

EFFICIENT ARSENIC REMOVAL FROM CONTAMINATED SLUDGE THROUGH ANAEROBIC VOLATILIZATION

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CERTIFICATION OF RECOMMENDATION

This is to certify that the thesis entitled “**EFFICIENT ARSENIC REMOVAL FROM CONTAMINATED SLUDGE THROUGH ANAEROBIC VOLATILIZATION**” is bonafide work carried out by NIBEDITA ROY under our supervision and guidance for partial fulfilment of the requirement for Post Degree of Master of Engineering in Water Resources & Hydraulic Engineering during the academic session 2021-2024.

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ABSTRACT

Arsenic contamination in sludge poses a significant environmental and public health concern worldwide. This study investigates an innovative and sustainable method for arsenic removal from contaminated sludge through enhanced anaerobic volatilization. By incorporating cow dung and septic sludge, this approach aims to improve the efficiency of arsenic removal while promoting the utilization of organic waste materials. The research explores the mechanisms of arsenic volatilization and evaluates the effectiveness of the proposed method in laboratory scale experiments. Results indicate promising outcomes, suggesting the potential for this approach to offer a cost-effective and environmentally friendly solution to arsenic remediation in sludge. Further research and implementation of this method could contribute to mitigating arsenic contamination and advancing sustainable waste management practices.

This research investigates the potential of utilizing anaerobic microorganisms, in conjunction with cow dung as an amendment, to effectively remove arsenic from arsenic-rich sludge through the process of volatilization. The study aims to evaluate the efficiency, feasibility, and environmental impact of this innovative approach, offering a sustainable solution to address arsenic contamination in sludge management.

The study achieved a maximum arsenic removal rate of 98.19% with a feed containing 5% ARP sludge relative to the total Cow Dung slurry. Additionally, a maximum arsenic removal rate of 94.54% was attained with a feed containing 5% ARP sludge relative to the total composite waste feed slurry, which included both septic sludge and cow dung, over a digestion period of 60 days.

Key Words: Arsenic-laden sludge (ALS), Anaerobic Volatilization, Digestor Bottle, Cow Dung, Septic Sludge.

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1 INTRODUCTION

Arsenic (As) is a toxic metalloid element that is present in air, water, and Earth's crust. Inorganic arsenic is generally more harmful than its organic counterparts. Examples of methylated organic arsenicals include monomethylarsonic acid MMA^V dimethylarsinic acid DMA^V. It is widely used in industrial processes such as mining, smelting, and agriculture, leading to its release into the environment. Over the past decade, the arsenic issue has garnered global concern because of its detrimental impacts on human health. Various techniques have been effectively devised for extracting arsenic from polluted water sources. These methods encompass ion exchange, reverse osmosis, lime softening, bioconversion to arsine, and coprecipitation/adsorption onto iron/aluminum oxyhydroxides. Among these, coprecipitation and adsorption onto iron and aluminum oxyhydroxides stand out as the most cost-effective and widely employed approach for purifying arsenic-contaminated drinking water. A significant amount of arsenic-laden sludge (ALS) is produced, containing an average of 6.10 g As/dm³ of sludge^[1] on a dry basis, which far exceeds the maximum permissible discharge limit of 0.2 g/m³^[2]. This level is considered hazardous according to the Resource Conservation and Recovery Act (RCRA) classification of the U.S. EPA (1986). Exposure to arsenic can have detrimental effects on human health, including skin lesions, respiratory diseases, and various types of cancer. One of the major sources of arsenic contamination is through the accumulation of arsenic-rich sludge, a by-product of industrial activities, in soil and water bodies. The traditional methods of arsenic removal, such as chemical precipitation, coagulation, and adsorption, have been proven to be inadequate and expensive. Thus, there is a need for alternative and sustainable methods for the removal of arsenic from contaminated sludge. In recent years, the use of anaerobic microorganisms treated with cow dung for the volatilization of arsenic from arsenic-rich sludge has gained attention as a potential solution. This thesis aims to explore the effectiveness of this method and its potential for large-scale applications.

Arsenic contamination in sludge, arising from various industrial, agricultural, and domestic sources, poses significant risks to human health and the environment. Conventional methods for arsenic removal from sludge often involve costly and energy-intensive processes. In recent years, there has been growing interest in exploring alternative approaches that are both effective and environmentally sustainable. Anaerobic volatilization has emerged as a promising method for arsenic remediation, leveraging microbial processes to convert arsenic into volatile forms

that can be easily removed. This study builds upon existing research by investigating the potential of enhancing anaerobic volatilization using cow dung and septic sludge as organic additives.

1.1 GENERAL BACKGROUND

Arsenic's prevalence in the Earth's crust and its long history of both beneficial and harmful applications highlight its complex role in human civilization. From industrial uses to traditional medicine, arsenic has left its mark on various aspects of human activity for centuries.

Its discovery by Albertus Magnus in 1250^[3] marked the beginning of our understanding of its properties and potential uses. Over time, arsenic found its way into numerous industrial processes, including alloy production, pesticide manufacturing, wood preservation, and semiconductor production. However, alongside its utility, the toxicity of arsenic has also been recognized, leading to efforts to regulate its use and minimize human exposure.

Despite its abundance, arsenic poses significant health risks, particularly through exposure via contaminated drinking water, consumption of certain foods like rice and seafood, occupational exposure in industries dealing with arsenic compounds, and certain cultural or traditional practices.

The World Health Organization (WHO) recognizes arsenic as a major public health concern chemical due to its well documented health effects. Chronic exposure to arsenic, primarily through drinking water, can lead to arsenic poisoning or arsenicosis, which manifests in various health problems ranging from skin lesions to cancers.

BIS 10500:2012^[4] is indeed the Indian standard for drinking water as per the specifications laid out by the Bureau of Indian Standards (BIS). As per BIS, from table no. 3

Table 1.1 Standard specifications for drinking water.

Characteristic	Requirement (Acceptable Limit) mg/l
Total arsenic (as As),	0.01
Iron (as Fe)	1

Efforts to regulate and mitigate arsenic exposure are crucial for protecting human health and the environment. This includes setting standards for arsenic levels in drinking water, implementing measures to reduce arsenic contamination in food sources, and promoting safer industrial practices.

Overall, arsenic's dual nature as both a useful substance and a potent toxin underscores the importance of responsible management and regulation to balance its benefits with the protection of human health and the environment.

1.2 NATURAL OCCURRENCE/ NATURAL SOURCES

Arsenic can naturally occur in various geological formations, leading to its presence in groundwater and surface water. Some natural sources of arsenic include:

1.2.1 MINERALS

Certainly, arsenic can be found in various minerals, some of which are present in specific geological formations and can release arsenic into the environment through weathering and erosion.



Figure 1.1 Natural arsenic-containing minerals, chemical formulas and Descriptions

Reference: <https://c7.alamy.com>

Here are some minerals that commonly contain arsenic:

Table 1.2 Natural arsenic containing minerals, chemicals formulas and Descriptions

Minerals	Chemical Formula	Description
Arsenite	As	Arsenite is a chemical compound consisting of arsenic in its trivalent state (arsenic with a +3 oxidation state). It can occur in various forms and is often found in aqueous solutions as arsenious acid (H ₃ AsO ₃).
Arsenopyrite	FeAsS	Arsenopyrite is an iron arsenic sulfide mineral. It is the most common arsenicbearing mineral and is often found in hydrothermal veins and metamorphic rocks. It has a metallic luster and can be pale bronzeyellow to white in color.
Arsenogentite	Ag₃As	Arsenogentite is a silver arsenide mineral. It is relatively rare and typically occurs in hydrothermal deposits associated with silver and other sulfide minerals.
Arsenolite	As₂O₃	Arsenolite is an arsenic trioxide mineral. It occurs as a white, gray, or yellowish powder and is formed as a product of the oxidation of arsenic minerals.
Adamite	Zn₂AsO₄(OH)	Adamite is a zinc arsenate hydroxide mineral. It is typically found in the oxidation zones of zinc and arsenic bearing mineral deposits. Adamite crystals are often green or yellow-green in color.
Antimony arsenide	AsSb	Antimony arsenide is a compound of arsenic and antimony. It is a rare mineral and is typically found in association with other arsenic and antimony minerals.
Beudantite	PbFe₃(AsO₄)SO₄	Beudantite is a lead iron arsenate Sulphate mineral. It forms in oxidized lead ore deposits and is often found in association with other lead and arsenic minerals.
Coaballite	CoAsS	Cobaltite is a cobalt arsenic sulfide mineral. It has a metallic luster and is often found in hydrothermal veins associated with other cobalt and arsenic minerals.
Domeykite	CuAs	Domeykite is a copper arsenide mineral. It typically occurs in association with other copper and arsenic minerals in hydrothermal deposits.

Enargite	CuAsS₄	Enargite is a copper arsenic sulfide mineral. It is an important ore of copper and is often found in porphyry copper deposits.
Gersdorffite	CoAsS	Gersdorffite is a nickel arsenide mineral. It is typically found in nickelcobalt sulfide deposits and is an important ore of nickel.
Jordanite	(Pb,Ti)₁₃As₇S₂₃	Jordanite is a complex lead arsenic sulfosalt mineral. It occurs in hydrothermal veins associated with other lead, arsenic, and sulfur minerals.
Loellingite	FeAs₂	Loellingite is an iron arsenide mineral. It is often found in hydrothermal veins and is associated with other arsenic and iron minerals.
Nicolite	NiAsS	Nicolite is a nickel arsenide mineral. It is typically found in nickelcobalt sulfide deposits and is often associated with gersdorffite and other nickel and arsenic minerals.
Orpiment	As₂S₃	Orpiment is an arsenic sulfide mineral. It occurs in hydrothermal deposits and volcanic fumaroles and is often associated with realgar.
Pearcite	Ag₁₆As₂S₁₂	Pearceite is a silver arsenic sulfosalt mineral. It occurs in hydrothermal veins associated with other silver, arsenic, and sulfur minerals.
Realgar	AsS	Realgar is an arsenic sulfide mineral. It occurs in hydrothermal veins and volcanic sublimation deposits and is often associated with orpiment.
Scorodite	(FeAl)AsO₄.2H₂O	Scorodite is an iron aluminum arsenate mineral. It forms as a secondary mineral in oxidized arsenicbearing mineral deposits and is often found in association with other arsenic minerals.
Sperrylite	PtAs₂	Sperrylite is a platinum arsenide mineral. It is one of the few minerals containing platinum as a primary component and is typically found in platinum bearing nickel copper deposits.
Tennantite	Cu₁₂As₄S₁₃	Tennantite is a copper arsenic sulfosalt mineral. It occurs in hydrothermal veins associated with other copper, arsenic, and sulfur minerals.

1.2.2 ROCKS AND SOIL

Yes, arsenic naturally occurs in rocks and soil. Over time, weathering and erosion processes break down these minerals, releasing arsenic into the environment. This can lead to contamination of groundwater and surface water sources with arsenic, posing risks to human health and ecosystems. Understanding the geological sources of arsenic is crucial for managing its presence in the environment and mitigating associated risks.

1.2.3 GROUNDWATER

Groundwater contamination with arsenic is a major concern in various parts of the world. Geological factors play a significant role in this contamination. For instance, in regions where arsenic rich minerals are present in geological formations, such as Bangladesh, West Bengal in India, and parts of Southeast Asia, groundwater can become naturally enriched with arsenic. Volcanic activity can also contribute to elevated levels of arsenic in groundwater.

In these areas, people often rely on groundwater as their primary source of drinking water, unaware of the arsenic contamination. Prolonged consumption of arsenic contaminated water can lead to serious health issues, including skin lesions, cancers, and various other ailments.

Addressing arsenic contamination in groundwater requires comprehensive efforts, including the development of alternative safe water sources, implementing effective water treatment technologies, and raising awareness among communities about the risks associated with arsenic exposure. Additionally, geological surveys and studies are essential for understanding the distribution of arsenic in groundwater and developing targeted mitigation strategies.

1.2.4 VOLCANIC ACTIVITY

Yes, volcanic emissions can indeed release arsenic into the atmosphere. Volcanoes can contain arsenic rich minerals like arsenopyrite and realgar, and during volcanic activity, these minerals can be heated and broken down, releasing arsenic compounds into the air.

Arsenic can be emitted in various forms during volcanic eruptions, including arsine gas (AsH_3) and volatile organic compounds such as mono, di, and trimethylarsine. These gases can be

carried by volcanic plumes and dispersed over wide areas, potentially affecting both local and distant environments.

Exposure to airborne arsenic compounds can pose health risks to humans and ecosystems. Inhalation of arsenic containing gases and particles can lead to respiratory problems and other health issues. Additionally, the deposition of arsenic from volcanic emissions onto soil and water bodies can contribute to environmental contamination, affecting plants, animals, and aquatic life.

Monitoring volcanic emissions and their impacts on air quality and environmental health is essential for assessing and mitigating the risks associated with arsenic exposure from volcanic activity. This involves both continuous monitoring of volcanic activity and conducting studies to understand the behaviour and fate of arsenic compounds in the atmosphere.

1.2.5 NATURAL WEATHERING AND EROSION

Natural weathering and erosion processes are significant contributors to the release of arsenic into the environment. As arsenic bearing minerals and rocks undergo weathering and erosion over time, arsenic is leached out and transported through surface water. This arsenic can then be deposited downstream, potentially contaminating soil and groundwater in the affected areas.

The levels of arsenic in natural sources can indeed vary widely depending on geological conditions and regional factors. Certain geological formations may have higher concentrations of arsenic bearing minerals, leading to elevated levels of arsenic in the surrounding environment.

Moreover, human activities such as mining and industrial processes can exacerbate environmental arsenic contamination. Mining activities, in particular, can disturb arsenic rich geological formations, releasing arsenic into the environment through processes like excavation and ore processing. Industrial activities may also contribute to arsenic pollution through emissions and waste disposal practices.

Given the diverse sources and pathways of arsenic contamination, comprehensive strategies are needed to mitigate its impact on human health and the environment. This includes implementing

measures to reduce arsenic emissions from industrial sources, regulating mining practices to minimize environmental disturbance, and developing effective methods for arsenic remediation in contaminated areas. Additionally, monitoring and research efforts are crucial for understanding the extent of arsenic contamination and guiding targeted interventions.

1.3 CHEMISTRY OF ARSENIC

The image shows a standard periodic table of elements. Arsenic (As) is highlighted in a blue box. It is located in Group 15 (the nitrogen family) and Period 4. Its atomic number is 33. The table includes elements from Hydrogen (1) to Oganesson (118), plus the Lanthanide and Actinide series at the bottom.

Figure 1.2 Arsenic position in Periodic Table

Reference: <https://www.chemistrylearner.com>

Arsenic, symbolized as **As** with an atomic number of **33**, is a unique chemical element situated in Group 15, also known as the nitrogen family, within the periodic table. It exhibits characteristics of both metals and non-metals, classifying it as a metalloid.

Naturally occurring in Earth's soil structure, arsenic manifests in diverse forms:

Inorganic Arsenic: This encompasses arsenic in its elemental state (arsenic metal, As), as well as arsenite (As^{III}) and arsenate (As^{V}), representing the trivalent and pentavalent states of arsenic. Inorganic arsenic compounds are commonly found in rocks, soil, and groundwater.



Figure 1.3 Chemical structure of Arsenite & Arsenate

Reference: <https://www.chemistrylearner.com>

Organic Arsenic: Arsenic compounds bound to carbon containing molecules fall under this category. Examples include monomethyl arsenic acid (MMA) and dimethyl arsenic acid (DMA), which may occur naturally or result from human activities such as the use of arsenic based pesticides.

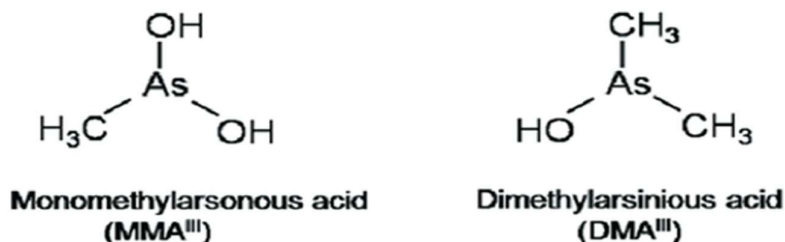


Figure 1.4 Monomethylarsonous Acid (MMA) and Dimethylarsinous Acid (DMA)

Reference: <https://www.chemistrylearner.com>

Arsine Gas: Arsine (AsH_3) is a toxic and flammable gas containing arsenic in the 3 oxidation state. It can form during industrial processes or the decomposition of organic arsenic compounds, posing significant health risks due to its toxicity.

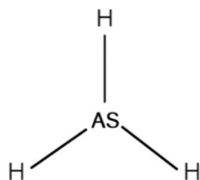


Figure 1.5 Chemical Structure of Arsine Gas

Reference: <https://www.chemistrylearner.com>

It's crucial to acknowledge that arsenic and its compounds carry high toxicity levels for all living organisms, humans included. The degree of toxicity varies depending on the form and concentration of arsenic. Ingesting or inhaling elevated levels of arsenic can result in severe health issues, including skin lesions, various cancers (such as lung, skin, bladder, and liver cancer), cardiovascular diseases, and neurological effects [5]. Consequently, handling arsenic and its compounds cautiously and adhering to safety protocols to minimize risks is imperative.

Moreover, arsenic contamination in the environment, especially in groundwater, presents a significant challenge. Certain regions globally grapple with naturally occurring arsenic in

groundwater, leading to widespread exposure and health complications among affected populations.

In summary, arsenic, existing in various forms like metallic arsenic, inorganic, and organic compounds, finds applications in industry and medicine. However, its highly toxic nature poses significant risks to both human health and the environment, mandating meticulous handling and disposal practices.

1.4 GROUNDWATER PROBLEMS OF ARSENIC

The timeline for arsenic exposure in India is not precisely defined, but it's believed to have started around the late 1960s coinciding with the introduction of tubewell digging as part of a largescale irrigation initiative [6]. Arsenic contamination in groundwater poses a significant challenge globally, notably in regions like South Asia's Bangladesh and West Bengal, India. It's also a concern in parts of Southeast Asia, America, and Europe. This issue arises from elevated levels of arsenic, a toxic element, in groundwater sources. The contamination primarily stems from natural sources, where arsenic from minerals in rocks and sediments dissolves into the water. However, human activities like mining, industrial processes, and arsenic based pesticide use exacerbate the problem. The consequences are severe, leading to various health issues such as skin lesions, cancers (like skin, lung, bladder, and kidney tumours), cardiovascular problems, and developmental impacts in children.

1.5 HEALTH EFFECTS DUE TO ARSENIC CONTAMINATION IN GROUNDWATER

Arsenic contamination in the environment is emerging as a significant public health concern in numerous regions globally. It is widely acknowledged that arsenite (As^{III}) is more toxic than arsenate (As^{V}), and inorganic arsenic is generally more toxic than organic arsenic. However, distinct organic arsenic species exhibit varying degrees of toxicity. For example, final arsenic metabolites like monomethylarsonic acid (MMA^{V}) and dimethylarsinic acid (DMA^{V}) are less toxic than inorganic arsenic. Conversely, intermediate metabolites such as monomethylarsonous acid (MMA^{III}) and dimethylarsinous acid (DMA^{III}) possess significantly higher toxicity levels compared to inorganic arsenic. The toxicity hierarchy of various arsenic species follows the order: $\text{As}^{\text{V}} < \text{MMA}^{\text{V}} < \text{DMA}^{\text{V}} < \text{As}^{\text{III}} < \text{MMA}^{\text{III}} \approx \text{DMA}^{\text{III}}$.

1.5.1 UPTAKE AND METABOLISM OF ARSENIC

In terrestrial environments, arsenic (As) predominantly exists as inorganic forms, with pentavalent arsenate (As^{V}) prevailing under aerobic conditions and trivalent arsenite (As^{III}) dominating under anaerobic settings. As^{III} , existing as a neutral species ($\text{As}(\text{OH})_3^\circ$, $\text{pK}_a = 9.2$) in aqueous solutions at physiological pH, and As^{V} exhibit distinct toxicological properties. As^{III} , structurally resembling glycerol, can enter cells via aquaglyceroporins, pore proteins facilitating the transport of small organic compounds like glycerol and urea. Conversely, As^{V} utilizes a pathway distinct from As^{III} , akin to phosphate, as both share similar dissociation constants. Found in water as oxyanions, $\text{H}_2\text{AsO}_4^{2-}$ and HAsO_4^{2-} at pH 5–7, As^{V} competes for entry via phosphate transporters. Once inside cells, As^{V} undergoes rapid reduction to As^{III} [7].

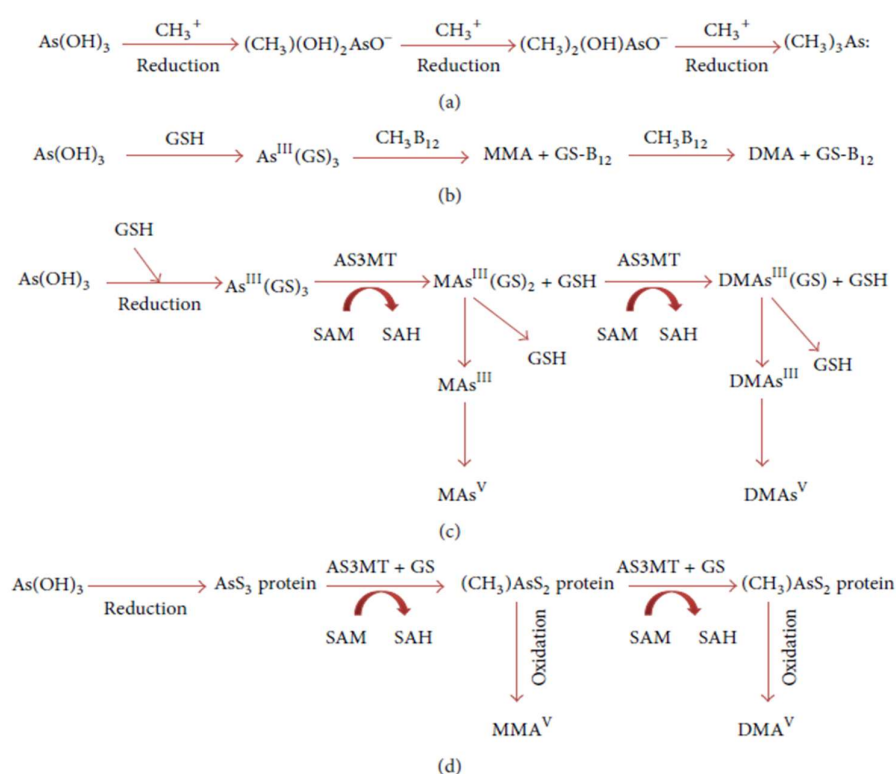


Figure 1.6 Pathways of arsenic metabolism in cells

(a) arsenic methylation in *Scopulariopsis brevicaulis*, (b) nonenzymatic As methylation in rat liver, (c) arsenic metabolic pathway in rat liver, and (d) metabolic pathway in rat liver, where SAM: Sadenosylmethionine; SAH: Sadenosylhomocysteine; CH_3^+ : methyl group; GSH: glutathione; $(\text{CH}_3)(\text{OH})_2\text{AsO}^-$: monomethylarsonous acid; $(\text{CH}_3)_2(\text{OH})\text{AsO}^-$: dimethylarsinic acid; $(\text{CH}_3)_3\text{As}$: trimethyl arsine oxide; $\text{As}(\text{GS})_3$: arsenic triglutathione; MMA: monomethylarsonic acid; DMA: dimethylarsinic acid; $\text{MAS}^{\text{III}}(\text{GS})_2$: monomethylarsonic diglutathione; $\text{DMAS}^{\text{III}}(\text{GS})$: dimethylarsinic glutathione; DMAS^{III} : trivalent monomethylarsonous acid; DMAS^{V} : pentavalent dimethylarsinic acid; MMA^{V} : pentavalent monomethylarsonic acid.

Reference: <https://doi.org/10.1155/2014/304524>

Subsequently, As^{III} undergoes multistep metabolism within cells, facilitated by arsenite methyltransferase (AS_3MT) using Sadenosylmethionine (SAM) as a methyl donor, resulting in the formation of various methylated As compounds, including MMA^{III} , DMA^{III} , MMA^{V} , and DMA^{V} . Initially proposed by Challenger, the classical pathway of As methylation involves a series of oxidation and reduction steps. Zakharyan and Aposhian later suggested a nonenzymatic methylation pathway in the presence of methylcobalamin and glutathione (GSH). However, subsequent studies have highlighted the crucial role of enzymes in arsenic methylation, depicting a new enzymatic metabolic pathway wherein $-\text{OH}$ groups of $\text{As}(\text{OH})_3$ are substituted by glutathionyl moieties, leading to the formation of GSH conjugates $\text{As}(\text{GS})_2^-$ OH and $\text{As}(\text{GS})_3$. As^{III} glutathione complexes, major substrates for AS_3MT , are further methylated to monomethylarsonic diglutathione ($\text{MMA}(\text{GS})_2$) and dimethylarsinic glutathione ($\text{DMA}(\text{GS})$). $\text{DMA}(\text{GS})$ is swiftly oxidized to pentavalent DMA^{V} , the major metabolite excreted from cells.

Additionally, Naranmandura et al. demonstrated an alternate pathway of arsenic metabolism, showing hepatic and renal metabolites of arsenic after intravenous injection of As^{III} in rats. They suggested that As^{III} bound to proteins (AsS_3 protein) undergoes successive reductive methylation by AS_3MT in the presence of GSH and SAM, with the reduced metabolites excreted outwardly. Consistent with these mechanisms, both trivalent and pentavalent inorganic and organic arsenicals have been detected in the urine of individuals chronically exposed to arsenic and in cell culture mediums post in-vitro arsenic exposure.

