
**Arsenic Contamination in Groundwater and Possible Mitigation
Using Suitable Eco-friendly Approaches: A Study in Selected
Endemic Areas of West Bengal, India**

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**Arsenic Contamination in Groundwater and Possible Mitigation
Using Suitable Eco-friendly Approaches: A Study in Selected
Endemic Areas of West Bengal, India**

A thesis

Submitted in partial fulfillment of the requirements for the award of the degree of

M. Tech in Environmental Biotechnology

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By

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DECLARATION

I hereby declare that the work presented in this thesis report titled “**Arsenic contamination in groundwater and possible mitigation using suitable eco-friendly approaches: A study in selected endemic areas of West Bengal, India**” submitted to Jadavpur University, Kolkata- 32, in partial fulfillment of the requirements for the award of the degree of M. Tech is a bonafide record of the research work carried out under the supervision of Dr. Tarit Roychowdhury and co-supervision of Dr. Subarna Bhattacharyya. The contents of the Thesis report in parts, have not been submitted to and will not be submitted by me to any other Institute or University in India or abroad for the award of any degree or diploma.



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CERTIFICATE

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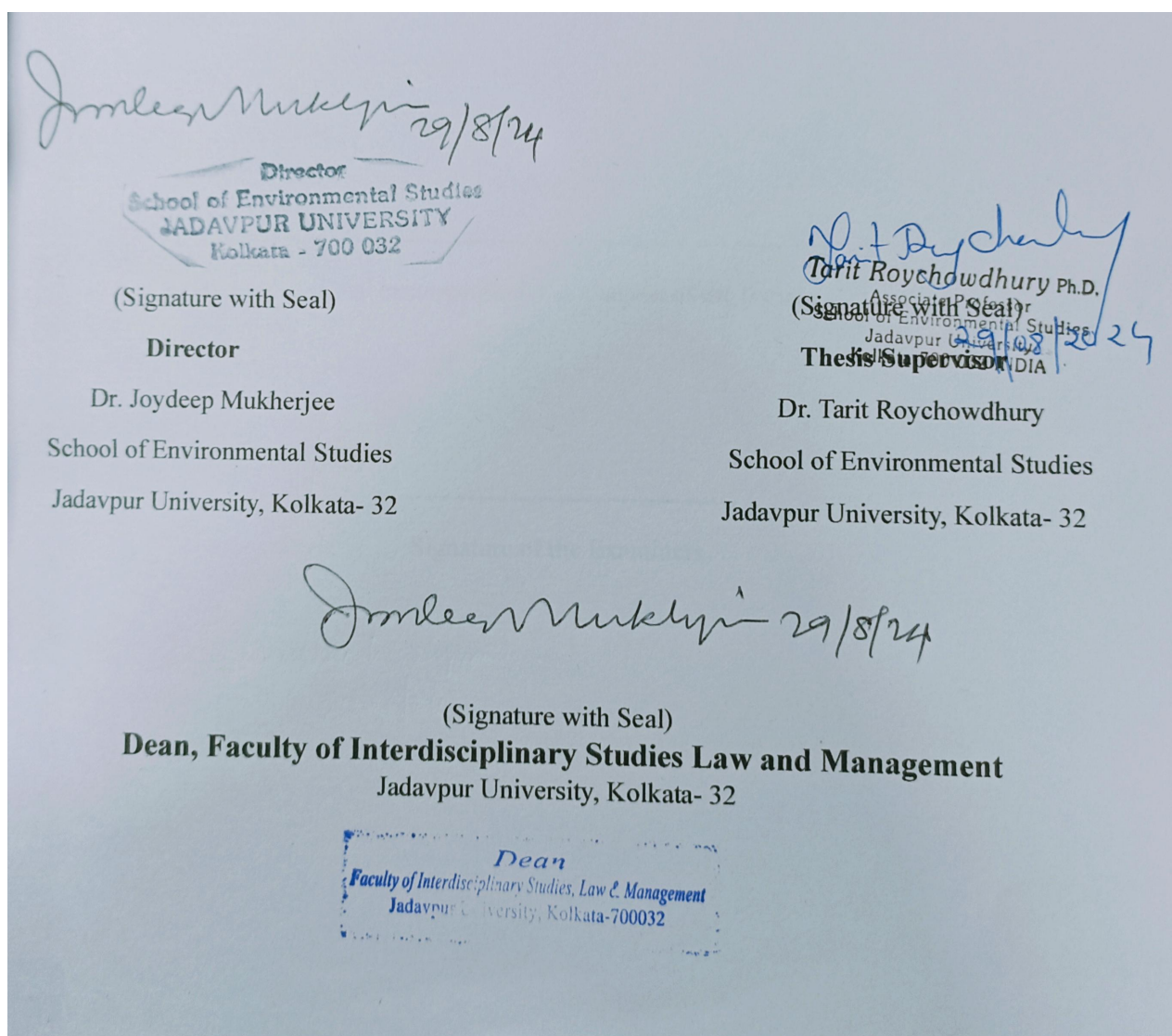
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TO WHOM IT MAY CONCERN

It is hereby notified that this thesis titled “Arsenic contamination in groundwater and possible mitigation using suitable eco-friendly approaches: A study in selected endemic areas of West Bengal, India”, is prepared and submitted for the partial fulfillment of the continuous assessment of Master of Technology in Environmental Biotechnology course of Jadavpur University by Sushmita Baidya (002230904006), a student of the said course for session 2022-2024. It is also declared that no part of this thesis has been presented or published elsewhere.



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Final examination for evaluation of the thesis

Signature of the Examiners

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ABSTRACT

88 available water samples from two gram-panchayats of the Bangaon subdivision were examined for 15 physicochemical parameters to evaluate the groundwater quality. 85% of the samples from Chowberia-I and 89% of the samples from Kalupur were found unsuitable for drinking, according to the Water Quality Index (WQI) modeling. The average range of anionic concentrations in groundwater appears to be $\text{HCO}_3^- > \text{Cl}^- > \text{CO}_3^{2-}$, which indicates that the water quality of the Bangaon is generally alkaline due to bicarbonate alkalinity. Calcium ion concentration (mean: 71.9 mg/L and 68.5 mg/L in Chowberia-I and Kalupur, respectively) prevailed over magnesium ion concentration (mean: 49.8 mg/L and 94 mg/L in Chowberia-I and Kalupur, respectively) which was determined for hardness. Both of the studied regions' groundwater is tainted with arsenic (As), with Kalupur having the highest quantity at 191 $\mu\text{g/L}$. Future cancer risk and non-carcinogenic health problems are highly likely due to As, as the C.R. value exceeds the relevant acceptability threshold for each of the studied regions. Elevated levels of As in water pollution pose serious health concerns to people, with the potential to induce both cancer and non-cancerous disorders. It is still difficult to remove arsenic from water effectively. To specifically remove total As (III + V) from water, this work produced green synthesized Fe-NPs using date seed powder. The removal effectiveness was 81.8% when the ideal parameters were met i.e., 180 rpm agitation, 120 min, pH 7, 1000 $\mu\text{g/L}$ starting concentration, 1 g/L adsorbent dosage. The highest absorption capacity was found to be around 818 $\mu\text{g/g}$ after adsorption isotherm models were examined. The pseudo-second kinetic model ($R^2 = 0.99$) best fitted the kinetic data and the chemisorption process of As adsorption onto iron nanoparticles was further validated by the amount of activation energy. However, general awareness, continuous maintenance, and monitoring are needed to achieve long-term safe water in respect to meet sustainable development goals.

Keywords – Arsenics contamination; Groundwater; Health risk; Arsenic removal; Suitable approaches

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CHAPTER 1: INTRODUCTION

A healthy lifestyle requires access to clean, potable water. According to the “United Nations World Water Development Report” (2015), groundwater provides 50% of all municipal water sources globally (Lezier et al., 2017), which is the primary source of drinking water for approximately 2.5 billion people worldwide (Amprako, 2016). Besides being essential for human consumption, groundwater is also necessary for maintaining ecosystems and agro-economic action (Giordano, 2009). In India, 30% of city inhabitants and over 90% of the population live in rural regions that receive water from reservoirs (Adimalla et al., 2022) for agriculture and drinking. Studies show that overuse of this resource has rendered around 33% of the nation's subterranean water sources unfit for human use (Chakraborti et al., 2010). This explains why illnesses transmitted by water are responsible for around 80% of human disorders (Das et al., 2020). The current agricultural methods pose a severe threat to human health, especially when it comes to the overuse of fertilizers, agricultural runoff, unpleasant circumstances, and the dumping of sewage into subsurface water (Panigrahi et al., 2012). The subsurface environment, seasonal variations, leached dissolved salts, and water depth may all impact the overall quality of groundwater (Ram et al., 2021). Along with inherent substances such as dissolved minerals and metals, anthropogenic chemicals, diseases, and microbes can also taint water quality which can destroy aquatic life, render water unsuitable for human use in industry or agriculture, and make it unpotable. The impacts of groundwater pollution can harm not just water supply wells and aquifers, but also surface water sources as they move toward rivers and lakes, thereby causing harm to the environment (Das et al., 2021; Taki et al., 2003).

Among the environmental disasters, the pollution of groundwater with arsenic (As) is naturally unearthed from its sediments (Chakraborti et al., 2013). Albertus Magnus made the discovery of As, a harmful metalloid with an atomic number of 33 and an atomic weight of 74.922. It is located in the 15th group of the

4th period of the periodic table (Uddin et al., 2020). This metalloid can be found in both oxidizing as well as reducing environments (Ni et al., 2016). Mainly, it is due to the oxidative dissolution of As-rich iron pyrite and the reductive dissolution of As-rich iron oxyhydroxide. The most widely accepted theory is that As is mobilized by the microbial decomposition of FeOOH in a reducing environment. This theory is further reinforced by some significant connections between dissolved As and Fe, methane, and ammonia in groundwater (Chakraborty et al., 2015). The Ganga Meghna Brahmaputra (GMB) plain populace, especially in India, is under constant threat from natural groundwater As poisoning (Chakraborti et al., 2018; Goswami et al., 2020). Many countries throughout the world, including the USA, Germany, Argentina, Bangladesh, Cambodia, China, Hungary, India, Mexico, Nepal, Pakistan, Romania, Vietnam, and the USA, have groundwater containing arsenic compounds at levels that are harmful to human health. Several West Bengal districts have been badly impacted, including Purba Bardhaman, Paschim Bardhaman, North 24 Parganas, South 24 Parganas, Hooghly, Nadia, and Maldah (Das Gupta and Shaw, 2014). The local populace from all these regions exhibits higher doses of As intake in their drinking water than the WHO's recommended limit of 10 µg/L (He et al., 2020).

Prolonged exposure to As contaminated groundwater can have adverse impacts on one's health, suppressing the immune system and boosting the risk of getting certain cancers, including kidney, lung, skin, and bladder cancers, as well as other medical conditions like diabetes, pulmonary diseases, cardiovascular diseases, keratosis, and issues with skin pigmentation (Guo et al., 2008; Rehman et al., 2020; Sanjrani et al., 2019). After absorption, As is notably accumulated in reserve in the heart, lungs, liver, and kidney. Muscles and neural tissues have a lower concentration of As (Singh et al., 2011). According to Goswami et al. (2020), methylation of arsenic is primarily influenced by the dose, form, and route of exposure as well as the exposed person's dietary history. A major factor in As toxicity is its metabolism, which is responsible for blocking around 200 enzymes that are involved in DNA synthesis and repair, cellular energy routes, and

other processes. This induced toxicity can be prevented by consuming a nutritious diet that includes vitamin C, α -tocopherol, flavonoids, polyphenols, and anti-toxic micronutrients like zinc (Zn) and selenium (Se) (Das et al., 2021; Rahman et al., 2019). For example, adequate consumption of Se produces more glutathione sulfhydryl (GSH) in the body, which counteracts free radical damage produced by As, which in turn maintains good health (Steinbrenner and Sies, 2009).

It had been thought that the shallow-depth aquifer's groundwater was more polluted with As than the deeper tube wells (Chakraborti et al., 2009; Das et al., 2024). But because of the depletion of groundwater, As has seeped into deep levels of the aquifers, contaminating the deep aquifers. Roughly 51.4% and 17.3% of the tube wells in the 17 blocks of Nadia district had As levels over 10 and 50 $\mu\text{g/L}$, respectively, indicating that groundwater in these blocks is contaminated with As (Rahman et al., 2014), which makes the water unpotable for human consumption. 50% of the tube-well in the Bangaon sub-division of the North 24 Parganas district exceeded the WHO drinking water standard of 10 $\mu\text{g/L}$, values varied from less than 10 $\mu\text{g/L}$ to 160 $\mu\text{g/L}$ (Bacquart et al., 2012). To address the As pollution in drinking water, several mitigation techniques have been implemented thus far. These include the use of pipeline water supply after appropriate treatment, the construction of new, relatively deeper hand pumps, the development of multiple As removal facilities, the drilling of wells, etc. (Halder, 2019). Yet, in remote border areas where pipeline infrastructures are impractical due to budgetary and logistical constraints, hand-pumped tube wells continue to serve as the principal source of drinking water (Jesoe, 2013; Sultana, 2011). This explains why it is now imperative to treat groundwater using low-cost, environmentally friendly, and sustainable methods to safeguard the health of at-risk people in the countryside. Groundwater may be treated to remove As using diverse methods, including membrane-based processes, ion exchange, and more conventional techniques, including adsorption followed by filtration, oxidation, coagulation, and co-precipitation.

Nonetheless, due to ignorance; lack of access to clean water, and reluctance to contribute to the costs of a community clean water supply program which is seen to be essential to the operation of an efficient sustainable approach, many people continue to use As-contaminated water. Thus, maintaining and monitoring overall water quality has become significant for safeguarding ecosystems and public health. Several physical (pH, temperature, total solids, color, conductivity, turbidity, odor) and chemical (alkalinity, acidity, total iron (Fe), phosphate, hardness, chloride, fluoride, As), tests are used to assess water quality. Scientists, responsible authorities, and environmental organizations can ascertain if water bodies satisfy regulatory criteria and locate possible sources of pollution by analyzing these parameters. Additionally, studies have indicated that knowledge and awareness help develop legislation in places where As-induced health problems are common.

CHAPTER 2: LITERATURE REVIEW

2.1. Biochemistry and different forms of arsenic

In the current periodic table, As (Latin: Arsenicum) is a metalloid compound classified in Group 15 (VA) and Period 4 between germanium and selenium. It is mostly found in three allotropic forms: metallic gray, black, and yellow. The most prevalent one is the gray one. As has 33 isotopes ranging from ^{60}As to ^{92}As , among these ^{75}As is the most stable form which makes it a monoisotopic compound in nature (Binkowski et al., 2019). There are four possible oxidation states for As in the environment: +V (arsenate), +III (arsenite), 0 (arsenic), and -III (arsine) (Sharma et al., 2009).

