ARSENIC REMEDIATION FROM WATER USING SUITABLE NANOMATERIAL AND BIOCHAR AMENDMENT

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ARSENIC REMEDIATION FROM WATER USING SUITABLE NANOMATERIAL AND BIOCHAR AMENDMENT

A thesis

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by

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DECLARATION

I hereby declare that the work presented in this thesis report title **“Arsenic Remediation from Water Using Suitable Nanomaterial and Biochar Amendment”** submitted to Jadavpur University, Kolkata in partial fulfilment of the requirement for the award of the degree of Master of Technology in Environmental Biotechnology is a bonafide record of the research work carried out under the supervision of Dr. Tarit Roychowdhury. The contents of 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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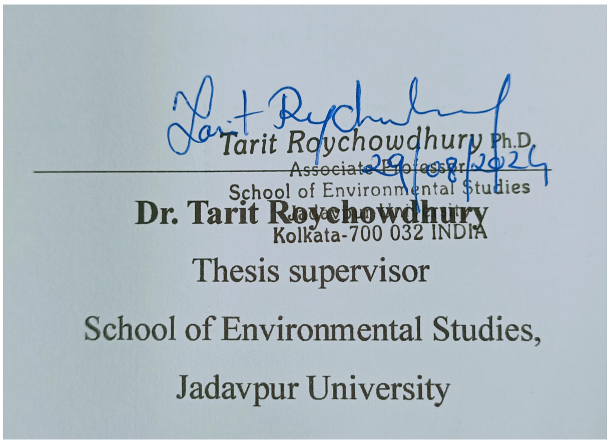
CERTIFICATE

This is to certify that the thesis report titled **“Arsenic Remediation from Water Using Suitable Nanomaterial and Biochar Amendment”**, submitted by Shuvankar Halder (Registration Number 163788 of 2022–2023; Class Roll No. 002230904003 and Exam Roll no: M4EBT24001), to Jadavpur University, Kolkata for the award of the degree of Master of Technology in Environmental Biotechnology in Environmental Biotechnology is a bonafide record of the research work done by him under my supervision. To the best of my knowledge, the constituents of this report, in full or in parts, have not been submitted to any Institute or University for the award of any degree or diploma.



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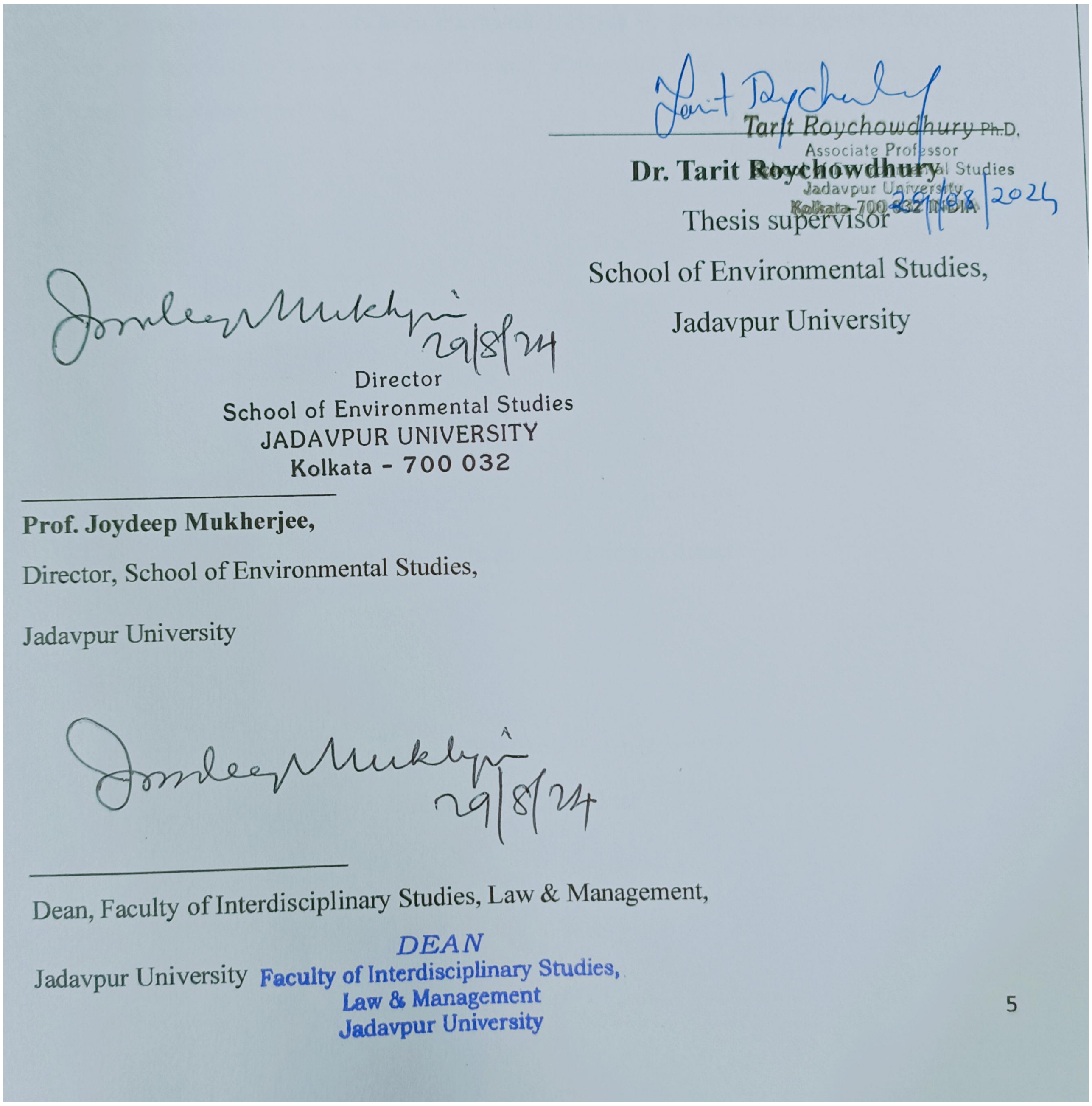
It is hereby notified that this thesis titled **“Arsenic Remediation from Water Using Suitable Nanomaterial and Biochar Amendment”**, is prepared and submitted for the partial fulfilment of the continuous assessment of Master of Technology in Environmental Biotechnology course of Jadavpur University by Shuvankar Halder (Registration Number 163788 of 2022–2023; Class Roll No. 002230904003 and Exam Roll no: M4EBT24001), a student of the said course for session 2022-2024. It also declared that no part of this thesis has been presented or published elsewhere.