1.5.2 TOXICITY OF ARSENIC

Arsenic toxicity is indeed a significant concern for both humans and animals, as extensively documented in various review articles. Arsenic's potency as a carcinogen is well-established, with links to several types of cancer including those affecting the skin, bladder, liver, and lungs. One of the mechanisms by which arsenic exerts its toxic effects is through the induction of oxidative stress, leading to the formation of excess reactive oxygen species (ROS), which in turn can cause damage to biological systems. Furthermore, arsenic exposure^[7] is associated with cytotoxicity and genotoxicity, indicating its damaging effects on cells and genetic material. Chronic exposure to arsenic can result in arsenicosis, a condition characterized by various symptoms including skin lesions, blackfoot disease, peripheral vascular disease, and an increased risk of developing cancers. Elevated levels of arsenic (As) in the environment have

been linked to the occurrence of arsenicosis in numerous studies. These findings underscore the importance of mitigating arsenic exposure to safeguard human and animal health.

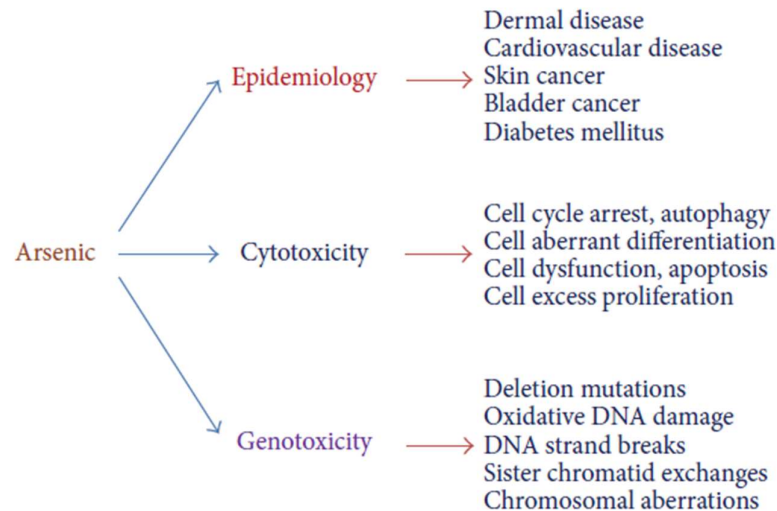


Figure 1.7 Arsenic toxicity in humans and rats

Reference: <https://doi.org/10.1155/2014/304524>

Epidemiology

Epidemiological research has extensively explored the mechanisms through which arsenic, a well-known human carcinogen, induces carcinogenesis. Numerous studies have provided compelling evidence that arsenic interferes with various cellular processes involved in gene proliferation, such as DNA damage and repair, cell cycle regulation, and cellular differentiation. Additionally, it disrupts important signalling pathways including the protein 53 signalling pathway, Nrf2-mediated redox signalling pathway, and MAPK pathway. The formation of reactive oxygen species (ROS) triggered by arsenic is also identified as a significant factor in cancer initiation.

Furthermore, research suggests that arsenic methylation metabolites are potent carcinogens. Studies have shown that dimethylarsinic acid (DMA) can induce bladder cancer in rats. Apart from its carcinogenic properties, arsenic is implicated in various noncancerous multisystemic diseases including cardiovascular diseases, dermal disorders, hypertension, and diabetes mellitus. Trivalent arsenicals (As^{III} , MMA^{III} , and DMA^{III}) are linked to diabetes through the distortion of glucose metabolism, as evidenced by studies using intact pancreatic islets from

mice. Moreover, inhibition of pyruvate and α ketoglutarate dehydrogenases by arsenic has been identified as a primary mechanism leading to diabetes.

Cardiovascular diseases, particularly hypertension, are closely associated with arsenic exposure. Arsenic induced hypertension involves multiple pathways including inflammation promotion, endothelial dysfunction, alterations in vascular tone, and kidney malfunction. Additionally, researchers concur on the pivotal role of ROS in mediating arsenic induced noncarcinogenic effects. Arsenic induced ROS contributes to alterations in cell signaling, apoptosis, increased cytokine production, and inflammation, which perpetuates a cycle leading to further ROS generation and mutagenesis, thereby exacerbating the pathogenesis of arsenic induced diseases.

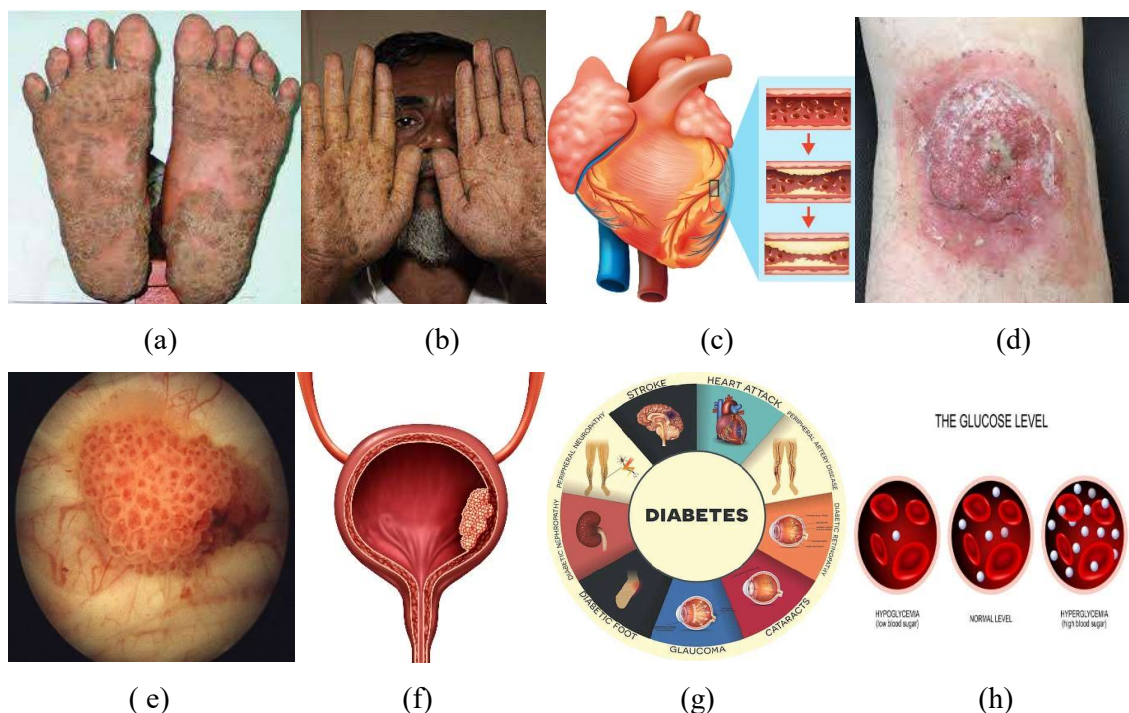


Figure 1.8 Pic of (a)(b) dermal diseases, (c) pic of Cardiovascular disease, (d) skin cancer, (e) (f) bladder cancer, (g) (h) diabetes mellitus

Reference: <https://www.medicalzone.net/uploads/1/2/7/3/12737542/4999601.jpg>

Cytotoxicity

Cytotoxicity arises when cells manifest abnormalities induced by toxic chemicals or contaminants. Numerous researchers have investigated the pathways through which arsenic

induces cytotoxicity in cells. Arsenic triggers cytotoxicity primarily by generating reactive oxygen species (ROS), leading to a significant increase in ROS levels within exposed cells. This increase in ROS is facilitated by arsenic's induction of NADPH oxidase. Elevated ROS levels cause damage to lipids and proteins and disrupt mitochondrial function, exacerbating cellular damage.

Studies have shown that ROS induced oxidative stress initiates a mitochondria dependent apoptotic pathway, as demonstrated by Shen et al. Furthermore, ROS exerts cytotoxic effects by activating cJun Nterminal kinases (JNK), a subgroup of mitogen activated protein kinases crucial for various cellular functions including proliferation, differentiation, and apoptosis. Additionally, ROS can modulate signal transduction pathways, impacting processes such as cell growth, apoptosis, adhesion, and HIV activation.

Arsenic induced cytotoxicity also involves the modulation of the tumour suppressor protein 53 (p53), which regulates diverse cellular functions including cell growth, cycle regulation, DNA repair, and apoptosis. Studies indicate that arsenic may induce the accumulation of p53 in human fibroblasts, leading to apoptosis by promoting Bax translocation to mitochondria, cytochrome c release, and activation of caspase9 through Apaf1 and the apoptosome. Moreover, p53 can induce cell cycle arrest at the G2/M stage by activating protein 21, an inhibitor of cyclin dependent kinases, and may induce autophagy in a DRAM (damage regulated autophagy modulator) dependent manner.

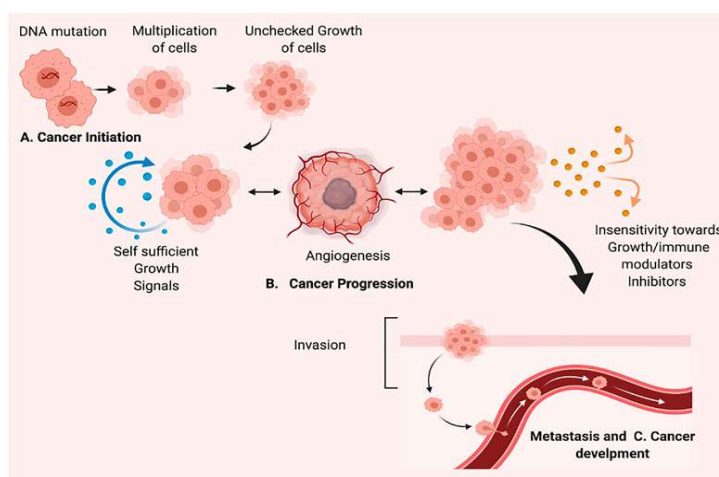


Figure 1.9 Pic of Cell dysfunction, apoptosis

Reference: <https://www.frontiersin.org/files/Articles/842376/fphar13842376HTML/imagem/fphar13842376g001.jpg>

Genotoxicity

Genotoxicity occurs when the genetic information within a cell sustains damage, ultimately leading to mutations. Numerous studies have investigated the genotoxic effects of arsenic (As). Arsenic induces genotoxicity through a mechanism similar to its cytotoxic effects by generating reactive oxygen species (ROS). Excessive ROS levels within the cell react with cellular components, resulting in genotoxicity. This occurs as ROS interact with both the deoxyribose and bases in DNA, causing base lesions and strand breaks. Additionally, ROS are implicated in DNA oxidation, alteration of DNA repair mechanisms, regulation of gene expression, and destabilization of genes.

Arsenic interacts with DNA repair proteins containing zinc finger motifs, crucial for transcription and DNA repair processes. Studies have demonstrated that arsenic trioxide (AsIII) disrupts zinc finger structures by binding to its target molecule, PARP1, leading to breaks in single and double strands of DNA and oxidative DNA damage. Furthermore, arsenic directly affects DNA repair efficiency by reducing the repair and expression of nucleotide excision repair pathway components such as ERCC1. Chronic exposure to elevated arsenic levels can deplete Sadenosylmethionine (SAM) in cells, leading to DNA hypomethylation and genomic instability. Arsenic and its trivalent methylated forms have been shown to interact with enzymes involved in SAM synthesis pathways, altering the activities of DNA methyltransferases and enzymes in SAM synthesis pathways.

Similarly to its cytotoxic effects, arsenic can also induce genotoxicity by affecting the status of the tumour suppressor protein p53. Arsenic's impact on p53 can further contribute to DNA damage and genomic instability.



Figure 1.10 Pic of Damaged DNA

Reference: <https://cdn.thescientist.com/assets/articleNo/70343/aImg/47182/article0822d2moico.jpg>

1.6 CURRENT STATUS OF ARSENIC

1.6.1 GLOBAL PERSPECTIVE OF ARSENIC

Arsenic contamination is a global issue affecting numerous regions, with high levels in drinking water posing significant public health hazards over the past two to three decades. This contamination primarily occurs in groundwater but can also impact surface water, soil, and food items. Natural geological processes, such as the dissolution of arsenic bearing minerals and leaching from rocks, are major contributors to this problem. Hotspots for arsenic contamination include parts of South Asia, Southeast Asia, Latin America, and other areas. For example, in Bangladesh and West Bengal, India, millions of people are exposed to arsenic levels far exceeding the World Health Organization's guideline of 10 µg/L. In these regions, chronic arsenic exposure is linked to serious health issues, including skin lesions, cancers, cardiovascular diseases, and developmental effects in children ^[8]. In Southeast Asia, Vietnam and Cambodia also face significant contamination, with many rural communities depending on arsenic laden tubewells for drinking water. In Latin America, countries like Mexico and Argentina have regions where natural arsenic levels in groundwater are high, putting local populations at risk ^[9]. Arsenic contamination is not only a developing world problem. In the United States, regions such as the Southwest and parts of the Midwest have reported elevated arsenic levels in private wells, affecting the health of those reliant on these water sources (Welch et al., 2000). In these affected areas, large populations are at risk of exposure to elevated arsenic levels through their drinking water sources, necessitating urgent public health interventions and the development of effective arsenic removal technologies.

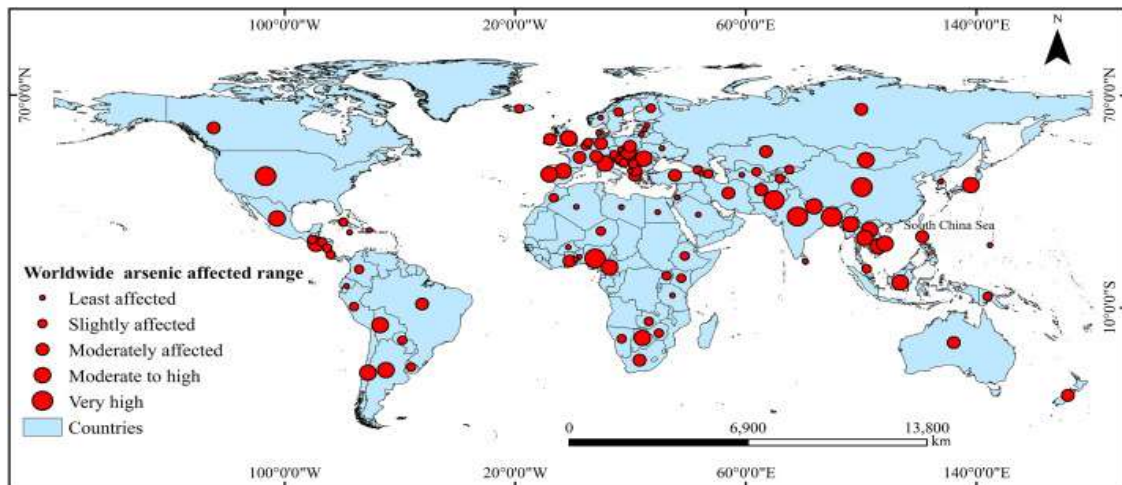


Figure 1.11 Arsenic affected countries

Reference: <https://ars.elscdn.com/content/image/1s2.0 S1674987120302115gr1.jpg>)

1.6.2 INDIAN PERSPECTIVE OF ARSENIC

In India, high levels of arsenic in groundwater present a significant public health problem. Drinking water contaminated with arsenic can lead to a wide range of health issues, as highlighted by the World Health Organization in 1996. This issue is particularly severe in states such as West Bengal, Bihar, Jharkhand, Uttar Pradesh, Chhattisgarh, Assam, and Manipur, where arsenic concentrations in groundwater exceed WHO's permissible limit of 10 µg/L.

In West Bengal, for instance, over 20 million people are estimated to be affected by arsenic contaminated water, with some areas reporting concentrations as high as 3,200 µg/L, vastly exceeding safe levels ^[10]. Chronic exposure in these regions has led to widespread health issues, including skin lesions, respiratory problems, and increased cancer risks. The district of Murshidabad is one of the most affected, with high prevalence rates of arsenicosis.

Bihar's arsenic crisis affects around 10 districts, particularly along the Ganges River, where the sediment deposits contribute to the high arsenic levels in the groundwater. Villages in the Bhojpur district have reported groundwater arsenic concentrations up to 1,500 µg/L, putting thousands at risk.

In Assam and Manipur, the issue is similarly dire. Studies have shown that several districts, such as Karimganj and Hailakandi in Assam, have groundwater arsenic levels above 300 µg/L. This has led to increased cases of arsenic related health issues, including gastrointestinal disorders and skin cancers.

Efforts to mitigate this crisis include the installation of Arsenic and Iron Removal Plants (AIRPs) and the promotion of alternative safe drinking water sources such as rainwater harvesting and treated surface water. However, the scale of contamination and the number of people affected call for more comprehensive and sustainable solutions, including regular monitoring of water quality, public health awareness programs, and investment in advanced arsenic removal technologies ^[11]

In conclusion, arsenic contamination in India's groundwater is a critical public health issue, particularly in states like West Bengal, Bihar, Jharkhand, Uttar Pradesh, Chhattisgarh, Assam, and Manipur. The extent of the contamination and the associated health risks underscore the urgent need for effective intervention and long-term solutions.

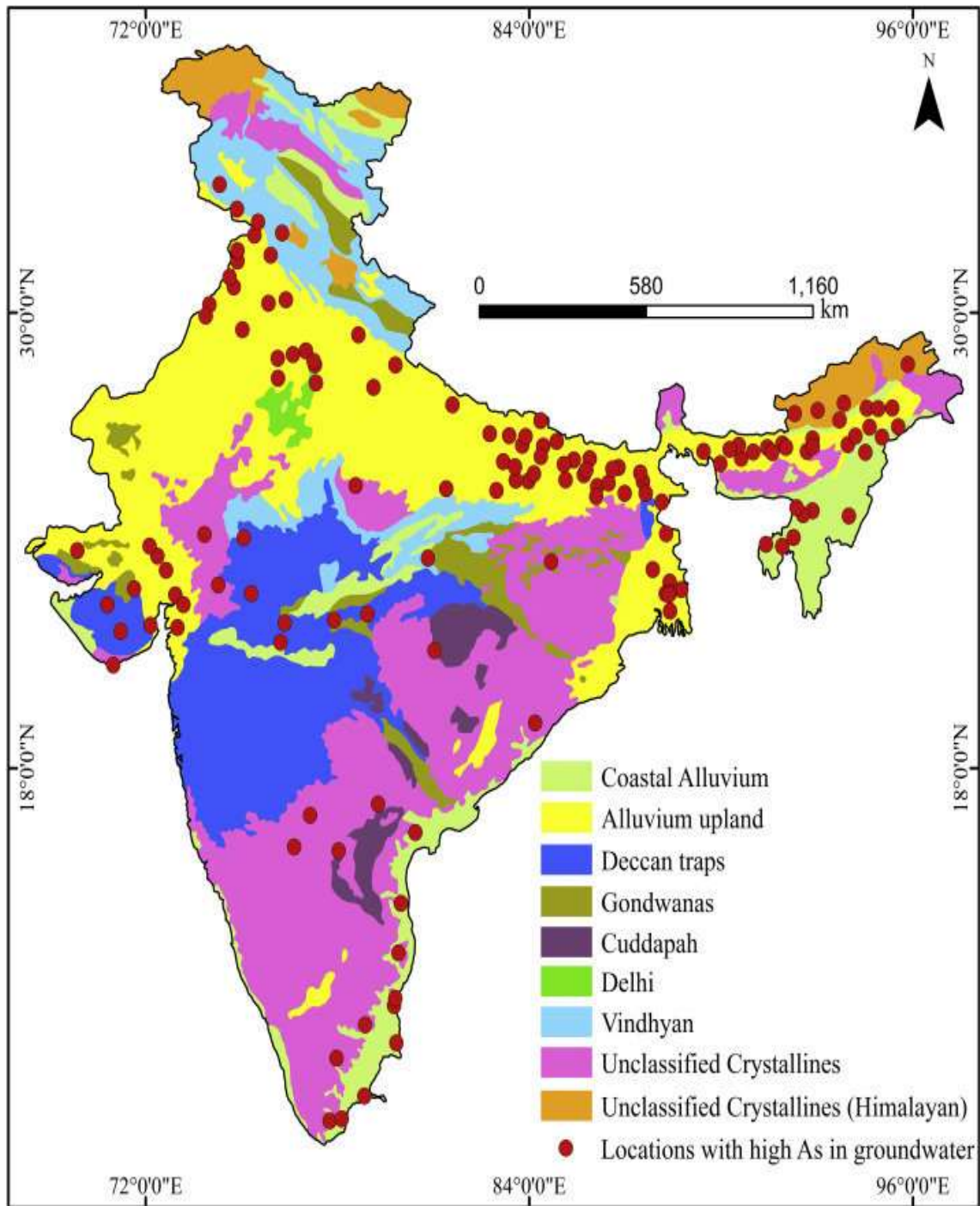


Figure 1.12 Arsenic contamination (hot spots of arsenic) in India

Reference: <https://www.researchgate.net/publication/346008548/figure/fig3/AS:960202870366210@1605941612678/ArsenicaffectedareassuperimposedonthegeneralgeologyofIndiaAlluvialaquifers.png>

1.6.3 EXTENT OF ARSENIC CONTAMINATION IN WEST BENGAL

In West Bengal, arsenic contamination is a significant environmental and public health issue, particularly in the Gangetic plains. First cases of Arsenicosis in West Bengal were detected in 1983. The groundwater contamination has severely affected 104 blocks across 11 districts, with the problem first identified in the late 1980s and early 1990s. The contamination is most severe in the districts of Nadia, Murshidabad, Malda, North 24 Parganas, South 24 Parganas, and parts of Hooghly, Howrah, and Bardhaman. The severity of contamination varies, with some areas having significantly higher arsenic concentrations in their groundwater.

In response to the crisis, the Public Health Engineering Department (PHED) of the Government of West Bengal has implemented several measures to provide safe drinking water, especially in areas where alternative sources are unavailable. One of the key interventions has been the installation of Arsenic and Iron Removal Plants (AIRPs). These plants use various technologies to remove arsenic and iron from water, including oxidation, coprecipitation, adsorption, ion exchange, and electrocoagulation [12]

Oxidation involves converting arsenite (As^{III}), which is more toxic and harder to remove, to arsenate (As^{V}), which can be more easily filtered out. Coprecipitation adds chemicals to the water to form precipitates that capture arsenic. Adsorption uses materials like activated alumina or iron hydroxides to bind arsenic ions. Ion exchange involves replacing arsenic ions with less harmful ions using resin beds, while electrocoagulation uses electrical currents to precipitate arsenic out of the water.

Despite these efforts, the scale of contamination in West Bengal remains a challenge. Continuous monitoring, maintenance of installed systems, and further research into more cost effective and sustainable solutions are essential to tackle the problem effectively. Furthermore, integrating community involvement and education into these efforts can enhance the sustainability and impact of arsenic mitigation strategies.

Overall, addressing arsenic contamination in West Bengal requires a multifaceted approach combining technology, education, and community engagement to ensure safe drinking water for all affected regions.

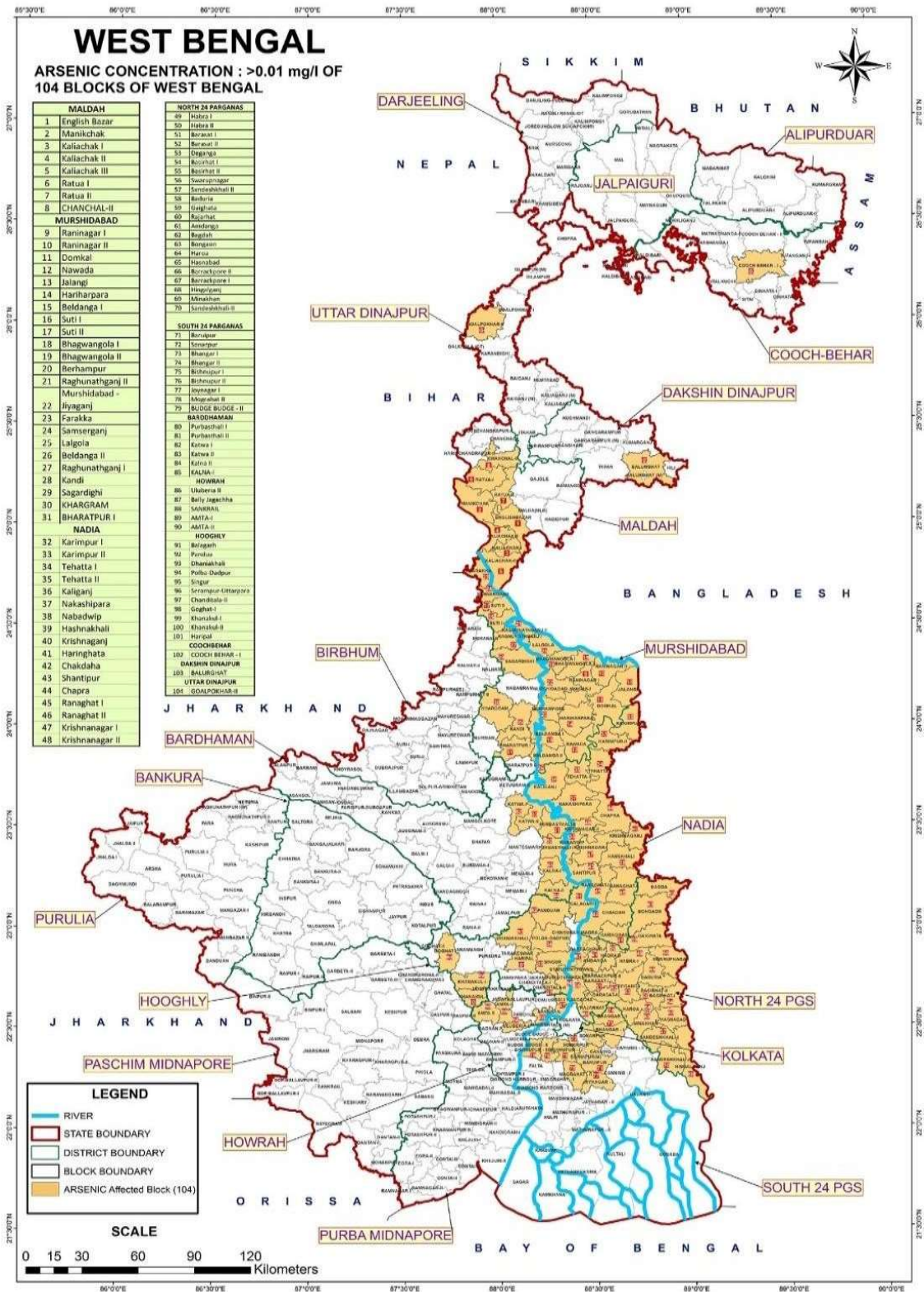


Figure 1.13 Arsenic contamination in West Bengal

Reference: PHED, W.B.