Table 1. Chemical properties of arsenic (Binkowski et al., 2019)

Atomic number	33	Melting Point (°C)	817
Atomic weight	74.922	Boiling Point (°C)	615
Oxidation numbers	(+)3, (+)5, 0, (-)3	Electronegativity (Pauling)	2.18
Density at 20°C (g/cm ³)	5.73	Heat of fusion (kJ/mol)	24.44
Electronic Configuration	[Ar]3d ¹⁰ 4s ² 4p ³	Radius: covalent (Å°)	1.19
1 st Ionization Energy (kg/mol)	947	Radius: Ionic (Å°)	0.72
Heat of vaporization (kJ/mol)	32.4	Critical temperature (atm)	1,427

Numerous kinds of As are available, but the two most common types are organic and inorganic compounds. Among these two inorganic forms of As are more toxic. Trivalent As (As^{3+} , Arsenite) and pentavalent As (As^{5+}), the two most prevalent types of As found in natural water bodies, are both extremely hazardous inorganic species (Singh et al., 2011). Some other inorganic As compounds are monomethyl arsinic (MMA) $[(\text{CH}_3\text{As}(\text{O})(\text{OH})_2)]$; dimethyl arsonic (DMA) $[(\text{CH}_3)_2\text{As}(\text{OH})]$; sodium arsenite, etc. Organic As

compounds, including arsenochlorine; arsenobetaine; and arsenosugars, which are non-carcinogenic, are found in marine environments. The toxicity of As is arranged in the following manner:

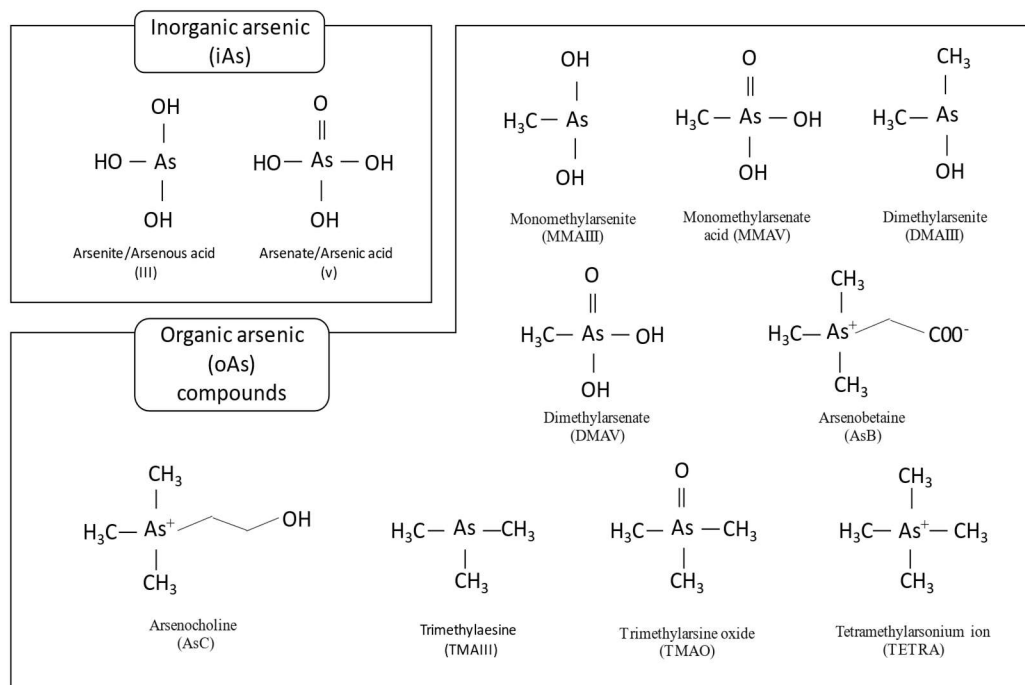
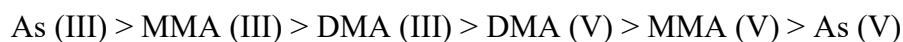


Fig. 1. Chemical structures inorganic and organic arsenic compounds

2.2. Occurrence, distribution, and sources of arsenic

It is omnipresent in the Earth's crust and makes up around 0.00015% of it, along with soil, air, water, and sediments (Chen et al., 2021). Thus, it can penetrate groundwater through the weathering of rocks and minerals. Major arsenic-containing minerals include realgar (AsS), cobaltite (CoAsS), orpiment (As₂S₃), arsenolite (As₂O₃), and arsenopyrite (FeAsS). It can also be entrapped in sulfide, iron, silicate, nickel, and carbonate-containing minerals such as quartz (SiO₂), magnetite (Fe₃O₄), and pyrite (FeS₂), among others. Other anthropogenic sources include burning fossil fuels, arsenical pesticides, herbicides, fertilizers, and

industrial and animal waste. Due to the trace amounts of pyrite found in sulfide-rich coals, burning coal can also increase the amount of As in the atmosphere (Neumann et al., 2010; Pacyna and Pacyna, 2001).

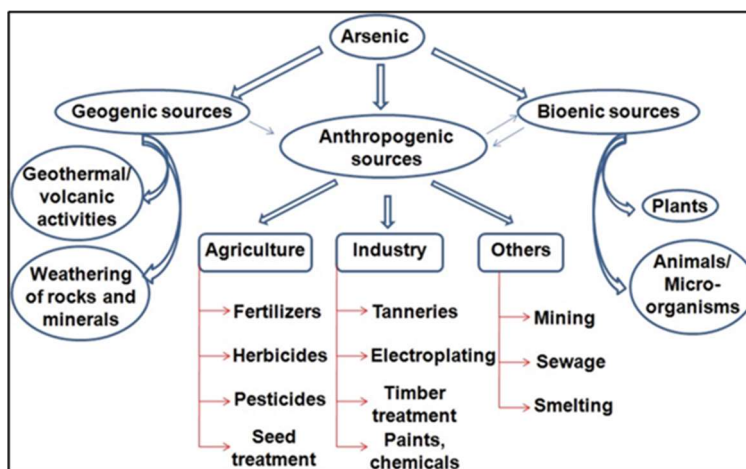
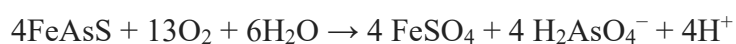


Fig. 2. Different sources of arsenic in groundwater (Hare et al., 2019)

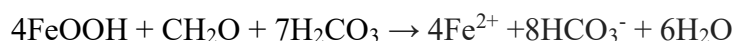
2.3. Arsenic mobilization in groundwater

The presence of As in natural water bodies has drawn a lot of interest in the last several years. According to WHO standards, the regulation limit for As in drinking water is normally 10 µg/L, with a maximum allowable content of 50 µg/L still in effect in a few countries. There are trace amounts of organic As in natural waterways whereas, the most prevalent species are inorganic As species, such as arsenite [As (III)] and arsenate [As (V)] (Herath et al., 2016). The intricate biogeochemical interactions that are influenced by an array of chemical, psychological, and natural factors—such as sedimentological settings, sedimentation history, groundwater abstraction, particle adsorption along with desorption actions, dissolved organic carbon, and microbes—are primarily responsible for the processes of As mobilization (Bhowmick et al., 2013; Nath et al., 2009). It is evident that the concentration of As increases somewhat when nitrate; sulfate concentrations decrease and pH is lower in groundwater which implies that reduced conditions within the aquifer system are linked to elevated As concentrations (Kar et al., 2010). The following are the mechanisms resulting in the release of As into groundwater:

- i. **Pyrite Oxidation Theory (group from Jadavpur University, Calcutta):** The oxidation of arsenopyrite led to the release of As into groundwater, confirming the underlying theory of pyrite oxidation. It is known that when the water table is lower than these deposits, atmospheric oxygen gets into the aquifers and diffuses into the pore space and groundwater, facilitating this process. As a result, the groundwater was exposed to a water-soluble form of As that was produced by the interaction between the arsenopyrite and the available oxygen (Chakraborti et al., 2003; Chowdhury et al., 1999; Singh et al., 2006).



- ii. **Theory of iron oxyhydroxide reduction (group from University College London):** After being abrasively transported down the Ganges, rocks containing As adhered to iron oxyhydroxide (FeOOH). An alluvial aquifer was created near the Gangetic Delta by the deposits of iron oxyhydroxides that were high in As. The aquifer received organic carbon via a variety of activities, including agriculture, flooding, and the burial of plants. Because of the organic carbon that served as food for the bacteria, the aquifer's anaerobic bacteria are using the organic matter, as evidenced by the methane that is present in the water. As so, this biological activity lowers the groundwater's redox potential. This reducing environment causes the iron oxyhydroxide to decompose, which allows absorbed As to enter the groundwater.



- iii. **Arsenic is exchanged competitively with other suitable ions, such as nitrate, phosphate** (Chowdhury et al., 1999), and bicarbonate (Nickson et al., 2000).

2.4. Arsenic contamination in groundwater

2.4.1 International status/ worldwide scenario

Since the previous 20 years, one of the most significant problems worldwide has been groundwater pollution. Numerous investigations conducted on various aquifers throughout the globe have revealed As concentrations over 50 µg/L, which can undoubtedly result in serious health issues. The countries with the greatest levels of As pollution worldwide include Argentina, Hungary, Mexico, and several regions of the United States. Arsenic pollution is a serious risk in Southeast Asian countries such as Bangladesh, China, Nepal, Vietnam, and India (Ali et al., 2019). Australia is the most As-contaminated nation in the world; concentrations of As have been recorded as high as 300 mg/L. Major sources of As release into groundwater have been identified as mineral extraction, weathering of sulfide-bearing rocks, and volcanic activity (Boyle et al. 1998). An arsenic concentration of 100 mg/L was found in groundwater from Canada, mostly contaminated due to geothermal springs and mining operations under oxidizing circumstances (Kim et al., 2002). Approximately 43% and 27%, respectively, of the over 50,000 hand tubewell water samples evaluated throughout every one of the 64 districts of Bangladesh had As concentrations over 10 µg/L and 50 µg/L, (Chakraborti et al., 2004). About 30 million individuals in Bangladesh are being exposed to 50 µg/L of As-contaminated water because of the naturally occurring high levels of As in the country's groundwater (Kinniburgh & Smedley 2001). Despite subsurface systems in Thailand not yet being shown to contain arsenic, adjoining surface contamination from metallic mineral extraction has resulted in a considerable amount of As. According to analyses, the amounts of dissolved As in surface and groundwaters in Thailand are up to 500 times higher than what is considered acceptable for human health which can cause skin and internal organ malignancies (Herath et al., 2016). The most frequent source of As-rich sub-surface waters is assumed to be the dissolution of As from iron oxide that has been accumulated in aquifer sediments. One of the main sources of As released into the alkaline groundwater of the western United States of America has been identified as iron oxide, which is connected to igneous volcanic rocks and saline aquifers. Additionally, sulfide minerals may function as both a source and a reservoir for As (Cummings et

al., 1999; Islam et al., 2013). Table 2 shows As concentration of groundwater from different countries throughout the world. **Table 2** shows As concentration in groundwater from different countries throughout the world.

Table 2. Arsenic concentration in groundwater from different countries throughout the world

Serial Number	Country	Region	Source	Groundwater Arsenic level (µg/L)	References
1	Africa	Ghana, Tanzania, and Ethiopia	Sulfide minerals, iron oxides, gold mining	<1–141, upto 1760	Irunde et al., 2022; Smedley et al., 1996
2	Argentina	southwest of the Chaco-Pampean plain	Limestone sediments; embedded ash layers from volcanic eruptions; iron and manganese oxides	< 13–621	Mariño et al., 2020
3	Bangladesh	Comilla	reduction of iron and manganese oxyhydroxides	2 - 360	Saha et al., 2020
4	Brazil	lower Paraíba do Sul River	Abundance of sulfate and organic substances	0.13 - 38.8	Meneguelli-Souza et al., 2020
5	China	Shaanxi	outflow of sewage from factories and natural sediments	1.2 – 19	Zhang et al., 2019
6	India	West Bengal	Reductive breakdown of iron-oxyhydroxide, excessive groundwater abstraction	<3–213	De et al., 2022
7	Nepal	Nawalparasi-West/Parasi	clastic minerals produced from weathering, glaciers, or landslides	1048 (pre-monsoon); 529 (wet season)	Gyawali et al., 2022
8	Pakistan	Pind Dadan Khan	waterlogging, mineral extraction, pesticides, iron hydroxide and bi-carbonate minerals	0.5 - 100	Ullah et al., 2023
9	South Korea	Chungcheong Province	Mining, precipitation of sulfide minerals (e.g., orpiment; As ₂ S ₃)	50	Kim et al., 2023
10	Thailand	Lampang Basin	weathered rocks, co-precipitated Fe (III)-oxyhydroxides in sediments	10.7 [shallow groundwater]; 51.0 [deep groundwater]	Santha et al., 2022

2.4.2. National status/Indian scenario with special emphasis on West Bengal

India's household, industrial, and irrigational water demands are mostly dependent on groundwater, especially in the fertile alluvial districts of the Ganga and Brahmaputra rivers. Because of the substantial drops in the water table caused by extensive extraction in this region, groundwater is contaminated with As (Khan et al., 2016; Saha et al., 2019). On the other hand, the Deccan plateau region of the Indian subcontinent consists of hard rock aquifers which is another source of As in groundwater. In the gold-mineralized regions in Karnataka, As is associated with sulfide mineralization, particularly arsenopyrite whereas, in Chhattisgarh, As contamination is linked to acid volcanics (Shaji et al., 2021).

Especially, in West Bengal, groundwater intoxication with As was first documented in 1984 (Garai et al., 1984). At the Department of Dermatology, School of Tropical Medicine, K. C. Saha provided the first treatment of As poisoning in West Bengal in 1983 (Bhowmick et al., 2018). Alluvium sediments which are the result of erosion of Himalayan sediments containing sulfide minerals, are the geogenic source of As in West Bengal (Mukherjee et al., 2009). **Table 3** shows As concentration of groundwater from different states/UT of India focusing on different states of West Bengal.

