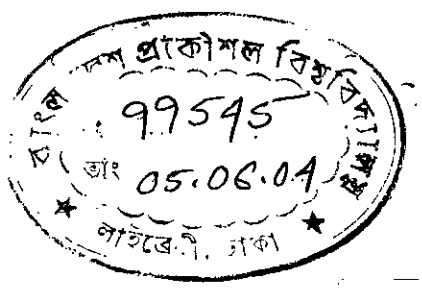
QUANTIFICATION OF ARSENIC RELEASE FROM ARSENIC RICH WASTES AND SOIL IN PRESENCE OF COWDUNG

A Thesis

by

MOHAMMAD AZIZUR RAHMAN

In partial fulfillment of the requirements for the degree
of
MASTER OF SCIENCE IN ENGINEERING (CIVIL)



Department of Civil Engineering
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A thesis approved as to style and content
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ABSTRACT

To combat the arsenic crisis, a number of household and community based arsenic removal technologies have been developed and a number of such technologies are currently being used in many arsenic affected areas in Bangladesh. All arsenic removal units generate some form of arsenic-rich wastes. Currently, disposal of such wastes in cow-dung bed is widely practiced. It has been suggested that biochemical processes in cow-dung bed transform inorganic arsenic into volatile forms and release them into air. In this study elimination of arsenic from arsenic solution, arsenic rich wastes and soil was evaluated in the laboratory. Role of phosphate in displacing arsenic from soil was also observed. Batch experiments were done to assess the elimination of arsenic from arsenic solution (unbound arsenic), arsenic rich wastes and soil (bound arsenic) in the presence of cowdung. Different concentrations of arsenic were mixed with different weight of fresh cowdung and the elimination of arsenic was studied under both cap-open condition (for simulating aerobic condition) and cap-closed condition (for simulating anaerobic condition).

Results of batch experiments performed on a wide range of arsenic aqueous solution suggest that, in general, significant elimination of arsenic (III) occurred from aqueous solution in the presence of fresh cowdung. The range of elimination was 13% to 96%. Majority of this elimination appeared to take place during the first few days. The results of this study suggest that the elimination of arsenic is not proportional to the amount of cowdung added to the aqueous solutions and initial concentration of arsenic in aqueous solution. Similar results were obtained for the batch experiments with As (V) aqueous solution. With arsenic rich wastes (Steven's Technology for arsenic Removal unit and Bucket Treatment Unit), the range of elimination was 9% to 69%. The elimination of arsenic from soil was observed 2% to 25% without using cowdung whereas the range of arsenic elimination was 52% to 89% with using cowdung. This study also suggest that elimination of unbound arsenic (aqueous solution) is quite high compared to bound arsenic (arsenic in wastes and soil.) In some cases it has been found that with increasing initial arsenic concentration elimination of arsenic decrease but more study is needed to ascertain this. The possible reason for great variation in the elimination of arsenic from solutions and wastes are variability in the number and type of microorganisms present in cowdung and in the availability of nutrients. Again, it has been found that As (V) reduced to As (III) before elimination, which has been suggested in literature. The ability of phosphate in displacing arsenic from soil was also

observed in laboratory. From the study it can be suggested that bio-chemical processes eliminate arsenic from arsenic rich wastes and soil in the presence of cowdung but the reaction involved, type of volatile arsine produced, characteristics of microorganism present in the cowdung should be studied in more detail for better understanding of the elimination process.

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Mohammad Azizur Rahman

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Chapter-I
Introduction

1.1 Background

Widespread arsenic contamination of groundwater has become a major threat to the water supply sector in Bangladesh. In Bangladesh, an estimated 268 Upazilla out of 465 have been affected with significantly high concentrations of arsenic (Ali et al., 2003). Here tubewell water extracted from shallow aquifers is the primary source of drinking/cooking water for most of its population. An estimated 28 million people are exposed to arsenic concentrations in tubewell water above the Bangladesh drinking water standard of 50 ppb (Begum, 2001) and many people are reported to have already been suffered from arsenicosis by drinking arsenic contaminated water (EES/DCH, 2000; Rahman et al. 2000).

The focus must now shift, and is shifting, away from identification of the problem towards finding solutions to the problem. There needs to be a parallel emphasis on both short and long term solutions to the arsenic problem. Now the arsenic problem not only associated with finding out the removal technologies but also to find out safe disposal options for the arsenic rich wastes produced from arsenic removal units.

1.2 Present State of the Problem:

All technologies that remove arsenic from groundwater produce arsenic rich waste either as a solid or a liquid. The volume of waste, and concentration and chemical stability of arsenic in the waste, depend the concentration of arsenic in the raw water and the treatment technology used. Broadly, the arsenic rich waste materials can be classified into: (a) wastes generated from coagulation/ precipitation based systems, and (b) wastes generated from systems based on adsorptive filtration and other techniques (e.g., ion exchange). The waste belonging to the first category is primarily slurry containing coagulated flocs of alum or iron salt, rich in arsenic. The waste belonging to the second category are primarily spent adsorbents or ion exchange resins, rich in arsenic.

In the absence of any clear guideline for safe disposal of wastes generated from arsenic removal units, the wastes are often disposed of in the open environment, especially on

cowdung bed. With increasing use of arsenic removal units, concerns have been raised regarding safe disposal of these wastes and possible contamination of environment from arsenic present in the wastes. However, there is only limited data on the quantities and characteristics of these wastes (e.g., Hamel and Zinia, 2001) and possible mobilization of arsenic from these wastes.

1.3 Rationale of the Study

The villagers usually dispose their arsenic rich wastes on cowdung bed . It has been suggested that microorganisms present in cowdung transform inorganic arsenic to volatile form and release it into air. Though little knowledge is available about the transformation of arsenic into volatile form in presence of cowdung, most of the researchers suggested to dispose the wastes from arsenic removal units on cowdung bed and this is now the common practice of household arsenic waste disposal. Cowdung is a widely available marvelous resource that is constantly being produced and deposited in large quantities in rural areas. Even though it has passed through an animal's digestive tract, dung retains many nutrients. Thus, it attracts its own fauna and flora consisting of bacteria, fungi, protozoa, platyhelminths, nematodes, annelids, and arthropods (Hauser, T. Juliana, 2000). There is much possibility of biotransformation of arsenic in the presence of cowdung. Again, as little work has been done to find out proper arsenic waste management, a study is needed to examine the extent of arsenic release from arsenic rich wastes in presence of cowdung. In rural areas cowdung is also used as fertilizer and bio-mass in agricultural land to improve the quality of soil. Literature suggests that there has been a lot of work done about bio-remediation of arsenic contaminated soil (Turpeinen et. al., 2001). So, the microorganism present in cowdung may also enhance the mobility of arsenic in soil. Again, chemical fertilizers are also applied to agricultural lands to enhance crop yield especially for irrigated crops. Arsenic from irrigation water may be adsorbed on the soil particles. The adsorbed arsenic may be transformed/bio-transformed and realesed in the presence of cowdung and phosphate fertilizer. But the processes of transformation/ biotransformation and release of arsenic in the agricultural fields are not clearly understood and quantified. Increased bio-methylation and volatilization of gases from soil can reduce arsenic accumulation in agricultural fields (McLaren et. al., 2001). A study is needed to quantify the release of arsenic under the above mentioned conditions. This quantification will help in developing appropriate arsenic waste management techniques and methodologies.

1.4 Objectives of the Study

The overall objective of this study is to get a better understanding and quantification of arsenic release from arsenic rich wastes and soil due to biochemical processes in the presence of cowdung.

The specific objectives of the study are:

i. To quantify the elimination of arsenic from aqueous solution in presence of cowdung.
ii. To asses the elimination of arsenic from arsenic rich slurry generated from different types of arsenic removal unit in presence of cowdung
iii. To quantify the elimination of arsenic from aqueous solution in presence of arsenic rich agricultural soil.
iv. To asses the elimination of arsenic from arsenic rich agricultural soil in presence of cowdung.
v. To quantify the role of phosphate in eliminating arsenic form arsenic rich agricultural soil.

1.5 Methodology

A brief description of the procedures followed to achieve the objectives of the research work is given below:

- As(V) stock solution was prepared by dissolving arsenic salts $Na_2HAsO_2.7H_2O$ in distilled water. As(III) stock solution was prepared by dissolving arsenic trioxide (As_2O_3) in distilled water containing sodium hydroxide (NaOH).
- Groundwater from a tap at the Environment Engineering Laboratory of the Department of Civil Engineering, BUET was used as the source of water to conduct the laboratory experiments.
- Arsenic elimination experiments in laboratory were conducted by placing arsenic rich wastes or soil in tubes in two experimental set up. In the first experimental set up all experiments were done under cap-open and cap-closed condition and in second experimental set up all experiments were done only for cap-open condition.
- In this study, caps of the tubes were kept open for simulating aerobic condition and for simulating anaerobic condition caps were kept closed after purging N_2 for two minutes.
- Arsenic-rich wastes were collected from two different types of coagulation-based systems. These were (i) STAR bucket treatment (based on iron coagulation) collected from Laksmipur district, and (ii) UNU-BUET bucket treatment unit (based on ferric

chloride coagulation) collected from the UNU-BUET field site at Adda village in Barura upazilla of Comilla district.

- Top soil of agricultural field was collected from Srinagar, Munshiganj for conducting experiments.
- Centrifuge machine was used to separate the liquid portion of the arsenic wastes from the solid portion. The centrifuge was done at the maximum speed (3200 rpm) for 20 minutes.
- Standard digestion procedure (with aqua-regia) was followed for digestion of cowdung, soil and the solid portion of the Cowdung-sludge mixture for determining the arsenic content
- Arsenic analysis of slurry samples was carried out with atomic absorption spectrophotometry using a GF-AAS (Shimadzu, AA6800).
- Some samples were analysed for several times in order to check the interference of organic carbon present in cowdung and no interference was observed.

1.6 Organization of the Study

A brief description of the organization of the thesis is enumerated below.

The thesis is composed of six chapters followed with a list of reference used for the study.

Chapter 1 gives a brief background of the study, the present state of problem, rationale of the study, objectives and the methodologies of the experiments that were adopted

Chapter 2 presents the detail review of existing literature. This chapter describes the properties and composition of arsenic, chemistry of arsenic, methylation of arsenic. This chapter also reviews the type of treatment waste and their disposal options inadditon with reviews of previous studies.

The methodology, results and discussion of the elimination of arsenic from aqueous solution in presence of cowdung are provided in chapter 3.

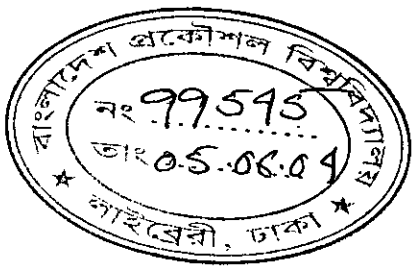
Chapter 4 provides the methodology, results and discussion of the elimination of arsenic from arsenic rich wastes in presence of cowdung

Chapter 5 presents the methodology, results and discussion of the elimination of arsenic from arsenic rich agricultural soil in presence of cowdung and arsenic solution. The study on the role of phosphate fertilizer in displacing arsenic from soil are also described in this chapter.

Chapter-6 presents the conclusions, limitations and recommendations of the study.

Chapter – 2

Literature Review



2.1 Introduction

The extent of the arsenic problem in Bangladesh is without doubt. Now the arsenic problem not only associated with finding out the removal technologies but also to find out safe disposal options for the arsenic rich sludges produced from arsenic removal units. Also the fate of arsenic, that is accumulated on to the top soil of the agricultural field is a quest of today. This chapter presents a review of literature concerning occurrence, source, chemistry and its behavior in the environment. Again, this chapter will also review the available arsenic removal techniques, types of waste generated, disposal options, microorganisms present in cowdung and role of microorganisms on arsenic chemistry (bound or unbound arsenic) and geo-chemistry.

2.2 Arsenic in the Environment

Arsenic is the 20^{th} most abundant element in the earth's crust and the 12^{th} most abundant element in the biosphere, where it is said to be an essential element at least for some animal species, but not for human. Arsenic is the king of poisons and has plagued human beings since the days of antiquity. As a carcinogen, it has been well known since early times. In Asia, arsenic is both a cause of large-scale environmental contamination and a serious health-hazard. Arsenic is a toxic chemical and may pollute air, soil, sediments and water causing health hazards to both human and animal's life. Arsenic is found to occur in nature as mineral form which, by way of erosion and deposition, soil may be contaminated. Water pollution by arsenic, below indicates the approximate environmental concentration levels and human exposure through the air, food and water.

At high concentrations (76 mg arsenite), arsenic could be lethal to human body. Arsenic is a dietary constituent and is present in many foods such as meat, fish, poultry, grain and cereals.

Table 2.1 Approximate Environmental Concentration Levels and Human Exposure Through the Air, Food and Water (Data from WHO, 1996).

Medium	Concentration	Daily Intake	Daily exposure	Remarks
Air	0.4-30 ng/m^3	20m^3	0.01-0.6µg	May be much higher in industrial areas
Food	0.4-120µg/kg	1kg	0.4-120µg	70% is organic As and 25% is inorganic As
Water, Generally	1-2µg/L	2 L	2-4µg	Mainly inorganic As(III) most toxic
Water, up to	12000µg/L	2 L	24000µg	Causing endemic illnesses

Arsenic is found in everywhere in the environment. It is found in atmosphere, biosphere, hydrosphere, pedosphere and geosphere and transferred from one to another by natural processes or human activities such as mining, agriculture, industrial processes etc. The environmental cycle of arsenic is shown in figure 2.1.

Arsenic is mainly found in the form of its mineral compounds and widely distributed in air, water, soils and in rocks and earth crust. The relative proportion of arsenic in rock, soil, water, biota and atmosphere with respect to soil is shown in Table 2.3. It may be seen that rocks and minerals are the main reservoirs of arsenic, which is mobilized in the other media of the environment by natural weathering processes, biological activity, volcanic eruption and anthropogenic activities.

The people of Bangladesh overwhelmingly depend on groundwater as their source of water. Since arsenic pollution of groundwater is a serious problem due to toxicity of arsenic, alternative sources or removal of arsenic from groundwater in the affected areas of Bangladesh are the options to provide safe drinking water.

Collection or purification may be more costly and laborious than treatment of groundwater contaminated with arsenic. Various methods are available for dearsination. Very little research has been carried out in Bangladesh to find the suitability of the available processes of arsenic removal. Hence it is very much appropriate to carry out a study to develop low cost treatment methods for dearsination.

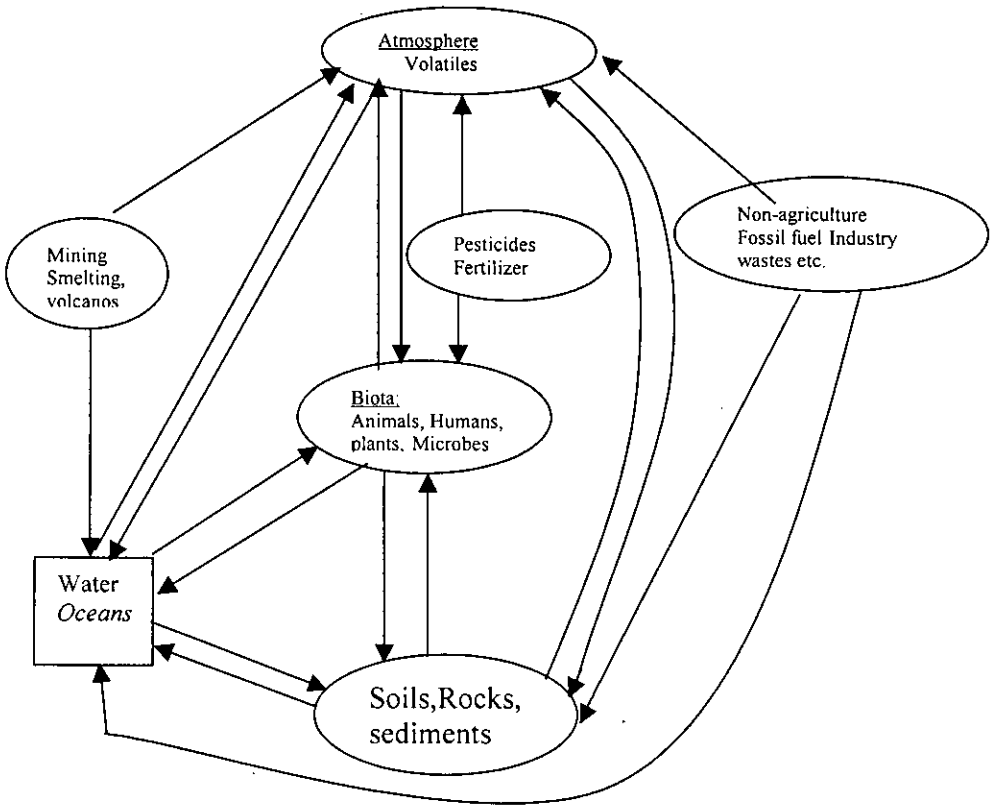


Figure 2.1: The Environmental Cycle of Arsenic (after Bhumbla and Keefer, 1994)

2.3 Principal Compound of Arsenic

Arsenic is a chemical element in the nitrogen family (group VA of the Periodic Table), existing in both grey and yellow crystalline forms. Although some forms of arsenic are metal-like, it is best classified as metalloid and non-metal. It can be manufactured in three allotropic forms, the yellow (α) form, the black (β) form and the steel grey (γ) form. These have different physical properties (Encyclopedia Britannica, 1994). Apart from the elementary arsenic, where the oxidation state by definition is 0, arsenic is stable in its states +5, +3 and -3. Some important properties of arsenic are listed in Table 2.2

Because arsenic has a range of oxidation states from -3 to +5, it can form a variety of different kinds of compounds. Among the most important commercial compounds are oxides, the principal forms of which are arsenious oxide (As_2O_3) and arsenic pentoxide (As_2O_5). Arsenious oxide, commonly known as white oxide, is the material most widely used for the synthesis of arsenic compounds. It is produced as a by product of the nonferrous metal industry, primarily from the smelting of copper ores. Naturally occurring metal arsenide's realgar and orpiment also convert to the trivalent oxide when roasted in air. The formation of the trioxide by the roasting of a sulfide ore is illustrated in Eq. (2-1) :

Table 2.2: Properties of Arsenic (Encyclopedia Britannica, 1994)

Parameter	Value
Atomic number	33
Atomic weight	74.92158
Melting point (gray form)	814^0C at 36 atm
Boiling point	616^0C (sublimes)
Density (gray form)	5.73 g/cm^3 at 14^0C
Density (yellow form)	2.03 g/cm^3 at 18^0C
Specific gravity (α, β, γ)	2.026, 4.700, 5.727
Latent heat of fusion	27,740 J/(mol-K)
Latent heat of sublimation	31,974 J/(mol-K)
Oxidation number	-3,0,+3,+5
Electronic configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$ (2-8-18-5)
Electrical resistivity	33.3 µohm cm (273 K)
Crystal system (grey form)	Hexagonal (rhombohedral)
Lattice constant at 26^0C	a = 0.376 nm, c = 1.0548 nm
Covalent radius	121 pm
Ionic radius (As^{+3})	69 pm
Metallic radius	139 pm
Hardness (Mohs' scale)	3.5

$$2\ FeAsS + 5\ O_2 \longrightarrow Fe_2O_3 + As_2O + 2\ SO_2 \qquad (2\text{-}1)$$

Elemental arsenic undergoes reaction with oxygen to yield the trioxide as follows:

$$4\ As + 3\ O_2 \longrightarrow 2\ As_2O_3 \qquad (2\text{-}2)$$

The trioxide is moderately soluble in water, but dissolves easily in aqueous alkali to produce a solution of arsenic, AsO^{2-}. It is slightly soluble in polar organic solvents such as alcohols and ethers and insoluble in benzene. The most useful reagent for the synthesis of pentoxide (As_2O_5) is concentrated nitric acid. The reaction between elemental arsenic and nitric acid gives H_3AsO_4. The controlled dehydration of this acid (Eq.3) gives the pentoxide.

$$4\ H_3AsO_4 \longrightarrow 6\ H_2O + As_4O_{10} \qquad (2\text{-}3)$$

Hypochlorous, hydrochloric and perchloric acids also oxidize the metal or As_2O_3 to the pentavalent state. Arsenic pentoxide dissolves readily in water to produce arsenic acid, H_3AsO_4. Arsine (AsH_3) is the best known of the hydrides of arsenic. It is a colorless poisonous gas composed of arsenic and hydrogen. The gas also called arsenic hydride is produced by the hydrolysis of metal arsenides and by the reduction by metals (e.g. zinc) of arsenic compounds in acidic solutions. Other hydrides of arsenic are diarsine (As_2H_4), diarsine hydride (As_2H_2), and polymeric diarsine monohydride $(As_2H)_x$.

Arsenic pentoxide, the anhydride of arsenic acid (H_3AsO_4) is very soluble in cold water and dissolves to form a solution of arsenic acid. The free acid can be obtained as a hydrate,

H_3AsO_4. 0.5 H_2O, by the evaporation of a cold aqueous solution. Arsenic trioxide is the anhydride of arsenious acid. The solubility of arsenic trioxide in water at 25^0C is 21.6 g/L. The rate of dissolution of trioxide in water is painstakingly slow, sometimes requiring up to 50 h of continuous agitation. The solubility of arsenic trioxide increases greatly and occurs much more rapidly in both acid and alkaline media, Metal salts containing orthoarsenate (AsO_4^{3-}), monohydroarsenate ($HAsO_4^{2-}$), and dihydrogen arsenate ($H_2AsO_4^-$) are known. Diarsenic disulfide (As_2S_2), but more properly written as As_4S_4, exists in nature as mineral realgar. As_2S_4 is normally prepared as an impure material and must be purified by sublimation under an atmosphere of CO_2. Diarsenic trisulfide (As_2S_3), found in nature in orpiment, has been referred to as yellow arsenic sulfide. Diarsenic pentasulfide (As_2S_5), has been described as brownish-yellow, glassy, amorphous, and highly refractive. When suspended in water and heated, it decomposes into the thermodynamically more stable As_2S_3 and free sulfur. Two binary As-P compounds have been reported. They are As_2P and AsP. Diarsenic phosphide is black and lustrous and turns brown on exposure to air. AsP is described as a lustrous and red brown powder.

Arsenic also forms numerous organic compounds, as for example, Methylarsine, Di methylarsine, Monomethyl arsenic Acid, Dimethyl arsenic (see figure 2.2). Several complex organic compounds of arsenic have been employed in the treatment of certain diseases, such as ameobic dysentery, caused by microorganisms. Some of the most important compounds and species of arsenic are shown in Table 2.2. Figure 2.3 (Dahi, 1997) shows a qualitative scale indicating that the toxicity of arsenic compounds varies to a large extent depending upon their chemical form.

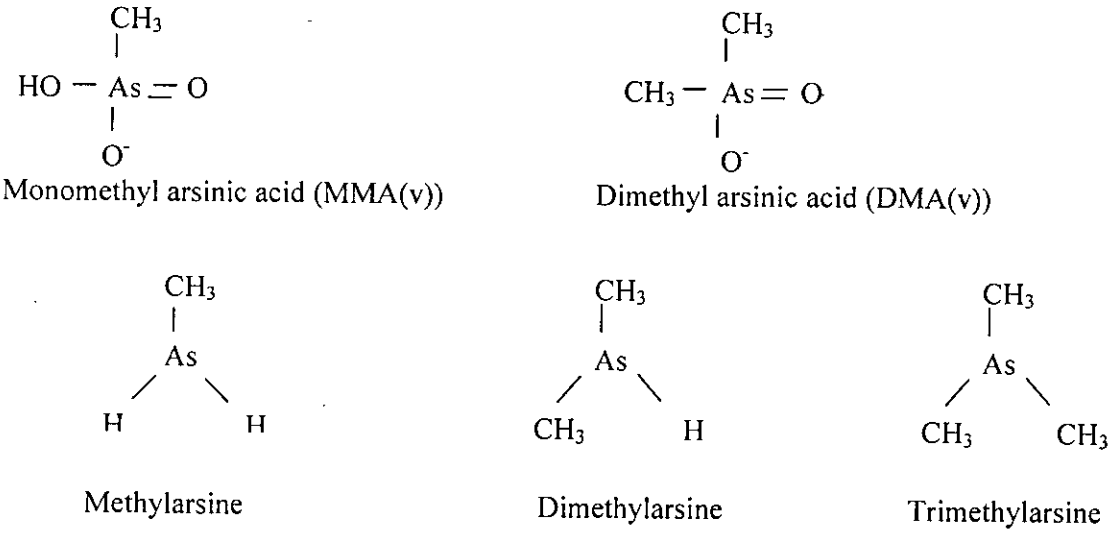


Figure 2.2: Common Methylated Species & Volatile Hydrides of Arsenic

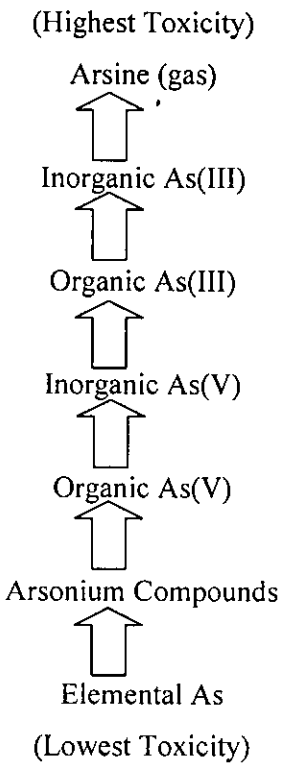


Figure 2.3: Arsenic Toxicity Scale (Dahi, 1997)

2.4 Chemistry of Arsenic

2.4.1 Acid-Base Reaction

Apart from the elementary arsenic with oxidation state 0, arsenic is stable in the oxidation states of +5, +3, and -3 (see Table2.2), but generally found in water only in the trivalent and pentavalent states. The oxides of both As (III) and As(V) are soluble in water. The dissolution implies direct reaction with water, hydration, where the oxides behave like non-metals and exhibit acidic character. Arsenic (III) forms arsenious also called arsonic acid. Arsenic (V) forms the arsenic acid, also called arsinic acid. The two acids dissociate to form respectively arsenite and arsenate ions as shown in the following reactions.

Arsenious Acid Dissociation:

$As_2O_3 + 3\ H_3O \quad = 2\ H_3AsO_3$ (2-4)

$H_3AsO_3 \quad = H^+ + H_2AsO_3^-$ pKa=9.22 (2-5)

$H_2AsO_3^- \quad = H^+ + HAsO_3^{2-}$ pKa=12.13 (2-6)

$HAsO_3^{2-} \quad = H^+ + AsO_3^{3-}$ pKa=13.40 (2-7)

Arsenic Acid Dissociation

$$As_2O_5 + 3\ H_2O = 2\ H_3AsO_4 \quad (2\text{-}8)$$

$$H_3AsO_4 = H^+ + H_2AsO_4^- \quad pKa=2.2 \quad (2\text{-}9)$$

$$H_2AsO_4^- = H^+ + HAsO_4^{2-} \quad pKa=7.08 \quad (2\text{-}10)$$

$$HAsO_4^{2-} = H^+ + AsO_4^{3-} \quad pKa=11.5 \quad (2\text{-}11)$$

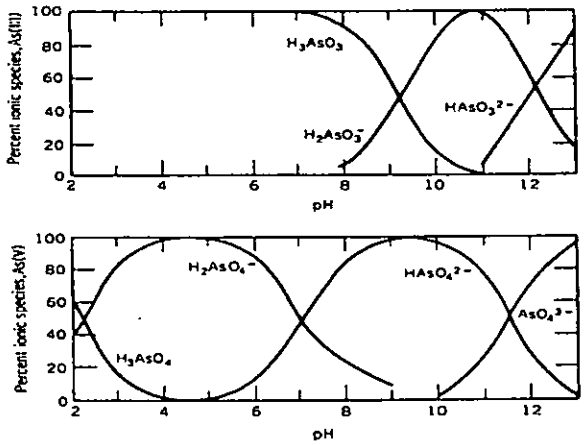


Figure 2.4: Predominance Diagram of As(III) and As(V) as a Function of pH (Montgomery, 1985)

Table 2.3 Arsenic Species and Their Environmental Importance in Water

Compounds	Example	Environmental Significance/Dominant pH Region
Arsine Oxidation state: -3	As^{3-}	Minor importance [Most toxic As species]
Elemental Arsenic Oxidation state: 0	As	Minor importance [Least toxic As species]
Trivalent Arsenic Oxidation state: +3	As(III)	Dominant under anaerobic condition [10 times more toxic than As(V)]
Arsenite, Inorganic	H_3AsO_3 $H_2AsO_3^{1-}$ $HAsO_3^{2-}$ AsO_3^{3-}	pH = 0 – 9 pH = 10 – 12 Important pH = 13 pH = 14
Methylated As(III) MMAs(III) DMAs(III) TMAs(III) Organo-As(III)	$CH_3As(III)O_2^{2-}$ $(CH_3)_2As(III)O^{1-}$ $(CH_3)_3As(III)$	Minor importance [Less toxic than inorganic As(III)]
Pentavalent Arsenic Oxidation state: +5		Dominant under aerobic condition [10 times less toxic than As(III)]
Arsenate, Inorganic	H_3AsO_4 $H_2AsO_4^{1-}$ $HAsO_4^{2-}$ AsO_4^{3-}	pH = 0 – 2 pH = 3 – 6 Important pH = 7 - 11 pH = 12 – 14

Figure 2.4 shows the predominance diagram of arsenic species as a function of pH. From Figure 2.4 it is seen that arsenic acid is stronger than arsenious acid. Within the range of natural waters (particularly groundwater), where pH is usually between 6 to 9, the trivalent inorganic arsenic is found as non-dissociated arsenious acid (H_3AsO_3); while the pentavalent arsenic is primarily found as the ionized dihydrogen arsenate ($H_2AsO_4^-$) and mono-hydrogen arsenate ($HAsO_4^{2-}$). The relatively more mobile monomethylated and dimethylated forms are observed in ocean and lake waters, but seldom in groundwater.

As most treatment processes are more capable to remove ions, the trivalent arsenic is more difficult to remove from the water than the pentavalent (Kartinen and Martin, 1995). Probably this ionization of arsenic (V) is also important for the fate of arsenic in the human body. The reduced toxicity of the arsenic (V) may be, to a large extent, due to its ionization, which enables easier control of its intracellular transportation (Dahi, 1997).

2.4.2 Redox Reaction

Arsenic is a redox sensitive element. Arsenate [As(V)] and Arsenite [As(III)] are common oxidation states of arsenic in water. The mobility of arsenic is controlled, in large part, by the oxidation-reduction (redox) transformations. The valence in which arsenic exists is related to both pH and the redox potentials, *Eh*. By determining the pH and Eh of water, it is possible to determine which species of arsenic will be prevalent.

2.4.3 Oxidation Reaction

As stated earlier, arsenate is dominant in oxygenated water, while arsenite is dominant in non-oxygenated water. While As(III) and As(V) acid-base reactions can be assumed to occur instantaneously, changes between oxidation states require indeterminate time periods in natural waters. For instance, the conversion of As(III) to As(V) in oxygenated water is thermodynamically favored, yet the transformation takes days, weeks or months depending on the specific conditions. The reduction of As(V) to As(III) is similarly kinetically constrained. This is the reason why arsenic (V) can be found in some anoxic waters (Dahi, 1997). This process is however also known to be facilitated through catalysis and bacterial mediation.

2.4.3.1 Photochemical Oxidation of Arsenic

Besides oxidation with chemical dosing, photo-oxidation using either UV or solar light has been used for converting arsenite to arsenate. Khoe et al. (1997) developed and patened an As-removal procedure using addition of Fe(II, III) followed by exposure to UV or solar light to accelerate oxidation of As(III). Here iron is used both as photo-absorber and co-precipitator.

Another arsenic removal technology – SORAS (Solar Oxidation and Removal of Arsenic), is also based on photochemical oxidation of As(III) followed by precipitation or filtration of As(V) adsorbed on Fe(III) oxides.

2.4.4 Adsorption-Desorption

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 are adsorbed on surfaces of a wide range of solids including iron, aluminum and manganese oxides (e.g., iron oxyhydroxides), and clay minerals.

As a result of pH dependence of arsenic adsorption, changes in groundwater pH can promote adsorption or desorption of arsenic. Similarly, redox reactions can control aqueous arsenic concentration by their effect on arsenic speciation and hence on adsorption-desorption reactions. For example reduction of arsenate to arsenite can promote arsenic mobility because arsenite is less strongly adsorbed than arsenate. It should be noted that in nature bacteria often mediate oxidation-reduction reactions.

2.4.5 Precipitation and Dissolution

Precipitation-dissolution reactions are important mechanisms controlling mobility of arsenic in the subsurface. Arsenic contained within solid phases, either as a primary structural component of arsenic bearing minerals (e.g., arsenopyrite) or an impurity in any of a variety of solid phases (e.g., pyrite), is released to groundwater when these solid phases dissolve. Similarly, arsenic is removed from groundwater when solid phases containing arsenic

precipitate from aqueous phase. As an example, because arsenic often coprecipitates with iron oxide, iron oxides may act as an arsenic source (case of dissolution) or a sink (case of precipitation) for groundwater (USGS, 1999). Besides, solid phase dissolution will contribute not only arsenic contained within that phase, but also any arsenic adsorbed to the solid-phase surface. In Bangladesh, reductive dissolution of iron oxyhydroxides and consequent release of adsorbed arsenic could be an important mechanism of arsenic mobilization in the subsurface.

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 biotransformation in the form of methylation. Besides microbial processes have been utilized in the bioremediation of arsenic contaminated soils.

Humans are exposed to arsenic mostly in the forms of arsenate/arsenite and organic arsenosugars/arsenobetaines and marine products. The inorganic forms are more toxic than organic forms. Methylation seems to be most important pathway of biotransformation of inorganic arsenic. The inorganic forms are metabolized by consecutive reduction and methylation reactions in humans and mammals to dimethylated arsenic (DMA) (see Fig. 2.7), which is excreted into urine (Suzuki, 2002). The toxicity of arsenite is highly dependent on animal species, which in turn depends on the differences in the metabolism shown in Fig. 2.7

The biomethylation of arsenic involves repeated steps of reductions, methylations, and oxidations (Challenger, 2000) methylation pathway is outlined in Figure 2.6 Recent studies indicate that the necessary intermediates monomethylarsonous acid (MMA III) and dimethylarsinous acid (DMA III) are more toxic than the inorganic arsenic species. Methylation in plants and animals was thought to detoxify inorganic arsenic (Suzuki, 2002) which is shown in Figure 2.6. However, recently Le et al. suggest that this should be reconsidered in light of the toxicity of MMA (III) and DMA(III)and their identification in human urine.

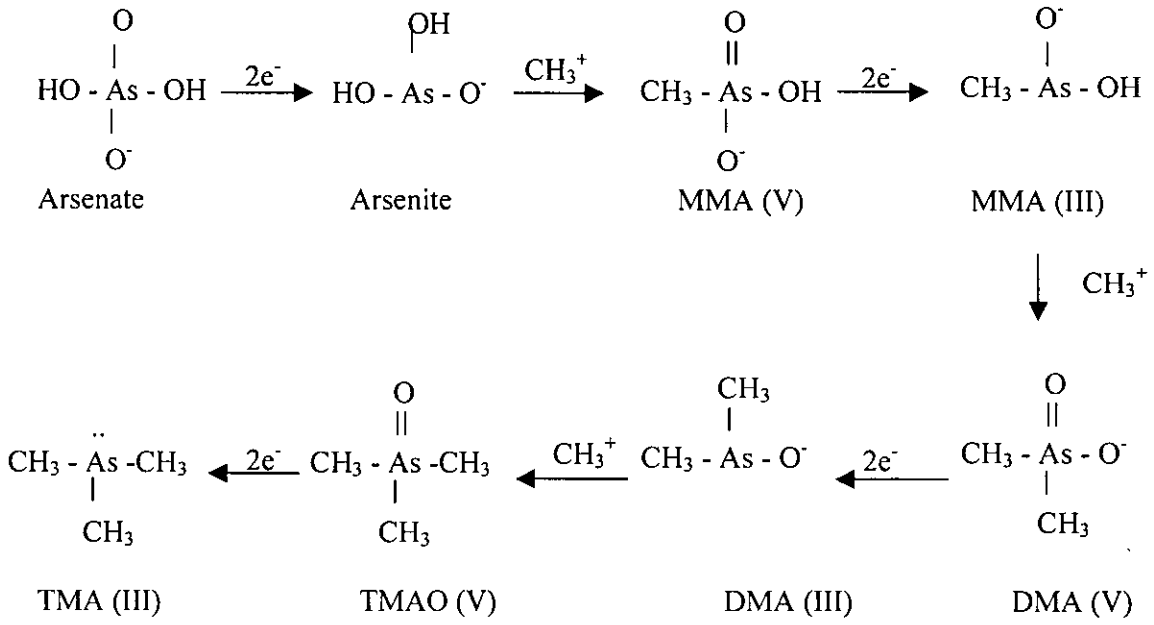


Figure 2.6 Pathway for Biomethylation of Arsenic as proposed by Challenger(2000)

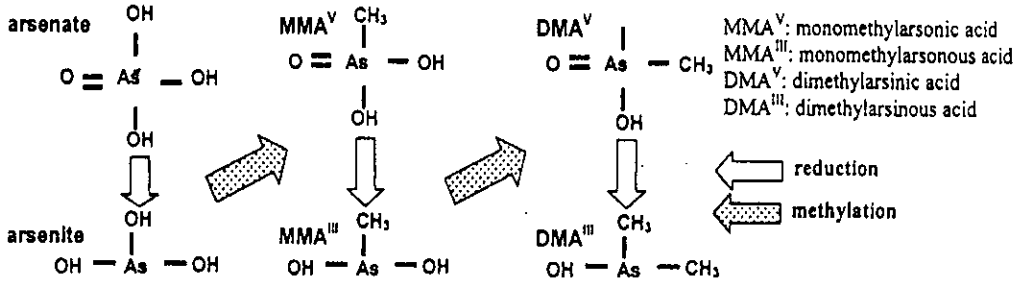


Figure 2.7 Reduction and methylation reactions in the metabolism of arsenic (Suzuki, 2002)

Several fungi and bacterial species have been demonstrated to methylate inorganic arsenic by an initially reducing arsenate fraction to arsenite, which then is methylated and released to the environment (Kartinen and Martin 1995). However, the concentration of methylated arsenic in the natural waters, whether ground or surface, is normally low. This is because the methylated arsenic is taken up by the biota where it undergoes metabolic conversion into organic arsenic. Compounds like arsenobetaine and arsenocholine, can thus be found in fish and crustaceans. These compounds do not have any toxicological significance. Upon consumption by man they are directly excreted through urine without any biotransformation (Vahter, 1994).

