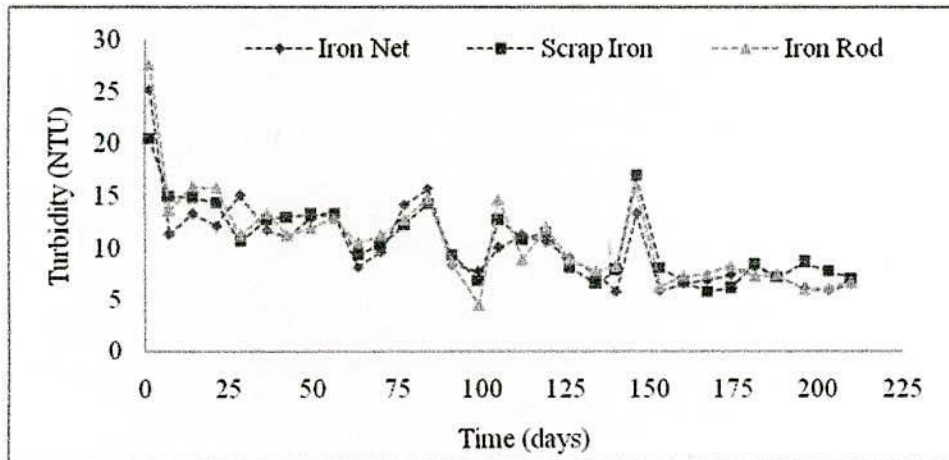
Figure 4.31: Turbidity concentration of various effluent options

Suspended clay, silt, finely divided organic and inorganic matters which cause the turbidity in water can be removed by filtration process easily. Therefore, turbidity removal was satisfactory. The effluent water from filters with iron net, scrap iron and iron rod have nearly the same values. The figures show that in the initial day the turbidity values were higher. It may be caused because of the presence of the suspended materials from the filter system like iron source, sludge and so on. Also in the 146th day the values were suddenly increased. It may be caused because of sudden increase in the amount of suspended solids from any kind of act in the operation procedure. The average values of turbidity for influent and effluent options are presented in Figure 4.32.

Figure 4.32: Average values of Turbidity of Influent and Effluent options

4.3.7 Salinity

Salinity is a measure of the amount of salts in the water. Because dissolved ions increase salinity as well as conductivity, the two measures are related.

In this study, only the salinity due to the presence of Chlorides was considered. So, the samples were tested for the chloride concentration which was determined by the titration method. Chloride ion may be present in combination with one or more of the cations of Calcium, Magnesium, Iron and Sodium. The Bangladesh standard for drinking purpose is 150 to 600 mg/L.

From the data, it was found that the filter unit had no significant capability to reduce the salinity level. The chlorides cannot be removed by simple filtration process. Therefore, the chloride and salinity removal was not satisfactory. The average salinity due to chloride ions was 62.42 mg/L. The salinity values of influent and effluents with iron net, scrap iron and iron rod are shown graphically in Figure 4.33. Figure 4.34 represents average values of various samples.

Table 4.7: Variation of Salinity of Influent and Effluent

	Average Salinity (mg/L)	Highest Salinity (mg/L)	Lowest Salinity (mg/L)	Standard Deviation
Influent	62.42	70	52.5	5.10
Effluent (Net)	61.37	70	52.5	5.47
Effluent (Scrap)	61.93	70	52.5	5.43
Effluent (Rod)	61.69	70	52.5	5.45

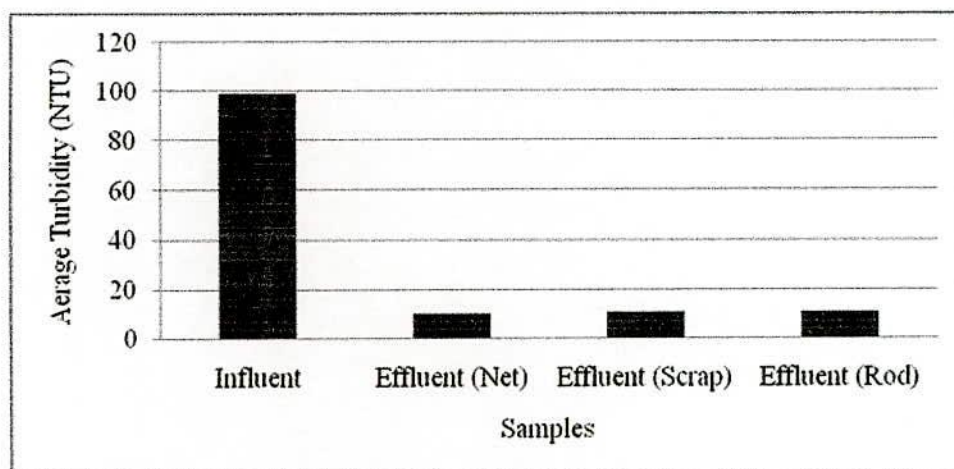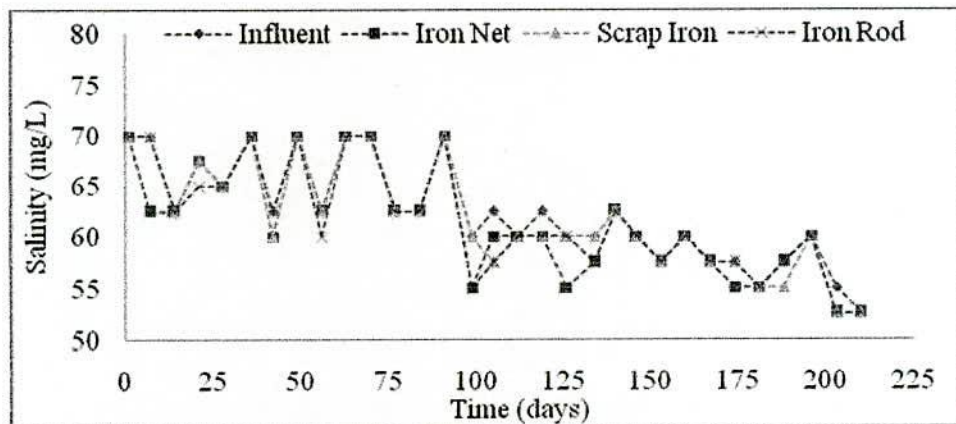Figure 4.33: Salinity of influent and various effluent options
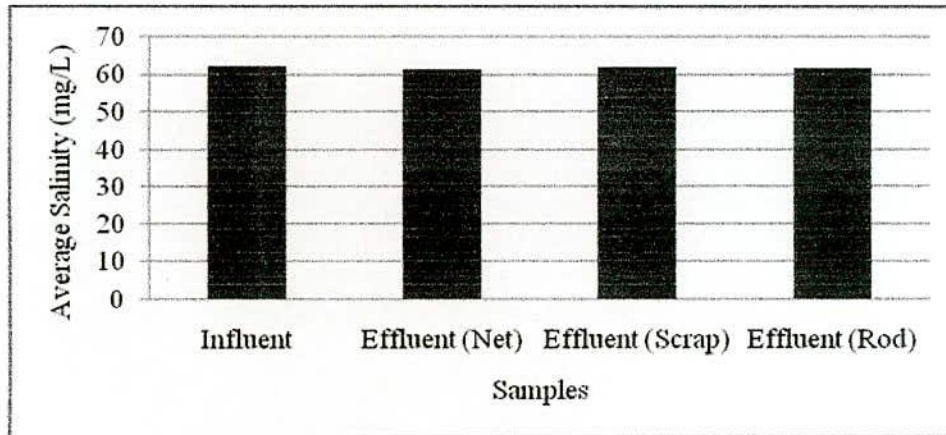
Figure 4.34: Average value of Salinity of Influent and Effluent options

4.3.8 Nitrate and Nitrite

The influent raw water of the Khulna site contained no nitrate and nitrite in almost every sampling through the monitoring period.

4.3.9 Hardness

It was found that the tubewell water of the household contained high amount of hardness. From the Aqua Check test the influent water hardness was determined as around 400 to 500 mg/L. It was also found that our filter system was not suitable for reducing the hardness significantly.

4.3.10 Alkalinity

The tubewell water of the household in Khulna contained high amount of hardness. From the Aqua Check test the influent water hardness was determined as around 180 to 200 mg/L in most cases. Also the proposed filter system was not suitable for reducing the alkalinity significantly.

The inability of removing nitrate, nitrite and alkalinity was conducted as the inability to removing Nitrogen, Calcium or Magnesium contents.

4.3.11 Iron (Fe)

By using Pack Test, the influent and effluent Fe (2+) concentrations were determined for the Khulna site. The influent water contained very high amount of iron. The average Fe (2+) concentration was 7.90 mg/L with highest and lowest value 10 mg/L and 5 mg/L respectively.

Figure 4.35: Iron of influent and various effluent options
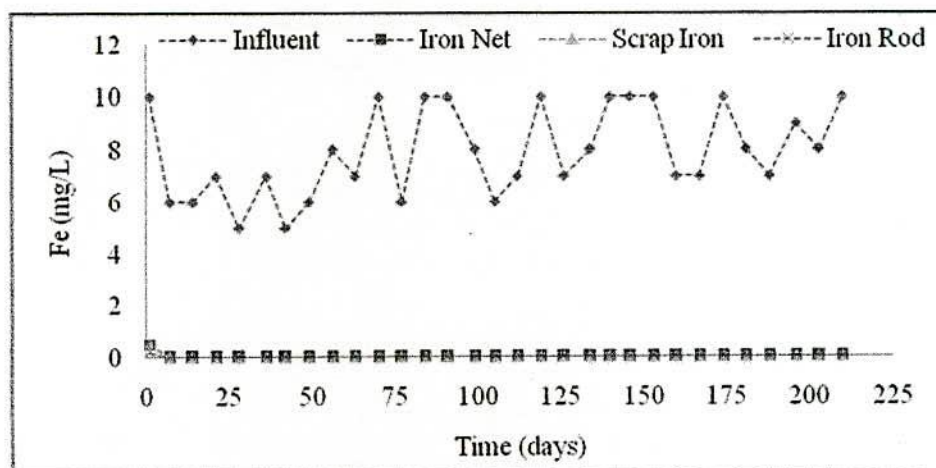
The proposed filter unit system was very much effective in reducing Fe (2+) concentration level. Soluble ferrous ions present in water were oxidized to insoluble ferric ions and then precipitated. Thus filter units with all the options as iron net, scrap iron and iron rod were able to remove Fe (2+) almost fully. Figure 4.35 shows Fe (2+) values of the influent and various effluent options.

4.3.12 Phosphorus (P)

The amount of Phosphate (PO_4^{3-}) was determined to determine the amount of Phosphorus in the samples. Bangladesh standard for drinking water for Phosphate is 6 mg/L. This was accomplished by Pack Test. The raw water of the contaminated tubewell contained high level of Phosphate of average 2.60 mg/L with highest and lowest value 3.5 mg/L and 1.5 mg/L, respectively. Average, highest and lowest Phosphorus and standard deviation (S.D.) for influent and effluent options are shown in Table 4.8.

Table 4.8: Variation of Phosphorus concentration of Influent and Effluent

	Average P (mg/L)	Highest P (mg/L)	Lowest P (mg/L)	Standard Deviation
Influent	2.60	3.5	1.5	0.62
Effluent (Net)	0.66	1.5	0.2	0.42
Effluent (Scrap)	0.68	1.5	0.2	0.40
Effluent (Rod)	0.67	1.5	0.2	0.36
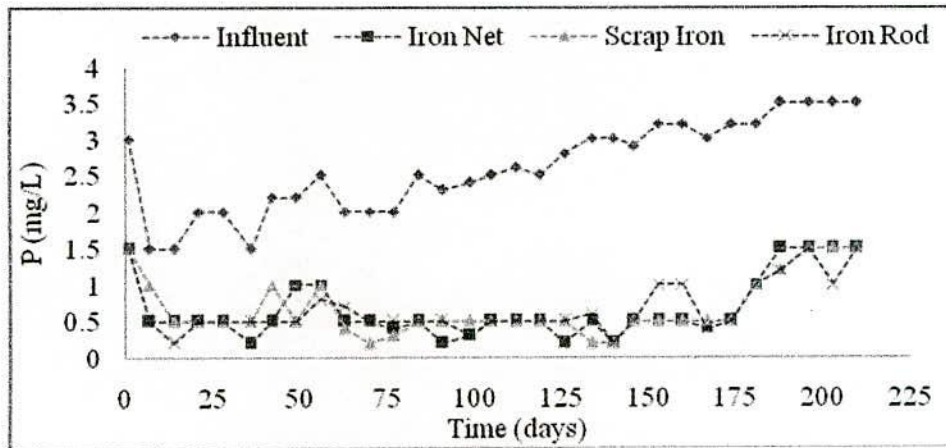
Figure 4.36: Phosphorus of influent and various effluent options
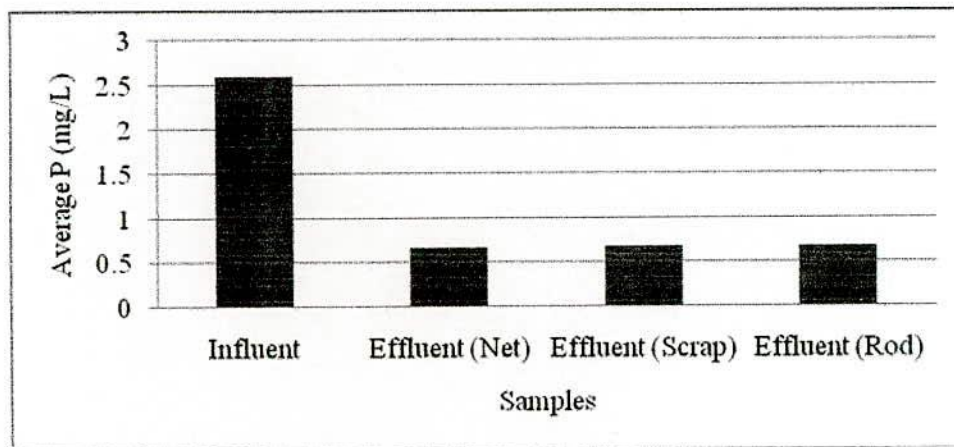
Figure 4.37: Average values of P of Influent and Effluent options

Figure 4.36 shows the P values of influent and effluent with various options with the filter unit. Figure 4.37 represents average values of various samples. It is clear from the figure that the amount of Phosphorus in the raw tubewell water sample increases with time. It was occurred due to the increase of Phosphate (PO_4^{3-}) concentration in the groundwater with time. Phosphate ions have chemical and biological properties to be adsorbed on iron hydroxides. The figures also depict that there is no big difference in the performance of phosphate removal.

4.3.13 Silica (Si)

Silica concentration of raw influent and treated effluent samples were tested by the Pack Test method.

Average, highest and lowest Si concentration and standard deviation (S.D.) for influent and effluent options are shown in Table 4.9. Figure 4.38 and 4.39 express graphical representation of influent and effluent values.