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This certifies that Shuvankar Halder thesis, **"Arsenic Remediation from Water Using Suitable Nanomaterial and Biochar Amendment"** is an authentic documentation of his work completed between September 2022 and August 2024, partially fulfilling the requirements for the Master of Engineering in Environmental Biotechnology degree from the Department of Environmental Studies (Registration Number 163788 of 2022–2023; Class Roll No. 002230904003 and Exam Roll no: M4EBT24001).It is acknowledged that the undersigned only approves the thesis for the purpose for which it has been presented, and that by granting this approval, they do not necessarily support or approve any statements made, opinions stated, or conclusions drawn within.

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ABSTRACT

Arsenic (As) contamination in water poses a severe risk to public health and the environment, necessitating effective remediation strategies. Biochar prepared from banana peels was utilised to remove As from As-contaminated water. To enhance the removal efficiency, iron oxide nanoparticles (FeONP) were prepared using waste tea residue which was doped with banana peel biochar (BPB). The prepared material was characterized by Energy Dispersive X-Ray Spectroscopy-Field Emission Scanning Electron Microscopy (EDX-FESEM). Iron oxide nanoparticles enriched banana peel biochar (FeONP-BPB) showed higher As removal efficiencies compared to BPB. For 100, 200, 300 and 400 µg/L As contaminated water at pH 7, BPB showed dearsenification capacity of 61.45%, 64.71%, 70.68% and 75.02%, respectively while FeONP-BPB showed 90.46%, 93.96%, 95.31% and 97.1%, respectively. The experimental value follows well with the Langmuir isotherm than the other models. Therefore, the modification of banana peel biochar with iron oxide nanoparticles provides an effective alternative adsorbent for arsenic removal from water. This study demonstrates the use of waste materials for removal of As from As-contaminated water.

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CHAPTER-I

1. Introduction

Arsenic (As) is a serious threat to global health due to contamination of groundwater, especially in areas like India and Bangladesh where both natural and man-made sources contribute to high concentrations of this dangerous substance. It is naturally present in soil and water (Mandal & Suzuki, 2002). Prolonged drinking water exposure to As can cause a number of serious health issues, such as internal cancers, skin lesions, and other systemic diseases (Mandal & Suzuki, 2002; Smedley & Kinniburgh, 2002). Consequently, effective remediation strategies are essential to mitigate As pollution and protect public health. Safe drinking water is dependent on the development of sustainable and affordable techniques for removing As, particularly in environments with limited resources. Arsenic in the environment can take many various forms, including methyl-arsenic acid, arsenic acids, arsenates, and arsine (Mohan & Pittmann, 2007). There are two main categories of sources of As contamination: natural sources and man-made sources. Arsenic from natural sources is released through sediment deposition, weathering, and geochemical processes. The use of fossil fuels, chemicals containing As, and additives in chicken feed are only a few of the human activities that cause As pollution (Smedley & Kinniburgh, 2002). A disease called arsenicosis, which has symptoms like skin blackening, skin and other cancer of internal organs, ailments of legs and feet, and diabetes, is brought on by chronic exposure to As from natural sources, drinking water, and food (Mohan & Pittman, 2007). Ion-exchange, ultrafiltration, co-precipitation, and reverse osmosis are a few methods that can be used to remove As from drinking water. Due to its low cost, adsorption has been a common approach for removing As from water (Rathi et al., 2021). Arsenic has been removed using a variety of adsorbents, including activated charcoal, iron oxides, treated slags, and activated aluminum (Meez et al., 2021; Mohan & Pittman, 2007). Materials that include iron have a significant ability to adsorb As (Yan et al., 2010). The most demanding is adsorption, which offers good financials and cheap installation and maintenance costs. In comparison to the others, it also uses less energy. Activated carbon is frequently employed as the adsorbent in adsorption, but it is not always readily available in sufficient quantities and is somewhat costly (Gupta & Chen, 1978). In recent years, there has been a lot of interest in the production of nanoparticles using tea extracts (Kamath et al., 2020; Shahwan et al., 2011; Wang et al., 2014). These extracts are biodegradable, non-toxic, and non-mutagenic. They are also reasonably priced. These factors make green synthetic nanoparticles suitable for use in the biological and medical domains (Shankar et al., 2004). For the treatment of groundwater, using green generated nanoparticles is more cost-effective and ecologically benign. Plant polyphenols serve as capping agents as well, therefore the green produced nanoparticles don't require an additional stabilizing ingredient (Shahwan et al., 2011). To remove heavy metals, researchers have using green produced zero-valent iron nanoparticles (Ehrampoush et al., 2015; Fazlzadeh et al., 2017; Jin et al., 2018; Martinez-Cabanas et al., 2016). Additionally, green produced zero-valent iron nanoparticles have also been applied for wastewater treatment (Devatha et al., 2016; Wang et al., 2014) and dye degradation (Shahwan et al., 2011; Weng et al., 2018). The applicability of adsorption-based methods can be considerably expanded in developing nations if a less expensive substitute for activated carbon is discovered. Materials that have previously been typically studied as inexpensive adsorbents include straw, microbial biomass, and tea waste (Amarasinghe & Williams, 2007; Aikpokpodion et al., 2010; Cay et al., 2004; Kamsonlian et al. 2011; Mahavi et al., 2005). There are also a number of other benefits to using waste products as an affordable adsorbent. It has been generally observed that tea waste's very porous shape and insoluble cell allow it to trap heavy metals (Amarasinghe & Williams, 2007; Aikpokpodion et al., 2010; Cay et al., 2004; Mahavi et al., 2005). The tea waste's functional groups contribute to the action of trapping as well. Therefore, this study thoroughly examines the ability of tea waste and banana peel to remove As with the goal of suggesting a low-cost substitute for activated carbon.