1.7 ARSENIC TREATMENT PROCEDURE

Arsenic removal from contaminated water involves various processes and technologies designed to reduce arsenic concentrations to safe levels. The choice of process depends on the specific conditions of the water source, including the arsenic concentration, water chemistry, and available infrastructure. Below are some commonly used arsenic removal processes:

1.7.1 OXIDATION AND FILTRATION

➤ **Steps:**

Oxidation: Add an oxidizing agent to convert arsenite (As^{III}) to arsenate (As^{V}).

Mixing: Ensure thorough mixing to allow complete oxidation.

Filtration: Filter the water to remove arsenate.

➤ **Materials Used:**

Oxidizing agents: Chlorine, potassium permanganate, ozone, hydrogen peroxide.

Filtration media: Sand filters, activated carbon.

➤ **Advantages:**

Effective for converting arsenite to arsenate.

Can be integrated with existing water treatment systems.

Relatively low cost for small scale operations.

➤ **Disadvantages:**

Requires careful handling and dosing of chemicals.

Chemical residues and byproducts need proper disposal.

Less effective in water with high organic content, which can consume oxidants.

1.7.2 COPRECIPITATION

➤ **Steps:**

Chemical Addition: Add co-precipitants like iron or aluminum salts.

Precipitation: Allow arsenic to bind with the precipitant to form insoluble compounds.

Sedimentation: Let the precipitate settle.

Filtration: Remove the settled precipitates.

➤ **MATERIALS USED:**

Co-precipitants: Ferric chloride, ferric Sulphate, aluminum Sulphate.

Filtration units: Sand filters, sedimentation tanks.

➤ **Advantages:**

Highly effective for both arsenite and arsenate.

Can treat large volumes of water.

Relatively low cost.

➤ **Disadvantages:**

Produces sludge that requires disposal.

Chemical handling and dosing are necessary.

Efficiency can be affected by the presence of other contaminants.

1.7.3 ADSORPTION

➤ **Steps:**

Pretreatment: Adjust pH if necessary to optimize adsorption.

Adsorption: Pass water through adsorption media.

Posttreatment: Monitor and replace or regenerate media as needed.

➤ **Materials Used:**

Adsorbents: Activated alumina, granular ferric hydroxide, ion exchange resins, synthetic media.

➤ **Advantages:**

Effective at low arsenic concentrations.

Simple operation and maintenance.

Some adsorbents can be regenerated and reused.

➤ **Disadvantages:**

Periodic replacement or regeneration of media is required.

Initial cost of adsorbents can be high.

Disposal of spent adsorbent must be managed.

1.7.4 ION EXCHANGE

➤ **Steps:**

Pre-treatment: Adjust water chemistry if necessary.

Ion Exchange: Pass water through ion exchange resins.

Regeneration: Periodically regenerate resins using a salt solution.

➤ **Materials Used:**

Ion exchange resins: Strong base anion exchange resins.

Regeneration solution: Typically, sodium chloride solution.

➤ **Advantages:**

Highly effective for both arsenite and arsenate.

Regenerable resins allow for repeated use.

Suitable for small to medium scale applications.

➤ **Disadvantages:**

Requires regeneration with salt solutions.

Sensitive to water chemistry, particularly competing ions.

High operational costs for largescale applications.

1.7.5 MEMBRANE FILTRATION

➤ **Steps:**

Prefiltration: Remove larger particles to prevent membrane fouling.

Membrane Filtration: Pass water through membranes (RO, NF, or UF).

Posttreatment: Treat the concentrate or brine waste.

➤ **Materials Used:**

Membranes: Reverse osmosis, nanofiltration, ultrafiltration.

Prefilters: Sand filters, activated carbon.

➤ **Advantages:**

Extremely effective in removing arsenic.

Also removes a wide range of other contaminants.

Produces high quality potable water.

➤ **Disadvantages:**

High initial capital and operational costs.

Requires regular maintenance and membrane replacement.

Generates concentrated brine that needs disposal.

1.7.6 ELECTROCOAGULATION

➤ **Steps:**

Electrolytic Dissolution: Apply electric current to dissolve metal electrodes.

Hydroxide Formation: Form metal hydroxides that capture arsenic.

Sedimentation: Allow precipitates to settle.

Filtration: Remove the settled precipitates.

➤ **Materials Used:**

Electrodes: Iron or aluminum.

Power supply: Electrical source for electrolysis.

➤ **Advantages:**

Effective for a wide range of contaminants, including arsenic.

Can be automated and requires minimal chemical additives.

Generates less sludge compared to chemical coprecipitation.

➤ **Disadvantages:**

High energy consumption.

Requires periodic replacement of electrodes.

Sludge management and disposal still necessary.

1.7.7 BIOLOGICAL METHODS

➤ **Steps:**

Microbial Activity: Utilize bacteria or plants that transform arsenic.

Phytoremediation/Bioremediation: Allow plants or bacteria to absorb or immobilize arsenic.

Harvest/Manage Biomass: Dispose of or treat biomass containing arsenic.

➤ **Materials Used:**

Bacteria: Specific arsenic transforming bacteria.

Plants: Hyperaccumulator plants used for phytoremediation.

➤ **Advantages:**

Environmentally friendly and sustainable.

Can be cost effective for certain applications.

Minimal chemical inputs are required.

➤ **Disadvantages:**

Slower process compared to chemical methods.

Limited to specific conditions and types of contamination.

Requires careful management to prevent secondary contamination.

CONCLUSION

Each arsenic removal procedure has unique steps, materials, advantages, and disadvantages, making them suitable for different situations. The choice of method depends on factors like arsenic concentration, water chemistry, available resources, and specific application requirements. In many cases, combining multiple methods can enhance efficiency and ensure more comprehensive arsenic removal.

1.8 PROBLEM OF SLUDGE GENERATED FROM THE ARSENIC CONTAMINATED WATER TREATMENT

The treatment of arsenic contaminated water generates sludge as a byproduct, posing several challenges and problems. Sludge refers to the solid residue remaining after the water treatment process. Here are some of the issues associated with the sludge generated from arsenic contaminated water treatment:

Arsenic Concentration

Problem:

The sludge contains high concentrations of arsenic, the primary contaminant removed from the water.

Elaboration:

This high concentration makes the sludge hazardous, necessitating careful handling and disposal to prevent environmental release. Arsenic levels in sludge can range from hundreds to thousands of milligrams per kilogram, far exceeding safe limits for direct disposal.

Toxicity and Environmental Impact

Problem:

Arsenic is a highly hazardous chemical, and improper management of the sludge can endanger human health and the environment.

Elaboration:

Improper disposal or release of arsenic containing sludge can contaminate soil, water bodies, and groundwater, leading to long term environmental and health consequences. For instance, leaching from improperly managed sludge can cause arsenic to enter agricultural lands, affecting crop safety and food security.

Regulatory Compliance

Problem:

The disposal and management of arsenic containing sludge are subject to strict regulations and guidelines to protect public health and the environment.

Elaboration:

Noncompliance with these regulations can result in severe penalties, legal action, and reputational damage. Regulations such as the Resource Conservation and Recovery Act (RCRA) in the U.S. mandate specific handling, storage, and disposal practices to prevent environmental contamination.

Volume and Storage

Problem:

The sludge generated from arsenic treatment processes can be significant in volume, requiring appropriate storage facilities.

Elaboration:

Managing large quantities of sludge poses logistical challenges, including space constraints and the need for containment structures to prevent leaks or spills. For example, a water treatment plant processing 100,000 gallons per day could generate several tons of sludge annually, requiring substantial storage and handling capacity.

Treatment and Disposal Options

Problem:

Arsenic containing sludge requires proper treatment and disposal methods to ensure long term safety and environmental sustainability.

Elaboration:

Treatment options include stabilization (e.g., mixing with lime to reduce solubility), solidification (e.g., encapsulating in cement), or immobilization techniques to reduce the mobility and bioavailability of arsenic. Disposal options can include landfilling in specialized hazardous waste facilities, incineration, or other approved methods that comply with local regulations. Each method has its advantages and limitations, balancing cost, effectiveness, and environmental impact.

Cost and Resource Requirements

Problem:

Proper management of arsenic containing sludge can incur significant costs.

Elaboration:

Treatment, storage, and disposal methods require appropriate infrastructure, equipment, and expertise. Implementing these measures can strain financial resources, especially for small scale water treatment facilities or communities with limited funding. For example, the cost of constructing a compliant hazardous waste landfill can be prohibitively high, running into millions of dollars.

Occupational Health and Safety

Problem:

Handling and managing arsenic containing sludge poses occupational health and safety risks for workers involved in the process.

Elaboration:

Proper training, protective equipment, and adherence to safety protocols are necessary to protect workers from potential exposure to arsenic and other hazardous substances present in the sludge. Workers handling arsenic laden sludge are at risk of skin contact, inhalation, and ingestion, which can lead to serious health issues, including skin lesions, respiratory problems, and increased cancer risk.

Conclusion

Managing sludge generated from arsenic contaminated water treatment involves addressing high arsenic concentration, toxicity, environmental impact, regulatory compliance, volume and storage challenges, treatment and disposal options, cost implications, and occupational health and safety risks. Comprehensive strategies are required to ensure safe and effective sludge management, safeguarding both human health and the environment. This involves utilizing advanced treatment technologies, ensuring regulatory compliance, and implementing robust health and safety protocols for workers.

1.9 MITIGATION MEASURES OF ARSENIC SLUDGE

Mitigating the risks and challenges associated with arsenic rich sludge requires a multifaceted approach. Here are several effective mitigation measures:

Stabilization and Solidification

Method:

Mixing the sludge with materials like lime, cement, or fly ash to immobilize arsenic.

Advantages:

Reduces the leachability and mobility of arsenic.

Converts sludge into a more stable, less hazardous form suitable for landfilling.

Disadvantages:

Adds bulk to the sludge, increasing the volume.

Requires careful handling and mixing to ensure complete stabilization.

Encapsulation

Method:

Encasing the sludge in materials such as concrete or polymer barriers to prevent leaching.

Advantages:

Provides a long-term containment solution.

Prevents direct contact with the environment.

Disadvantages:

High cost of materials and process.

Potential for future degradation of encapsulation materials.

Landfilling in Hazardous Waste Facilities

Method:

Disposing of the stabilized sludge in specially designed hazardous waste landfills.

Advantages:

Isolates the arsenic rich sludge from the environment.

Complies with regulatory requirements for hazardous waste.

Disadvantages:

High cost of landfill disposal.

Limited availability of hazardous waste landfill sites.

Thermal Treatment (Incineration)

Method:

Using high temperature incineration to destroy organic contaminants and reduce the volume of the sludge.

Advantages:

Significantly reduces the volume of waste.

Destroys organic contaminants effectively.

Disadvantages:

High energy consumption and cost.

Requires air pollution control systems to handle emissions.

Phytoremediation

Method:

Using plants that can absorb and concentrate arsenic from the sludge.

Advantages:

Environmentally friendly and sustainable.

Can be integrated into landscape management.

Disadvantages:

Slow process requiring long term commitment.

Biomass containing arsenic must be handled and disposed of properly.

Vitrification

Method:

Heating the sludge to form a glasslike material, immobilizing arsenic.

Advantages:

Produces a stable, inert product.

Minimizes leaching potential.

Disadvantages:

High energy costs.

Requires specialized equipment.

Chemical Treatment

Method:

Adding chemicals to the sludge to convert arsenic into less soluble forms.

Advantages:

Reduces the solubility and mobility of arsenic.

Can be tailored to specific sludge characteristics.

Disadvantages:

Requires careful control of chemical dosing.

Potential secondary waste generation.

Reuse in Construction Materials

Method:

Incorporating treated sludge into bricks, concrete, or other building materials.

Advantages:

Reduces waste volume by creating useful products.

Encapsulates arsenic within a solid matrix.

Disadvantages:

Potential leaching over time if not properly stabilized.

Regulatory and market acceptance challenges.

Electrochemical Treatment

Method:

Applying electric current to precipitate arsenic from the sludge.

Advantages:

Can achieve high removal efficiencies.

Generates less secondary waste compared to chemical treatments.

Disadvantages:

Requires specialized equipment and energy input.

May need posttreatment of precipitates.

Community Education and Training

Method:

Educating workers and local communities about safe handling, disposal practices, and potential risks.

Advantages:

Reduces accidental exposure and improper disposal.

Empower communities to manage arsenic risks effectively.

Disadvantages:

Requires ongoing efforts and resources.

Effectiveness depends on community engagement and participation.

Conclusion

Implementing these mitigation measures requires a balanced approach considering cost, effectiveness, regulatory compliance, and environmental sustainability. Combining multiple methods, where appropriate, can enhance overall effectiveness in managing arsenic rich sludge. Continuous monitoring and adaptation of these strategies are crucial to addressing evolving challenges in sludge management.

2 LITERATURE REVIEW

2.1 INTRODUCTION

The literature review chapter of this study aims to deliver a thorough overview of the current knowledge and research by critically analysing and synthesizing the available literature. This chapter will establish a solid foundation for the subsequent research and investigation carried out in this study.

2.2 LITERATURE REVIEW

Mahapatra et al., 2008^[13] investigated the microbial mediated volatilization of arsenic via anaerobic digestion, employing cultures of methanogenic bacteria. Cow dung served as the primary substrate for bacterial growth during this process. Analysis of contact time revealed a linear kinetics of arsenic volatilization for up to 40 days, beyond which the kinetics became negligible. Arsenic volatilization kinetics were modelled using a first order plot, yielding a reaction rate constant (k) of 0.0282 mg/L/day. The bacteria's regeneration time was determined to be 53.3 hours. The impact of substrate (cow dung) concentration on arsenic volatilization was assessed, indicating that a concentration of 25 g/L could volatilize approximately 35% of arsenic. However, higher substrate concentrations led to a decrease in the volatilization rate, likely due to methane formation, which inhibited higher arsenic doses and promoted the formation of non-volatile compounds. The maximum arsenic uptake was determined to be 1.08 mg of As^V per gm of substrate. Furthermore, the study delved into the effects of various organic acids on arsenic mobilization during anaerobic digestion, providing valuable insights for future research and optimization efforts.

Banerjee 2010^[14] said that when alum or iron salts are used for arsenic removal, they create a hefty batch of arsenic infused sludge, roughly averaging 6.10 grams of arsenic per decimetre cubed of sludge on a dry basis, in your typical arsenic removal plant (ARP). This sludge, teeming with toxicity, gets mixed in with a concoction of partially broken down market waste, sewage treatment plant sludge, and liquefied water hyacinth, forming a composite organic waste slurry. This slurry, comprising 1–10% of the total volume, undergoes anaerobic digestion for about 30–50 days. At the pinnacle of this process, a whopping 99.69% of arsenic is successfully removed after 50 days of digestion. Even at the lower end, with just 30 days of digestion, the biogas production hits a minimum of 0.560 cubic meters at standard temperature and pressure

per cubic meter of composite feed slurry, with 10% of ARP sludge. What's interesting is that the presence of arsenic doesn't throw a significant wrench into the anaerobic digestion works, given that the composite feed sludge is properly acclimated. This suggests that anaerobic digestion could be a feasible route for safely and economically disposing of arsenic laden sludge from existing arsenic removal water plants in affected areas.

Clancy 2015^[15] the quest for effective arsenic removal from groundwater has spurred extensive research into water treatment technologies. However, one crucial aspect often overlooked is what to do with the arsenic laden waste produced during treatment. Sadly, specific guidelines for its disposal are often scarce, leaving it as a gap for future exploration. This lack of clarity poses a significant hurdle to the widespread adoption of arsenic removal systems. This review delves into current disposal methods for arsenic laden waste, ranging from landfilling to stabilization, even innovative approaches like mixing with cow dung or passive aeration. Each method's efficacy is scrutinized, comparing results from both simulated disposal conditions and regulatory tests. It's often found that short-term regulatory tests fall short in reflecting the diverse conditions encountered in real disposal environments. Moving forward, there's a pressing need to establish regulatory tests that mirror actual disposal conditions better. Additionally, exploring nonlandfill disposal options, particularly relevant for developing nations, holds promise for more sustainable arsenic waste management.

Banerjee, et al. 2005^[4], recovered that, the disposal of arsenic laden sludge generated from water treatment plants poses a significant environmental challenge due to its toxicity. In addressing this issue, various stabilization processes have been explored, including briquette production, cement mortar, and concrete making. This literature review examines the efficacy of these methods in managing arsenic bearing sludge and their compliance with regulatory standards. When arsenic is coprecipitated with iron hydroxide in water treatment processes, a substantial amount of sludge is produced, containing an average of 6.1 kg As /m³ of sludge. To mitigate the environmental impact of this sludge, stabilization techniques have been investigated. One such method is briquette production, which involves compressing the sludge with other common ingredients. In this study, it was observed that incorporating up to 10% of arsenic bearing sludge by volume did not exceed the permissible leachate levels set by regulatory standards. Similarly, cement mortar and concrete making were explored as potential disposal solutions. It was found that mixing up to 18% and 40% of arsenic bearing sludge by

volume in cement, sand mortar and concrete, respectively, did not result in leachate concentrations surpassing the prescribed limits for direct inland water discharge. Furthermore, the study investigated the possibility of replacing a portion of cement with fly ash to stabilize arsenic laden sludge. Results indicated that 25% of cement could be substituted with fly ash in a cement, sand mortar mix (1:3 ratio), enabling the stabilization of arsenic laden sludge up to 11% by volume.

Overall, these findings suggest that stabilization processes such as briquette production, cement mortar, and concrete making offer viable means of disposing of arsenic bearing sludge without compromising environmental safety. Moreover, the incorporation of fly ash presents a potential avenue for enhancing the efficiency of stabilization while reducing the reliance on traditional cement-based approaches. Compliance with regulatory standards, particularly those set by the Ministry of Environment & Forest, Government of India, underscores the suitability of these methods for managing arsenic contaminated waste streams in water treatment facilities.

Mestrot, et al. 2013^[16], categorized Arsenic, as a class 1 nonthreshold carcinogen, pervades various environmental settings due to its widespread presence. Within these environments, arsenic undergoes diverse transformations, both biotic and abiotic, across different compartments, resulting in various chemical species with distinct properties and toxicities. One particular transformation, As biotic volatilization coupled with As biomethylation, remains understudied due to challenges in sampling. In regions like China, rice straw and animal manure are commonly utilized for biogas production, yet they may harbour elevated arsenic levels, particularly if sourced from areas with intense mining or smelting activities, or if animals are fed Roxarsone. Roxarsone, an arsenic containing drug widely used in China for controlling intestinal parasites and enhancing feed efficiency, can degrade into inorganic arsenic under anaerobic conditions. This study focuses on the biotic transformations of arsenic within small scale biogas digester models (BDMs), employing recently validated arsenic traps to directly quantify and identify volatile arsenic species. The findings reveal a loss of soluble arsenic in the BDMs, indicating conditions conducive to biomethylation. Notably, all reactors produce volatile arsenic, particularly those spiked with monomethylarsonic acid, suggesting that the initial methylation step from inorganic arsenic may be a limiting factor. Trimethylarsine emerges as the most abundant species, with toxic arsine also detected in the headspace of numerous BDMs. These results underscore the importance of monitoring volatile arsenic species in biogas digesters to assess potential risks to individuals working in biogas plants and

those utilizing biogas for various purposes. Such monitoring is essential for ensuring occupational safety and evaluating the potential hazards associated with biogas utilization.

Webster et al. 2016^[17], examined that removal of arsenic from drinking water sources produces arsenic bearing wastes, which are disposed of in various ways. Some disposal methods involve anaerobic environments, such as mixing arsenic waste with cow dung, landfills, anaerobic digesters, and pond sediments. The production of gaseous arsenic species in these environments can be either an intended goal (e.g., cow dung mixing) or an unintended consequence (e.g., anaerobic digesters). Once formed, these gaseous arsenic species are readily diluted in the atmosphere. Arsenic volatilization can be mediated by the enzyme arsenite Sadenosylmethionine methyltransferase (ArsM) or through enzymes involved in methanogenesis. In this study, methanogenic mesocosms containing arsenic bearing ferric iron waste from an electrocoagulation drinking water treatment system were used to evaluate the role of methanogenesis in arsenic volatilization, using methanogen inhibitors. Arsenic volatilization was highest in methanogenic mesocosms, but accounted for less than 0.02% of the total arsenic added. Analyses including 16S rRNA cDNA sequencing, qPCR of mcrA transcripts, and functional gene array based analysis of arsM expression revealed that arsenic volatilization correlated with methanogenic activity. Aqueous arsenic concentrations increased in all mesocosms, indicating that unintended contamination might result from disposal in anaerobic environments. This underscores the need for further research before recommending anaerobic disposal methods intended to promote arsenic volatilization.

Rahman et al. 2013^[8] With the increasing use of arsenic (As) removal units to treat As contaminated groundwater in rural Bangladesh, concerns have arisen about the safe disposal of As rich wastes from these units and the potential for environmental contamination. In the absence of clear guidelines for the safe disposal of wastes generated from As removal units, these wastes are often disposed of openly, frequently on cow dung beds in backyards. Short-term (up to 6 weeks) batch experiments conducted in this study suggest that biochemical processes, such as biomethylation, in the presence of fresh cow dung can significantly remove As from both aqueous solutions and As rich treatment wastes. The study indicates that arsenic removal increases as the As to cow dung weight ratio decreases. It also suggests that arsenate transforms into arsenite before being removed from aqueous As solutions in the presence of cow dung. Most As removal occurs within the first few days. Similar removal rates of As were

observed under both cap open (aerobic conditions) and cap closed (anaerobic conditions) setups. No significant variation was found in the removal of As from aqueous solutions and from treatment wastes (As bound to iron solids).

The study concludes that disposing of As rich treatment wastes in cow dung pits could be an effective method for managing As sludge disposal in rural areas of Bangladesh.

Mueller & Steiner, 1992^[18], both authors said that the severity of heavy metal inhibition on anaerobic digestion depends on the specific metal species and their dissolved concentrations in the digester. The inhibition sequence for anaerobic digestion of municipal sewage sludge is $Ni > Cu > Cd > Cr > Pb$, with metal immobilization affinity in the sludge following the reverse order. Due to sulfide production during digestion, significant quantities of heavy metals precipitate as highly insoluble sulfide salts. Nickel was immobilized up to 94% in the digester and had the most dramatic effect on anaerobic digestion, with toxicity occurring at concentrations of 250 to 300 g Ni/m³. Lower nickel concentrations resulted in reversible process inhibition. Copper, at concentrations up to 1000 g Cu/m³, caused reversible inhibition of acid producing, fermentative, and methanogenic bacteria. The recovery time for the process depended on the initial copper concentration in the digester, with organisms showing an ability to adapt to copper. Copper uptake in the digester reached 97%. Cadmium inhibited the digestion of sewage sludge by approximately 50% at 650 g Cd/m³. However, with long durations of acclimation, there was a tendency toward recovery. Cadmium uptake in the digested sludge was 99%. Chromium and lead were both up taken at 99.9% during digestion, and their addition up to 1000 mg Cr/L and 600 mg Pb/L showed minimal effects on anaerobic digestion.

Sankar et al. 2014^[7], said that arsenic contamination of groundwater worldwide results from both natural and anthropogenic sources, leading to serious adverse effects on human health and ecosystems. Millions of people in various countries rely on groundwater with elevated levels of arsenic for drinking. This contamination poses a significant risk to human health. Prolonged exposure to inorganic arsenic through drinking water leads to arsenicosis, a debilitating disease characterized by skin lesions, pigmentation changes, and patches on the palms and soles. Arsenic poisoning can also result in potentially fatal diseases such as skin and internal cancers. This paper reviews the sources, speciation, and mobility of arsenic, providing a global overview of groundwater arsenic contamination. It also critically examines the health risks associated

with arsenic, including its uptake, metabolism, and toxicity mechanisms. Additionally, the paper offers an overview of current knowledge on alternative arsenic free drinking water sources and various technologies (such as oxidation, coagulation, flocculation, adsorption, and microbial methods) used to mitigate the problem of groundwater arsenic contamination.

Mestrot, et al. 2013^[19], said that Arsenic, a class 1 nonthreshold carcinogen, is highly ubiquitous and undergoes numerous transformations, both biotic and abiotic, within and between environmental compartments. These transformations result in various chemical species with different properties and toxicities. One specific transformation is the biotic volatilization of arsenic, which is coupled with arsenic biomethylation and has been rarely studied due to inherent sampling challenges. Arsenic methylation and volatilization are also linked to methanogenesis and occur in anaerobic environments. In China, rice straw and animal manure are frequently used to produce biogas and can contain high amounts of arsenic, especially if the rice is grown in areas with heavy mining or smelting industries or if animals are fed Roxarsone, an arsenic containing drug widely used to control intestinal parasites, improve feed efficiency, and promote rapid growth. Roxarsone degrades to inorganic arsenic under anaerobic conditions. This study focuses on biotic transformations of arsenic in small microcosms designed as biogas digester models (BDMs) using recently validated arsenic traps, enabling direct quantification and identification of volatile arsenic species. The study found that although there was a loss of soluble arsenic in the BDMs, the conditions favored biomethylation. All reactors produced volatile arsenic, particularly those spiked with monomethylarsonic acid, which produced 413 ± 148 ng arsenic (mean $\pm$ SD, $n = 3$), suggesting that the initial methylation step from inorganic arsenic is a limiting factor. The most abundant species was trimethylarsine, but toxic arsine was also present in the headspace of most BDMs. These results indicate that volatile arsenic species should be monitored in biogas digesters to assess risks to workers in biogas plants and users of biogas.