Table 3. Arsenic concentration in groundwater from different states/UT of India focusing on different states of West Bengal

Serial Number	State/ Union Territory	Region	Source	Groundwater Arsenic level ($\mu\text{g/L}$)	References
1	Bihar	Patna, Saran, Vaishali	Holocene aquifers with Iron oxide films on clay and quartz rocks	2 - 780.1	Pal et al., 2023
2	Maharashtra	Mumbai (Malad landfill)	Landfill leachate	1800	Gani et al., 2024
3	Uttar Pradesh	Bahraich	Anthropogenic, geogenic (Alluvium Plain)	14.82	Singh et al., 2022
4	Assam	Majuli Island	Iron oxide minerals, Holocene rocks	137	Goswami et al., 2020
5	West Bengal	Nadia	Geogenic, agricultural runoff	350	Das et al., 2016
		Murshidabad	Weathered Arsenic bearing rocks, agricultural runoff	86 - 513 (pre-monsoon) and 59–431 (post-monsoon)	Mishra et al., 2022

		Kolkata	Reductive dissolution of FeOOH	825	Chakraborti et al., 2017
		South 24 Parganas	Dissolution of Arsenopyrite mineral	56.2	De et al., 2022
		North 24 Parganas (Gaighata block)	Aquifers rich in As-bearing minerals, excessive extraction of groundwater	154	Das et al., 2024
		Howrah	Geogenic, industrial discharge	275	Bhattacharya et al., 2018
6	Chhattisgarh	Rajnandgaon	Excessive amounts of dissolved organic carbon, and reductive ferric oxyhydroxides	150 - 990	Patel et al., 2017
7	Tamil Nadu	Tuticorin	Leachate of industrial waste, arsenic trioxide	0.87 - 84	Selvam et al., 2017

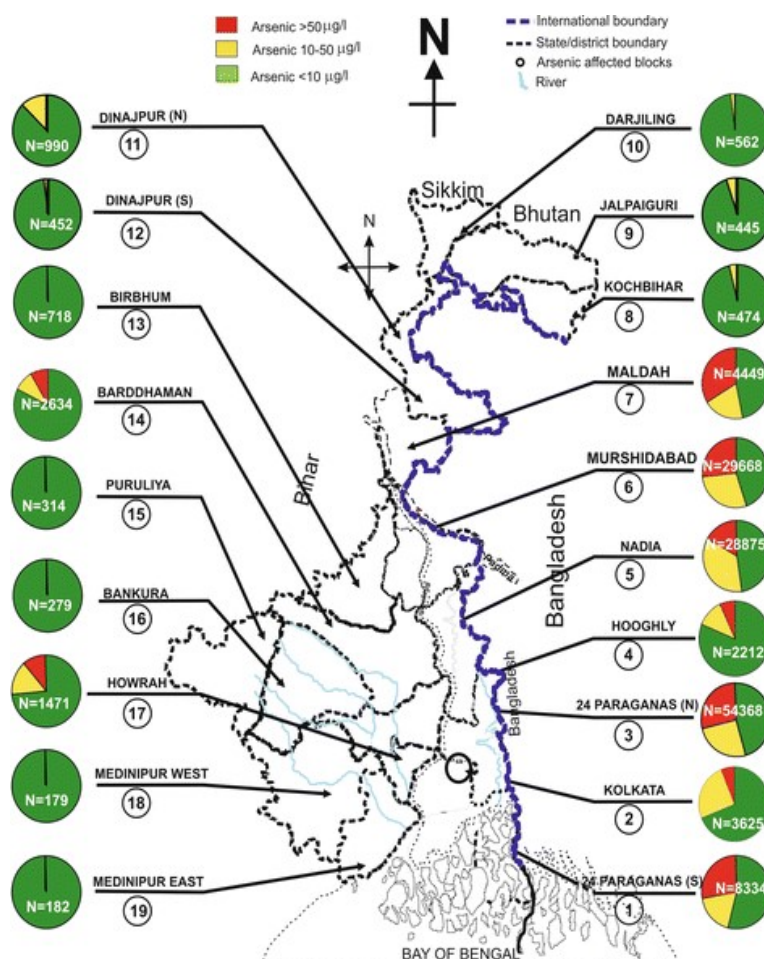


Fig. 3. Groundwater arsenic contamination status in West Bengal (Till 2009) (Chakraborti et al., 2009)

2.5. Different mitigation techniques for arsenic removal

When it comes to eliminating As from drinking water as well as groundwater treatment, many techniques are frequently used. These techniques are:

- Adsorption
- Oxidation
- Coagulation
- Biological treatment
- Ion exchange
- Membrane filtration
- Electrokinetic method
- Chemical precipitation

2.5.1. Adsorption: The process of molecules or particles adhering to a solid surface from a fluid state (gas, liquid, or dissolved solids) is known as adsorption. The material being adsorbed is known as the adsorbate, and this surface is commonly referred to as the adsorbent. This process can be done in two ways; physical adsorption (a non-specific weak force such as Van Der Waals force between adsorbent and adsorbate which is reversible and varies with temperature and pressure), chemical adsorption or chemisorption (stronger chemical bonds formation between adsorbate and adsorbent surface). The difference between physical adsorption and chemisorption is shown in **Table 4**. Adsorption isotherms provide insight into the study of the adsorption process. The key trend lines that define the processes controlling the adsorption or migration of compounds through a liquid state to a solid surface at an optimum temperature and pH are called adsorption isotherms (Sarkar et al., 2016). Freundlich, BET, and Langmuir isotherms are the most favored isotherm models (Chakraborty et al., 2012). Activated charcoal (Eguez et al., 1987), activated alumina grains (Lin et al., 2001), granular ferric hydroxide (Driehaus et al., 1998), iron oxide-coated sand (Gupta et al., 2005), red mud (Altundogan et al., 2002), aluminum alginate (Gupta et al., 2009), Portland cement (Kundu et al., 2004) and activated carbon doped with silver and copper (Jubinka et al., 1993) are some of the materials that are used as adsorbent in the context of arsenic adsorption. Nowadays, academics are becoming interested in using bio-adsorbents mostly from waste substances—like modified fly ash

(Pattanayak et al., 2000), coconut shell (Mohan et al., 2005), chitosan (Kwok et al., 2014), powdered eggshells (Oke et al., 2008), chicken feathers (Khosa et al., 2014), sugarcane straw (Soares et al., 2021), rice husk (Amin et al., 2006), flower petals (Upadhyay et al., 2023) and nanomaterials made of iron and oxides (Luther et al., 2012) or carbon nanotubes (Sankararamakrishnan et al., 2014) to remove As from contaminated water.

According to Goyal et al. (2022), aluminum oxides/hydroxides nanoparticles which were synthesized by electrolyzing aluminum electrodes in distilled water at a current density of 195 A/m² (Rathore et al., 2017), have shown effective simultaneous removal of As, with maximal Langmuir adsorption capacity 0.833 mg/g under the ideal working substances (pH 7, contact time 300 min, temperature 25 °C).

Chitosan, a non-toxic biopolymer made up of chitin that occurs naturally in the exoskeleton of crustaceans like crabs; and shrimps, has remarkable effectiveness in adsorbing arsenic ions due to the presence of amino (-NH₂) and hydroxyl (-OH) groups that enhance ion exchange, hydrogen bonding, and chelation. Its effectiveness is attributed to its hydrophilic nature, biocompatibility, biodegradability, and antibacterial qualities. The ability to absorb the molecules of this polymer is regulated by pH, mostly in acidic environments. Gupta et al. (2013). have shown the effective use of chitosan-Fe composites for As remediation.

Adsorption capacity depends on different variables, such as pH, temperature, agitation speed, starting concentration, adsorbent dose, and equilibrium duration. Using kinematic and equilibrium isotherm models, such as Langmuir, Freundlich, Temkin, D-R, and their analogs, single and competitive adsorption systems were examined. The competitive interactions, affinity, and adsorption capacity are clarified by these models. The ability of adsorbents to be utilized for both simultaneous and single-contaminant removal was confirmed by regeneration testing.

Table 4. Difference between physical adsorption and chemisorption (Aljamali et al., 2021; Rouquerol et al., 2013)

Property	Physical Adsorption	Chemisorption
The character of the bond	Weak van der Waals forces	Strong chemical bonds (covalent or ionic)
Adsorption Heat	20-40 kJ/mol	80-200 kJ/mol
Specificity and layer formation	Form non-specific multilayer	Form highly specific multilayer
Reversibility	Generally reversible	Generally irreversible
Correlation with temperature	Decreases with increasing temperature	Increases with increasing temperature until optimal point
Surface Interaction	No significant alteration of the adsorbent surface	May cause surface rearrangement or modification
Example	Adsorption of water vapor on silica gel, adsorption of gases like N ₂ , and O ₂ on activated carbon	Adsorption of oxygen on a silver (Ag) surface, adsorption of carbon monoxide (CO) on palladium (Pd)

Table 5. Comparison between the adsorption capacities of various adsorbents

Sl. No	Adsorbent material	Adsorption capacity (mg/g)	Mechanism	References
1	Fe (III) oxide-hydroxide and charcoal	As (III) -0.72	Porous surface area and formation of inner-sphere complexes	Hossain et al., 2023
2	municipal solid waste and KOH mixed municipal solid waste biochar	24.49 and 30.98	Porous surface area	Srivastav et al., 2022
3	graphene oxide-iron nanohybrid	As (V)-431, As (III) -306	Redox reactions	Das et al., 2020
4	Fly Ash agglomerates	5.7	Binding with reactive sites and minerals	Ulatowska et al., 2014
5	activated laterite	32.5	Ion exchange and surface complexation	Mondal et al., 2017
6	Poly (Zirconyl dimethacrylate)	As (V)- 4.26, As (III)-4.22	Forming an inner-sphere complex with ZrOH	Gupta et al., 2024
7	Fe-Bentonite	0.5637	Increasing adsorption sites	Meena et al., 2023
8	Aligned α -FeOOH nanorods	56.4	ligand exchange	Fu et al., 2017

2.5.2. Oxidation: It is a chemical process where a substance loses electrons which frequently increases the oxidation state of that substance with the help of oxidizing agents (Maity et al., 2021). Some of the oxidizing agents are Oxygen (O₂), hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), and chlorine (Cl₂). For example, H₂O₂ oxidized ferrous ion (Fe²⁺) to produce ferric ion (Fe³⁺).



This process can be categorized into several types.

- a) Thermal Oxidation
- b) Chemical Oxidation
- c) Electrochemical Oxidation
- d) Photochemical Oxidation
- e) Biological Oxidation

2.5.3. Coagulation and precipitation: These chemical processes are used for eliminating dissolved elements and suspended particles from liquids, especially water, and wastewater. While coagulation destabilizes particles and permits them to combine, precipitation is the process by which solid large particles are formed from dissolved substances through sedimentation, filtration, or centrifugation process (Garelick et al., 2005).

- a) Mechanism of coagulation- Coagulants (e.g., aluminum sulfate, ferric chloride, etc.) that carry positive charge neutralize the negatively charged colloids present in water and as a result Van der Waals forces cause them to aggregate, generating micro-flocs. By moderate mixing, these micro-flocs grow into bigger, more settleable flocs. It can be divided into three types, such as Chemical Coagulation, Electrocoagulation, and Biological Coagulation.
- b) Mechanism of precipitation- Reagents such as lime, and sodium hydroxide react with the dissolved compounds to form an insoluble substance that can be separated through

sedimentation and filtration processes. It can be divided into two types, such as Chemical Precipitation and hydroxide Precipitation (Pio et al., 2015).

For this these methods are used in different industries such as the treatment of river water in municipal drinking water plants; textile wastewater treatment; and industrial wastewater treatment.

2.5.4. Ion exchange: It is a reversible process that involves exchanging ions on a solid phase—typically an ion exchange resin—for ions in a liquid phase. The resin retains the exchanged ions as the liquid moves along a column, leaving it with a different ionic composition (Karakurt and S., 2019). The pharmaceutical, metal recovery, food and beverage, wastewater treatment, soil conditioning, and radioactive waste management industries are among the industries that employ this technique extensively for ion removal and purification (Hu et al., 2018). This process can be categorized into two types, such as Cation Exchange, and Anion Exchange

2.5.5. Membrane filtration: Semi-permeable membranes, such as polyether sulfone, polysulfone, or polyvinylidene fluoride, are used in this separation process to filter particles, microbes, and dissolved compounds out of liquids. Water treatment, medicines, ceramics, metals, and polymers are among the materials employed extensively in the production of these thin, porous, or nonporous membranes (Zakhar et al., 2018).

This process is classified into five categories.

- a) Reverse Osmosis (RO) - Pore sizes of the membrane are <0.001 micrometers
- b) Nanofiltration (NF) - pore size of the membrane is 0.001 - 0.01 micrometers
- c) Microfiltration (MF) - membrane pore sizes vary from 0.1 - 10 micrometers
- d) Ultrafiltration (UF) - membrane pore sizes vary from 0.01 - 0.1 micrometers

- e) Forward Osmosis (FO) - water is driven through a semi-permeable membrane using this technique creating a natural osmotic pressure difference between an inflow solution and a draw solution.

2.5.6. Electro-kinetic method: This technique involves passing a low-voltage direct current (DC) electric field across the material to treat soils, sediments, and sludge (Li et al., 2019). Through a variety of electromigration (ions and charged particles move toward electrode with opposite charge- cations to the cathode, anions to the anode), electrophoretic (via sludge or soil, electrified colloidal particles and fine solids go in the direction of the opposing charge electrode), electro-osmotic (under an electric field, water travels from the anode to the cathode through a porous media carrying dissolved pollutants) and electrolysis processes (decomposition of water and compounds at electrodes generates gases and causes pH change), this procedure mobilizes and eliminates pollutants (Mao et al., 2016). This method is used in various fields like wastewater treatment plants; road construction; mining and metallurgy; and remediation of a site contaminated with lead and arsenic.

2.5.7. Biological treatment: In this process, microorganisms break down organic matter and convert harmful substances into less toxic forms through aerobic or anaerobic metabolism (Hayat et al., 2017). Some of these are- aerobic treatment (municipal wastewater treatment); anaerobic Treatment (industrial wastewater treatment); constructed wetlands (agricultural runoff treatment); biofilters (industrial effluents and stormwater treatment) etc.

Table 6. Working principle, advantages, and limitations of multiple techniques

Technique	Working principle	Advantages	Limitations
Adsorption	Employing diverse physical forces, contaminants are drawn to the outermost layer of a	High As removal effectiveness, inexpensive, easy to handle, use, and maintain.	Water chemistry can have an impact on adsorption capacity.
		Less hazardous residues.	It might be problematic to dispose of used adsorbent.

	solid substance known as an adsorbent.	Regenerative and reusable	Adsorbent may need regular refilling.
Oxidation	The oxidizing agent is added to water to chemically change pollutants into less dangerous ones.	Useful in getting rid of organic pollutants like pesticides, pharmaceuticals, and volatile organic compounds by oxidized metals.	Exorbitant chemical expenses.
		Taste and odor are eliminated.	Possibility of hazardous by-product formation.
		Contaminants' biological degradation may be enhanced.	Demands that oxidants be handled carefully.
Coagulation	Coagulants are chemicals that agglomerate and destabilize colloids and suspended matter to facilitate removal.	Successful elimination of solids in suspension.	Chemical utilization.
		Pathogen elimination.	Creation of sludge.
		Adaptable—it may be applied to other procedures.	Expense (chemicals and processing of sludge).
		Improves filtration and sedimentation.	Needs careful dose management.
Biological treatment	Organic substances and biodegradable contaminants are broken down by microorganisms into nontoxic byproducts.	Rapid procedure	Adjusting the pH can be necessary.
		Economical when it comes to organic contaminants.	Proceed slowly.
		Microbiological procedure that occurs naturally.	pH, temperature, and pollutants all affect it.
		Elimination of nutrients.	Has to be closely observed.
		Lowers COD and BOD.	could create an odor.
Ion exchange	Different ions are released in exchange for the ions that the ion exchange resin specifically adsorbs from the water.	able to manage substantial wastewater flows.	Needs room for medical facilities
		The elimination of certain ions only.	Fouling of resin.
		Resins that can regenerate.	Chemically dependent for regeneration.
		Enhanced effectiveness.	Expense (first setup and upkeep).
		May attain very low ion concentrations.	Restricted ability to handle heavy pollutant loads.
Membrane filtration	Depending on the size of their pores, semi-permeable membranes physically segregate dissolved materials and particles.	Comparatively easy to use	Possibility of secondary waste
		High effectiveness of elimination.	The clogging of membranes.
		An actual physical defense against pollutants.	High energy content.
		Adaptable to various capacities.	High cost of capital at first.
		Eliminates dissolved materials, particles, and bacteria.	Has to be replaced or cleaned on a regular basis.
		Little to no chemical usage	Membranes' limited lifetime

Chemical precipitation	It is via sedimentation or filtering that chemicals that cause the production of insoluble precipitates are eliminated.	Effective against inorganics and heavy metals and also decreases the soluble nature of pollutants.	Chemicals like lime, alum, or ferric salts that are used for precipitation, generate sludge.
		Straightforward process.	Expenses can be high (for sludge management and chemicals).
		Speedy medical attention.	A pH correction could be necessary.
		Can be paired with additional techniques.	The possibility of just partially eliminating pollutants
Electrokinetic method	By a variety of electrochemical techniques, electrical fields improve the transportation and treatment of pollutants.	Groundwater and soils are treated in situ.	Excessive energy use and time taken process.
		Pollutants are removed selectively (organics and heavy metals).	Complicated setup that needs certain tools and knowledge
		Minimal chemical usage which makes it non-intrusive during the treatment procedure.	Restricted application (certain pollutants and circumstances).