CHAPTER-II

2. Objectives of the Study

1. **To evaluate the environmental benefits of green synthesis:** The objective of this study is to promote environmental advantages of using waste materials for nanoparticle synthesis promoting sustainable practices in nanotechnology and water treatment.

2. **To synthesize iron oxide nanoparticles using green methods**: The goal of the study is to reduce the amount of toxic chemicals used in usual conventional synthesis processes by using the natural reducing characteristics of the chosen waste materials to create iron oxide nanoparticles in an environmentally responsible way.

3. **Evaluate the effectiveness of tea waste**: To investigates the potential of processed tea waste as an alternative adsorbent to conventional activated carbon for removing arsenic.

4. **Assess treatment methods**: To determine the effect of aqueous $FeCl_3$ treatment on the tea waste's capacity to absorb arsenic from tainted water.

5. **Establish feasibility for use**: To determine whether it is possible to use tea waste as an easily available and reasonably priced substitute for As removal in water treatment processes, especially in underdeveloped nations.

6. **Quantify removal capacities**: To determine the various materials' capacities for removing As under various operating temperatures and conditions, offering a thorough evaluation of their efficacy.

7. **Contribute to environmental solutions**: The aim is to address the public health issues related to As exposure by aiding in the development of environmentally effective methods for treating water contaminated with arsenic.

CHAPTER-III

3. Brief history of arsenic contamination in groundwater: a review

3.1 Literature review

3.2. Arsenic

Arsenic is a naturally occurring element that can be found in different minerals, water, and soil. Due of its harmful impact on both the environment and human health, it is well known for its poisonous qualities and has been the subject of extensive research. When As-containing fertilizers or As-laden water are used for irrigation, As can contaminate crops, especially rice. Significant health hazards from this contamination include skin lesions, cancer, and developmental problems in children (Smith et al., 2002; Williams et al., 2007). Especially in areas where groundwater is contaminated, the presence of As in the food chain is a serious problem. Research has indicated that communities that largely depend on rice as a staple diet may be more exposed to As due to its ability to accumulate in rice grains (Rahman et al., 2007; Zhao et al., 2010). Moreover, As can interfere with plant metabolism and growth, which can lower agricultural yield and quality (Abedin et al., 2002).

3.3 Source of arsenic in the environment

Arsenic is a naturally occurring element that may be found in the crust of the Earth. Both natural and man-made sources can contribute to its presence in the environment. Addressing As pollution in soil and water requires an understanding of these sources.

Natural Sources:

(i) Geological sources: Volcanic activity and the weathering of minerals that contain arsenic, including arsenopyrite, release arsenic into the atmosphere. Arsenic can be mobilized into groundwater by natural geological processes, especially in regions where geological arsenic concentrations are high (Smedley & Kinniburgh, 2002).

(ii) Sediment deposition: Arsenic can also be present in sediments and soils, where it may leach into groundwater systems. This is particularly true in areas where naturally occurring arsenic levels are high.

Anthropogenic Sources:

(i) Industrial activities: Arsenic pollution is mostly caused by human activities including mining, smelting, and the use of arsenic in various industrial processes. For example, arsenic is frequently produced as a byproduct during the manufacture of metals like copper and lead (Mandal & Suzuki, 2002).

(ii) Agricultural practices: Historically, the use of pesticides and herbicides containing As in agriculture has led to soil and water contamination. Furthermore, fertilizers may include arsenic, which can cause it to build up in agricultural soils and then leak into groundwater.

(iii) Fossil fuel burning: Burning fossil fuels, especially coal, can release arsenic into the atmosphere. This gas can then return to Earth as precipitation, poisoning nearby water and soil resources.

(iv) Contaminated water sources: Due to a combination of human activity and naturally occurring geological formations, groundwater utilized for irrigation and drinking in many locations, especially in South Asia, is contaminated with arsenic. For the populations that depend on these water sources for their daily requirements, this contamination poses serious health hazards (Smith et al., 2000).

3.4 Arsenic in drinking water

Arsenic is hazardous to human health, its presence in drinking water is a serious public health concern. The World Health Organization (WHO) has established a 10-part per billion (ppb) thres hold as a temporary recommendation value for arsenic in drinking water because arsenic exposure can result in major health problems, such as internal cancers, skin cancer, and other disorders (WHO, 2011). Chronic exposure to low quantities of arsenic has been associated with a number of malignancies, including those of the skin, lungs, bladder, and kidneys, as well as diabetes and cardiovascular disorders (Navas-Acien et al., 2008; Smith et al., 2002).

3.5 Permissible limit of arsenic in drinking water

A recommended level of arsenic in drinking water is set by the World Health Organization (WHO) at 0.01 mg/L (10 µg/L). Based on the possible health risks—such as cancer and other serious health effects—associated with prolonged exposure to arsenic, this limit has been set (WHO, 2011). Long-term exposure to arsenic, even at low concentrations, can raise the risk of developing kidney, bladder, skin, and lung cancers, as well as other health problems such diabetes and cardiovascular illnesses (Navas-Acien et al., 2008; Smith et al., 2002). The Bureau of Indian Standards (BIS) has established a permitted level of 0.01 mg/L, or 10 parts per billion (ppb), for arsenic in drinking water. The World Health Organization's (WHO) recommendations for safe drinking water are in line with this standard (BIS, 2012; WHO, 2011). Based on the possible health risks—such as the possibility of cancer and other severe health effects—associated with prolonged exposure to arsenic, these limitations have been set.