2.5 Arsenic in Soil

In uncontaminated soils, average arsenic concentration varies from about 5 to 6 mg/kg, but this varies among geographic regions. However, significantly high arsenic concentrations have been found in agricultural soil irrigated with arsenic contaminated groundwater. Concentrations as high as 51 mg/kg and 83 mg/kg have been reported in soils of Faridpur and Comilla districts, respectively of Bangladesh (Ullah, 1998). A concentration varying from 1.5 to 19 mg/kg showing higher concentration in the top layers of soil has been found in Samta village in Jessore (Kubota, 1998).

2.5.1 Chemical Forms of Arsenic in Soils

The chemical forms of arsenic in soil have been illustrated in Fig. 2.5 (Bhumba and Keefer, 1994). The reactions and processes involved in the transformation of different forms of arsenic include oxidation, reduction, adsorption, dissolution, precipitation and volatilization. The most often detected arsenic species is As(V) (Cullen and Reimer,1989). Alexander and Woolson (1977) proposed that the major pathway by which arsenic is lost from soil is through reduction of As(V) to As(III) and a series of reactions of As(III) with trimethylarsine (TMA) as a final product. Arsines may travel in the air long distances or they are oxidized rapidly

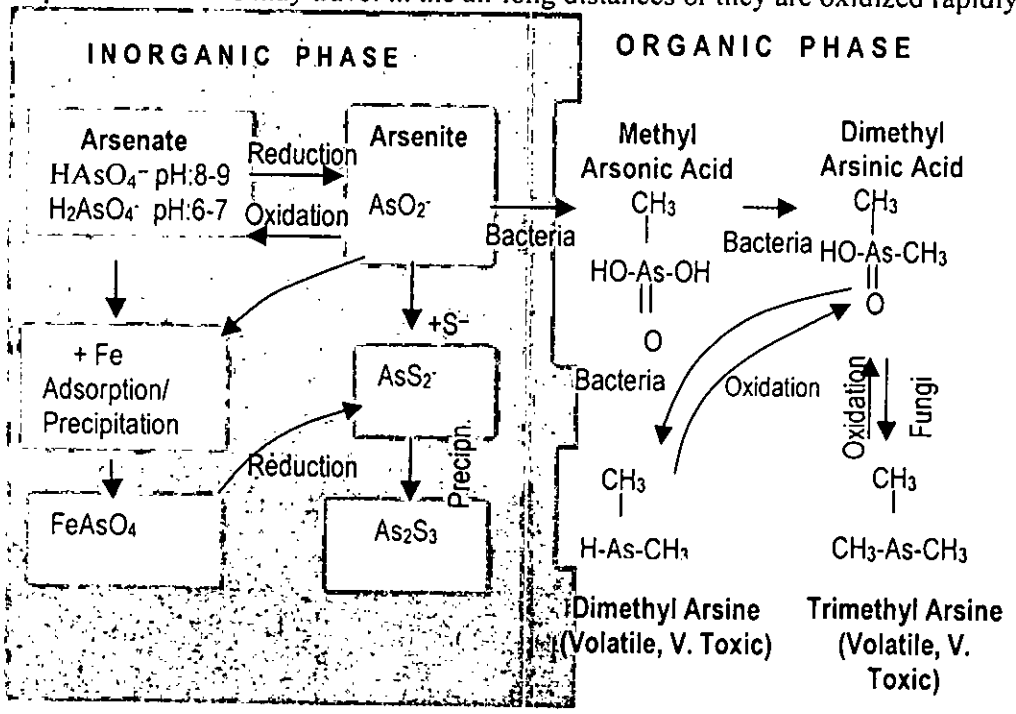


Figure 2.5: Chemical Forms of Arsenic and Their Transformations in Soils (Bhumba and Keefer, 1994)

depending on environmental conditions (Pongratz,1998) Oxidations returns arsenic back to inorganic species and the cycle of arsenic is completed because atmospheric inorganic arsenic is deposited back to soil by rain or by dry deposition(Pongratz., 1998)

Bacteria and fungi play important roles in chemical transformation of arsenic to volatile arsine gases, which are extremely toxic. Limited data suggest presence of both As(III) and As(V) as well as organic arsenic in agricultural soil and the process of transformation/bio-transformation of arsenic are not clearly understood. Soil components that contribute to arsenic sorption and retention include oxides of Al, Fe and Mn, soil mineralogy, and organic matter.

2.6 Role of Microorganisms in Transformation of Arsenic

Microbial activities are ubiquitous in the geochemical environment, and they can exert tremendous influence on the biogeochemical cycles of elements by interconverting species that display remarkably different behaviors. Arsenic is one such element, possessing a multi-dimensional biogeochemical cycle with important components contributed both directly, by microbial transformations of arsenic itself, and indirectly, by microbial transformations of elements with biogeochemical cycles that intersect that of arsenic. Much of the environmental chemistry of arsenic is governed by the existence of a wide range of methyl compounds, produced as natural products by microorganisms in the environment.

2.6.1 Microbial Energy Generation by Catalyzing Redox Reactions

One of the primary tasks of a microorganism is to catalyze chemical reactions that will help it to obtain energy for metabolic growth from its environment, and as a result, many of the biogeochemically significant transformations that microorganisms catalyze are the result of energy-generating endeavors. The greatest energy-generating reactions available to the biosphere are those in which electrons are transferred from one element or compound to another, also known as oxidation-reduction or "redox" reactions (Stumm, W., and J. J. Morganm, 1996). Redox reactions necessarily alter the electronic configurations of the compounds involved, and because electronic associations form the basis for much chemical reactivity, redox reactions frequently create dramatic alterations in the behaviors of their substrates (Schlesinger, W. H. 1997). In addition, because the microbial incentive to catalyze energy-generating reactions is so great, and because the abiotic rates of redox reactions are frequently so slow, such reactions frequently proceed much more rapidly and to a much

greater extent in the presence of microbial catalysis than they would do otherwise (Morel, F. M. M., and J. G. Hering. 1993).

2.6.2 Aerobic and Anaerobic Respiration

Microorganisms catalyze redox reactions by means of "respiratory" processes, which are those that catalyze the transfer of electrons from one reactant to another. Aerobic respirations couple the oxidation of an electron donor such as organic carbon, H_2, or Fe(II) to the reduction of molecular oxygen, O_2, forming water. These processes necessarily occur in unsaturated soils or well-mixed or oligotrophic surface waters where oxygen is abundant (Brock, T. D., and M. T. Madigan. 1991). In contrast, anaerobic respirations couple the oxidation of an electron donor to the reduction of an alternative electron acceptor such as nitrate, Fe(III), or sulfate, generating N_2, Fe(II), or sulfide, for example (Zehnder, A. J. B., and W. Stumm. 1988). Aerobic and anaerobic respiratory processes form one central class of processes that strongly influence arsenic biogeochemistry, both directly and indirectly.

Respiratory Arsenic Transformations

In recent years, microorganisms have been discovered in a great diversity of anoxic environments that are able to generate energy by coupling the oxidation of H_2 or organic carbon to the reduction of inorganic As (V), arsenate, forming inorganic As (III), arsenite (Ahmann, D., A. L. Roberts, L. R. Krumholz, and F. M. M. Morel, 1994). Arsenite behaves much differently than arsenate in natural environments; in particular, its sorption onto clay minerals and metal oxides appears to be less rapid and/or less stable, with the result that As (III) is generally much more mobile than As(V) in aqueous systems (Aggett, J., and M. R. Kriegman. 1988.). Because arsenate reduction is an energy-generating process for the microorganisms involved, and because arsenite is both more toxic and more mobile than arsenate, this process has the potential to influence greatly the geochemistry of arsenic in anoxic systems, particularly with respect to arsenic mobilization (Ahmann, D., et.al. 1997). The converse respiratory process, the oxidation of arsenite to arsenate, coupled to the reduction of O_3 to water, has the theoretical potential to generate energy for microbial growth, but has been indicated in only one microorganism to date (Ilyaletdinov, A. N., and S. A. Abdrashitova. 1981). Nevertheless, a variety of other microorganisms have been shown to oxidize arsenite to arsenate by non-energy-generating mechanisms (Phillips, S. E., and M. L. Taylor. 1976). Again , reduction of As (V) to As (III) in anoxic environments is thought to occur primarily by dissimilatory reduction where microorganisms utilize As(V)

as a terminal electron acceptor for anaerobic respiration. To date, dissimilatory reduction has been characterized in at least seven bacteria:

- Sulfurospirillum barnesii
- Bacillus arsenicoselenatis
- B.selenitireducenes
- S. arsenophilum.
- Desulfotomaculum auripigmentum
- Chrysiogenes arsenatis &
- Desulfomicrobium stain Ben-RB

They represent genera scattered throughout the bacterial domain. Microorganisms may also posses reduction mechanisms that are not coupled to respiration but instead are thought to impart As resistance. Microorganisms that express As resistance genes are able to withstand higher concentration of arsenic through the intercellular reduction of As (V) and the subsequent excretion of As(III) into the surrounding media. It is thought that this pathway may function in aerobic as well as anaerobic environments and may contribute to apparent non-equilibrium conditions where As (III) has been often observed in oxic surface waters.

Role of micro organisms in Toxic Environment

In addition to energy generation, a second important task of microorganisms is to protect themselves from toxic substances. Arsenate, with its structural similarity to phosphate, enters microbial cells readily through phosphate-uptake proteins. Its primary mode of toxicity is then to displace phosphate in the production of adenosine triphosphate (ATP), the primary energy currency of the cell. The resulting molecules hydrolyze spontaneously, causing the cell to deplete its energy stores rapidly (Winship, K. A. 1984). Although this mechanism of toxicity is quite effective, many cells are able to induce highly phosphate-specific uptake proteins that improve the exclusion of arsenate (Willsky, G. R., and M. H. Malamy. 1980). Arsenite, in contrast, is uncharged at neutral pH and appears to gain access to the cytoplasm by less specific mechanisms, possibly including diffusion across the membrane. Once inside, it crosslinks sulfhydryl groups on enzymes, forming stable adducts that permanently disable the enzyme. This mechanism is even more destructive to the cell than that of arsenate (Winship, K. A. 1984).

Arsenic Detoxification

To protect themselves against the toxic effects of arsenic, many microorganisms have evolved strategies for detoxification. The best-studied among these is the microbial

reduction of arsenate to arsenite by means of the *Ars* system, an enzymatic process in which energy is actually consumed to drive the reduction. The *Ars* system is borne on plasmids that are easily transferred among both Gram-positive and Gram-negative bacteria, and it is induced at arsenic concentrations low enough to be relevant to contaminated environments, with the result that this process is potentially rapid, extensive, and ubiquitous in both oxic and anoxic environments (. Ji, G., and S. Silver. 1995). Certain other bacteria and fungi appear to detoxify arsenicals by reducing them to arsine, As(-III), in both inorganic and methylated forms (Cheng, C.-N., and D. Focht. 1979). In addition, some algae have been shown to reduce arsenate to arsenite, presumably for detoxification purposes, but this purpose has not been confirmed (Sanders, J. G., and H. L. Windom. 1980). Finally, certain bacteria and algae, as well as many higher organisms, may incorporate arsenic into organic compounds such as arsenocholine, arsenobetaine, and other arsenosugars (Cullen, W. R., and K. J. Reimer. 1989). Regardless of the utility to the microorganism, however, it is clear that many non-energy-generating microbial transformations of arsenic occur both rapidly and extensively in natural environments, and should be considered potentially important contributors to arsenic geochemistry.

Passive Nucleation

Microbial cell surfaces possess an abundance of surface functional groups that can form complexes with dissolved ions, including arsenic oxyanions, and such complexes have been shown to function as sites of nucleation in the precipitation of certain minerals (. Beveridge, T. J. 1989). In the case of arsenic, it may be possible that microbial cell surfaces contribute to arsenic geochemical cycling in this passive manner as well, particularly in the instance of nucleating arsenic sulfide precipitation (Rittle, K. A., J. I. Drever, and P. J. S. Colberg. 1995).

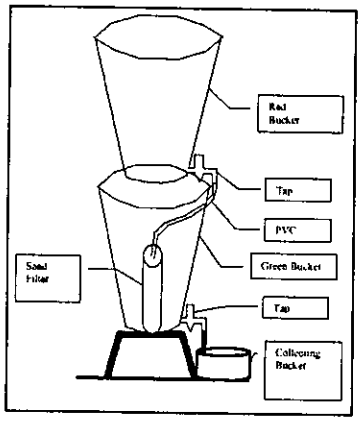
In oxic environments, the dominant microbial influences on arsenic geochemistry appear to be the bacterial and algal oxidations of arsenite to arsenate, diminishing both toxicity and mobility of the arsenic, as well as confirmed detoxification processes, including the *Ars*-mediated reduction of arsenate to arsenite and fungal generation of arsines. In anoxic environments, in contrast, the dominant microbial roles are expected to be the respiratory reductions of arsenate, iron, and manganese, all of which promote arsenic desorption and enhance its mobility, and the respiratory reduction of sulfate, which promotes arsenic immobilization into sulfide solids. While the mechanisms underlying these processes are well understood in many cases, and their geochemical influences are potentially great, the

ability to quantify and, more importantly, to predict the rates and extents of these processes in natural environments, remains a tremendous challenge for the future.

2.7 Arsenic Removal Technologies

A number of studies have been conducted to develop suitable technologies to treat arsenic withdrawn from groundwater. Most of these are aimed at developing household or small scale community level units. A number of such units/ technologies have been used in Bangladesh. In this section a brief description of some of those technologies/units is provided.

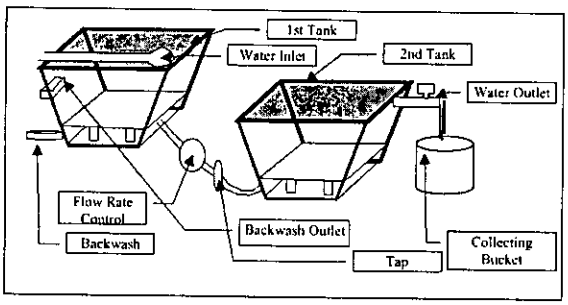
2.7.1 DPHE/Danida Bucket Treatment Unit



TECHNOLOGY	TECHNOLOGY DPHE/Danida Bucket Treatment Unit
Process	Oxidation/coagulation/flocculation/filtration
Chemical controls	Relies on enhanced coagulation Less dependent upon groundwater Fe Chemical oxidant enhances arsenite removal PO4 > ASO4 >> SiO4 >F High HCO3 has –ve impact High Ca/Mg has +ve impact Ideal pH 6.5 to 8 for optima functioning of alum Possible residual Mn
Physical controls	Agitation and duration of coagulation. Sand packing in filter. Distribution of water over filter Sand grain size and clays . Sand Fe and Organic C content. Character and rate of flow through filter
Operating procedure	procedure Pour water into the top bucket. Add mixture of aluminium sulphate and potassium permanganate and stir vigorously 20 times. Leave to settle for 2 hours. Turn tap to send water to lower bucket where it passes through a sand filter. Turn tap in bottom bucket to get drinking water
Flow rate -	

TECHNOLOGY	TECHNOLOGY DPHE/Danida Bucket Treatment Unit
-low turbidity -high turbidity	70 litres per hour (but 23 l/hr including 2 hours preparation) 50 litres per hour (but 17 l/hr including 2 hours preparation)
Time for 20 litres to pass	Approx. 3 hours (1 hour settling + 1 hour filtration)
Litres in 12 hours	Approx. 240 litres
Batches before deterioration - low turbidity - high turbidity	 17 batches – no deterioration 40% fall in flow after 6 batches, then constant to 15 batches
Claims on effectiveness (Results and references)	Noakhali – 100% As below 50ppb after treatment (initial levels 120-1000ppb.) DPHE/Danida Arsenic Mitigation Pilot Project Information leaflet 'Arsenic Removal at Household Level' Sitakunda and Gomastapur – 100% As below 50ppb after treatment (initial levels 116-201 ppb) Water Aid, March 2000. Household Level Arsenic Removal Methodologies, Preliminary Research Report.
Costs (capital and recurrent)	Tk. 300-350 depending on the production cost of the flat cover for the lower bucket.

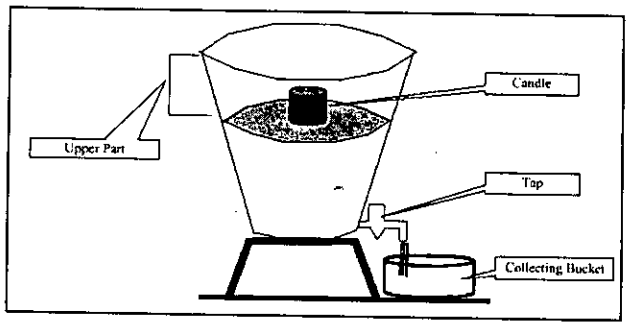
2.7.2 Alcan Enhanced Activated Alumina Filter



TECHNOLOGY	ALCAN ENHANCED ACTIVATED ALUMINA FILTER
Process	Sedimentation, filtration, actived alumina (AAFS-50)
Chemical controls	Semi-reversible adsorption to Al_2O_3 Arsenite removal occurs (through oxidative step- chlorine)
Physical controls	Formulae to calculate bed-volumes to exhaustion (for 0.1mg/l ASO_4, 15000 bed volumes) Potentially prone to clogging by FeOH
Operating procedure	Usually attached to well head and pump directly into the filter
Flow rate - -low turbidity -high turbidity	 >300 litres per hour >300 litres per hour
Time for 20 litres to pass	3-5 minutes
Litres in 12 hours	>3600 litres
Batches before deterioration - low turbidity	 No deterioration

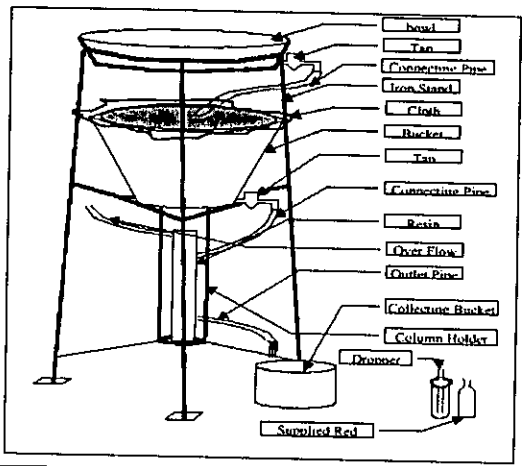
TECHNOLOGY	ALCAN ENHANCED ACTIVATED ALUMINA FILTER
- high turbidity	No deterioration
Claims on effectiveness (Results and references)	Studies by Department of Chemistry, Dhaka University, and BRAC (Sonargaon) show a removal rate of 100%.
Costs (capital and recurrent)	US$500 (US$200 for the unit and US$300 for the material (5 year warranty, expected life 10 years). Annual filter material costs US$300. Costs could fall if demand is high

2.7.3 Adarsha



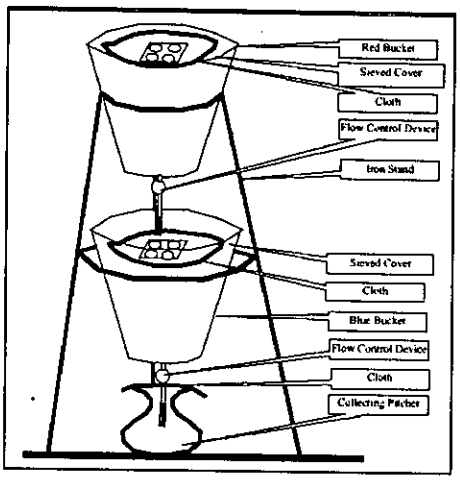
TECHNOLOGY	ADARSA
Process	Filtration
Chemical controls	Semi-reversible adsorption to Al_2O_3 Arsenite removal occurs (through oxidative step-chlorine)
Physical controls	Character and flow rate through filter
Operating procedure	Pour water into tray within bucket. Use tap to get treated water from bottom of bucket.
Flow rate - -low turbidity -high turbidity	 1.1 litres per hour 1.1 litres per hour
Time for 20 litres to pass	19 hrs
Litres in 12 hours	13 litres
Batches before deterioration - low turbidity - high turbidity	 No deterioration in 15 Batch No deterioration in 15 Batch
Claims on effectiveness (Results and references)	DPHE R& D have done some assessment and think it reduces As below 50ppb. They are not sure why.
Costs (capital and recurrent)	Tk 500 Costs could fall if demand is high

2.7.4 BUET Activated Alumina Filter



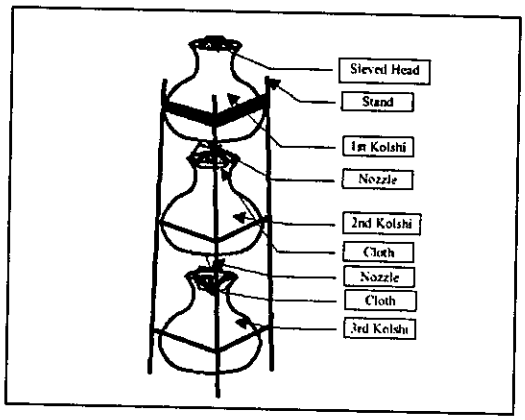
TECHNOLOGY	TECHNOLOGY BUET ACTIVATED ALUMINA
Process	Oxidation, sedimentation, filtration, actived alumina
Chemical controls	Semi-reversible adsorption to Al_2O_3 Arsenite removal occurs (through oxidative step)
Physical controls	Formulae to calculate bed-volumes to exhaustion (for 0.1mg/l ASO_4, 15000 bed volumes) Potentially prone to clogging by FeOH
Operating procedure	Fill top bucket and add chemicals as directed. Stir vigorously and leave for one hour. Turn tap to allow water into the activated alumina column. Retrieve water from bottom of column.
Flow rate -low turbidity -high turbidity	Approx. 8 litres per hour Approx. 8 litres per hour
Time for 20 litres to pass	Approx. 2.5 litres
Litres in 12 hours	13 litres
Batches before deterioration - low turbidity - high turbidity	Steady gentle deterioration (<10% over 15 batches) Steady gentle deterioration (<10% over 15 batches)
Claims on effectiveness (Results and references)	DPHE R& D have done some assessment and think it reduces As below 50ppb. They are not sure why.
Costs (capital and recurrent)	Tk 1000

2.7.5 Garnet Filter



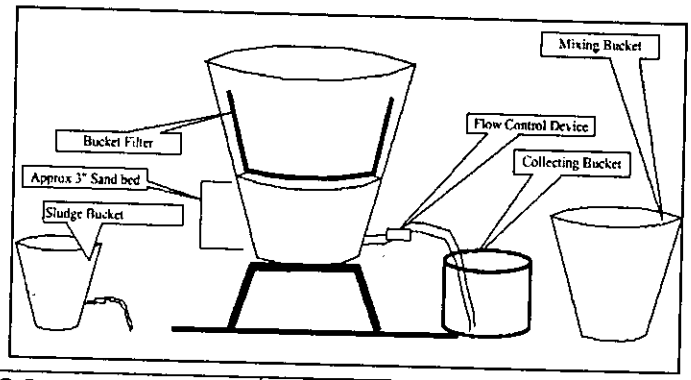
TECHNOLOGY	GARNET FILTER
Process	Coagulation, adsorption and filtration
Chemical controls	Relies on passive coagulation with Fe and/or adsorption to sand matrix PO4 > ASO4 >> SiO4 >F High HCO3 has –ve impact High Ca/Mg has +ve impact
Physical controls	Sand packing in filter. Distribution of water over filter.Sand grain size and clays. Sand Fe and Organic C content. Character and rate of flow through filter
Operating procedure	Water frequently topped up in top bucket. Flow regulated to second bucket – regular checking required.
Flow rate -low turbidity -high turbidity	0.7 litres per hour 0.4 litres per hour
Time for 20 litres to pass	Approx. 30 hrs
Litres in 12 hours	7 litres
Batches before deterioration - low turbidity - high turbidity	50% initial flow after 7 batches 30% initial flow after 5 batches
Claims on effectiveness (Results and references)	Removal efficiencies of 70-100% cited in GARNET's own literature, depending on the presence of As and Fe in the feed water.
Costs (capital and recurrent)	Tk.250-600 based on materials

2.7.6 Sono 3-Kolshi Filter



TECHNOLOGY	SONO 3-KOLSHI FILTER
Process	Coagulation, adsorption, filtration
Chemical controls	Relies on passive coagulation with Fe and/or adsorption to sand matrix PO4 > ASO4 >> SiO4 >F High HCO3 has –ve impact High Ca/Mg has +ve impact
Physical controls	Sand/iron filings/charcoal packing in filter Distribution of water over filter Sand grain size and clays Sand Fe and Organic C content Character and rate of flow through filter
Operating procedure	Pour water into top kolshi. Use water from the bottom kolshi.
Flow rate -low turbidity -high turbidity	Approx. 5 litres per hour Approx. 5 litres per hour
Time for 20 litres to pass	Approx. 4 hrs
Litres in 12 hours	Approx. 60 litres
Batches before deterioration - low turbidity - high turbidity	15 batches with no major deterioration 15 batches with no major deterioration
Claims on effectiveness (Results and references)	As (III) from 800ppb to less than 50ppb (2ppb) As (total) from 1100ppb to less than 50ppb (10ppb)
Costs (capital and recurrent)	Tk. 325/-

2.7.7 Steven's Institute Technology



TECHNOLOGY	STEVENS INSTITUTE TECHNOLOGY
Process	Coagulation, adsorption, filtration
Chemical controls	Relies on enhanced coagulation and co-precipitation (ferrous suphate) Less dependent upon groundwater Fe Chemical coagulant (ferric chloride) enhances arsenite removal PO4 > ASO4 >> SiO4 >F High HCO3 has –ve impact High Ca/Mg has +ve impact
Physical controls	Sand cleaning and packing in filter.Distribution of water over filter.Sand grain size and clays. Sand Fe and Organic C content .Character and rate of flow through filter
Operating procedure	Collect 20 l in a bucket, add chemicals and stir rapidly for s minute. Pour into filter (bucket with holes on top of sand in larger bucket) and wait for water
Flow rate -low turbidity -high turbidity	18 litres per hour 18 litres per hour
Time for 20 litres to pass	Just over one hour
Litres in 12 hours	Approx. 240 litres
Batches before deterioration - low turbidity - high turbidity	Steady decline to 50% initial flow after 10 batches Steady decline to 50% initial flow after 10 batches
Claims on effectiveness (Results and references)	Kachua - less than 50ppb As in treated water (max. 25ppb) from initial As concentrations of 300-800ppb). Kishoreganj and Munshiganj – max. As was 19ppb from initial untreated concentrations of 280-468ppb. Xiaoguang Meang and George P. Korfiatis, 'Removal of Arsenic from Bangladesh Well Water by the Stevens Technology for Arsenic Removal (STAR)'. Occasional Paper.
Costs (capital and recurrent)	Tk. 500/- on contact

2.7.8 Passive Sedimentation

TECHNOLOGY	PASSIVE SEDIMENTATION
Process	Co-precipitation with iron upon oxidation
Chemical controls	Relies on passive coagulation with iron Main control is iron in the water PO4 > ASO4 >> SiO4 >F High HCO3 has –ve impact High Ca/Mg has +ve impact
Physical controls	Duration of settling. Final water could be contaminated by stirring. Bacteriological contamination could be an issue
Operating procedure	Fill kolshi and leave to settle for over 12 hours. Pour top 2/3 ^{rds} for use and discard lower 1/3rd
Flow rate -low and high turbidity	N/A
Time for 20 litres to pass	12 hours (depends on size of kolshi)
Litres in 12 hours	20 litres (depends on size of kolshi)
Batches before deterioration - low and high turbidity	N/A
Claims on effectiveness (Results and references)	2 out of 17 wells tested took As below 50ppb. Greatest influence seen was negative correlation between As removal and Electrical Conductivity.
Costs (capital and recurrent)	20 litre aluminium kolhsi – approx. Tk. 200/-

2.8 Wastes From Arsenic Removal Units

All technologies that remove arsenic from groundwater will at some point produce arsenic waste either as a solid or a liquid. The volume of waste, and concentration and chemical stability of arsenic, will depend upon the initial concentration of arsenic and the treatment technology used.

The main types of waste that will be produced from the household level technologies are as follows (base on nine technology described earlier)

1.When no coagulant is used, the main type of arsenical sludge will be an iron oxyhydroxide onto which arsenic is strongly adsorbed. This oxyhydroxide will either be trapped within the matrix of filters (eg in the 3 Kolshi or Garnet filters) or may potentially occur as a separate sludge at the bottom of a bucket or kolshi (e.g. passive sedimentation).

2. When a coagulant is used (e.g. DPHE/Danida, BUET-UNU BTU and Steven's Institute) aluminium and iron are introduced into the water producing larger volumes of co-

precipitated arsenic-rich sludge that will, in the case of DPHE/Danida also contain aluminium hydroxides. These co-precipitates again may either occur trapped in filter matrices or as a sludge from the pre-filtration settlement stages.

3. Ion exchange (IE) and activated alumina (AA) processes do not, under typical use, produce a solid waste stream because the media are regenerated. However, the periodic process of regeneration produces alkaline and acidic brines enriched in arsenic and other elements.A summary of the main types of waste likely to be associated with the nine technologies being tested in this project is shown in Table 2.3.

Stability of Arsenic Wastes

For the majority of the technologies, arsenic will be associated (through co precipitation and adsoprtion) with iron (or aluminium) oxyhydroxides. There are three main factors that can lead to the release of arsenic from these precipitates. These factors are listed below:

1. Dissolution of oxyhydroxides under mildly reducing conditions associated with solid waste can cause the release of arsenic. Since mildly reducing conditions can well develop in latrines, disposal pits and landfills, disposal to these settings needs to consider the possibility of arsenic remobilisation.
2. Bacterial activity in animal manure when mixed with arsenic-rich sludges has been shown to methylate arsenic transforming it into less toxic compounds. Transformation to arsine gas and release in to air may occur in this setting.
3. Arsenic tends to desorb from oxyhydroxides under high pH conditions. This behaviour is opposite to that of typical metals which tend to be more strongly adsorbed under high pH conditions. When identifying disposal options, consideration should be given to the potential remobilisation of arsenic in alkaline settings.

Table 2.4 Summary of the main types of waste likely to be associated with the nine Technologies being Tested by Water Aid, 2000

Method	Nature of sludges and waste products
Passive sedimentation	Arsenic-bearing iron oxyhydroxide flocs may settle to the base of the kolshi.
Ardasha	• The filter "candle" block will contain iron and arsenic as an iron oxyhydroxide. • Arsenic-bearing iron oxyhydroxide flocs will accumulate in the base of the upper compartment of the bucket.
Sono 3-Kolshi Garnet	• Arsenic-bearing iron oxyhydroxide will accumulate in both kolshis/ buckets containing filter materials
DPHE/ Danida Steven's Institute	• Coagulation will give rise to an amorphous arsenic, iron bearing sludge that will accumulate i) at the bottom of the pre-filtration bucket, and ii)within the sand filter. Additional elements present in the coagulant will occur in the sludge. For DHPE/ Danida this will include alum.
BUET	• Coagulation will give rise to an amorphous arsenic, iron bearing sludge that will accumulate i) at the bottom of the pre-filtration bucket, and ii)within the sand filter. • Alumina in the column would need to be periodically regenerated (see below).
ALCAN	• Arsenic-bearing iron oxyhydroxide on the activated alumina can be back washed out of the system – this effluent will need to be disposed of. • Regeneration of the alumina will also be necessary – this requires flushing with strong acids and alkalis and will need to be done at a centralize facility. The frequency will depend on the nature of the water being treated.
Tetra Hedron	• No backwashing facility appears to be available, but regeneration of the resin will also be necessary – this requires flushing with strong acids and alkalis and will need to be done at a centralised facility. As for the ALCAN system, the frequency will depend on the nature of the water being treated.

In order to identify the likely leachate characteristics of wastes, the United Sates Environmental Protection Agency has developed a standard procedure known as the toxicity characteristic leaching procedure (TCLP). The method involves crushing the waste and leaching with weak acids to simulate conditions that may prevail in landfill, for example. This procedure is widely used and has been applied to wastes arising from arsenic treatment technologies.

The general controls on the stability of arsenic wastes are reasonably well understood. However, research on wastes arising from household level removal technologies is active and a more comprehensive review of this current research is considered to be worthwhile.

2.9 Possible Disposal Options

Chemical stability is only one of several factors that needs to be considered when identifying potential disposal options. For example, in view of the relatively small volumes of waste that will be produced, it may be more advantageous to dispose of sludge to a setting where remobilisation (and consequently dilution and dispersal) could occur but that is unlikely to give rise to direct human exposure, particularly by ingestion. In addition, consideration needs to be given to the practicalities of disposal options in rural settings.

Estimates on the mass of oxyhydroxide wastes that need to be disposed of by a household over a yearly period are less than 200 g when no coagulants are used and around 2 kg of oxyhydroxide for a coagulant treatment technique such as the DPHE/Danida two bucket system (Water Aid, 2000). Bearing these volumes in mind and the rural setting, the main options and associated issues are summarised in Table- 2.4.

Disposal to latrines or shallow pits would seem to be favorable option. Disposal to latrines is the currently advised option for the DPHE/ Danida two bucket system. However, given the potential future scale arsenic removal treatment in Bangladesh it is recommended that further investigation of waste disposal issues are carried out.

Other Waste Disposal Issue

Arsenic-rich wastes produced from the majority of household level removal technologies will be in one of two forms:

1. Oxyhydroxide flocs in relatively large volumes of water such as the passive sedimentation bucket, settlement buckets from multi-stage systems or backwash waters from ALCAN
2. Oxyhydroxide flocs trapped in the matrices (e.g. sand and bricks) of filter systems.

In the first form, a particulate-rich liquid waste, disposal to latrines should be feasible. For the flocs trapped in filter matrices the issue of separation / regeneration needs to be considered. Separation/regeneration methods will need to be considered on a technology-specific bases.

With regard to the activated alumina (ALCAN and BUET) and ion exchange (Tetrahedron) systems, treatment and disposal of regeneration wastes needs to be considered. Regeneration typically involves flushing with highly acid and alkaline solutions and the resultant wastes

will be saline, rich in arsenic and potentially other toxic elements, and will require pH correction. These sorts of activities should be carried out at a centralized facilit

Table 2.5: Preliminary Summary of Sludge Disposal Options Issues (adopted from Water Aid, 2000)

Disposal Option		Issues
1.	Disposal in latrines.	• Likely to be feasible for most households. • Awareness/training likely to be relatively straightforward. • The risk of remobilization into shallow aquifers and re-abstraction from wells needs to be assessed. • Potential impacts of arsine release to confined space should be investigated either by desk or field trials.
2.	Mixture with animal manure and disposal to shallow pit.	• Likely to be feasible for most households. • Dedicated pit may need to be constructed. • The risk of remobilization into shallow aquifers and re-abstraction from wells needs to be assessed. • Awareness/training required.
3.	Disposal on land.	• Logistically difficult for the some households. • Scavenging from waste disposal sites could lead to human exposure. • The bulk of land is committed to agricultural production and intuitively this option seems illogical. • Seasonal considerations (wet/dry seasons and harvesting) would need to be taken into account. • Could be further assessed through a risk assessment.
5.	Solidification by incorporation into bricks.	• Logistically difficult for the majority of households. • Probably not justified if other options prove viable.
6.	Solidification by incorporation into cement	• Logistically difficult for the majority of households

2.10 Microorganisms Present in Cowdung

Cowdung is a marvelous resource that is constantly being produced and deposited in large quantities rural areas. Even though it has passed through an animal's digestive tract, dung retains many nutrients. Thus, it attracts its own fauna and flora consisting of bacteria, fungi, protozoa, platyhelminths, nematodes, annelids, and arthropods. Coprophilous (dung-loving) fungi are uniquely adapted to herbivore dung. They are deposited with dung, and they grow and reproduce there.

Dung consists of the macerated and undigested remains of plant food plus vast quantities of bacteria (mostly dead) as well as animal waste products, such as broken-down red blood cells and bile pigments. The nature of herbivore dung depends on the efficiency of the digestive tract, which, in turn, depends on the animal's digestive anatomy and its microflora. Ruminants produce a fine-textured dung of fibrous plant material whereas horses, with a less

efficient system, produce much coarser dung. Dung decomposes rapidly because the macerated material has a high nitrogen content, available aeration, and a high water content that is protected from fluctuations.

Although there is little available protein in dung, many other undigested food components are present. Dung is rich in water-soluble vitamins, growth factors, and mineral ions, some of which are metabolic by-products of the microbes in a herbivore's gut. For example, coprogen, an organo-iron compound found in dung, is necessary for the growth and reproduction of the fungus Pilobolus crystallinus. Dung also contains a large amount of readily available carbohydrates.

Considering the great variation in the feeding habits, habitats, and digestive systems of herbivores, it is surprising how universal coprophilous fungi are. All classes of the Kingdom Fungi are found in dung, with the Zygomycetes usually appearing first, followed by the Ascomycetes, and finally the Basidiomycetes. Their distribution is influenced locally by the number of herbivores in an area. Some species are restricted to a particular herbivore; for example, Lasiobolus cainii is found only on porcupine dung. However, many coprophilous fungi grow indiscriminately on any herbivore dung.

Coprophilous fungi are highly specialized for growth on dung, and some never occur elsewhere. While some dung fungi show few modifications peculiar to their habitat, most do have some unique features. Many exhibit some very specialized structures to ensure survival in their unique habitat.

Many of the coprophilous fungal spores will not germinate until after passing through an herbivore's digestive tract: They must be heated inside the gut, digested by the gut enzymes and/or bacteria, or stimulated by the higher pH of dung.

The dung heap is not inhabited exclusively by fungi. As mentioned previously, vast populations of bacteria, protozoa, platyhelminths, nematodes, annelids, and arthropods coexist with the fungi. These compete for resources, and some parasitize or consume the fungi while others provide substrates for them. Also, these organisms can deplete the dung of nutritionally necessary compounds, such as nitrogenous one, and can produce waste products that enhance or retard the growth and reproduction of some fungi. For instance, ammonia, a waste product of the bacterial degradation of proteins, stimulates sporangial production of Pilobolus, which grows better in the presence of other microbes.

Coprophilous bacteria enhance the growth of some of the coprophilous fungi, but retard the growth of others. Also, the number of fly larvae, Lycoriella mali (Diptera: Sciaridae) that survive to pupate increases as fungal competition increases. It could be that as fungal growth is inhibited, more resources are available to the fly larvae, or that larvae may be favored by the enzymes produced by fungi to inhibit other fungi.

The success of coprophilous fungi, as measured by their ability to produce and maintain a fruiting body, is not simply a matter of competing against other fungi. Instead, it is a complex web of interactions, some combative, some inhibitive, some mutually or exclusively beneficial between and among the bacteria, fungi, protozoans, platyhelminths, nematodes, annelids, and arthropods.