Table 4.9: Variation of Silica concentration of Influent and Effluent

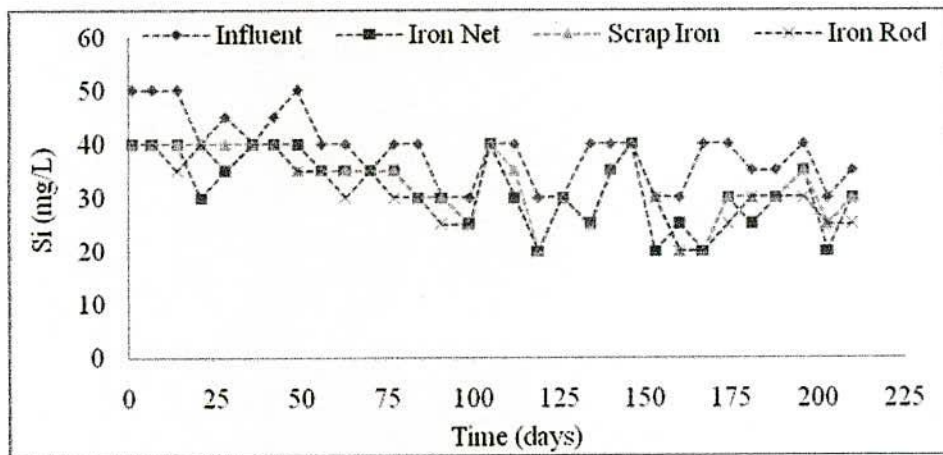|	Average Si (mg/L)	Highest Si (mg/L)	Lowest Si (mg/L)	Standard Deviation
Influent	38.71	50	30	6.32
Effluent (Net)	31.77	40	20	6.78
Effluent (Scrap)	32.74	40	20	6.43
Effluent (Rod)	31.29	40	20	6.45

Figure 4.38: Silica of influent and various effluent options
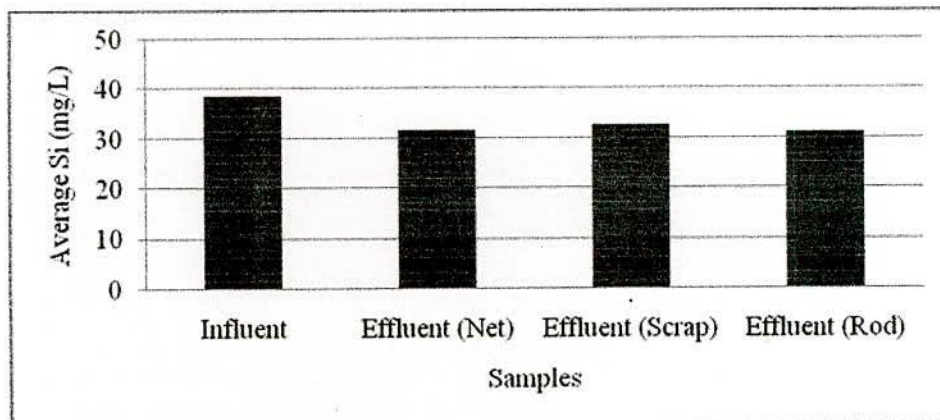

Figure 4.39: Average values of Si of Influent and Effluent options

The above figures show that the filter systems are not suitable enough to reduce the high Si level of raw groundwater samples. Also there was almost no change in the performances for the filter systems with different iron sources. Because Si removal occurred as a result of adsorption on to oxidized iron-hydroxides produced in the filter due to iron release and no change was found among the iron released from different sources like iron net, scrap iron or iron rod.

4.3.14 Arsenic (As)

The raw water of the household tubewell contained very high level of arsenic concentration (average 489.7µg/L). Filter units with iron net, scrap iron and iron rod were run in the same household and samples were collected for testing in every week. Average, highest and lowest arsenic concentration for influent and effluent options are shown in Table 4.10.

Table 4.10: Variation of Arsenic concentration of Influent and Effluent

	Average As (µg/L)	Highest As (µg/L)	Lowest As (µg/L)	Standard Deviation
Influent	489.7	582.7	399.2	42.60
Effluent (Net)	125.6	211.4	100.3	23.40
Effluent (Scrap)	125.5	235.3	94.6	25.09
Effluent (Rod)	127.5	254.9	95.2	30.23
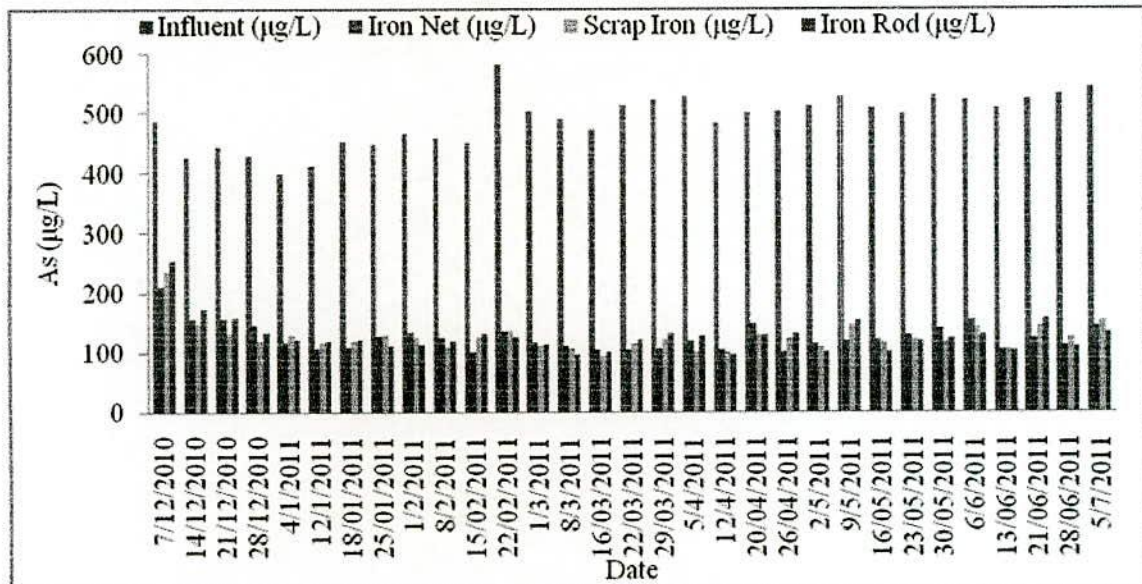
Figure 4.40: Arsenic concentration of influent and various effluent options with date
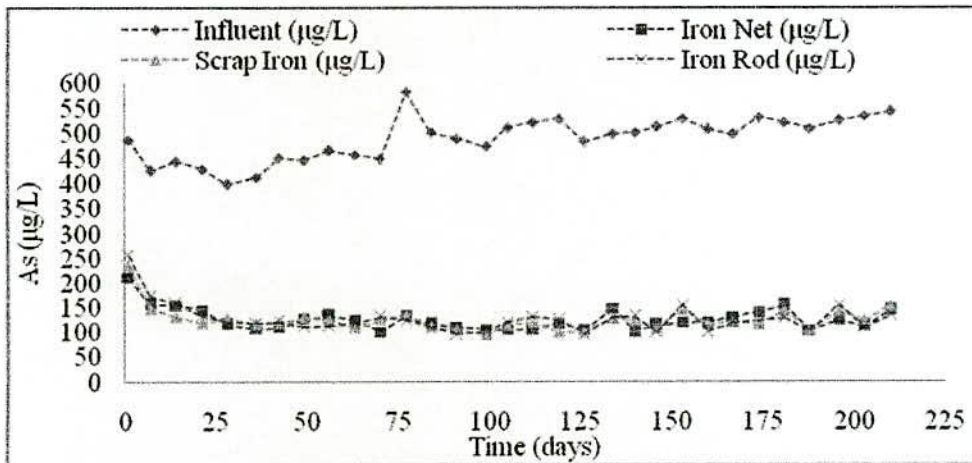
Figure 4.41: Arsenic concentration of influent and various effluent options
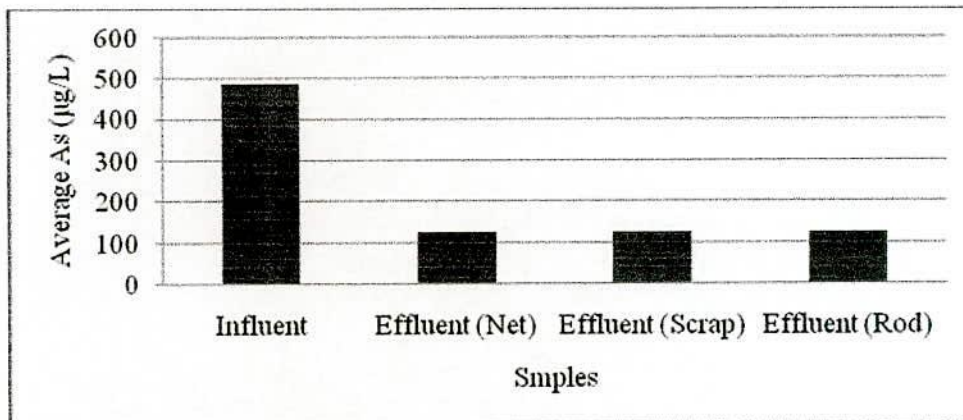
Figure 4.42: Average values of Arsenic of Influent and Effluent options

The removal of arsenic occurred due to the oxidation of iron and arsenic followed by their subsequent adsorption and precipitation on and with biologically produced iron hydroxides. Figure 4.40 represents the values of arsenic concentration of influent and effluent samples with respect to the date of sampling. This figure describes that the filter units reduce the arsenic concentration from the raw samples greatly, though not enough to reduce up to standard for drinking purpose. It is also clear that whatever the source of iron in the system is the removal performance do not change enough.
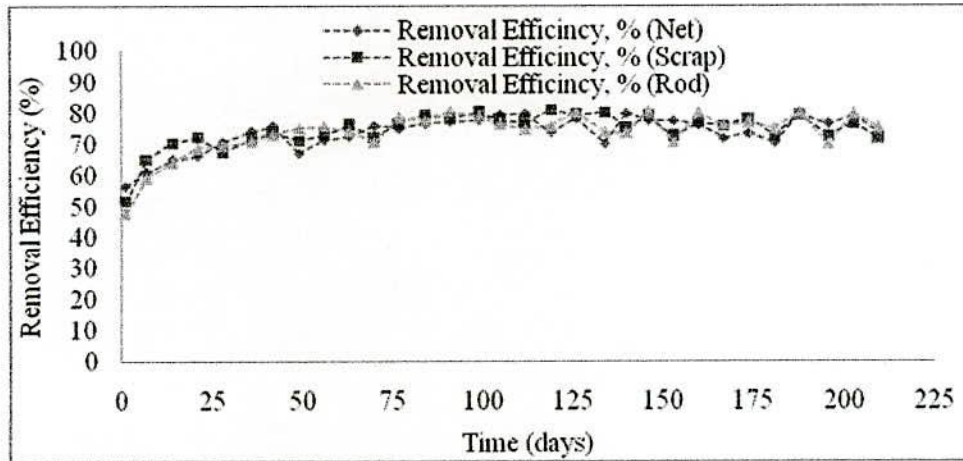
Figure 4.43: Removal Efficiency (%) for various filter options

Figure 4.41, 4.42 and 4.43 represents influent and effluent concentrations, average concentrations and removal efficiencies of the filter units, respectively. The figures show that the removal efficiency is smaller initially as some time was required to start adsorption process. After that the arsenic removal curves for different filter options follow same pattern.

4.3.15 Flow Rate

Flow rate is an important factor. It was found from the study that, the zero-valent iron source options did not affect the flow rate characteristics of the filter unit. The flow rate tendency was more or less same. Figure 4.44 shows flow rates of different filters with different iron options. It was found that the flow rates were satisfactory enough for the filter running period.

Figure 4.44: Flow rate of filters with various options

CHAPTER 5

Performance of Double Unit Filter Systems

5.1 Introduction

In the previous chapter, it was tried to elaborate the performance and testify the suitability of single unit filter system. It is clear that the single unit system is capable of reducing the arsenic concentration in the tubewell water of rural Bangladesh, though the arsenic level did not settle down to the guideline value of arsenic concentration for drinking water. So, one had to think again some modification or addition with the filter system.

Double unit filter system may be one of the solutions. Arsenic concentration may be reduced significantly in this system. To check the suitabil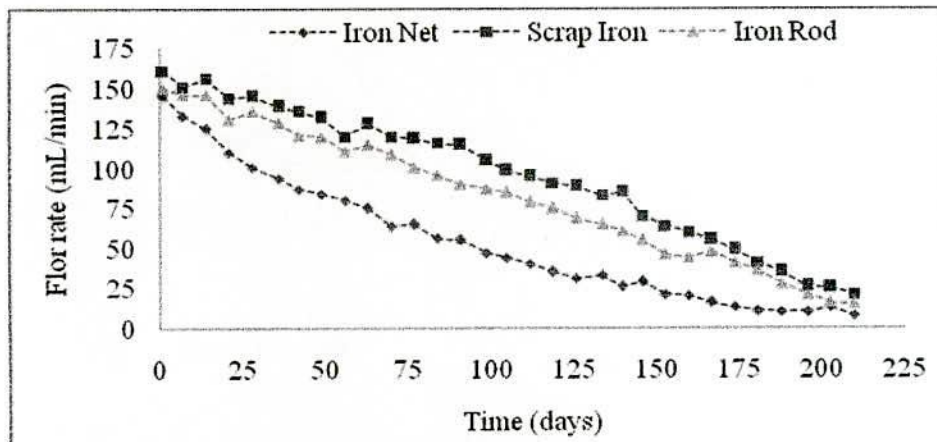ity of Double unit filter system, filter systems ('R1double' and 'R2double') were installed in Rupsha site. To have a specific, compareable and fruiful result, the Double unit filter systems were installed in the same household where Single unit filter systems were installed earlier.

The Double unit filter system may be conducted in two ways described in Chapter 3 (Art. 3.7). Both 'W-system' and 'Connect system' of double unit filter system were tried in my study. Firstly, a short study of 12 days with two times sampling in each day was conducted to find the difference in performance and sustainibility of the ways of double unit filter system. Secondly, a long term monitoring of the filter ystem was conducted.

5.2 Comparison between W-System and Connect System of Double Unit Filter System

In two households in Rupsha, the W-System and Connect System double unit filter unit was monitored for Arsenic, Iron, Phosphorus, Silica, pH, Dissolved Oxygen (DO), Electro conductivity (EC), Nitrate, Nitrite, Hardness, Alkalinity, Flow rate etc.

5.2.1 pH

pH values of the influnt raw water samples were increased significantly after filtration. The pH values of the 2nd effluent values in W-system and final effluent values in Connect system

were greater than the 1st efflunt values in W-system. Also the 2nd effluent water and Connect final effluent contained nearly same values. The average values of pH for influent, 1st effluent, 2nd effluent and final effluent were 7.33, 8.05. 8.20 and 8.18, respectively for 'R1double' and 7.24, 7.99, 8.08 and 8.06, respectively for 'R2double'.
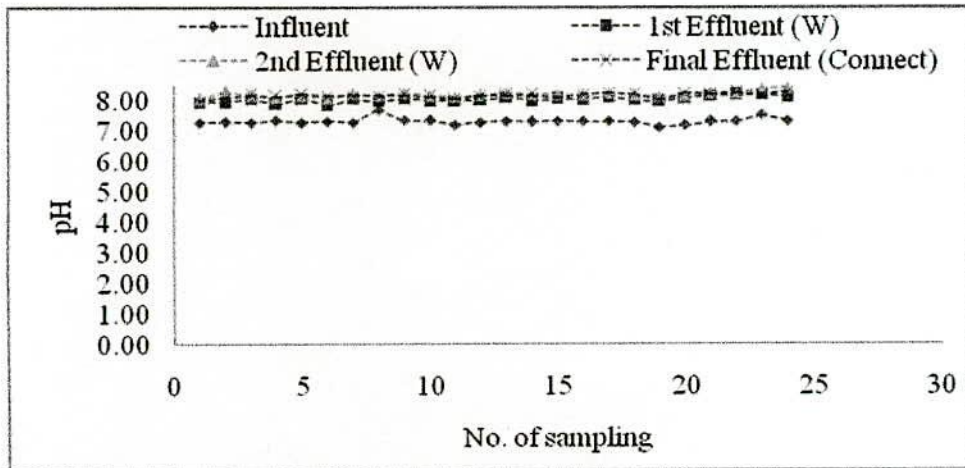
Figure 5.1: pH of samples of W and Connect system double unit filter system for 'R1double'

Figure 5.1 represents the variation of pH values for the samples for the filter system 'R1double'. In the Figure 5.2, this variation for the filter system 'R2double'of pH is presented.
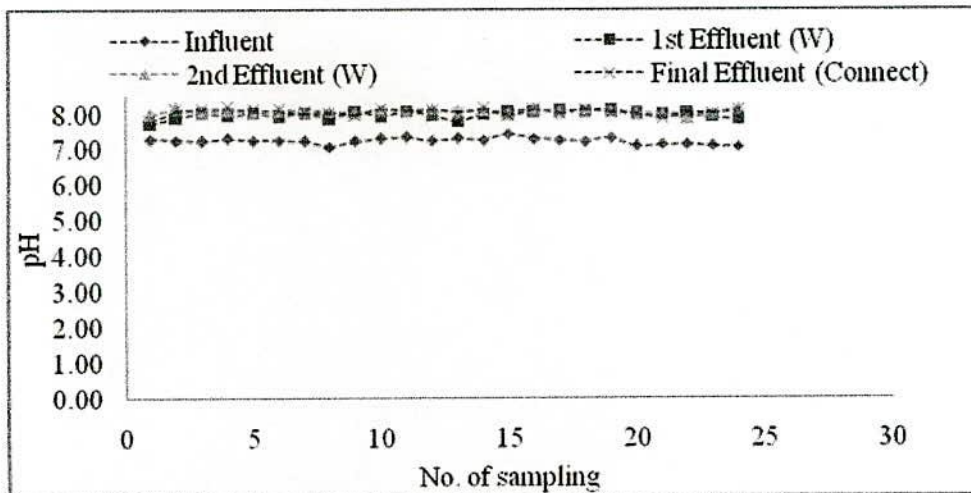
Figure 5.2: pH of samples of W and Connect system double unit filter system for 'R2double'

pH increases as a result of release of OH⁻ groups. It was caused because of the water decomposition by various iron sources present in the system and also by the sorption reaction

of arsenic, which released OH⁻ groups from sorbents. The above figures also clarify that 2nd effluent samples contain comparatively high level of pH as a result of consecutive filtrations which increase the level of release of OH⁻ groups.