Table 3.1: Permissible levels of arsenic in drinking water as set by various organizations

Name of the Organization	Permissible Limit (mg/l)
Bureau of Indian Standards (BIS)	0.01
Indian Council of Medical Research (ICMR)	0.05
Committee on Public Health Engineering Manual and code of Practice, Government of India	0.05
World Health Organization (WHO)	0.01

3.6 Adverse health effects of arsenic

Ingestion of inorganic As for a prolonged period causes respiratory problems, including cough, chest sound, bronchitis, and shortness of breath (Islam et al., 2013; Mazumder et al., 2000). (Mazumder et al., 2000) examined the rate of respiratory signs and symptoms including cough, chest sounds, and shortness of breath and As exposure via drinking water in the population of the As-affected 24-South Paraganas district of West Bengal in India. This study involved 7,683 participants of all ages (≤9 to ≥60 years). The concentration of As in their drinking water ranged from <3 to 3,400 µg/L. It was reported that the prevalence odds ratio (POR) for cough were 5.0 and 7.8 for males and females, respectively; for chest sounds, the POR was 6.9 and 9.6, for males and females, respectively, after adjustment of age. For shortness of breath, the POR was 3.7 and 23.2 in males and females, respectively.

Figure 3.1: renal system affected by arsenic toxicity

Source:
https://www.google.com/search?q=black+foot+disease

(i) Lung cancer: Exposure to arsenic has been strongly linked to an elevated risk of lung cancer, according to epidemiological research. Inhaling arsenic can cause cancer in the tissues of the lungs, especially in work environments (such as mining and smelting).

(ii) Chronic respiratory conditions: Long exposure to arsenic has been linked to bronchitis and chronic obstructive pulmonary disease (COPD), among other chronic respiratory conditions.

Table 3.2: Physiological effects of arsenic based on exposure concentrations and types

Arsenic Concentration	**Type of Exposure**	**Physiological Effects**	**References**
< 0.01 mg/L (10 µg/L)	Drinking water (low exposure)	No immediate health effects, but prolonged exposure may increase cancer risk.	WHO, 2021
0.01 - 0.05 mg/L (10-50 µg/L)	Drinking water (moderate exposure)	Skin lesions (hyperpigmentation, keratosis), potential cardiovascular effects.	NRC, 1999
0.05 - 0.1 mg/L (50-100 µg/L)	Drinking water (high exposure)	Increased risk of skin, bladder, and lung cancer; possible respiratory issues.	Smith et al., 2012
> 0.1 mg/L (100 µg/L)	Drinking water (very high Exposure)	Severe toxicity, including multi-organ failure, pronounced cancer risk, and respiratory complications	Mazumder et al., 2011
< 0.1 µg/m³	Air (low occupational exposure)	Minimal to no immediate effects; long-term exposure may still pose a cancer risk.	IARC, 2012
0.1 - 1 µg/m³	Air (moderate occupational exposure)	Respiratory irritation, chronic obstructive pulmonary disease (COPD), increased lung cancer risk.	Navas-Acien et al., 2005

> 1 µg/m³	Air (high occupational exposure)	High risk of lung cancer, severe respiratory issues, and cardiovascular problems.	Enterline et al., 1987
Acute Exposure (e.g., > 100 mg/m³ in air)	Accidential or High level exposure	Acute poisoning, leading to nausea, vomiting, abdominal pain, diarrhea, cardiovascular collapse, and death if untreated.	WHO, 2001

Arsenic keratoses (below) on the palms of a patient who ingested arsenic from a contaminated well over a prolonged period (photo courtesy Dr. Joseph Graziano).

Figure 3.2: Arsenic keratoses on plams

Source: https://www.google.com/search?q=black+foot+disease

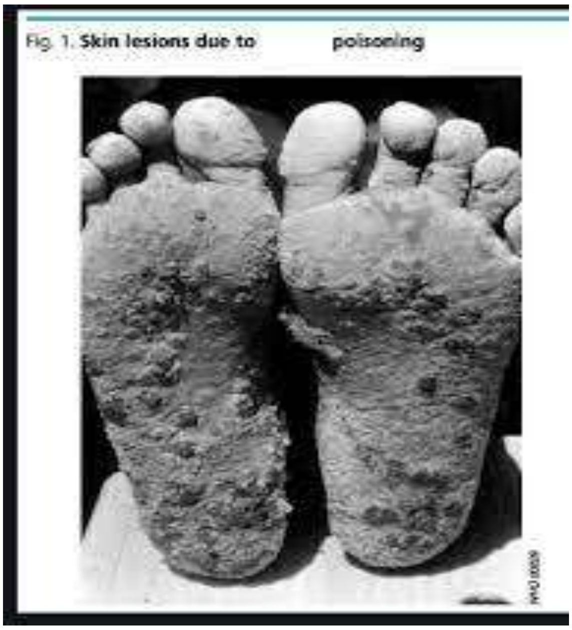


Fig. 1. Skin lesions due to poisoning

Figure 3.3: Skin lesions due to As poisoning

Source: https://www.google.com/search?q=black+foot+disease

(iii) Chronic Exposure and Long-term Effects

(a) Lung Function Decline: Long-term exposure to arsenic has been linked to a reduction in forced expiratory volume (FEV1) and forced vital capacity (FVC), two measures of lung function.

(b) Increased Risk of Respiratory Infections: Due to weakened immune systems and lung function, those exposed to arsenic may be more susceptible to respiratory infections.