2.11 Microbial Growth:

There are a number of factors that affect the survival and growth of microorganisms in food. The parameters that are inherent to the food, or intrinsic factors, include the following:

- nutrient content
- moisture content
- pH
- available oxygen
- biological structures
- antimicrobial constituents

Nutrient Requirements:

While the nutrient requirements are quite organism specific, the microorganisms of importance in foods require the following:

- water
- energy source
- carbon/nitrogen source
- vitamins
- minerals

In a typical bacterial cell, Escheria coli about 90% of the dry weight of cell is composed of four elements; carbon, oxygen, nitrogen and hydrogen. These elements, plus phosphorous and sulfur , comprise the macromolecules of the cell. The remaining 4% of the dry weigh of

the cell includes a large number of elements – potassium, sodium, calcium, magnesium, chlorine, iron, manganese, cobalt, copper, boron, zinc, molybdenum and others

Moisture Content:
All microorganisms require water but the amount necessary for growth varies between species. The amount of water that is available in food is expressed in terms of water activity (aw), where the aw of pure water is 1.0. Each microorganism has a maximum, optimum, and minimum aw for growth and survival. Generally bacteria dominate in foods with high aw (minimum approximately 0.90 aw) while yeasts and moulds, which require less moisture, dominate in low aw foods (minimum 0.70 aw).

pH:
Most microorganisms have approximately a neutral pH optimum (pH 6-7.5). Yeasts are able to grow in a more acid environment compared to bacteria. Moulds can grow over a wide pH range but prefer only slightly acid conditions. Milk has a pH of 6.6 which is ideal for the growth of many microorganisms.

Available Oxygen:
Microorganisms can be classified according to their oxygen requirements necessary for growth and survival:

- Obligate Aerobes: oxygen required
- Facultative: grow in the presence or absence of oxygen
- Microaerophilic: grow best at very low levels of oxygen
- Aerotolerant Anaerobes: oxygen not required for growth but not harmful if present
- Obligate Anaerobes: grow only in complete absence of oxygen; if present it can be lethal

Biological Structures:
Physical barriers such as skin, rinds, feathers, etc. have provided protection to plants and animals against the invasion of microorganisms. Milk, however, is a fluid product with no barriers to the spreading of microorganisms throughout the product.

Antimicrobial Constituents:
As part of the natural protection against microorganisms, many foods have antimicrobial factors. Milk has several nonimmunological proteins which inhibit the growth and metabolism of many microorganisms including the following most common:

- lactoperoxidase

- lactoferrin
- lysozyme
- xanthine

Where the intrinsic factors are related to the food properties, the extrinsic factors are related to the storage environment. These would include temperature, relative humidity, and gases that surround the food.

Temperature:

As a group, microorganisms are capable of growth over an extremely wide temperature range. However, in any particular environment, the types and numbers of microorganisms will depend greatly on the temperature. According to temperature, microorganisms can be placed into one of three broad groups:

- Psychrotrophs: optimum growth temperatures 20 to 30° capable of growth at temperatures less than 7° C. Psychrotrophic organisms are specifically important in the spoilage of refrigerated dairy products.
- Mesophiles: optimum growth temperatures 30 to 40° C; do not grow at refrigeration temperatures
- Thermophiles: optimum growth between 55 and 65° C

It is important to note that for each group, the growth rate increases as the temperature increases only up to an optimum, after which it rapidly declines.

2.12 Review of Previous Studies

In early 1815 cases of arsenic poisoning were reported to have been caused by wall paper containing such arsenic compounds as scheel's green $Cu(AsO_2)_2$, $CuHAsO_3$ and paris green $Cu(CH_3COO)_2 . 3Cu(AsO_2)_2$. (Challenger et al., 1933)

It was first thought to be the ingestion of arsenic particulate materials from the paper; but latter on it was revealed that particular poisoning occurred from the paper was not responsible, hence the theory was abandoned. From the literature it was found that the rooms where symptoms occurred had a garlic odors and it was found to be a volatile arsenic compound produced by molds on damp arsenic-pigmented wall paper (Challenger et. al., 1933). After proper investigation & research it was possible to identify the chemical nature of this volatile arsenicals as Methylated compounds of arsenic. (Challenger et. al., 1933)

Gosio used pure cultures of bacteria and fungi on a potato medium and found that, although no bacteria produced a garlic odor, a mold *Penicillium brevicaule* was very much active. He analysed the gas formed and calculated that it was an alkylarsine (actually trimethylarsine, called Gosio gas) (Gosio et. al., 1893). Sodium cocodylate also produce garlic odor in cultures of *S.Brevecaulis* (Borgeaud, 1902) and Monilia sitophila Saccardo(Saccardo et. al., 1912). From the literature, it was found that a volatile substance was produced from breadcrumb cultures of four strains of *S. brevicaulis* as trimethylarsines (Challenger et. al., 1933). Bird et. al. reported that trimethylarsines ws produced from sodium arsenite , sodium methylarsonate and Sodium cocdylate (Bird et. al., 1948). In 1932, Thom and Raper isolated from soil several strains of fungi that were active in producing trimethylarsine (Thom et. al., 1932). They also found that the strains were with wide variety of arsenicals used commercially and suggested that any arsenical could probably be acted on by fungi. Several fungi isolated from sewage (Cox et. al., 1973) can reduce arsenic compounds to trimethylarsine (TMA). More recently, the methylation of arsenic by mrthanoganic bacteria (Mcbride et. al., 1971) and by reaction which methyl cobalamine or L- metthionine- methyl-d_3- has been demonstrated in laboratory work. Mcbride et. al. reported that dimethylarsine was mainly produced by anaerobic organisms, while trimethylarsine resulted from aerobic methylation. . Challenger proposed that As (V) has tobe reduced to As (III) before being methylated. in a recent study by Huysmans et. al., it was found that in the central valley of california , arsenic is present in soil at naturally high concentrations. being derived from marine sedimentary parent material of the coastal range. Due to intense agricultural irrigation, soluble arsenic is leach from the soil and accumulates in evaporation ponds where it may pose an environmental threat to the waterflow and wildlife. A penicillium sp. isolated from evaporation pond water was found to be capable of methylating and subsequently volatilizing organic arsenic.

Turpeinen (2002), in his study the influence of microbes on the speciation of arsines in contaminated soils investigated under laboratory conditions. Microbes were able to carry out reactions that resulted in changes in the speciation of arsenic in soil. The transformation of soil dominating species, arsenate [As (V)], under both aerobic and anaerobic conditions to arsenite [As (III)], monomethylarsonic acid [MMAA], dimethyl arsenic acid [DMAA] and to volatile trimethylarsine [TMA] was, however, less than 0.5%, of which the production of TMA represented 0.02-0.3%. The volatilization was also verified in the field, in the soil of a dumping area. The 'life-time' of arsines in air was, however, short and they were rapidly converted back to water-soluble species, As (V) and trimethyl arsine oxide (TMAO)

Rahman (2000) his study the methylation of arsenic in presence of cowdung was studied in laboratory. Two types of experiment were done. In first experiment virgin soil mixed with arsenic contaminated fly ash candle and fresh cowdung and the

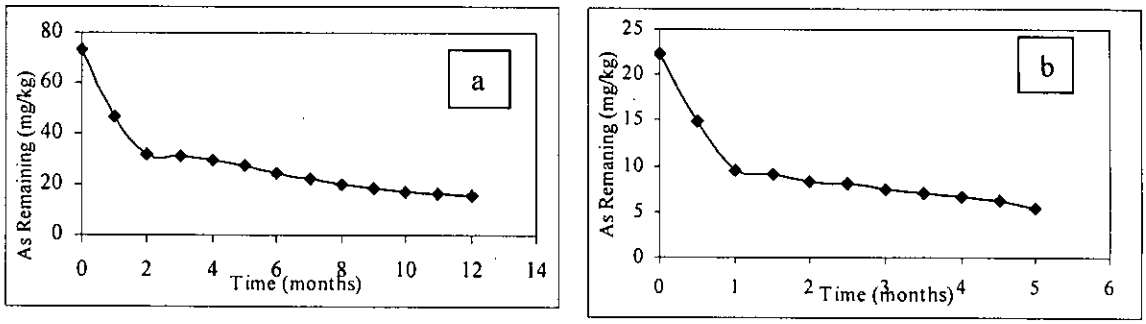


Figure 2.8: Elimination of Arsenic from Soil (a) initial (b) addition of more cowdung (Rahman, 2000)

samples were tested after certain intervals. Results shown in Figure 1(a). The maximum elimination occurs with the first few days and then elimination occurred very little. About 79% elimination occurred after 12 months. Again in second experiment some portion of soil from first experiment was taken and again cowdung was added and arsenic content of the mixture was tested as before (Figure 1 (b). This figure indicates that addition of cowdung increased the elimination of arsenic.

Macur (2001) studied microbial reduction of arsenate to arsenite and the subsequent effects on As mobilization in contaminated mine tailings were studied under transport condition. The results (Figure 2.9) of the study indicate that microbial reduction of As(V) in As contaminated soils may occur under aerobic conditions over relatively short time scales resulting in enhanced As mobilization.

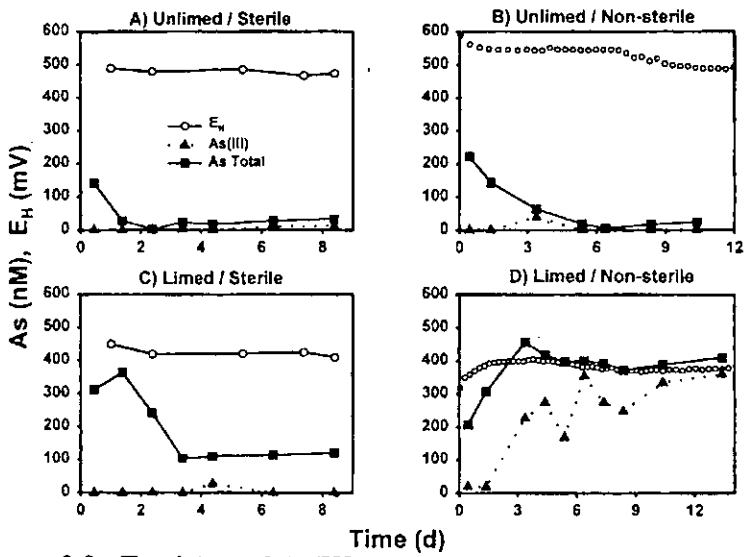


Figure 2.9 : Total As and As(III) concentrations in the effluent with time under different conditions (Macur,2001)

Badruzzaman (2003), studied leaching of arsenic from arsenic removal wastes. The author concluded that for the solid wastes and multiphasic sludge the leaching of arsenic concentration peaked within the first week and then tapered off and disappeared after twelve weeks. Absence of residual arsenic in the solids following anaerobic leaching indicate that a significant amount of arsenic is lost through bio-methylation induced by the presence of organic matters used in the leaching experiments

Chapter-3

Elimination of Arsenic from` Arsenic Solution in the Presence of Cowdung

3.1 Introduction

Liquid and / or solid arsenic wastes are generated during the operation and maintenance of arsenic removal units/plants. These wastes are often disposed into cowdung bed where transformation and release of arsenic occurs. Experiments have been performed to quantify the elimination of arsenic from aqueous solution in the presence of cowdung. In this chapter, the experiments are described and the results are presented and discussed.

3.2 Materials and Methods

In order to the assess the transformation and release of arsenic in the presence of cow-dung, batch experiments were conducted in 15-mL falcon centrifuge tubes. Stock solutions of As(III) and As(V) were prepared with Hach-NIST arsenic standards. Aqueous arsenic solutions (12 ml) with known concentrations (varying from 80 ppb to 500 ppb) of either As(III) or As(V) were taken in a series of tubes (a total of 8 to 10 tubes for each set of experiment). Fixed quantities (1, 2 and 6 grams) of fresh cow-dung were added to each of the tubes. One set of tubes was capped after purging N_2 gas and a similar other set was left uncapped. After particular time intervals, one tube from each set was taken out and centrifuged to separate the solid (cow-dung) from the liquid. The capped tubes were uncapped and left open for few minutes. Then pH and Eh of each sample wad recorded. The liquid portion from each tube was then separated by decanting and its arsenic concentration was measured (after acidification). Arsenic content of the solid (cow-dung) portion was determined after digestion with aqua regia. Arsenic content of the fresh cow-dung was also determined after digestion. Thus total arsenic present in the tubes were determined as a function of time to see any change in total arsenic content in the presence of cow-dung. The arsenic concentrations were measured with graphite-furnace AAS (Shimadzu AA6800).

The digestion procedure of cowdung consists of the following steps:

i. 5 grams of fresh cowdung was taken in a volumetric flask and it was made moist by adding a few milliliters of deionized water, then 2.5 mL nitric

acid and 7.5 mL hydrochloric acid was added to the flask and was kept overnight

ii. deionized water was added and the flask was heated for two hours

iii. if color of the sample turns yellow, digestion was assumed to be completed.

iv. deionized water was then added to make the volume 100 mL

v. After filtering the sample was stored in a bottle

In order to assess the elimination of arsenic from aqueous solution in presence of cowdung through transformation/bio-transformation, the same experiments were done again in 2nd set up using the same methodology. But from the experience gained from the results of 1st experimental set up, the experiments in the 2nd set up were done with As (III) solution under cap-open condition in presence of 1g, 2g and 6g cowdung.

From the results presented at section 3.3 it is seen that arsenic elimination from As (III) and As (V) solution is similar under both cap-open and cap-closed conditions. To quantify arsenic elimination from aqueous solution, 2nd experimental set up was prepared. But this time the batch tests were done with As (III) solution under cap-open condition only.

Test methods and digestion procedure were same in the 2nd experimental set up as described earlier. But the initial arsenic content of the solution was 6.632 μg.

3.3 Results and Discussion

3.3.1 1st Experimental Set Up

The main objective of this part of the study was to assess the elimination of arsenic from aqueous solution with different ratio of arsenic content and weight of cowdung. The batch experiments were conducted with aqueous arsenic solutions (12 ml) with known concentrations (varying from 80 ppb to 500 ppb) of either As (III) or As (V) in presence of fixed weight of cowdung (1g, 2g and 6g). All the results of this study are presented in Annex A. The pH was recorded 6.2-6.8 and Eh was – 175mV to –350mV.

Figures 3.1 and 3.2 show the arsenic remaining in the solution with time for both cap-open and cap-closed conditions. In most cases elimination of arsenic under cap-open and cap-closed conditions were similar. Majority of this elimination appears to take place during the first few days and then arsenic contents appear to reach a plateau. Similar results obtained for different weights of cowdung added to the solution with same arsenic

content. The reason for elimination of majority of arsenic within the first few days may be the decay of microorganisms in first few days of the experiment. Arsine and methyl arsines are undoubtedly very toxic (Bantley and Chasteen, 2002). So these types of gases may reduce the activity of microorganism within a few days when they are produced through biotransformation process and the elimination recorded after 16 days may be the elimination that occurred within first few days. Thus the elimination may have occurred within first few days, after which microorganisms became ineffective.

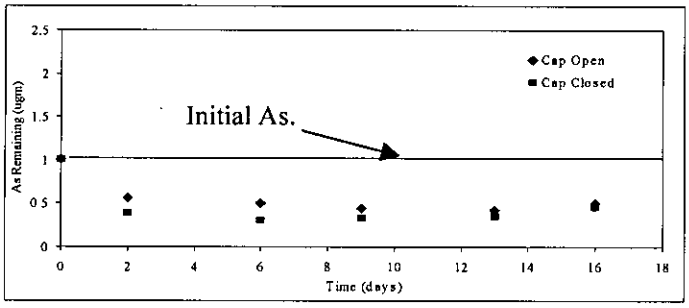


Figure 3.1: Arsenic Remaining in Arsenic (III) solution with time in presence of 1 g Cowdung (Initial As 1.031 μg)

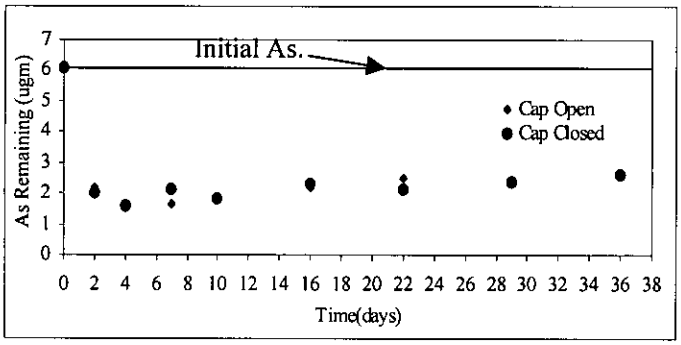


Figure 3.2: Arsenic Remaining in Arsenic (V) solution in presence of 2g cowdung (initial As 6.11 μg)

Figure 3.3 shows As elimination (in percentage) at different time intervals from four aqueous solutions (arsenic content vary from 1.031μg to 2.24μg) mixed with 1g cowdung. About 93% arsenic is eliminated from the solution with initial arsenic content 1.75 μg, where as about 20%-80% arsenic was eliminated from the other three solutions.

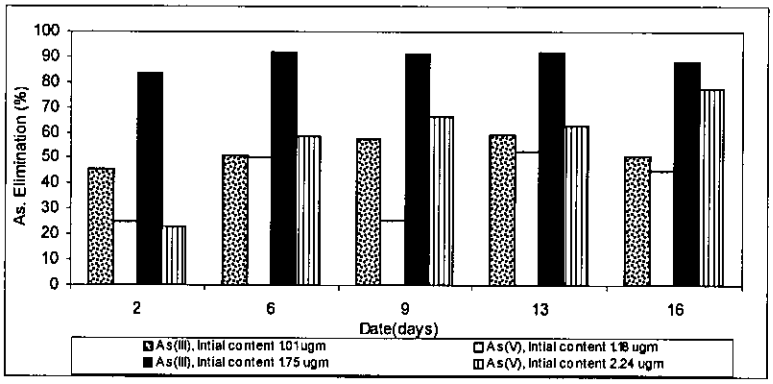


Figure 3.3: Elimination of Arsenic (%) from Arsenic solution with time in presence of 1 g cowdung

This figure does not give any clue about the relationship between percentage of arsenic elimination with initial arsenic content of the solution. The type of microorganism present in the solutions may also play a role in this case, as all microorganisms do not contribute to volatilization process.

Again though Fig 3.4 and Fig 3.5 show that arsenic elimination from cap-closed condition is higher than that of cap-open condition but Fig 3.6 shows that the elimination is almost same for both conditions, cap-open and cap-closed. Arsenic elimination under these condition ranges from 45%-75%.

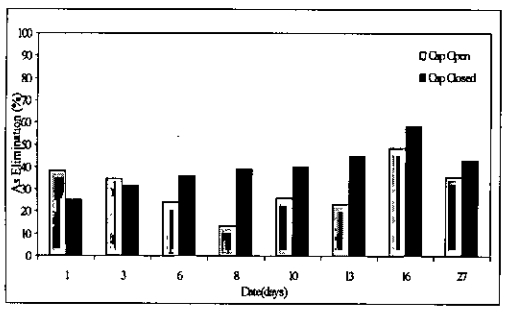


Figure 3.4:Elimination of Arsenic(%) from Arsenic (III) solution in presence of 1 g cowdung (Initial As 5.90 µg)

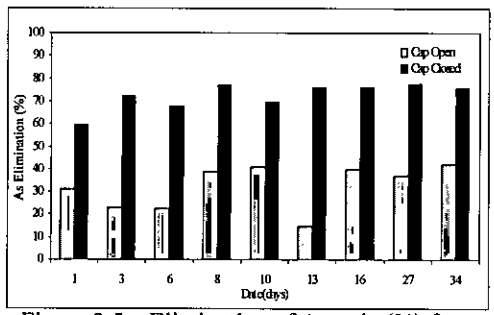


Figure 3.5: Elimination of Arsenic (%) from Arsenic (V) solution in presence of 1 g cowdung (Initial As 5.90 µg)

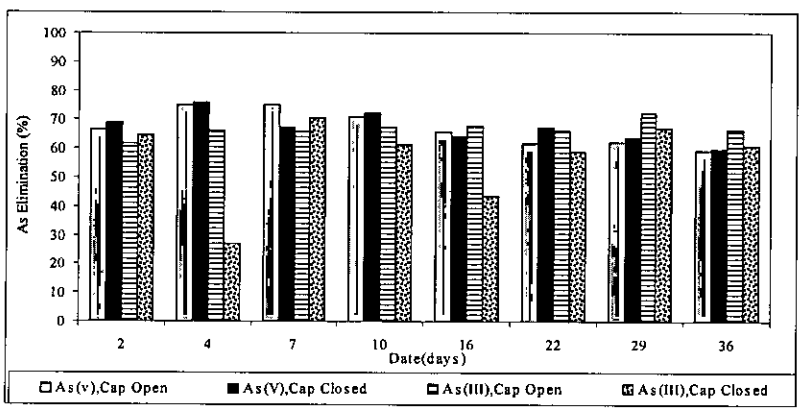


Figure 3.6: Elimination of Arsenic (%) from Arsenic solution in presence of 2 g cowdung (Initial As 6.11 µg)

Figures 3.7 and 3.8 show Arsenic elimination (in percentage) versus Arsenic/cowdung (µg/g) ratio. Here total Initial arsenic content of the mixture and total weight of fresh cowdung added to the solution are considered. In Fig 3.7 the ratios are calculated only for cases where only 1g fresh cowdung was added to As (III) solution. Figure 3.8 has been drawn taking the ratios which are calculated based on different weight of cowdung added to different arsenic content of the mixtures.

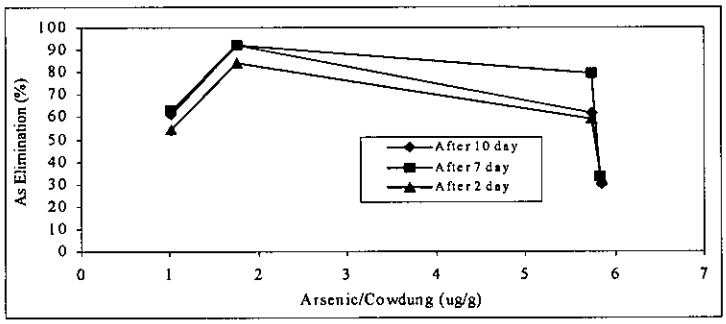


Figure 3.7 : Comparison of Arsenic Elimination from Arsenic (III) Solution with Arsenic/cowdung(μg/g) Ratio in different days.

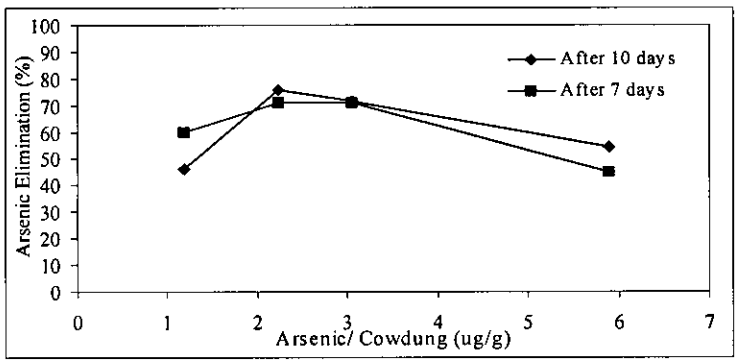


Figure 3.8: Comparison of Arsenic Elimination from Arsenic (V) solution with Arsenic/cowdung(μg/g) Ratio in different days.

Each arsenic elimination data of the curves is the average of arsenic elimination under cap-open and cap-closed condition. It appears that elimination after 2 days, 7 days and 10 days is similar. At first elimination tends to increase with increasing arsenic/ cowdung ratio but then decreases. This phenomenon may be explained by considering that with increasing arsenic/ cowdung ratio, there might be also an increase in amount of toxic gas that are produced in the solution by biotransformation process within first few days and these gases may reduce the activity of the living microorganisms that are present at that time. As nutrient, oxygen and other essential elements for microbial growth were not supplied in the mixture, the microorganisms could not get any way to reproduce themselves in this adverse situation and elimination of arsenic may decrease.

3.3.2 2nd Experimental Set Up

In the second experimental set up, The batch tests were performed under cap-open condition with As (III) solution in the presence of 1g , 2g and 6g cowdung. Fig 3.9 shows variation of arsenic remaining in the solution with time. But the results do not show any trend between the remaining arsenic content in the mixture and the time allowed for biotransformation. The pattern of arsenic elimination in not the same as observed in the first experiments. Solution mixed with 6g cowdung shows low percentage of arsenic elimination where solution mixed with 2g cowdung shows maximum elimination among the three cases (Figure 3.10) with same initial arsenic content. Range (min - max) of

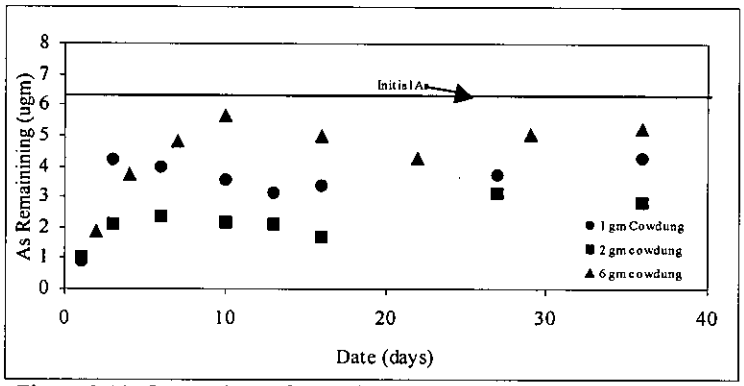


Figure.3.11: Comparison of Arsenic Remaining in the As (III) solution in presence of 1 gm, 2 gm and 6 gm cowdung, Cap Open Condition, (initial As 6.632 μg)

arsenic elimination from the solution in the presence of 2 g cowdung is 53%-85% whereas 36% to 86% and 15% to 44% for the solution mixed with 1g and 6g cowdung respectively. The number of microorganism present in the mixture and the type of microorganism is an important factor. In these three cases the cowdung was added from the same source. Though the cowdung was added to the mixture after uniform mixing, there might be uneven distribution of microorganism in mixtures that probably have some effect of arsenic elimination. Again, type of microorganism (either it is capable of volatilization or not) is also an important factor in arsenic elimination from solution in the presence of cowdung. As we did not the count the population and also did not identify the type of microorganism, we could not assess the actual cause of these variations.

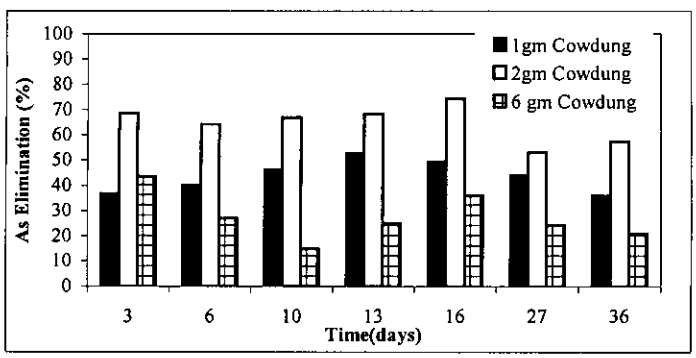


Figure 3.10:Comparison of Elimination of As (III) in batch Tests in Presence of 1 g, 2g & 6g Cowdung (Initial As 6.632 μg); Cap open Condition

Elimination of arsenic from different Arsenic/ cowdung(μg /g) ration at certain fixed interval were plotted in Fig 3.11. It has seen from the figure that at a certain day eliminination (%) increases as the Arsenic/ cowdung ratio increases but then decreases again. The same pattern was followed at every interval.

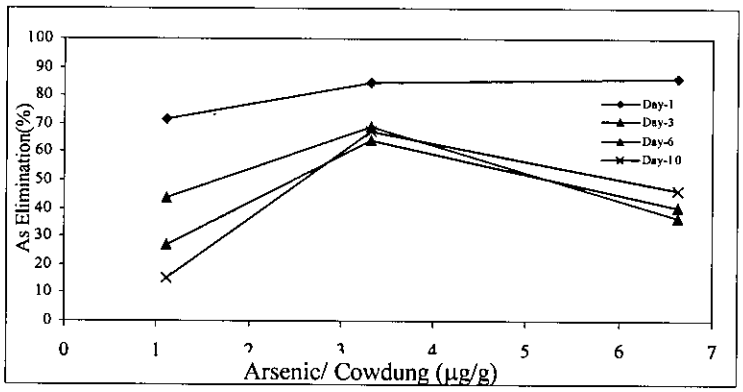


Figure 3.11: Comparison of Arsenic Elimination with Arsenic/cowdung(µg/g) ratio in different days

3.3.3 Comparison of Arsenic Elimination from As (III) Solution in 1st and 2nd Experimental Set Up

To assess the elimination of arsenic from As (III) solution in the presence of cowdung, batch tests were performed in two experimental set up. Comparison was made for only cap-open condition for As (III) solution and also the initial arsenic content of the tests were quite similar. Almost no variation was found in elimination of arsenic in the presence of 1g and 2 g cowdung from As (III) solution. But the elimination of arsenic from the solution in the presence of 6 g cowdung was quite higher in 1st experimental set up compared to the 2nd experimental set up (Fig 3.12). This is may be due to the difference of type and number of microorganisms in the cowdung. In general, it can be suggested that arsenic elimination increases with increasing weight of cowdung.

Table-3.1 Arsenic Elimination (Average in %) from Arsenic Aqueous Solution in Presence of Cowdung

	Cowdung Mixed with As(III) solution				Cowdung Mixed with As(V) solution			
	Initial As Conc (µg)	Wt of Cowdung (g)	Range (min – max) of As Elimination (%)		Initial As Conc (µg)	wt of Cowdung (g)	Range of As Elimination (%)	
			Cap-open	Cap-closed			Cap-open	Cap-closed
1st Phase	1.03	1.00	46 - 59	56 - 71	1.175	1.00	24 - 52	20 - 73
	1.75	1.00	84 - 92	85 - 93	2.24	1.00	23 - 78	75 - 87
	5.86	1.00	13 - 45	25 - 58	5.86	1.00	14 - 42	59 - 78
	6.11	2.00	62 - 72	27 - 71	6.11	2.00	60 - 75	60 - 76
	6.36	6.00	58 - 96		6.36	6.00	60 - 94	
	6.63	1.00	36 - 86					
2nd Phase	6.63	2.00	53 - 74					
	6.63	6.00	15 - 72					

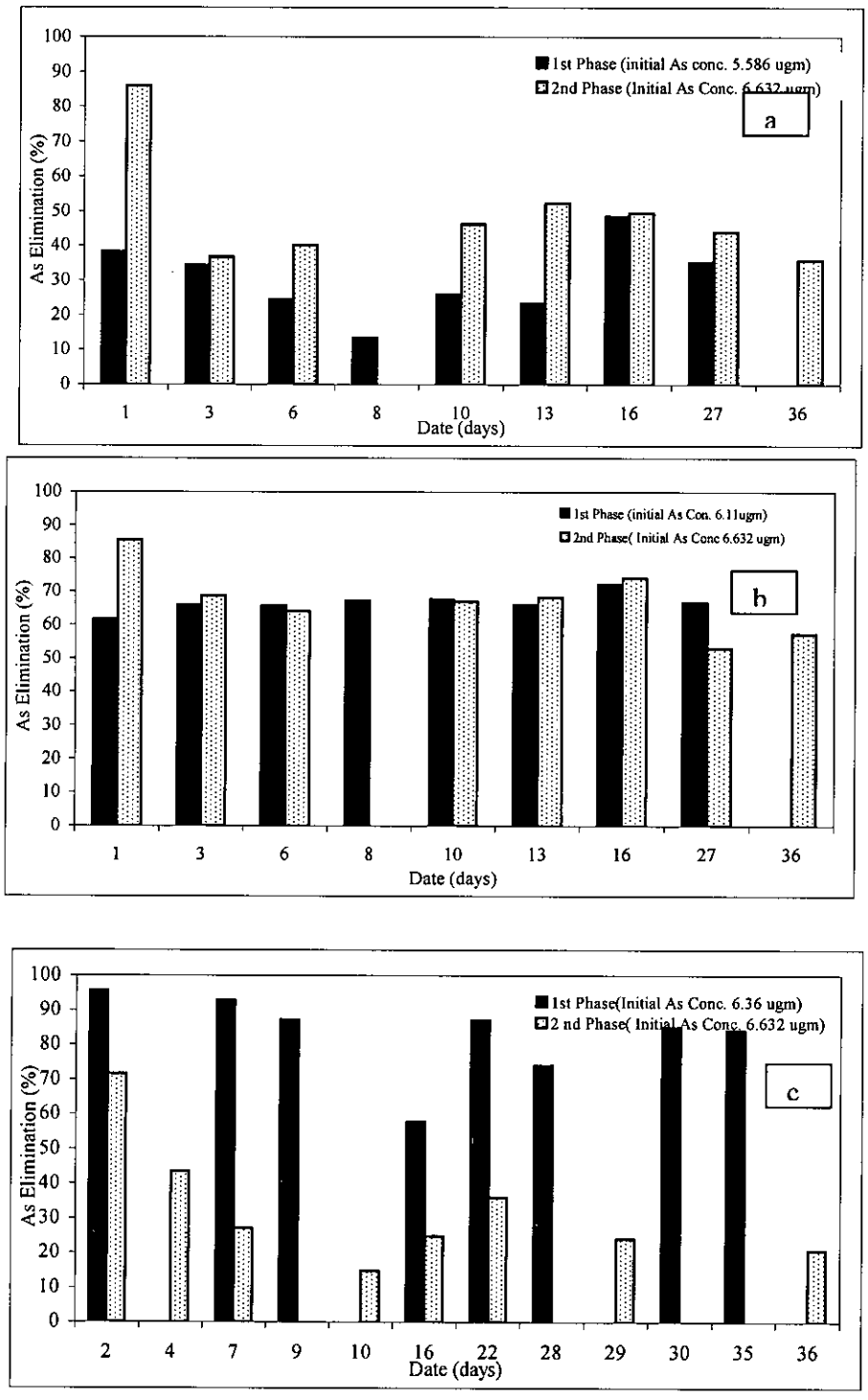


Figure 3.12: Comparison of Arsenic Elimination from As(III) solution between the batch tests performed in 1st and 2nd phase in presence of(a) 1g (b) 2g (c) 6g cowdung

3.4 Transformation of As (V) to As(III)

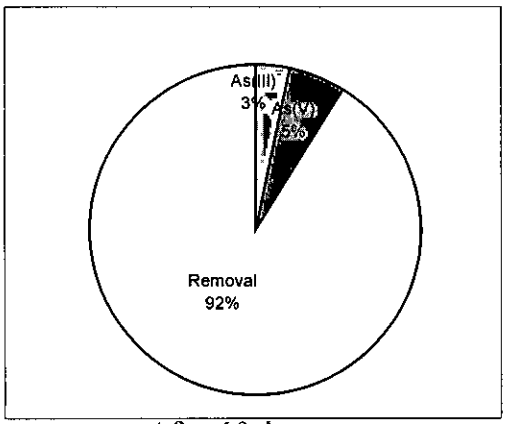
Challenger (1954) proposed that As(V) transformed to As(III) before methylation. Reduction of arsenic (V) to As (III) in anoxic environments is thought to occur primarily by dissimilatory reduction where microorganisms utilize As (V) as a terminal electron acceptor for anaerobic respiration. In this study the conversion of As(V) to As(III) before eliminated from solution was assessed through batch experiments.

3.4.1 Materials and Methods

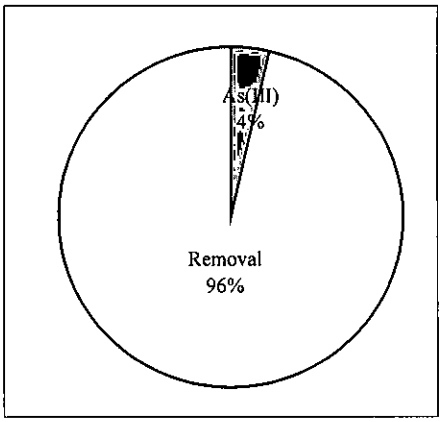
In order to assess transformation of arsenic in the presence of cow-dung, batch tests were conducted in 15-mL falcon centrifuge tubes. . Stock solutions of As (V) were prepared with Hach-NIST arsenic standards. Aqueous arsenic solutions (12 ml) with known concentrations (varying from 80 ppb to 400 ppb) of As(V) were taken in a series of tubes. 1 g of fresh cow-dung were added to each of the tubes. The tubes were left uncapped. After particular intervals, one tube from each set was taken out and centrifuged to separate the solid (cow-dung) from the liquid. The liquid portion from each tube was then separated by decanting and 2 ml was taken to measure arsenic concentration (after acidification). The remaining liquid portion was then analyzed for transformation of As(V) to As(III).The solution was acidified with 24μL to lower the pH to 2.7-3.0. One gm of Biorad moist resin was then added from pre-measured vial and shaked for 1 minute. It was allowed to settle for 4/5 minutes after which it was centrifuged to separate the liquid from solid. The liquid portion containing As (III) was then analysed for arsenic. The resin containing adsorbed As (V) of the solution was then treated with 10 mL 1.1316N HC to extract the adsorbed As (V) and measured with graphite-furnace AAS (Shimadzu AA6800).