3 OBJECTIVE AND SCOPE OF THE STUDY

3.1 OBJECTIVE OF THE STUDY

- The primary objective of this study is to evaluate the efficiency of arsenic removal from contaminated sludge through anaerobic volatilization.
- The study aims to identify the optimal conditions that promote the biotic volatilization of arsenic, quantify the extent of arsenic removal, and assess the resulting chemical species.
- This includes understanding the role of microbial processes and specific environmental parameters in enhancing arsenic volatilization, with the ultimate goal of developing a sustainable and effective method for arsenic removal from sludge.
- This study indicates that biochemical processes, such as biomethylation in the presence of fresh cow dung, can significantly remove arsenic (As) from aqueous solutions and As rich treatment wastes. The transformation of As into a volatile species appears to be the main mechanism for this removal. The study suggests that arsenic reducing bacteria present in cow dung are responsible for converting As(V) to As(III). Given the socioeconomic conditions in rural India, there is a need for low cost and user friendly arsenic removal and sludge management systems.

3.1 SCOPE OF THE STUDY

✓ **Literature Review:**

- Review existing research on arsenic contamination in sludge and current remediation techniques.
- Analyse the biochemical pathways involved in arsenic methylation and volatilization.

✓ **Experimental Setup:**

- Design and construct anaerobic microcosms simulating biogas digester conditions.
- Use contaminated sludge samples from various sources with known arsenic concentrations.

✓ **Biotic and Abiotic Factors:**

- Investigate the impact of different microbial communities on arsenic volatilization.
- Study the influence of various environmental parameters (e.g., pH, temperature, redox conditions) on the volatilization process.

✓ **Chemical Analysis:**

- Employ advanced analytical techniques to identify and quantify volatile arsenic species produced during the anaerobic digestion process.
- Measure the concentrations of arsenic in the sludge before and after treatment.

✓ **Optimization Studies:**

- Explore the effects of adding various substrates (e.g., cow dung, rice straw) to enhance microbial activity and arsenic volatilization.
- Determine the optimal conditions for maximum arsenic removal efficiency.

✓ **Risk Assessment:**

- Assess the potential risks associated with the release of volatile arsenic species into the environment and to human health.
- Develop guidelines for safe handling and disposal of treated sludge.

✓ **Technology Evaluation:**

- Compare the efficacy of anaerobic volatilization with other arsenic removal technologies.
- Evaluate the scalability and practicality of implementing this method in real world scenarios.

✓ **Recommendations and Future Research:**

- Provide recommendations for improving the anaerobic volatilization process.
- Identify areas for future research to further enhance arsenic removal efficiency and environmental safety.

4 STUDY AREA

The study area was selected based on its status as an arsenic affected village with preinstalled Arsenic and Iron Removal Plants (AIRPs) to treat contaminated groundwater. It is located in the Palla region of the Bongaon block, within the North 24 Parganas district of West Bengal. This district, situated in the eastern part of India, is known for significant arsenic contamination issues in its groundwater.

Table 4.1 General details of the AIRP (source PHED)

Water Supply Scheme	Commencement date of AIRP	Population served	AIRP capacity (cum/hr.)	Working time (hrs./d)
PALLA	March, 2017	28145	175	6

Table 4.2 Technology details of the AIRP

Water Supply Scheme	Technology
PALLA	Aeration Coagulation Precipitation followed by Adsorption

Table 4.3 List of Chemicals Used for Arsenic Treatment in the AIRP

Water Supply Scheme	Chemicals
PALLA	Sodium Hypochlorite; Ferrous Sulphate; Alum: Conc; Activated Alumina

The study focuses on the North 24 Parganas district to address the specific challenges and opportunities associated with managing arsenic sludge in this region. It involves collecting arsenic sludge samples from AIRPs within the district. By concentrating on this area, the study aims to provide targeted recommendations and insights for the effective utilization of sludge in stabilization and solidification techniques, such as incorporating it into brick and concrete, to manage arsenic sludge in the North 24 Parganas district of West Bengal, India.

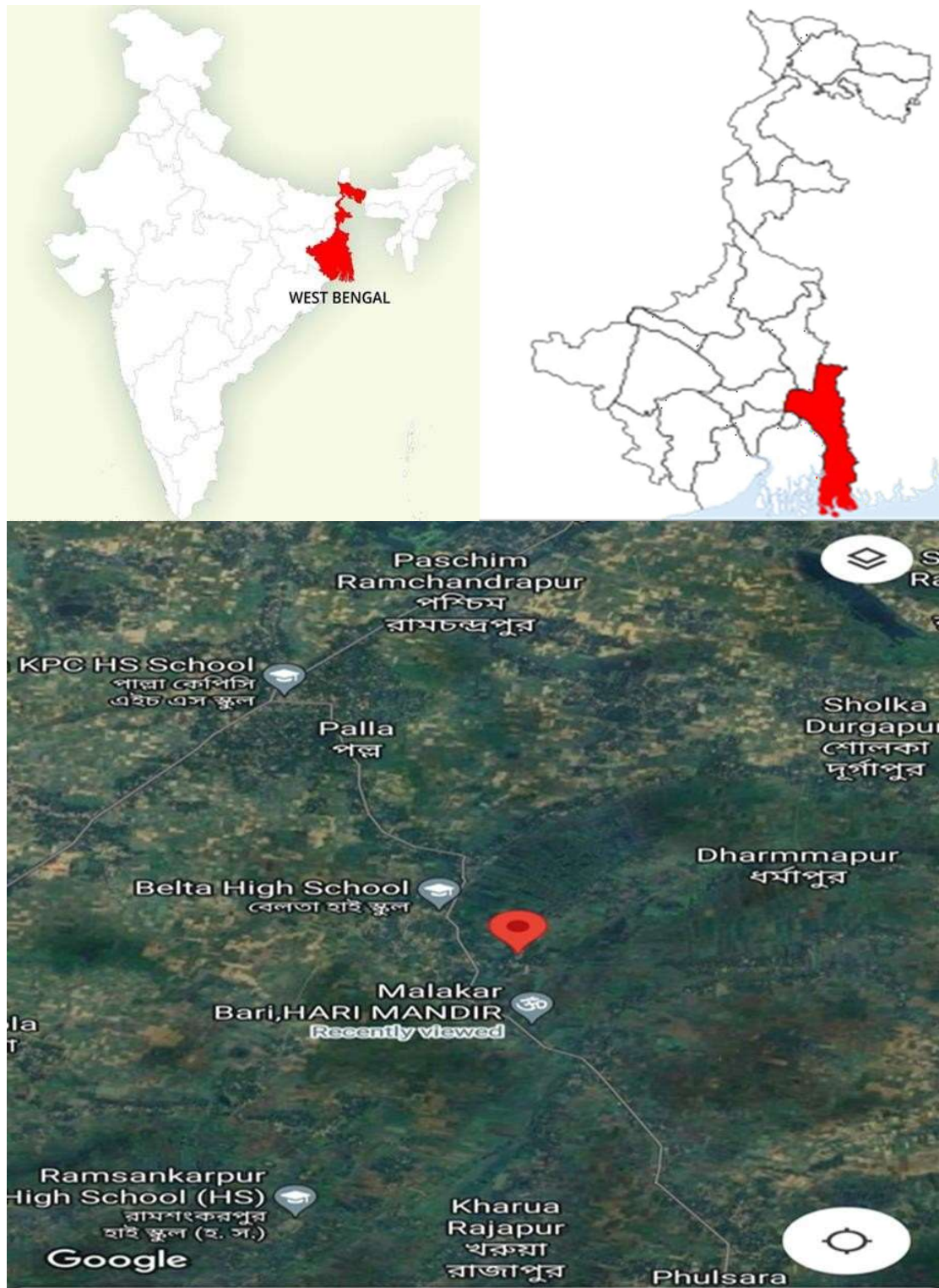


Figure 4.1 Location of the AIRPs (Study Area)

Reference: Wikipedia, Google Map.

5 MATERIALS AND METHODOLOGY

5.1 COLLECTION OF MATERIALS

5.1.1 COLLECTION OF ARSENIC SLUDGE

Arsenic sludge refers to the solid residue or by-product that is generated during the treatment of arsenic-contaminated water. It is produced as a result of various treatment processes designed to remove arsenic from water sources, such as groundwater or surface water. Arsenic sludge typically contains high concentrations of arsenic, which is a toxic heavy metal known to have harmful effects on human health and the environment.



Figure 5.1 Arsenic-rich sludge samples in Semi-solid State

Characteristics of Arsenic Sludge:

High Arsenic Concentration: Arsenic sludge contains elevated levels of arsenic, which is the primary contaminant being removed from the water. The concentration of arsenic in the sludge can vary depending on the source water and the effectiveness of the treatment process.

Physical Properties: Arsenic sludge can vary in texture and consistency, ranging from a thick, viscous material to a more solid, sediment-like substance. It may also contain other impurities or contaminants present in the water.

Hazardous Nature: Due to its high arsenic content, arsenic sludge is considered hazardous and poses risks to human health and the environment if not managed properly. Direct contact or ingestion of arsenic-containing sludge can lead to poisoning and other adverse health effects.

The safe handling and disposal of arsenic sludge present significant challenges. Specialized procedures and precautions are required to minimize exposure and prevent environmental

contamination. Arsenic sludge management requires careful planning, strict adherence to safety protocols, and compliance with regulatory requirements to mitigate the hazards associated with arsenic contamination and protect both human health and the environment.

Collecting arsenic sludge from an arsenic removal plant involves specific procedures to ensure safety, accuracy, and compliance with environmental regulations.

Equipment and Materials Needed:

- Personal Protective Equipment (PPE):
 - ✓ Gloves (preferably chemical resistant)
 - ✓ Safety goggles or face shield
 - ✓ Protective clothing (coveralls)
 - ✓ Respirator or mask
- Sample Collection Tools:
 - ✓ Sterile sampling containers (usually 1liter capacity or larger)
 - ✓ Sampling scoops or shovels (nonreactive material like stainless steel or plastic)
 - ✓ Sealable plastic bags
- Cleaning Supplies:
 - ✓ Disinfectant solution
 - ✓ Clean water for rinsing
- Labelling and Documentation:
 - ✓ Waterproof markers
 - ✓ Labels
 - ✓ Notebook

Collection:

A sludge sample was collected from the Arsenic cum Iron Removal Plant (AIRP) established as part of a water supply scheme in the Palla region of North 24 Parganas district, West Bengal, and transported to the Water Quality Laboratory at the School of Water Resources Engineering, Jadavpur University. At the time of collection, the sludge was in a semi-solid state. At that time 14% of solid was present in that collected sample. During the conveying process, foreign particles were carefully removed to ensure the purity of the sample. Any extraneous materials, such as stones, debris, or other impurities, were identified through careful inspection and subsequently removed, leaving behind a purified sample.

5.1.2 COLLECTION OF COW DUNG

Cow dung, also known as cow manure, is the fecal matter produced by cows. It is rich in organic matter and nutrients, making it a valuable resource in agriculture and various traditional practices.



Figure 5.2 Cow Dung collection at Chakdaha, Nadia

Characteristics of Cow Dung

Composition:

- **Organic Matter:** High in decomposable organic material.
- **Nutrients:** Contains nitrogen, phosphorus, potassium, and trace elements.
- **Moisture Content:** Fresh cow dung has a high moisture content, which decreases as it dries.

Physical Properties:

- **Texture:** Fresh cow dung is typically soft and malleable.
- **Colour:** Generally greenish when fresh, turning brown as it dries.
- **Odour:** Characteristic earthy smell when fresh, becoming milder as it decomposes.

Microbial Content:

- Contains beneficial microbes that help in the decomposition process and contribute to its fertilizing properties.

Cow dung is a versatile and valuable resource with numerous applications in agriculture, energy production, construction, and traditional practices. Its use promotes sustainability and eco-

friendliness, particularly in rural and agricultural communities. However, proper handling and treatment are essential to mitigate potential health risks and maximize its benefits.

Collecting cow dung requires careful handling to ensure safety and hygiene. Here's a step-by-step procedure for collecting cow dung effectively:

Equipment and Materials Needed:

- Personal Protective Equipment (PPE):
 - ✓ Gloves
 - ✓ Shovel
 - ✓ Bucket and Container
 - ✓ Cleaning Supplies: Soap, water, and disinfectant etc.

Collection:

The cow dung sample was collected from a house located at Chakdaha, Nadia District, West Bengal, and transported to the Water Quality Laboratory at the School of Water Resources Engineering, Jadavpur University. Firstly, reached the aforesaid location and confirmed fresh dung from all of the cow owners. Fresh dung was lifted into the container by shovel and properly sealed and labelled and brought to our laboratory.

5.1.3 SAMPLE FROM THE SECOND CHAMBER OF SEPTIC TANK

Septic sludge, also known as septage, is the semi-solid material that accumulates in the second chamber of a septic tank. This sludge primarily consists of settled solids, organic matter, and various microorganisms that are not broken down in the primary chamber of the septic tank.

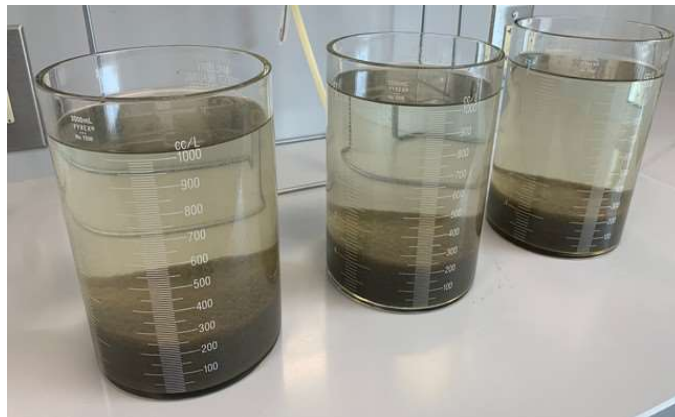


Figure 5.3 Septic Sludge collected from second Chamber

Characteristics of Septic Sludge

Composition:

- **Organic Matter:** Includes fecal matter, food waste, and other biodegradable materials.
- **Inorganic Solids:** Sand, grit, and other non-biodegradable particles.
- **Pathogens:** Contains bacteria, viruses, and parasites that can be harmful to human health.
- **Nutrients:** High levels of nitrogen and phosphorus.
- **Moisture Content:** This varies depending on the retention time and tank design, but typically has a high moisture content.

Physical Properties:

- **Texture:** Thick, viscous, and semi-solid.
- **Colour:** Generally black or dark brown.
- **Odour:** Strong, unpleasant smell due to the decomposition of organic matter.

Microbial Content:

- Contains anaerobic bacteria that aid in the decomposition of organic materials.

Septic sludge from the second chamber of a septic tank requires careful handling, treatment, and disposal to prevent environmental pollution and health hazards. Proper management practices, including regular maintenance, safe handling protocols, and effective treatment methods, are essential for maintaining the functionality of septic systems and protecting public health and the environment.

Collecting samples from the second chamber of a septic tank involves several steps to ensure safety and accuracy. The second chamber typically allows solids to settle and promotes further decomposition of wastewater. Here's a detailed procedure for collecting samples from this chamber:

Equipment and Materials Needed:

- Personal Protective Equipment (PPE):
 - ✓ Gloves (preferably chemical resistant)

- ✓ Safety goggles or face shield
- ✓ Protective clothing (coveralls)
- ✓ Respirator or mask
- Sample Collection Tools:
 - ✓ Rope & Plastic Mug
 - ✓ Sterile sampling Barrel (5liter capacity)
 - ✓ Sealable plastic bags
- Cleaning Supplies:
 - ✓ Disinfectant solution
 - ✓ Clean water for rinsing
- Labelling and Documentation:
 - ✓ Waterproof markers
 - ✓ Labels
 - ✓ Sample collection forms or notebook

Collection:

First, we identify the location of the septic tank, within our university campus and also locate the second chamber's appropriate access cover. By the use of proper tools cover was removed safely from the chamber. A visual inspection was conducted of the chamber to check the liquid level and overall condition. Using proper accessories, the sample was collected from the middepth of the liquid layer to get a representative sample of the effluent. the sample bottle was removed carefully, ensuring it did not touch the sides of the tank or any other surfaces to avoid contamination. After that, we sealed it properly, labelled it, and transported it to the Water Quality Laboratory at the School of Water Resources Engineering, Jadavpur University. And kept it safe position where it was protected from direct sunlight.

5.1.4 ANAEROBIC DIGESTER BOTTLE

An anaerobic digester bottle is a laboratory-scale system used to simulate the anaerobic digestion process. It is a valuable tool for studying the microbial breakdown of organic material in the absence of oxygen, resulting in the production of biogas (methane, carbon dioxide, etc.) and digestate.



Figure 5.4 Digester Bottle with gas collection unit

Components of an Anaerobic Digester Bottle

Bottle or Reactor Vessel:

Typically made of glass or high-grade plastic to withstand chemical reactions. Size can vary, but common volumes are between 250 mL to 2 litres. Here I chose volume of 500ml.

Sealing Cap:

Airtight cap to maintain anaerobic conditions.

Gas Collection System:

Tubing is connected to the gas disposal nozzle and the other end is attached with two types of items like balloons and a gas collecting bag with a lock system.

5.1.5 OTHER NECESSARY EQUIPMENTS

- Beaker
- Burette, Burette stand & Clamp
- Graduated cylinder
- Pipette
- Spatula
- Funnel

- Flask
- Weighing machine



Figure 5.5 Other Necessary Equipments

5.2 METHODOLOGY

5.2.1 PREPARATION OF FEED SLURRY

The preparation of feed slurry for anaerobic digestion involves creating a homogeneous mixture of various organic and inorganic materials that will be subjected to microbial breakdown in an anaerobic digester. In this context, the feed slurry is composed of three different combinations, first, septic sludge, cow dung, and arsenic-laden sludge, second, cow dung, surface water, and arsenic-laden sludge and third, septic sludge and arsenic-laden sludge. Each of these components brings unique properties and challenges to the digestion process.

Septic Sludge: This is the semi-solid material that accumulates in septic tanks from the treatment of domestic wastewater. It is rich in organic matter and microorganisms, making it a suitable substrate for anaerobic digestion. However, it can also contain pathogens and contaminants that need to be managed carefully.

Cow Dung: A traditional and widely used material in anaerobic digestion, cow dung is an excellent source of organic matter and microbial inoculum. It helps in stabilizing the digestion process and enhancing biogas production due to its balanced nutrient content and high microbial activity.

Arsenic-Laden Sludge: This is the by-product from water treatment processes aimed at removing arsenic from contaminated water. It contains high levels of arsenic, which makes it hazardous. The inclusion of arsenic-laden sludge in the feed slurry requires careful handling and specific treatment strategies to prevent environmental contamination and ensure the safety of the digestion process.



Figure 5.6 Various Stages of Mixing of Feed Slurry

Steps of Preparation of Feed Slurry:

▪ Mixing of Feed Slurry

The mixing of feed slurry is a crucial step in preparing a homogeneous substrate for anaerobic digestion. The feed slurry, composed of septic sludge, cow dung, surface water, and arsenic-laden sludge in different combinations needs to be thoroughly mixed to ensure uniformity in composition and consistency, which is essential for effective microbial breakdown and biogas production. Below is a detailed procedure for mixing the feed slurry:

▪ Materials Needed:

- ✓ Septic sludge
- ✓ Cow dung
- ✓ Arsenic-laden sludge
- ✓ Mixing container
- ✓ pH meter
- ✓ Protective equipment (gloves & mask)
- ✓ Mixing tool
- ✓ Surface Water

▪ Procedure:

Safety Precautions:

At the time of the experiment, appropriate protective equipment, including gloves and a mask, were taken to protect against potential hazards from the sludge materials. It was a well-ventilated place where this mixing was done.

Measurement and Preparation:

All the materials were carefully measured according to the required quantities and thoroughly mixed to achieve a homogeneous consistency, ensuring the experiment proceeded correctly. In this study, a 30% solid cow dung solution was used as the standard reactor, while a 14% solid arsenic-laden sludge solution was used in varying concentrations (5%, 10%, 15%, 20%, 25%, and 30%) to determine which concentration yields the best results for arsenic reduction. During the mixing process, the arsenic-laden sludge was added slowly and gradually to ensure even distribution and to avoid any localized concentration of arsenic. Mixing continued until the

sludge was fully integrated into the slurry, resulting in a smooth, uniform texture without clumps or uneven distribution of materials. A pH meter was utilized to ensure that the mixture maintained a pH value within the range of 6.2 to 7.2. Once the mixture was properly prepared, it was transferred to an anaerobic digester bottle, as previously described, and left for a specific period to facilitate arsenic removal. The desired results from this process are discussed in detail later.

In this experiment, three different feed slurry combinations were used. The mixing percentages and sample batching days for each combination are presented in a tabular form, which was utilized throughout the experiment.

Table 5.1 Composite Waste Sludge Preparation

Sl. No.	Combination made by	Percentage of Cow Dung [%]	Percentage of ALS [%]	Marked As	Batching Days			
					10 Days	20 Days	30 Days	60 Days
1	Combination 1: Septic Sludge, Cow Dung & Arsenic Laden Sludge (ALS)	30	5	SM05	SM05-10	SM05-20	SM05-30	SM05-60
			10	SM10	SM10-10	SM10-20	SM10-30	SM10-60
			15	SM15	SM15-10	SM15-20	SM15-30	SM15-60
			20	SM20	SM20-10	SM20-20	SM20-30	SM20-60
			25	SM25	SM25-10	SM25-20	SM25-30	SM25-60
			30	SM30	SM30-10	SM30-20	SM30-30	SM30-60
2	Combination 2: Surface Water, Cow Dung & Arsenic Laden Sludge (ALS)	30	5	SC05	SC05-10	SC05-20	SC05-30	SC05-60
			10	SC10	SC10-10	SC10-20	SC10-30	SC10-60
			15	SC15	SC15-10	SC15-20	SC15-30	SC15-60
			20	SC20	SC20-10	SC20-20	SC20-30	SC20-60
			25	SC25	SC25-10	SC25-20	SC25-30	SC25-60
			30	SC30	SC30-10	SC30-20	SC30-30	SC30-60
3	Combination 3: Septic Sludge & Arsenic Laden Sludge (ALS)	-	5	SS05	SS05-10	SS05-20	SS05-30	SS05-60
			10	SS10	SS10-10	SS10-20	SS10-30	SS10-60
			15	SS15	SS15-10	SS15-20	SS15-30	SS15-60
			20	SS20	SS20-10	SS20-20	SS20-30	SS20-60
			25	SS25	SS25-10	SS25-20	SS25-30	SS25-60
			30	SS30	SS30-10	SS30-20	SS30-30	SS30-60

In Combination 1, the composite waste sludge, which includes a mixture of septic sludge and cow dung, is combined with varying percentages of arsenic-laden sludge. Initial testing showed that the raw composite feed slurry contains approximately 0.06 mg/L of arsenic. Arsenic-laden

sludge was then added to this slurry in specific measured percentages. A table is provided that details the actual weight (mg/L) of arsenic used for each percentage and the final concentration of arsenic after it is blended with the composite waste sludge.

Table 5.2 Weight of Arsenic present in Composite Waste Sludge: Combination 1

Sl. No.	Sample Name	Actual Weight of As present in Feed Slurry (mg/L)	As Present as per Lab Test (mg/L)
1	SM05	10.92	10.98
2	SM10	21.84	21.90
3	SM15	32.76	32.82
4	SM20	43.68	43.74
5	SM25	54.60	54.66
6	SM30	65.52	65.58

Combination 2 involves mixing composite waste sludge, composed of tap water and cow dung, with arsenic-laden sludge in varying proportions. Initial analysis indicated that the raw composite feed slurry has an arsenic concentration of approximately 0.10 mg/L. Arsenic-laden sludge was subsequently added to this slurry in carefully measured percentages. A table is included that outlines the specific weight (mg/L) of arsenic for each proportion and the resulting concentration of arsenic after it has been mixed with the composite waste sludge.

Table 5.3 Weight of Arsenic present in Composite Waste Sludge: Combination 2

Sl. No.	Sample Name	Actual Weight of As present in Feed Slurry (mg/L)	As Present as per Lab Test (mg/L)
1	SC05	10.92	11.02
2	SC10	21.84	21.94
3	SC15	32.76	32.86
4	SC20	43.68	43.78
5	SC25	54.60	54.70
6	SC30	65.52	65.62

In Combination 3, septic sludge is combined with arsenic-laden sludge in varying proportions. Initial testing revealed that the raw composite feed slurry contains approximately 0.01 mg/L of

arsenic. Arsenic-laden sludge was then added to this mixture in specific, measured percentages. The accompanying table details the exact weight (mg/L) of arsenic used for each proportion and the resulting arsenic concentration after blending with the septic sludge.

Table 5.4 Weight of Arsenic present in Composite Waste Sludge: Combination 3

Sl. No.	Sample Name	Actual Weight of As present in Feed Slurry (mg/L)	As Present as per Lab Test (mg/L)
1	SS05	10.92	10.93
2	SS10	21.84	21.85
3	SS15	32.76	32.77
4	SS20	43.68	43.69
5	SS25	54.60	54.61
6	SS30	65.52	65.53

5.3 TESTING OF SAMPLE

5.3.1 BOD TESTING OF SAMPLE

The Biochemical Oxygen Demand (BOD) test measures the amount of oxygen that microorganisms will consume while decomposing organic matter in water. This test is crucial for assessing the organic pollution level in water and wastewater. The standard procedure for conducting the BOD test as per IS 3025 (Part 44): 1993 involves several steps to ensure accurate measurement.



Figure 5.7 Aeration of Distilled Water

Sample Collection and Storage:

Collect water or wastewater samples in clean, airtight BOD bottles.

Samples should be tested as soon as possible to prevent changes in their biochemical properties.

If immediate testing is not possible, store the samples at 4°C (without freezing) to minimize biological activity.

Preparation of Dilution Water:

Use distilled water as dilution water. It should be free from chlorine, organic matter, and other impurities.

Aerate the distilled water for at least 1 hour to ensure it is saturated with oxygen.

Add nutrients to the dilution water to promote microbial growth. The standard nutrients include phosphate buffer, magnesium Sulphate, calcium chloride, and ferric chloride solutions.

Preparation of Samples:

If the sample has high BOD, dilute it with the prepared dilution water to bring it within the range of the BOD test (2-6 mg/L).