5.2.2 Dissolved Oxygen (DO)

Dissolved oxygen is very much essential for the arsenic removal mechanism of this proposed filter unit of this study. Figure 5.3 and 5.4 represent the variation of DO values for the samples for the filter system 'R1double' and 'R2double'.

Figure 5.3: DO of W and Connect system double unit filter system for 'R1double'
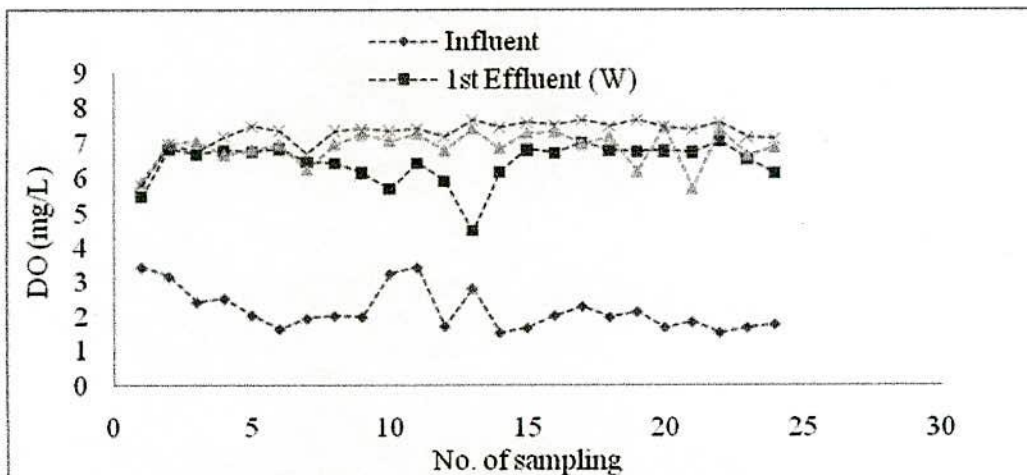
Figure 5.4: DO of W and Connect system double unit filter system for 'R2double'

The average values of DO for influent, 1st effluent, 2nd effluent and final effluent were 2.08, 6.45, 7.30 and 7.19 mg/L, respectively for 'R1double' and 2.18, 6.43, 6.89 and 7.28 mg/L, respectively for 'R2double'.

The graphs show that the amount of dissolved oxygen increased with the degree of filtration. Initially before pouring in the reactor, manual aeration was performed for influent water. Because, high level of DO was required for the arsenic removal mechanism. The DO values of the 2nd effluent values in W-system and final effluent values in Connect system were greater than the 1st efflunt values in W-system. Also the 2nd effluent water and Connect final effluent contained nearly same values. It was occured for the addition of oxygen from air.

5.2.3 Electrconductivity (EC)

There was no big change of EC values for filtration in my study. However, the average values of EC for influent, 1st effluent, 2nd effluent and final effluent are as follows 0.752, 0.702, 0.638 and 0.644 mS/cm, respectfully for 'R1double' and 0.742, 0.695, 0.636 and 0.647 mS/cm, respectfully for 'R2double'.

Figure 5.5: EC of W and Connect system double unit filter system for 'R1double'
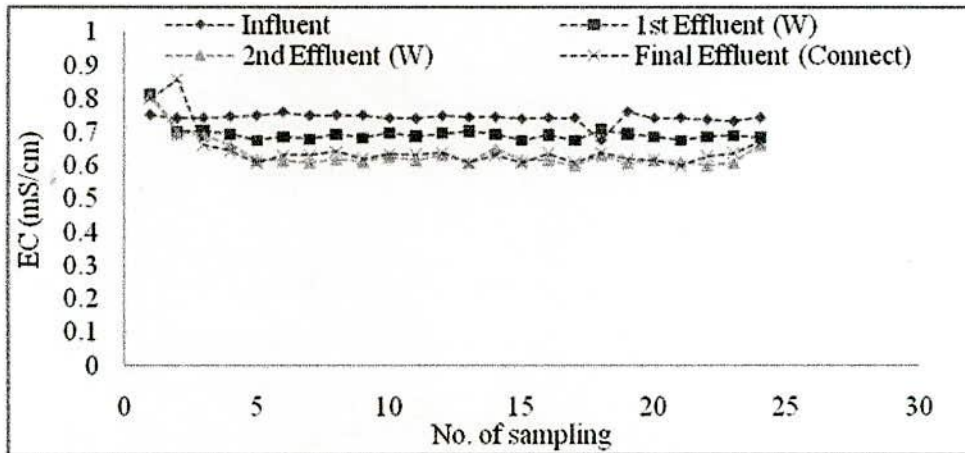
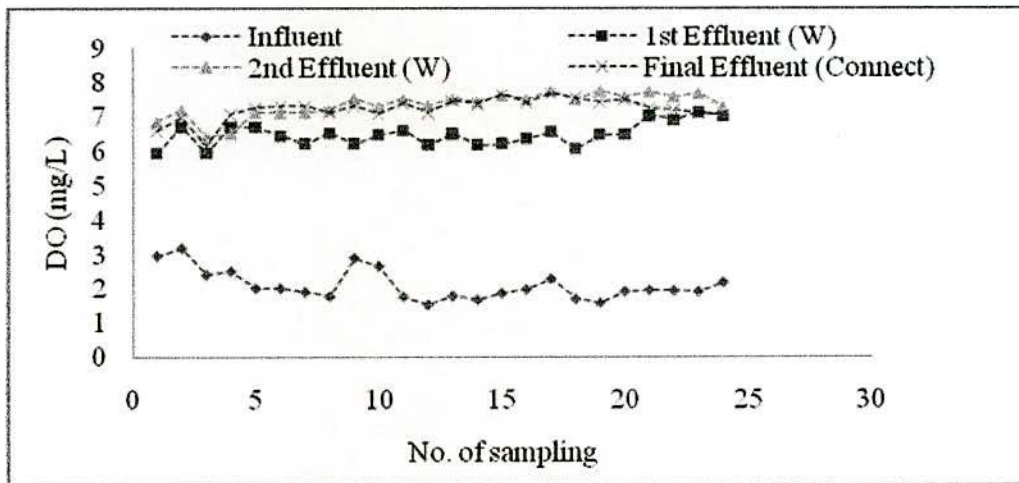Figure 5.6: EC of W and Connect system double unit filter system for 'R2double'

It is clear from the above graphs that no option, even double filtration, is suitable enough to reduce the EC of the influent greatly. These also depict that the contributor ions for electroconductivity could not be filtrated by consecutive double filtration.

5.2.4 Nitrate and Nitrite

Raw samples contained almost no nitrate and nitrite. So, the filter unit had no effect on nitrate or nitrite concentrations.

5.2.5 Hardness

Both tubewells of this study contained water of high hardness values. The hardness values ranged from about 400 to 500 mg/L. But, not even double unit filter units were effective for the removal or reduction.

5.2.6 Alkalinity

The raw water sample contained high amount of alkalinity concentration (around 200 mg/L). No way of filtration system was suitable to reduce the alkalinity level.

5.2.7 Iron (Fe)

Influent water contained very high amount of iron. The average Fe (2+) concentration was 7.63 mg/L with highest and lowest value 10 mg/L and 4 mg/L, respectively for 'R1double' and 7.63 mg/L with highest and lowest value 10 mg/L and 5 mg/L, respectively for 'R2double'.
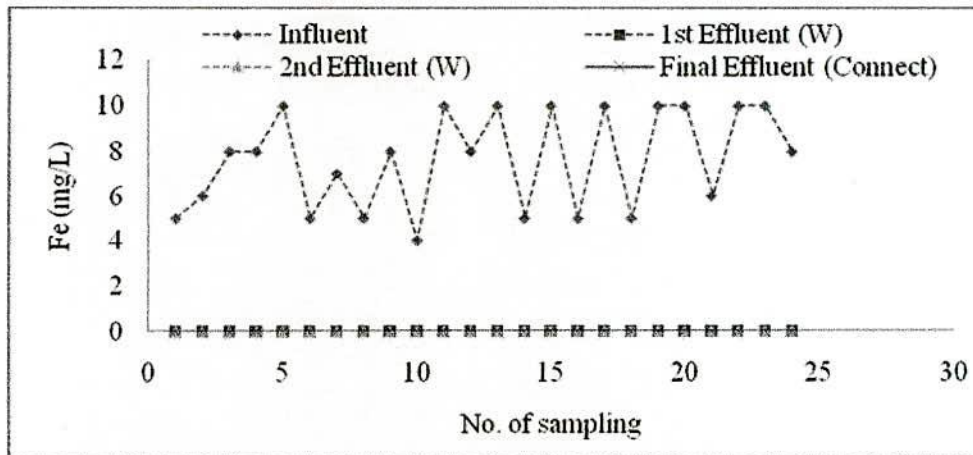
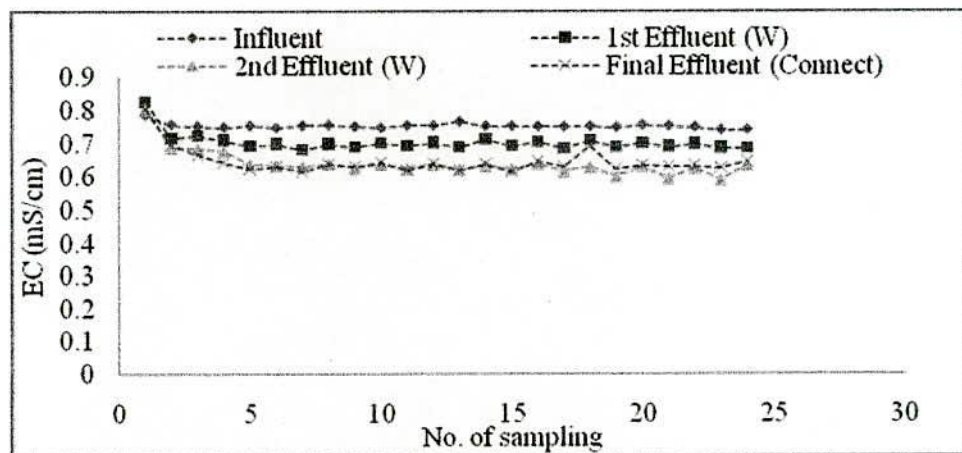Figure 5.7: Fe (2+) of W and Connect system double unit filter system for 'R1double'
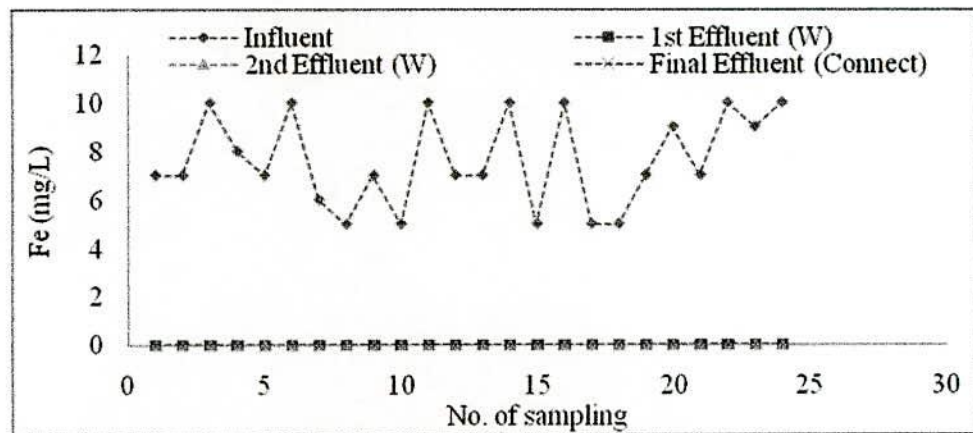
Figure 5.8: Fe (2+) of W and Connect system double unit filter system for 'R2double'

The figures clarify that the proposed filter unit systems (both single and double units) were very much effective in reducing Fe (2+) concentration level. 1st effluent, 2nd effluent, final effluent contained almost no Fe (2+) concentration. Soluble ferrous ions present in water were oxidized to insoluble ferric ions and then precipitated. As a result, high iron removal performances were found.

5.2.8 Phosphorus (P)

By using Pack Test method, the concentration of Phosphorus was determined easily. The data for influent and effluent options for 'R1double' and R2double' is shown in Table 5.1 and Table 5.2, respectively.

Table 5.1: Variation of Phosphorus concentration of Influent and Effluent for 'R1double'

	Average P	Highest P	Lowest P	Standard

	(mg/L)	(mg/L)	(mg/L)	Deviation
Influent	1.33	1.5	1.5	0.35
1st Effluent (W)	0.29	1	0.1	0.24
2nd Effluent (W)	0.25	1	0.1	0.20
Final Effluent (Connect)	0.32	1	0.1	0.26

Table 5.2: Variation of Phosphorus concentration of Influent and Effluent for 'R2double'

|	Average P (mg/L)	Highest P (mg/L)	Lowest P (mg/L)	Standard Deviation
Influent	1.35	2.50	0.75	0.44
1st Effluent (W)	0.36	2	0.15	0.38
2nd Effluent (W)	0.32	2	0.10	0.39
Final Effluent (Connect)	0.26	2	0.10	0.38
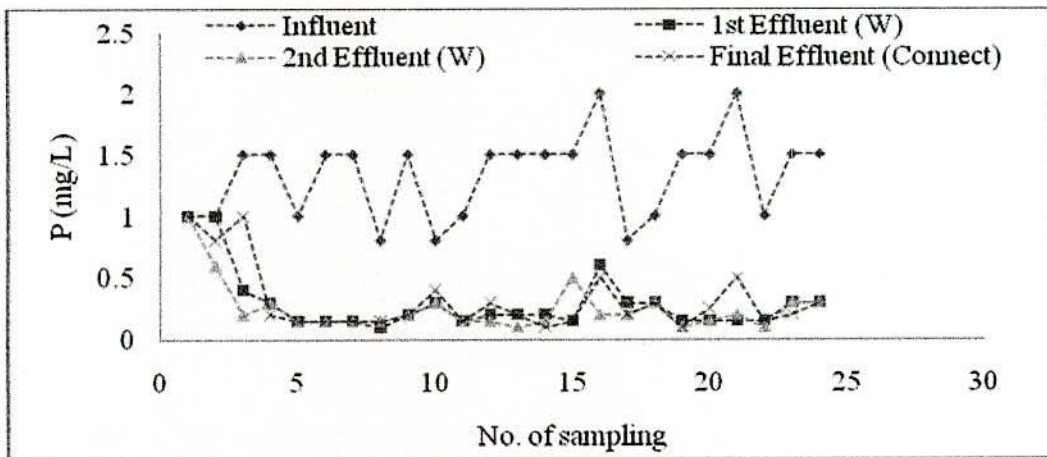
Figure 5.9: P of W and Connect system double unit filter system for 'R1double'

Figure 5.10: P of W and Connect system double unit filter system for 'R2double'

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Figure 5.9 and Figure 5.10 show the P values of influent and effluent with various options with the filter unit for both 'R1double' and 'R2double'. It is clear from the data and graphs above that, second time filtration is not reducing the Phosphorus level significantly.