CHAPTER 3: STUDY OBJECTIVES

The objective of this study, titled “**Arsenic contamination in groundwater and possible mitigation using suitable eco-friendly approaches: A study in selected endemic areas of West Bengal, India**” is the following-

- Estimation of As to evaluate its present contamination status in groundwater and assessment of community health risk through the consumption of contaminated groundwater.
- An approach to find out the suitable mitigation approaches using waste plant parts through the green synthesis of iron nanoparticles (Fe-NPs)
- Creating awareness among the local populace of affected areas.

For this, we used geographic data, physicochemical features, the water quality index, health risk assessments, and statistical analysis, such as Pearson’s correlation analysis to examine the As pollution in groundwater from two-gram panchayats (Kalupur and Chowberia-I) in the Bangaon sub-division of the North 24 Parganas district of West Bengal. The Bangaon subdivision's overall water quality has never been evaluated in a previous study using a variety of physicochemical factors. Secondly, develop a waste-derived Fe-NPs to investigate the extent to which it reduces As in water that is contaminated. The purpose of this research is to mitigate As pollution in a way that is both ecologically and economically viable, while also educating local populations and guiding policy choices.

CHAPTER 4: MATERIALS & METHODS

4.1. Study area

Bangaon subdivision is one of the administrative regions of the North 24 Parganas district of West Bengal, India. It is a section of the Ichhamati-Raimangal Plain, which is one of the district's three physiographic parts. The district lies in the lower Ganges Delta. The eastern region of this district is traversed by the Ichhamati. The hydrogeology of this area appears to be comprised of an unconfined aquifer with a high As threshold inside a mature layer of black or brownish loam, which is topped by a more recent layer of alluvium. According to the 2011 census, with an area of 838.17 km², Bangaon has a residence of 1,063,028 inhabitants. There are 150 mouzas, 16-gram panchayats, 1 panchayat samity, 230-gram sansads (village councils), and 149 inhabited villages. Two of sixteen Gram Panchayats, Kalupur, and Chawberia-I, had been selected as the study sites. Chawberia-I is located at 22.98°N, 88.66°E, while Kalupur is located at 23.02° N, 88.80° E.

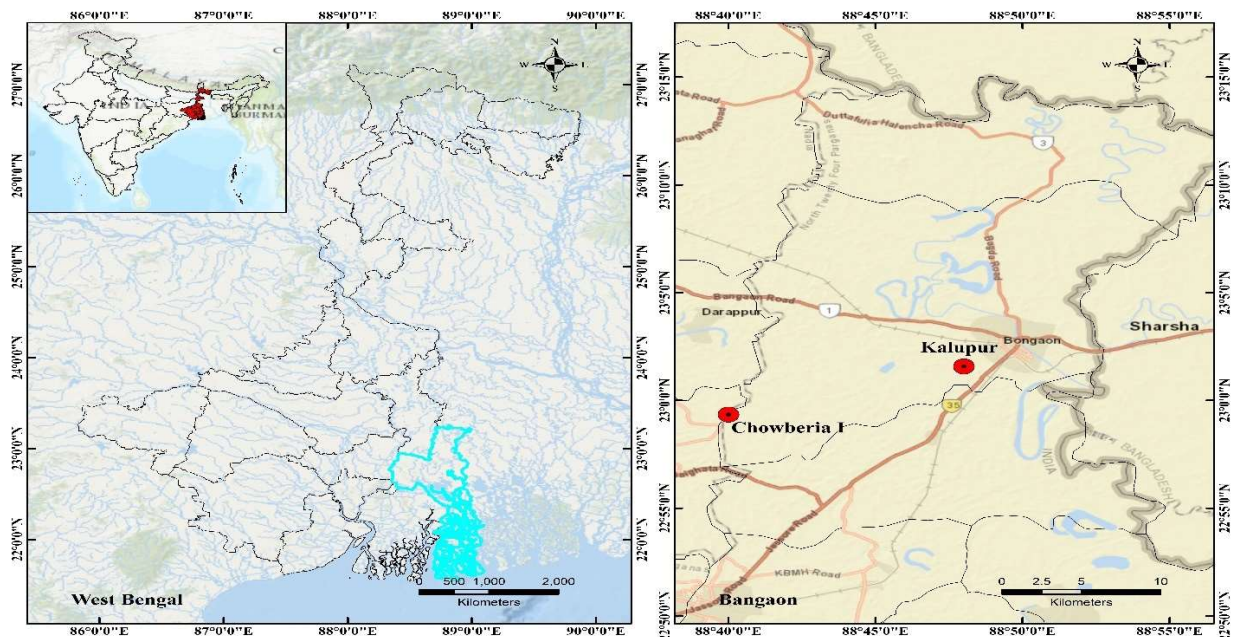


Fig. 4. Location map of studied areas

4.2. Sample collection, preparation and preservation

The raw and treated groundwater samples ($n = 88$) used for both drinking and irrigation purposes were collected from the 2-gram panchayats in the studied area and stored in airtight polyethylene containers (50 and 250 mL) in duplicates. The collected water samples in 50 mL containers were preserved with an addition of 0.1% v/v of 69% concentrated nitric acid (HNO_3) to estimate As and Fe (Ghosh et al., 2019). Water samples were taken and preserved in the other (250 mL) containers without the use of preservatives to estimate further physico-chemical characteristics (Das et al., 2024). Before analysis, the containers were carried in an ice box to the laboratory and stored at 4 °C.

4.3. Analysis procedure

4.3.1. Arsenic estimation

- Chemicals used: 10% Potassium iodide (KI), Hydrochloric acid (HCl), 0.5% Sodium borohydride (NaBH_4), Sodium hydroxide pellets (NaOH)
- Reagents used: To prepare 500 mL of 10% KI – 3 g of NaBH_4 was added with 2.5 g of NaOH in a volumetric flask and made up to the mark by double distilled water. The solution was then filtered through the suction filter.
- Instrument used: Atomic absorption spectroscopy (AAS)
- Standard preparation: From 1000 ppm stock solution of As (III) and As (V), 10 ppm of each stock was prepared. From which 5 mL of 1 ppm of each solution was prepared. Then 50 mL of 100 ppb As (V) and 50 mL of 100 ppb As (III) is made. From these two various concentrations 5 ppb, 10 ppb, 20 ppb, 25 ppb, 30 ppb, 40 ppb are prepared. Then each of those was added with KI, HCl, and volume made up to the mark with double distilled water.
- Sample preparation: Sample water was filtered using filter paper before measuring.

4.3.2. Water quality index

Several water quality indices, including total and calcium hardness, arsenic, total calcium, total suspended solids, total dissolved solids, alkalinity, chloride, turbidity, pH, conductivity, total sodium, total potassium, total sulfate, carbonate, bicarbonate, and total iron content, were evaluated in the samples that were obtained.

4.3.2.1. Estimation of pH

- Chemical used: Diluted Hydrochloric acid (HCl)
- Instrument used: pH meter with temperature and pH probe
- Calibration: calibrated using three solutions having known pH values of 4.0, 7.0, and 10.0.

4.3.2.2. Estimation of Conductivity (EC)

- Chemical used: Standard Potassium chloride (KCl) solution with concentrations of 0.01 M, 0.001 M.
- Instrument used: Conductivity meter with probe
- Calibration: Calibrated in standard solution according to cell constant.

4.3.2.3. Estimation of Turbidity

- Chemicals used: 5 mL of each Solution 1 (1 g of Hydrazine sulfate $[N_2H_6SO_4]$ in 100 mL of distilled water) and solution 2 (10 g of Hexamethylene tetramine $[(CH_2)_6N_4]$ in 100 mL of distilled water) in volumetric flask with 90 mL of distilled water
- Instrument used: Nephelometer
- Calibration: A blank solution was made to set the instrument with zero turbidity-free water and adjusted to '000' with the set zero knobs. Then calibrated using the standard solutions of 1000 NTU and 100 NTU.

4.3.2.4. Estimation of total suspended solids (TSS) and total dissolved solids (TDS)

- Equipment used: Drying oven, filter paper

- Method used: Simple gravitational method

4.3.2.5. Estimation of Total Sulfate

- Chemicals used: Conditioning reagent (mixture solution of 50 mL glycerol, 30 mL hydrochloric acid, 300 mL of double distilled water, 100 mL of 95% ethyl or isopropyl alcohol, 75 g of sodium chloride); SO_4^{2-} stock solution from Sodium sulfate [Na_2SO_4] (100 ppm); Barium chloride (BaCl_2)
- Instrument used: Orion Aquamate 8000 UV-VIS spectrophotometer at 420 nm wavelength.
- Calibration: From 100 ppm stock solution 10, 15, 25, and 35 ppm was prepared and then the calibration curve was prepared using blank, 10, 15, 25, and 35 ppm sulfate standard solution.
- Sample preparation: Sample water was filtered using filter paper before measuring.

4.3.2.6. Estimation of Total Sodium

- Chemical used: Sodium chloride (NaCl)
- Reagents used: To prepare 250 mL of 1000 ppm NaCl standard solution- 0.625 g of NaCl was added in a volumetric flask and made up to the mark by double distilled water.
- Instrument used: HPG Systems Microcontroller Flame photometer G- 301
- Calibration: From 1000 ppm stock solution 10, 20, 50, 80, and 100 ppm was prepared. The calibration curve was prepared using blank, 10, 20, 50, 80, and 100 ppm sodium standard solution.
- Sample preparation: Sample water was filtered using filter paper before measuring.

4.3.2.7. Estimation of Total Potassium

- Chemical used: Potassium chloride (KCl)
- Reagents used: To prepare 250 mL of 1000 ppm KCl standard solution- 0.625 g of KCl was added in a volumetric flask and made up to the mark by double distilled water.

- Instrument used: HPG Systems Microcontroller Flame photometer G- 301
- Calibration: From 1000 ppm stock solution 10, 20, 50, 80, and 100 ppm was prepared. The calibration curve was prepared using blank, 10, 20, 50, 80, and 100 ppm potassium standard solution.
- Sample preparation: Sample water was filtered using filter paper before measuring.

4.3.2.8. Estimation of Total Calcium

- Chemicals used: Calcium carbonate (CaCO_3), 35% hydrochloric acid (HCl)
- Reagents used: To prepare 250 mL of 1000 ppm CaCO_3 standard solution- 0.625 g of CaCO_3 + 1:1 HCl (dropwise) is added in a volumetric flask and made up to the mark by double distilled water.
- Instrument used: HPG Systems Microcontroller Flame photometer G- 301
- Calibration: From 1000 ppm stock solution 10, 20, 50, 80, and 100 ppm is prepared. The calibration curve was prepared using blank, 10, 20, 50, 80, and 100 ppm potassium standard solution.
- Sample preparation: Sample water was filtered using filter paper before measuring.

4.3.2.9. Estimation of Total Hardness (TH)

- Chemicals used: M/100 Na_2EDTA solution, NH_4Cl - NH_4OH buffer, Eriochrome Black Tea (EBT) indicator.
- Reagents used: To prepare 250 mL of NH_4Cl - NH_4OH buffer solution- 17.5 g of NH_4Cl and 142 mL of ammonia (NH_3) were added in a volumetric flask and made up to the mark by double distilled water. For preparing the indicator 0.5 g of EBT and 4.9 g of Potassium Nitrate (KNO_3) were grinded in a mortar.
- Equipment used: Burette

- Procedure: In a conical flask 10 mL of water sample + 1 mL buffer solution + a pinch of indicator was titrated against standard Na₂EDTA solution.
- Color change: Pinkish to blue

4.3.2.10. Estimation of Calcium Hardness (CH)

- Chemicals used: M/100 Na₂EDTA solution, 10% NH₄OH buffer, murexide indicator.
- Equipment used: Burette
- Procedure: In a conical flask 10 mL of water sample + 4 mL of 10% NaOH + a pinch of indicator is titrated against standard Na₂EDTA solution.
- Color change: Pink to light purple

4.3.2.11. Estimation of Alkalinity

- Chemicals used: 0.02 N Sulfuric acid (H₂SO₄), 0.02 N sodium carbonate (Na₂CO₃), methyl orange indicator
- Equipment used: Burette
- Standardization of 0.02 N H₂SO₄: In a conical flask 10 mL 0.02 N Na₂CO₃ + 2 to 3 drops of indicator was titrated against standard 0.02 N H₂SO₄ solution
- Procedure: In a conical flask 10 mL of water sample + 2 to 3 drops of indicator was titrated against standard 0.02 N H₂SO₄ solution.
- Color change: Yellowish orange to pink

4.3.2.12. Estimation of Chloride

- Chemicals used: Silver nitrate (AgNO₃), Potassium chromate (K₂CrO₄), Sodium chloride (NaCl)
- Equipment used: Burette
- Method used: Argentometric method

- Procedure: In a conical flask 10 mL of water sample + 2 to 5 drops of K_2CrO_4 indicator was titrated against standard $AgNO_3$ solution taken in burette
- End point color: Reddish brown

4.3.2.13. Estimation of Carbonate and Bicarbonate

- Chemicals used: 0.01 N Sulfuric acid (H_2SO_4), Phenolphthalein indicator (for carbonate estimation), 0.1% methyl orange indicator (for bicarbonate estimation)
- Equipment used: Burette
- Procedure: In a conical flask 10 mL of water sample + 1 drop of Phenolphthalein indicator was titrated against standard 0.01 N H_2SO_4 solution after, 2 drops of 0.1% methyl orange indicator were added to this and again titrated against standard 0.01 N H_2SO_4
- Color change: At first, solution will change from pink color to colorless and then at last it will turn into orange color.