For samples with low BOD, it might not be necessary to dilute.

Inoculation:

If the sample is not expected to contain sufficient microorganisms for the oxidation of organic matter, inoculate the diluted water with a seed (microbial culture) from a source like fresh sewage.

Filling BOD Bottles:

Fill two sets of BOD bottles (300 ml capacity) completely with the diluted sample, ensuring there are no air bubbles.

One set of bottles is for the initial dissolved oxygen (DO) measurement (Day 0), and the other set is incubated for 3 days for the final DO measurement (Day 3).

Measurement of Initial Dissolved Oxygen (DO):

Measure the DO of one set of the sample bottles immediately using a DO meter or the Winkler titration method.

Incubation:

- Incubate the second set of BOD bottles at 20°C in a BOD incubator in the dark to prevent photosynthesis, which could alter oxygen levels.

Measurement of Final Dissolved Oxygen (DO):

After 3 days, measure the DO in the incubated bottles using a DO meter or the Winkler titration method.

Calculation of BOD:

The BOD is calculated using the difference between the initial and final DO values, corrected for dilution:

$$\text{BOD (mg/L)} = \frac{(\text{DO Initial} - \text{DO Final}) \times \text{Dilution Factor}}{\text{Volume of Sample (mL)}}$$

Important Considerations:

Blank Determination: Perform a blank determination using dilution water without any sample to ensure that the dilution water and seed are free from BOD.

Dilution Factor: The dilution factor is determined by the ratio of the total volume of the mixture (sample + dilution water) to the volume of the sample.

Temperature Control: The test should be conducted at a constant temperature of 20°C to ensure consistent results.

Quality Control: To ensure accurate and reliable results, quality control checks such as blank controls, duplicates, and use of standard samples are essential.

The BOD test as per IS 3025 (Part 44): 1993 is a standard procedure widely used for evaluating the organic pollution load in water and wastewater. Following these steps precisely ensures an accurate determination of the biochemical oxygen demand of a sample, which is crucial for water quality monitoring and environmental management.

5.3.2 COD TESTING OF SAMPLE

The Chemical Oxygen Demand (COD) test is a measure of the amount of oxygen required to chemically oxidize organic and inorganic matter in water. Here is the procedure for determining COD as per the Indian Standard (IS) 3025 (Part 44):1993:

Apparatus and Materials Required:

COD Digestion Apparatus: Refluxing unit with a heating block or water bath.

Conical Flask or Digestion Tubes: 250 mL capacity.

Pipettes and Burettes: For accurate measurement.

Measuring Cylinders: Various capacities.

Volumetric Flasks: Various capacities.

Mercuric Sulphate (HgSO_4): Reagent grade.

Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) Solution (0.25 N): Standard solution.

Silver Sulphate (Ag_2SO_4): As a catalyst.

Concentrated Sulfuric Acid (H_2SO_4): Reagent grade.

Ferrous Ammonium Sulphate (FAS) Solution (0.1 N): Standard solution for titration.

Ferriin Indicator: A redox indicator.

Distilled Water.

Preparation of Reagents:

Standard Potassium Dichromate Solution (0.25 N): Dissolve a known weight of $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled water and dilute to a specific volume.

Concentrated Sulfuric Acid (with Ag_2SO_4): Add silver Sulphate to concentrated H_2SO_4 and mix well.

Ferrous Ammonium Sulphate Solution (0.1 N): Dissolve ferrous ammonium Sulphate in distilled water and dilute to a specific volume.



Figure 5.8 Prepared Reagents and it's Raw Materials

Sample Preparation:

Collect Sample: Obtain the water sample to be tested, ensuring that it is representative and free from particulate matter.

Preserve Sample: If immediate analysis is not possible, preserve the sample by acidifying it with H_2SO_4 to a pH of less than 2.0



Figure 5.9 Reflux Digestion & Titration

Test Procedure:

Take the Sample:

Pipette 50 mL of the water sample into a 250 mL conical flask or a digestion tube.

Add Reagents:

Add 1 g of mercuric Sulphate (HgSO_4) to the flask to eliminate chloride interference. Add 10 mL of standard potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) solution.

Reflux Digestion:

Slowly add 20 mL of concentrated sulfuric acid containing silver Sulphate to the flask while swirling to mix thoroughly. Be cautious to avoid any violent reaction.

Attach the flask to a refluxing unit and heat it for 2 hours. Ensure the mixture is gently boiling throughout the period.

Cool the Sample:

Allow the flask to cool to room temperature after digestion.

Dilution and Titration:

Dilute the contents of the flask to about 150 mL with distilled water.

Add 2-3 drops of ferroin indicator to the diluted solution.

Titrate with standard ferrous ammonium Sulphate (FAS) solution until the color changes from blue-green to reddish-brown (end point).

Calculation:

Calculate the COD using the formula:

$$\text{COD (mg/L)} = \frac{(A - B) \times N \times 8000}{\text{Volume of Sample (mL)}}$$

Where:

A = Volume of FAS used for blank (mL)

B = Volume of FAS used for sample (mL)

N = Normality of FAS solution

Reporting:

Report the COD value in mg/L to the nearest whole number.

Safety and Precautions:

Wear appropriate protective equipment such as gloves, goggles, and lab coats.

Handle all chemicals, especially concentrated sulfuric acid, with care to avoid burns or injuries.

Work in a well-ventilated area or under a fume hood to avoid inhalation of fumes.

Quality Control:

Use standard quality control samples to verify the accuracy of the test.

Conduct the test in duplicates to ensure consistency in results.

This method provides a reliable measure of the organic pollution level in water, helping to assess the treatment efficiency of water and wastewater treatment processes.

5.3.3 TDS & pH VALUE TESTING OF SAMPLE

The Hanna pH/Conductivity/TDS Tester is a multifunctional digital device that measures the pH, conductivity, and total dissolved solids (TDS) of a solution. These testers are particularly useful in various applications where it is essential to monitor the quality of water or solutions, such as in aquariums, hydroponics, pools, wastewater treatment, environmental monitoring, and laboratory settings.



Figure 5.10 Hanna pH/Conductivity/TDS Tester

Key Features of Hanna pH/Conductivity/TDS Testers:

Multi-parameter Measurement:

The tester combines the functionality of three different meters (pH, conductivity, and TDS) into a single, compact device, providing convenience and versatility.

Digital Display:

It features a clear digital display that shows readings for pH, conductivity, and TDS. Some models have a dual-level LCD that can display two parameters simultaneously.

Automatic Temperature Compensation (ATC):

The meter automatically adjusts readings based on temperature changes, ensuring accurate measurements for pH, conductivity, and TDS.

Waterproof and Durable:

Many Hanna pH/Conductivity/TDS testers are designed to be waterproof, which makes them durable and suitable for use in various environmental conditions.

Calibration:

The device typically supports automatic or manual calibration for pH and conductivity. It can be calibrated using standard solutions to maintain accuracy.

Replaceable Electrodes:

Some models come with replaceable electrodes or probes, which extend the lifespan of the device and maintain measurement accuracy over time.

Battery Operated:

These testers are generally powered by batteries, making them portable and convenient for fieldwork.

How to Use a Hanna pH/Conductivity/TDS Tester:**Calibration:**

pH Calibration: Immerse the electrode in a standard pH buffer solution (commonly pH 4.01, 7.01, or 10.01). Follow the device's instructions to calibrate. Most Hanna testers allow for single or multi-point calibration.

Conductivity Calibration: Use a standard conductivity solution (e.g., 1413 $\mu\text{S}/\text{cm}$). Follow the instructions to calibrate the conductivity sensor.

- Ensure the meter is properly calibrated before taking measurements.

Sample Preparation:

Collect the water or solution sample in a clean container. Ensure it is free from bubbles and debris to avoid contamination or inaccurate readings.

Measurement:

pH Measurement: Turn on the device and select the pH mode. Immerse the pH electrode in the sample, ensuring it is fully submerged. Wait for the reading to stabilize.

Conductivity/TDS Measurement: Switch to conductivity or TDS mode. Immerse the probe in the sample, ensuring the electrodes are fully covered. Wait for the reading to stabilize.

The device will display the readings on the screen.

Maintenance and Cleaning:

After use, rinse the probes with distilled water to remove any residual sample.

Store the device according to the manufacturer's guidelines, often with a protective cap or in a storage solution to maintain electrode functionality.

Hanna pH/Conductivity/TDS testers are versatile, easy-to-use instruments that provide accurate and reliable measurements for multiple water quality parameters. Their multifunctionality makes them a valuable tool for a wide range of applications, from environmental monitoring to industrial and agricultural use. Proper calibration, usage, and maintenance are crucial for obtaining precise measurements and prolonging the life of the device.

5.3.4 NITRATE, NITRITE, SULPHATE & PHOSPHATE TESTING

The Spectroquant® DR2800 Spectrophotometer by Hach is a versatile, portable spectrophotometer designed for water and wastewater analysis. This spectrophotometer is capable of measuring a wide range of parameters using various pre-programmed methods or customized methods developed by the user. It is widely used in environmental laboratories, industrial settings, and water treatment facilities due to its reliability and ease of use.



Figure 5.11 Spectroquant® DR2800 Spectrophotomete

Use procedure of the Hach DR2800 Spectrophotometer:

Sample Preparation:

Prepare the water sample according to the test procedure. Depending on the parameter being tested, this may involve adding reagents, filtering, or diluting the sample.

Cuvette Preparation:

Pour the prepared sample into a clean cuvette. Ensure that the outside of the cuvette is clean and free from fingerprints or smudges, which can affect the accuracy of the measurement.

Select the Method:

On the DR2800 touchscreen, select the pre-programmed method for the parameter you wish to measure. Alternatively, use a user-defined method if you are following a custom protocol.

Insert the Cuvette:

Place the cuvette in the designated holder inside the spectrophotometer. Make sure it is correctly aligned to ensure accurate readings.

Perform the Measurement:

Close the lid and press the 'Read' button to start the measurement. The DR2800 will measure the absorbance or transmittance of the sample at the selected wavelength(s) and display the concentration or result on the screen.

Data Recording and Transfer:

Record the results or transfer the data to a computer or USB storage device for further analysis or documentation.

Maintenance and Cleaning:

After use, clean the cuvette holder and the exterior of the device to maintain its performance. Regularly calibrate and service the spectrophotometer to ensure accuracy and reliability.

The Hach DR2800 Spectrophotometer is a versatile and robust instrument widely used for water quality analysis in various industries. Its ability to measure multiple parameters, combined with ease of use and portability, makes it an essential tool for ensuring the safety and quality of water and wastewater.

5.3.5 ARSENIC TESTING OF SAMPLE

Testing sludge involves conducting various analyses to determine its composition, characteristics, and potential environmental and health impacts. Below are some common tests and procedures used to analyse sludge:

➤ Sludge Digestion:

Sludge digestion is a process used to break down the complex organic and inorganic components of sludge into soluble forms, allowing for subsequent analysis of specific elements or compounds. According to EPA guidelines, two primary methods for sludge digestion are available:

- **Nitric Acid Digestion:** Add 10 ml of 1:1 Nitric acid (HNO_3) and reflux the sample.
- **Mixed Acid Digestion:** Add 10 ml of concentrated Hydrochloric acid (HCl) and 2.5 ml of Nitric acid (HNO_3) to the sample and reflux.

Overview of Digestion Processes Used in This Study:

a) Digestion of Sludge for Spectrophotometric Analysis:

Sample Preparation: 0.5 grams of dried and powdered sludge sample were accurately weighed.



Figure 5.12 Digestion & Filtration for Spectrophotometric Analysis

Acid Selection: Concentrated Hydrochloric acid (HCl) and Nitric acid (HNO_3) were chosen for their strong oxidizing properties and ability to dissolve a wide range of organic and inorganic materials.

Digestion Procedure:

10 ml of concentrated HCl and 2.5 ml of concentrated HNO₃ were added to the sludge sample and shaken well.

An additional 5 ml of distilled water was then added to form a mixture in a 250 ml digestion vessel.

The mixture was digested for 40 minutes. After digestion, the vessel was allowed to cool down. The digested sludge was then diluted with water to a final volume of 100 ml to achieve the desired concentration range.

The SDDC test was performed, and the arsenic concentration in the sample was measured using a spectrophotometer.

b) Digestion of Sludge for ICP-OES Analysis:

Sample Preparation: 0.3-0.5 grams of dried and powdered sludge sample were accurately weighed.

Acid Selection: Concentrated Nitric acid (HNO₃) was used for its strong oxidizing properties and broad dissolution capacity for organic and inorganic materials.

Digestion Procedure:

6 ml of concentrated HNO₃ was mixed with the sludge and shaken well.

Distilled water was added to bring the volume up to 50 ml in a 50 ml digestion vessel.

The mixture was digested in a microwave for 40 minutes, including cooling time.

The digested sludge was then diluted with water to a final volume of 100 ml to achieve the desired concentration range.

The ICP-OES test was performed to measure the arsenic concentration in the sludge sample.

➤ **Spectrophotometric Silver Diethyldithiocarbamate (SDDC) Method:**

Principle:

In groundwater, total arsenic is mostly found as inorganic arsenates (AsO₄³⁻) and arsenates (AsO₄³⁻). In the Gutzeit generator, Zinc, Hydrochloric acid (HCl), and Stannous Chloride (SnCl₂) are used as reducing agents, where Stannous Chloride fully evolves Arsine gas (AsH₃) by reducing Arsenate (As^V) to Arsenite (As^{III}). The Arsine gas passes through a scrubber tube containing absorbent cotton with lead acetate [(CH₃COO)₂Pb] to remove sulfide interference (Hydrogen Sulfide, H₂S). The Arsine gas is absorbed in a Silver Diethyldithiocarbamate

(SDDC) solution, which produces an orange-red color. This color is measured with a spectrophotometer at 520 nm.

Apparatus:

- Spectrophotometer capable of measuring at 520 nm.
- Gutzeit generator.



Figure 5.13 SDDC Test in laboratory

Reagents:

- Concentrated Hydrochloric acid (HCl).
- 15% Potassium Iodide (KI) solution: 15 gm KI in 100 ml distilled water.
- 40% Stannous Chloride (SnCl_2) solution: Dissolve 40 gm $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 ml conc. HCl, dilute to 100 ml with conc. HCl.
- 10% Lead Acetate $[(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}]$ solution: Dissolve 10 gm in 100 ml distilled water.
- Zinc flakes, arsenic-free.
- Silver Diethyldithiocarbamate (SDDC) solution: Dissolve 1 ml morpholine in 70 ml chloroform, add 0.3 gm SDDC, and shake in a stoppered flask until dissolved. Dilute to 100 ml with chloroform, filter through a Whatman filter paper, store in a moisture-free container in a refrigerator.
- Standard arsenic stock solution: Dissolve 0.17876 gm sodium arsenite (Na_2AsO_2) in 1000 ml distilled water.

Procedure:

- A 100 ml measuring cylinder was used to take the water sample into a clean generator flask. Then, 35 ml of the water sample was added.

- Successively, 5ml of concentrated HCl, 2ml of KI solution, and 0.5 ml of SnCl_2 solution were added to the flask with proper mixing.
- The mixture was kept for 15 minutes to allow the reduction of Arsenate (As^{V}) to Arsenite (As^{III}).
- The scrubber tube was prepared by impregnating glass wool with a lead acetate solution.
- In the absorber tube (U-tube), 10 ml of SDDC solution was pipetted.
- Arsine generation and measurement were initiated by adding 3-4 grams of zinc flakes to the water sample in the generator flask. The scrubber-absorber assembly was immediately connected.
- A period of 30 minutes was allowed for complete arsine evolution.
- The resulting solution was poured directly into a clean 20 mm cuvette/cell, and the absorbance was measured at 520 nm using a spectrophotometer.

This rewritten version consolidates the procedures and explanations, presenting them in a clear and concise format suitable for technical documentation or academic writing.

6 RESULTS AND DISCUSSION

This study involves collecting arsenic sludge from an Arsenic cum Iron Removal Plant (AIRP) for the purpose of Efficient Arsenic Removal from Contaminated Sludge Through Anaerobic Volatilization.

Samples were prepared with different percentages of arsenic-rich sludge solution (5%,10%,15%,20%25% & 30%) with composite septic sludge with three different combinations and then tested all samples for the desirable results, the details of which are given in the table below:

6.1 BOD TEST RESULTS

The Biochemical Oxygen Demand (BOD) test is conducted to quantify the amount of oxygen that microorganisms will utilize while breaking down organic matter in a water sample over a specified period, typically five days at 20°C (68°F). The BOD test is a crucial parameter in environmental monitoring and management, as it indicates the potential impact of organic pollutants on the oxygen levels in water bodies and, subsequently, on the health and sustainability of aquatic ecosystems.

Table 6.1 BOD Test Results for Three type of Combinations

Sl. No.	Parameters	Unit	Minimum Detection Limit	SM _{Raw}	SM _{at} 10Days	SM _{at} 20Days	SM _{at} 30Days	SM _{at} 60Days
1	Biochemical Oxygen Demand,3 Days at 27°C, mg/L	mg/L	2	7260	5590	4937	3920	1960
2				SC _{Raw}	SC _{at} 10Days	SC _{at} 20Days	SC _{at} 30Days	SC _{at} 60Days
				6203	4776	4218	3350	1675
3				SS _{Raw}	SS _{at} 10Days	SS _{at} 20Days	SS _{at} 30Days	SS _{at} 60Days
				3325	2560	2261	1796	898

In this study, initial BOD measurements were recorded on the first day of the experiment, designated as SM Raw, SC Raw, and SS Raw for the three different combinations. Further measurements were taken at intervals of 10, 20, 30, and 60 days for each combination. The results show that after 10 days, BOD levels had decreased by approximately 23-25% across all combinations. By day 20, this reduction reached about 32-35%, further increasing to 46-50% by day 30, and around 72-75% by day 60. These findings illustrate a consistent decline in BOD levels over time, indicating a reduction in the rate of oxygen consumption by microorganisms. All reported figures are average values obtained from multiple samples taken at the same intervals.

6.2 COD TEST RESULTS

The Chemical Oxygen Demand (COD) test is conducted to determine the amount of oxygen needed to chemically oxidize both organic and inorganic matter in a water sample. This test provides a comprehensive evaluation of water quality by quantifying the total amount of pollutants that can be oxidized chemically. In the experiment, COD was initially measured immediately after setting up the sample. Further measurements were taken at intervals of 10 days, 20 days, 30 days, and 60 days across three different sample combinations.

The data revealed a decrease in COD over time, signifying a reduction in the concentration of organic pollutants or chemically oxidizable substances in the water sample. This decline in COD suggests that the organic matter or pollutants are being broken down, either through chemical reactions or microbial activity, leading to improved water quality. Initially, all combinations exhibited very high COD levels, with Combination 1, labelled as SM_{Raw} , showing the highest value among them. Over the course of 10, 20, 30, and 60 days, the COD reduction percentages for Combination 1 were approximately 25-27%, 36-38%, 60-65%, and 71-73%, respectively.

Table 6.2 COD Test Results for Three type of Combinations

Sl. No.	Parameters	Unit	Minimum Detection Limit	SM_{Raw}	SM_{at} 10Days	SM_{at} 20Days	SM_{at} 30Days	SM_{at} 60Days
1	Chemical Oxygen Demand	mg/L	2	31300	24101	21284	16902	8451
2				SC_{Raw}	SC_{at} 10Days	SC_{at} 20Days	SC_{at} 30Days	SC_{at} 60Days
				27856	21449	18942	15042	7521
3				SS_{Raw}	SS_{at} 10Days	SS_{at} 20Days	SS_{at} 30Days	SS_{at} 60Days
				11752	9049	7991	6346	3173

6.3 TDS TESTING RESULTS

An increase in Total Dissolved Solids (TDS) value over time typically indicates that the concentration of dissolved substances in the feed slurry is rising. TDS represents the total amount of dissolved inorganic and organic matter in a water sample, including salts, minerals, and other particles.

For Combination 1, the average percentage increases from SM_{Raw} to SM at 10, 20, 30, and 60 days were 1%, 2%, 10%, and 6%, respectively. In Combination 2, the increases from SC_{Raw} to SC at the same intervals were 2%, 3%, 5%, and 13%. For Combination 3, the average percentage increases from SS_{Raw} to SS_{AT} over the 10, 20, 30, and 60-day periods were 3%, 5%, 5%, and 8%, respectively.

Table 6.3 TDS Test Results for Three type of Combinations

Sl. No.	Parameters	Unit	SM_{Raw}	SM_{at} 10Days	SM_{at} 20Days	SM_{at} 30Days	SM_{at} 60Days
1	Total solved Solid (TDS)	ppm	5360	5398	5482	6047	6420
2			SC_{Raw}	SC_{at} 10Days	SC_{at} 20Days	SC_{at} 30Days	SC_{at} 60Days
			4750	4863	4985	5213	5897
3			SS_{Raw}	SS_{at} 10Days	SS_{at} 20Days	SS_{at} 30Days	SS_{at} 60Days
			4521	4652	4895	5124	5542

6.4 pH VALUE TESTING RESULTS

In an anaerobic sludge mixture, a decreasing pH value generally signifies increased acidity, which is a common outcome of several processes:

Production of Organic Acids: During anaerobic digestion, microorganisms break down organic matter into simpler compounds. This process produces organic acids like acetic acid, propionic acid, and butyric acid. The accumulation of these acids leads to a decrease in pH.

Volatile Fatty Acid Accumulation: In the initial stages of anaerobic digestion, volatile fatty acids (VFA) can accumulate as organic material is broken down. High VFA concentrations can significantly lower the pH.

Hydrogen Sulfide Formation: Sulfate-reducing bacteria in anaerobic conditions may convert sulfates into hydrogen sulfide, which can further acidify the sludge.

Microbial Activity: The metabolism of anaerobic microorganisms produces acidic by products as they decompose organic matter. If the production of these acids exceeds their removal, the pH will decrease.

Inhibitory Conditions: A very low pH can inhibit the activity of methanogenic microorganisms, which are essential for the stabilization of the sludge and the production of biogas. This can disrupt the anaerobic digestion process and lead to further pH drop.

A decreasing pH in anaerobic conditions can affect the efficiency of the digestion process and may require pH management to maintain optimal conditions for microbial activity and ensure effective sludge treatment.

Table 6.4 pH Test Results for Three type of Combinations

Sl. No.	Parameters	Unit	SM _{Raw}	SM _{at 10Days}	SM _{at 20Days}	SM _{at 30Days}	SM _{at 60Days}
1	Total solved Solid	ppm	7.1	6.5	6.1	5.5	5.2
2			SC _{Raw}	SC _{at 10Days}	SC _{at 20Days}	SC _{at 30Days}	SC _{at 60Days}
			6.9	6.6	5.8	5.3	4.9
3			SS _{Raw}	SS _{at 10Days}	SS _{at 20Days}	SS _{at 30Days}	SS _{at 60Days}
			7.0	6.7	6.2	5.7	5.4

6.5 SOME OTHER TEST RESULTS

An increase in nitrate, nitrite, and Sulphate concentrations over time in a solution containing arsenic sludge, septic sludge, and cow dung suggests several potential biochemical and environmental processes are occurring. Here's what this increase might mean:

Microbial Activity and Organic Decomposition:

Nitrate and Nitrite: In the presence of organic matter (such as cow dung and septic sludge), microbial activity can break down nitrogen-containing organic compounds into simpler forms like ammonia. Through nitrification, ammonia is further oxidized to nitrite (NO_2^-) and then to nitrate (NO_3^-) by nitrifying bacteria. An increase in nitrate and nitrite over time could indicate ongoing microbial activity and the conversion of organic nitrogen to these oxidized forms.

Sulphate: Sulphate (SO_4^{2-}) can increase as a result of the oxidation of sulfur-containing organic compounds present in the sludge. Microbial processes, particularly those involving sulfur-oxidizing bacteria, can lead to an increase in Sulphate levels over time.

Breakdown of Organic Matter:

As the cow dung, septic sludge, and arsenic-laden sludge undergo decomposition, organic nitrogen and sulfur compounds are mineralized. This process releases nitrates, nitrites, and Sulphates into the solution. The presence of these compounds suggests that organic matter is actively being broken down and converted into simpler inorganic forms.

Chemical Reactions and Oxidation:

The increase in these anions could also result from chemical reactions occurring within the mixture. For example, if the sludge mixture is exposed to oxygen, aerobic conditions can promote the oxidation of organic sulfur to Sulphate and organic nitrogen to nitrate/nitrite.

In summary, the increase in nitrate, nitrite, and Sulphate levels over time in a solution containing arsenic sludge, septic sludge, and cow dung suggests that organic matter is being decomposed by microbial activity, releasing these compounds into the solution. It also points to active biochemical processes such as nitrification and oxidation occurring within the mixture,

which could indicate the ongoing breakdown of organic and inorganic substances present in the sludge.

In other hand, a decrease in sulfide as (S), total solids (TS), volatile solids (VS), total coliform, and fecal coliform over time in a mixture containing arsenic sludge, septic sludge, and cow dung indicates several biological, chemical, and physical processes occurring within the solution. Here's what the decrease in each parameter might mean:

Decrease in Sulfide (as S):

Microbial Oxidation: Sulfide (S^{2-}) is often present in anaerobic conditions and can be reduced by Sulphate-reducing bacteria. Over time, in the presence of oxygen or under slightly aerobic conditions, sulfide can be oxidized to elemental sulfur or Sulphate (SO_4^{2-}) by sulfur-oxidizing bacteria. A decrease in sulfide levels suggests that these bacteria are active and that there is a shift towards more oxidized forms of sulfur.

Volatilization: Under certain conditions, especially if the environment becomes less anaerobic, hydrogen sulfide gas (H_2S), which is a form of sulfide, may volatilize and escape into the air, leading to a decrease in sulfide concentration in the liquid phase.

Decrease in Total Solids (TS):

Biodegradation of Organic Matter: Total solids include both suspended and dissolved solids. Over time, the organic portion of the solids is broken down by microorganisms. This biodegradation reduces the mass of organic material, leading to a decrease in total solids.

Sedimentation and Settling: Some solids may settle out of the solution over time due to gravity. If the solids settle at the bottom, the concentration of total suspended solids in the liquid portion will decrease, resulting in a lower total solids measurement.