5.2.9 Silica (Si)

Average, highest and lowest Silica and standard deviation (S.D.) for influent and effluent options for 'R1double' and R2double' are shown in Table 5.3 and Table 5.4 respectively.

Table 5.3: Variation of Silica concentration of Influent and Effluent for 'R1double'

	Average Si (mg/L)	Highest Si (mg/L)	Lowest Si (mg/L)	Standard Deviation
Influent	35.21	50	25	6.16
1st Effluent (W)	31.25	40	20	4.48
2nd Effluent (W)	29.79	35	20	2.75
Final Effluent (Connect)	30.00	35	25	1.47

Table 5.4: Variation of Silica concentration of Influent and Effluent for 'R2double'

|	Average Si (mg/L)	Highest Si (mg/L)	Lowest Si (mg/L)	Standard Deviation
Influent	36.04	50	30	6.42
1st Effluent (W)	31.88	40	20	4.38
2nd Effluent (W)	30.42	40	20	4.40
Final Effluent (Connect)	30.63	40	25	2.68
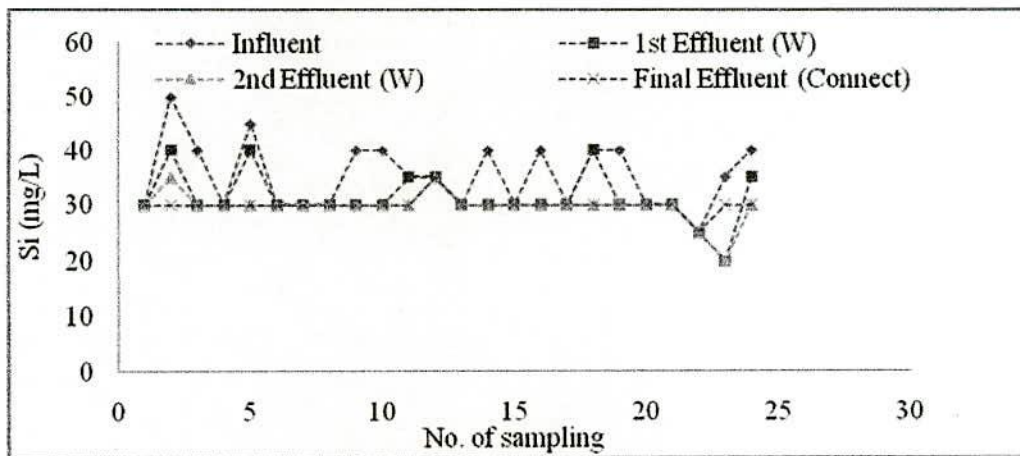
Figure 5.11: Si of W and Connect system double unit filter system for 'R1double'
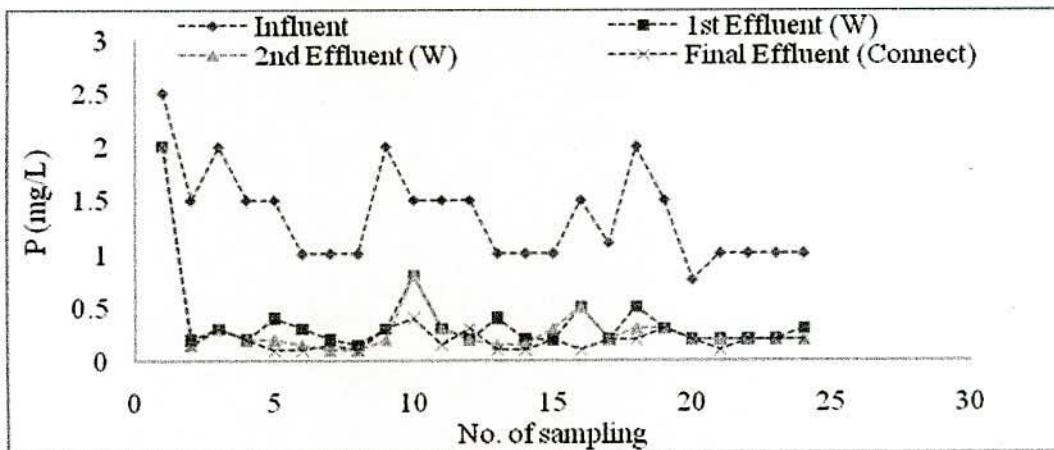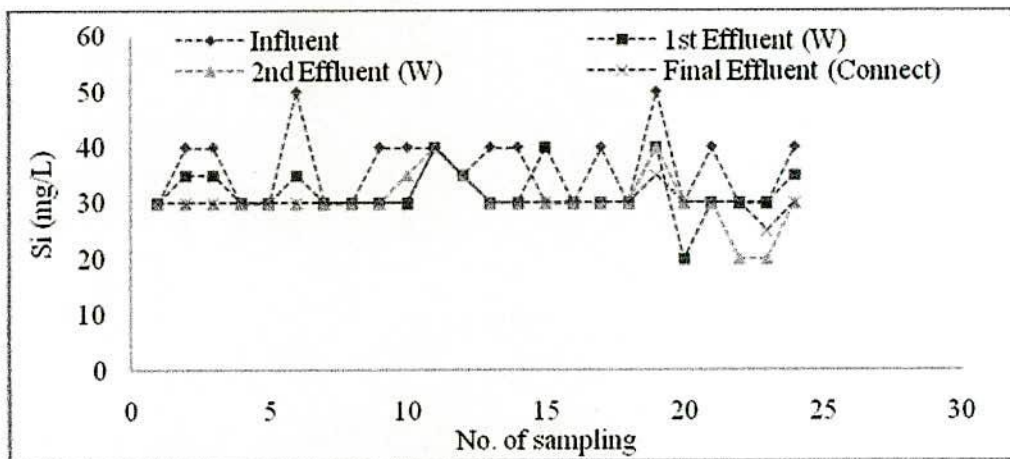

Figure 5.12: Si of W and Connect system double unit filter system for 'R2double'

Figure 5.11 and Figure 5.12 show the Si values of influent and effluent with various options with the filter unit for both 'R1double' and 'R2double'. It can be easily seen from the tables and graphs that the Si concentrations are not greatly affected by the degree of filtration. Si removal occurred as a result of adsorption on to oxidized iron-hydroxides produced in the filter due to iron release. May be the iron release rate was low for every option and the Si removal is not satisfactory.

5.2.10 Arsenic (As)

The performances of single unit filter systems are presented in previous chapter. In this portion, the performances of double unit filter systems are being evaluated. W-system and Connect system are two different ways of double unit systems. The household tubewell of the study contained very high level of arsenic concentration. The arsenic concentration was

reduced in 1st effluent, 2nd effluent of W-system and final effluent in Connect system. The average, highest and lowest Arsenic and standard deviation (S.D.) for influent and effluent options for 'R1double' and R2double' are shown in Table 5.5 and Table 5.6 respectively.

Table 5.5: Arsenic concentration of Influent and Effluent for 'R1double'

	Average As (µg/L)	Highest As (µg/L)	Lowest As (µg/L)	Standard Deviation
Influent	406.25	469	334	31.32
1st Effluent (W)	148.58	364	87	55.74
2nd Effluent (W)	56.88	165	39	27.99
Final Effluent (Connect)	64.88	186	37	32.82

Table 5.6: Arsenic concentration of Influent and Effluent for 'R2double'

	Average As (µg/L)	Highest As (µg/L)	Lowest As (µg/L)	Standard Deviation
Influent	420.92	501	356	35.96
1st Effluent (W)	151.42	286	84	44.44
2nd Effluent (W)	56.63	156	35	25.65
Final Effluent (Connect)	62.21	189	41	34.77

Figure 5.13 and Figure 5.14 show data for 'R1double' and 'R2double', respectively.
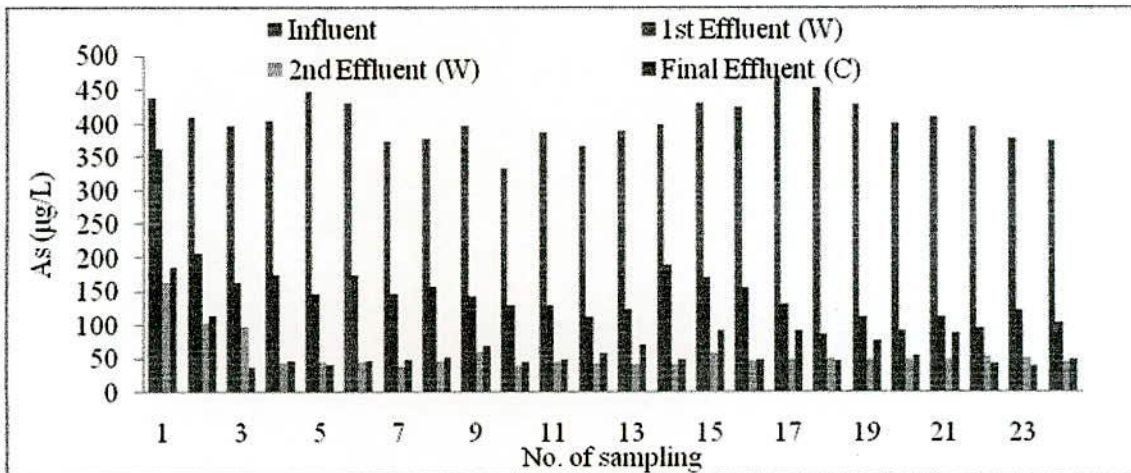
Figure 5.13: Arsenic concentration of influent and various effluent options for 'R1double'
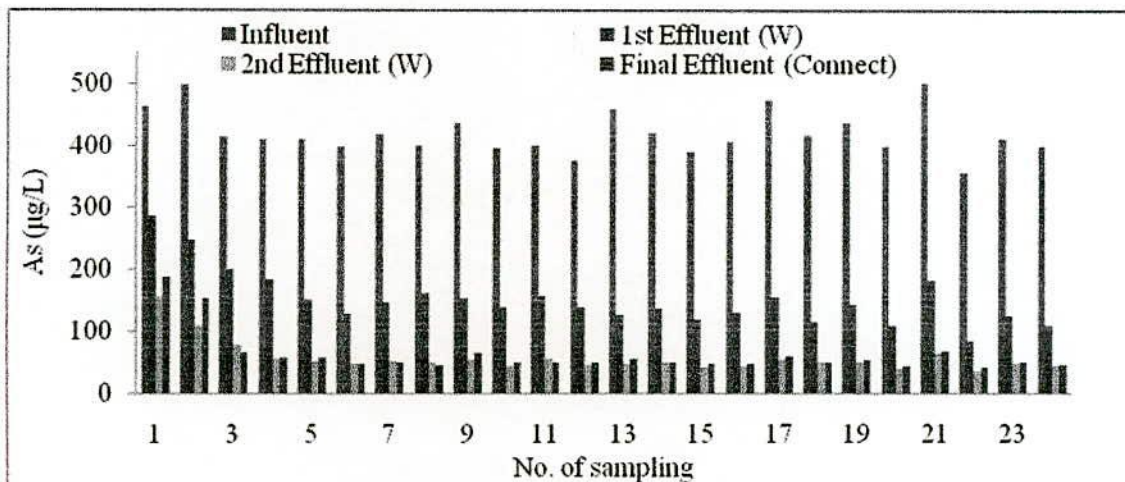
Figure 5.14: Arsenic concentration of influent and various effluent options 'R2double'

The tables and graphs show that, the 2nd effluent for W-system and final effluent for Connect system produced water of arsenic concentration around the guideline value for drinking purpose (50 µg/L). The effluent from 2nd effluent from W-system and final effluent from Connect system contained nearly same values of arsenic concentrations. The average values of influent and effluent options are presented graphically in Figure 5.15 and 5.16.
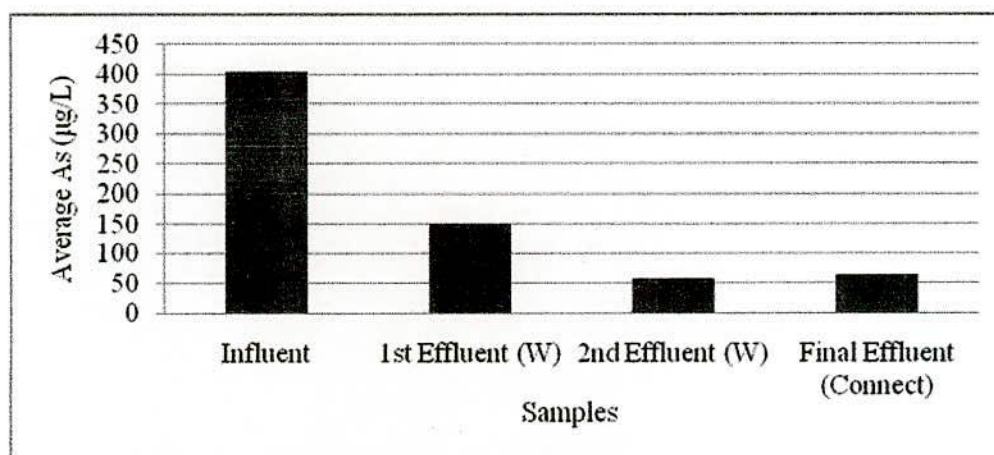
Figure 5.15: Average values of Arsenic of Influent and Effluent options for 'R1double'
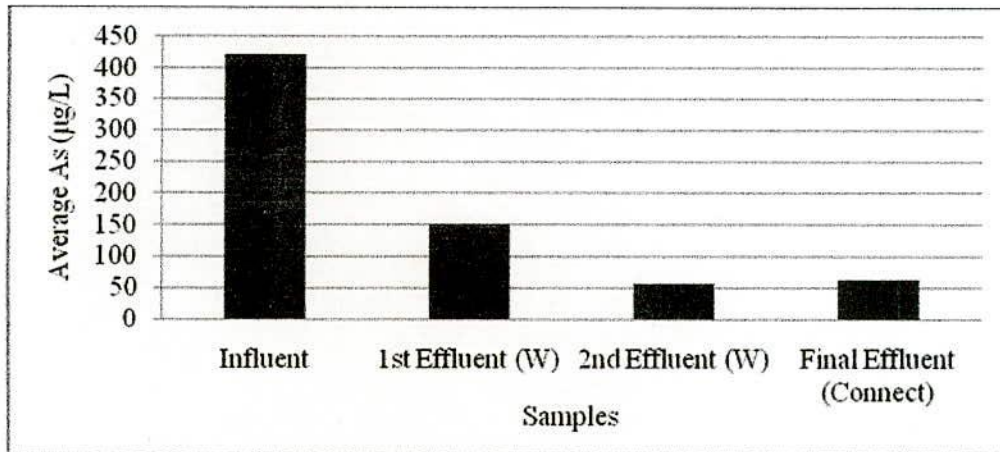
Figure 5.16: Average values of Arsenic of Influent and Effluent options for 'R2double'

5.3 Monitoring of the Performance of 'Connect System' of Double Unit Filter System

The performances of both W-system and Connect system of Double unit filter system for a short period of 12 days are described in the earlier section (Art. 5.2). The main objective of this short study was to find out the preferable, easy and suitable form of double unit filtration system for the long run. From the discussion, it is clear that there is no big difference between the performances of the filtration procedure. So, we can run any form of filter unit to evaluate the performance of double unit filter system.