4.3.2.14. Estimation of Total Iron

- Chemicals used: 100 ppm iron (Fe) stock solution, sodium acetate-acetic acid ($CH_3COONa + CH_3COOH$) buffer solution, hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), O-phenanthroline reagent
- Reagents: To prepare 1000 mL of Fe buffer solution- 3.8 g CH_3COONa and 48 mL CH_3COOH were added in a volumetric flask and made up to the mark by double distilled water. 10% of the entire volume was $NH_2OH \cdot HCl$ and 0.25% of the entire volume is O-phenanthroline reagent.
- Equipment used: Orion Aquamate 8000 UV-VIS spectrophotometer at 510 nm wavelength.
- Calibration: From 100 ppm Fe stock solution 10 ppm was prepared and from this 0.25, 0.50, 1.0 ppm were prepared and then the calibration curve was prepared using blank, 10, 15, 25, 35 ppm sulfate standard solution.

- Sample preparation: In a 25 mL volumetric flask, 5 mL of water sample + 10 mL of Fe buffer solution + 2.5 mL of $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 2 mL of O-phenanthroline were added and volume made up to the mark with double distilled water.

4.3.3. Quality control and assurance

By standardizing, performing regular blank measurements, and analyzing spiked samples, the control and accuracy of the analytical data that were produced were verified ($\pm 5\%$ variation). ICP-OES and AAS (variance of $\pm 10\%$) were used for interlaboratory testing to detect As in a subset of 88 water samples.

4.3.4. Water quality index (WQI)

According to Das et al. (2020); Gupta and Misra (2018) and Meng et al. (2016), WQI is a rating system that provides a thorough overview of the fundamental water quality of the studied areas. The parameters are assigned a numerical value, or "weight," based on their significance to the quality of the water, and then their "relative weight" (W_i) is computed. The W_i is computed as

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i}$$

Here,

W_i = relative weight; n = number of parameters and w_i = weight of each parameter

After that, the concentration of each parameter in each water sample is divided by the corresponding standard in accordance with the BIS's recommendations, and the result is multiplied by 100 to provide a quality rating scale (q_i) for each parameter.

$$q_i = \frac{C_i}{S_i} \times 100$$

In this case, q_i = quality rating; C_i = concentration of each chemical parameter in a given water sample; and S_i = the Indian drinking water standard for each chemical parameter in accordance with BIS (2012) recommendations.

First, the SI is computed for every chemical parameter in order to determine the WQI using the following equation (Anim-Gyampoa et al. 2019):

$$SI_i = W_i \times q_i$$

$$WQI = \sum SI_i$$

In which,

q_i = rating relying on the i th parameter's concentration;

SI_i = subindex of the i th parameter

Ultimately, the computed WQI values are classified into five water quality groupings: < 50 (very good), < 100 (fair), < 200 (poor), < 300 (extremely bad), and > 300 (unfit for consumption).

4.3.5. Health risk assessment

4.3.5.1. Cancer and non-cancer health risk assessment

An investigation of potential health risks to the public from the treated drinking water supplied was done as part of the health risk assessment. According to United States Environment Protection Agency, Specifically the cancer risk is computed for As; non-cancer risk has been assessed considering the occurrence of various other heavy metals (USEPA, 1986). Average daily dosage (ADD) is initially used to calculate the daily exposure to As.

$$ADD = \frac{C \times IR \times ED \times EF}{BW \times AT}$$

Here,

C = Concentration of the element in drinking water ($\mu\text{g/L}$);

IR = Ingestion rate (Adult males= 5 L/day; Adult females= 4 L/day; Children = 2 L/day);

ED = Exposure duration (Average age)

EF = Exposure frequency (365 days/year);

BW = Body weight (kg); (Adult males = 60 kg; Adult females= 55 kg; Children= 30 kg)

AT = Average lifetime = $365 \times 70 = 25,550$ days.

Consequently, cancer risk (CR) is calculated as,

$$CR = ADD \times CSF$$

And, non-cancer risk or hazard quotient (HQ) is calculated as,

$$HQ = \frac{ADD}{RfD}$$

Here, for As,

CSF = Cancer Slope Factor (1.5 per mg/kg BW/day)

RfD = Oral Reference Dose (0.0003 mg/kg BW/day)

4.3.5.2. Risk characterization through the severity adjusted margin of exposure (SAMOE)

The Swedish National Food Agency suggests applying a "Risk thermometer" to classify the threat to human health posed by any chemically hazardous substance. The difference between "exposure" and "reference points" (RP) or "tolerable daily intake" (TDI) which is generally toxicant's health-based recommendation value, is known as the "margin of exposure" (MOE) (Sand et al., 2015). It is estimated as,

$$SAMOE = (RP \text{ or } TDI) / (AF_{BMR} \times AF \times SF \times E)$$

Here,

TDI (Total daily intake) = $3.0 \mu\text{g/kg BW/day}$;

$AF_{BMR} = 1/10$; if the effect of the toxicant is thought to be non-linear in the $BMD_{0.5}$ – BMD_{10} range (BMD = Benchmark Dose)

AF (Assessment factor) = 10;

SF (Severity factor) = 100;

E (Daily exposure) = (Mean concentration \times Intake rate) / Body weight

4.3.6 Statistical analysis

In order to determine the dependency and significance of the samples, correlation matrices, and other mathematical and statistical linkages were carried out using Excel 2016 (Microsoft Office).

4.3.7. Protocol for arsenic removal from water

p4.3.7.1. Preparation of date seed powder and extract

Phoenix sylvestris plant seeds were collected from markets of Kolkata, West Bengal, India. Before thoroughly washing the date seeds with distilled water to eliminate any meat that stuck to them, the date fruits were peeled. After that, the seeds were dried for 24 hours at 50 °C in an oven. Next, using a ring sieve with 10 mm ZM-200 ConidUR Holes, the dried seeds were crushed into a powder using an ultra-centrifugal mill ZM-200. Up until its next usage, the fine powder was kept in glass containers that were tightly sealed and kept at 4 °C. Up until its next usage, the fine powder was kept in glass containers that were tightly sealed and kept at 4 °C. 50 mL of deionized water and 5 g of date seed powder have been mixed and boiled for 45 minutes to create the date seed extract. After removing suspended particles by centrifuging the mixture for 5 minutes at 5000 rpm, the supernatant was filtered through a 0.45 µm filter, yielding a clear, brownish date seed extract solution with a total solids (TS) content of 7 g/L.

4.3.7.2. Synthesis of Fe-NPs using date seed extract (ds-Fe-NPs)

For the preparation of Fe-NPs, 20 mL iron sulfate stock solution which was prepared by dissolving 2 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 50 mL of deionized water, and 40 mL date seed extract were mixed and heated to 70 °C while being constantly stirred. The mixture turned from brownish to black as the temperature rose to 70 °C, implying the synthesis of nanoparticles. After 45 minutes of stirring at 70 °C, the suspension was centrifuged at 5000 rpm for 10 minutes to separate the particles from the solution, and the supernatant was then decanted. After that, the particles were cleaned four times by adding deionized water, sonicating the suspension for 20 minutes in a bath sonicator, centrifuging for 10 minutes at 5000 rpm, and finally straining

the supernatant. After drying in a hot air oven at 55 °C, the particles were kept for testing or characterization in an anoxic chamber.

4.3.7.3. Adsorption Experiments

Using a batch approach, the adsorption of As on Fe-NPs as a nano-adsorbent was investigated. A weighed quantity of total As (As III + As V) was dissolved in double distilled water to create the stock solution of 1000 mg/L. After that, the stock solution was progressively diluted to the appropriate concentrations in double distilled water to prepare the required solutions (100, 500, and 1000 µg/L). Numerous factors were examined for their impact on the adsorption process, including pH, concentrations, contact duration, and adsorbent dose. Fe-NPs' adsorption tendencies toward total As were examined at 25 °C and a pH range of 3.0 to 11.0, which was balanced using 1 M HCl or 1 M NaOH aqueous solution. By contacting different doses (0.01, 0.02, 0.03, 0.04, and 0.05 g) of the Fe-NPs with 10 mL of varied concentrations of total As from 100 to 1000 µg/L for a studied period on an electric stirrer, the adsorption isotherm was carried out. To conduct adsorption kinetics investigations, 10 mL of total As solution was added to 0.01 g of Fe-NPs within a flask with different concentrations and constantly swirled for 15, 30, 60, 120, 240, and 360 minutes. AAS was used to determine the concentration of total As left in the solution after the adsorbent was removed using centrifugation after adsorption equilibrium was reached. The best conditions for removing the greatest amount of As from an aqueous solution were determined using the findings of these investigations. The following formula was used to determine how much As was adsorbed onto the unit quantity of the adsorbents, q_e (mg/g):

$$q_e = \frac{(C_0 - C_e) \times V}{W}$$

Here, V is the volume of the As solution (L), W is the dried weight of the adsorbent (g), and C_0 and C_e are the starting and final As concentrations (mg/L), respectively. It was determined that the percentage of As adsorption was as follows: $\text{Adsorption\%} = [(C_0 - C_e) / C_0] \times 100$

CHAPTER 5: RESULTS & DISCUSSION

5.1. Arsenic exposure status

5.1.1. Arsenic contamination in household water

The present As concentration in household water from As exposed studied areas showed a considerable risk to the population using these for drinking, cooking, and other household purposes. The concentration of As in household water from two different studied areas is shown in **Fig. 5a**. The mean As concentration in household water from Kalupur and Chowberia-I GP in North 24 Parganas district were $68.3 \pm 48.9 \mu\text{g/L}$ ($n = 19$; range: 0.9-191 $\mu\text{g/L}$) and $33.8 \pm 36.7 \mu\text{g/L}$ ($n = 14$; range: 0.05-104 $\mu\text{g/L}$) respectively. All water samples from these two studied areas exceed the WHO recommended value of As by 6.8 and 3.3 times higher in respective of Kalupur and Chowberia-I (WHO, 2011).

Distribution of As in these household water from two GPs is shown in **Fig. 5b** where the percentage of higher concentrations of As were more pronounced in Kalupur i.e., 89.5% samples had As concentration $>10 \mu\text{g/L}$ ($n = 19$) and 63.2% samples with As concentration $>50 \mu\text{g/L}$ and maximum As concentration was found to be 191 $\mu\text{g/L}$. Out of 14 groundwater samples from Chowberia-I GP, 57.1% of samples had As concentration $>10 \mu\text{g/L}$ (WHO limit) with 4 water samples (28.6%) having As concentration $>50 \mu\text{g/L}$. According to research by Das et al. (2021), about 54.6% of the total water samples taken ($n = 366$) had As levels higher than 10 $\mu\text{g/L}$ in groundwater samples from the Raninagar-II block in Murshidabad, which were severely polluted. Additionally, different research conducted by Joardar et al. (2021) discovered that the groundwater at Sutia gram Panchayat in the Gaighata block was polluted, with a mean As value of 49 $\mu\text{g/L}$ (range: 3-786 $\mu\text{g/L}$, $n = 83$).

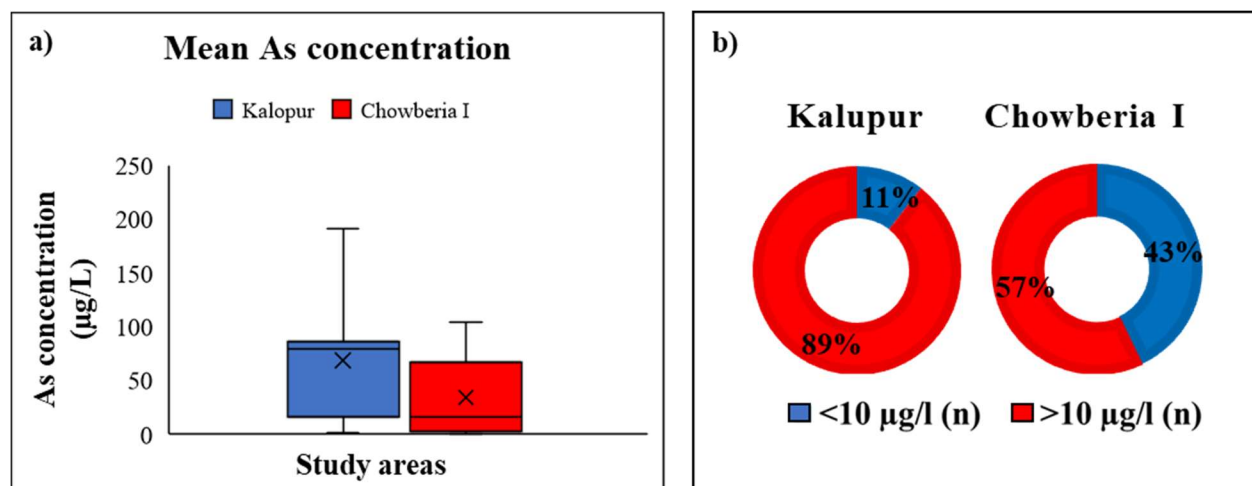


Fig. 5. (a) The mean arsenic concentration in household water from Kalupur and Chowberia-I;

(b) Distribution of arsenic (percentage) in these household tube wells from Kalupur and Chowberia-I

5.1.2. Arsenic contamination in alternative drinking water sources

The study regions do not have access to the water supplied from the government-supplied pipeline water service, deep tube wells, or any other water treatment plants throughout the area. Therefore, most of the rural populations from the study areas are still reliant on domestic-level shallow tube wells. In this study, government-implanted tube wells (GTW) and irrigational shallow tube wells (IW) from Kalupur and Chowberia-I, and water from arsenic removal plants (ARPs) from Kalupur were considered as alternative sources of water. The GTW in Kalupur and Chowberia-I showed a mean As concentration of $86.7 \pm 33.2 \mu\text{g/L}$ (range: $30.9 \pm 132 \mu\text{g/L}$; $n = 12$) and $99.2 \pm 42.4 \mu\text{g/L}$ (range: $24.1\text{--}182 \mu\text{g/L}$; $n = 16$), respectively. In the case of, water from IW i.e., in Kalupur and Chowberia-I, have been found with a mean As concentration of $69.5 \pm 35.9 \mu\text{g/L}$ (range: $7.35\text{--}1133 \mu\text{g/L}$; $n = 12$), $30.4 \pm 36.5 \mu\text{g/L}$ (range: $2.2\text{--}99.7 \mu\text{g/L}$; $n = 11$), respectively and for, ARPs in Kalupur $7.43 \pm 6.39 \mu\text{g/L}$ (range: $0.49\text{--}13.9 \mu\text{g/L}$; $n = 4$) showed in (Fig. 6).

All the GTW samples of the analyzed samples had As concentration above the permissible limit for Kalupur and Chowberia-I, whereas, about 8.33% of the analyzed samples ($n = 12$) in Kalupur and 54.6% of the

analyzed samples ($n = 11$) in Chowberia-I from IW had been found with As concentration below the permissible limit, therefore, it is not a safe alternative source for drinking water, while about 2% of the evaluated water samples ($n = 4$) from ARPs were found to be safe for consumption Which showed in (Fig. 7). Among all these alternative sources, treated water from ARPs was safer to use.