Decrease in Volatile Solids (VS):

Microbial Decomposition: Volatile solids represent the organic fraction of the total solids. As microorganisms digest organic matter, the volatile solids content decreases. This is a key indicator of the biodegradability of the organic matter present. A reduction in volatile solids suggests that a significant amount of the organic material is being consumed or converted into gases (such as CO₂ and CH₄) during the anaerobic digestion process.

Decrease in Total Coliform:

Microbial Die-Off: Total coliform bacteria, which are indicators of fecal contamination and general microbial pollution, decrease over time due to environmental stressors such as temperature, pH changes, and competition with other microbes. As the conditions in the sludge mixture become less favourable (due to depletion of nutrients or accumulation of toxic by-products), the coliform bacteria population declines.

Natural Attenuation: Over time, pathogenic and non-pathogenic bacteria can naturally die off or get outcompeted by other more dominant or specialized microorganisms. This leads to a reduction in their numbers.

Decrease in Fecal Coliform:

Environmental Stress and Natural Die-Off: Similar to total coliform, fecal coliform bacteria, which are specific indicators of fecal contamination, can decrease over time as a result of natural die-off due to adverse environmental conditions. High temperatures, pH shifts, and other environmental factors can negatively impact their survival rates.

Predation and Competition: Other microorganisms, such as protozoa, can prey on fecal coliform bacteria, or they may get outcompeted by other bacteria that are better adapted to the changing conditions in the sludge mixture.

The decrease in sulfide, total solids, volatile solids, total coliform, and fecal coliform in a mixture of arsenic sludge, septic sludge, and cow dung over time indicates that various biological, chemical, and physical processes are actively occurring. These include the breakdown and oxidation of organic and inorganic compounds, sedimentation of solids, and the

natural die-off or reduction of microbial populations. Overall, these decreases reflect the ongoing stabilization, digestion, and treatment of the sludge mixture, suggesting an improvement in the quality of the sludge over time.

Table 6.5 Key Test Results for Other Parameters: Combination 1

Sl. No.	Parameters	Unit	Minimum Detection Limit	SM _{Ra} w	SM _{at} 10Days	SM _{at} 20Days	SM _{at} 30Days	SM _{at} 60Days
1	Nitrate (as NO ₃)	mg/L	0	68	-	-	-	72
2	Nitrite (as NO ₂)	mg/L	0	16	-	-	-	18
3	Sulphate (as SO ₄)	mg/L	3	316	-	-	-	139
4	Sulphide (as S)	mg/L	1	180	-	-	-	58
5	Total Solids	mg/L	10	42320	-	-	-	29201
6	Volatile Solids	mg/L	10	22240	-	-	-	16458
7	Total Coliform	MPN/100 mL	<1.8	32 x 10 ⁹	23 x 10 ⁸	6 x 10 ⁸	84 x 10 ⁵	4 x 10 ²
8	Fecal Coliform	MPN/100 mL	<1.8	7 x 10 ⁹	11 x 10 ⁸	4 x 10 ⁸	75 x 10 ⁵	3 x 10 ²

Table 6.6 Key Test Results for Other Parameters: Combination 2

Sl. No.	Parameters	Unit	Minimum Detection Limit	SC _{Raw}	SC _{at} 10Days	SC _{at} 20Days	SC _{at} 30Days	SC _{at} 60Days
1	Nitrate (as NO ₃)	mg/L	0	72	-	-	-	63
2	Nitrite (as NO ₂)	mg/L	0	12	-	-	-	11
3	Sulphate (as SO ₄)	mg/L	3	402	-	-	-	213
4	Sulphide (as S)	mg/L	1	168	-	-	-	62
5	Total Solids	mg/L	10	35741	-	-	-	26091
6	Volatile Solids	mg/L	10	21356	-	-	-	15163
7	Total Coliform	MPN/100 mL	<1.8	24 x 10 ⁹	15 x 10 ⁸	7 x 10 ⁸	73 x 10 ⁵	3 x 10 ²

Table 6.7 Key Test Results for Other Parameters: Combination 3

Sl. No.	Parameters	Unit	Minimum Detection Limit	SS_{Raw}	SS_{at} 10Days	SS_{at} 20Days	SS_{at} 30Days	SS_{at} 60Days
1	Nitrate (as NO ₃)	mg/L	0	35	-	-	-	41
2	Nitrite (as NO ₂)	mg/L	0	6	-	-	-	6
3	Sulphate (as SO ₄)	mg/L	3	231	-	-	-	122
4	Sulphide (as S)	mg/L	1	78	-	-	-	29
5	Total Solids	mg/L	10	11254	-	-	-	8215
6	Volatile Solids	mg/L	10	9845	-	-	-	6990
7	Total Coliform	MPN/100 mL	<1.8	12 x 10 ⁹	5 x 10 ⁸	4 x 10 ⁸	54 x 10 ⁵	2 x 10 ²
8	Fecal Coliform	MPN/100 mL	<1.8	4.5 x 10 ⁹	8 x 10 ⁸	2 x 10 ⁸	41 x 10 ⁵	1.8 x 10 ²

6.6 ARSENIC TEST RESULT

A decrease in arsenic concentration over time in a mixture containing arsenic sludge, septic sludge, and cow dung suggests that various physical, chemical, or biological processes are reducing the bioavailability or mobility of arsenic within the mixture. Here are some possible explanations for this decrease:

Adsorption to Solids:

Binding to Organic and Inorganic Matter: Arsenic can bind to organic matter present in the cow dung or septic sludge or to inorganic particles like iron oxides in the sludge. Over time, these particles can adsorb arsenic from the solution, effectively reducing its concentration in the liquid phase. The presence of iron and other minerals in the sludge or cow dung can facilitate this adsorption process, as arsenic has a high affinity for iron oxides and hydroxides.

Co-precipitation:

Formation of Insoluble Compounds: Arsenic may co-precipitate with iron, aluminium, or calcium compounds present in the sludge. For instance, if the pH conditions are favourable, arsenic can co-precipitate with ferric hydroxide or form other insoluble arsenic compounds. This process reduces the concentration of soluble arsenic in the liquid phase, thereby decreasing its overall concentration in the mixture.

Microbial Transformation:

Microbial Reduction or Methylation: Certain microorganisms can transform arsenic into less toxic forms or convert it into volatile methylated species that can escape into the atmosphere. For example, some bacteria can reduce arsenate (As^{V}) to arsenite (As^{III}), or even further to dimethylarsine or trimethylarsine, which are volatile and can be lost from the mixture, reducing the overall arsenic content.

Bioremediation: Some microbes can also immobilize arsenic by converting it into a form that precipitates out of the solution, such as arsenic sulfide, especially under anaerobic conditions prevalent in septic sludge or cow dung slurry.

Volatilization:

Release of Arsenic Gas: If microbial activity leads to the production of methylated arsenic species, these volatile arsenic compounds can be released into the air, leading to a decrease in arsenic concentration in the liquid and solid phases of the mixture.

Dilution or Settling of Arsenic-Laden Particles:

Sedimentation of Arsenic-Containing Particles: Over time, particles containing arsenic may settle to the bottom of the mixture, effectively reducing the arsenic concentration in the overlying liquid. This physical separation can result in a decrease in measured arsenic concentration in the liquid sample.

Immobilization and Stabilization:

Chemical Stabilization Processes: In some cases, chemical additives or naturally occurring substances in the cow dung or septic sludge may lead to the immobilization of arsenic in more stable solid phases. This process effectively reduces its mobility and bioavailability, contributing to a decrease in measurable arsenic concentration in the liquid phase.

The decrease in arsenic concentration over time in the mixture of arsenic sludge, septic sludge, and cow dung suggests that the arsenic is being removed from the solution or converted into less soluble or volatile forms. This could be due to adsorption onto solid particles, co-precipitation with minerals, microbial activity that transforms or volatilizes arsenic, or sedimentation of arsenic-laden particles. These processes contribute to the stabilization and reduction of arsenic levels, making the mixture potentially less hazardous over time.

Detailed Analysis of Arsenic Removal Efficiency Based on ALS Percentage Added

Table 6.8 Reduction of Arsenic with 5% ALS at different time intervals of Combination 1

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SM05-Raw	10.98	-
SM05-10	9.36	14.75
SM05-20	6.00	45.36
SM05-30	3.20	70.86
SM05-60	0.60	94.54

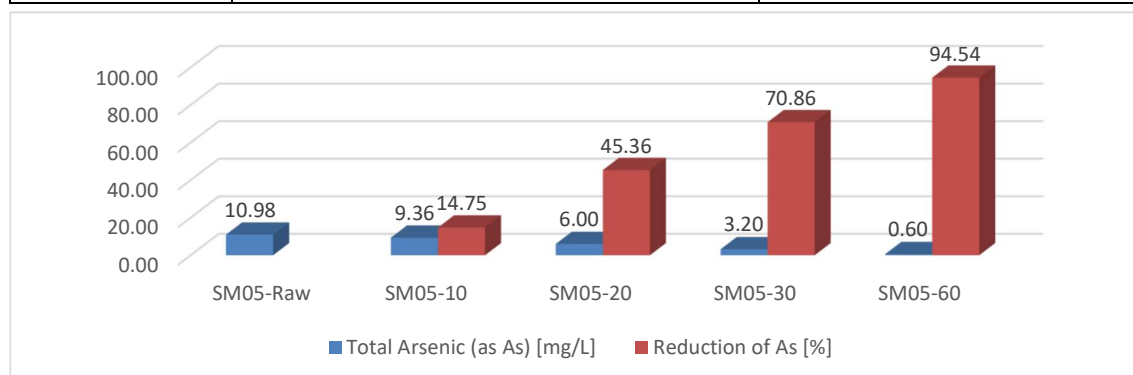


Figure 6.1 Reduction of Arsenic with 5% ALS at different time intervals of Combination 1

Table 6.9 Reduction of Arsenic with 10% ALS at different time intervals of Combination 1

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SM10-Raw	21.90	-
SM10-10	16.20	26.03
SM10-20	9.80	55.25
SM10-30	6.30	71.23
SM10-60	2.10	90.41

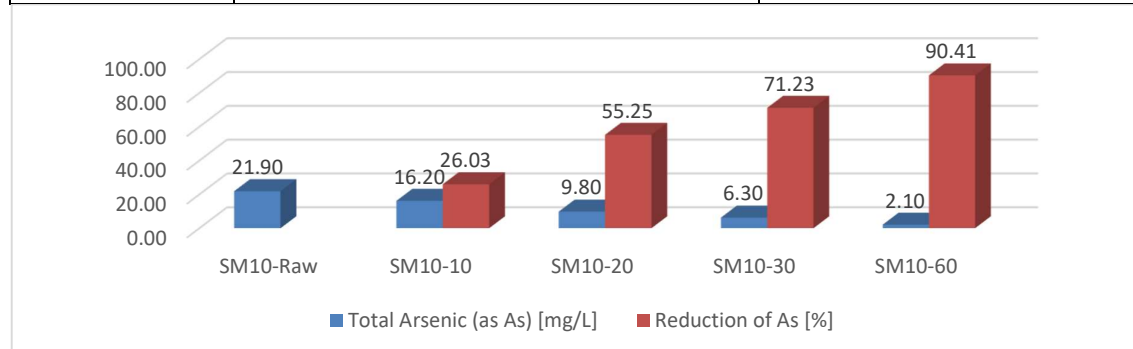


Figure 6.2 Reduction of Arsenic with 10% ALS at different time intervals of Combination 1

Table 6.10 Reduction of Arsenic with 15% ALS at different time intervals of Combination 1

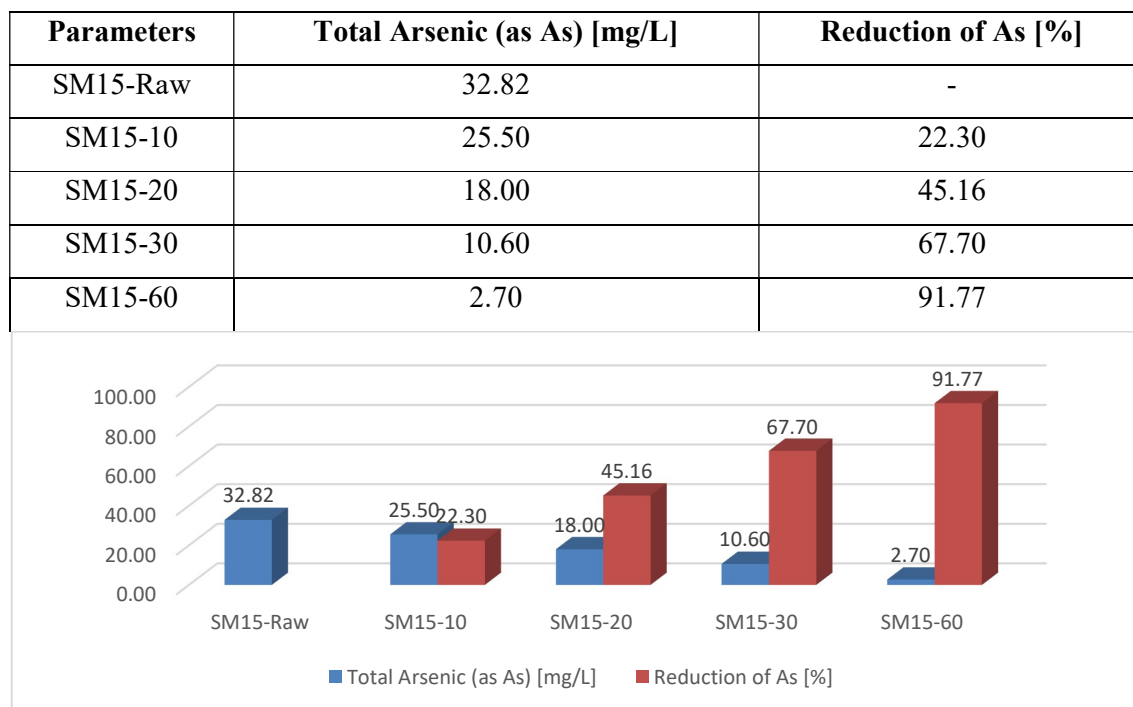


Figure 6.3 Reduction of Arsenic with 15% ALS at different time intervals of Combination 1

Table 6.11 Reduction of Arsenic with 20% ALS at different time intervals of Combination 1

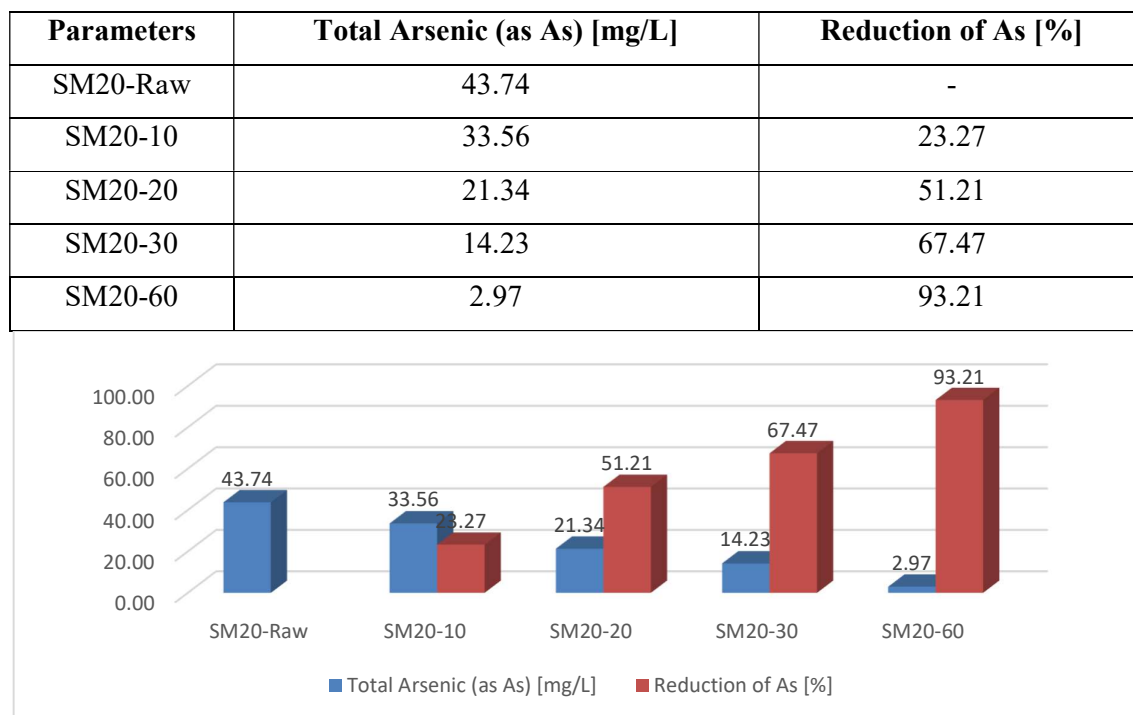


Figure 6.4 Reduction of Arsenic with 20% ALS at different time intervals of Combination 1

Table 6.12 Reduction of Arsenic with 25% ALS at different time intervals of Combination 1

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SM25-Raw	54.66	-
SM25-10	43.25	20.87
SM25-20	40.00	26.82
SM25-30	22.90	58.10
SM25-60	5.60	89.75

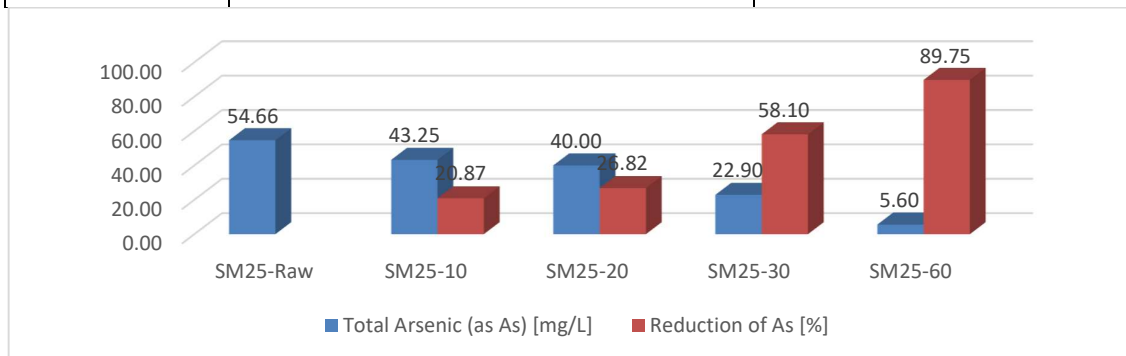


Figure 6.5 Reduction of Arsenic with 25% ALS at different time intervals of Combination 1

Table 6.13 Reduction of Arsenic with 30% ALS at different time intervals of Combination 1

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As
SM30-10	65.58	-
SM30-10	51.62	21.29
SM30-20	37.30	43.12
SM30-30	26.35	59.82
SM30-60	7.35	88.79

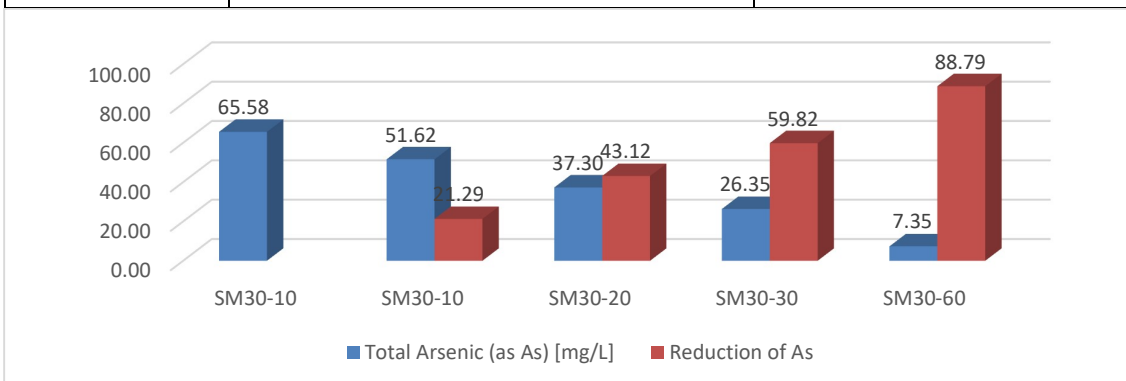


Figure 6.6 Reduction of Arsenic with 30% ALS at different time intervals of Combination 1

Table 6.14 Reduction of Arsenic with 5% ALS at different time intervals of Combination 2

Parameters	Total Arsenic (as As)	Reduction of As
SC05-Raw	11.02	-
SC05-10	10.5	4.72
SC05-20	5.6	49.18
SC05-30	1.3	88.20
SC05-60	0.2	98.19

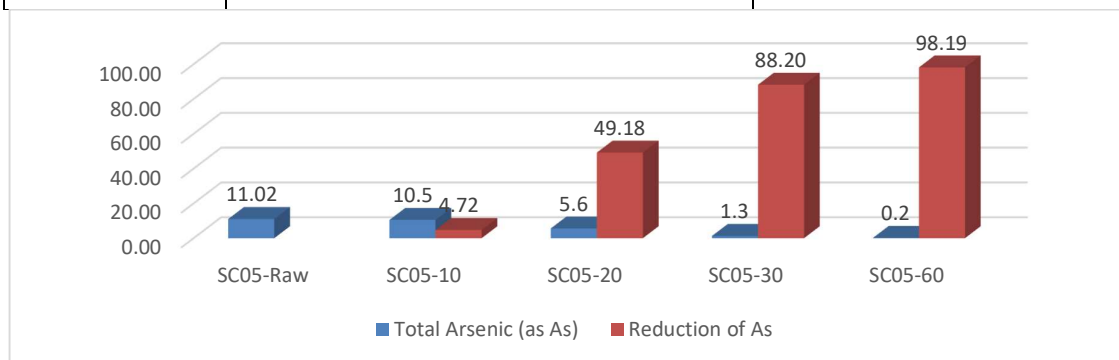


Figure 6.7 Reduction of Arsenic with 5% ALS at different time intervals of Combination 2

Table 6.15 Reduction of Arsenic with 10% ALS at different time intervals of Combination 2

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SC10-Raw	21.94	-
SC10-10	20.5	6.56
SC10-20	9.5	56.70
SC10-30	5.4	75.39
SC10-60	0.8	96.35

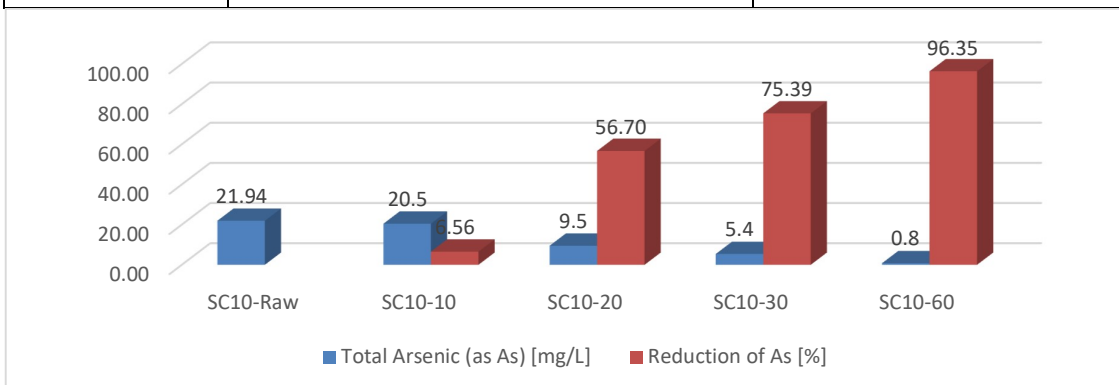


Figure 6.8 Reduction of Arsenic with 10% ALS at different time intervals of Combination 2

Table 6.16 Reduction of Arsenic with 15% ALS at different time intervals of Combination 2

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SC15-Raw	32.86	-
SC15-10	32.5	1.10
SC15-20	20.5	37.61
SC15-30	7.6	76.87
SC15-60	2.3	93.00

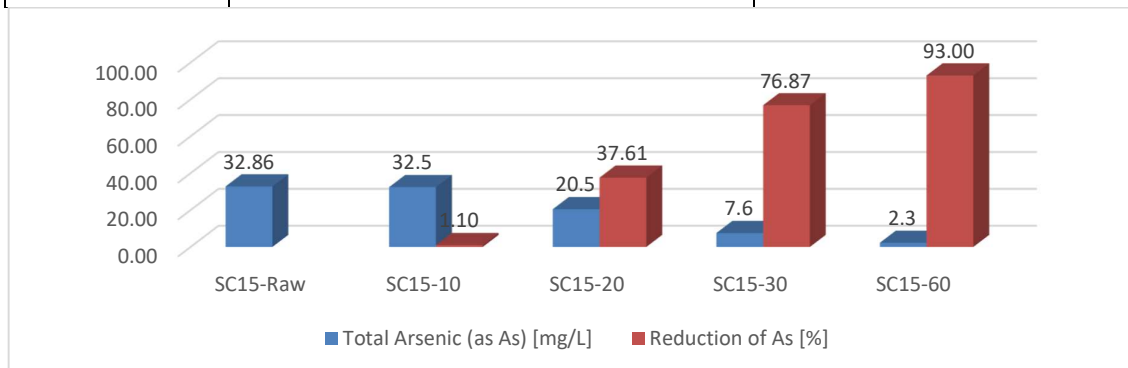


Figure 6.9 Reduction of Arsenic with 15% ALS at different time intervals of Combination 2

Table 6.17 Reduction of Arsenic with 20% ALS at different time intervals of Combination 2

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SC20-Raw	43.78	-
SC20-10	36.8	15.94
SC20-20	22.6	48.38
SC20-30	10.7	75.56
SC20-60	5.2	88.12