In case of running or using the filter unit, the Connect system was easier and suitable for the household people. Because, the Connect system required pouring of raw water once and then the final effluent came out accomplishing double filtration, and in case of W-system, after completion of 1st filtration, the water required to be poured to another filtration reactor. So, for the ease of using for the household people, the Connect system of double unit filter unit was being run and the W-system was stopped. The samples were tested in every 2 weeks for about 10 months. Arsenic, Iron, Phosphorus, Silica, pH, Color, TDS, Turbidity, Nitrite, Nitrate, Hardness, Alkalinity etc. were determined.

5.3.1 pH

pH concentration for both 'R1double' and 'R2double' was increased due to double filtration. Table 5.7 and Table 5.8 present the average, highest, lowest values of samples and standard deviation of the data. pH concentrations are also presented in Figure 5.17 and Figure 5.18.

Table 5.7: pH concentrations of samples for long run of 'R1double'

	Average pH	Highest pH	Lowest pH	Standard Deviation
Influent	7.18	7.56	6.88	0.17
Final Effluent	8.05	8.34	7.67	0.18

Table 5.8: pH concentrations of samples for long run of 'R2double'

	Average pH	Highest pH	Lowest pH	Standard Deviation
Influent	7.12	7.41	6.88	0.13
Final Effluent	7.95	8.17	7.42	0.20

Figure 5.17: pH concentration of samples for long run of 'R1double'
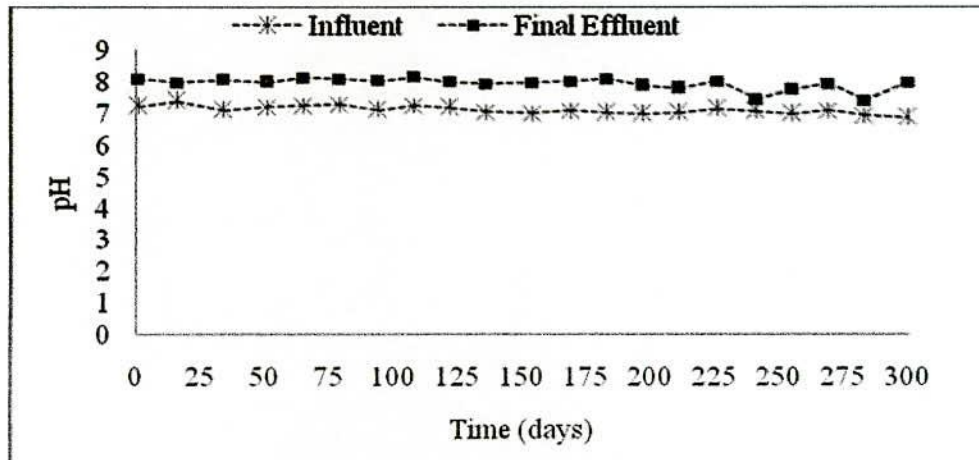
Figure 5.18: pH concentration of samples for long run of 'R2double'

It can be observed from the above figures that the concentration of pH in the influent raw water increased a little bit after the filtration. It is caused because of the presence of OH⁻ groups in the effluent and these OH⁻ groups were attributed to water decomposition by the iron and to the sorption reaction of arsenic. Also the patterns of pH concentrations are same for the both filter systems.

5.3.2 Dissolved Oxygen (DO)

Dissolved oxygen level is an important factor for the performance of this proposed filter units. Because, arsenic removal was mainly attributed to the adsorption on iron hydroxides, and which were produced through the oxidation of zero-valent iron by dissolved oxygen. The DO values are presented in the following tables and figures.

Table 5.9: DO concentrations of samples for long run of 'R1double'

	Average DO (mg/L)	Highest DO (mg/L)	Lowest DO (mg/L)	Standard Deviation
Influent	1.75	2.47	1.39	0.28
Final Effluent	7.11	7.68	6.89	0.18

Table 5.10: DO concentrations of samples for long run of 'R2double'

	Average DO (mg/L)	Highest DO (mg/L)	Lowest DO (mg/L)	Standard Deviation
Influent	1.82	2.43	1.33	0.30
Final Effluent	7.10	7.77	6.67	0.22
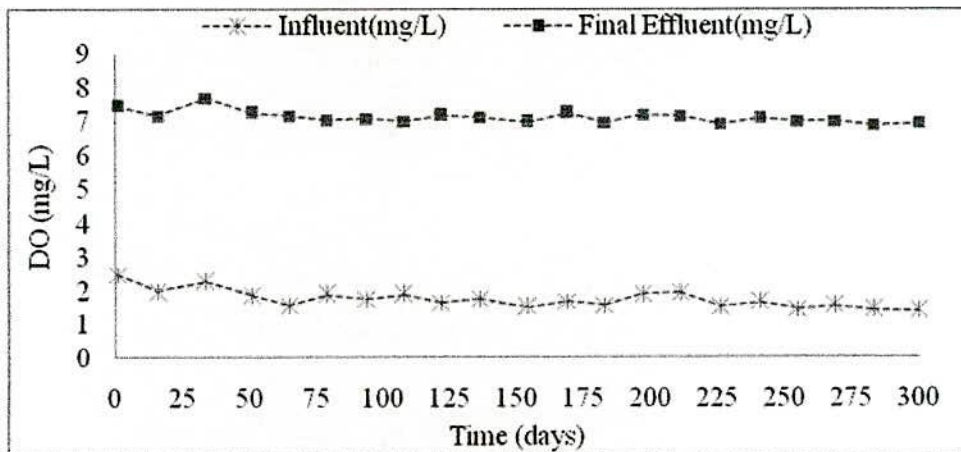
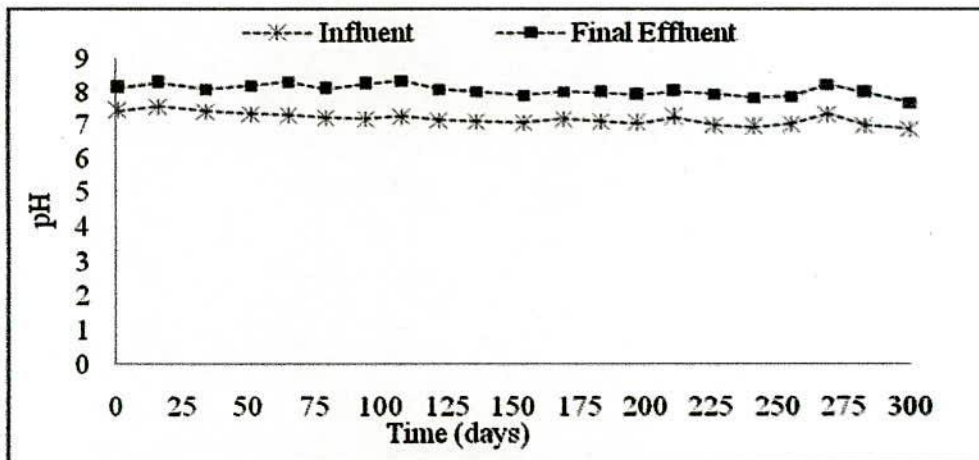Figure 5.19: DO concentration of samples for long run of 'R1double'
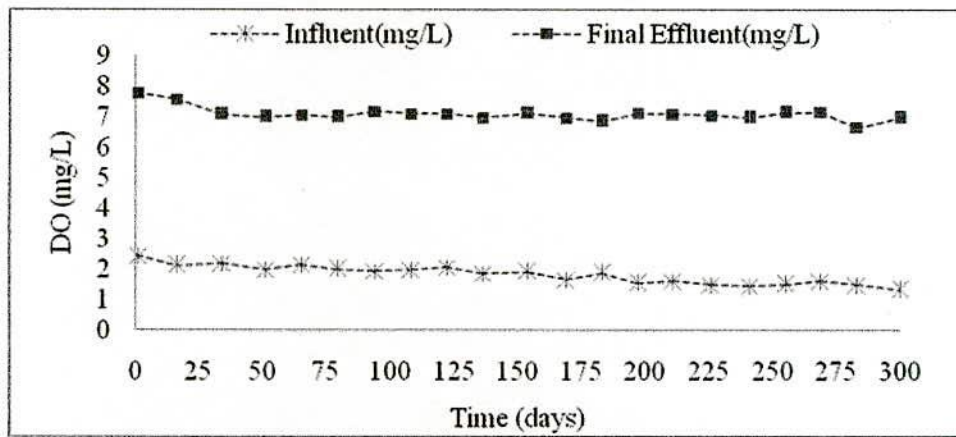
Figure 5.20: DO concentration of samples for long run of 'R2double'

It is clear from the figures that, the influent water contained low level of DO values. Before pouring in the 1st reactor, the raw water was manually aerated to increase the DO concentration of raw water. Also the system was open to air and that's why some amount of oxygen may be contributed to the DO of the effluent samples. So, finally the effluent samples showed high level of DO.

5.3.3 Electroconductivity (EC)

Conductivity is the ability of water to conduct an electrical current, and the dissolved ions are the conductors. The major contributors to conductivity are positively charged ions Na^+, Ca^{+2}, K^+ and Mg^{+2} while negatively charged ions Cl^-, SO_4^{-2}, CO_3^{-2}, HCO_3^-, NO_3^{-2} and PO_4^-. Table 5.11 and Table 5.12 present the average, highest, lowest values of samples and standard deviation of the data for both filter units.

Table 5.11: EC concentrations of samples for long run of 'R1double'

	Average EC (mS/cm)	Highest EC (mS/cm)	Lowest EC (mS/cm)	Standard Deviation
Influent	0.721	0.765	0.682	0.021
Final Effluent	0.648	0.701	0.600	0.026

Table 5.12: EC concentrations of samples for long run of 'R2double'

|	Average EC (mS/cm)	Highest EC (mS/cm)	Lowest EC (mS/cm)	Standard Deviation
Influent	0.718	0.756	0.689	0.019
Final Effluent	0.655	0.711	0.601	0.031

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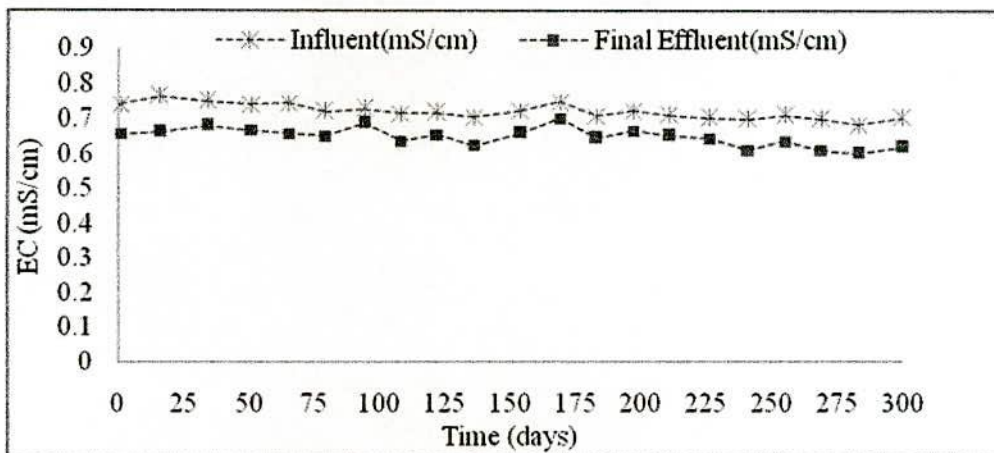
Figure 5.21: EC concentration of samples for long run of 'R1double'
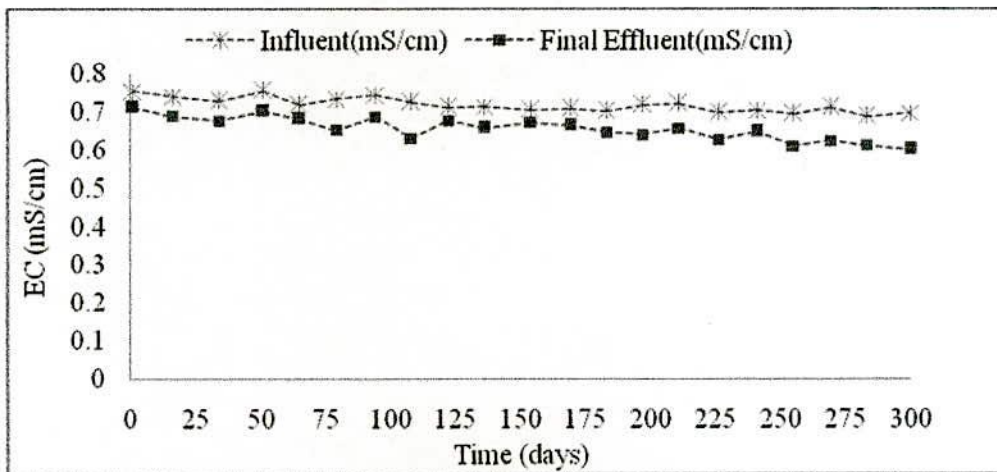
Figure 5.22: EC concentration of samples for long run of 'R2double'

Figure 5.21 and Figure 5.22 represent the EC values of the samples graphically. There was a small change of values of Electroconductivity in the samples of the study. The EC values of raw influent decreased with time. For 'R1double', the average value of influent was 0.721 mS/cm and average final effluent value was 0.648 mS/cm. For 'R2double', the average value of influent was 0.718 mS/cm and average final effluent value was 0.655 mS/cm. Also there is a steady pattern in the data of both influent and effluent in the figures.

5.3.4 Total Dissolved Solids (TDS)

TDS is a measure of all dissolved substances in water, including organic and suspended particles that can pass through a very small filter. So, the performance of reducing TDS of the raw water of this field study was quite poor. Table 5.13 and 5.14 show the data for the data for both filter units.

Table 5.13: TDS concentrations of samples for long run of 'R1double'

	Average TDS (mg/L)	Highest TDS (mg/L)	Lowest TDS (mg/L)	Standard Deviation
Influent	254.57	322	189	42.36
Final Effluent	223.57	290	162	36.26

Table 5.14: TDS concentrations of samples for long run of 'R2double'

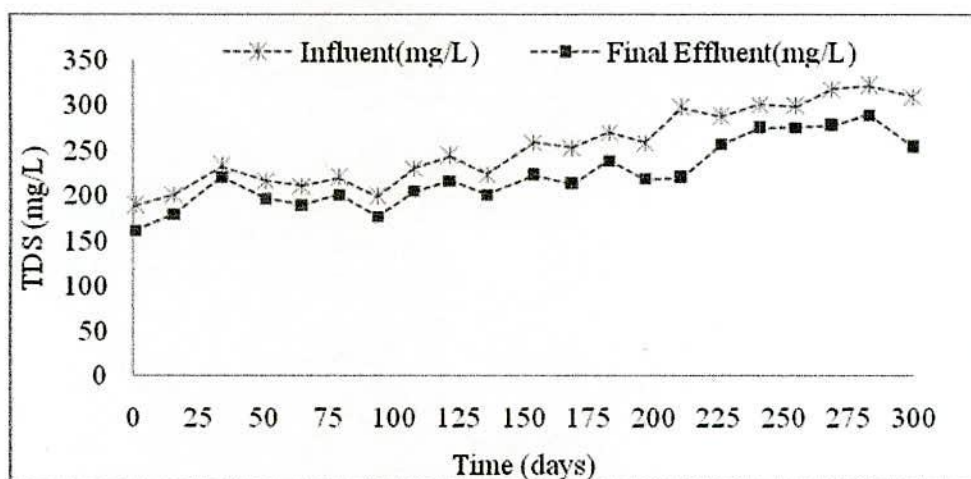|	Average TDS (mg/L)	Highest TDS (mg/L)	Lowest TDS (mg/L)	Standard Deviation
Influent	244.62	302	189	32.19
Final Effluent	204.00	251	143	31.34

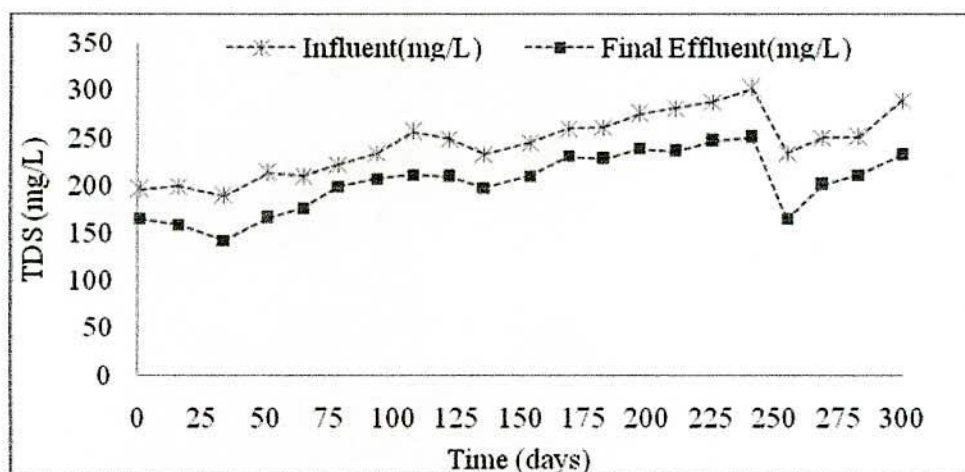Figure 5.23: TDS concentration of samples for long run of 'R1double'

Figure 5.24: TDS concentration of samples for long run of 'R2double'

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The data and the figures show that even double filtration is not suitable for reducing the amount of TDS of the influent water. "Filtration" systems are designed to selectively reduce contaminants and to leave in dissolved trace minerals, such as calcium and magnesium. The proposed simple filter system was also not designed to reduce the dissolved minerals responsible for TDS in groundwater. It can also be observed from the graph that the curve showing the influent TDS is ascending with time. Because, in the dry season the groundwater contains higher level of dissolved minerals and reduces in the rain. May be that's why the curves are ascending (www.aquariacentral.com).