3.4.2 Results and Discussion

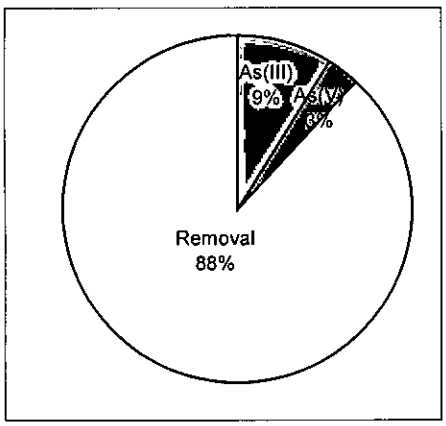
Figure 3.13 shows the elimination of arsenic from arsenic solution and transformation of arsenic in terms of percentage from As (V) converted to As (III) as well as As(V) remaining in the solution after certain period of time. About 92% of arsenic was eliminated from As(V) solution with an initial As concentration 1.05 mg /L after 10 days, where about 96% arsenic was eliminated after 15 days, with the same initial arsenic concentration This indicate that most of the arsenic



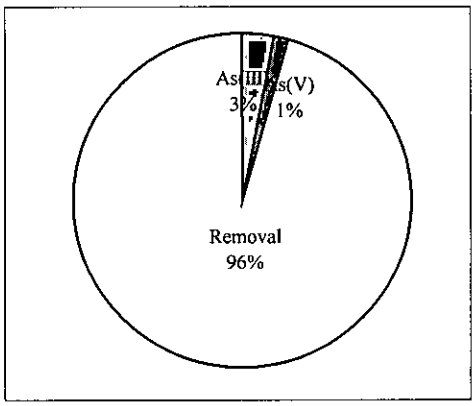
After 10 days
Initial As 1.05 μg



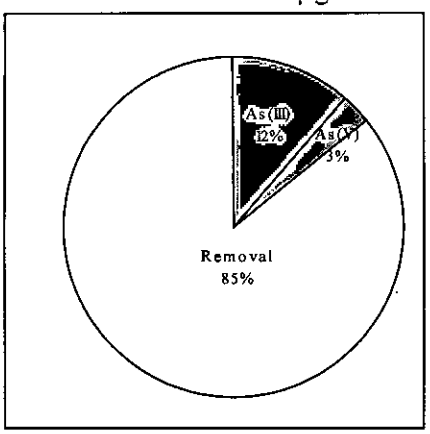
After 15 days
Initial As 1.05 μg



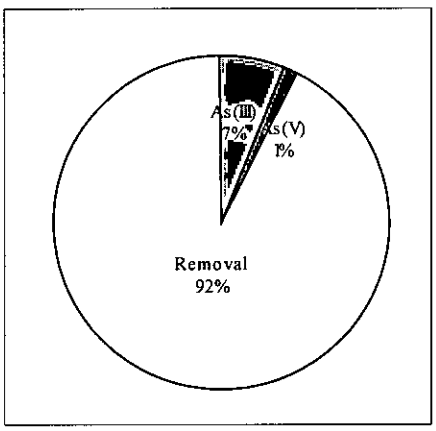
After 10 days
Initial As 2.21 μg



After 15 days
Initial As 2.21 μg



After 5 days
Initial As 4.74 μg



After 8 days
Initial As 4.74 μg

Figure 3.13: Conversion of As(V) to As(III) before Elimination

has been eliminated from the aqueous solution. Again, the results clearly state that As (V) is transformed into As (III) before elimination. With the progress of time percentage of As (V) reduced from the solution.

The remaining As(III) and As(V) portion in solution is quite low in compared to the elimination of arsenic from the solution. The results also suggest that the transformation of arsenic is not proportional to the initial concentration of arsenic (V).

Table 3.1 shows the mass balance estimates from the laboratory experiments. Mass balance error varied from 6% to 35%.

It should be noted here that Richard et al. (2001) found in their study that microbial reduction of arsenic (V) to arsenic (III) enhance arsenic mobilization. From the study so far, it appears that arsenic (V) convert to arsenic (III) before elimination. However, studies are needed to understand the process.

Table 3.2: Mass Balance of Total As and As (V) &As (III)

Total As	As(III)	As(V)	Cumulative As(III)+As(V)	Difference Between Total As And Cumulative	% Difference in terms of Total As
(µg)	(µg)	(µg)	(µg)	(µg)	
0.12	0.0413	0.055	0.0963	0.0237	19.75
0.046	0.0367	0	0.0367	0.0093	20.22
0.27	0.194	0.059	0.253	0.017	6.30
0.2	0.121	0.03	0.151	0.049	24.50
1.02	0.5517	0.136	0.6877	0.3323	32.58
0.57	0.308	0.065	0.373	0.197	34.56

Chapter-4

Quantification of Arsenic Release from Arsenic Rich Sludge

4.1 Introduction

To combat the arsenic crisis, a number of household and community based arsenic removal technologies have been developed and a number of such technologies are currently being used in many arsenic affected areas in Bangladesh. All arsenic removal units generate some form of arsenic-rich wastes. The wastes are usually disposed into cowdung bed where transformation/ biotransformation may occur with consequent arsenic release from the water. On of the objectives of this study is to quantify the release of arsenic from the wastes generated from coagulation based arsenic removal systems (STAR and BTU unit). In this chapter, the experiments are described and the results are presented and discussed.

4.2 Collection of Treatment Waste Samples

In this study, arsenic-rich wastes have been collected from two different types of coagulation-based systems. These are (i) STAR bucket treatment unit (based on iron coagulation), and (ii) UNU-BUET bucket treatment unit (based on ferric chloride coagulation). All samples have been collected from operational arsenic removal units. Wastes from the first type of arsenic removal units were collected from Laksmipur district. Wastes from the UNU-BUET unit (BTU) have been collected from the UNU-BUET field site at Adda village in Barura Thana of Comilla district.

4.3 STAR Unit

4.3.1 Materials and Methods

In order to assess transformation of arsenic present in treatment wastes in the presence of cow-dung, similar experiments, as described in Chapter-3, were conducted with slurry wastes collected from STAR treatment units. At first, arsenic contents of well mixed slurry wastes collected from STAR treatment units were determined after digestion with aqua regia. For batch experiments, fixed volumes of slurry wastes (5-mL for STAR waste and 30-mL for BUET-UNU-waste) were taken in a series of 50-mL falcon centrifuge tubes (a total of 8 to 10 tubes for each set of experiment). Fixed quantities (2, 4 and 8 grams) of freshly collected cow-dung were added to each of the tubes. One set of tubes was capped and a similar other set was left uncapped. The tubes were capped after purging nitrogen gas for 2/3 minutes from the gas cylinder. After particular intervals, one tube from each set was taken.

The capped tubes were uncapped and left open for sometime. Eh of each tubes was measured by Eh probe and then arsenic concentration of its contents was determined after digestion (with aqua-regia). As before, arsenic content of freshly collected cow-dung was also determined after digestion. Thus changes in total arsenic content in the tubes were determined as a function of time.

The digestion procedure of cowdung consists of the following steps:

i. 5 grams of fresh cowdung was taken in a volumetric flask and it was made moist by adding a few milliliters of deionized water, then 2.5 mL nitric acid and 7.5 mL hydrochloric acid was added to the flask and was kept overnight
ii. deionized water was added and the flask was heated for two hours
iii. if color of the sample turns yellow, digestion was assumed to be complete.
iv. deionized water was then added to make the volume 100 mL
v. After filtering the sample was stored in a bottle

Briefly the digestion procedure of the slurry consists of the following steps: .

i. 25 mL slurry was taken from the collected sample and 2.5 mL nitric acid and 7.5 mL hydrochloric acid was added to the flask and was kept overnight
ii. deionized water was added and the flask was heated for two hours
iii. if color of the sample turns yellow, digestion was assumed to be completed.
iv. deionized water was then added to make the volume 500 mL
v. After filtering the sample was stored in a bottle

Same procedure was followed for digestion of cowdung mixed slurry.

Arsenic analysis of slurry samples was carried out with Graphite Furnace atomic absorption spectrophotometry using an AAS (Shimadzu, AA6800).

4.3.2 Results and Discussion

1st Experimental Set Up

The main objective of this part of the study is to assess the elimination of arsenic from arsenic rich wastes generated from arsenic removal units for different ratio of arsenic content and weight of cowdung. The batch experiments were conducted with arsenic rich slurry (5mL) in the presence of fixed weight of cowdung (2g, 4g and 8g). All the results of the study are shown in Annex B. The recoded pH and Eh is 6.3-6.8 and –155 mV to –375mV.

Fig 4.1 shows the arsenic remaining in the mixture as a function of time for both cap-open and cap-closed conditions. In most cases elimination of arsenic under cap-open and cap-closed conditions were similar. Majority of this elimination appears to take place during the first few days and then arsenic contents appear to reach a plateau. Again, the same result has been found for different weights of cowdung added to the slurry with same arsenic content.

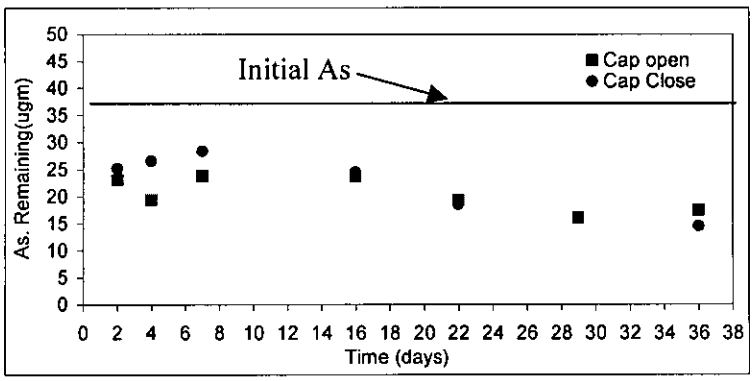


Figure 4.1: Arsenic Remaining in Arsenic rich STAR slurry in presence of 4 g Cowdung (Initial As 36.41 μg)

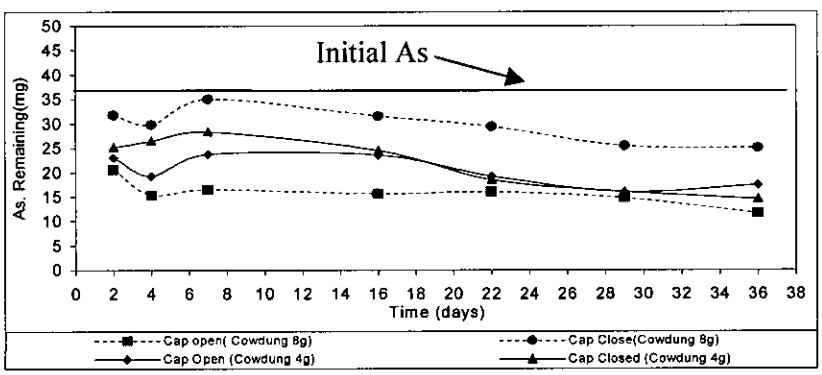


Figure 4.2: Comparison of Arsenic Remaining from Arsenic Rich STAR Slurry Mixed with of 4 g and 8 g Cowdung

Elimination of arsenic from arsenic rich STAR slurry is shown in Fig 4.2. In this figure elimination of arsenic from STAR slurry is shown in the presence of 4g and 8g cowdung. Initial Arsenic contents of the two samples were almost same (36.41 μg As for the sample mixed with 4g cowdung and the other is 37.07 μg.) Ranges (min – max) of percentages of arsenic elimination from the STAR slurry in the presence of 4 g cowdung under cap-open condition is

35%-47% and 22%-60% for cap-closed condition. Ranges (min – max) of arsenic elimination from the STAR slurry in the presence of 8g cowdung are 44%-69% and 5%-33%

in case of cap-open, cap-closed respectively. Arsenic elimination under cap-closed condition is lower than cap-open condition for the batch experiments performed in presence of 4g and 8g cowdung. Maximum arsenic elimination was recorded 50% and 60% in cap-open and cap-closed conditions respectively in the presence of cowdung 2g cowdung. The results do not indicate a significant correlation between the percent elimination of arsenic to the weight of fresh cowdung added to the STAR slurry for both cap- open and cap-closed condition. Again, from Fig 4.2 and 4.3, it has been observed that arsenic elimination from the mixture under cap-closed condition is quite low in comparison to that of under cap- open condition. The number of microorganism present in fresh cowdung might have some effect on this case. In this study a fixed amount of cowdung was added to the mixture after mixing in a vial. So each sample contained the same weight of cowdung but the number of microrganism and type may be different. Thus there might be a possibility of not getting same trend in arsenic elimination not only under different condition (cap- open and cap-closed), but also under similar capping condition, but for different amount of cowdung.

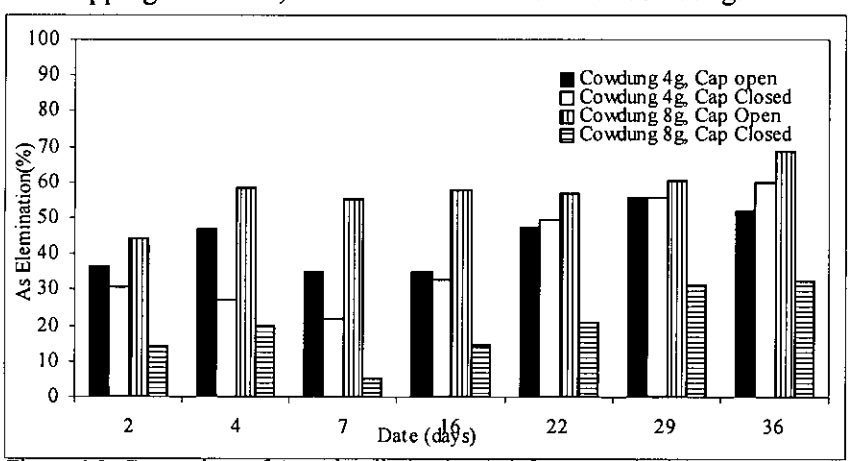


Figure 4.3: Comparison of Arsenic Elimination (%) from arsenic rich STAR Slurry mixed with of 4 gm And 8 gm Cowdung

2nd Experimental Set Up:

In 2nd experimental set up batch experiments were performed to assess the elimination of bound arsenic from arsenic rich STAR slurry and to compare these results with the results obtained in the 1st experimental set up. As from the results of the batch experiments performed at 1st set up it is seen that there was no significant variation of results under cap-open and cap-closed condition. Thus in 2nd experimental set up the tests were performed

only for cap- open condition. In the second phase initial amount of arsenic rich STAR slurry was higher.

The initial amount of arsenic of STAR slurry was 1488 μg. Fig 4.4 shows arsenic remaining in the slurry after fixed interval in the presence of 4g and 8g cowdung under cap-open condition. Like the results of first experimental set up, majority of this elimination appears to take place during the first few days (Fig 4.4) and then arsenic contents appear to reach a plateau. Percent elimination of arsenic is

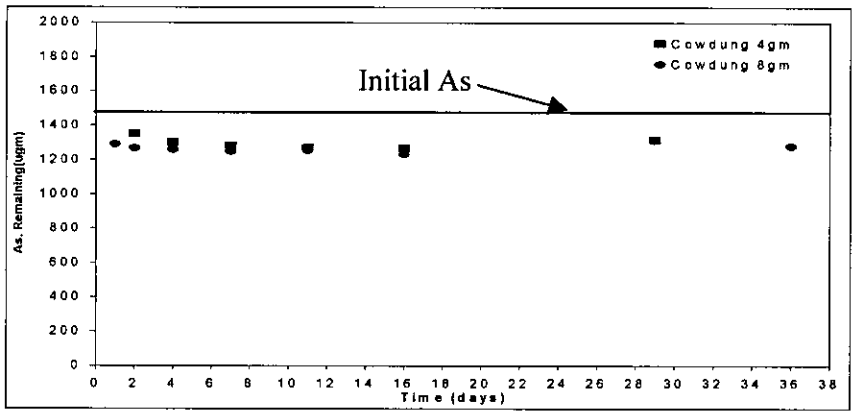


Figure 4.4: Elimination of arsenic present in treatment wastes from STAR unit in the presence of 4g and 8 g Cowdung (initial As 1488 μg)

almost same throughout the period of the experiments. Again elimination of arsenic for 4g and 8g cowdung were found to be similar. As the initial concentration is quite high, average percent of elimination is quite low. Range of percent elimination of arsenic are 9%-15% and 12%- 17% for the samples mixed with 4g and 8g fresh cowdung, respectively.

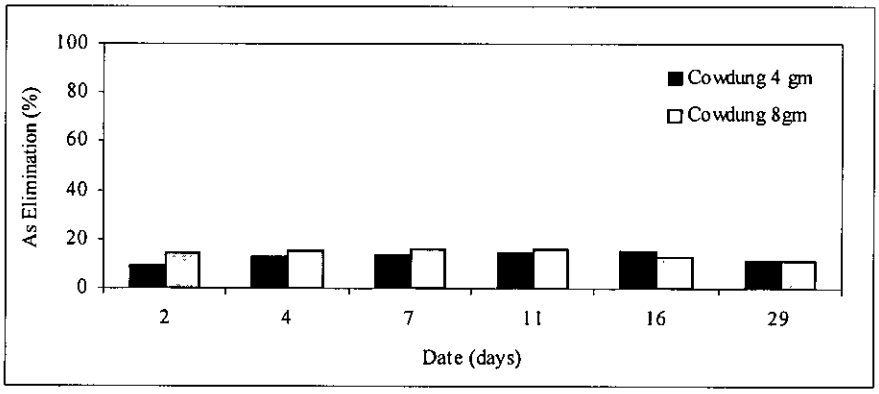


Figure 4.5: Elimination (%) of arsenic present in treatment wastes from STAR units in the presence of 4g and 8 gm Cowdung (initial As 1488 μg)

4.4 Comparison of Results Between 1st Experimental Set Up and 2nd Experimental Set Up

In both phases , it has been observed that majority of the elimination appears to take place during the first few days and then As content appears to reach plateau.

Table 4.1: Range (min –max) of percent elimination of arsenic in the Presence of Cowdung (Cap- open)

Experimental Set Up	Initial Arsenic content µg	Weight of cowdung added g	Range (min – max) of elimination of arsenic %
1st	36.41	4	35% - 57%
2nd	1488	4	9%-15%
1st	37.07	8	44% - 69%
2nd	1488	8	12%-17%

From Table 4.1, it can be suggested that with increasing arsenic concentration in slurry elimination of bound arsenic decreases. But percent elimination has no proportional relationship to the amount of cowdung added to the slurry. Microorganism may not be much efficient in eliminating arsenic from treatment waste as the arsenic is chemically bound with the treatment waste .

4.5 BTU Unit

4.5.1 Materials and Methods

In order to assess transformation of arsenic present in treatment wastes in the presence of cow-dung, similar experiments (as described earlier) were conducted with slurry wastes collected from BUET-UNU bucket treatment units. At first, arsenic contents of well mixed slurry wastes collected from BTU were determined after digestion with aqua regia. For batch experiments, fixed volumes of slurry wastes (30-mL) were taken in a series of 50-mL falcon centrifuge tubes (a total of 8 to 10 tubes for each set of experiment). Fixed quantities (2, 4 and 8 grams) of freshly collected cow-dung were added to each of the tubes. One set of tubes was capped and a similar other set was left uncapped. The tubes were capped after purging nitrogen gas for 2/3 minute from the gas cylinder. After particular intervals, one tube from each set was taken. The capped tubes were uncapped and left open for sometime. Eh of each tubes was measured by Eh probe and then arsenic concentration was determined after

digestion (with aqua-regia). As before, arsenic content of freshly collected cow-dung was also determined after digestion. Thus changes in total arsenic content in the tubes were determined as a function of time.

The digestion procedure of cowdung consists of the following steps:

i. 5 grams of fresh cowdung in a volumetric flask was taken and it was made moist by adding a few milliliters of deionized water, then 2.5 mL nitric acid and 7.5 mL hydrochloric acid was added to the flask and was kept overnight
ii. deionized water was added and the flask was heated for two hours
iii. if color of the sample turns yellow, digestion was assumed to be complete.
iv. deionized water was then added to make the volume 100 mL
v. After filtering the sample was stored in a bottle

Briefly the digestion procedure of the slurry consists of the following steps: .

i. 25 ml slurry was taken from the collected sample and 2.5 mL nitric acid and 7.5 mL hydrochloric acid was added to the flask and was kept overnight
ii. deionized water was added and the flask was heated for two hours
iii. if color of the sample turns yellow, digestion was assumed to be completed.
iv. deionized water was then added to make the volume 500 mL
v. After filtering the sample was stored in a bottle

Same procedure was followed for digestion of cowdung mixed slurry.

Arsenic analysis of slurry samples was carried out with Graphite Furnace atomic absorption spectrophotometry using an AAS (Shimadzu, AA6800)..

4.5.2 Results and Discussion

1st Experimental Set Up

Batch experiments, similar to other carried out with STAR Unit, were conducted with the slurry of BTU. The batch experiments were conducted with arsenic rich slurry (30mL) in

presence of fixed weight of cowdung (2g, 4g and 8g). All the results of the study are shown in Annex B.

Figure 4.6 shows the arsenic remaining in the mixture after certain interval for both cap-open and cap-closed condition in presence of 2g cowdung. In most cases elimination of arsenic under cap-open and cap-closed conditions were similar. Majority of this elimination appears to take place during the first few days and then arsenic contents appear to reach a plateau. Similar results have been found for different weights of cowdung added to the slurry with same arsenic content (See Annex B)

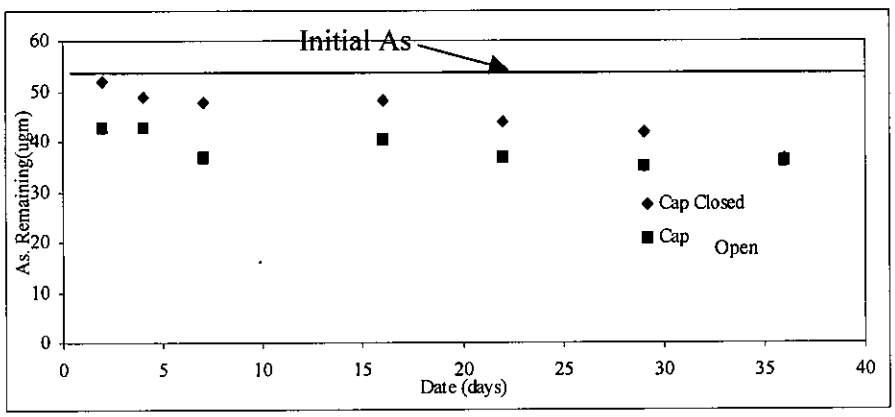


Figure 4.6: Arsenic Remaining in treatment wastes from BTU units in the presence 2gm Cowdung (initial As 53.3 μg)

Elimination of arsenic from arsenic rich BTU slurry is shown in Fig 4.6. In this figure elimination of arsenic from BTU slurry is shown in the presence of 4g and 8g cowdung. Initial amount of arsenic of the two samples were 53.30 μg. Range (min – max) of percentages of arsenic elimination from the BTU slurry in the presence of 4 g cowdung under cap-open condition is 20%-44% and 27%-35% for cap-closed condition. Range (min – max) of arsenic elimination from the BTU slurry in the presence of 8g cowdung are 5%-28% in case of cap-open condition. Arsenic elimination under cap-closed condition is lower than cap-open condition for the batch experiments performed in the presence of 4g cowdung. Maximum arsenic elimination was recorded 32% and 34% in cap-open and cap-closed conditions respectively in the presence of cowdung 2g cowdung. The results do not indicate a significant correlation between the percent elimination of arsenic to the weight of fresh cowdung added to the BTU slurry for both cap- open and cap-closed condition. Again, from

Fig 4.7, it is seen that arsenic elimination from the mixture under cap-closed condition is quite low in comparison to that of under cap- open condition. The number of microorganism present in fresh cowdung might have some effect on this case. In this study a fixed amount of cowdung was added to the mixture after mixing in a vial. So each sample contained the same weight of cowdung but the number of microorganisms and type of them may have been different. Thus there might be a possibility of not getting same trend in arsenic elimination not only under different condition (cap- open and cap-closed), but also under similar capping condition, but for different amount of cowdung.

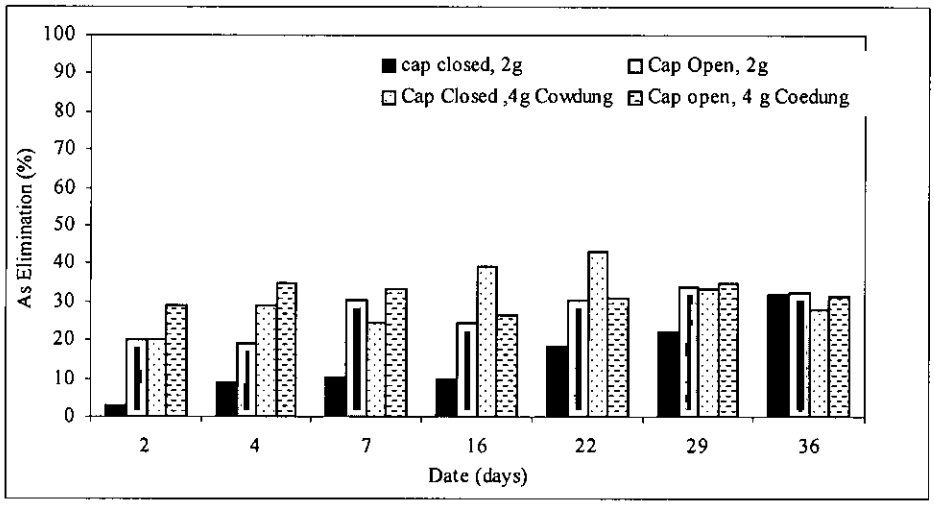


Figure 4.7: Elimination (%) of arsenic present in treatment wastes from BTU unit in the presence 2g and 4gm Cowdung (initial As. conc 53.3 μg)

2nd Experimental Set Up

In 2nd experimental set up batch experiments were performed to assess the elimination bound arsenic from arsenic rich BTU slurry and to compare these results with the results obtained in the 1st experimental set up. As from the results of the batch experiments performed at 1st phase it is seen that there was no significant variation of results under cap- open and cap-closed condition. Thus in 2nd experimental set up the tests was performed only for cap- open condition. In the second phase initial amount of arsenic rich BTU slurry was higher.

The initial amount of arsenic of BTU slurry was 31.12 μg. Fig 4.8 shows arsenic remaining in the slurry after fixed interval in the presence of 4g and 8g cowdung under cap-open

condition. Like the results of first experimental set up, majority of this elimination appears to take place during the first few days (Fig 4.8) and then arsenic contents appear to reach a plateau. Percent elimination of arsenic is almost same throughout the period of the

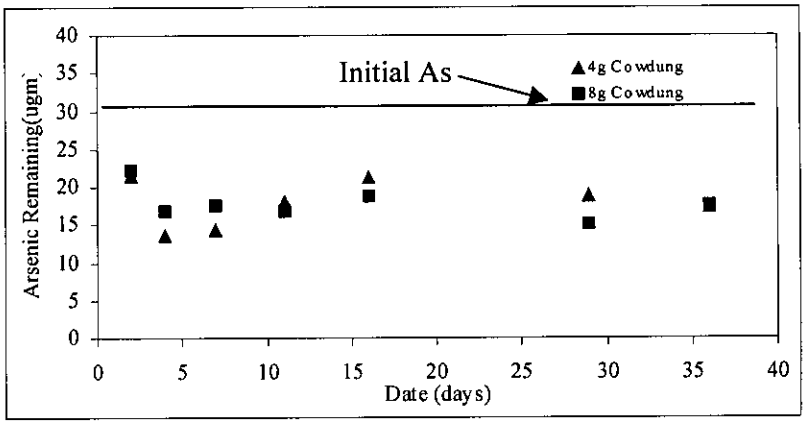


Figure 4.8: Elimination of arsenic with time present in treatment wastes from BTU unit in the presence of 4g and 8 g Cowdung (intial As. conc 31.12 µg)

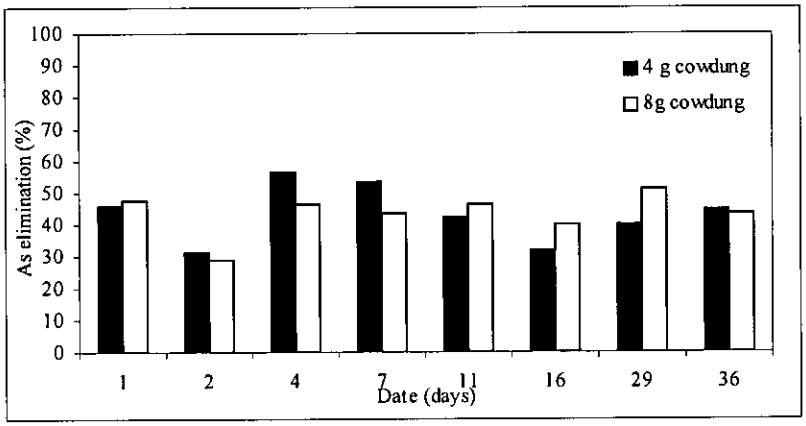


Figure 4.9: Elimination (%) of arsenic present in treatment wastes from BTU unit in the presence 2g and 4g Cowdung (initial As. conc 53.3 µg)

Again elimination of arsenic for 4g and 8g cowdung were found to be similar. Range of percent elimination of arsenic are 31%-57% and 29%- 52% for the samples mixed with 4g and 8g fresh cowdung, respectively.

4.5.3 Comparison of Results Between 1st And 2nd Experiment Set Up

In both phases, it has been observed that majority of the elimination appears to take place during the first few days and then As content appears to reach plateau.

Table 4.2: Range (min-max) of percent of arsenic elimination in Presence of Cowdung(Cap- open)

Experimental Set up	Initial Arsenic content µg	Weight of cowdung added g	Range (min – max) of Arsenic elimination %
1st	53.30	4	20%-44%
2nd	31.12	4	31%-57%
1st	53.02	8	5%-28%
2nd	31.12	8	29%- 52%

From Table 4.2 and Figure 4.10, it can be suggest that with increasing arsenic concentration in slurry elimination of bound arsenic decreases.

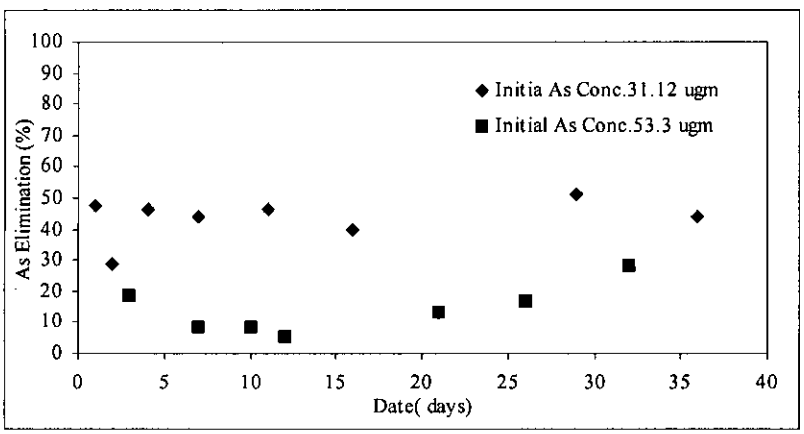


Figure 4.10: Comparison of arsenic elimination with time in presence of 8g cowdung with different arsenic concentration

It should be mentioned that Rahman (2002) investigated elimination of arsenic from treatment wastes in the presence of soil and cowdung over a longer time periods and observed significant elimination of arsenic during the first one to two months, after which removal rates dropped significantly.

The results of the experiment of this give an idea that arsenic elimination may decrease with increase of initial arsenic content of the wastes. But no proportionality has been found with amount of fresh cowdung added to elimination of arsenic from wastes. Again, from the results it can be said that amount of arsenic elimination from both STAR and BTU unit almost similar when same amount of cowdung is added but more data is needed to establish this phenomena.

Chapter- 5

Elimination of Arsenic from Arsenic Rich Soil

5.1 Elimination of Arsenic from Arsenic Solution Mixed with Arsenic Rich Soil

5.1.1 Introduction

Various forms of arsenic in soil are interconverted by geo-chemical reactions and microbial activities. Soil microorganisms convert small amount of arsenic to volatile arsine. These volatile arsines are released to the air. In this study, one of the objectives is to quantify the amount of arsenic eliminated by microbial activity from arsenic-rich soil mixed with aqueous solution. In this chapter, the experiments are described and the results are presented and discussed.

5.1.2 Materials and Methods

In order to assess transformation of arsenic present in arsenic solution in the presence of soil rich in arsenic, similar experiments as described in chapter three and four were conducted. At first, arsenic contents of well mixed soil collected from agricultural field were determined after digestion with aqua-regia. For batch experiments, fixed weight of soil (5 g, oven dry weight) was taken in a series of 15-mL falcon centrifuge tubes (a total of 5 to 7 tubes for each set of experiment) containing As(III) solution (23.45 μg) . One set of tubes was capped and a similar other set was left uncapped. The capped tubes were uncapped and left open for sometime. The liquid portion from each tube was then separated by decanting and its arsenic content was measured (after acidification). Arsenic content of the solid (soil) portion was also determined after digestion with aqua-regia. Thus changes in total arsenic content in the tubes were determined as a function of time. In all cases arsenic concentrations were measured with graphite-furnace AAS (Shimadzu AA6800). The same type of batch tests were performed with AS(V) solution.

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The digestion procedure of soil consists of the following steps:

i. The soil was taken in a volumetric flask and was made moist by adding a few milliliters of deionized water, then 2.5 mL nitric acid and 7.5 mL hydrochloric acid was added to the flask and was kept it overnight
ii. deionized water was added and heated the flask for two hours
iii. if color of the sample turns yellow, digestion was assumed to be complete.

iv. demonized water was added to make 500 mL solution of the sample and bottled after filtration.

5.1.3 Results and Discussion

Figure 5.1 and figure 5.2 shows results of batch experiments conducted to assess transformation of arsenic from aqueous solutions in the presence of arsenic rich agricultural soil. All the figures of the batch test experiment have been given in Annex-C. These figures show little elimination of As (III) from the solution in presence of arsenic rich soil.

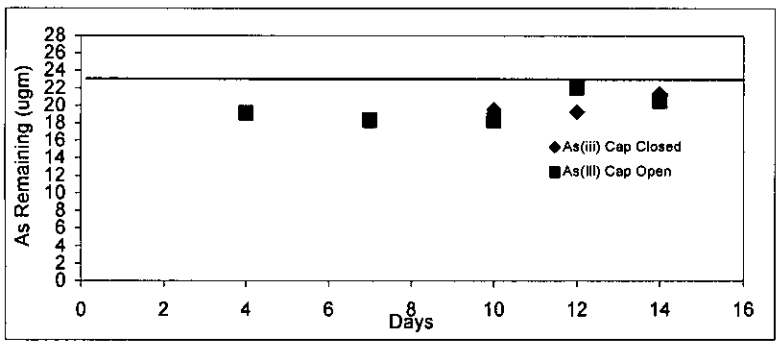

Figure 5.1: Arsenic Remaining in As(III) Solution mixed with 5g Arsenic contaminated Soil.

This may be due to the microbial activity of the microorganisms present in the soil. In most cases elimination of arsenic under cap-open and cap-closed conditions were similar. Majority of this elimination appears to take place during the first few days. Similar results were also obtained from experiments with aqueous solutions of As (V) (Fig 5.2).

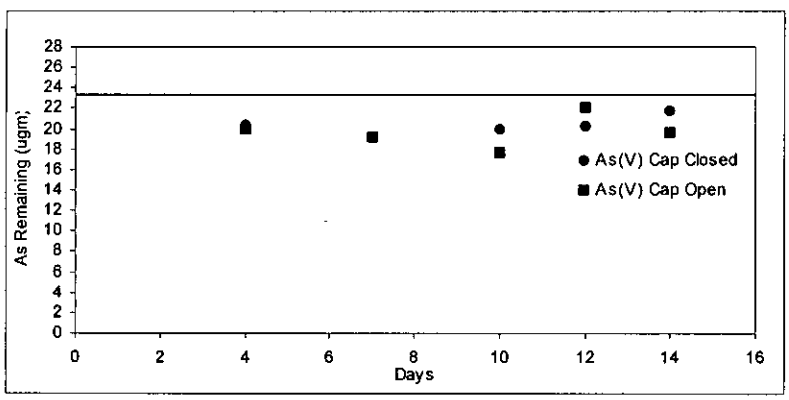

Figure 5.2: Arsenic Remaining in As(V) Solution mixed with 5g Arsenic contaminated Soil.

Fig 5.3 shows elimination of arsenic (%) from arsenic (III) and arsenic (V) solution mixed with arsenic rich soil. About 5%-20% arsenic was eliminated from the solution as well as from the soil. Again this figure also shows almost all elimination take place in early few days and the

elimination is similar for both cap-open and cap-closed condition. These results may not be the representative picture of the field condition. In field there is a lot of source of nutrient, which was not supplied in batch experiments. Again, temperature, solar energy, algal activity influences the activity of microorganism that was not achieved in laboratory environment. In a publication U. S. EPA (1999) suggests that various form of arsenic in soil is interconverted chemical reactions and microbial activity and soil microorganisms convert small amount of arsenic to volatile form.

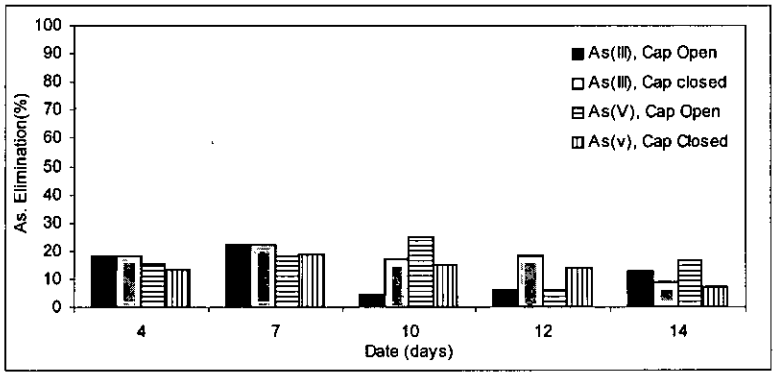

Figure 5.3: Arsenic Elimination from Arsenic Rich Soil under both Cap Open and Cap Closed Condition (Initial As 23.45μg)

5.2 Elimination of Arsenic from Arsenic Rich Agricultural Soil in the Presence of Cowdung

To see any possible effect of cowdung, which might eliminate bound arsenic, some batch tests were performed adding fresh cowdung with arsenic rich soil and the same procedure was followed as mentioned above. In these experiments tap water was used in place of arsenic solution.

5.2.1 Materials and Methods

In order to assess transformation of arsenic from arsenic rich agricultural soil in the presence of cow-dung, batch tests were conducted in 15-mL falcon centrifuge tubes. At first, arsenic contents of well mixed soil collected from agricultural field were determined after digestion with aqua-regia. For batch experiments, fixed weight of soil (2 g, oven dry weight) were taken in a series of 15-mL falcon centrifuge tubes (a total of 5 to 7 tubes for each set of experiment). Fixed quantitities (1g, 2 g, 6 g) of freshly collected cow-dung were added to each of the tubes. Tap water (8 to 10 mL) was also taken in each tube. The tubes were left uncapped. Decanting then separated the liquid portion from each tube and its arsenic concentration was measured (after

acidification). Arsenic content of the solid (cow-dung and soil) portion was also determined after digestion with aqua regia. The initial Arsenic content of freshly collected cowdung and arsenic content of distilled water was also determined. Thus changes in total arsenic content in the tubes were determined as a function of time. In all cases arsenic concentrations were measured with graphite-furnace AAS (Shimadzu AA6800).

Briefly the digestion procedure of solid (cowdung and soil) consists of the following steps:

i. 5g oven dry soil was taken in a volumetric flask and it was made moist by adding a few milliliters of deionized water, then 2.5 mL nitric acid and 7.5 mL hydrochloric acid was added to the flask and was kept overnight

ii. deionized water was added and heated the flask for two hours

iii. if color of the sample turns yellow, digestion was assumed to be complete.

iv. deionized water was added to make 500 mL solution of the sample and bottled after filtration.

5.2.2 Results and Discussion

The main objective of this part of the study is to assess the elimination of arsenic from arsenic rich agricultural soil mixed with cowdung in tap water solution. It was observed that only 5%-20% arsenic is eliminated from soil and aqueous solution. All the results and graphs of the study are shown in Annex C.