3.6.1 Respiratory system

The kidneys are the main organ system in humans that excrete arsenic (As), and they seem to be less sensitive to the metal than other organ systems (Mandal & Suzuki, 2002). Capillaries, tubules, and glomeruli are the kidney's target sites for arsenic damage (Mandal & Suzuki, 2002). According to Wang et al. (2009), renal disease was related to arsenic exposure in a community examined in Xinjiang, China. According to Chakraborti et al. (2011), As inhibits a number of mitochondrial enzymes and interferes with oxidative phosphorylation to reduce cellular respiration. Because arsenite (As^{3+}) species increase reactive oxygen species (ROS), they inactivate sulfhydryl (-SH) groups in proteins and enzymes, which damages cells. As^{3+} can disrupt vital enzymes due to its greater solubility, which can have multi-systemic non-cancerous effects (Chakraborti et al., 2011). Numerous species of arsenic have been identified through studies, such as As^{3+}, As^{5+}, MMA (V), DMA (V), MMA (III), and DMA (III) (Smedley & Kinniburgh, 2002). By causing chromosomal abnormalities, oxidative stress, and enhanced cell proliferation while blocking DNA repair processes, inorganic arsenic indirectly contributes to cancer (Chen et al., 2008). Because of their structural similarities, arsenate (AsO_4^{3-}) can replace phosphate (PO_4^{3-}), which will cause ADP to be substituted and prevent ATP creation, which will interfere with the production of cellular energy (Mandal & Suzuki, 2002). The health effects of As, including those on the skin, heart, lungs, digestive system, liver and spleen, diabetes mellitus, endocrinology, neurological system, reproductive and developmental system, cancer, and other systemic effects, have been reported before (Daryabor et al., 2020).

3.7 Distribution of arsenic in groundwater from India

Table 3.3: Distribution of arsenic in groundwater in India

State	District/Place	General range of arsenic concentration (mg/l)	References
West Bengal	Murshidabad	0.05 - 1.2	Chakraborti et al., 2009
Bihar	Bhojpur	0.01 – 1.5	Saha et al., 2009
Uttar Pradesh	Ballia	0.05 – 0.95	Bhattacharya et al., 2006
Assam	Nalbari	0.01 – 0.6	Mahanta et al., 2009
Punjab	Amritsar	0.01 – 0.07	Singh et al., 2006
Jharkhand	Sahebganj	0.01 – 0.45	Yadav et al., 2012
Haryana	Palwal	0.01 – 0.15	Kumar et al., 2010
Chhattisgarh	Raipur	0.01 – 0.08	Chandrasekharam et al., 2010

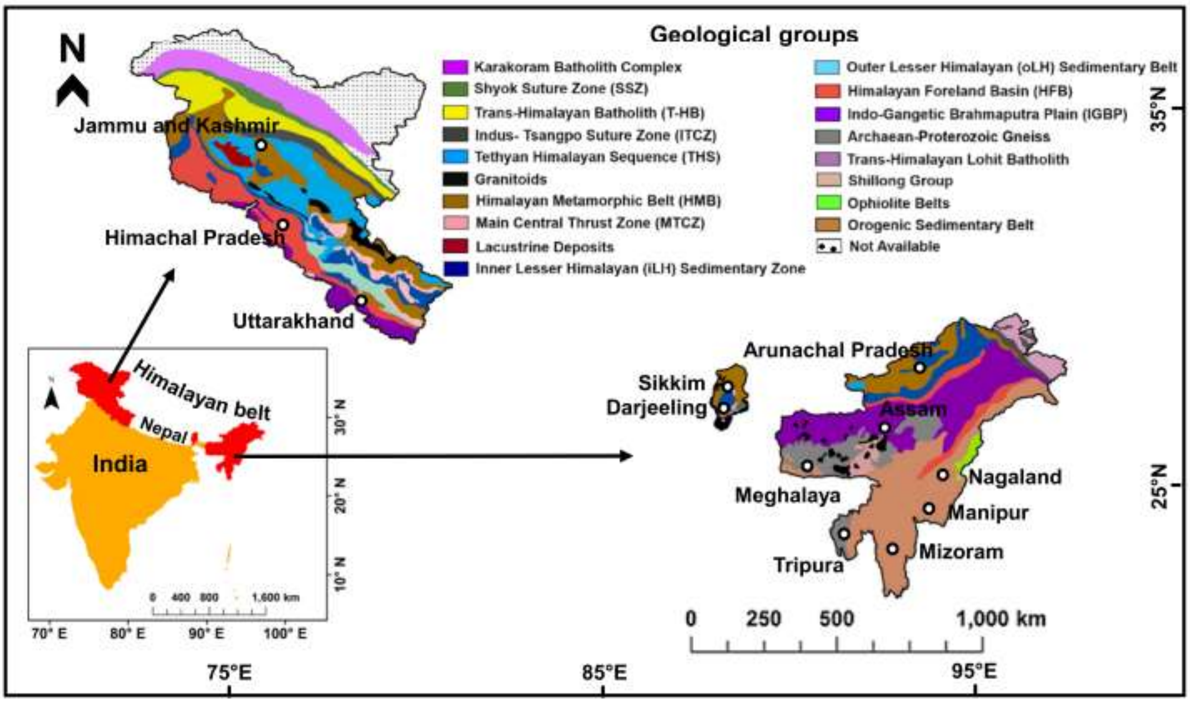


Figure 3.4: Contamination of Arsenic in various states in India (Das et al., 2022)