5.3.5 Color

Color may occur due to the presence of colored organic substances originating in the decay or aqueous extraction of natural vegetation and the presence of metals such as iron, manganese and copper. Color removal is important from the aesthetic view mainly.

Table 5.15: Color concentrations of samples for long run of 'R1double'

	Average Color (Pt-Co)	Highest Color (Pt-Co)	Lowest Color (Pt-Co)	Standard Deviation
Influent	428.67	494	388	32.49
Final Effluent	11.43	24	3	6.21

Table 5.16: Color concentrations of samples for long run of 'R2double'

	Average Color (Pt-Co)	Highest Color (Pt-Co)	Lowest Color (Pt-Co)	Standard Deviation
Influent	383.38	453	309	43.32
Final Effluent	8.95	25	2	5.93
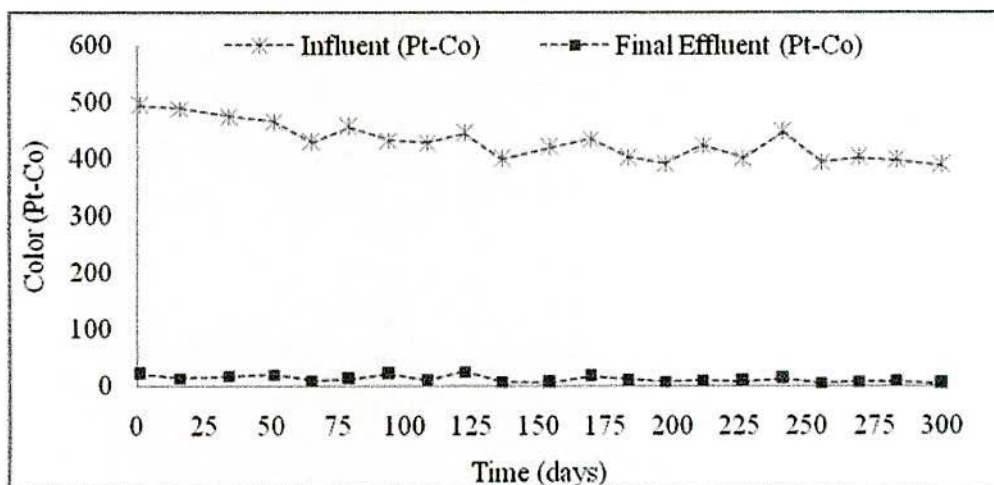
Figure 5.25: Color concentration of samples for long run of 'R1double'

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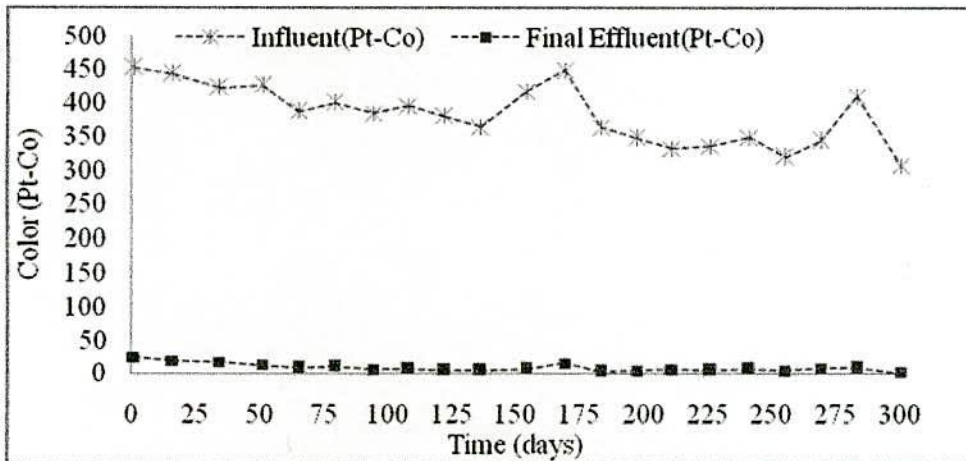
Figure 5.26: Color concentration of samples for long run of 'R1double'

Table 5.15, Table 5.16 and Figure 5.25 and Figure 5.26 represent various data of the filter units. The influent samples of both the tubewells contained highly colored groundwater. The color concentration curve was descending with time, as the amount of suspended solid causing color of groundwater decreased with time elapse. The filtration can filtrate most of the suspended solids. That's why after double filtration the filtrated water became very less-colored.

5.3.6 Turbidity

Suspended clay, silt, finely divided organic and inorganic matters cause the turbidity of the groundwater. Double unit filter units were very much effective for the turbidity reduction in this study.

Table 5.17: Turbidity concentrations of samples for long run of 'R1double'

	Average Turbidity (NTU)	Highest Turbidity (NTU)	Lowest Turbidity (NTU)	Standard Deviation
Influent	84.95	112.1	66.6	13.09
Final Effluent	2.41	6.1	0.6	1.67

Table 5.18: Turbidity concentrations of samples for long run of 'R2double'

|	Average Turbidity (NTU)	Highest Turbidity (NTU)	Lowest Turbidity (NTU)	Standard Deviation
Influent	91.18	132.8	55.2	22.91
Final Effluent	2.62	8.3	0.4	2.41
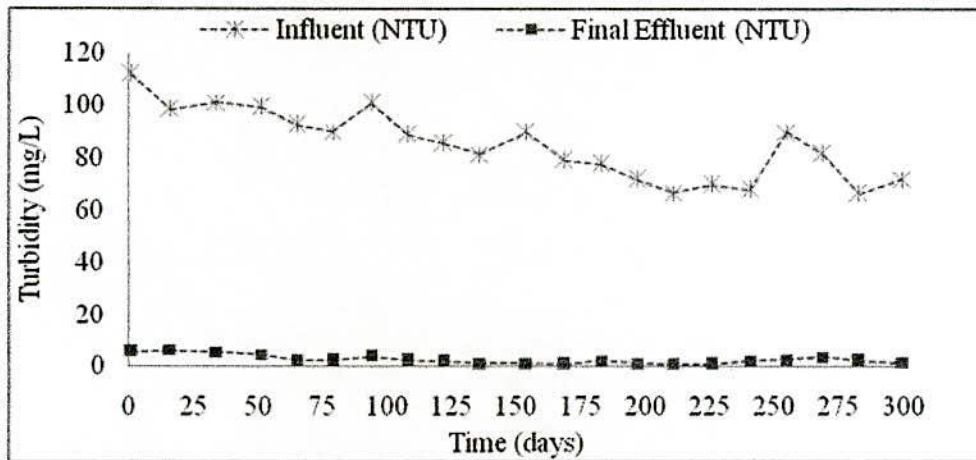
Figure 5.27: Turbidity concentration of samples for long run of 'R1double'
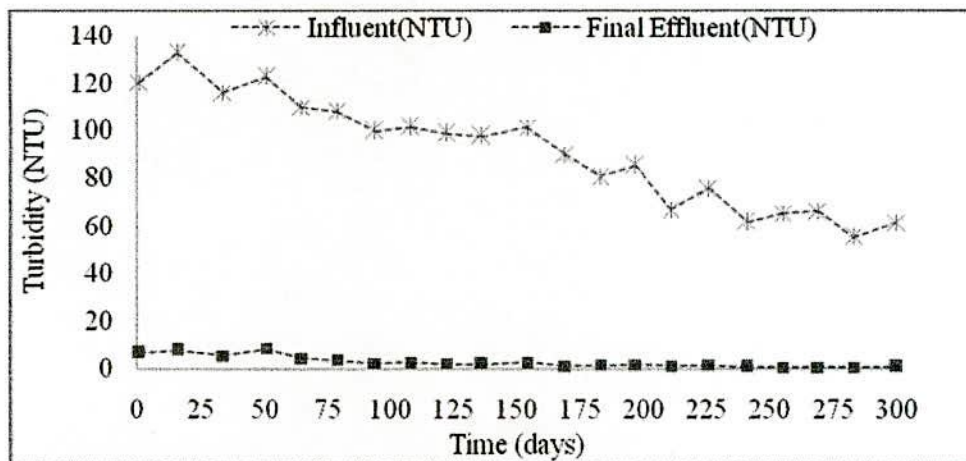
Figure 5.28: Turbidity concentration of samples for long run of 'R2double'

The tables and figures above show that the influent water was highly turbid (average 84.95 NTU for 'R1double' and 91.18 NTU for 'R2double'), which represent that the groundwater contained high level of suspended clay, silt, and finely divided organic and inorganic materials. But the filtration process was suitable enough to reduce the turbidity of the samples quite satisfactorily. Moreover, the consecutive filtration in double filtration system increased the performance. That's why the effluent samples contained very low turbidity concentrations.

5.3.7 Salinity

The samples were tested for the chloride concentration to determine the salinity and this chloride concentration was determined by the titration method. This proposed filter unit was

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not suitable for reducing the salinity level of the tubewell waters. Table 5.19 and Table 5.20 present the average, highest, lowest values of samples and standard deviation of the data.

Table 5.19: Salinity concentrations of samples for long run of 'R1double'

	Average Salinity (mg/L)	Highest Salinity (mg/L)	Lowest Salinity (mg/L)	Standard Deviation
Influent	63.69	70	55	5.57
Final Effluent	63.33	70	55	5.83

Table 5.20: Salinity concentrations of samples for long run of 'R2double'

|	Average Salinity (mg/L)	Highest Salinity (mg/L)	Lowest Salinity (mg/L)	Standard Deviation
Influent	68.81	75	60	4.15
Final Effluent	68.45	75	60	3.91

Figure 5.29: Salinity concentration of samples for long run of 'R1double'
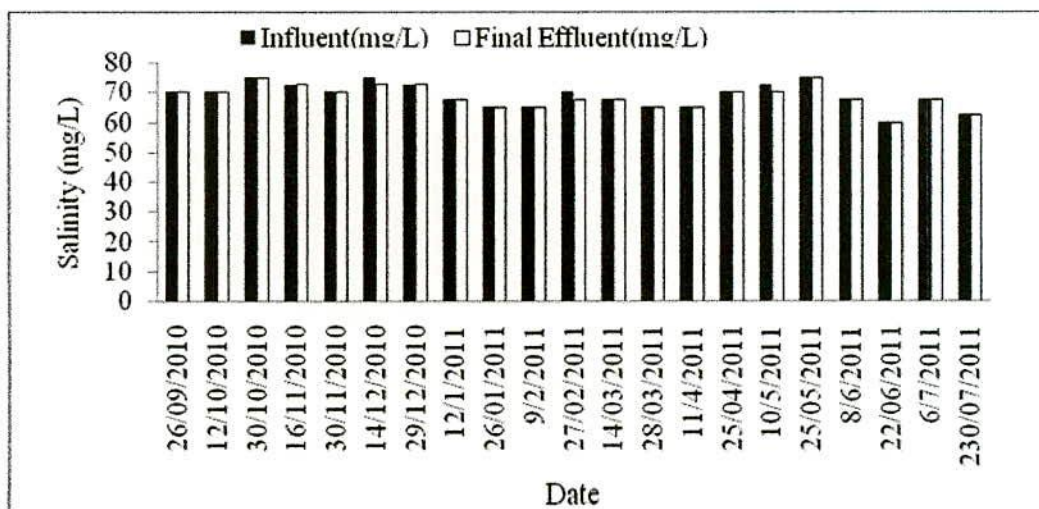
Figure 5.30: Salinity concentration of samples for long run of 'R2double'

Figure 5.29 and 5.30 express the concentrations of salinity for influent and effluent samples with respect to the dates of sampling. There is rarely any change in the salinity concentrations. The chlorides cannot be removed by simple filtration process. Therefore, the chloride and salinity removal was not satisfactory.

5.3.8 Nitrate and Nitrite

The raw water of the Rupsha sites contained no concentration of nitrate and nitrite through the monitoring period of the study.

5.3.9 Hardness

A very high level of hardness was found in the tubewell water of the households and the concentration was almost same (around 400 to 500 mg/L) all around the monitoring period. Double filtration system had almost no effect on the hardness concentration in the influent.

5.3.10 Alkalinity

The raw water was highly alkaline with values around 200 mg/L. Also the proposed filter units were no effective to reduce this alkalinity level.