Figure 5.4 and 5.5 shows the arsenic remaining in the solution and arsenic elimination from the solution after certain interval for both cap-open and cap-close condition respectively. In most cases majority of this elimination appears to take place during the first few days and then arsenic contents appear to reach a plateau. Again, the same result has been found for different weights of cowdung added to the soil with same arsenic content. From Fig 5.5 we can see that about

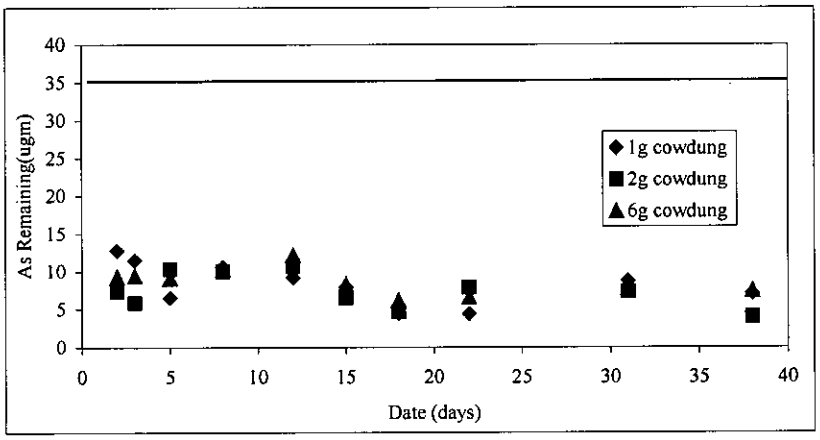

Figure 5.4: Arsenic Remaining with time in Solution mixed with 2g Soil and different weight of cowdung

52%-89% arsenic was eliminated from the soil, whereas the percentage was 5-20% when no cowdung was used. Range (min-max) of percentage elimination of arsenic from soil are 64%-88%, 70%-89% and 52%- 82% corresponding to 1g, 2g and 6g of fresh cowdung. Thus it can be said that microorganism present in cowdung might have significant effect in elimination of arsenic from arsenic rich soil.

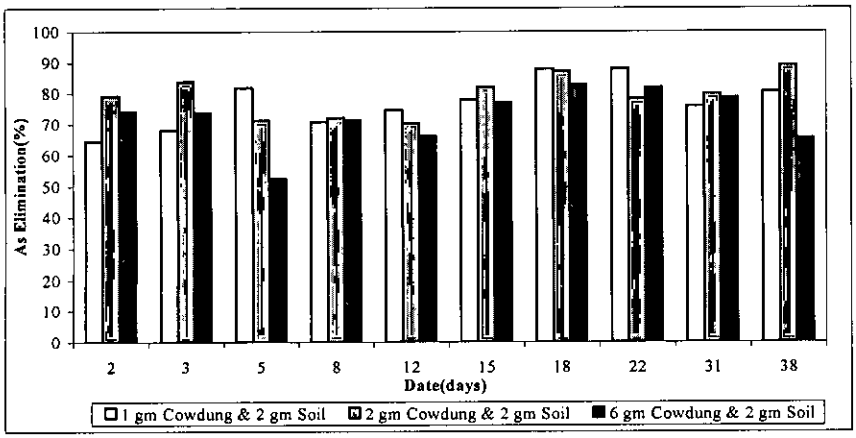

Figure 5.5: Arsenic Elimination (%) in Solution mixed with 2g Soil and different weight of cowdung

A comparison of elimination of arsenic (%) from the soil vs Arsenic concentration / Cowdung (μg /g) ratio has been shown in Fig 5.6. At a particular ratio the percentage elimination of arsenic from soil is apparently same as mentioned earlier and at the same time no significant change has been seen in elimination of arsenic with increase of arsenic/cowdung ratio .

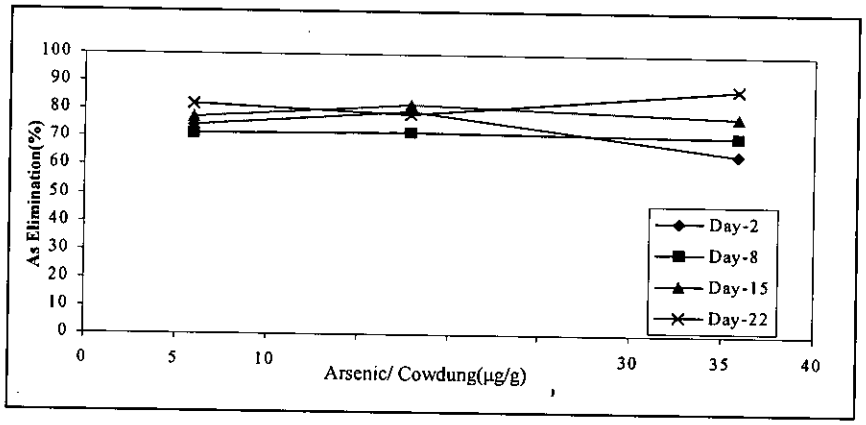

Figure 5.6: Arsenic Elimination (%) from Solution mixed with 2g Soil and different weight of cowdung

From the results of the two cases; arsenic elimination from arsenic solution mixed with soil and arsenic elimination from soil mixed with cowdung, it is clearly seen that arsenic elimination is much higher when it is mixed with cowdung . Again, when cowdung is mixed with soil, there may be variety of microorganism available at that mixture and the interdependency of microorganism may enhance their activity. Also the microorganism present in soil may get nutrient from cowdung for their growth and vice versa. However, as we did not measure the conditions, we are not at the stage to clearly assess the kinetics. Further study is needed for this.

5.3 Role of TSP in Desorbing of Arsenic

In Bangladesh fertilizers are frequently used in agricultural field and TSP is on of them.

With the use of these fertilizers, phosphate is directly been applied to the field. Phosphate addition to arsenic contaminated soils has been shown to enhance arsenic release from the soil through competitive anion exchange (Peryea and Kammereck, 1997). So in this study experiments were done to assess the performance of TSP, a source of phosphate in soil, was observed in displacing arsenic from arsenic rich agricultural soil.

5.3.1 Material and Methods

At first, arsenic contents of well mixed soil collected from agricultural field were determined after digestion with aqua-regia. For batch experiments, fixed weight of soil (5 g, oven dry weight) with different arsenic concentration (6.3 mg/kg to 11 mg/ kg) were taken in a series of 15-mL falcon centrifuge tubes (3 tubes for each set of experiment). 10 mL of phosphate solution (6.08 mg/L to 9.03 mg/L) made up from TSP fertilizer was added to each tube. Among three different concentrations of phosphate solutions, the concentration of phosphate in solution which is close to the concentration of arsenic in soil was added to that tube i.e., The solution containing 6.08 mg/kg of phosphate was added to the tube that contains the soil of arsenic

concentration 6.3 mg/kg and similarly the other two experiments were designed. For each soil type one set of experiment was carried out with deionized water instead of the particular phosphate solution. The tubes were left under cap-closed condition and end-over rotated for 24 hrs(1st set of tubes of each type of soils) , 48 hrs(2nd set) and a third set was end-over rotated for 72 hrs. The tubes filled with distilled water were end-over rotated for 48 hrs. Afterwards, the samples were centrifuged and the liquid portion of solution was taken for measuring arsenic concentration. Two replicates of each sample were done in a completely same design.

In all cases arsenic concentrations were measured with graphite-furnace AAS (Shimadzu AA6800).

5.3.2 Results and Discussion

In these experiments no significant displacement of total arsenic from soil into solution was found in the presence of phosphate. Besides the initial total arsenic concentration of the arsenic containing soil, initial phosphate and arsenic concentration of the solution was also measured and then arsenic concentration of the solution was measured after fixed time intervals (1d, 2d and 3days). Figure 5.7 shows total arsenic in solution after fixed interval. Initial arsenic content of the soil sample was 55 μg and amount of Phosphate was 60.75 μg total arsenic displacement from the soil by phosphate is significantly small (about 0.3 μg at day 2) in comparison to the initial arsenic content of the soil. This is may be due to that all arsenic are bound in soil matrix. Again a small amount of arsenic displacement was also found when tap water was used instead of phosphate solution. Similar results were found for the other 2 samples.

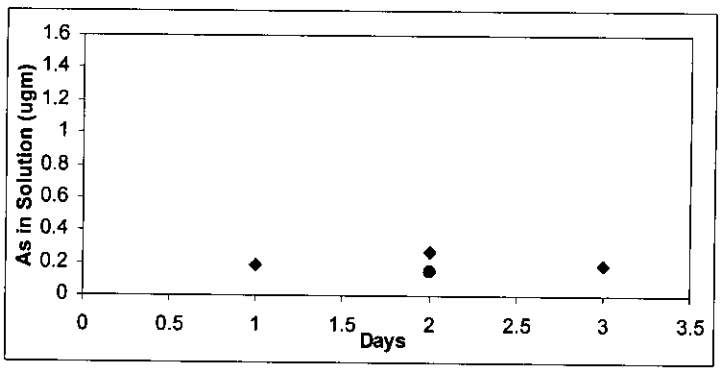

Figure 5.7: Arsenic Displacement from Arsenic Contaminated soil (Initial As 55 μg) in Presence of Phosphate

Again, Fig 5.8 shows comparison of arsenic displacement from three contaminated soil samples in the presence of phosphate solution and tap water after 48 hrs end-over rotation. Displacement

of arsenic from soil in presence of Phosphate solution is higher than the displacement by tap water.

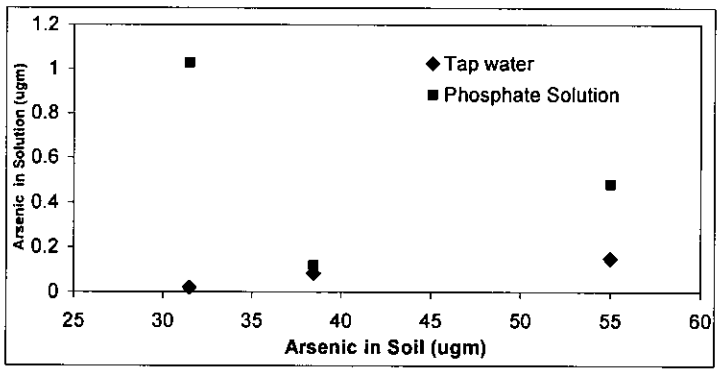

Figure 5.8: Arsenic Displacement from Arsenic Contaminated soil in Presence of Phosphate Solution and Tap water after 48 end over rotation

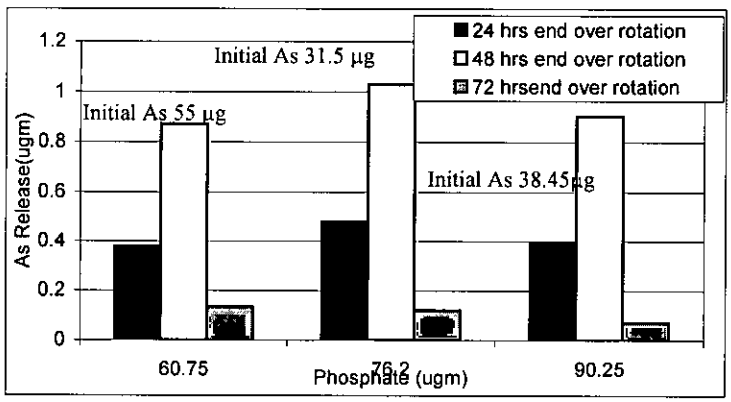

Figure 5.9: Displacement of total arsenic from arsenic contaminated soil samples in presence of phosphate of different concentrations.

Displacement of arsenic from arsenic rich agricultural soil by phosphatic fertilizers has been observed to be very low and also the experiments did not show any relationship of amount of arsenic released to the initial arsenic content of the soil or the concentration of the phosphate solution that was applied (Fig 5.9). It should be noted that Acharyya et al., (1999) have suggested that phosphatic fertilizers might enhance mobilization of arsenic in the soil zone by displacing of arsenic from adsorption site.

Chapter-6
Conclusions and Recommendations

6.1 Introduction

The overall objective of this study is to get a better understanding andquantificationof arsenic release from arsenic solution, arsenic-rich wastes and soil due to biochemical processes in the presence of cowdung. In this study batch experiments were performed with different initial arsenic content in presence of different amount of cowdung under cap-open and cap-closed condition. In this chapter conclusions, limitation of the study and recommendations for future works are described.

6.2 Conclusions

After analyses of the results, obtained from the batch experiments, the following conclusions can be drawn.

1. Batch experiments performed in this study on a wide range of arsenic aqueous solution in presence of cowdung suggest that, in general, significant elimination of arsenic occurred from aqueous solution in presence of cowdung.

   Addition of 83 g/L cowdung to the solution with arsenic concentration 79μg/L, the arsenic elimination was to be 46%-71% under cap- open and cap–closed condition whereas 84%-93% and 13% -58% arsenic elimination was observed when initial arsenic concentration was 180μg/L and 468μg/L respectively. Maximum 96% arsenic elimination was recorded from the solution with initial arsenic concentration 730 μg/L in the presence of 750 g/L cowdung.

   Similar trend has been found in arsenic elimination from As(V) solution in presence of cowdung under cap open and cap closed condition.

2. The results of the study suggest that As(V) may reduce to As(III) before elimination.

3. From STAR unit, range of arsenic elimination was found to be 9%-50%, 35%-56% and 44%-69% in the presence of 400g/L, 800g/L and 1600g/L cowdung respectively (the initial arsenic content was about 7400μg/L) .In cap-closed condition the range of arsenic elimination was found to be 19%-60%, 22%-60% and 5%-32% in the presence of 400g/L, 800g/L and 1600g/L cowdung respectively (the initial arsenic content was about 7400μg/L). Lower elimination (13% to 16%) of arsenic has been observed when slurry waste with high arsenic content (297.6 mg/L) was used in the experiments.

4. From Bucket Treatment Unit, range of arsenic elimination was found to be 3%-31%, 20%-44% and 5%-28% in the presence of 400g/L, 800g/L and 1600g/L cowdung respectively (the initial arsenic content was 7400 μg/L) .In cap-closed condition the range of arsenic elimination was found to be 19%-34% and 27%-35% in the presence of 400g/L and 800g/L cowdung respectively (the initial arsenic content was 7400 μg/L). Higher elimination (28% to 57%) of arsenic was observed when slurry waste with comparatively lower arsenic content (1307μg/L) was used in the experiments.

5. Addition of 83 g/L cowdung to an aqueous solution with arsenic concentration 464 μg/L about 2% to 25% arsenic elimination was observed. Again maximum arsenic elimination was to be 89% in presence of 1g, 2g and 6g cowdung mixed with 2g soil (initial As 18 mg/kg)

6. The results of this study suggest that phosphate can displace arsenic from soil matrix. The amount of arsenic displace from the soil is quite low (maximum displacement found 1.43 μg with initial arsenic content 31.5 μg and the concentration of phosphate solution was 6.075 mg/L after 24 hrs end over rotation).

7. In most of the cases majority of this elimination appears to take place during first few days. The results of this study suggest that, in general, elimination of arsenic from wastes (bound arsenic) is lower to some extent than that of arsenic from aqueous solution (unbound arsenic) and soil mixed with cowdung. Results of this study also suggest that bio-chemical (e.g. bio-methylation) process in the

presence of fresh cowdung may lead to significant elimination of arsenic from arsenic- rich treatment wastes and soil. The process appears to slow down significantly with time, under the experimental conditions followed in this study. No proportionality has been found with amount of fresh cowdung added to elimination of arsenic from wastes and soil.

6.3 Limitations of The Study

In this study experiments setup was designed after reviewing a lot of literature and care was taken during study period to perform the experiments with precision and also care was taken to analyse arsenic with Atomic Adsorption Sectophotometer (Shimadzu AA6800). However, due to lack of proper laboratory facility and other inconvenience some limitation of this study are as follows:

1. All the results of this study were observed in laboratory environment, which is some extent different from that of field condition i.e. algal activity.
2. While analyzing arsenic, Total arsenic was measured only, As (V), As (III) . Organic arsenic acid (MMA, DMA etc) was not measured separately, which may be also a product of bio-geochemical process of arsenic biotransformation.
3. The results are plotted taking the measurement of only one sample. More than one sample at a particular interval might give better and confident plot.
4. In addition to arsenic rich contaminated agricultural soil, pond sediment rich in arsenic might be used for batch experiments, as the structure of microorganism is different.
5. We did not inject any nutrient for microbial growth to the samples
6. Type of gas, Type of organic acid did not identified due to lack of laboratory facility.
7. In batch experiments with phosphate solution, phosphate concentration was taken is same as the concentration of arsenic in soil but in field phosphate fertilizers contain much higher concentration of phosphate.

6.4 Recommendations

After analyzing the results, obtained from a number of batch experiments performed in different experimental set up (i.e. different initial as concentration, different weight of cow dung), and reviewing a number of literature some recommendation have been suggested for further activities which are as follows:

1. In this study only quantification of arsenic released from arsenic rich wastes and soil was studied under different batch experiments in the laboratory. In order to understand better biogeochemical cycles of arsenic and production of arsenic in soil and wastes, the speciation analysis of water soluble arsenic species together with the analysis of gaseous species is of crucial importance. Again, it is important to study how microbial activities are linked to the biogeochemistry of arsenic and thus increasing the understanding of microbial mediated mechanisms behind environmental hazards and risk involved in arsenic contaminated soil and their remediation.

2. In all experiments, only total arsenic, As (V), As (III) was measured. Other products of transformation/bio-transformation such as Mono-methyl Arsonic Acid (MMA), Di-methyl Arsinic Acid (DMA), etc was not analysed separately due to lack of facilities in the laboratory.

3. In future study, at least three sets of samples under the same condition should be analysed to obtain average results.

4. The batch test may be continued for a long period in order to assess the long term evaluation of arsenic elimination in presence of cow dung from arsenic rich wastes and soil

5. Microorganisms such as bacteria, Fungi, yeast present in cow dung and soil should be identified. In addition to the identification works, the decay of microorganisms should be studied.

6. In this experiment samples were analysed from different tubes at different days. The samples should be analysed from one source in different days. So there may be homogeneity in microbial activity in all results.

7. Arsenic elimination in field condition should be checked.

8. Transformation / biotransformation of arsenic from agricultural field, irrigated by arsenic contaminated groundwater, should be studied.

9. In future study there should be consideration to measure soil moisture and temperature, abundance of different species of arsenic and microbial population in soil.

10. Chemical composition of cowdung should be investigated.

11. In this study, the main emphasis was given to get an overall idea in arsenic elimination in presence of cowdung. An in-depth study of arsenic elimination from arsenic solution or arsenic rich treatment waste or soil should be carried out to enhance the knowledge on biotransformation in the presence of cowdung.

Chapter-7

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ANNEX-A
Experimental Results on Elimination of Arsenic from Arsenic Solution in Presence of Cowdung

A.1 Arsenic Remaining in Arsenic Solution After fixed interval in Presence of Cowdung

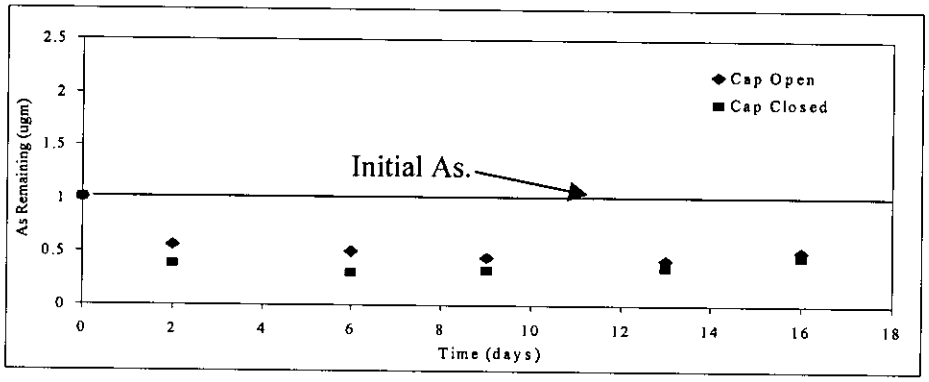


Figure A.1.1: Arsenic Remaining in Arsenic (III) solution with time in presence of 1 gm Cowdung (Initial As 1.01 μgm)

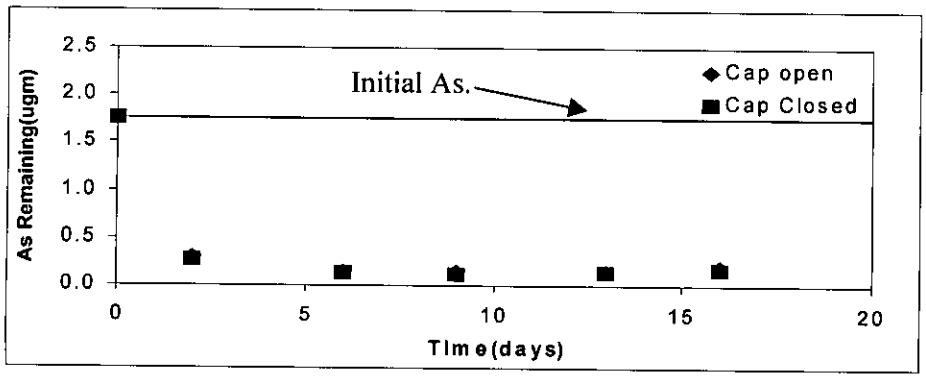


Figure A.1.2: Arsenic Remaining in Arsenic (III) solution with time in presence of 1 gm Cow dung (initial As 1.75 μgm)

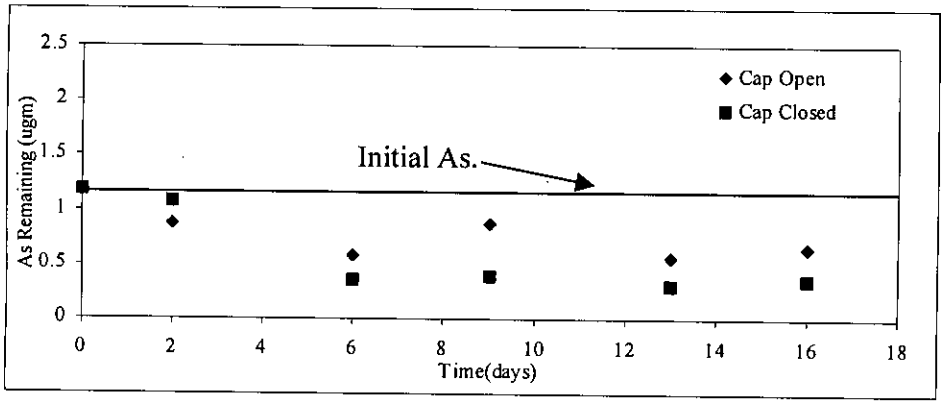


Figure A.1.3: Arsenic Remaining in Arsenic (V) Solution with time in presence of 1 gm Cow dung (initial As 1.18 μgm)

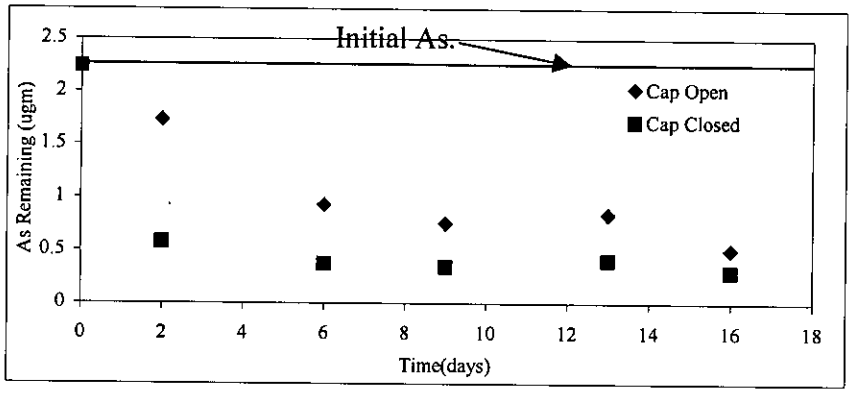


Figure A.1.4: Arsenic Remaining in Arsenic (V) solution with time in presence of 1 gm cowdung (initial As 2.24 μgm)

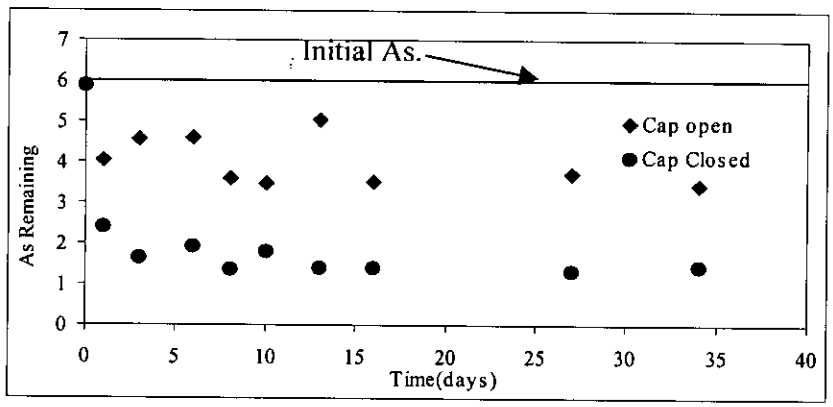


Figure A.1.5: Arsenic Remaining in Arsenic (V) solution with time in presence of 1 gm cowdung (initial As 5.90 μgm)

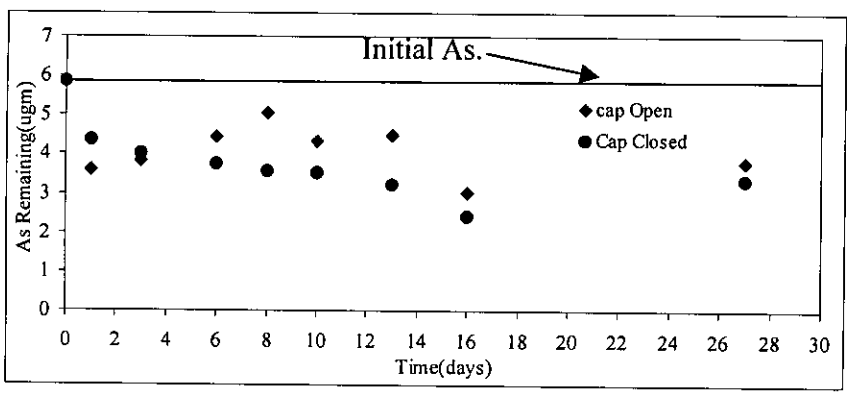


Figure A.1.6: Arsenic Remaining in Arsenic (III) solution with time in presence of 1 gm cowdung (initial As 5.90 μgm)

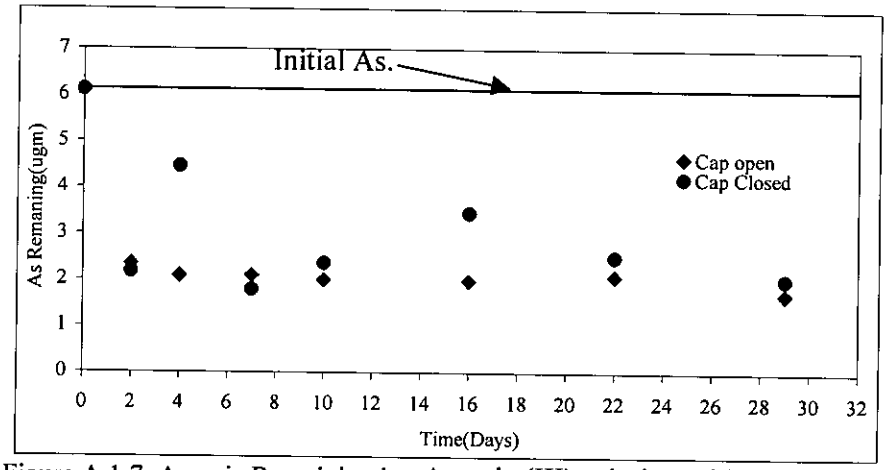


Figure A.1.7: Arsenic Remaining in Arsenic (III) solution with time in presence of 2 gm cowdung (initial As 6.11 μgm)

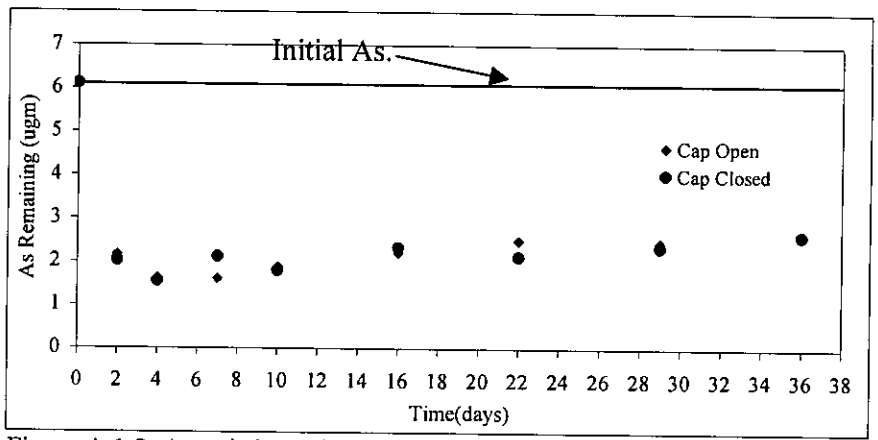


Figure A.1.8: Arsenic Remaining in Arsenic (V) solution with time in presence of 2 gm cowdung (initial As 6.11 μgm)

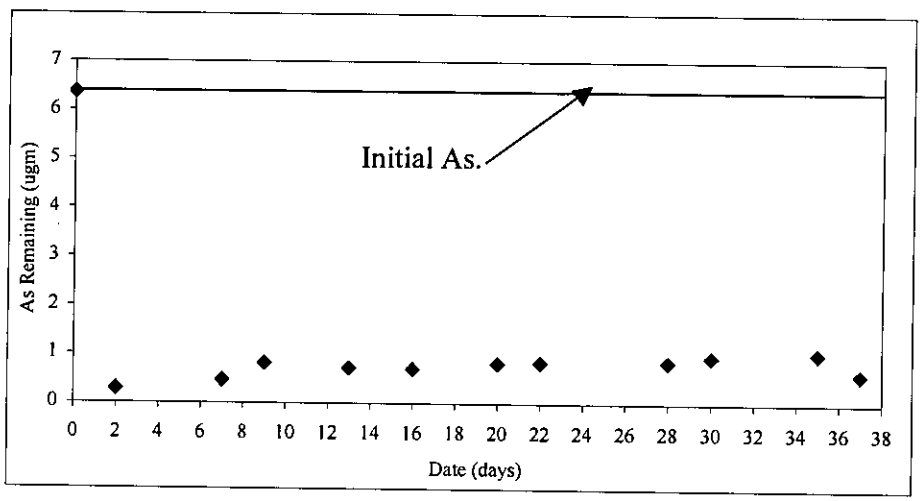


Figure A.1.8: Arsenic Remaining in Arsenic (V) solution with time in presence of 6 gm cowdung (initial As 6.36 μgm)

A.2 Arsenic Remaining in Arsenic Solution After fixed interval in Presence of Cowdung

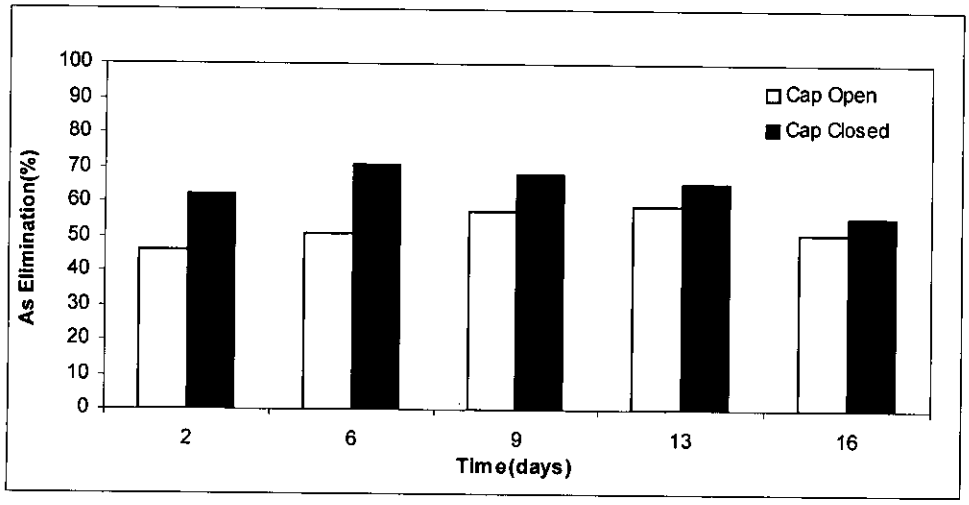


Figure A.2.1 Elimination of Arsenic from Arsenic (III) solution in presence of 1 gm cowdung (Initial As 1.01 μgm)

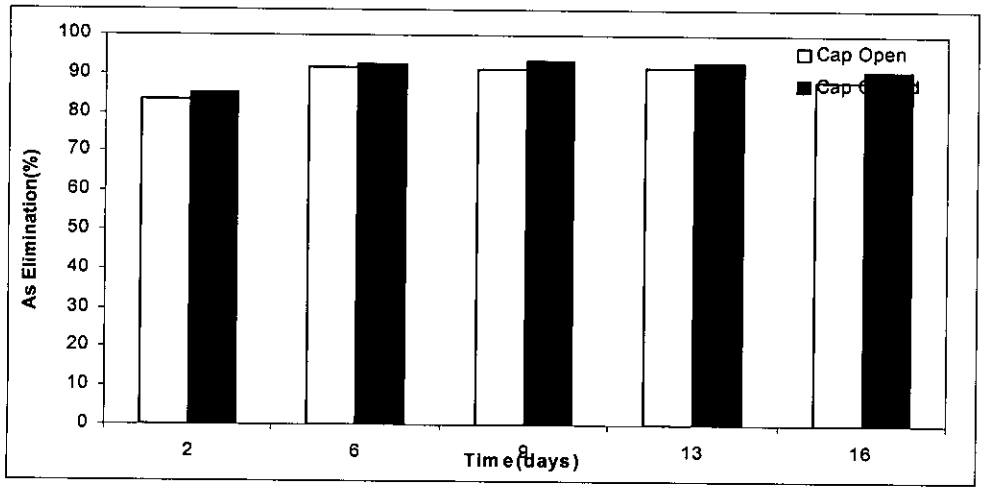


Figure A.2.2 Elimination of Arsenic from Arsenic (III) solution in presence of 1 gm cow dung (Initial As 1.75 μgm)

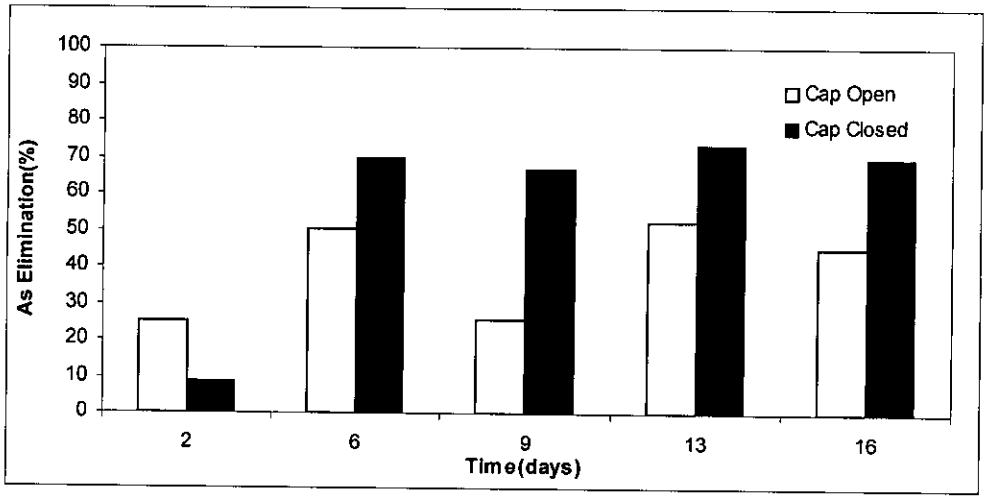


Figure A.2.3: Elimination of Arsenic from Arsenic (V) solution in presence of 1 gm cow dung (initial As 1.18 μgm)

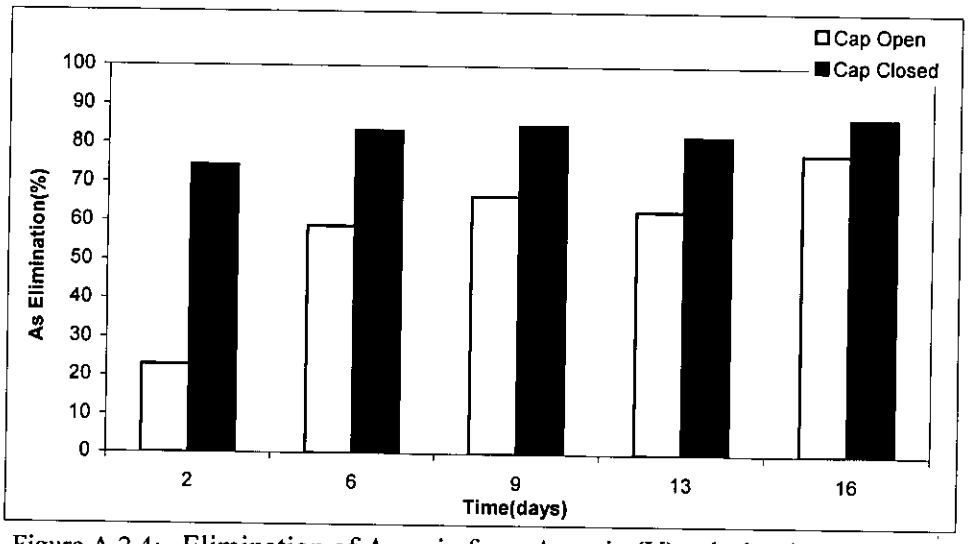


Figure A.2.4: Elimination of Arsenic from Arsenic (V) solution in presence of 1 gm cowdung (initial As 2.24 μgm)