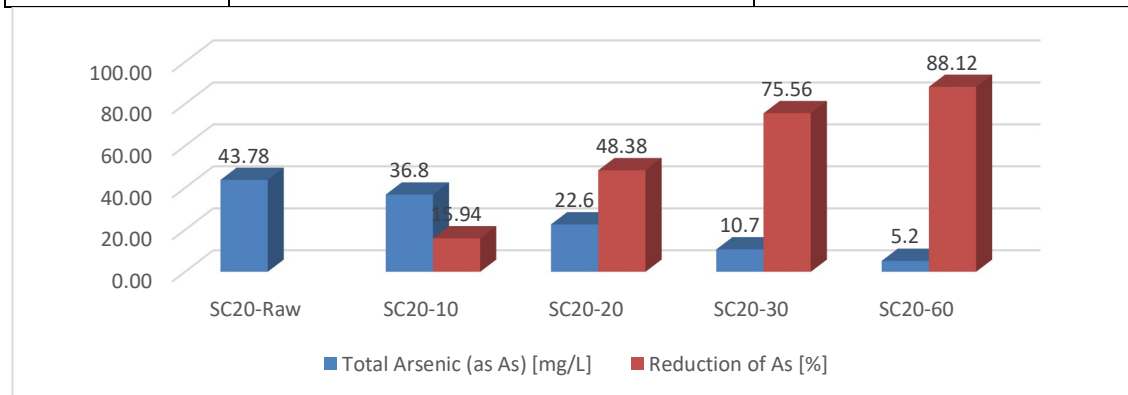


Figure 6.10 Reduction of Arsenic with 20% ALS at different time intervals of Combination 2

Table 6.18 Reduction of Arsenic with 25% ALS at different time intervals of Combination 2

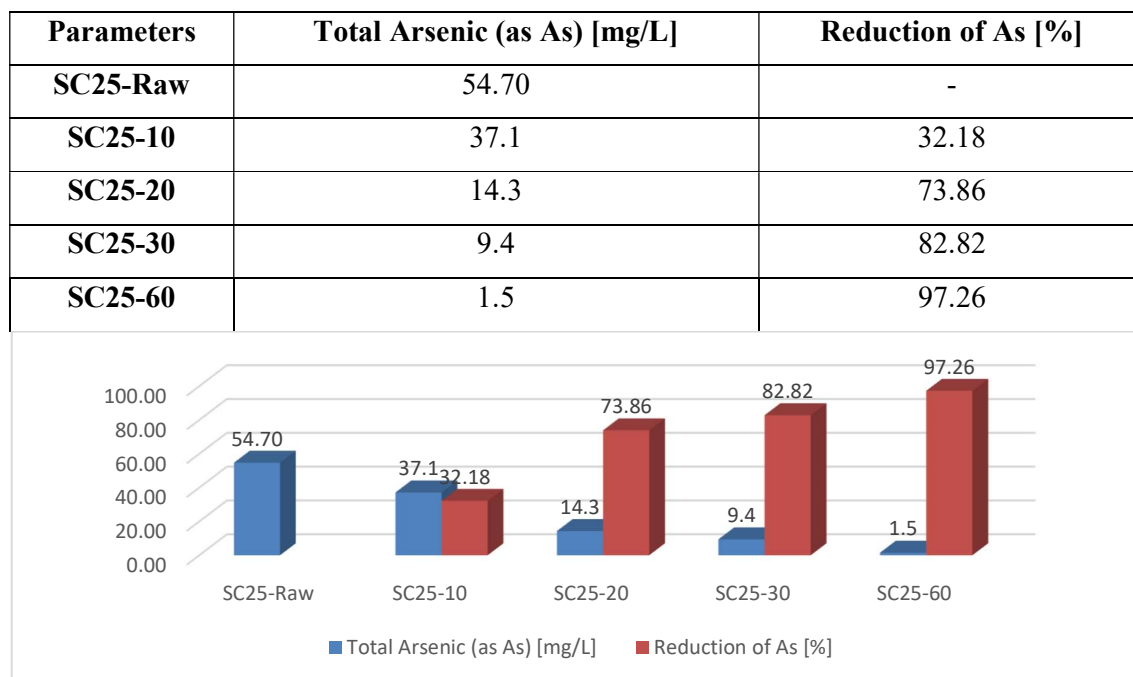


Figure 6.11 Reduction of Arsenic with 25% ALS at different time intervals of Combination 2

Table 6.19 Reduction of Arsenic with 30% ALS at different time intervals of Combination 2

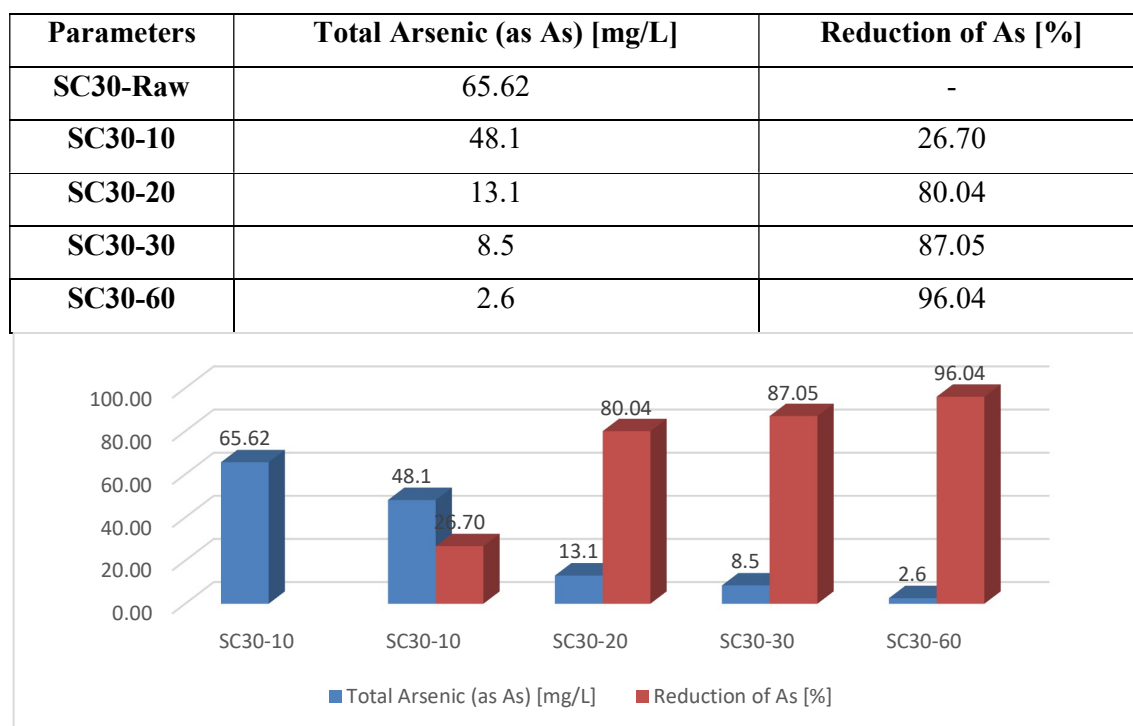


Figure 6.12 Reduction of Arsenic with 30% ALS at different time intervals of Combination 2

Table 6.20 Reduction of Arsenic with 5% ALS at different time intervals of Combination 3

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SS05-Raw	10.93	
SS05-10	8.6	21.32
SS05-20	5.6	48.76
SS05-30	3.41	68.80
SS05-60	1.26	88.47

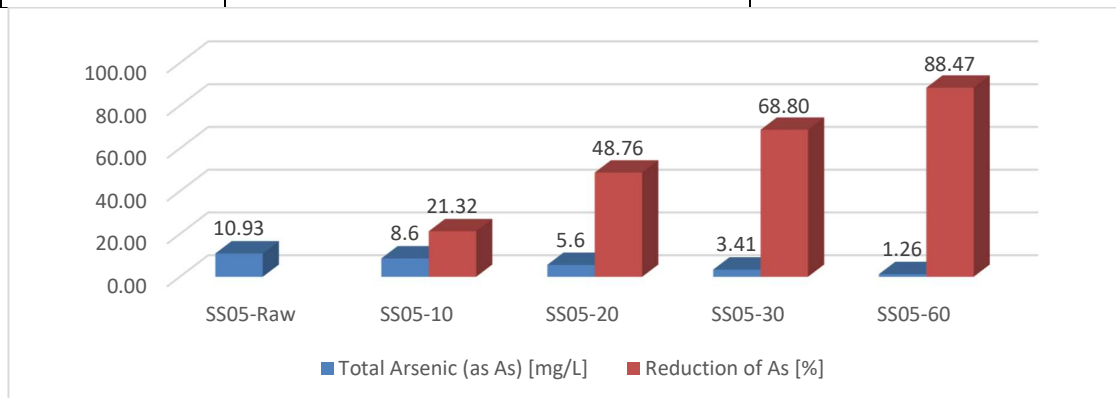


Figure 6.13 Reduction of Arsenic with 5% ALS at different time intervals of Combination 3

Table 6.21 Reduction of Arsenic with 10% ALS at different time intervals of Combination 3

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SS10-Raw	21.85	-
SS10-10	16.58	24.12
SS10-20	10.2	53.32
SS10-30	7.42	66.04
SS10-60	2.07	90.53

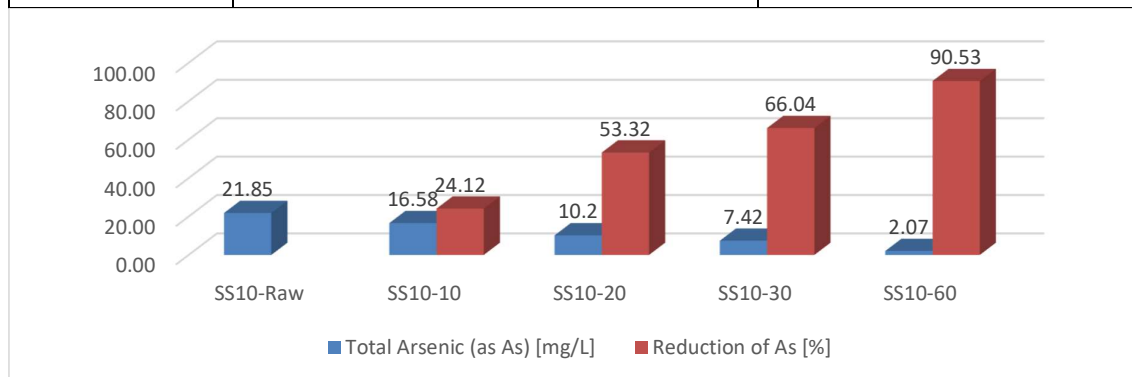


Figure 6.14 Reduction of Arsenic with 10% ALS at different time intervals of Combination 3

Table 6.22 Reduction of Arsenic with 15% ALS at different time intervals of Combination 3

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SS15-Raw	32.76	-
SS15-10	24.87	24.08
SS15-20	18.23	44.35
SS15-30	11.74	64.16
SS15-60	4.9	85.04

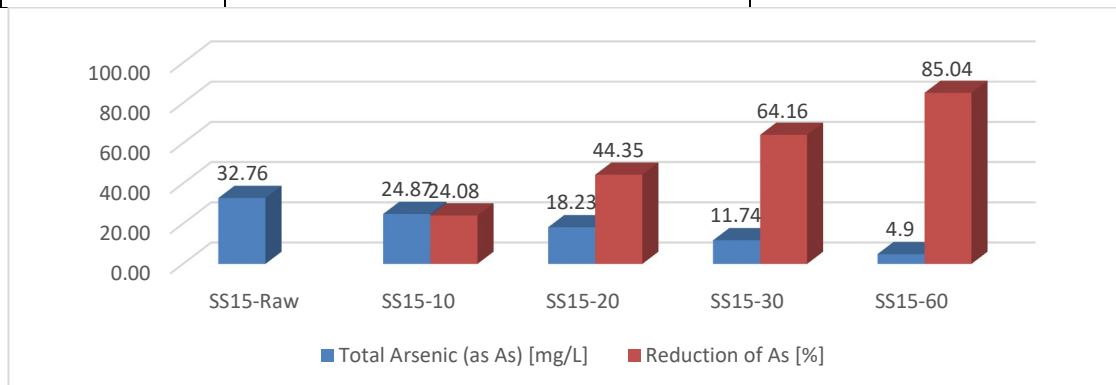


Figure 6.15 Reduction of Arsenic with 15% ALS at different time intervals of Combination 3

Table 6.23 Reduction of Arsenic with 20% ALS at different time intervals of Combination 3

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SS20-Raw	43.69	-
SS20-10	32.6	25.38
SS20-20	24.7	43.47
SS20-30	13.67	68.71
SS20-60	4.48	89.75

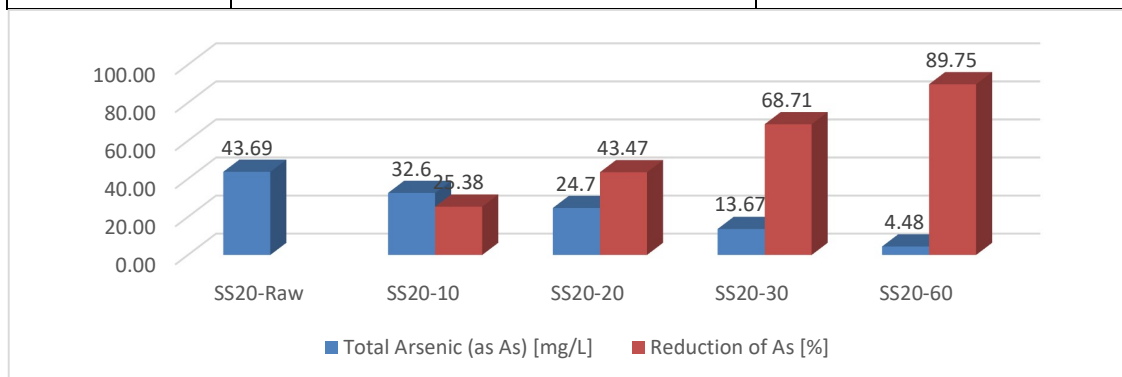


Figure 6.16 Reduction of Arsenic with 20% ALS at different time intervals of Combination 3

Table 6.24 Reduction of Arsenic with 25% ALS at different time intervals of Combination 3

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SS25-Raw	54.61	
SS25-10	41.78	23.49
SS25-20	30.6	43.97
SS25-30	18.45	66.21
SS25-60	7.3	86.63

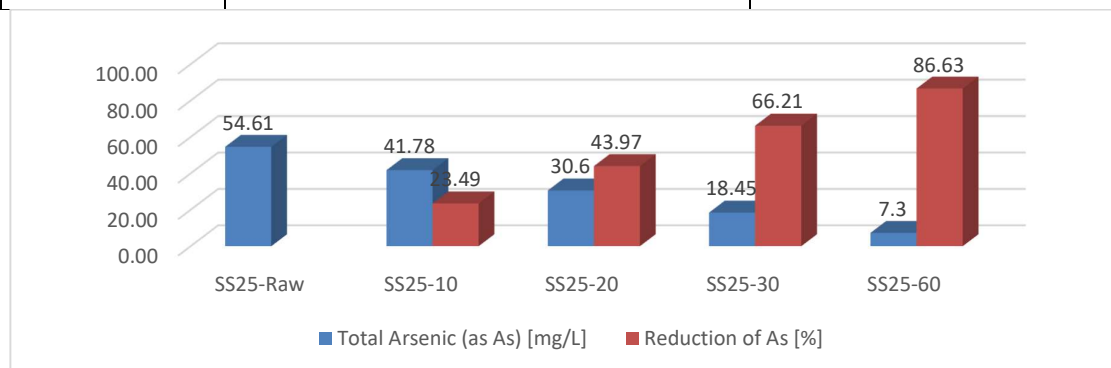


Figure 6.17 Reduction of Arsenic with 25% ALS at different time intervals of Combination 3

Table 6.25 Reduction of Arsenic with 30% ALS at different time intervals of Combination 3

Parameters	Total Arsenic (as As) [mg/L]	Reduction of As [%]
SS30-10	65.53	
SS30-10	49.52	24.43
SS30-20	36.78	43.87
SS30-30	19.45	70.32
SS30-60	9.2	85.96

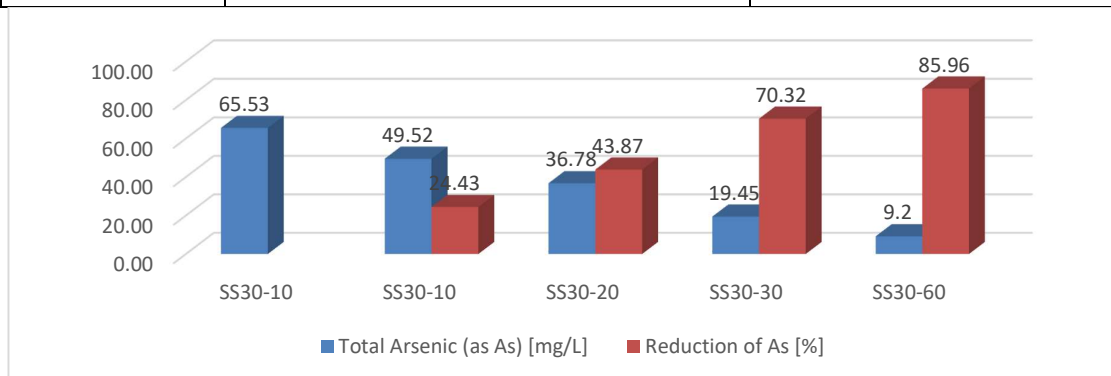


Figure 6.18 Reduction of Arsenic with 30% ALS at different time intervals of Combination 3

Based on the data presented in the tables and charts, the following conclusions can be drawn regarding the effectiveness of arsenic removal in the three different sludge combinations used in the experiment:

For Combination 1, which involves blending composite sludge with varying percentages of arsenic-laden sludge (ALS), the most effective arsenic removal rates were observed with 5% and 20% ALS. After 60 days, the initial arsenic concentrations for these mixtures were 10.98 mg/L and 43.74 mg/L, respectively. The final concentrations after the same period were reduced to 0.60 mg/L and 2.97 mg/L, corresponding to removal efficiencies of approximately 94% and 93%. These results suggest that incorporating lower to moderate levels of ALS in the composite sludge optimizes arsenic removal over time. In contrast, the mixture with 30% ALS exhibited the lowest removal efficiency after 60 days, indicating that higher ALS concentrations may impede the removal process or suggest a saturation point beyond which additional ALS does not enhance arsenic reduction.

In Combination 2, the composite sludge consistently achieved an arsenic removal rate of 95% after 60 days across all tested percentages of arsenic-laden sludge (ALS), which were 5%, 10%, 15%, 25%, and 30%. The initial arsenic concentrations for these mixtures were 11.02 mg/L, 21.94 mg/L, 32.86 mg/L, 54.70 mg/L, and 65.62 mg/L, respectively. After 60 days, the final arsenic concentrations were reduced to 0.2 mg/L, 0.8 mg/L, 2.31 mg/L, 1.5 mg/L, and 2.6 mg/L, respectively. This consistent performance across various ALS concentrations indicates that the sludge matrix in Combination 2 is highly effective at stabilizing and removing arsenic, regardless of the initial ALS concentration. This effectiveness may be attributed to the specific properties of the composite sludge used in this combination, which likely enhances arsenic binding or transformation under anaerobic conditions.

For Combination 3, which involved only one sludge sample achieving significant arsenic removal, the highest efficiency was observed with 10% ALS, reaching 90% removal after 60 days (Initial weight of arsenic 21.85 mg/L and final weight was 2.07 mg/L). This suggests that, within this combination, a lower percentage of ALS (specifically 10%) is optimal for arsenic removal. The limited performance with other percentages indicates that the conditions or interactions in Combination 3 are less favourable for arsenic removal compared to the other combinations.

Overall, the data suggest that Combination 1 and Combination 2 are the most effective for arsenic removal from sludge mixtures, with Combination 2 showing a particularly robust performance across all tested ALS concentrations. These findings imply that the sludge matrix and the proportion of ALS are critical factors influencing the efficiency of arsenic removal. The results underscore the importance of optimizing the mixture proportions and conditions to achieve maximum contaminant reduction in practical applications.

Detailed Analysis of Arsenic Removal Efficiency Over Time

In this study, the effectiveness of arsenic removal was evaluated across different combinations of composite sludge and varying durations. For Combination 1, which included different concentrations of arsenic-laden sludge (ALS) at 5%, 10%, 15%, 20%, 25%, and 30%, several significant trends in arsenic reduction were observed over time:

At the 10-day mark, the highest arsenic removal rates were noted in samples containing 10%, 15%, and 20% arsenic sludge, achieving reductions of approximately 23-26%. These samples are designated as SM10-10, SM15-10, and SM20-10, respectively. This early observation indicates that a moderate concentration of arsenic sludge is effective in initiating the removal process within a relatively short timeframe.

By 20 days, samples with 10% and 20% arsenic sludge (SM10-20 and SM20-20) continued to show optimal arsenic removal, maintaining reduction rates of around 23-26%. This consistency suggests a sustained efficiency in the removal process for these specific concentrations, highlighting their potential for longer-term treatment applications.

At 30 days, the efficiency of arsenic removal increased significantly, particularly in samples SM10-30, SM15-30, and SM20-30. These samples exhibited arsenic removal rates between 65-70%, indicating that as the digestion period extends, the removal efficiency becomes more pronounced, especially for these intermediate concentrations of arsenic sludge.

By the 60-day mark, arsenic removal reached its highest observed levels in samples SM10-60, SM15-60, and SM20-60, with reduction rates escalating to between 80-94%. This peak

performance underscores the effectiveness of longer digestion periods combined with optimal sludge concentrations (10%, 15%, and 20%) for maximizing arsenic removal.

The data reveals a clear pattern: arsenic removal efficiency improves with time and is most effective at intermediate concentrations of arsenic sludge. These specific concentrations (10%, 15%, and 20%) consistently showed superior performance across all time intervals, suggesting they provide an ideal balance for microbial activity and chemical reactions necessary for arsenic removal. The findings indicate that optimizing the concentration of arsenic-laden sludge and extending the digestion period are critical factors in enhancing the removal process, thereby providing valuable insights for designing effective wastewater treatment strategies.

Table 6.26 Reduction of Arsenic at 10 Days with different % of ALS of Combination 1

Parameters	Reduction of As [%]
SM05-10	14.75
SM10-10	26.03
SM15-10	22.30
SM20-10	23.27
SM25-10	20.87
SM30-10	21.29

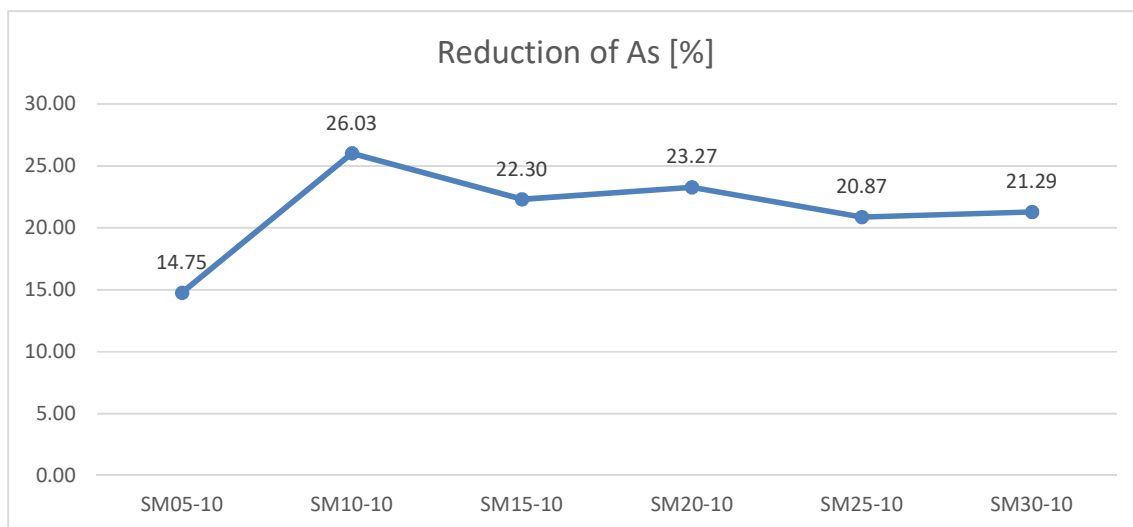


Figure 6.19 Reduction of Arsenic at 10 Days with different % of ALS of Combination 1

Table 6.27 Reduction of Arsenic at 20 Days with different % of ALS of Combination 1

Parameters	Reduction of As [%]
SM05-20	45.36
SM10-20	55.25
SM15-20	45.16
SM20-20	51.21
SM25-20	26.82
SM30-20	43.12

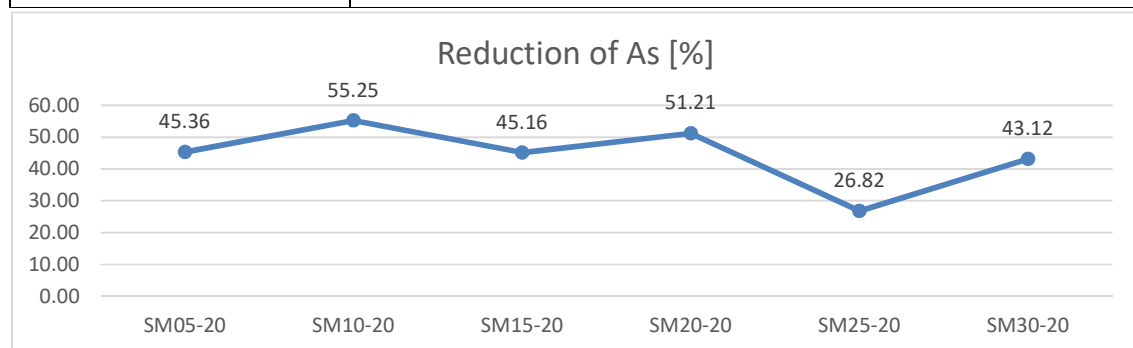


Figure 6.20 Reduction of Arsenic at 20 Days with different % of ALS of Combination 1

Table 6.28 Reduction of Arsenic at 30 Days with different % of ALS of Combination 1

Parameters	Reduction of As [%]
SM05-30	70.86
SM10-30	71.23
SM15-30	67.70
SM20-30	67.47
SM25-30	58.10
SM30-30	59.82

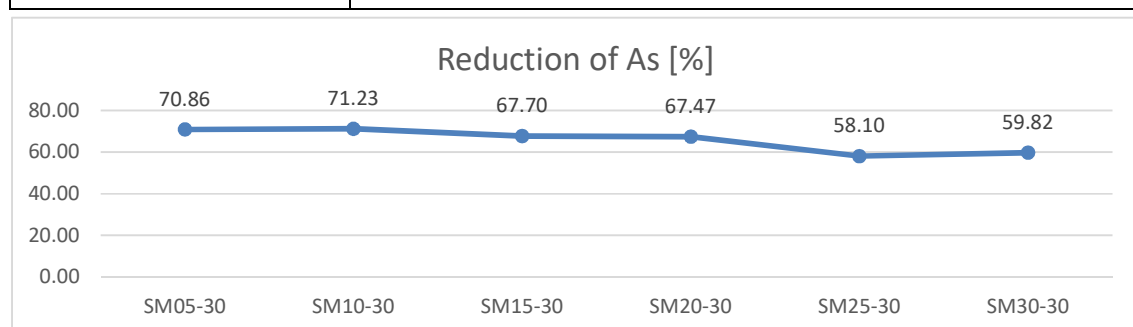


Figure 6.21 Reduction of Arsenic at 30 Days with different % of ALS of Combination 1

Table 6.29 Reduction of Arsenic at 60 Days with different % of ALS of Combination 1

Parameters	Reduction of As [%]
SM05-60	94.54
SM10-60	90.41
SM15-60	91.77
SM20-60	93.21
SM25-60	89.75
SM30-60	88.79

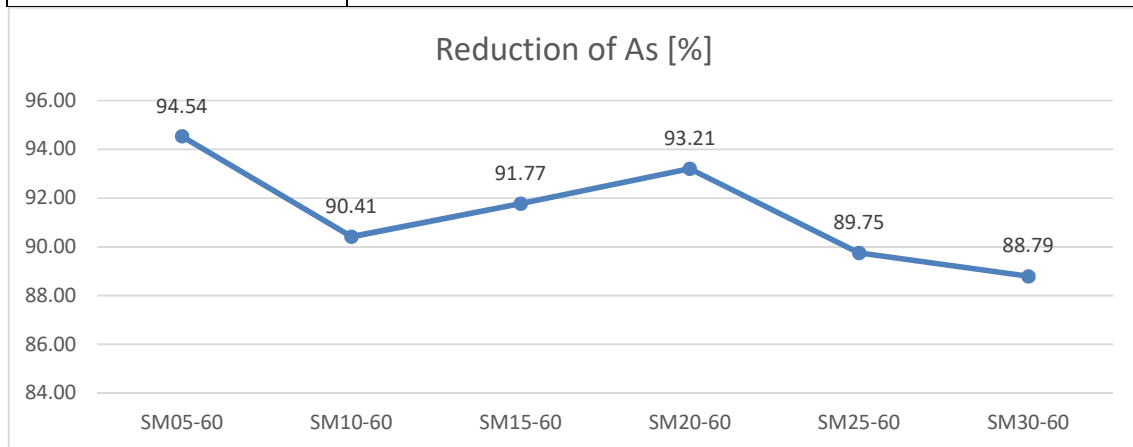


Figure 6.22 Reduction of Arsenic at 60 Days with different % of ALS of Combination 1

For Combination 2, the study observed the highest levels of arsenic removal in specific samples across different time intervals, highlighting the effectiveness of certain sludge concentrations in reducing arsenic levels:

At the 10-day interval, the samples identified as SC25-10 and SC30-10 showed the greatest arsenic reduction, achieving removal rates in the range of approximately 25-30%. This early result indicates that higher sludge concentrations, specifically 25% and 30%, are effective in initiating substantial arsenic removal within a short period, possibly due to enhanced contact between the arsenic and the active components of the sludge.