5.3.11 Iron (Fe)

Influent water contained high level of iron concentration. Average values of influent Fe (2+) concentrations were 8.71 mg/L and 8.10 mg/L for 'R1double' and 'R2double', respectively.
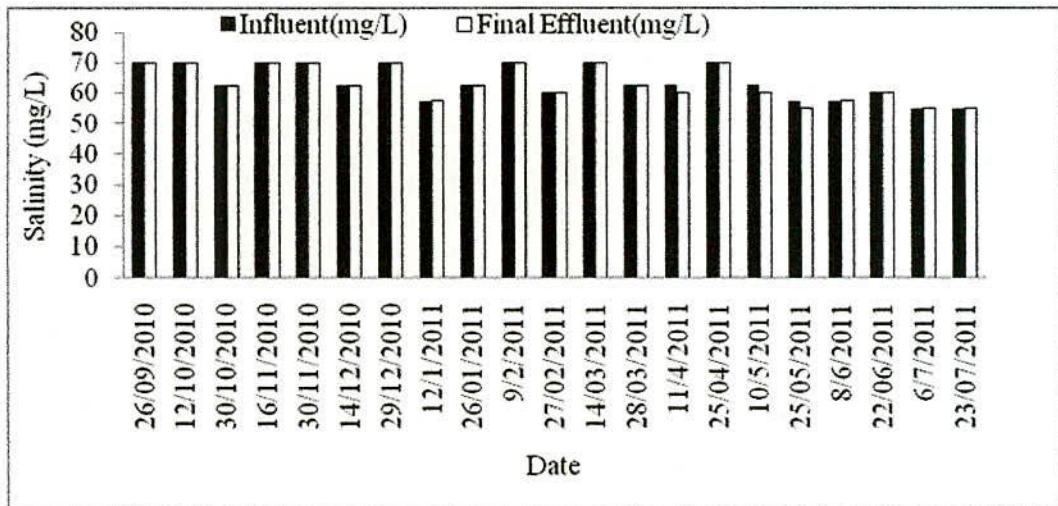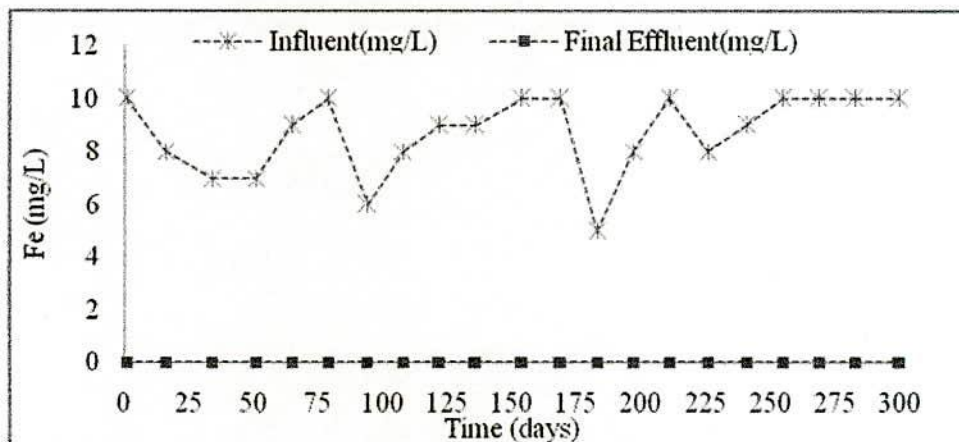

Figure 5.31: Iron concentration of samples for long run of 'R1double'

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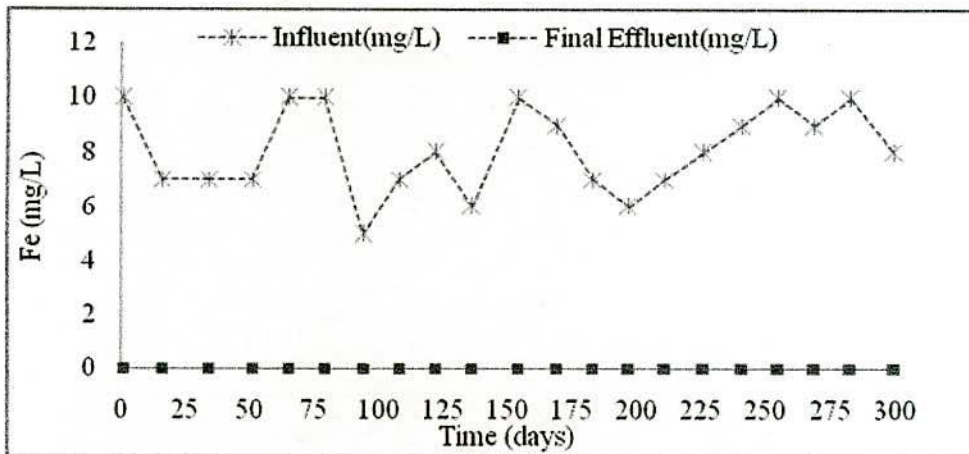
Figure 5.32: Iron concentration of samples for long run of 'R2double'

Figures show that double filtration system is fully satisfactory in iron removal. Aeration was conducted in the raw sample to increase the DO level before pouring in to the reactor. Soluble ferrous ions present in water were oxidized to insoluble ferric ions. Then the adsorption of arsenic on the ferric ions occurred, and the precipitated. As a result, high iron removal efficiency was achieved. It is clear that, Fe (2+) was completely removed by the double unit filter system.

5.3.12 Phosphorus (P)

The amount of Phosphate (PO_4^{3-}) was determined to determine the amount of Phosphorus in the samples. Table 5.21 and 5.22 describe the data for P in the samples. The determination of P concentration was accomplished by Pack Test.

Table 5.21: P concentrations of samples for long run of 'R1double'

	Average P (mg/L)	Highest P (mg/L)	Lowest P (mg/L)	Standard Deviation
Influent	1.83	2.5	0.8	0.51
Final Effluent	0.66	1	0.2	0.27

Table 5.22: P concentrations of samples for long run of 'R2double'

	Average P (mg/L)	Highest P (mg/L)	Lowest P (mg/L)	Standard Deviation
Influent	1.69	2.4	1	0.44
Final Effluent	0.69	1.5	0.2	0.40

The following figures depict the data of influent and effluent samples for P concentration for the monitoring period.

Figure 5.33: P concentration of samples for long run of 'R1double'
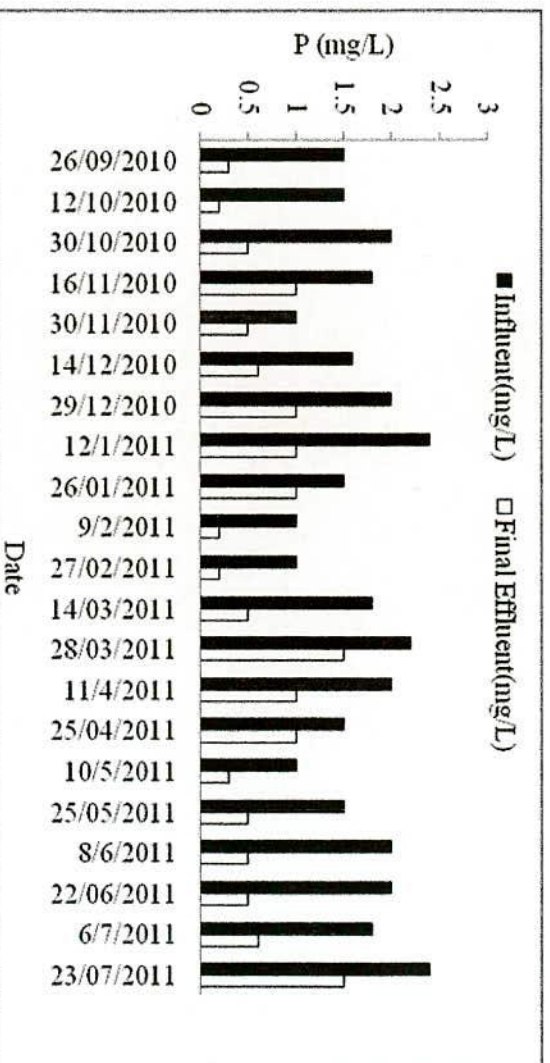
Figure 5.34: P concentration of samples for long run of 'R2double'

The graphs show influent and effluent concentration in every sampling date. Arsenate and phosphate have similar chemical and biological properties and they compete with each other in iron hydroxides adsorption. In this double filtration, consecutive filtration occurs and performance in P removal improves.

5.3.13 Silica (Si)

Average, highest and lowest Si concentration and standard deviation (S.D.) for influent and effluent data is shown in Table 5.23 and Table 5.24. Figure 5.35 and Figure 5.36 represent the values of Si for various samples with sampling dates for both 'R1double' and 'R2double'.

Table 5.23: Si concentrations of samples for long run of 'R1double'

	Average Si (mg/L)	Highest Si (mg/L)	Lowest Si (mg/L)	Standard Deviation
Influent	47.38	65	30	10.20
Final Effluent	31.67	45	20	6.39

Table 5.24: Si concentrations of samples for long run of 'R2double'

	Average Si (mg/L)	Highest Si (mg/L)	Lowest Si (mg/L)	Standard Deviation
Influent	47.38	65	30	10.20
Final Effluent	31.67	45	20	6.39

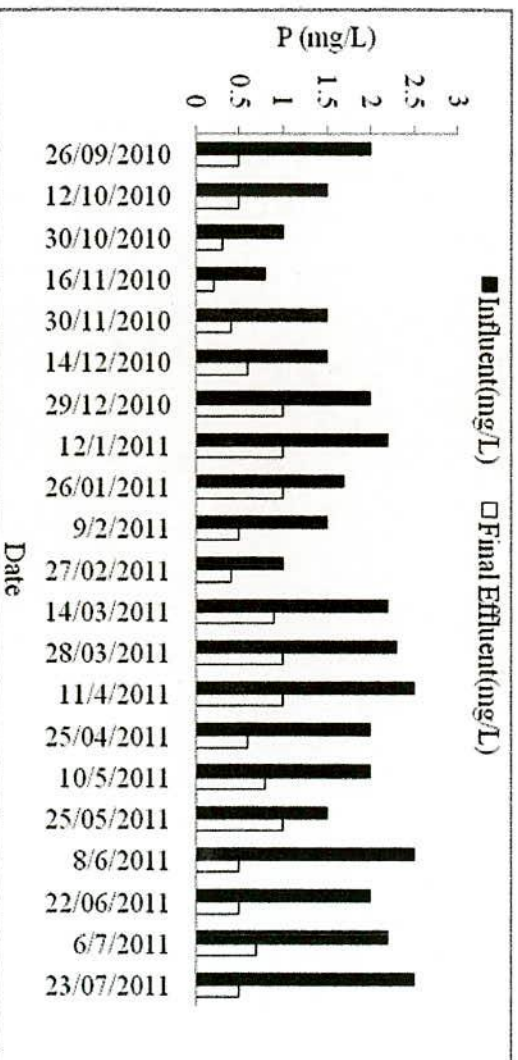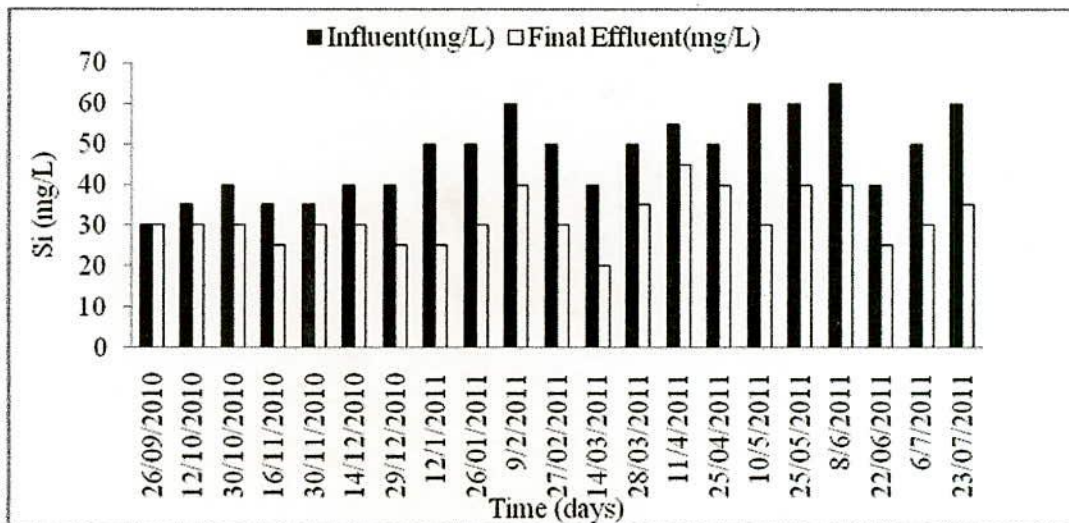Figure 5.35: Si concentration of samples for long run of 'R1double'
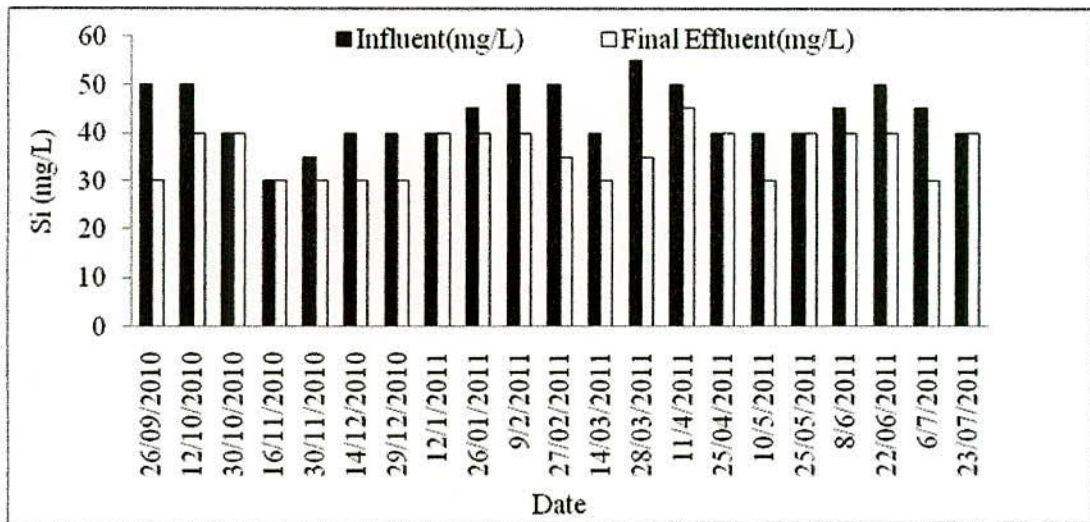
Table 5.36: Si concentrations of samples for long run of 'R2 double'

It can be easily observed from the above graphs that the filter system, even with double filtration, is not suitable enough to reduce the Si concentration from the raw water. Because the adsorption of Si on oxidized iron-hydroxides present in the system was not enough. Also the there was a competition for the adsorption on iron-hydroxides among As, Si, P and others. As a result, there was a chance to decrease the performance of individual adsorption rate.

5.3.14 Arsenic (As)

Tubewell water was highly arsenic contaminated. Double unit filter system was being run and monitored to evaluate the performance of the double unit system, as it was found earlier that single unit systems could not be able to reduce the arsenic level to allowable limit. The performances of double unit filters are presented by the following tables and figures.

Table 5.25: As concentrations of samples for long run of 'R1double'

	Average As (μg/L)	Highest As (μg/L)	Lowest As (μg/L)	Standard Deviation
Influent	418.86	465	387	19.03
Final Effluent	50.10	71	38	8.98

Table 5.26: As concentrations of samples for long run of 'R2double'