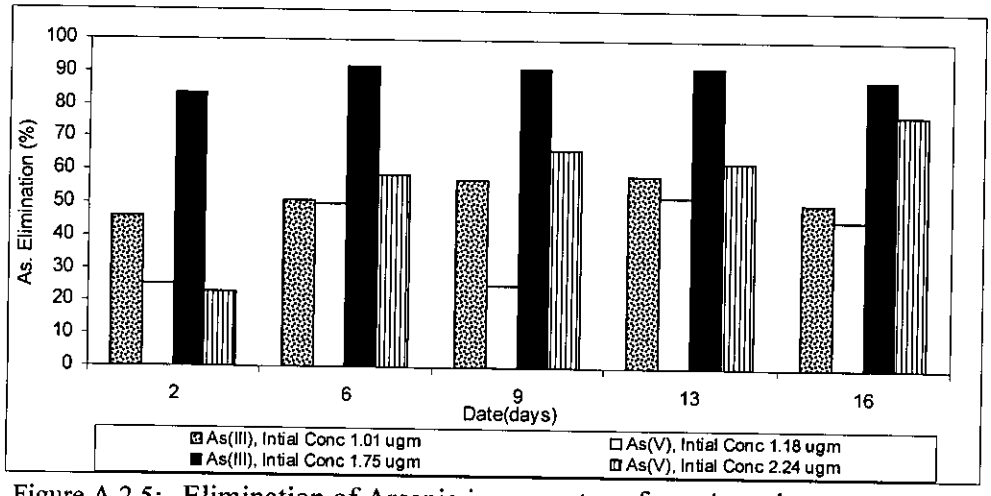


Figure A.2.5: Elimination of Arsenic in percentage from Arsenic solution in presence of 1 gm cowdung

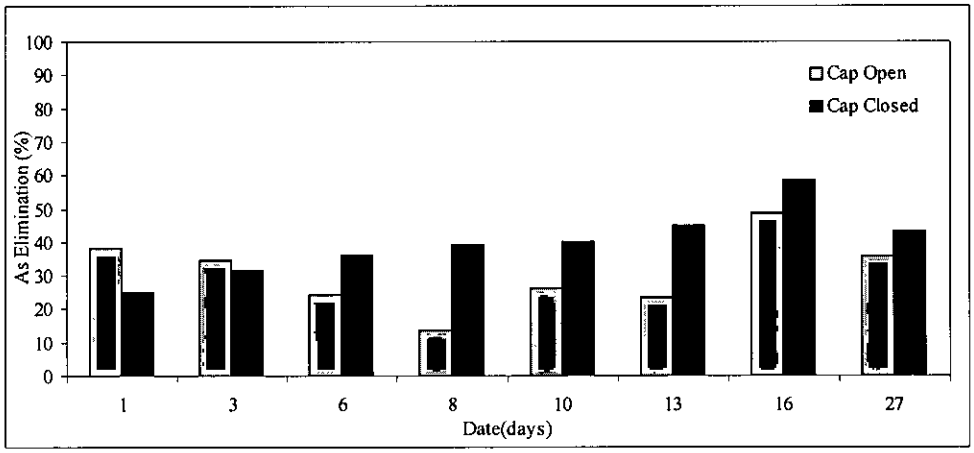


Figure A.2.6: Elimination of Arsenic(in percentage) from Arsenic (III) solution in presence of 1 gm cowdung (Initial As 5.90 μgm)

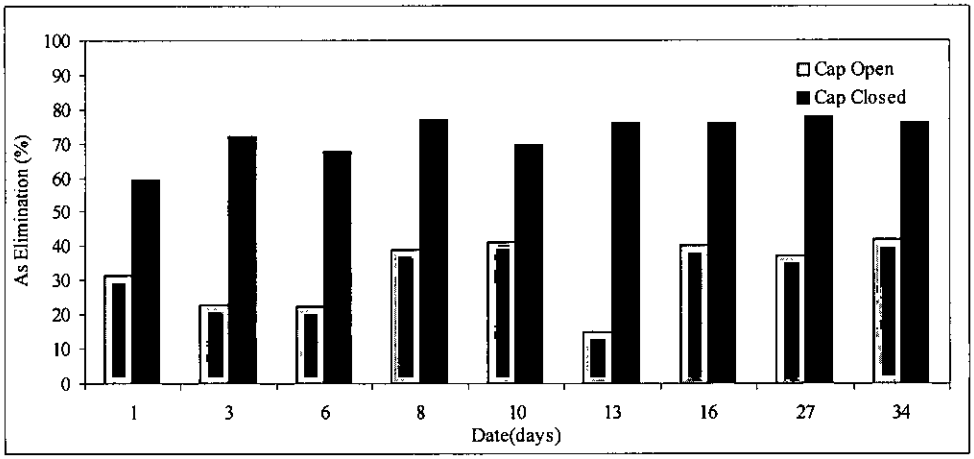


Figure A.2.7: Elimination of Arsenic in percentage from Arsenic (V) solution in presence of 1 gm cowdung (Initial As 5.90 μgm)

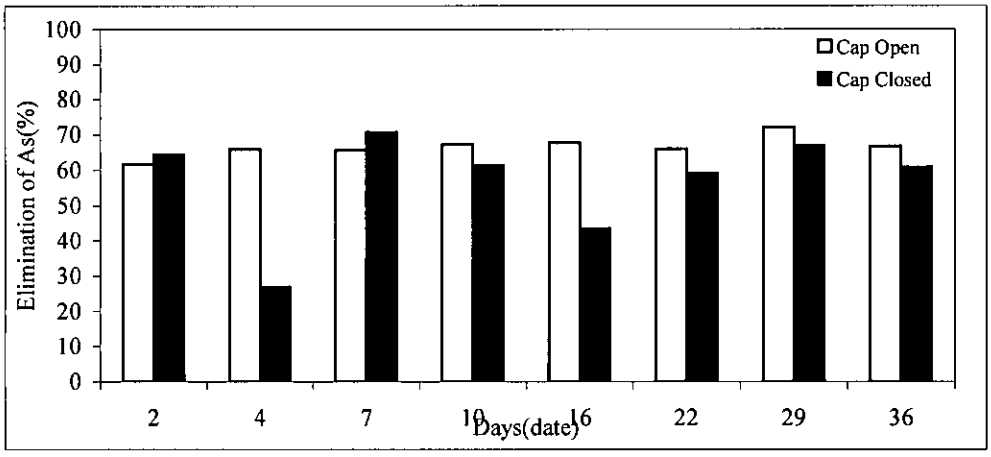


Figure A.2.8: Elimination of Arsenic in percentage from Arsenic (III) solution in presence of 2 gm cowdung (Initial As 6.11 μgm)

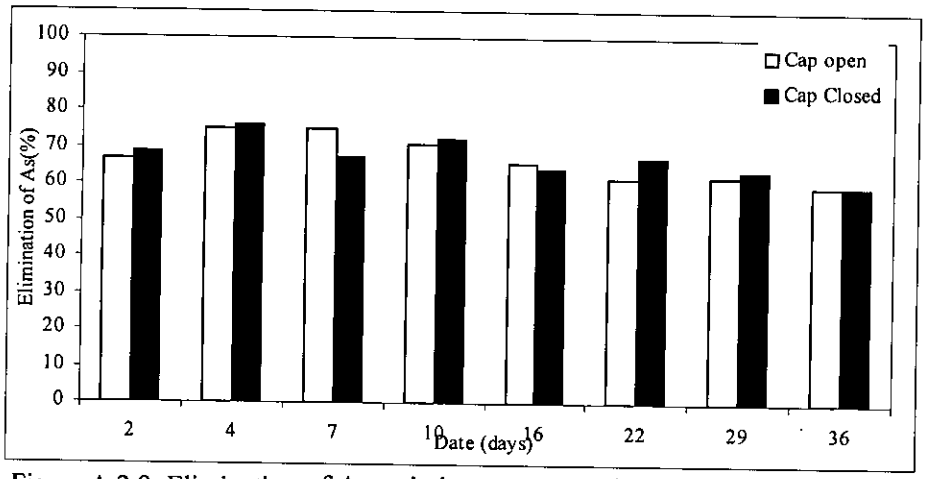


Figure A.2.9: Elimination of Arsenic in percentage from Arsenic (III) solution in presence of 2 gm cowdung (Initial As 6.11 µgm)

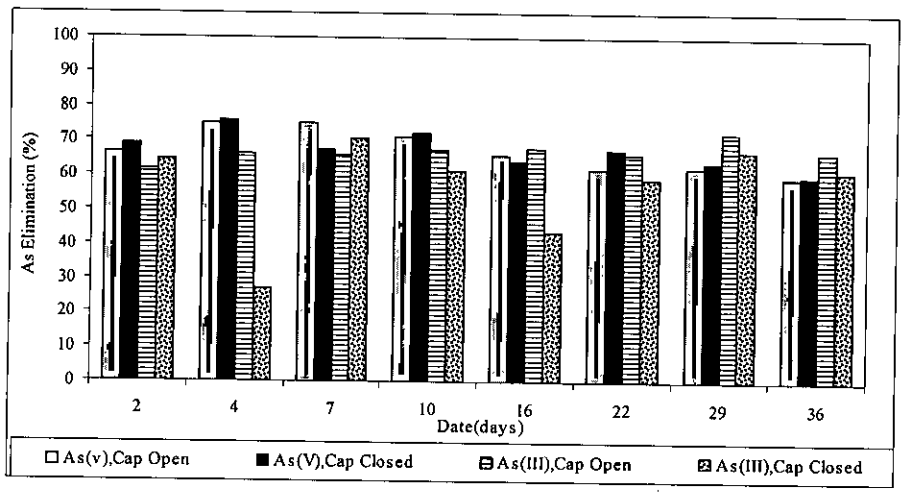


Figure A.2.10 Elimination of Arsenic in percentage from Arsenic solution in presence of 2 gm cowdung (Initial As 6.11 µgm)

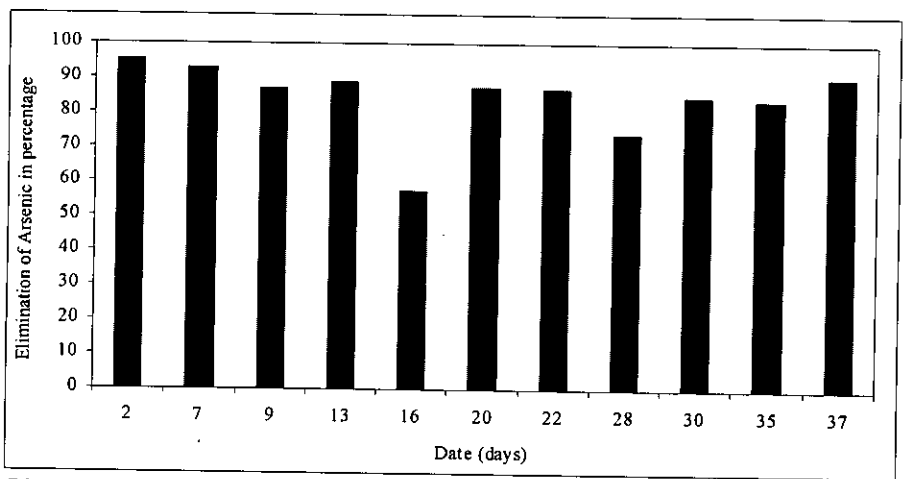
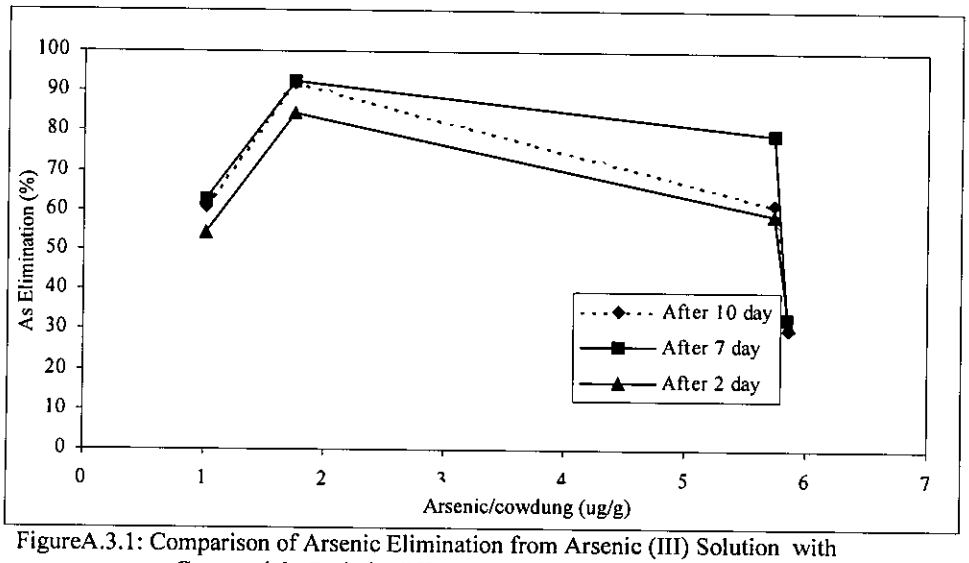
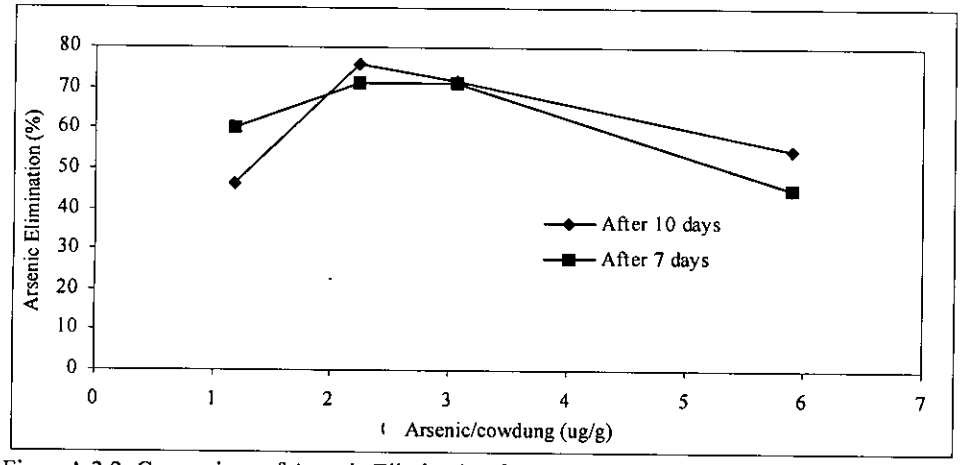


Figure A.2.11: Elimination of Arsenic(in percentage) from Arsenic (III) solution in presence of 6 gm cowdung (Initial As 6.36 µgm)

A.3 Comparison Of Arsenic Elimination From Arsenic (III) Solution With Arsenic/Cowdung Ratio In Different Day.



FigureA.3.1: Comparison of Arsenic Elimination from Arsenic (III) Solution with Conc-weight Ratio in different day.



FigureA.3.2: Comparison of Arsenic Elimination from Arsenic (V) Solution with Conc-weight Ratio in different day.

A.4: Arsenic Remaining in Arsenic Solution in Presence of Cowdung (2nd Phase)

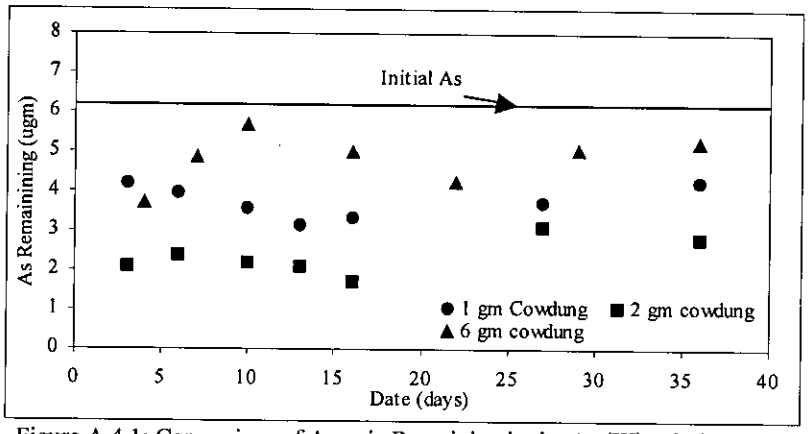


Figure.A.4.1: Comparison of Arsenic Remaining in the As (III) solution in presence of 1 g, 2 g and 6 g cowdung, Cap Open Condition, (initial As 6.632 µg)

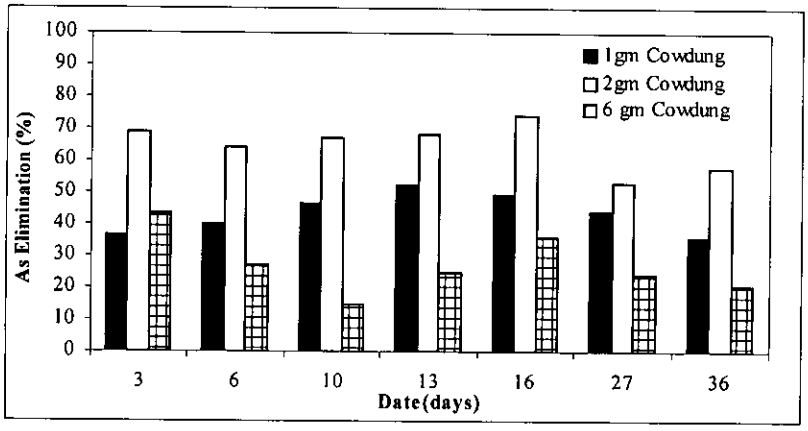


Figure A.4.2:Comparison of Elimination of As (III) in batch Tests in Presence of 1 g, 2g & 6g Cowdung (Initial As. 6.632 µg); Cap open Condition

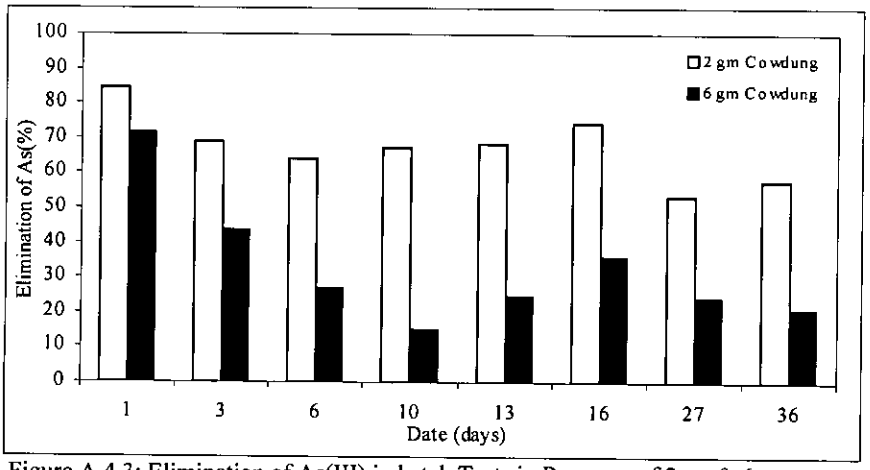


Figure A.4.3: Elimination of As(III) in batch Tests in Presence of 2gm & 6gm Cowdung (Initial As 6.632 µgm); Cap open Condition

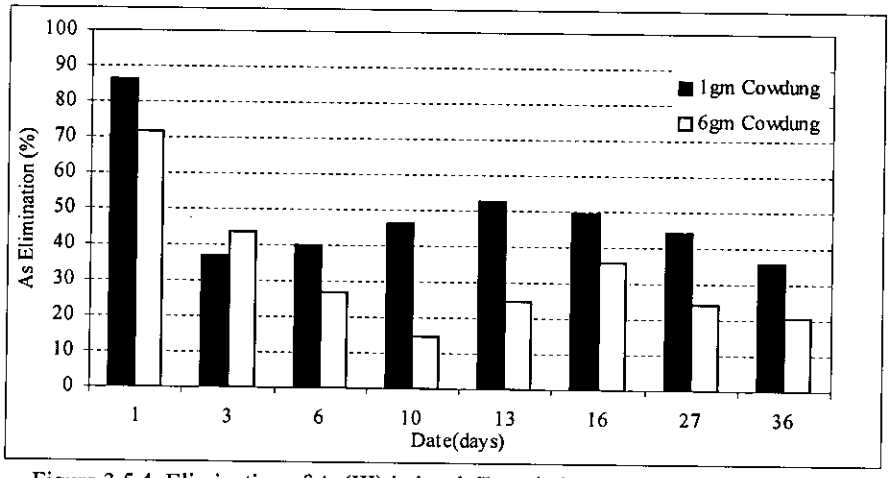


Figure 3.5.4: Elimination of As(III) in batch Tests in Presence of 2gm & 6gm Cowdung (Initial As 6.632 μgm); Cap open Condition

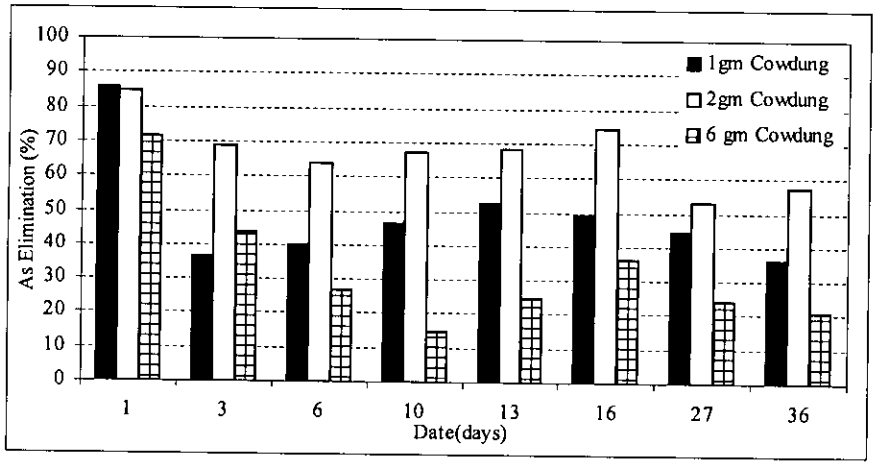


Figure 3.5.5:Comparison of Elimination of As(III) in batch Tests in Presence of 1 gm, 2gm & 6gm Cowdung (Initial As 6.632 μgm); Cap open Condition

A.6 Comparison of Arsenic Elimination

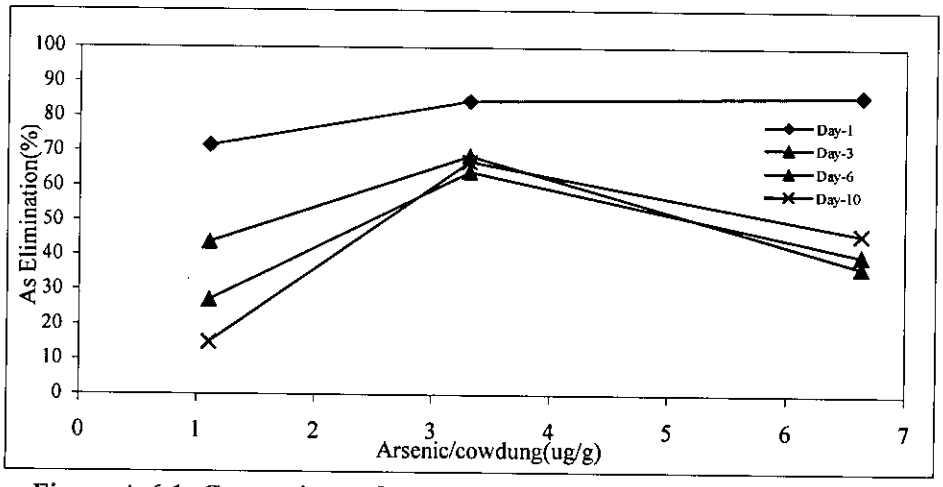


Figure A.6.1: Comparison of Arsenic Elimination with arsenic/cowdung μg/g) ratio in different days

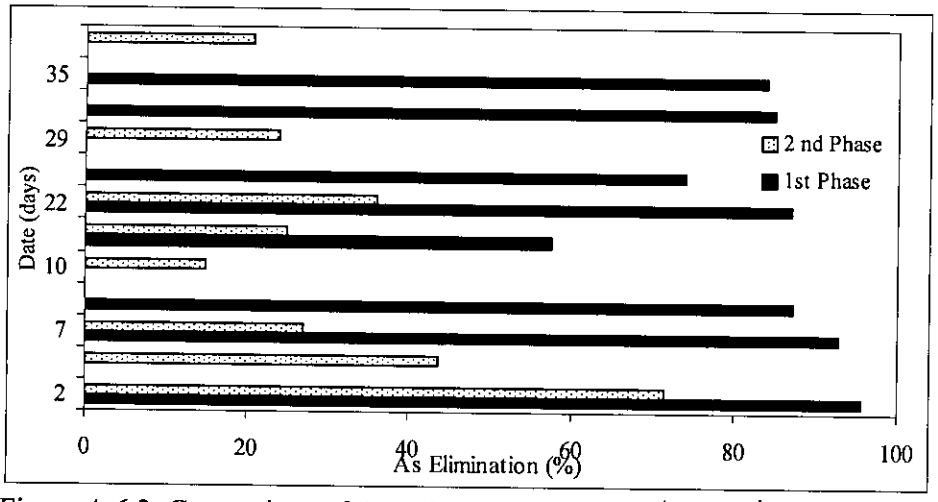


Figure A.6.2: Comparison of Arsenic Elimination in 1st and 2nd phase from As (III) solution in presence of 6 gm cowdung

ANNEX-B

Experimental Results on Elimination of Arsenic from Arsenic Rich Wastes in Presence of Cowdung

B.1 Arsenic Remaining in Slurry (STAR Filter) in Presence of Cowdung

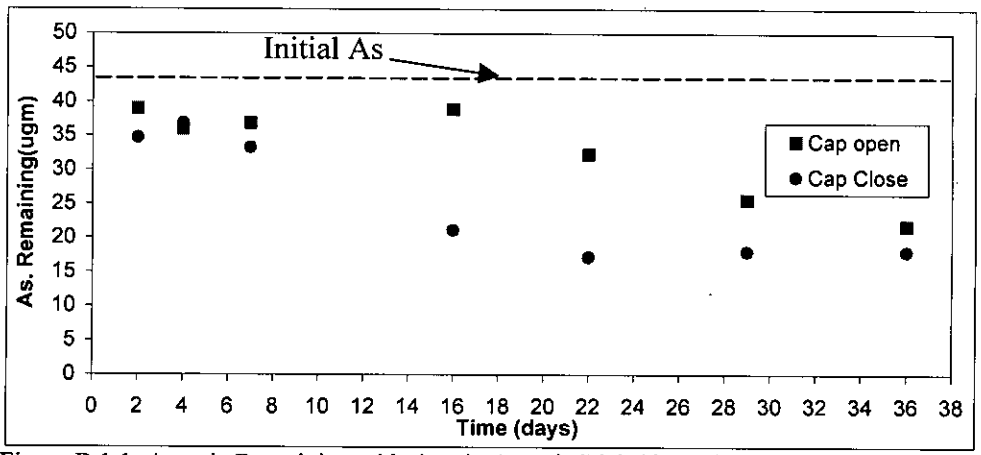


Figure B.1.1: Arsenic Remaining with time in Arsenic Rich Slurry (STAR) Mixed with 2g cowdung (Initial Arsenic 42.7 μg)

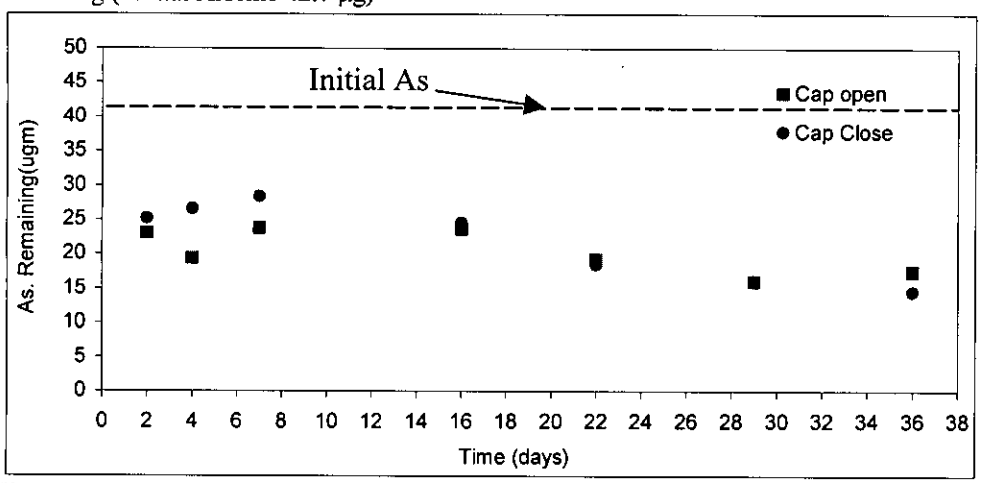


Figure B.1.2: Arsenic Remaining with time in Arsenic Rich Slurry (STAR) Mixed with 4g cowdung (Initial Arsenic 36.41 μg)

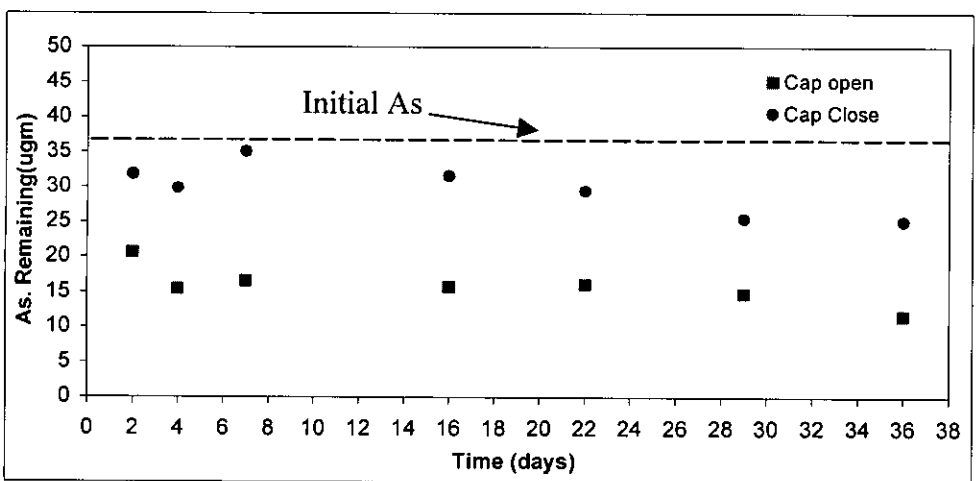


Figure B.1.3: Arsenic Remaining with time in Arsenic Rich Slurry (STAR) Mixed with 8g cowdung (Initial Arsenic 36.41 μg)

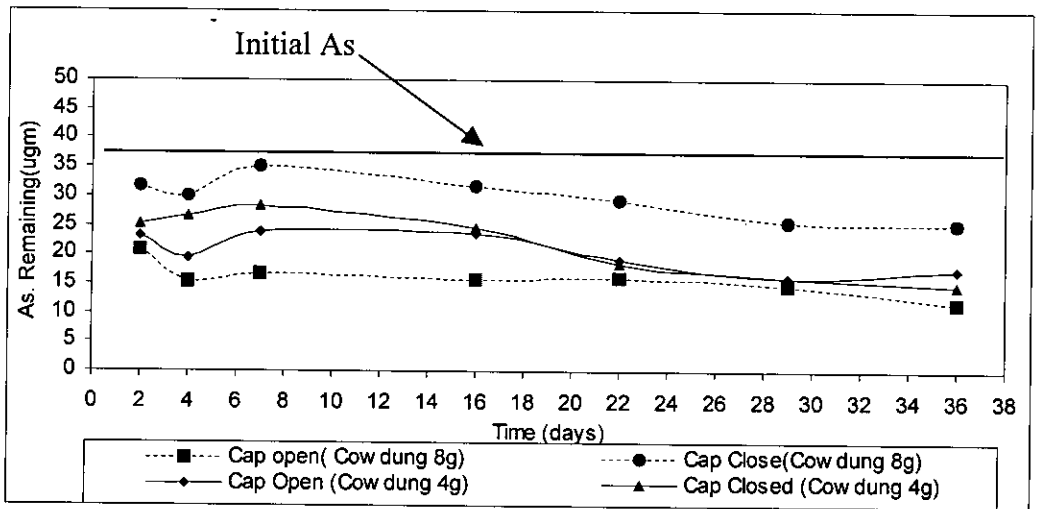


Figure B.1.4: Comparison of Arsenic Remaining in Slurry (STAR) mixed with 4g and 8g Cowdung

B.2 Elimination of Arsenic from Slurry (STAR Filter) In Presence of Cowdung

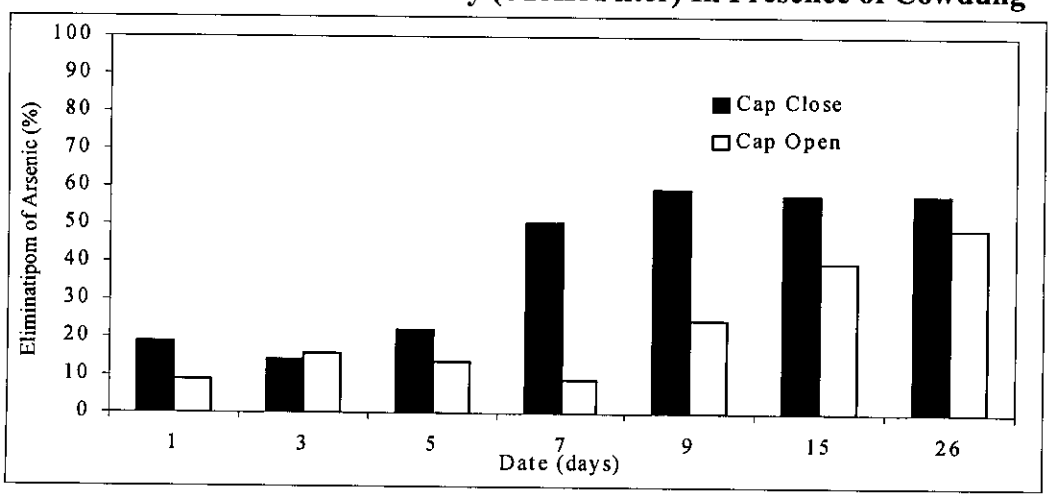


Figure B.2.1: Elimination of Arsenic from Arsenic Rich Slurry (STAR Filter) in Presence of 2 gm Cowdung (initial As 42.7 μg)

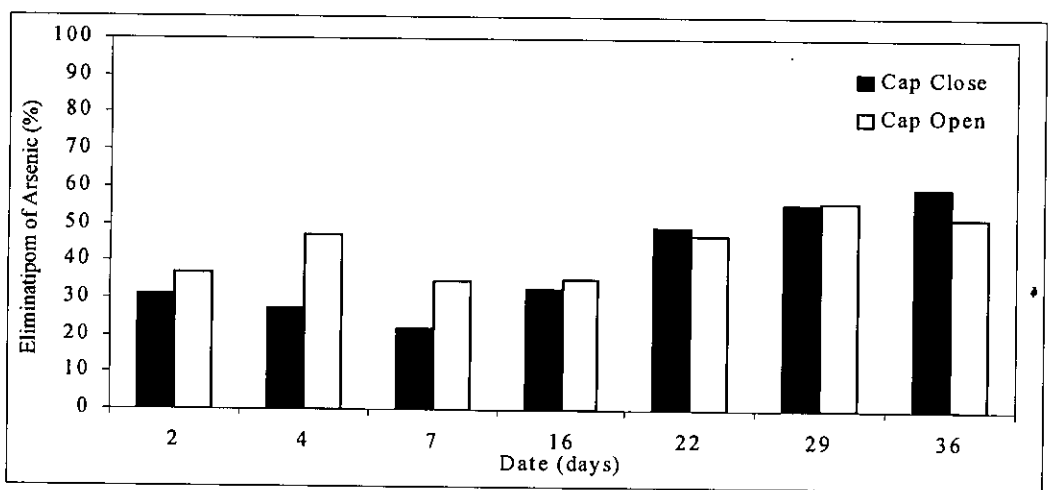


Figure B.2.2: Elimination of Arsenic from Arsenic Rich Slurry (STAR Filter) in Presence of 4 gm Cowdung (initial As 36.41 μg)

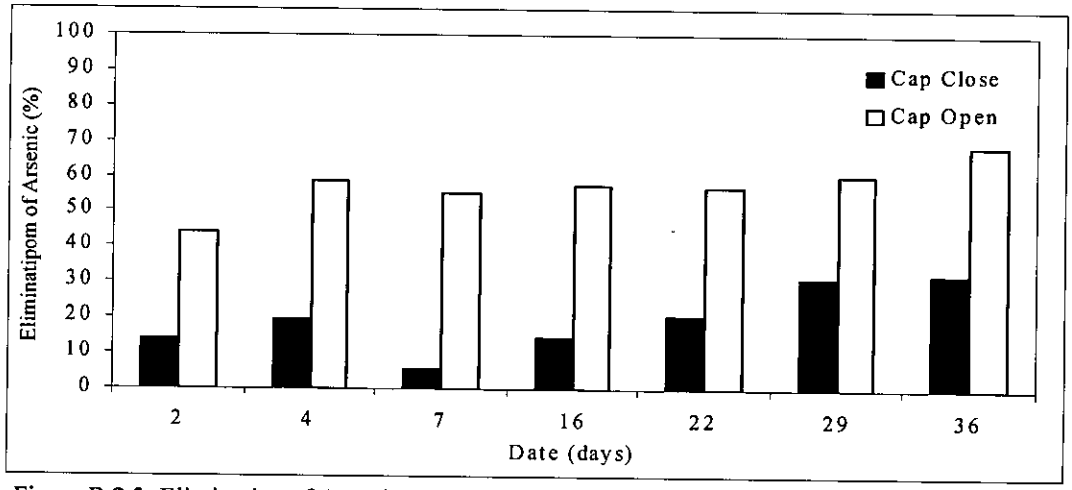


Figure B.2.3: Elimination of Arsenic from Arsenic Rich Slurry (STAR Filter) in Presence of 8 gm Cowdung (initial As 37.07 µg)

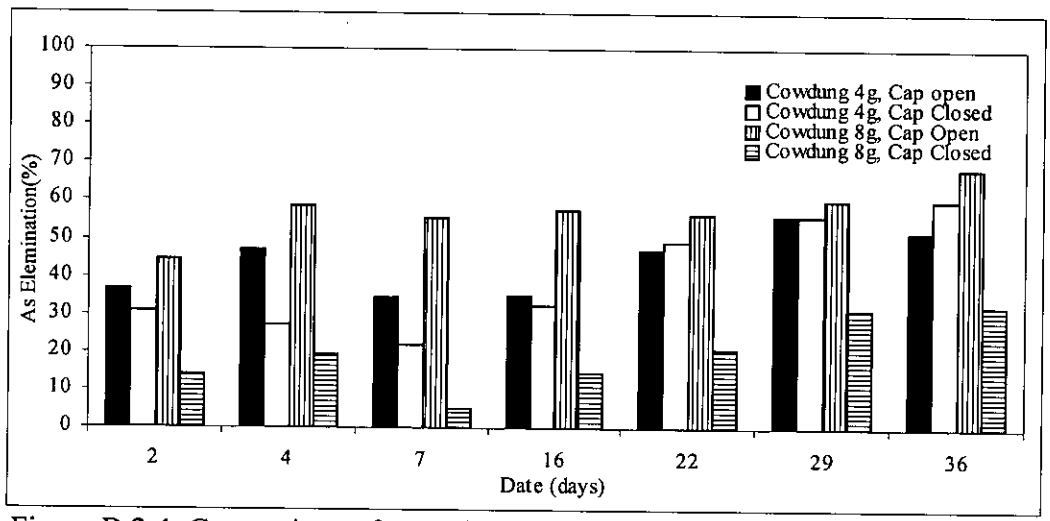


Figure B.2.4: Comparison of Arsenic Elimination Present in Arsenic Rich Sludge (STAR Filter) in presence of 2g, 4g & 8g Cowdung