3.8 Arsenic affected zone in West Bengal

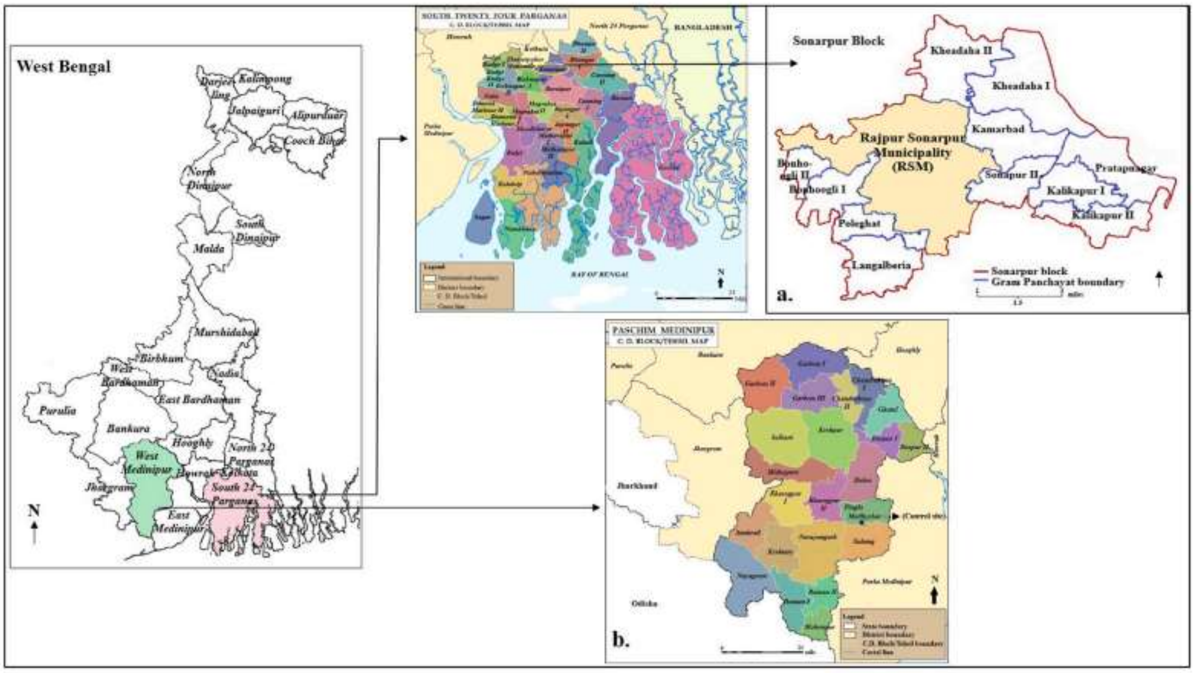


Figure 3.5: Affected areas in West Bengal (De et al., 2022)

CHAPTER-IV

4. Remediation Techniques

4.1 Amendments for arsenic remediation from water

4.2 Use of green synthesized nanoparticles in remediation

Nanoparticles range in size from 1-100 nm. They are widely used for various kinds of purposes such as adsorption and catalysis. Nanoparticles due to their nanometer size and large surface area, show great properties of adsorption. Therefore, these nano-sized particles are exploited for wastewater treatment. Even nanoparticles have been highly investigated and researched in this field of treating wastewater for removal of heavy metals, inorganic pollutants and pathogenic microorganisms (Lunge et al., 2016). Nanoparticles' effectiveness in eliminating harmful compounds have also been documented in a number of studies For example, it has been demonstrated that metal oxide nanoparticles, such as zinc oxide (ZnO) and titanium dioxide (TiO_2), may efficiently remove organic contaminants from water via photocatalytic degradation (Khin et al., 2012). Numerous physical and chemical techniques can be used to create nanoparticles. Nonetheless, one major disadvantage of these methods is their high level of toxicity (Durán et al., 2015). Alternative production techniques that are safer and more environmentally friendly are being developed in response to these worries (Iravani, 2011). These developments are intended to lessen the negative consequences of traditional physical and chemical synthesis techniques, which frequently use toxic solvents and produce dangerous byproducts (Mittal et al., 2013).

4.3 Iron nanoparticles use in arsenic remediation

Iron nanoparticles' exceptional chemical and dimensional stability allows for a larger capacity to remove As from waterbodies. Iron nanoparticles allow reactive areas to be exposed upon application due to their excellent surface distribution. The consistent size and charge distribution of iron nanoparticles created through green synthesis contribute to their increased efficiency. These bioinspired magnetic nanoparticles' superior adsorption and degradation properties stem from their high volume-to-surface ratio and quantum size. These magnetic nanoparticles may therefore be more effective in eliminating As3+ and As5+.

4.4 Properties of iron nanoparticles

Magnetic nanoparticles are another name for iron nanoparticles (FeNPs). Since these nanoparticles have no toxicological consequences, cleanup can be done with them. The most significant feature is its huge surface area, which aids in absorbing the majority of the material. It has thermal and electrical conductivity as well. Iron nanoparticles from tea residue are found to be either cuboid or of pyramid shape (Fahmy et al., 2018). Iron nanoparticles have potential implementation in adsorption of As, removal of harmful toxic dyes and also possess antibacterial activities. The size of the particles mainly ranges from 5-25 nm (Lunge et al., 2014). These FeNPs have high dimensional stability, high electrical conductivity and also high thermal conductivity (Batool et al., 2021). FeNPs are extremely reactive because they can instantly create Fe ions when they come into contact with water or air. As a result, these Fe_3O_4 nanoparticles possess super-paramagnetic qualities as well.

4.5 Use of biochar in arsenic remediation

Because of its excellent capacity for immobilizing impurities and effectively absorbing heavy metals and organic pollutants, biochar has been gaining popularity in recent years. Biochar can be produced by burning the waste products produced by homes and farms. This encourages the recycling and reuse of waste products, leading to a more ecologically friendly approach to environmental remediation. The usage of biochar is growing rapidly as a result of its extraordinary potential for remediation (Vithanage et al., 2016). The type of feedstock and thermochemical processes employed in its synthesis determine the production and effectiveness of biochar. High carbon content and extremely high temperatures produce biochar with a high ash percentage. Moreover, a higher ash concentration speeds up the immobilization of contaminants. Pyrolytic temperature has a huge influence on the potentiality of the biochar. Increased pyrolytic temperature subsequently increases the pore size, surface area and the volume of the pore (Ahmad et al., 2014). Also, high pyrolysing temperature converts aliphatic carbons to aromatic carbons which latter forms rings like structures of graphene. Therefore, biochar can be used for remediating both As^{3+} and As^{5+} from waterbodies. In this study, domestic waste like tea waste and banana peel was used as biochar.