	Average As (μg/L)	Highest As (μg/L)	Lowest As (μg/L)	Standard Deviation
Influent	416.19	450	355	25.37
Final Effluent	52.86	75	38	9.28
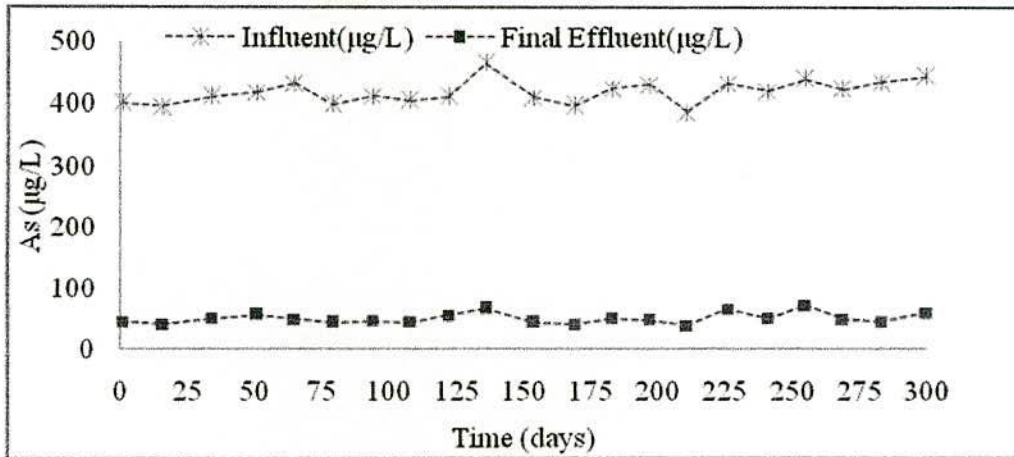
Figure 5.37: Arsenic concentration curves for 'R1double'
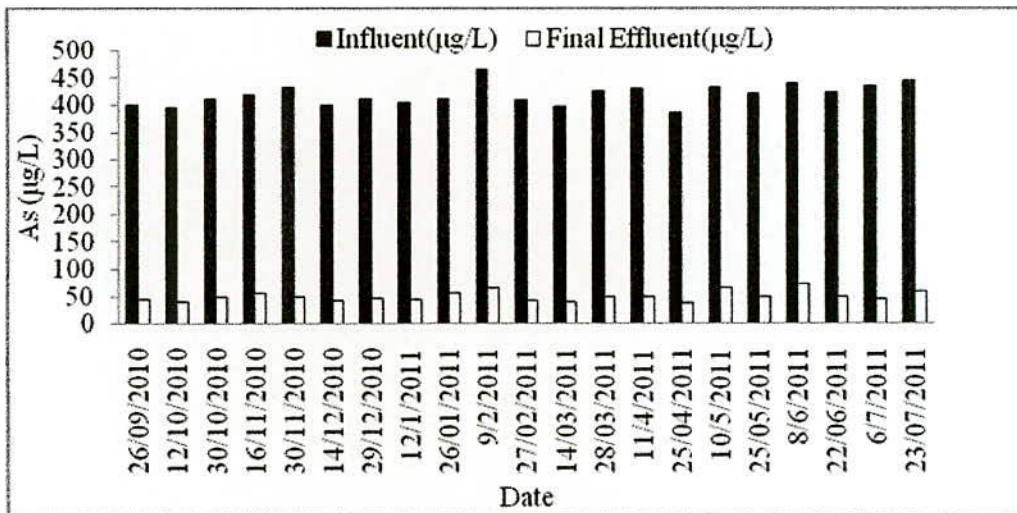
Figure 5.38: Arsenic concentrations of influent and effluent of 'R1double'
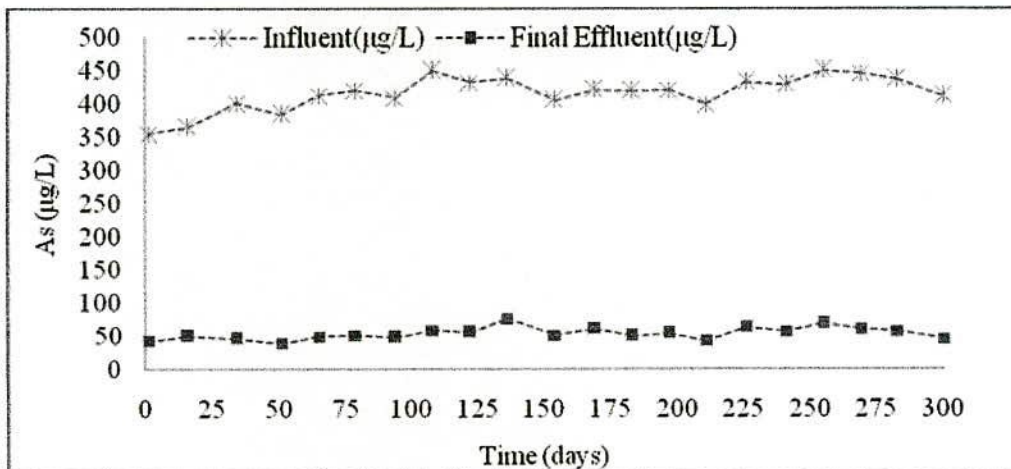
Figure 5.39: Arsenic concentration curves for 'R2double'
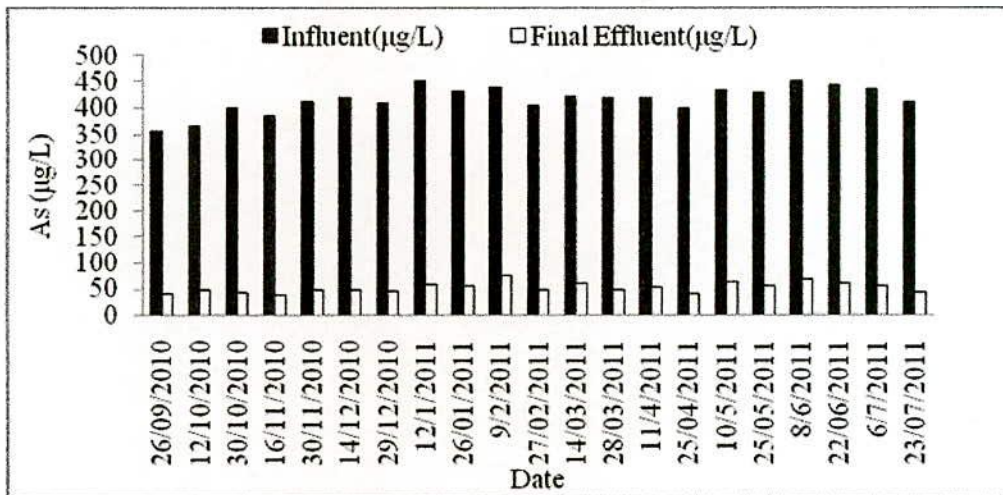
Figure 5.40: Arsenic concentrations of influent and effluent of 'R2double'

It was found that, in most cases, the effluent water of the Connect system of double unit system contained arsenic concentration around the allowable limit. The removal efficiency was nearly same for the whole study period. And influent arsenic concentration did not differ much. Average removal efficiency for 'R1double' and 'R2double' were 88.19% and 87.33%, respectively. The consistency in the performance also indicates that the release rate of iron-hydroxides and the consequent adsorption were also consistent.

5.3.15 Flow Rate

It was natural that, the flow rate decreased in case of double unit filtration systems. In the long run of monitoring, the flow rate decreased significantly with time.
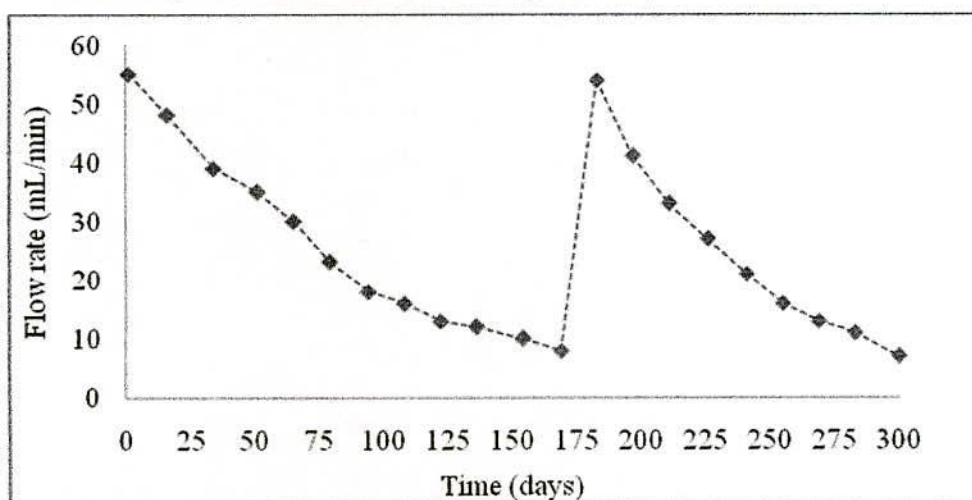
Figure 5.41: Flow rate with time for 'R1double'

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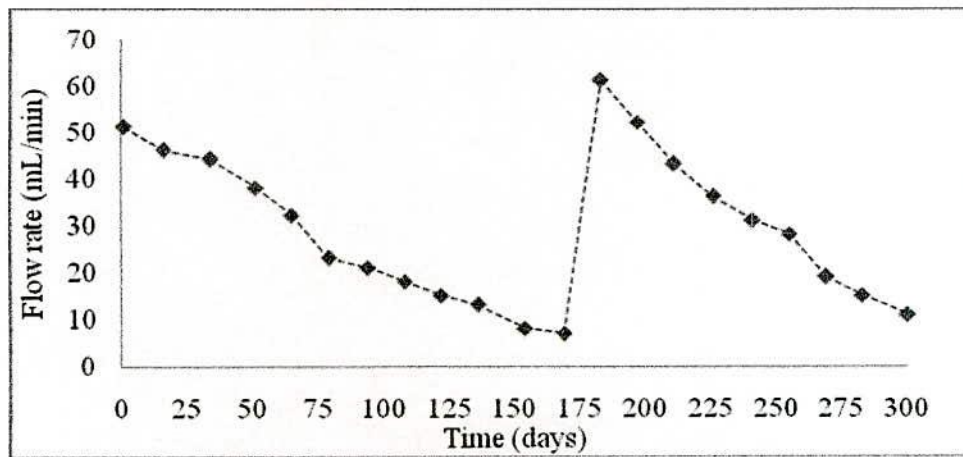
Figure 5.42: Flow rate with time for 'R2double'

However, the flow rate curves for 'R1double' and 'R2double' are presented in Figure 5.41 and 5.42. With every operation, the surface of the filter was having clog. As a result flow rate decreased every day. In every sampling point, the filter surface was cleaned with soft clothes. When the flow rate was below 10 mL/min, then the upper filter was changed. That's why there is sudden increase in flow rate. In these points the filter with the upper reactors were changed due to very low flow rate. This change occurred in 183 days from the starting of the monitoring.

CHAPTER 6

Conclusion and Recommendations

6.1 Introduction

The project focused on the development, and also the checking of the performances of that filter unit. The filter unit worked in the biological oxidation process by the cultured iron bacteria for arsenic removal. This filter unit was firstly installed with iron net as the source of the iron. After that, single unit filter systems with different iron options as iron net, scrap iron and iron rod were installed and run for long time. These two attempts were taken to check the suitability of single unit filter systems in case of household tubewells with highly arsenic contaminated water. Double unit filter systems were then developed and installed in the field. Firstly double unit filter systems with both 'W-system' and 'Connect system' were installed and run to compare the performances. It was found that, there was no big change in the performances of these two systems. Then double unit filter systems with 'Connect system' were being run continuously for the long run.

The detail results were presented in Chapter 4 and Chapter 5 in this report. Now the main findings of this whole study are going to be mentioned in very precise form.

6.2 Major Findings for Single Unit Filter Systems with Iron Net

- In case of arsenic removal, the single unit system was not able to reduce the arsenic concentration level to allowable limit, as the raw waters of all the sites were highly contaminated. For 'R1single', average influent and effluent values were 361 µg/L and 128 µg/L, the removal efficiency was 65.56%. For 'R2single', the influent and effluent values were 396 µg/L and 130 µg/L, the removal efficiency was 67.34%.

- In case of iron removal, single unit filter system was fully successful and was able to reduce to zero concentration in almost every stage. Average influent values were 8.56 mg/L and 9.16 mg/L for 'R1single' and 'R2single' respectively, while average effluent value was nearly zero, removal efficiency was 100%.

- Phosphorus removal performances were quite more satisfactory, but not the Silica removal. For 'R1single' single unit filter system with iron net, average P influent and effluent values were 1.72 mg/L and 0.45 mg/L. For 'R2single', the values were 1.3 mg/L and 0.36 mg/L respectively. For 'R1single', average Si influent and effluent values were 44.53 mg/L and 34.84 mg/L, while for 'R2single', the values were 40.63 mg/L and 34.22 mg/L respectively.

- The flow rates decreased with time for both filters. In 32 days from starting, it decreased from 156 mL/min to 66 mL/min for 'R1single' and from 194 mL/min to 60 mL/min for 'R2single'.

6.3 Major Findings for Comparison among Single Unit Filter Systems with Iron Net, Scrap Iron and Iron Rod

- Arsenic removal efficiency of single unit filter systems with iron net, scrap iron and iron rod were more or less same. The average removal efficiency of filters with iron net, scrap iron and iron rod were 73.63%, 74.42% and 73.73% respectively during the long run of the filter units in the field level.

- Iron removal was successfully accomplished by every option as iron net, scrap iron or iron rod and reduced average 7.90 mg/L of influent concentration to zero concentration.

- Phosphorus removal was completed almost satisfactorily. Average values of P of influent, and effluents with iron net, scrap iron and iron rod were 2.60 mg/L, 0.66 mg/L, 0.68 mg/L and 0.67 mg/L respectively. Silica values were not reduced due to filtration by any one of the iron options.

- The turbidity of the raw water samples were reduced significantly by the filtration process. Average influent, and effluents with iron net, scrap iron and iron rod values for turbidity were as follows 98.99, 10.25, 10.65 and 10.79 NTU.

- Color removal efficiency was very high for our proposed single unit filter systems. Color removal efficiency for influent, and effluents with iron net, scrap iron and iron rod were as follows 97.15%, 94.70% and 97.11%.

- From the flow rate values of the long run, it was found that the flow rate decreasing patterns for different filter options were nearly same.

6.4 Major Findings for Comparison between W-System and Connect System of Double Unit Filter System

Prior to the long run of the double unit filter system in field level; a short study was performed in the same household to choose the way of double filtration ('W-system' or 'Connect system'). The results are shown in points as follows:

- Arsenic removal efficiency was nearly same in case of double unit filter systems with 'W-system' and 'Connect system'. In 'W-system', the removal efficiency in 1st effluent and 2nd effluent were as 63% and 86.21%. And in 'Connect system', the final removal efficiency was 83.96%. The average values of influent, 1st effluent, 2nd effluent and final effluent were as 406 µg/L, 149 µg/L, 57 µg/L and 65 µg/L for 'R1double'; while 421 µg/L, 151 µg/L, 57 µg/L and 62 µg/L for 'R2double'.

- Iron removal was fully satisfactory in both ways of double filtration.

- Naturally flow rates decreased rapidly in case of double unit filter system as the final effluents were found after 2 steps of filtration. There was no big effect on the way of double filtration on the flow rates.

So, from these points of view it may be concluded that, whatever the way of double filtration ('W-system' or 'Connect system'), the performances had no huge change. But, from the comments of the user of the filter systems in the field it was found that they prefer 'Connect system' to run as the 1st effluent automatically fell in the 2nd reactor in the system. So, for long run in the next stage of the study, 'Connect system' was selected.

6.5 Major Findings for Monitoring of the Performance of 'Connect System' of Double Unit Filter System

- Most of the cases, the double unit filter system was proved effective to reduce the arsenic concentration to the allowable standard limit (Bangladesh Standard 50 µg/L). Average removal efficiency of 'R1double' and 'R2double' for the long monitoring study was 88.19% and 87.33% respectively. Average influent and final effluent arsenic concentrations were 419 µg/L and 50 µg/L for 'R1double', and 416 µg/L and 53 µg/L for 'R2double'.

- Iron removal was 100% for both 'R1double' and 'R2double' through the full study time.

- Phosphorus removal efficiency was quite satisfactory for the double unit filter system. The removal efficiency was 63.55% and 60.88% respectively for 'R1double' and 'R2double'. Silica removal efficiency was not good enough. Average removal efficiency was 31.77% and 16.49% respectively.

- Turbidity removal was great by double unit filter systems. The removal efficiency was 97.30% and 97.50% for 'R1double' and 'R2double' respectively.

- In case of color removal the double unit filter system was successful as the removal efficiency for 'R1double' and 'R2double' filter units were 97.40% and 97.77% respectively.

- For the long run of the study, the DO values increased in high amount. The average influent and effluent values were 1.75 mg/L and 7.11 mg/L for 'R1double' and 1.82 mg/L and 7.10 mg/L for 'R2double'.

- Flow rate or the production rate was one of the main needs for the sustainability of the treatment technology. In our study, the flow rate started to reduce in every sampling period. The cleaning of the filter surface was conducted in about every 2 or 3 weeks. The upper filter unit was required to change due to very low flow rate for the both unit systems in 183rd days from the starting of the monitoring.

6.6 Concluding Remarks

The major findings of the projects can be concluded as:

- The single unit system of this study was proved 'not fully successful' in case of very highly arsenic contaminated tubewell water treatment. Whatever the iron producing option in the single unit filter system (Iron net, scrap iron or iron rod), the performances remain almost same.

- There is no big difference in the performance of two ways of double filtration ('W-system' or 'Connect system').

- Arsenic removal was satisfactory for double filtration in case of highly arsenic contaminated groundwater treatment.

- Iron, color and turbidity removal were satisfactory for single and double filtration.

6.7 Recommendations for Future Works

The study recommends that the proposed single unit filter system can be successfully used in case moderately contaminated groundwater treatment. Also, in most cases the double unit systems may be effective for more intensely contaminated groundwater treatment. But, before mass-utilization, more research and monitoring should be conducted specially covering following areas.

- Field study in different water quality conditions
- Microorganism characteristics of samples
- Sludge characteristics and disposal procedure
- Clogging on filter surface and provision for flow rate increasing
- Effect of DO on arsenic removal efficiency
- Correlation among various water quality field data, etc.

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