B.3 Elimination of Arsenic from Slurry (STAR Filter) In Presence of Cowdung (2nd Phase)

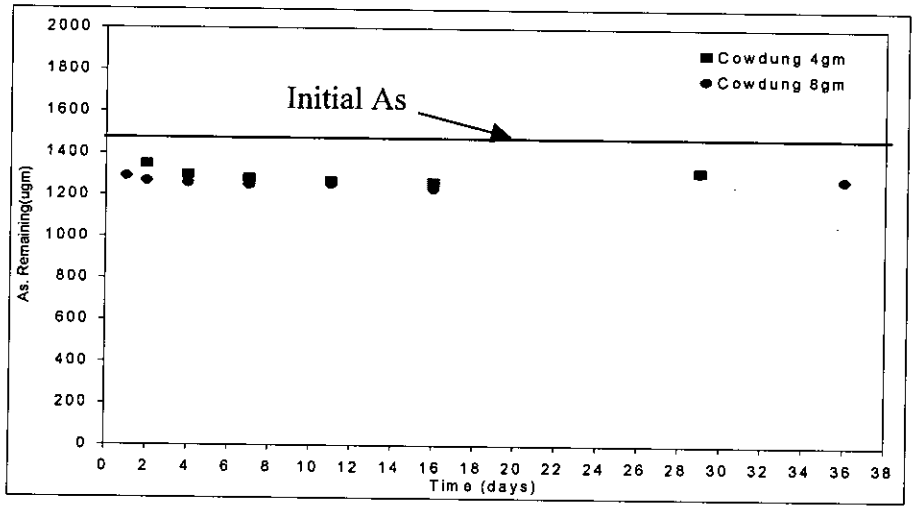


Figure B.3.1: Elimination of arsenic present in treatment wastes from STAR unit in the presence of 4gm and 8 gm Cowdung (initial As 1488 μg)

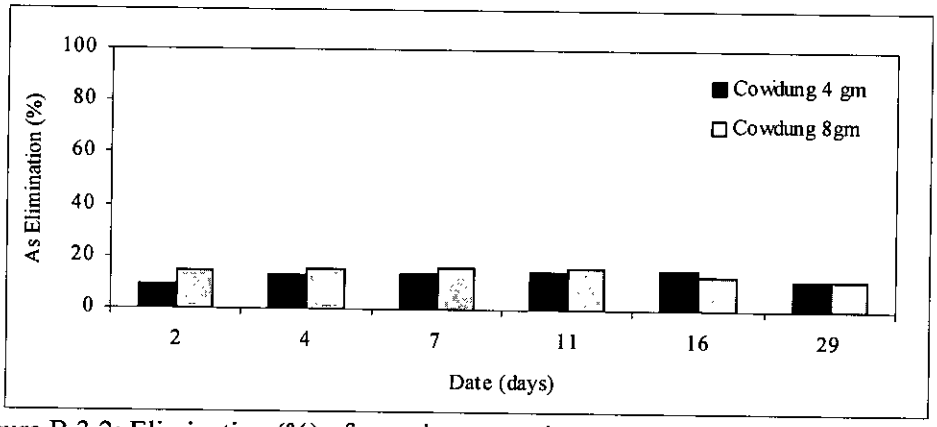


Figure B.3.2: Elimination (%) of arsenic present in treatment wastes from STAR units in the presence of 4gm and 8 gm Cowdung (initial As 1488 μg)

B.4 Arsenic Remaining in BTU Slurry in Presence of Cowdung(1st Phase)

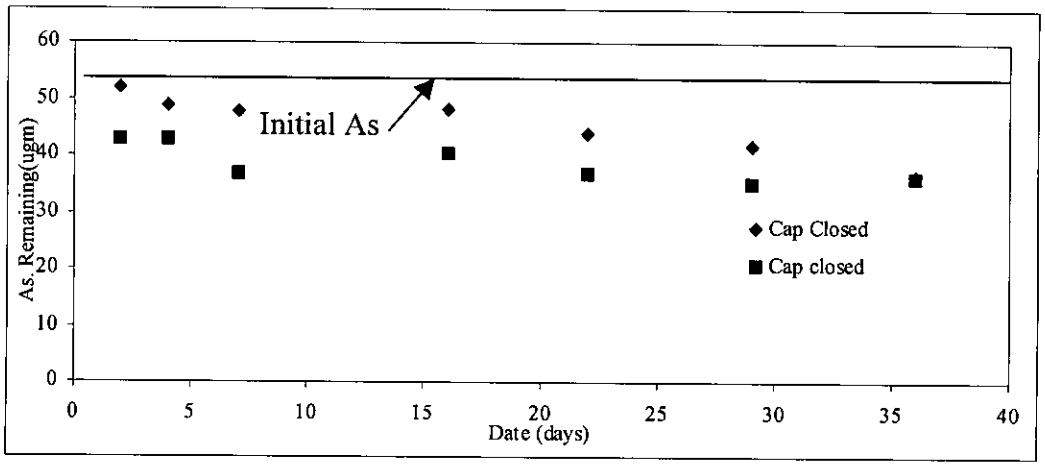


Figure B.4.1: Arsenic Remaining with time in treatment wastes from BTU units in the presence 2gm Cowdung (initial As 53.3 μg)

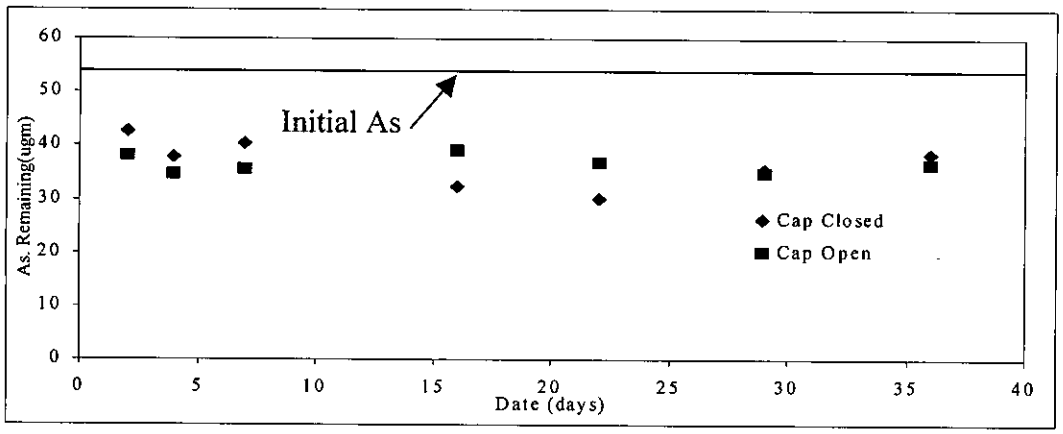


Figure B.4.2: Arsenic Remaining with time in treatment wastes from BTU units in the presence 4 gm Cowdung (initial As 53.3 μg)

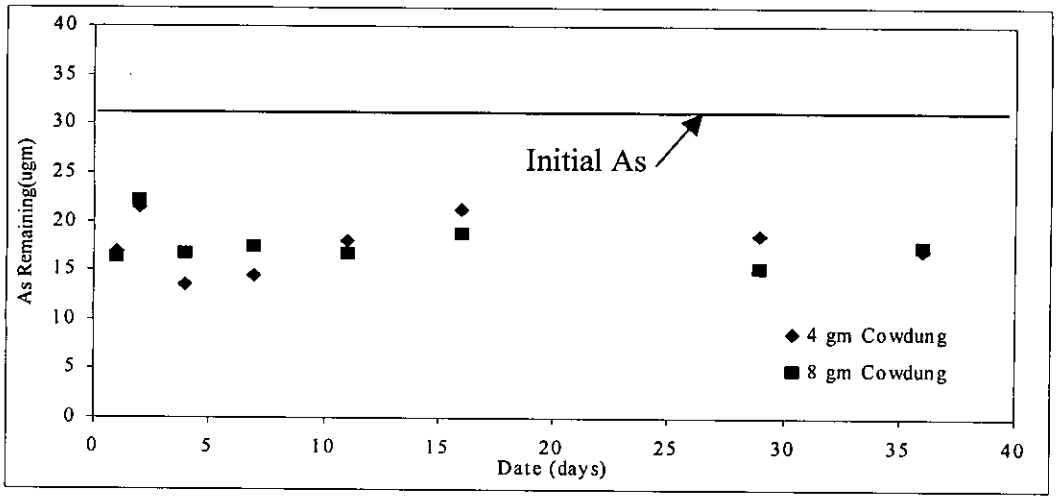


Figure B.4.3: Comparison of arsenic Remaining with time in treatment wastes from BTU units in the presence 4g& 8gm Cowdung, Cap Open Condition (initial As 31.12 μgm)

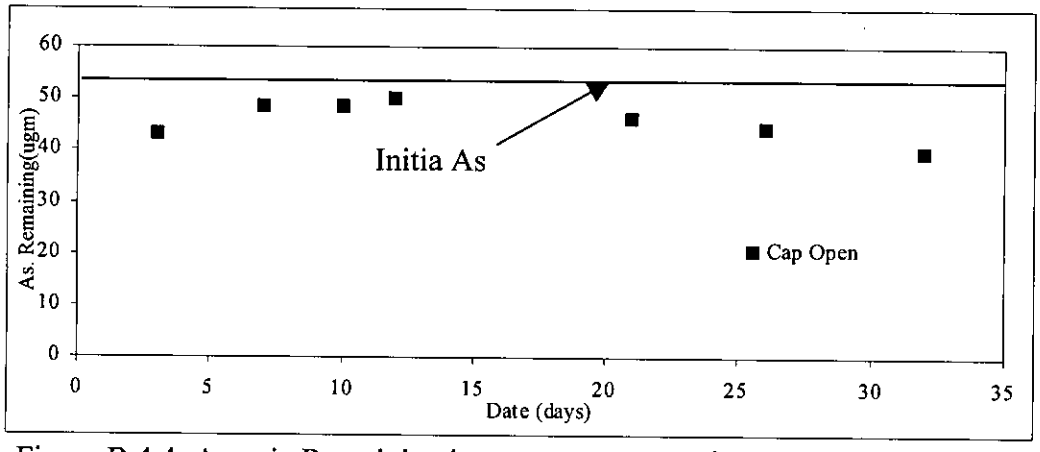


Figure B.4.4: Arsenic Remaining in treatment wastes from BTU units in the presence 8gm Cowdung (initial As 53.02 μg)

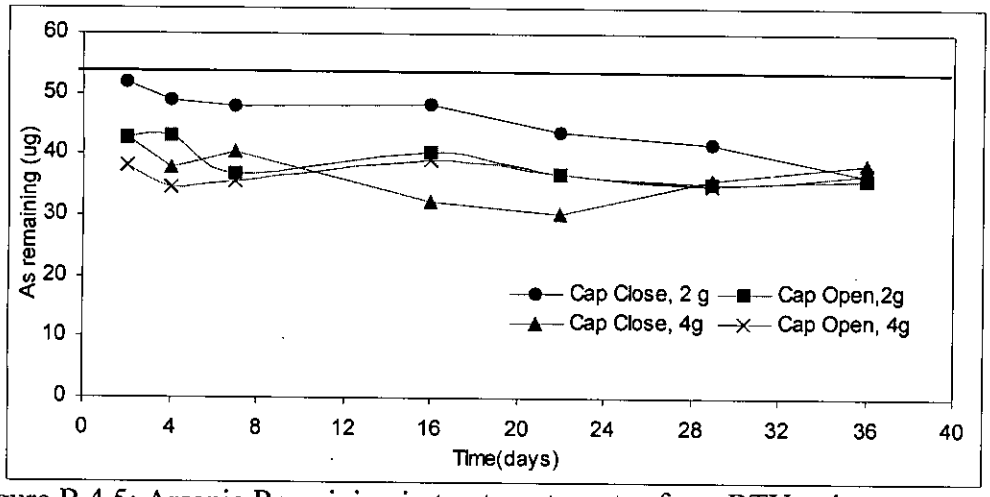


Figure B.4.5: Arsenic Remaining in treatment wastes from BTU units in the presence 2g and 4gm Cowdung (initial As 53.3 μg)

B.5 Elimination of Arsenic from BTU Slurry in Presence of Cowdung

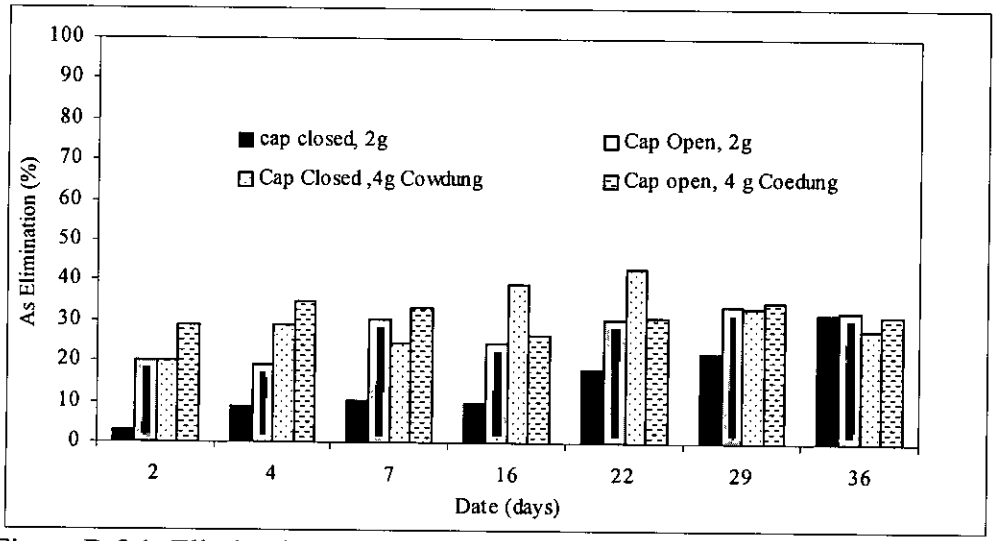


Figure B.5.1: Elimination (%) of arsenic present in treatment wastes from BTU units in the presence 2g and 4gm Cowdung (initial As 53.3 μg)

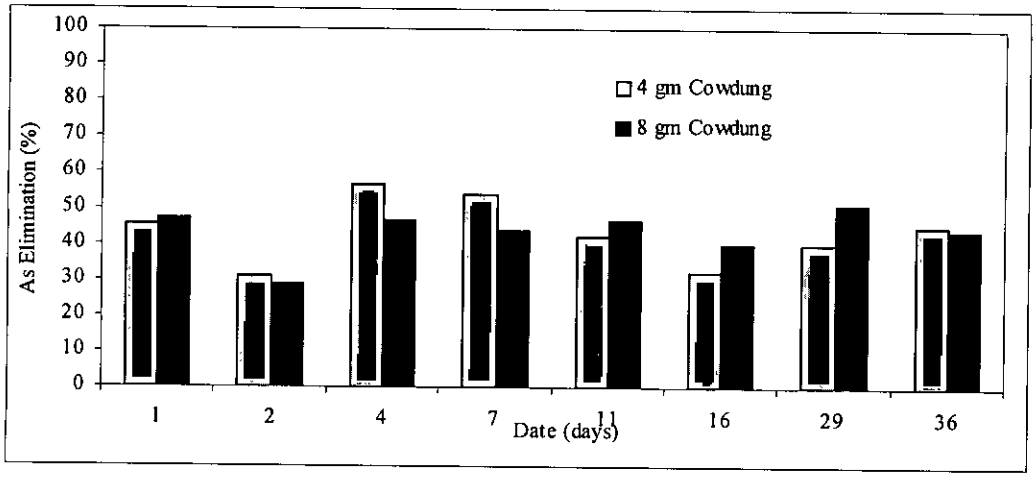


Figure B.5.2: Elimination (%) of arsenic present in treatment wastes from BTU units in the presence 4g and 8gm Cowdung (initial As 31.12 μg)

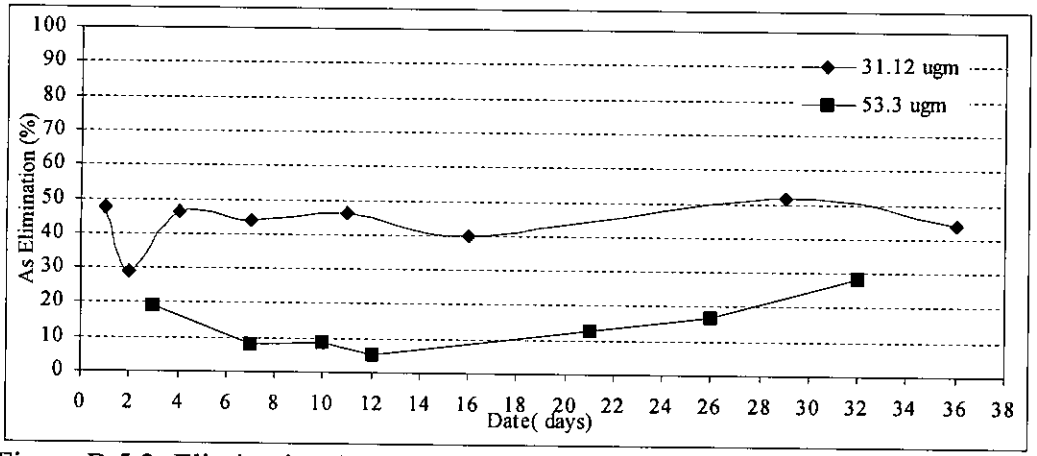


Figure B.5.3: Elimination (%) of arsenic present in treatment wastes from BTU units in the presence 8gm Cowdung with different concentration

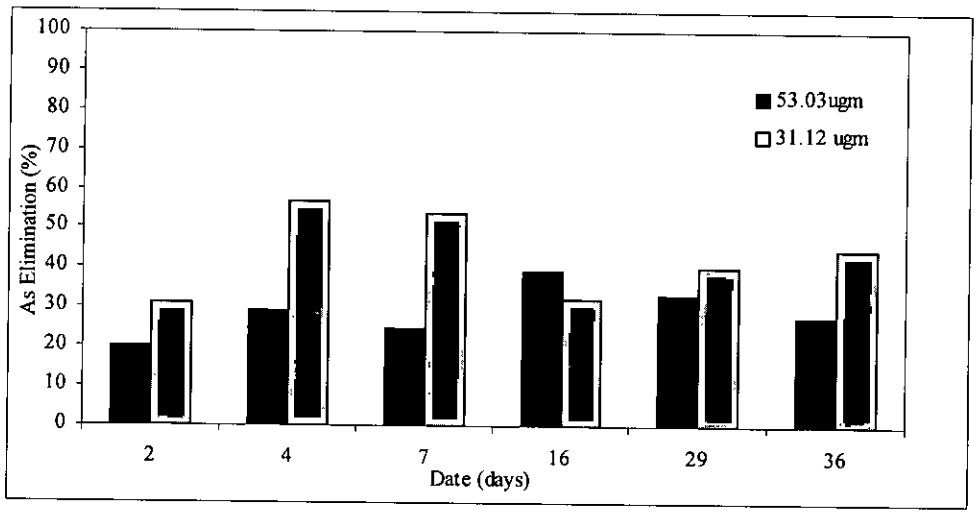


Figure B.5.4: Elimination (%) of arsenic present in treatment wastes from BTU units

B.6 Arsenic Remaining in Arsenic Rich BTU Slurry in Presence of Cowdung (2nd Phase)

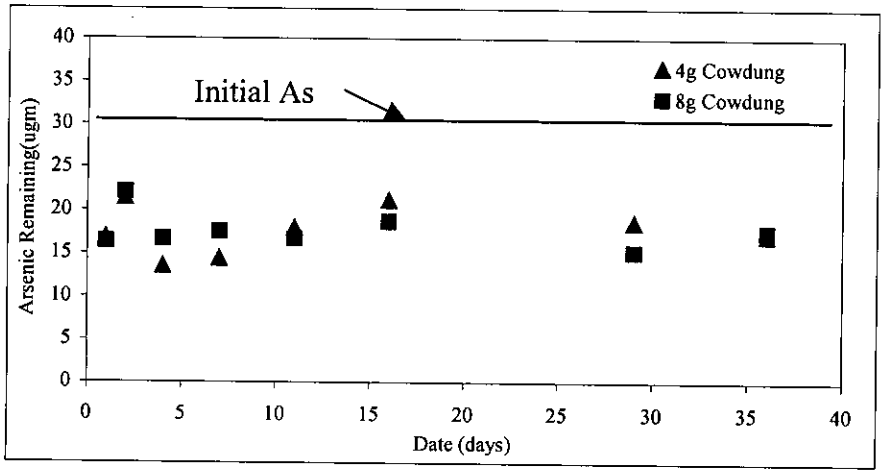


Figure B.6.1: Arsenic Remaining with timein Arsenic rich BTU Slurry in Presence of Cowdung (Initial As 31.12 µg)

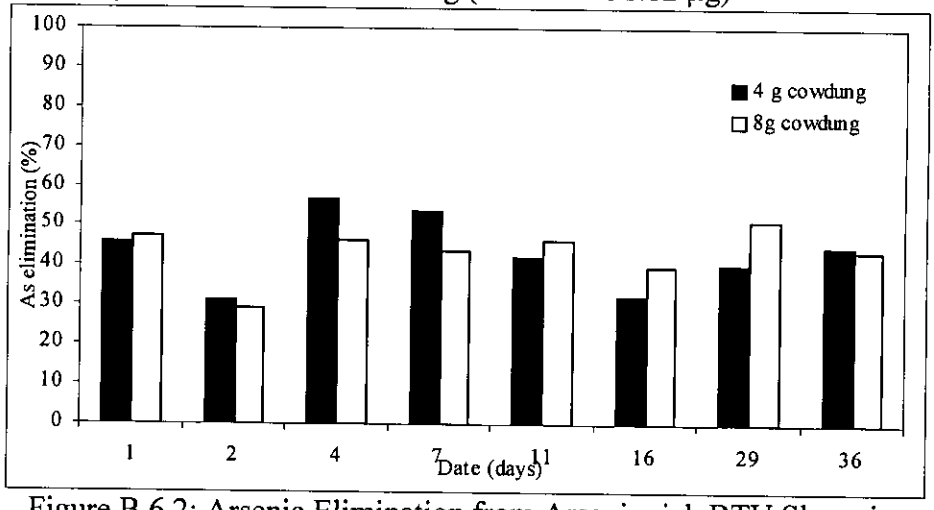


Figure B.6.2: Arsenic Elimination from Arsenic rich BTU Slurry in Presence of Cowdung (Initial As 31.12 µg)

ANNEX-C
Experimental Results on Elimination of Arsenic from Arsenic Rich Soil

C.1: Graphs Showing Comparisons of Arsenic Elimination from Arsenic (III) &(V) Solution mixed with Different Weight of Cowdung and 5 g Soil.

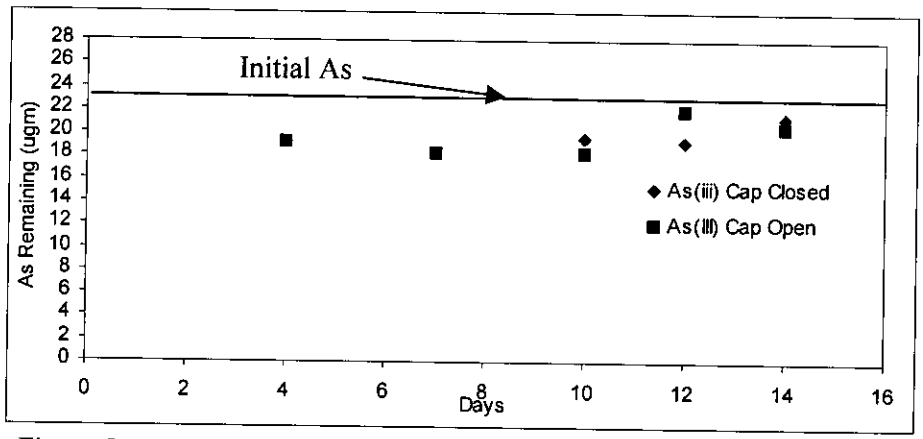


Figure C.1.1: Arsenic Remaining in As(III) Solution mixed with 5g Arsenic contaminated Soil.

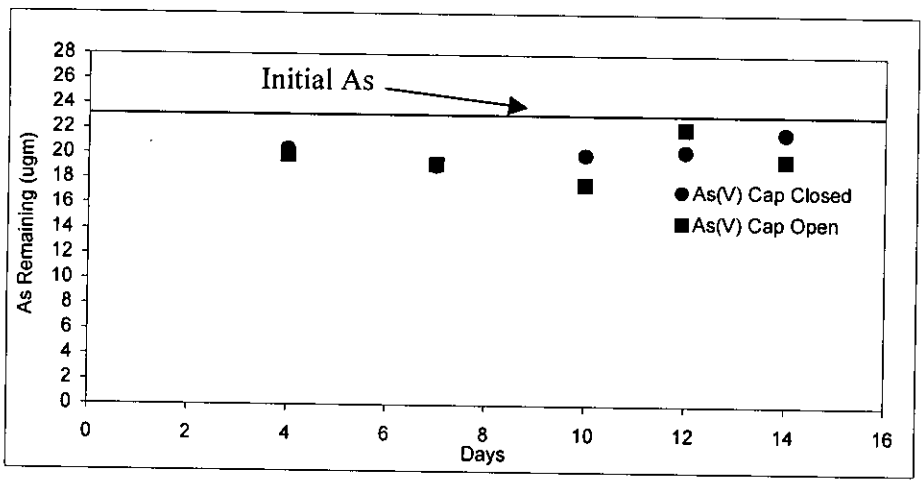


Figure C.1.2: Arsenic Remaining in As(V) Solution mixed with 5g Arsenic contaminated Soil.

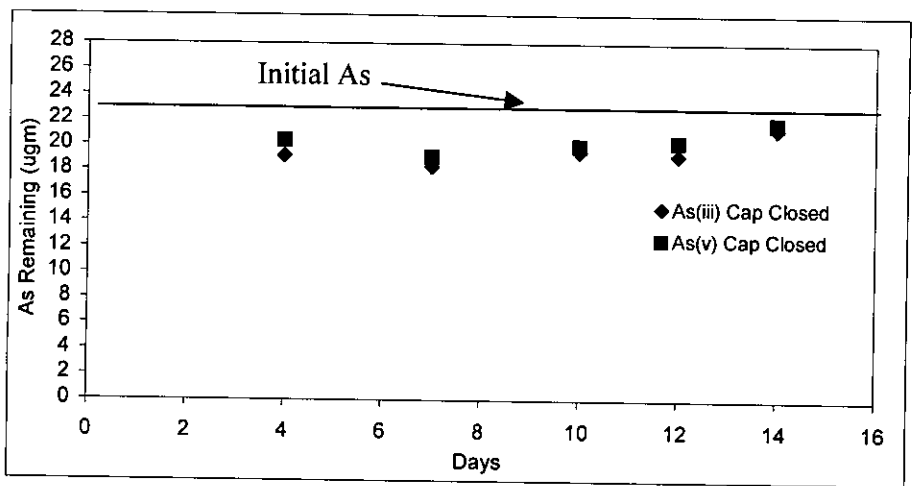


Figure C.1.3: Arsenic Remaining in As(V) and As(III) Solution mixed with 5g Arsenic contaminated Soil in Cap Closed Condition.

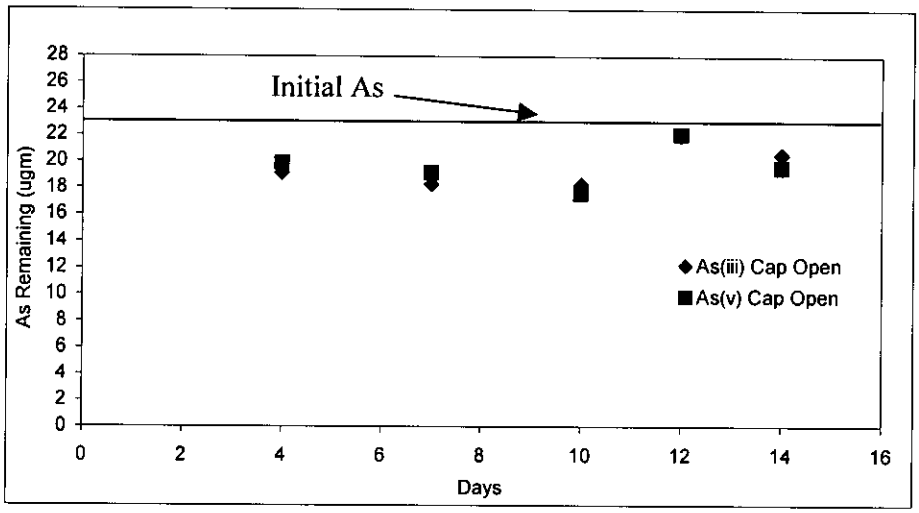


Figure C.1.4: Arsenic Remaining in As(V) and As(III) Solution mixed with 5g Arsenic Contaminated Soil in Cap Open Condition.

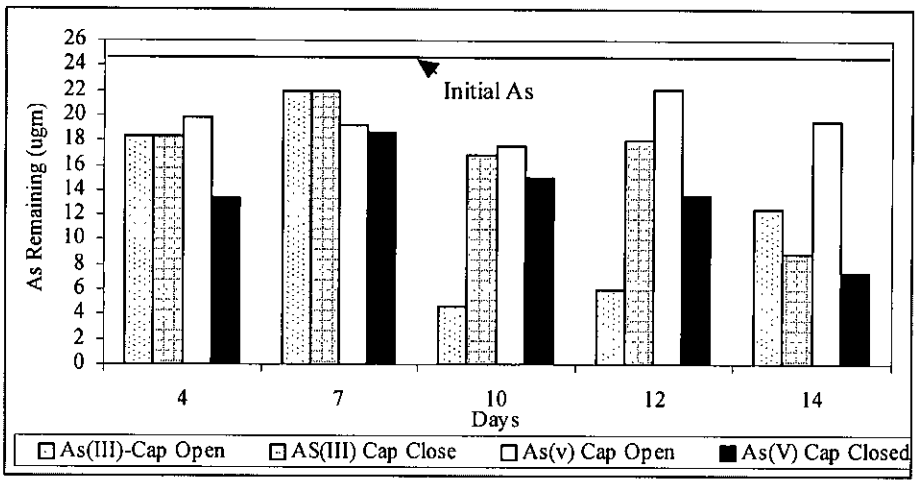


Figure C.1.5: Arsenic Remaining in As(V) and As(III) Solution mixed with 5g Arsenic Contaminated Soil .

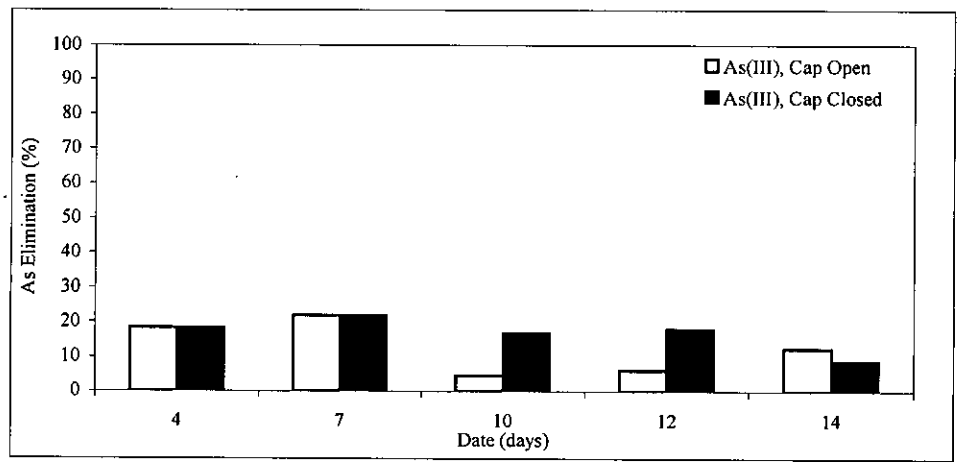


Figure C.1.6: Elimination of Arsenic Present in Soil in presence of 1g Cowdung (initial As 23.45 μg)

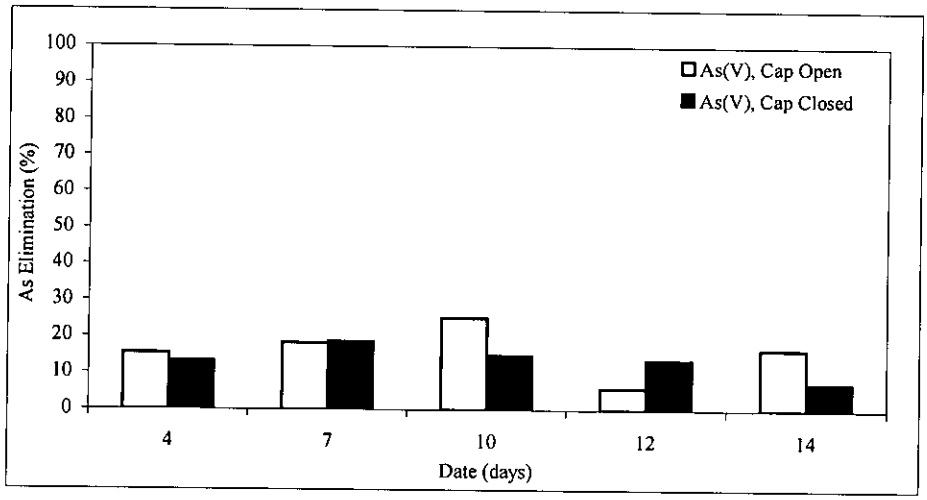


Figure C.1.7: Elimination of Arsenic Present in Soil (initial As 23.45 μg) in As(III) Solution

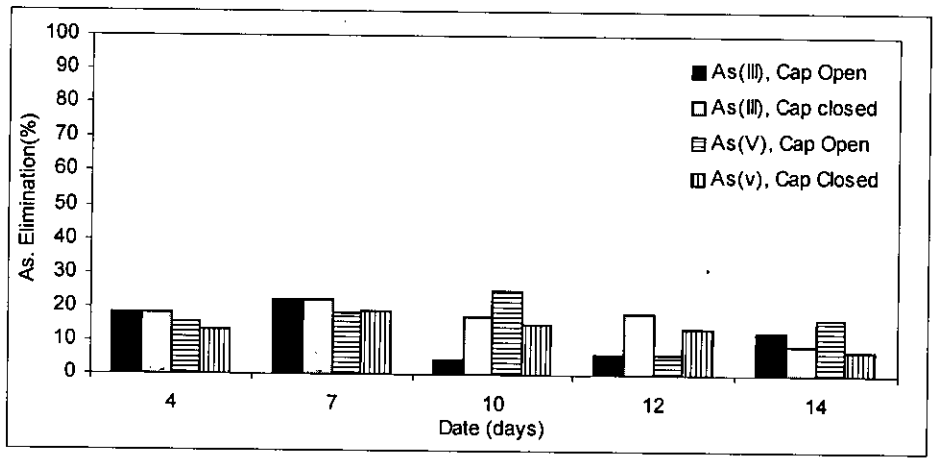


Figure C.1.8: Arsenic Elimination from Arsenic Rich Soil under both Cap Open and Cap Closed Condition (Initial As 23.45μg)

C.2: Graphs Showing Comparisons of Arsenic Elimination from Arsenic Rich Soil mixed With Different Weight of Cowdung

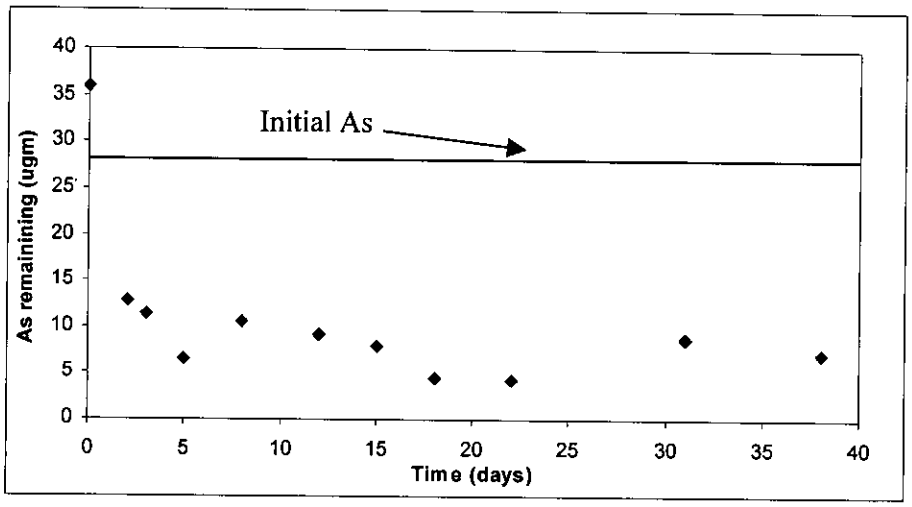


Figure C.2.1: Arsenic remaining in Aqueous Solution mixed with 2g soil and 1 g Cowdung

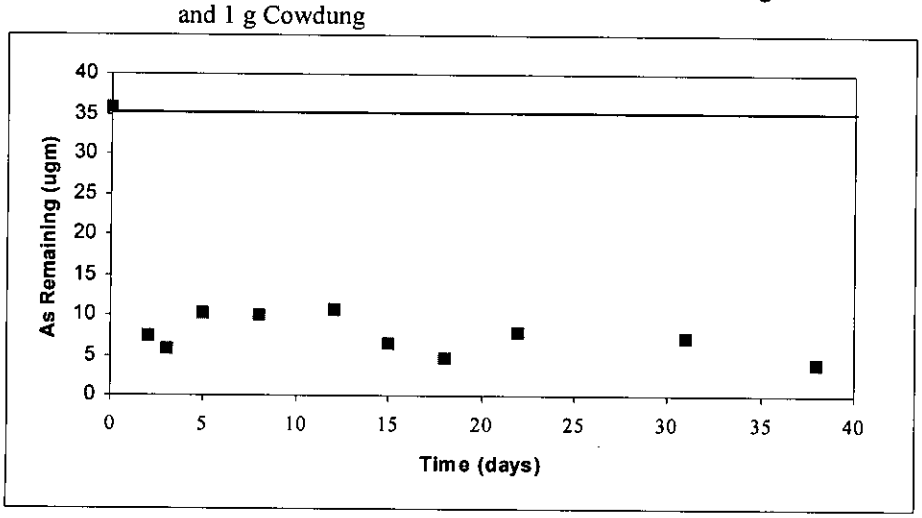


Figure C.2..2: Arsenic Remaining in Aqueous Solution mixed with 2g soil and 2 g Cowdung