CHAPTER-V

5. Materials and Methods

5.1 Green synthesis of iron nanoparticles

Iron nanoparticles were synthesized using the procedure outlined by (Lunge et al., 2016). After gathering the discarded tea, it was properly cleaned with distilled water and allowed to air dry. 150 mL of distilled water was used to dissolve 30 g of dry tea trash. addition of 15 g $FeCl_3.2H_2O$ was made to a 150 mL mixture. After that, it was shaken for four hours and left to incubate overnight. Subsequently, the residue was collected and dried in a hot air oven after suction filtration. To get rid of any contaminants, the residues were cleaned twice with distilled water. The tea residue was cleaned, dried fully in a hot air oven, and then heated for six hours at 450 °C in a muffle furnace. On cooling down, the product obtained was homogenized using a mortar and pestle.

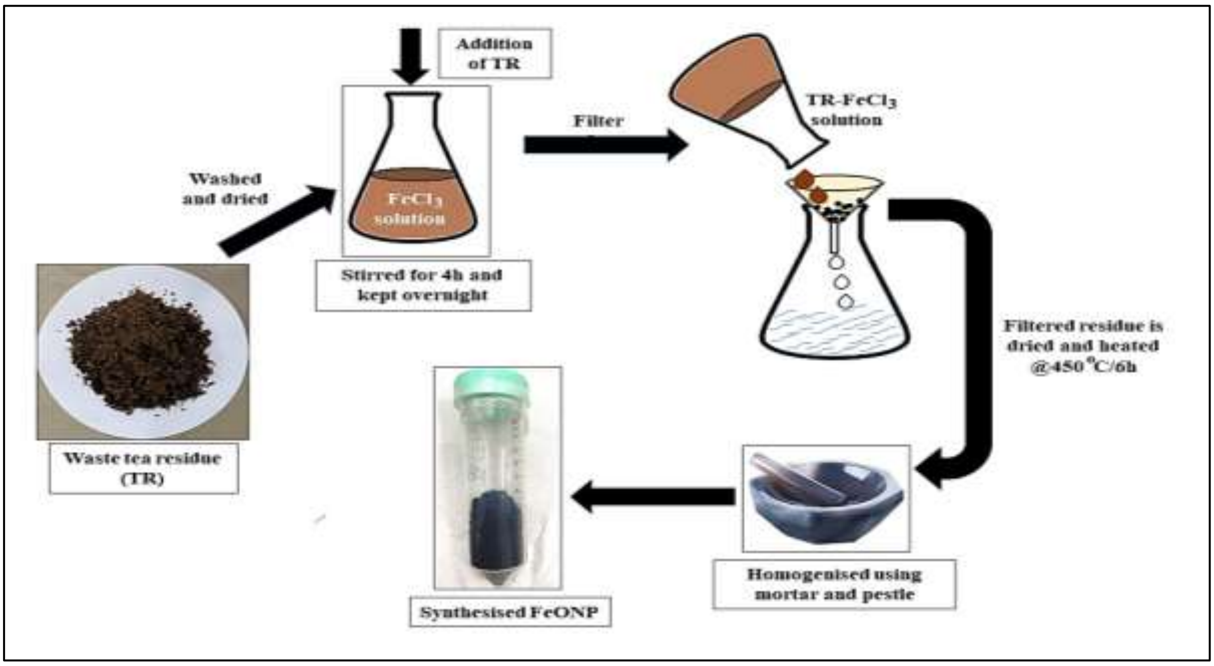


Figure 5.1 : Green synthesis of iron nanoparticles

5.2 Preparation of biochar from banana peel

Banana peels were used to create biochar. To ensure that the banana peel was completely free of contaminants, it was first cleaned with distilled water and then the cleaned banana peels were chopped into little pieces. After being allowed to air dry, the banana peels were placed in a hot air oven set at 50 °C until they were completely dry. Using silicon crucibles, the dried banana peels were now heated to a very high temperature of 600 °C for two hours in the muffle furnace. After allowing the heated crucibles to cool, they were put away in airtight containers for later use.