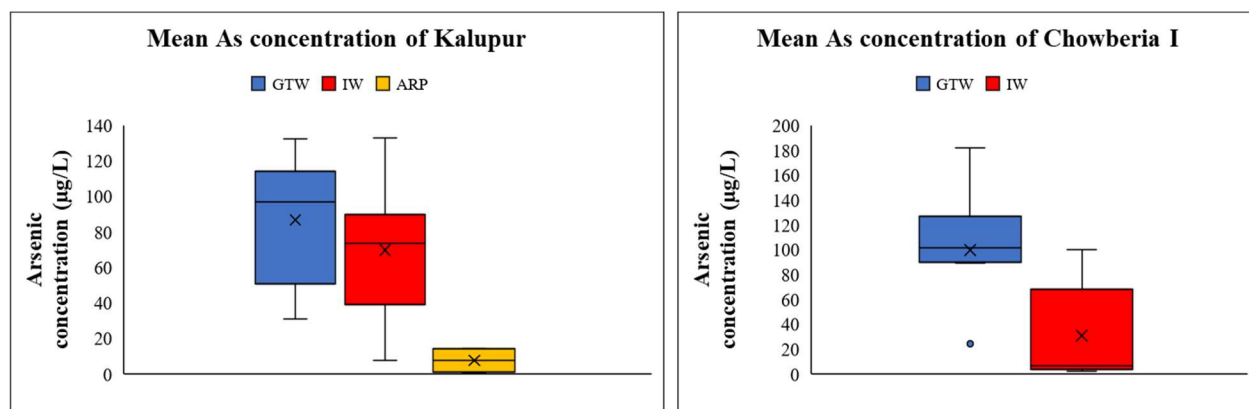


Fig 6. Mean arsenic concentration in alternative drinking water from Kalupur, and Chowberia-I

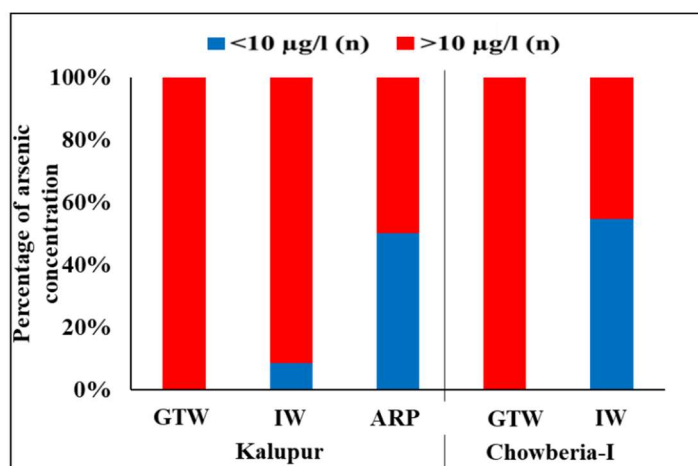


Fig 7: Distribution of arsenic in alternative drinking water from Kalupur, and Chowberia-I

5.2. Physico-chemical properties, correlation analysis, and water quality index

5.2.1. Physico-chemical properties

Groundwater samples ($n = 88$) were collected, and several physical and chemical characteristics were determined to analyze the overall quality of the water. **Table 7** displays the statistical presentation of the

water quality metrics for each sample from Kalupur and Chowberia-I. The water quality of both Kalupur and Chowberia-I groundwater samples is somewhat alkaline, as indicated by their respective mean pH values of 7.55 and 7.63 out of 88 groundwater samples. This was further supported by their respective mean total alkalinity values of 600 mg/L and 602 mg/L. Two such metrics that aid in comprehending the overall concentration of soluble salts in water are EC and TDS. While EC measures the electrical current in water, TDS describes the total amount of inorganic salts, including organic stuff, in the water. There is a high correlation between these characteristics (Rusydi, 2018). The range of EC in the instance under study was 16.1 to 833 $\mu\text{S}/\text{cm}$ (mean = 538 $\mu\text{S}/\text{cm}$) and 22.3 to 1288 $\mu\text{S}/\text{cm}$ (mean = 568 $\mu\text{S}/\text{cm}$), which provided insight into the high potential for salts and minerals in the water from Kalupur and Chowberia-I. It was discovered that the mean TDS value was 946 mg/L and 587, which was more than the maximum amount of TDS that is allowed in drinking water. TDS is influenced by chloride (Cl^-) ions (Balakrishnan et al., 2011; Nelson, 2002), and TDS determines the salinity of groundwater. For drinking purposes, this is crucial for the flavor of groundwater. The mean Cl^- value lay at 35 mg/L and 38.5 mg/L for Kalupur and Chowberia-I respectively. Based on 88 samples taken from the two blocks, the mean iron (Fe) content in Chowberia-I was 2.33 mg/L with a range of 0-8.52 mg/L, while in Kalupur it was 3.4 mg/L with a range of 0-9.86 mg/L. These results suggest that the groundwater was rich in Fe. Total Hardness (TH) and Total Alkalinity (TA) mean values in drinking water were found to be greater than their respective guideline limits. The average TH content in Kalupur and Chowberia-I was found to be 359 mg/L and 205 mg/L, respectively, indicating a rather hard groundwater quality. Calcium (Ca^{2+}), magnesium (Mg^{2+}), iron (Fe), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-) ions were the main causes of hardness in water. Mean Ca^{2+} ion concentration in Chowberia-I (71.9 mg/L; range = 4.9-111 mg/L) was found to be higher than that of Mg^{2+} ion (49.8 mg/L; range = 0-150 mg/L) whereas, in Kalupur mean concentration of Mg^{2+} (94 mg/L) was higher than Ca^{2+} (65.8 mg/L). Mean HCO_3^- concentration (Kalupur: 69.5 mg/L; range = 5-109 mg/L, and Chowberia-I:

76.2 mg/L; range = 15-121 mg/L) was found to be higher than mean CO_3^{2-} concentration (18.4 mg/L; range = 4-112 mg/L and 30.5 mg/L; range = 4-84 mg/L in Kalupur and Chowberia-I respectively). The mean concentration of Na^+ was observed to be 33.4 mg/L in Chowberia-I and 31.8 mg/L in Kalupur, and that of K^+ was 6.09 mg/L and 4.45 mg/L respectively. The water quality of the Bangaon subdivision is considered basic due to the mean ionic concentration range in both study areas being $\text{HCO}_3^- > \text{Cl}^- > \text{CO}_3^{2-}$ and the cationic concentration range being $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$. The elevated concentration of HCO_3^- ions may cause carbonate minerals in the surveyed area's groundwater to dissolve.

Table 7. Normal statistics of water quality parameters of available water sources from Kalupur and Chowberia-I

Parameters	Chowberia-I		Kalupur		Acceptable limit in drinking water
	Mean	Range	Mean	Range	
TSS (mg/L)	763±483	20-3080	1502±1579	220-7360	5
TDS (mg/L)	587±1244	0-6950	946±558	0-2050	500
TA (mg/L)	602±194	160-1040	600±280	40-1300	200
Cl^- (mg/L)	38.5±33.9	10.7-146	35±21.9	10.7-107	250
TH (mg/L)	205±76.9	20-360	359±118	20-600	200
CH (mg/L)	155±49.5	20-240	265±97.5	10-460	100
MH (mg/L)	49.8±44.5	0-150	94±34.6	10-150	30
Turbidity (NTU)	21.7±19.8	9-109	18.4±22.9	2-102	5
PH	7.63±0.23	7.08-8.33	7.55±0.33	6.75-8.07	6.5–8.5
EC ($\mu\text{S}/\text{cm}$)	568±300	22.3-1288	538±199	16.1-833	<1500
Ca^{2+} (mg/L)	71.9±24.9	4.9-111	65.8±22.6	2.3-103	75
Na^+ (mg/L)	33.4±36.8	2.8-138	31.8±20.5	1.3-130	200
K^+ (mg/L)	6.09±7.14	0.4-32.8	4.45±5.75	0.3-39.6	12
Total As ($\mu\text{g}/\text{l}$)	58.4±51.5	0.05-182	68.1±45	0.49-191	10
Total Fe(mg/L)	2.33±2.69	0-8.52	3.4±2.64	0-9.86	0.3
CO_3^{2-} (mg/L)	30.5±16.1	4-84	18.4±16.8	4-112	200
HCO_3^- (mg/L)	76.2±24.7	15-121	69.5±23.7	5-109	200

5.2.2. Correlation analysis among the physicochemical parameters

The inter-relation among the physicochemical parameters analyzed for different water sources are shown in **Fig. 8** and **Fig. 9**. The degree of positive correlation is classified into 3 categories and designated with 3

different colors (yellow color for strongly correlated, red color for moderately correlated, and green color for weakly correlated) whereas the negative associations are highlighted in a blue box. In the present study of Kalupur, TH is strongly associated with Ca^{2+} ions ($r = 0.966$), HCO_3^- ($r = 0.894$), moderately correlated with Na^+ ions ($r = 0.543$), weakly correlated with pH ($r = 0.346$), k^+ ions ($r = 0.260$), and negatively associated with CO_3^{2-} ions ($r = -0.194$). Whereas in Chowberia-I, TH was found to be very strongly correlated with Ca^{2+} ions ($r = 0.953$), Na^+ ($r = 0.774$), and HCO_3^- ($r = 0.831$), while, EC was also very strongly associated with TDS ($r = 0.859$) and TA ($r = 0.839$). The strong relation of Cl^- with Na^+ ($r = 0.901$) and TH ($r = 0.751$) suggested that the treated water quality tends to be alkaline in nature and also causes the temporary hardness of the water. The TA was moderately correlated with Cl^- ions ($r = 0.476$), Na^+ ions ($r = 0.493$), TH ($r = 0.690$), weakly associated with k^+ ions ($r = 0.237$), and negatively allied with CO_3^{2-} ions ($r = -0.024$). In Kalupur, pH has a negative correlation with most parameters except turbidity, EC, and TDS ($r = 0.086$; 0.034 ; 0.196 respectively), unlike, in Chowberia-I, pH has a strong correlation with TA ($r = 0.711$), moderate association with TSS, and TDS, negative correlation with Cl^- ($r = -0.002$), turbidity ($r = -0.395$), EC ($r = -0.068$), and rests make the weak association. In the same way, in Kalupur, TDS in water samples from different sources is moderately linked with Cl^- ($r = 0.525$) and HCO_3^- ($r = 0.645$), strongly correlated with Ca^{2+} ($r = 0.707$), Na^+ ($r = 0.720$), and negatively associated with CO_3^{2-} ions ($r = -0.050$). Quite a strong correlation between TDS and TH ($r = 0.741$) signifies that the minerals responsible for TDS value in water cause the hardness of the water. In Chowberia-I, TDS is also moderately associated with Cl^- ($r = 0.476$) but weakly associated with Ca^{2+} ($r = 0.315$), TA ($r = 0.159$). A weak positive association in water samples from Kalupur is observed between arsenic and iron ($r = 0.156$), and a moderate positive association ($r = 0.623$) in Chowberia-I. Arsenic concentration in water samples from different sources is found to be insignificantly or negatively related with CO_3^{2-} ions ($r = -0.047$) and ($r = -0.031$) from Kalupur and Chowberia-I respectively. In Kalupur, As concentration is negatively related to K^+ ($r = -0.134$), TSS (r

= -0.077) and Fe are also conversely related to K^+ ($r = -0.084$), while in Chowberia-I, As concentration is negatively related to different ions: Ca^{2+} ($r = 0.023$), Na^+ ($r = -0.250$), K^+ ($r = -0.382$), Cl^- ($r = -0.464$), and Fe is conversely associated with Cl^- ($r = -0.238$), Na^+ ($r = -0.127$), K^+ ($r = -0.250$). Similar interactions between the cations and anions in groundwater have also been reported in several other Indian investigations (Jain et al., 2018; Memon et al., 2023).

	TSS	TDS	TA	Cl^-	TH	CH	MH	Turbidity	PH	EC	Ca^{2+}	Na^+	K^+	As	Fe	CO_3^{2-}	HCO_3^-
TSS	1																
TDS	0.503	1															
TA	0.423	0.593	1														
Cl^-	0.082	0.525	0.124	1													
TH	0.297	0.741	0.617	0.540	1												
CH	0.346	0.754	0.637	0.516	0.966	1											
MH	0.036	0.399	0.306	0.389	0.686	0.475	1										
Turbidity	-0.307	-0.274	-0.176	0.183	0.118	0.074	0.194	1									
PH	0.506	0.612	0.711	-0.002	0.346	0.410	0.024	-0.395	1								
EC	0.161	0.033	-0.030	0.074	-0.053	-0.116	0.145	0.239	-0.068	1							
Ca^{2+}	0.306	0.707	0.570	0.529	0.947	0.928	0.609	0.138	0.296	-0.020	1						
Na^+	0.193	0.720	0.292	0.768	0.543	0.526	0.370	-0.048	0.259	0.129	0.590	1					
K^+	0.001	0.351	0.085	0.152	0.260	0.202	0.318	-0.132	0.027	0.047	0.260	0.290	1				
As	-0.077	0.250	0.335	0.111	0.450	0.435	0.308	0.253	0.131	-0.007	0.477	0.155	-0.134	1			
Fe	0.047	0.032	0.265	0.133	0.290	0.295	0.157	0.552	0.018	0.326	0.306	0.067	-0.084	0.156	1		
CO_3^{2-}	-0.003	-0.050	0.210	-0.194	-0.055	-0.024	-0.121	-0.046	0.197	0.013	-0.066	-0.120	0.025	-0.047	0.039	1	
HCO_3^-	0.184	0.645	0.511	0.424	0.894	0.840	0.682	0.113	0.221	0.002	0.874	0.490	0.402	0.488	0.194	-0.265	1

Fig. 8. Pearson correlation among the parameters in different water samples from Kalupur

	TSS	TDS	TA	Cl ⁻	TH	CH	MH	Turbidity	PH	EC	Ca ²⁺	Na ⁺	K ⁺	As	Fe	CO ₃ ²⁻	HCO ₃ ⁻
TSS	1																
TDS	0.053	1															
TA	-0.113	0.159	1														
Cl ⁻	0.224	0.476	0.479	1													
TH	0.159	0.385	0.690	0.751	1												
CH	0.099	0.317	0.643	0.599	0.839	1											
MH	0.164	0.314	0.477	0.632	0.795	0.337	1										
Turbidity	-0.124	-0.116	0.210	-0.184	0.018	0.169	-0.157	1									
PH	-0.054	0.034	-0.439	-0.194	-0.575	-0.537	-0.397	0.086	1								
EC	-0.123	-0.122	-0.226	-0.211	-0.127	-0.148	-0.055	0.195	0.196	1							
Ca ²⁺	0.143	0.315	0.741	0.689	0.953	0.838	0.714	0.069	-0.665	-0.201	1						
Na ⁺	0.185	0.531	0.493	0.901	0.774	0.618	0.649	-0.107	-0.237	-0.184	0.689	1					
K ⁺	0.285	0.107	0.237	0.570	0.577	0.522	0.415	-0.211	-0.297	-0.150	0.532	0.522	1				
As	-0.435	-0.195	0.135	-0.464	-0.032	0.057	-0.119	0.417	-0.100	0.369	-0.023	-0.250	-0.382	1			
Fe	-0.299	-0.083	0.329	-0.238	0.104	0.220	-0.066	0.793	-0.038	0.391	0.144	-0.127	-0.250	0.623	1		
CO ₃ ²⁻	0.528	0.092	-0.024	-0.042	0.086	0.132	0.002	-0.074	-0.076	-0.111	0.112	-0.080	0.051	-0.031	-0.225	1	
HCO ₃ ⁻	-0.203	0.211	0.697	0.536	0.799	0.708	0.593	0.234	-0.535	-0.037	0.803	0.638	0.347	0.208	0.314	-0.243	1

Fig. 9. Pearson correlation among the parameters in different water samples from Chowberia-I

5.2.3. Water quality index

A complete water quality indexing (WQI) of water samples from different sources has been conducted taking into account 15 parameters (pH, TSS, TDS, EC, Cl⁻, SO₄²⁻, TH, CH, TA, Ca²⁺, CO₃²⁻, HCO₃⁻, Na⁺, K⁺, Turbidity, Fe, As). Fifteen important parameters are assigned a weight (wi) based on how important they are in terms of the general condition of the water that is fit for drinking. Supplementary **Table 8** contains the parameters, their assigned weights, and the relative weights that were computed for the WQI assessment. The parameters with the most potential for harm, such as As, have been provided a maximum weight of 5, owing to their significance in groundwater pollution. Approximately 89% and 88% of the water samples from Kalupur and Chowberia-I were determined to be unfit for household use and consumption, with the overall WQI score varying between 21.6 and 519. In the case of Kalupur, all the water samples collected from different sources (HTW, GTW, IW) except from ARP, which is 100% good in quality, are

unsuitable for drinking. Whereas, in Chowberia-I, only 14.3% HTW; 18.8% GTW; and 27.3% IW are good in quality. **Fig. 10** shows the percentage contribution of available water sources towards its quality.