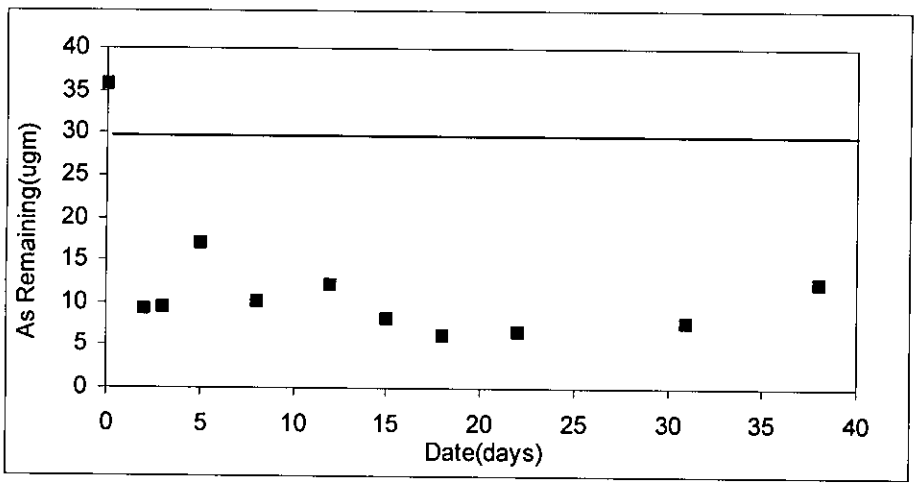


Figure C.2.3: Arsenic Remaining in Aqueous Solution mixed with 2g soil and 6 g Cowdung

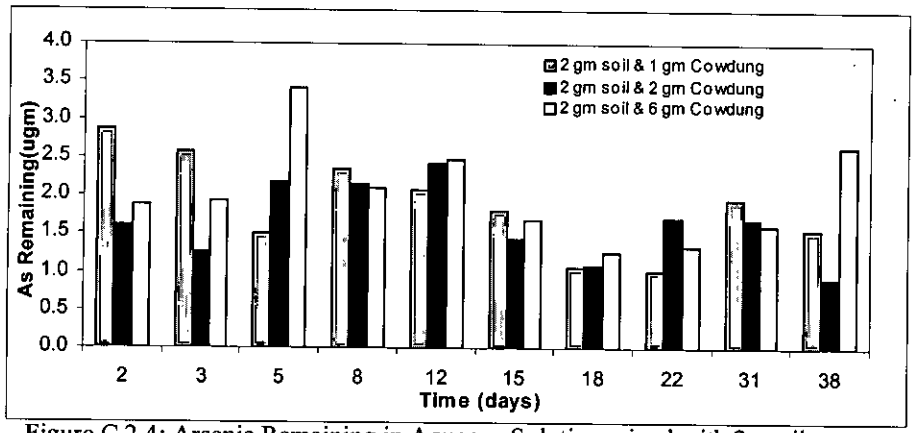


Figure C.2.4: Arsenic Remaining in Aqueous Solution mixed with 2g soil and Different weight of Cowdung

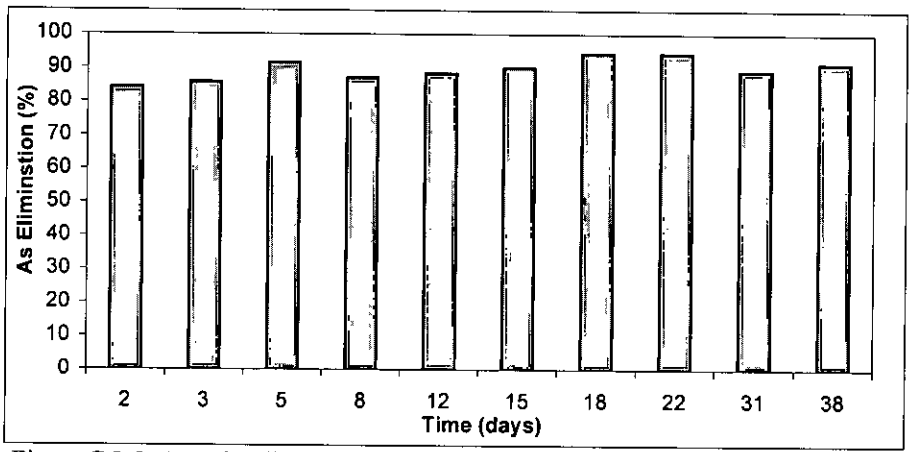


Figure C.2.5: Arsenic Elimination (%) in Aqueous Solution mixed with 2g soil and 1 g Cowdung

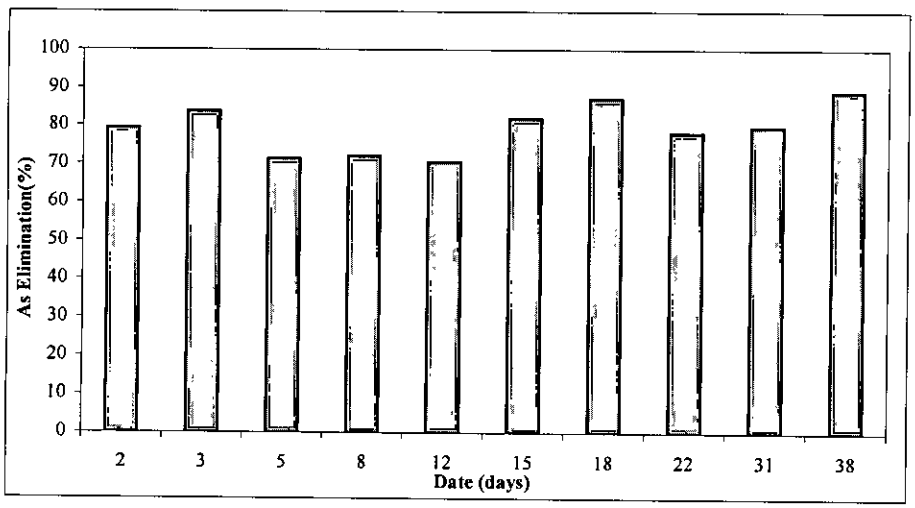


Figure C.2.6: Arsenic Elimination (%) in Aqueous Solution mixed with 2g Soil and 2 g Cowdung

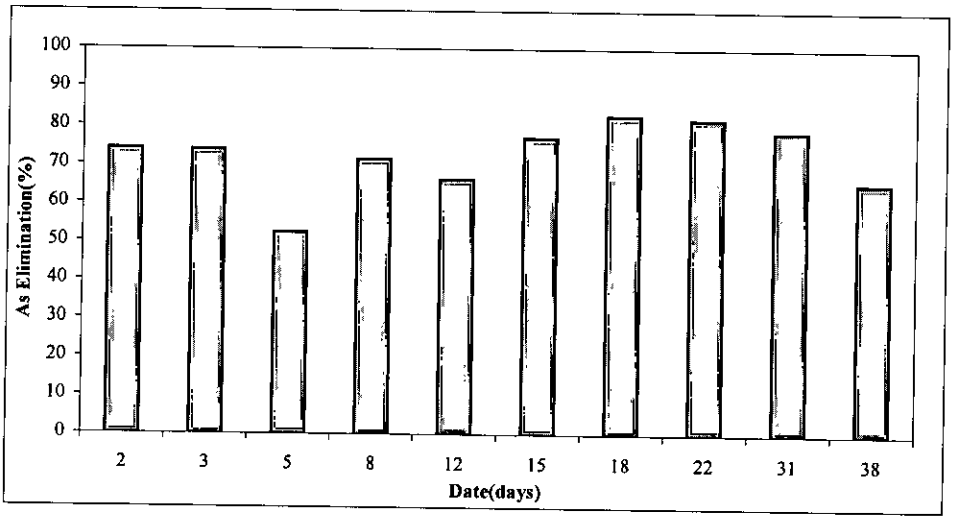


Figure C.2.7: Arsenic Elimination (%) in Aqueous Solution mixed with 2g Soil and 6 g Cowdung

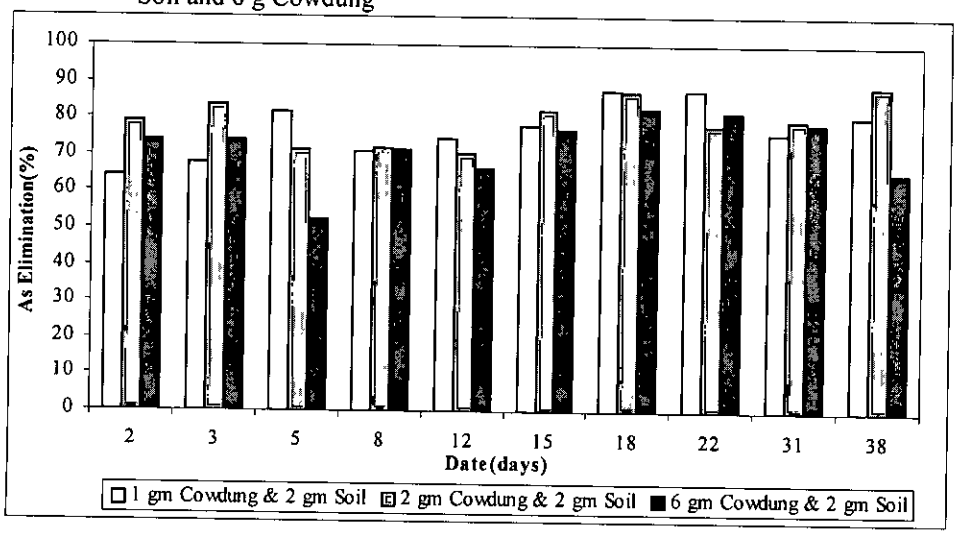


Figure C.2.8: Arsenic Elimination (%) in Aqueous Solution mixed with 2g Soil and different weight of cowdung

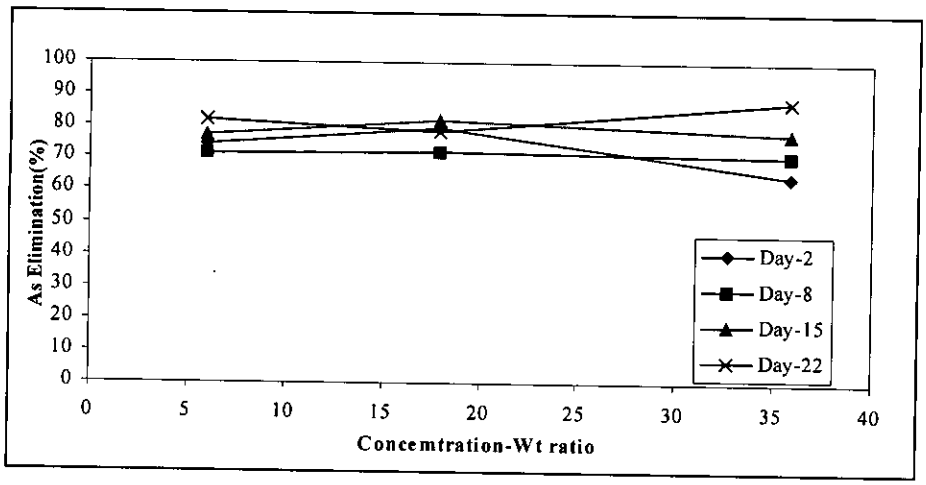


Figure C.2..9: Arsenic Elimination (%) in Aqueous Solution mixed with 2g Soil and different weight of cowdung

C.1: Graphs Showing Comparisons of Arsenic Elimination from Arsenic (III) &(V) Solution mixed with Different Weight of Cowdung and 5 g Soil.

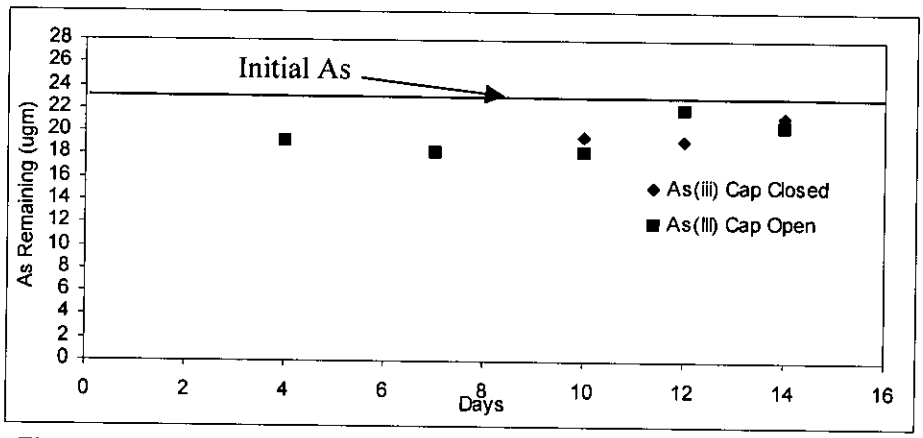


Figure C.1.1: Arsenic Remaining in As(III) Solution mixed with 5g Arsenic contaminated Soil.

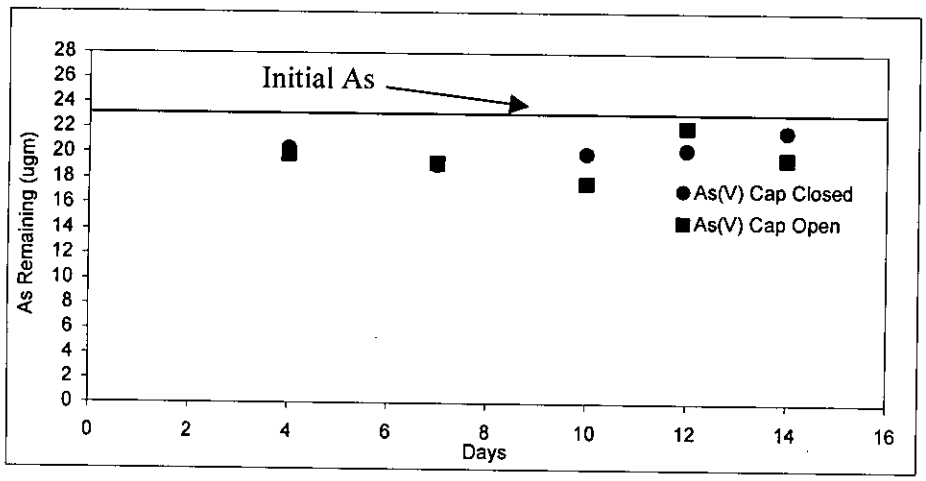


Figure C.1.2: Arsenic Remaining in As(V) Solution mixed with 5g Arsenic contaminated Soil.

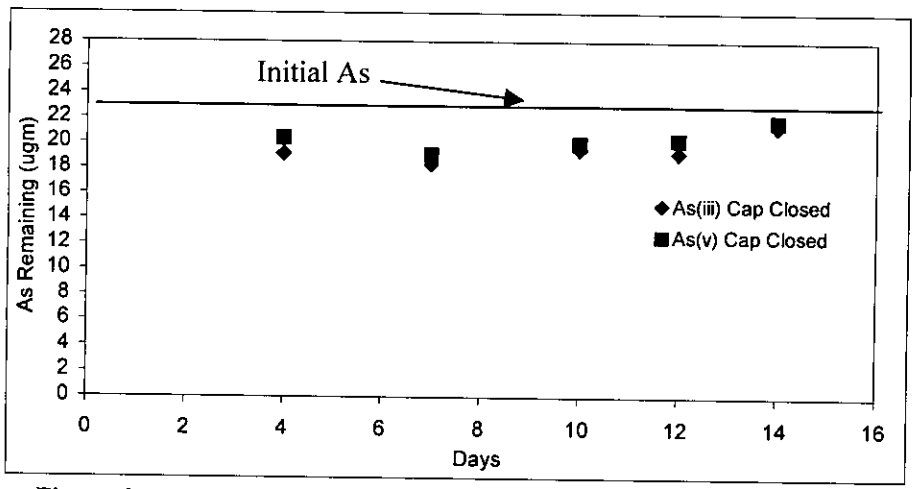


Figure C.1.3: Arsenic Remaining in As(V) and As(III) Solution mixed with 5g Arsenic contaminated Soil in Cap Closed Condition.

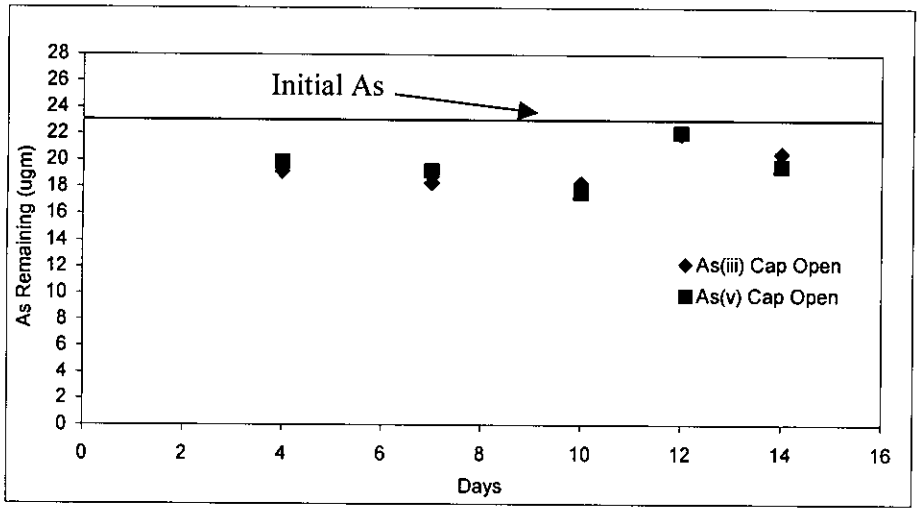


Figure C.1.4: Arsenic Remaining in As(V) and As(III) Solution mixed with 5g Arsenic Contaminated Soil in Cap Open Condition.

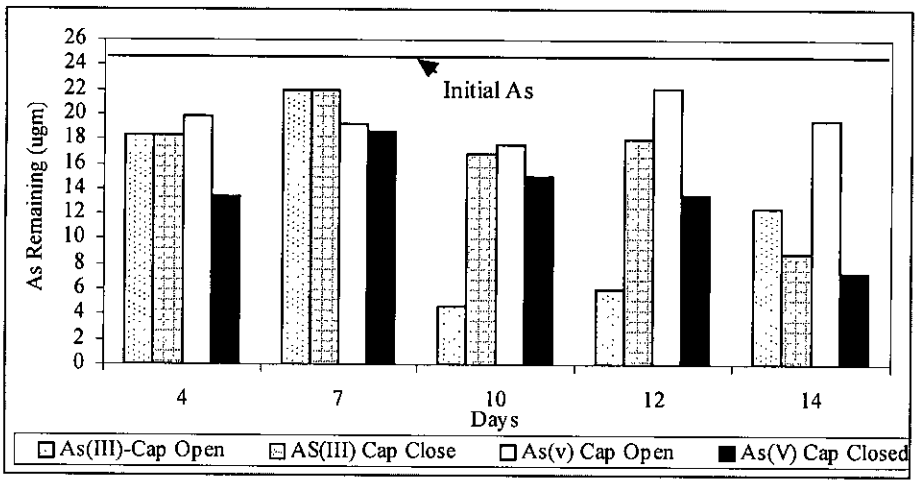


Figure C.1.5: Arsenic Remaining in As(V) and As(III) Solution mixed with 5g Arsenic Contaminated Soil .

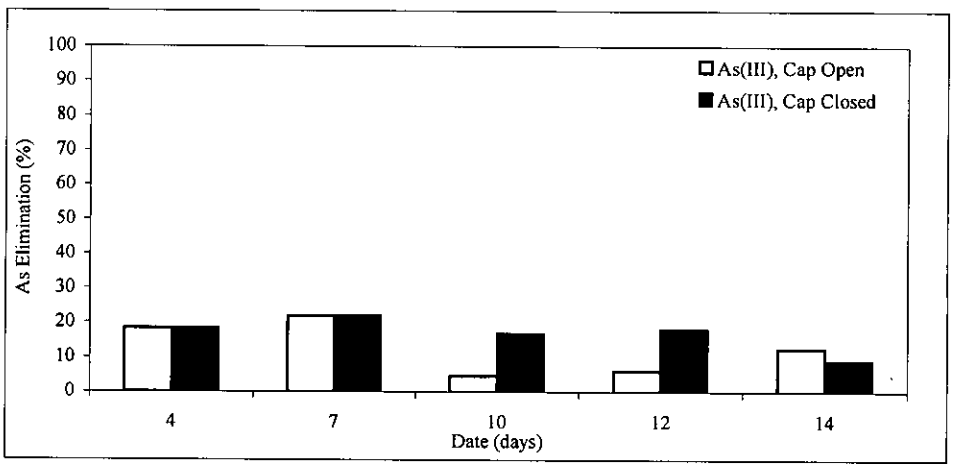


Figure C.1.6: Elimination of Arsenic Present in Soil in presence of 1g Cowdung (initial As 23.45 μg)

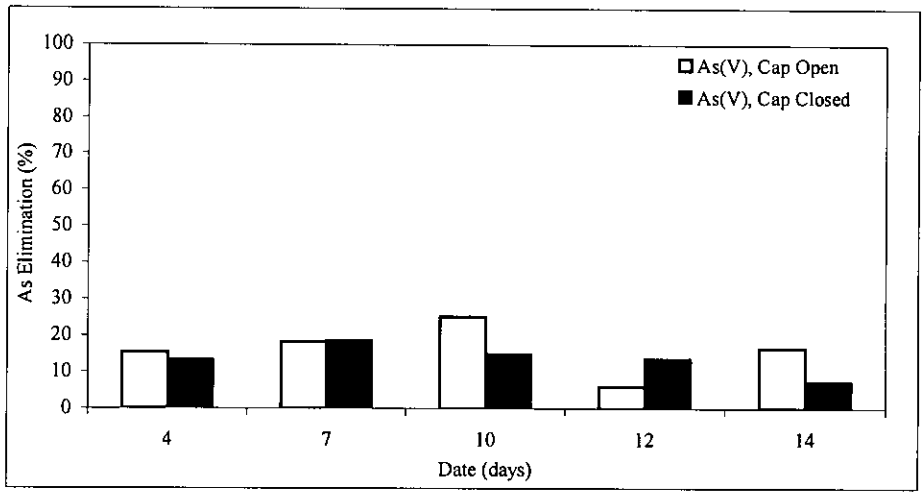


Figure C.1.7: Elimination of Arsenic Present in Soil (initial As 23.45 μg) in As(III) Solution

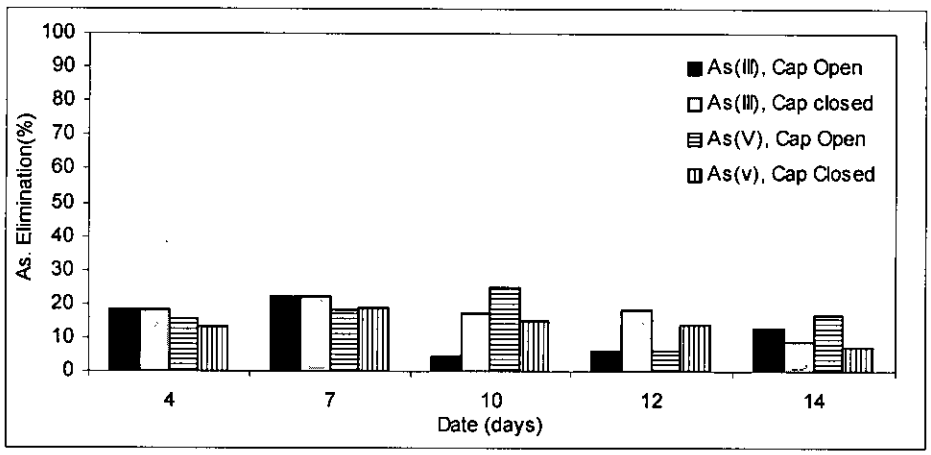


Figure C.1.8: Arsenic Elimination from Arsenic Rich Soil under both Cap Open and Cap Closed Condition (Initial As 23.45μg)

C.2: Graphs Showing Comparisons of Arsenic Elimination from Arsenic Rich Soil mixed With Different Weight of Cowdung

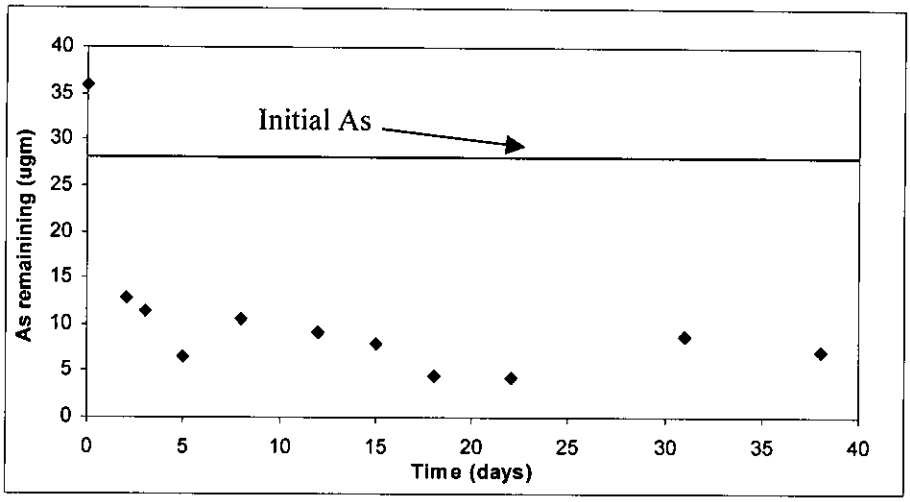


Figure C.2.1: Arsenic remaining in Aqueous Solution mixed with 2g soil and 1 g Cowdung

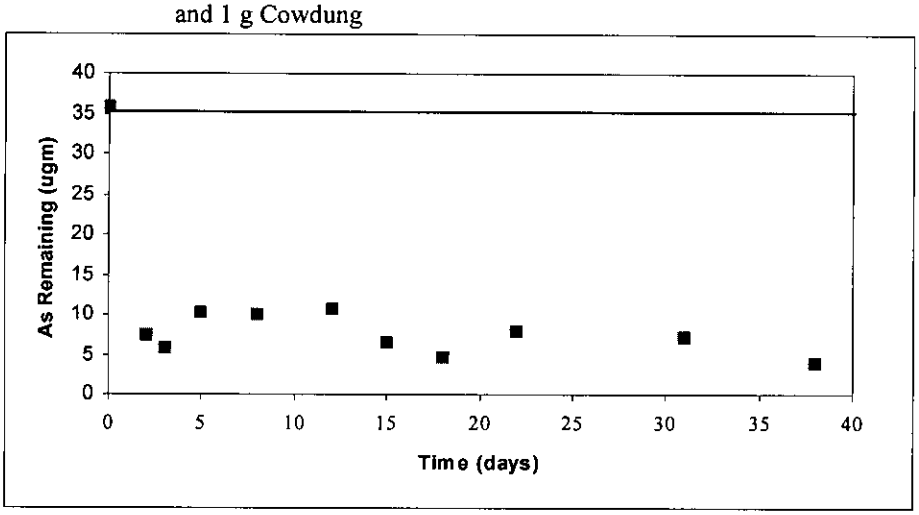


Figure C.2..2: Arsenic Remaining in Aqueous Solution mixed with 2g soil and 2 g Cowdung

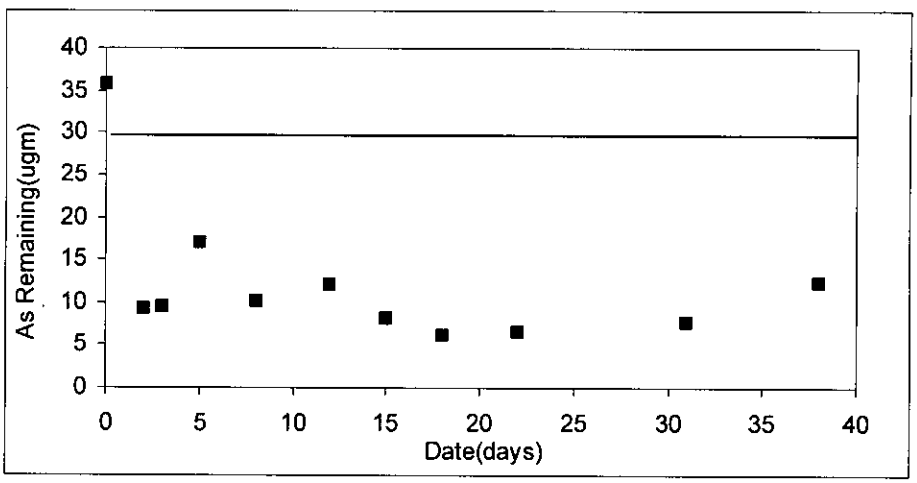


Figure C.2.3: Arsenic Remaining in Aqueous Solution mixed with 2g soil and 6 g Cowdung

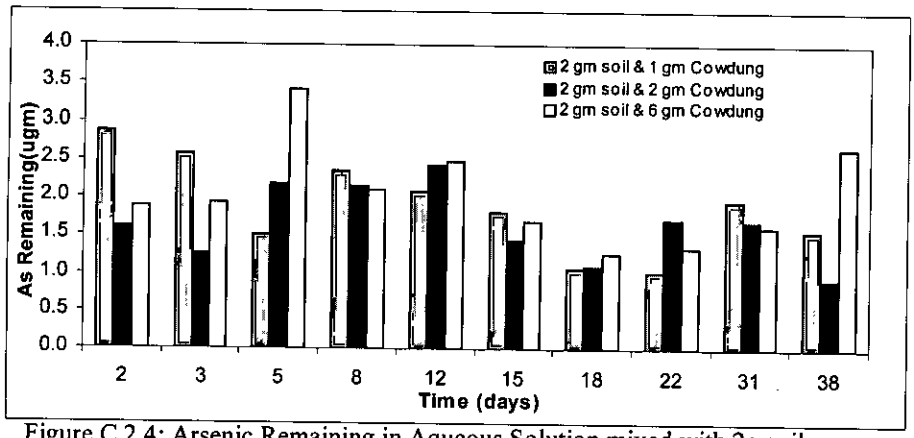


Figure C.2.4: Arsenic Remaining in Aqueous Solution mixed with 2g soil and Different weight of Cowdung

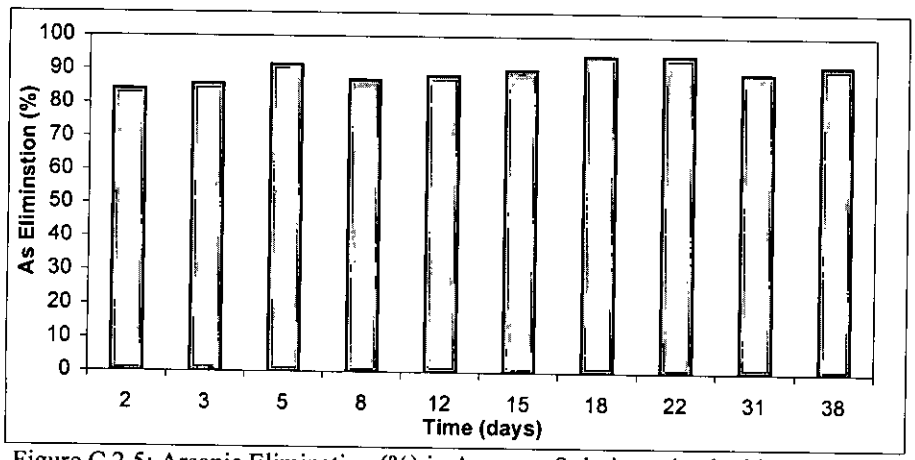


Figure C.2.5: Arsenic Elimination (%) in Aqueous Solution mixed with 2g soil and 1 g Cowdung

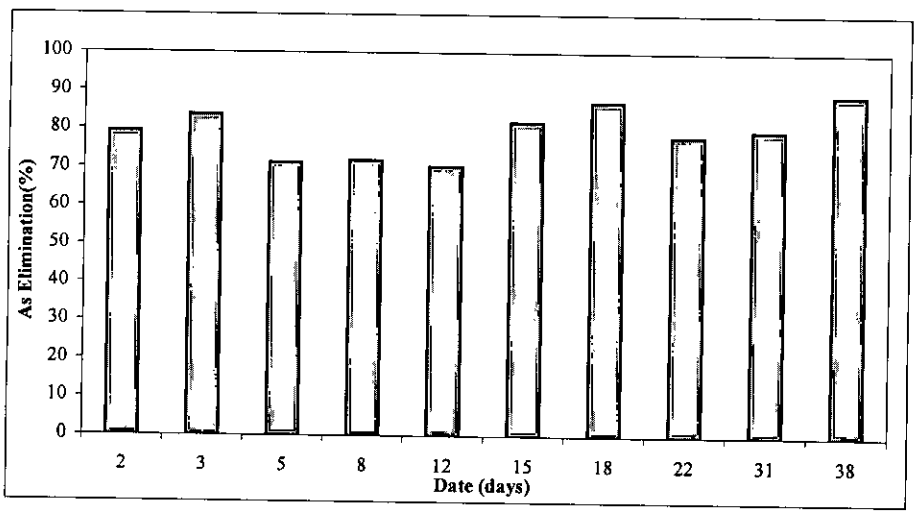


Figure C.2.6: Arsenic Elimination (%) in Aqueous Solution mixed with 2g Soil and 2 g Cowdung

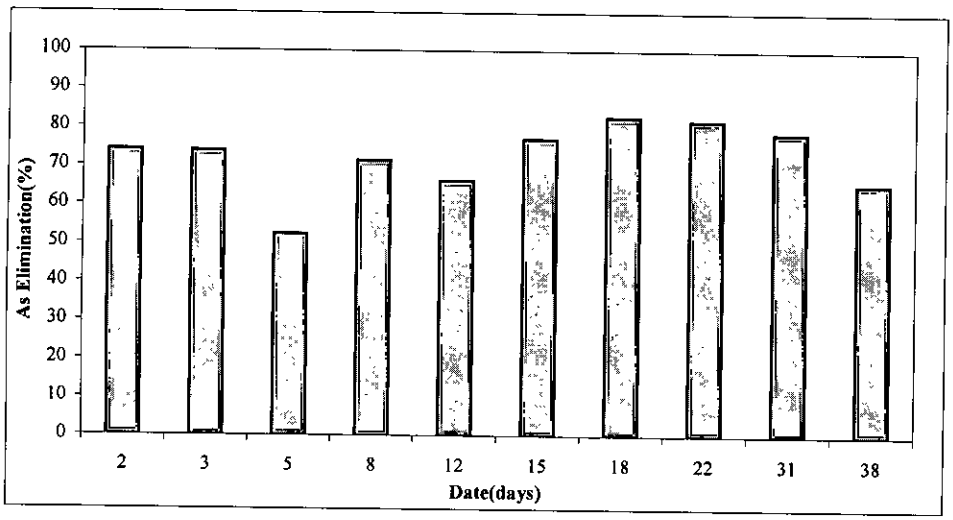


Figure C.2.7: Arsenic Elimination (%) in Aqueous Solution mixed with 2g Soil and 6 g Cowdung

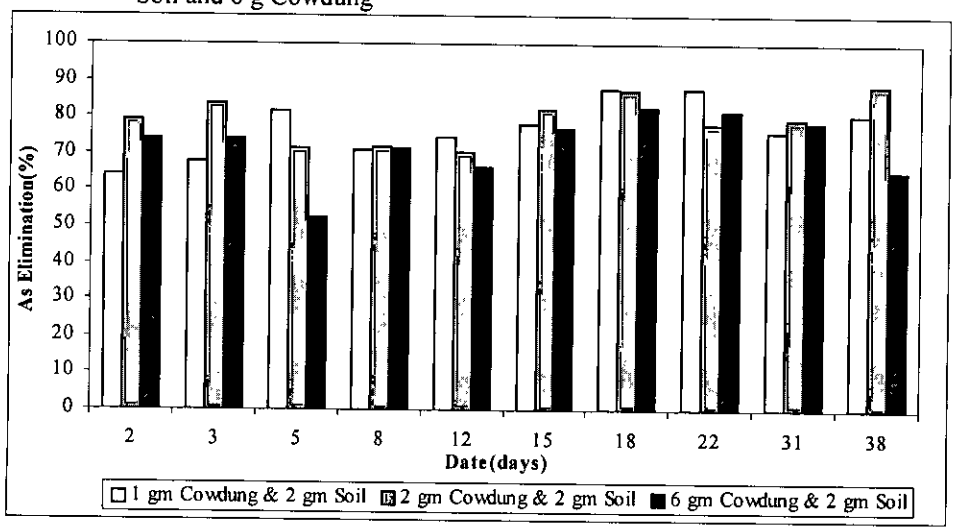


Figure C.2.8: Arsenic Elimination (%) in Aqueous Solution mixed with 2g Soil and different weight of cowdung

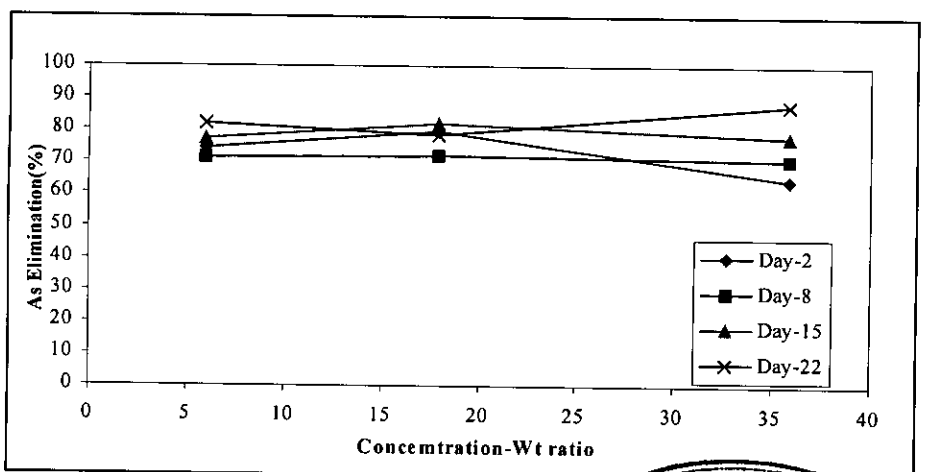


Figure C.2..9: Arsenic Elimination (%) in Aqueous Solution mixed with 2g Soil and different weight of cowdung

বাংলাদেশ প্রকৌশল বিশ্ববিদ্যালয়
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