By 20 days, there was a significant improvement in arsenic removal efficiency, particularly in the samples SC25-20 and SC30-20. The removal rates escalated dramatically, reaching approximately 73-80%. This sharp increase suggests that as the digestion process continues, the conditions within the sludge become more favourable for the breakdown and removal of arsenic, especially at these higher concentrations.

At the 30-day mark, the maximum arsenic removal was recorded in samples SC05-30, SC25-30, and SC30-30, with efficiencies ranging between 82-88%. The data from this interval shows that even lower concentrations, such as 5%, began to achieve significant removal rates when given a longer time to act. However, the highest concentrations (25% and 30%) still demonstrated superior performance, indicating a strong correlation between sludge concentration and removal efficiency over time.

After 60 days, the samples SC05-60, SC25-60, and SC30-60 achieved the highest arsenic removal rates observed in the study, with efficiencies between 96-98%. This result demonstrates that extended digestion periods greatly enhance arsenic removal, especially in samples with higher sludge concentrations. The consistent performance of the 25% and 30% concentrations across all time periods suggests these are the most effective for achieving maximum arsenic reduction in anaerobic conditions.

These findings illustrate a clear trend of progressively increasing arsenic removal efficiency over time, particularly for samples with higher sludge concentrations (25% and 30%). The data suggests that the effectiveness of arsenic removal is not only a function of time but also

significantly influenced by the concentration of arsenic-laden sludge in the composite mixture. Higher concentrations provide more binding sites and reactive surfaces, which likely facilitate the breakdown and removal of arsenic compounds. Thus, for optimal results in treating arsenic-laden sludge, both the concentration of sludge and the duration of treatment are critical factors to consider.

Table 6.30 Reduction of Arsenic at 10 Days with different % of ALS of Combination 2

Parameters	Reduction of As [%]
SC05-10	4.72
SC10-10	6.56
SC15-10	1.10
SC20-10	15.94
SC25-10	32.18
SC30-10	26.70

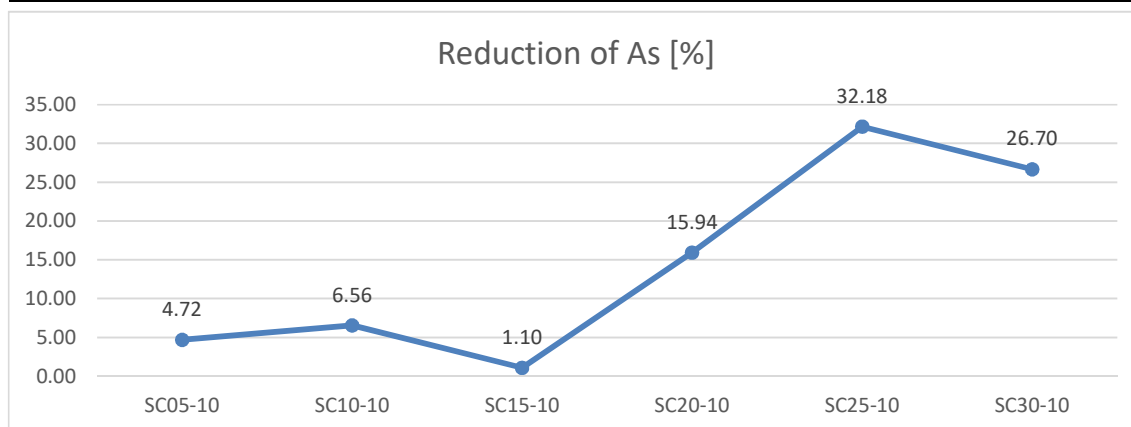


Figure 6.23 Reduction of Arsenic at 10 Days with different % of ALS of Combination 2

Table 6.31 Reduction of Arsenic at 20 Days with different % of ALS of Combination 2

Parameters	Reduction of As [%]
SC05-20	49.18
SC10-20	56.70
SC15-20	37.61
SC20-20	48.38
SC25-20	73.86
SC30-20	80.04

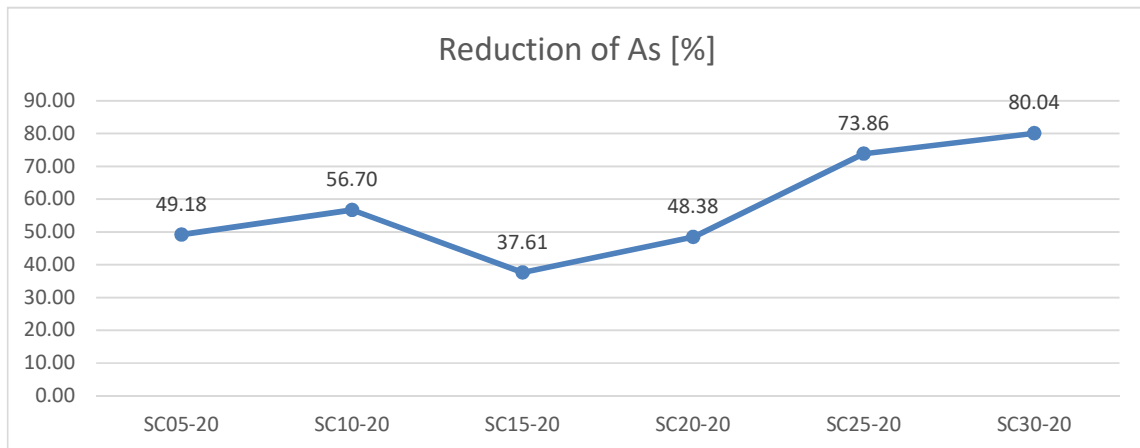


Figure 6.24 Reduction of Arsenic at 20 Days with different % of ALS of Combination 2

Table 6.32 Reduction of Arsenic at 30 Days with different % of ALS of Combination 2

Parameters	Reduction of As [%]
SC05-30	88.20
SC10-30	75.39
SC15-30	76.87
SC20-30	75.56
SC25-30	82.82
SC30-30	87.05

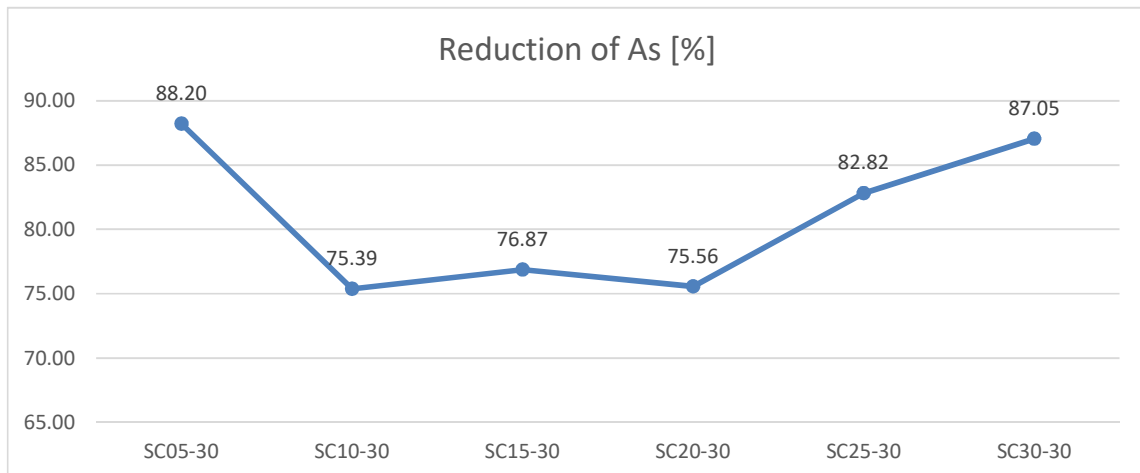


Figure 6.25 Reduction of Arsenic at 30 Days with different % of ALS of Combination 2

Table 6.33 Reduction of Arsenic at 60 Days with different % of ALS of Combination 2

Parameters	Reduction of As [%]
SC05-60	98.19
SC10-60	96.35
SC15-60	93.00
SC20-60	88.12
SC25-60	97.26
SC30-60	96.04

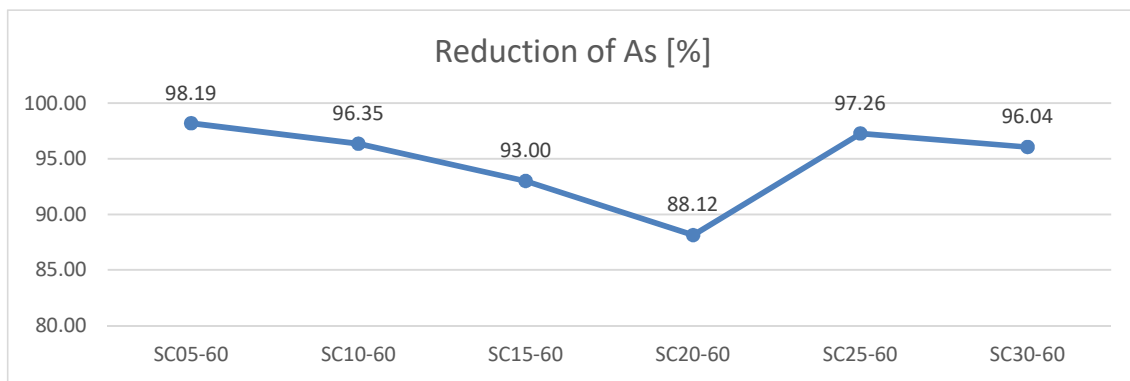


Figure 6.26 Reduction of Arsenic at 60 Days with different % of ALS of Combination 2

For Combination 3, the study found that the maximum arsenic removal occurred at different time intervals, with varying efficiencies depending on the sludge concentration used in the samples:

At the 10-day mark, the samples labelled SS10-10 and SS25-10 exhibited the highest arsenic removal rates, achieving approximately 24-25%. This indicates that even within a relatively short period, samples with 10% and 25% sludge concentrations were effective in initiating the arsenic removal process. The moderate levels of removal suggest that the early stages of treatment benefit from these specific concentrations, likely due to optimal conditions for initial arsenic adsorption or binding.

After 20 days, there was a notable increase in arsenic removal efficiency, particularly in the samples SS05-20 and SS10-20. These samples showed removal efficiencies ranging from 48-53%. This significant rise suggests that as the anaerobic digestion process progresses, the sludge environment becomes more conducive to breaking down or binding arsenic compounds, especially at 5% and 10% concentrations. The results from this interval reflect a critical phase where the ongoing reactions within the sludge are increasingly effective at reducing arsenic levels.

At the 30-day interval, the highest removal rates were observed in samples SS05-30, SS20-30, and SS30-30, reaching efficiencies between 68-70%. The data from this period highlights that both lower (5%) and higher concentrations (20% and 30%) are effective in arsenic removal when given sufficient time. The ability of the sludge to maintain and enhance removal rates at both ends of the concentration spectrum suggests a dynamic interaction between the sludge constituents and arsenic compounds, possibly involving both adsorption and microbial transformation processes.

By the 60-day mark, the samples SS05-60, SS10-60, and SS20-60 achieved the highest arsenic removal efficiencies, ranging from 88-90%. This final phase demonstrates that extended treatment durations are crucial for maximizing arsenic removal, particularly for samples with moderate sludge concentrations (5%, 10%, and 20%). The consistent increase in efficiency over time and across these specific concentrations indicates that prolonged exposure to anaerobic

conditions enhances the breakdown or stabilization of arsenic compounds within the sludge matrix.

These findings indicate a clear trend of progressively increasing arsenic removal efficiency over time, with specific sludge concentrations showing the most significant improvements across different intervals. The data suggests that both time and the concentration of arsenic-laden sludge play vital roles in optimizing removal rates. The variation in performance across different concentrations and time points highlights the complex interplay between chemical and biological processes within the sludge, where both adsorption and microbial degradation may contribute to the overall arsenic removal. Thus, for optimal treatment strategies, a careful balance of sludge concentration and treatment duration is essential to achieve the highest arsenic reduction in anaerobic conditions.

Table 6.34 Reduction of Arsenic at 10 Days with different % of ALS of Combination 3

Parameters	Reduction of As [%]
SS05-10	21.32
SS10-10	24.12
SS15-10	24.08
SS20-10	25.38
SS25-10	23.49
SS30-10	24.43

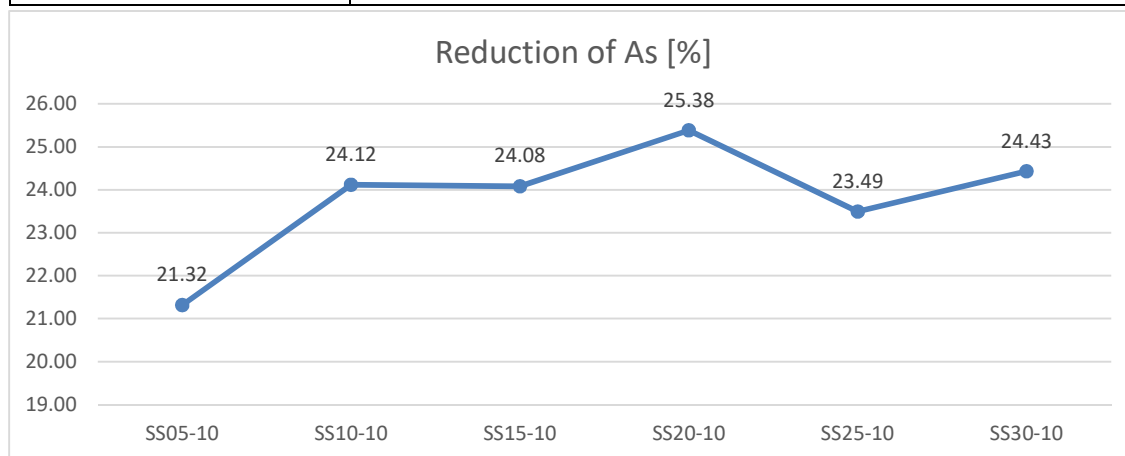


Figure 6.27 Reduction of Arsenic at 10 Days with different % of ALS of Combination 3

Table 6.35 Reduction of Arsenic at 20 Days with different % of ALS of Combination 3

Parameters	Reduction of As [%]
SS05-20	48.76
SS10-20	53.32
SS15-20	44.35
SS20-20	43.47
SS25-20	43.97
SS30-20	43.87

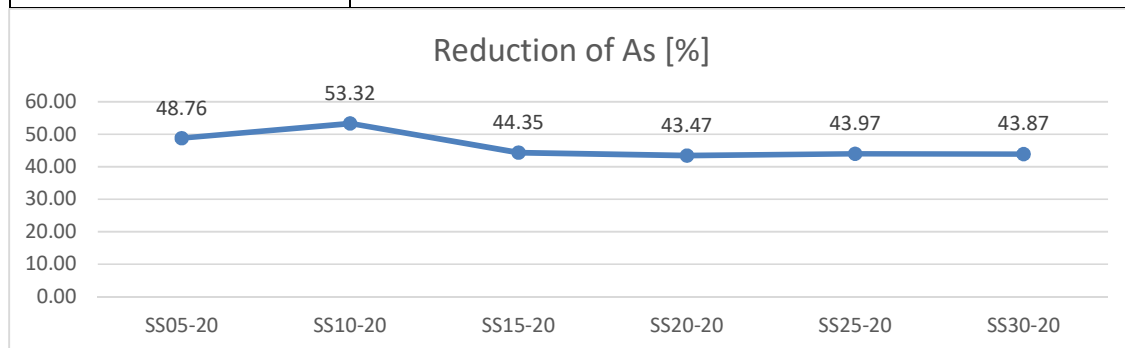


Figure 6.28 Reduction of Arsenic at 20 Days with different % of ALS of Combination 3

Table 6.36 Reduction of Arsenic at 30 Days with different % of ALS of Combination 3

Parameters	Reduction of As [%]
SS05-30	68.80
SS10-30	66.04
SS15-30	64.16
SS20-30	68.71
SS25-30	66.21
SS30-30	70.32

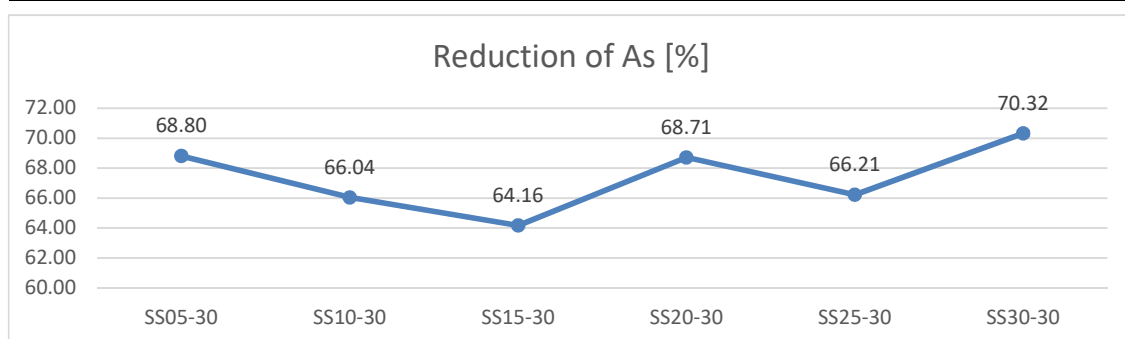


Figure 6.29 Reduction of Arsenic at 30 Days with different % of ALS of Combination 3

Table 6.37 Reduction of Arsenic at 60 Days with different % of ALS of Combination 3

Parameters	Reduction of As [%]
SS05-60	88.47
SS10-60	90.53
SS15-60	85.04
SS20-60	89.75
SS25-60	86.63
SS30-60	85.96

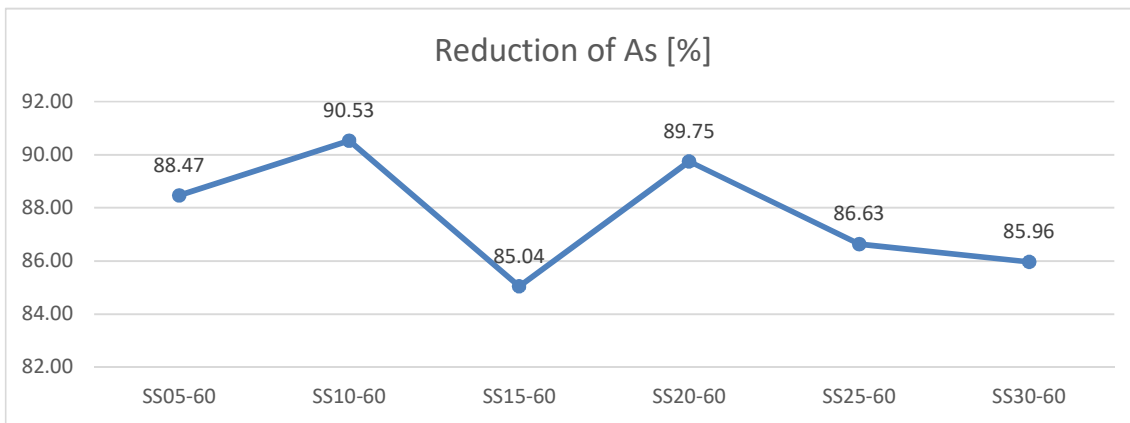


Figure 6.30 Reduction of Arsenic at 60 Days with different % of ALS of Combination 3

7 CONCLUSIONS

The treatment of hazardous, arsenic-laden inorganic sludge from water treatment plants can be effectively managed through anaerobic digestion when combined with a mixture of composite Cow Dung and Septic Sludge.

Key findings from this study include:

Efficiency of Digestion: When arsenic-laden sludge is mixed with composite organic waste sludge, it can undergo effective anaerobic digestion. However, introducing a high concentration of arsenic-laden sludge (ALS) into the feed slurry can disrupt bacterial growth, impairing both the methanization process and overall digestion efficiency. The presence of arsenic-laden inorganic sludge from arsenic removal water plants (ARWP) can further detract from the digester's performance compared to digesting organic composite waste sludge alone. This suggests that while organic waste promotes the breakdown process, the inorganic arsenic content poses significant challenges that necessitate meticulous management.

Arsenic Removal Efficiency: The study achieved a maximum arsenic removal rate of 98.19% with a feed containing 5% ARP sludge relative to the total Cow Dung slurry and maximum arsenic removal rate of 94.54% with a feed containing again 5% ARP sludge relative to the total composite waste feed slurry with septic sludge and cow dung over a digestion period of 60 days. This high removal rate demonstrates the potential of anaerobic digestion in significantly reducing arsenic levels in mixed waste streams.

Biogas Production: The production of biogas during a digestion period of the experiments highlights the impact of arsenic-laden sludge on the microbial activity within the digester, potentially influencing the efficiency of biogas generation. To effectively release the produced biogas, it is necessary to install a tall vent pipe at the experiment site. This setup ensures that the biogas, which may contain arsine gas, is adequately discharged into the air. The height of the vent pipe facilitates the dispersion of the gas, minimizing the risk of accumulation and allowing for its safe diffusion into the atmosphere.

Regulatory Compliance: we have to ensure the safe disposal of arsenic while maintaining compliance with environmental standards.

Mechanism of Arsenic Removal: The pathway for arsenic removal in the anaerobic digestion process is likely attributed to the formation of dimethyl arsine, although this compound was not directly measured in this study. Additionally, under anaerobic conditions, particularly in the presence of hydrogen, arsenic may be reduced to arsine gas, which can further facilitate its removal from the sludge.

Practical Applications: In regions affected by arsenic contamination, this method of sludge management could be effectively implemented by disposing of ARP sludge in manure pits, pit latrines, or cow dung-based biogas plants in rural areas. In semi-urban and urban settings, ARP sludge could be processed in septic tanks or STP digesters, offering a viable and sustainable approach to managing arsenic-laden waste.

This comprehensive approach to sludge management not only addresses the environmental and health risks associated with arsenic but also promotes sustainable practices in waste treatment and resource recovery. Moving forward, we will certainly explore additional combinations and various types of arsenic-laden sludge (ALS) with different concentrations to identify the most effective formulation.

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9 ANNEXTURE

WHO - World Health Organization

ALS- Arsenic-laden sludge

ROS- Reactive oxygen species

AIRPs- Arsenic and Iron Removal Plants

CWFS- Composite waste feed slurry

VFA- Volatile Fatty Acids

BOD- Bio-Chemical Oxygen Demand

COD- Chemical Oxygen Demand

DO- Dissolved Oxygen

MMA - Monomethylarsonous Acid

DMA - Dimethylarsinous Acid