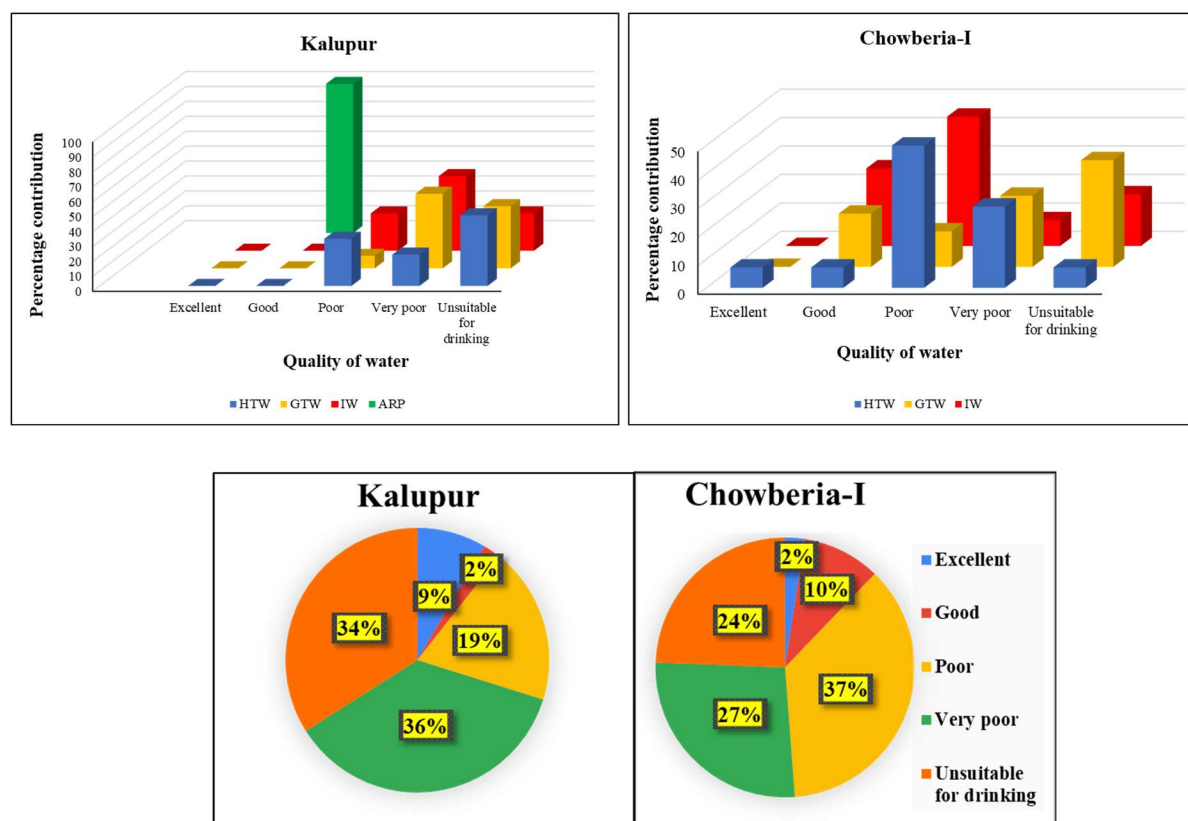


Fig. 10. Percentage contribution of available water sources towards its quality

Table 8. Relative weight of chemical parameters

Parameters	Weight (wi)	Relative weight (Wi)
pH	4	0.090909091
TDS (mg/l)	5	0.113636364
EC	4	0.090909091
Cl ⁻ (mg/l)	3	0.068181818
SO ₄ ²⁻ (mg/l)	4	0.090909091
TH (mg/l)	2	0.045454545
TA (mg/l)	3	0.068181818
Fe (mg/l)	3	0.068181818
Ca ²⁺ (mg/l)	2	0.045454545
Mg ²⁺ (mg/l)	2	0.045454545
As (µg/l)	5	0.113636364

Na ⁺ (mg/l)	2	0.045454545
Turbidity (NTU)	3	0.068181818
K ⁺ (mg/l)	1	0.022727273
HCO ₃ ⁻ (mg/l)	1	0.022727273
	$\Sigma=44$	$\Sigma=1$

5.3. Health risk assessment

5.3.1. Risk assessment among available drinking water sources through risk thermometer

The risk of As exposure through the consumption of available drinking water by the population from particular areas has been estimated with the help of a risk thermometer (**Fig. 11**). SAMOE value and risk level of drinking water sources from different study areas have been shown in **Table 9**. According to Sand et al. (2015), there are five categories to classify the degree of exposure risk. The categories are starting with ‘low’ to ‘high’ i.e., class 1 = no (>10), class 2 = no-low (>1-10), class 3 = low-moderate (>0.1-1), class 4 = moderate-high (0.01-0.1) and class 5 = high (<0.01). It is observed that adult males, adult females, and children from Kalupur and Chowberia-I are exposed to arsenic mainly through drinking household water (class 5, SAMOE 0.0053, 0.0061, and 0.0066 in Kalupur; class 4, SAMOE: 0.0106, 0.0122 and 0.013302365 in Chowberia-I for adult males, adult females and children respectively) followed by deep tube-wells (class 5, SAMOE: 0.0042, 0.0048 and 0.0052 in Kalupur; class 5, SAMOE: 0.0036, 0.0042 and 0.0045 in Chowberia-I for adult males, adult females and children respectively), irrigation water (class 5, SAMOE: 0.0052, 0.0059 and 0.0065 in Kalupur; class 4, SAMOE: 0.012, 0.014 and 0.0148 in Chowberia-I for adult males, adult females and children respectively). Arsenic removal plant was observed to have class 3 i.e. low-moderate risk with SAMOE values 0.0485, 0.0556, and 0.0606 for adult males, adult females, and children respectively. The calculated values show the following trend of increasing the risk for all the sources: ATP < irrigation water < household water < deep tube well.

Table 9. SAMOE value of adult males, adult females, and children through consuming water from different sources from both Kalupur and Chowberia-I.

Study area	Drinking water source	SAMOE value		
		Adult males	Adult females	Children
Kalupur	HTW	0.0053	0.0061	0.0066
	DT	0.0042	0.0048	0.0052
	IW	0.0052	0.0059	0.0065
	ARP	0.0485	0.0556	0.0606
Chowberia-I	HTW	0.0106	0.0122	0.0133
	DT	0.0036	0.0042	0.0045
	IW	0.0118	0.0136	0.0148

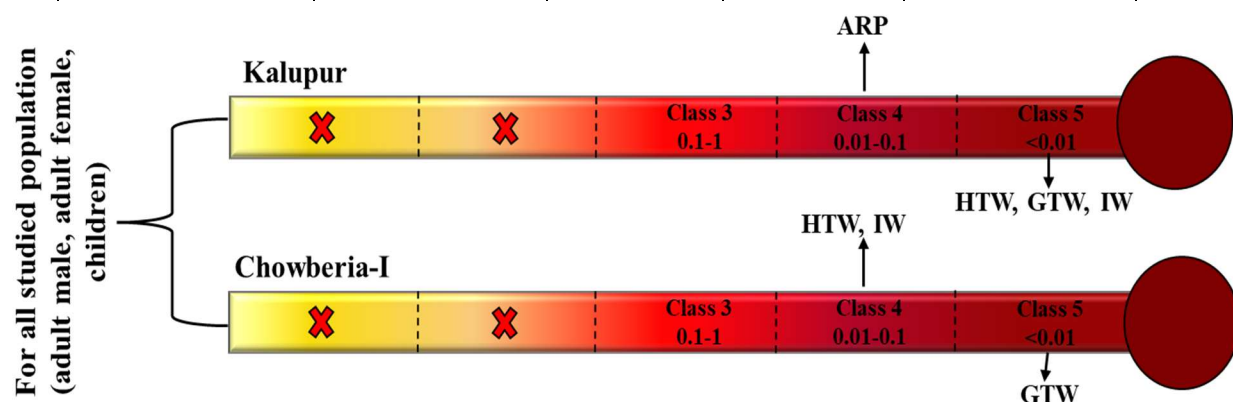


Fig. 11. Risk assessment through SAMOE

5.3.2. Cancer risk (CR) and non-cancer risk (HQ)

The CR and HQ of three studied population groups from four respective areas are shown in **Table 10**. The carcinogenic risk for the population of Kalupur from HTW (8.5×10^{-3} , 6.3×10^{-2} and 7.4×10^{-3} , respectively for adult males, females, and children); GTW (1.1×10^{-2} , 4.2×10^{-3} and 9.5×10^{-3} , respectively for adult males, females, and children); IW (8.7×10^{-3} , 1.4×10^{-2} and 7.6×10^{-3} , respectively for adult males, females, and children); ARP (9.3×10^{-4} , 3.8×10^{-3} and 8.1×10^{-4} , respectively for adult males, females and children);. Likewise, for the population of Chowberia-I from HTW (4.2×10^{-3} , 5.3×10^{-3} and 3.7×10^{-3} , respectively for adult males, females, and children); GTW (1.2×10^{-2} , 3.8×10^{-3} and 1.1×10^{-2} , respectively for adult males, females and children); IW (3.8×10^{-3} , 5.3×10^{-3} and 3.3×10^{-3} , respectively for adult males, females and children). The carcinogenic risk among all was higher than the USEPA prescribed limit (1×10^{-4}) (USEPA

2011) in both Kalupur and Chowberia-I. Even each population group from all studied areas was under serious NCR as all of them exceeded the threshold for HQ ($HQ > 1$). The HQ for the population of Kalupur from HTW (19.0, 16.6, and 15.2, respectively for adult males, females, and children); GTW (24.1, 21.0, and 19.3 respectively for adult males, females, and children); IW (19.3, 16.9 and 15.4, respectively for adult males, females, and children); ARP (2.06, 1.80 and 1.65, respectively for adult males, females, and children); Likewise, for the population of Chowberia-I from HTW (9.40, 8.20 and 7.52, respectively for adult males, females, and children); GTW (27.6, 24.1 and 22.1, respectively for adult males, females, and children); IW (8.44, 7.37 and 6.75, respectively for adult males, females, and children). The study's findings indicate that drinking raw water from a deep tube well without treating it is not advised because of the potential for anthropogenic activity-related pollution.

Table 10. Cancer and non-cancer risk from different available water sources

Study area	Source of water	CR			HQ		
		Adult males	Adult females	Children	Adult males	Adult females	Children
Kalupur	HTW	8.5×10^{-3}	6.3×10^{-2}	7.4×10^{-3}	19.0	16.6	15.2
	DTW	1.1×10^{-2}	4.2×10^{-3}	9.5×10^{-3}	24.1	21.0	19.3
	IW	8.7×10^{-3}	1.4×10^{-2}	7.6×10^{-3}	19.3	16.9	15.4
	ARP	9.3×10^{-4}	3.8×10^{-3}	8.1×10^{-4}	2.06	1.80	1.65
Chowberia-I	HTW	4.2×10^{-3}	5.3×10^{-3}	3.7×10^{-3}	9.40	8.20	7.52
	DTW	1.2×10^{-2}	3.8×10^{-3}	1.1×10^{-2}	27.6	24.1	22.1
	IW	3.8×10^{-3}	5.3×10^{-3}	3.3×10^{-3}	8.44	7.37	6.75

Despite having both CR and HQ values greater than the threshold level (9.3×10^{-4} , 3.8×10^{-3} and 8.1×10^{-4} and 2.06, 1.80, and 1.65, respectively for three studied population groups), ARP-treated water from Kalupur can be used with least risk among other collected available water sources. The risk was found to be higher in males followed by females, and children for both Kalupur and Chowberia-I. **Figure 12** displayed the risk of (a) cancer and (b) non-cancer for adult males, adult females, and children from the various water sources.

Research conducted in North 24 Parganas, West Bengal, likewise found that adults were at higher risk than children (Joardar et al., 2021).

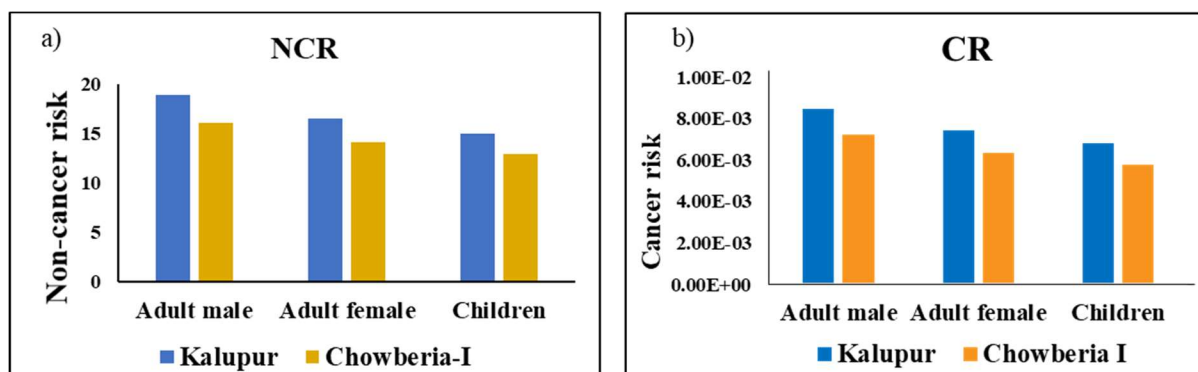


Fig. 12. (a) Non-cancer and (b) cancer risk from all available water sources for adult males, adult females, and children

5.4. Removal of total arsenic by batch experiments

5.4.1. Impact of various factors

Effect of initial solution pH: Since pH has an impact on both the shape of As and the electrical properties of the Fe-NPs, it was determined to be an important parameter impacting As removal. To investigate how pH affects total As adsorption by the generated Fe-NPs, constants were used for the adsorbent dosage, reaction temperature, contact time, and total As concentration- 1 g/L, 25 °C, 120 min, and 1000 µg/L, respectively. **Fig. 13a** presents the findings. It was evident that with the increasing pH, adsorption was first increased and then reduced. Since most water bodies naturally have a pH of 7.0, the highest adsorption occurred at that pH (81.8%), thus pH 7.0 was thought to be ideal.

Effect of contact time: Through a range of contact periods, from 15 to 360 minutes, the experiment shows how much total As is removed. It was evident (**Fig. 13b**) that, with the increasing time, adsorption was also increased (18.98 to 87.15%). Within 120 minutes, 72.8% of the arsenic was removed; this safe zone peaked at 360 minutes. However, it took 120 minutes for the adsorption to achieve equilibrium; as a result,

120 minutes was the ideal duration. Adsorbent dosage, reaction temperature, pH, and total As concentration were held constant at 1 g/L, 25 °C, 7, and 1000 µg/L throughout this experiment.

Effect of adsorbent dose: 10 mL of a 1000 µg/L total As solution at 25.0 °C were exposed to a pH 7.0 adsorbent dose variation of 1.0 to 5.0 g/L for 120 minutes of contact time. The result showed that with the increase of doses from 1.0 to 5.0 g/L the removal of total As also rose (from 90.25 to 91.2%; **Fig. 13c**). The higher adsorbent surface area is responsible for an increase in adsorption with adsorbent dose. The percentage of removal changed barely from 1 g/L to 5 g/L, although the removal reached its maximum at 5.0 g/L. The ideal dosage was therefore established at 1.0 g/L.

Effect of initial concentration: Analyses were conducted to figure out the impact of starting concentrations (100–1000 µg/L) of total As at 25.0 °C, 1.0 g/L of Fe-NPs, pH 7.0, and 120 minutes of contact time. The results are shown in **Fig. 13d**. It is evident that with the increasing initial concentration, the removal of total As decreased (from 92.4 to 81.8%).

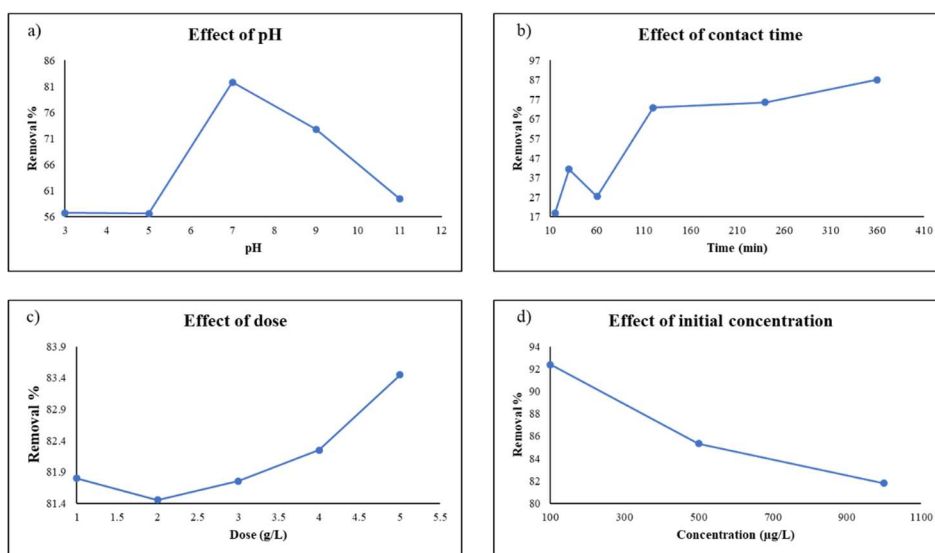


Fig. 13. Impact of different variables on the adsorption experiment of total arsenic- (a) pH, (b) contact time, (c) dose, and (d) concentration

5.4.2. Adsorption isotherms

The correlation between the quantity of As adsorbed and its equilibrium concentration in solution had been explained using the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D-R) isotherm models. These isotherms were also used to understand the adsorption process's kinetics.

Freundlich isotherm: The Freundlich isotherm is suggested based on the theory that the heat of adsorption is not dispersed equally over the heterogeneous surface of the adsorbent. This led to its use for total As adsorption on Fe-NPs as well. The linear form of the Freundlich isotherm, as it applies to the experimental data, is shown below (Friedrich 1906):

$$\text{Log } q_e = \log KF + \frac{1}{n} \text{Log } C_e$$

Here, q_e = Adsorption capacity at equilibrium ($\mu\text{g/g}$); C_e = Adsorbate concentration at equilibrium ($\mu\text{g/L}$); K_F (isotherm constant) = Heterogeneous adsorption capacity; n (isotherm constant) = Adsorption intensity. Calculating the value of K_F and n from the intercept and slope was done by plotting $\text{Log } q_e$ versus $\text{Log } C_e$ (**Fig. 14a**). Regression coefficient values K_F , n , and R^2 were computed and are displayed in **Table 11**.

Temkin isotherm: Adsorbate-adsorbate interactions on the adsorbent surface are considered by the Temkin isotherm. Temkin observed via experimentation that as saturation increases, adsorption temperatures more frequently drop. The Temkin isotherm's linear form is provided by the following equation. (Temkin and Pyzhey 1940):

$$q_e = B_T \times \ln A_T + B_T \times \ln C_e$$

Here, q_e = Adsorption capacity at equilibrium ($\mu\text{g/g}$); C_e = Adsorbate concentration at equilibrium ($\mu\text{g/L}$); A_T = The energy of the adsorbent-adsorbate interaction; B_T = Heat of adsorption. Calculating the value of B_T and A_T from the intercept and slope was done by plotting q_e versus $\ln C_e$ (**Fig. 14b**). Regression coefficient values B_T , A_T , and R^2 were computed and are displayed in **Table 11**. A higher B_T value suggests stronger and more consistent contacts throughout the surface since it shows that the heat of adsorption

increases less as the surface is saturated, indicating the energy needed to adsorb more molecules stays constant.

Langmuir isotherm: Based on the Langmuir isotherm, monolayer sorption triggered uptake on a homogenous surface. Furthermore, it anticipates that the adsorbent will not transmigrate and that adsorption energies will be uniformly applied to the surface. This equation represents the Langmuir isotherm in linear form. (Langmuir 1918):

$$\frac{1}{q_e} = \frac{1}{K_L q_{\max}} \times \frac{1}{C_e} + \frac{1}{q_{\max}}$$

Here, q_e = Adsorption capacity at equilibrium ($\mu\text{g/g}$); C_e = Adsorbate concentration at equilibrium ($\mu\text{g/L}$); q_{\max} = maximum adsorption capacity ($\mu\text{g/g}$); K_L = Langmuir constant ($\text{L}/\mu\text{g}$). Plotting $1/q_e$ versus $1/C_e$ yields an almost straight line (**Fig. 14c**), indicating that the Langmuir isotherm was followed by the adsorption of total As. Regression coefficient values K_L , n , and R^2 were computed and are displayed in **Table 11**. Using the dimensionless separation factor (K_L), these factors were utilized to forecast the affinity between the adsorbent and adsorbate.

Dubinin-Radushkevich (D-R) isotherm: To differentiate between chemical and physical adsorption, the D-R model was used. Additionally, it is employed in defining the Gaussian energy distribution adsorption process onto a heterogeneous surface. The linear form of the D–R isotherm (Chen 2015) can be written as follows:

$$\ln q_e = \ln q_m - K\varepsilon^2$$

Here, q_e = Adsorption capacity at equilibrium (mol/g); q_m = max adsorption capacity; K = constant; ε = Polanyi potential. Calculating the value of K and q_m from the slope and intercept was done by plotting $\ln q_e$ versus ε^2 (**Fig. 14d**). Regression coefficient values q_m , E , and R^2 were computed and are displayed in **Table 11**. ε and the energy (E) were calculated using the following formula:

$$\epsilon = RT \times \left(1 + \frac{1}{Ce}\right)$$

$$E = \frac{1}{\sqrt{2K}}$$

The adsorption process could include chemisorption, which implies stronger chemical bonding since the E value (11.18 kJ/mol) was more than 8 kJ/mol.

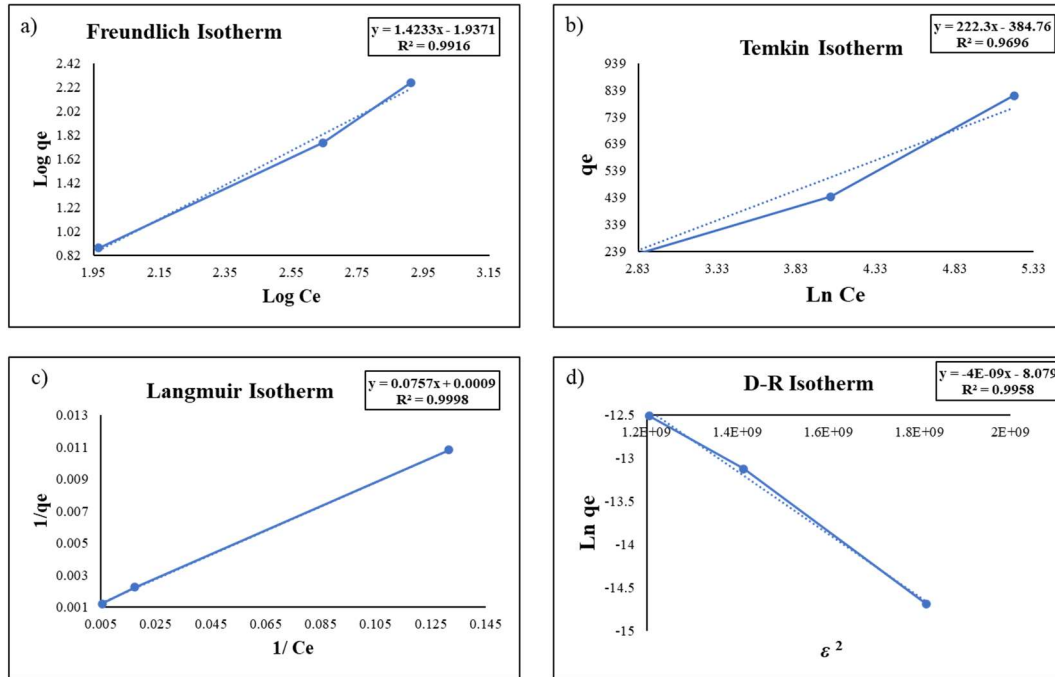


Fig. 14. Graphs displaying the (a) Freundlich; (b) Temkin; (c) Langmuir; and (d) D-R isotherms for the removal of total arsenic

Table 11. Values of isotherm parameters

Freundlich Isotherm	k_F	n	R^2
	0.011558	0.702593	0.9916
Langmuir Isotherm	k_F	n	R^2
	1.002074	13.21004	0.9998
Temkin Isotherm	B_T	A_T	R^2
	11.15	3.125E-35	0.9696
D-R Isotherm	q_m (mol/g)	E (KJ/mol)	R^2
	0.00031	11.18	0.9958

The adsorption behavior of total As on Fe-NPs was found to be well-described by both the Langmuir and Freundlich isotherm models, as indicated by the R^2 values of any system or model.

5.4.3. Kinetic studies

The rate at which Fe-NPs absorbed arsenic ions was defined by the kinetics. First-order, second-order, pseudo-first- and pseudo-second-order equations were utilized to analyse the sorption data kinetics.

Pseudo-second-order reaction: The pseudo-second-order kinetics formula is commonly utilized in the format suggested by Ho and McKay, which is:

$$\frac{t}{q_e} = \frac{1}{K_2 \times q_e^2} + \frac{1}{q_e}$$

The surface adsorption in this model, which includes chemisorption and causes the removal from a solution due to physicochemical interactions between the two phases, is the rate-limiting step (Ho et al., 1999). At 25°C, Fe-NPs remove As ions with fitted pseudo-second-order-model kinetic parameters (R^2 , and K_2) were calculated by plotting t/q_t versus t (**Fig. 15**). The values of R^2 , and K_2 were 0.9992, and 6.47059E-05 respectively.

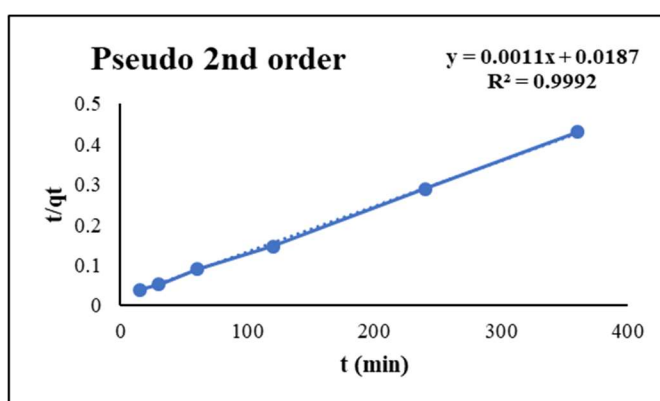


Fig. 15. Impact of contact duration on arsenic ion adsorption by Fe-NP surfaces

CHAPTER 6: CONCLUSION

The groundwater quality of Kalupur and Chowberia-I from the Bangaon subdivision, North 24 Parganas, West Bengal was not found suitable for drinking purposes. 89% and 88% of samples from these places, according to the WQI, are unfit for human consumption; bicarbonate alkalinity makes the water typically alkaline. More Ca^{2+} than Mg^{2+} is involved in the hardness of water. In Kalupur and Chowberia-I, amounts of As up to 191 and 182 $\mu\text{g/L}$ respectively. It was also noted that in 50% of the ARPs from Kalupur, the mean concentration is higher than the permissible limit due to a lack of routine maintenance, which has raised severe concerns about potential health consequences, including cancer. It is not enough to just deploy ARPs in As-affected regions. Regular maintenance, water quality testing, and a complete strategy incorporating infrastructure, trained staff, education, and contemporary technology are all necessary for effective risk reduction. Water monitoring and ARP maintenance must be given top priority by officials and legislators. Besides, the research showed that, under ideal circumstances, Fe-NPs derived from date seed powder efficiently lowered 81.8% of arsenic, with chemisorption through monolayer adsorption on a homogeneous or a heterogeneous surface serving as the main mechanism of As removal. Thus, by using this cost-effective waste product a sustainable technology of water As remediation can be possible. However, technologists, legislators, and villagers must work together to ensure that these innovations are accepted and maintained properly for long-term sustainability by the community and adapted to the local environment.

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