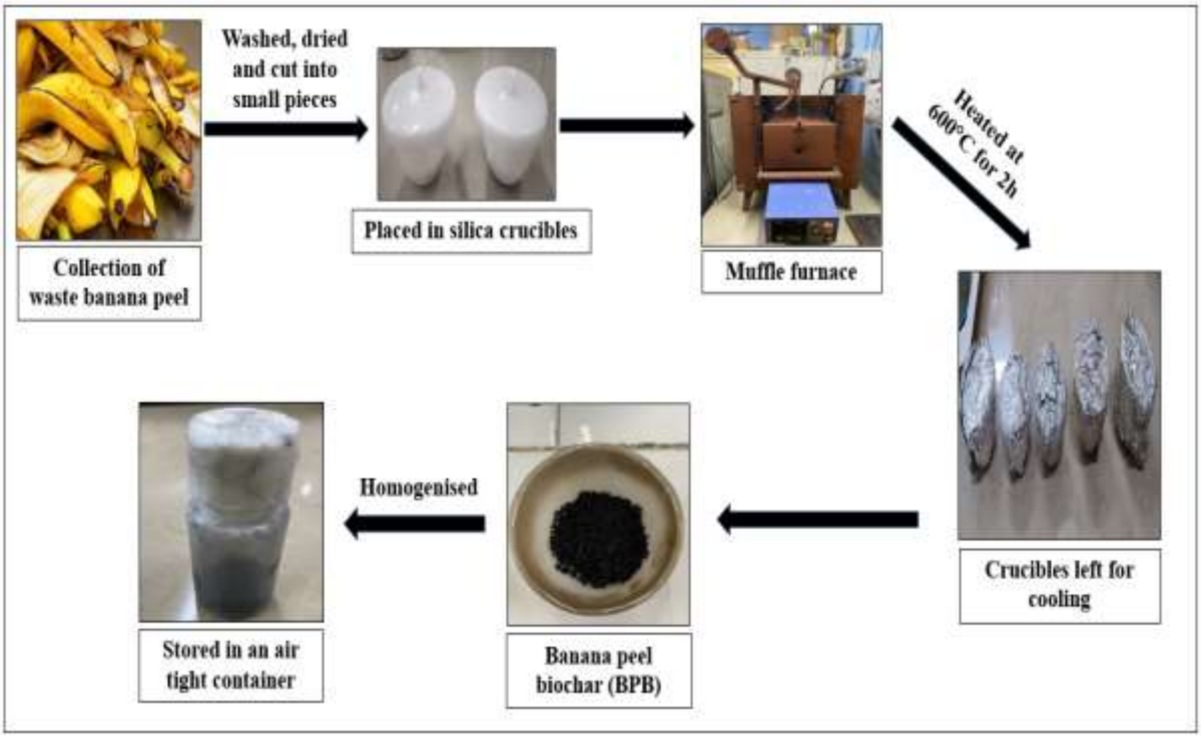


Figure 5.2 : Preparation of banana peel biochar

5.3 Preparation and characterization of FeONP doped banana peel biochar

For the synthesis of biochar doped FeONPs, both FeONP and banana peel biochar were taken in a ratio of 1:1. Five (5.0) g of both banana peel biochar (BPB) and FeONPs were weighed. Now this mixture was added with 50 mL of double distilled water in a 100 mL of conical flask. The mixture was kept for stirring overnight. Next day the mixture was suction filtered and the residues were taken. Now the residues were allowed to dry in a hot air oven at 50 ºC. It was then stored until further use. A part of it was processed for analysis of surface morphology and elemental composition using EDX-FESEM.

5.4 Application of FeNP doped biochar in removal of arsenic

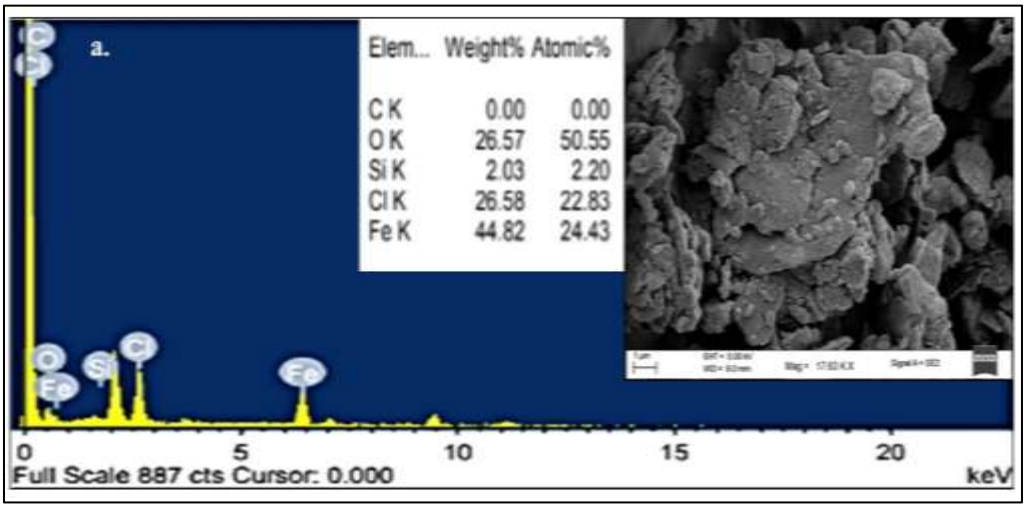
0.05g of iron-oxide doped biochar (FeONP-BPB) particles were weighed for 50mL of arsenic spiked water to make dosage of 1g/L. The concentration of arsenic spiked water was taken as 100 ppb, 200 ppb, 300 ppb and 400 ppb. The As spiked water was kept in contact with the particles by constant stirring at different time intervals such as 0 min, 20 min, 40 min, 60 min. The mixture was suction filtered at the respective time intervals and the filtrate was collected to measure the arsenic content in VGA-AAS after treating with iron-oxide doped biochar particles.

CHAPTER-VI

6. Results and Discussion

6.1 Characterization of FeONP-BPB

The surface morphology and elemental composition of FeONP-BPB was studied from EDX-FESEM as shown in **Fig. 5.1** It was observed that the size of the particles of FeONP-BPB lied in the range of 180–250 nm. The magnetic particles of FeONP-BPB tend to cluster and agglomerate as they are magnetic in nature. There may be a possibility of exposure of the adsorbent to moisture during sample preparation and handling which also cannot be ruled out.



Elem...	Weight%	Atomic%
C K	0.00	0.00
O K	26.57	50.55
Si K	2.03	2.20
Cl K	26.58	22.83
Fe K	44.82	24.43

Figure 6.1 : PEDX-FESEM analysis of FeONP-BPB

6.2 Batch Adsorption Studies

6.2.1. Initial arsenic concentration effects

The initial As solution concentration exerts an influence upon the adsorption capacity. The initial As concentrations were 100, 200, 400 and 500 µg/L under different pH conditions (5, 7 and 9), the amount of adsorbent was 1 g/L and the adsorption time was set upto 1 h. **Fig. 6.2** represents the As removal efficiencies at different initial As concentrations. In case of BPB, the As removal efficiency increased from 61.45% to 75.0% when the initial As concentration increased from 100 to 500 µg/L under pH 7. Similar trend was noticed with increasing initial As concentration in other pH conditions. FeONP-BPB also exhibited increase in As removal efficiency with increasing As conditions, the highest being ranging from 90.46% to 97.1% under pH 7.

6.2.2. Influence of contact time

The effect of contact time with the capacities of both BPB and FeONP-BPB under different pH conditions is presented in **Fig. 6.2** The adsorption ability of the adsorbents increased with time in the beginning. This may be attributed to the sufficient active sites on the surface of the adsorbent which is filled up with time in the process of adsorption. FeONP-BPB, however, showed faster adsorption rate compared to BPB. As the contact period was further increased and the adsorbent was fully saturated, desorption was noticed which was confirmed with the slow increase in As concentration.

6.2.3. Influence of pH

The adsorption of As was better at pH 7. Both BPB and FeONP-BPB showed maximum d dearsenification capacities in solutions of pH 7. The surface of adsorbent and As forms complexes due to adsorption and co-precipitation.

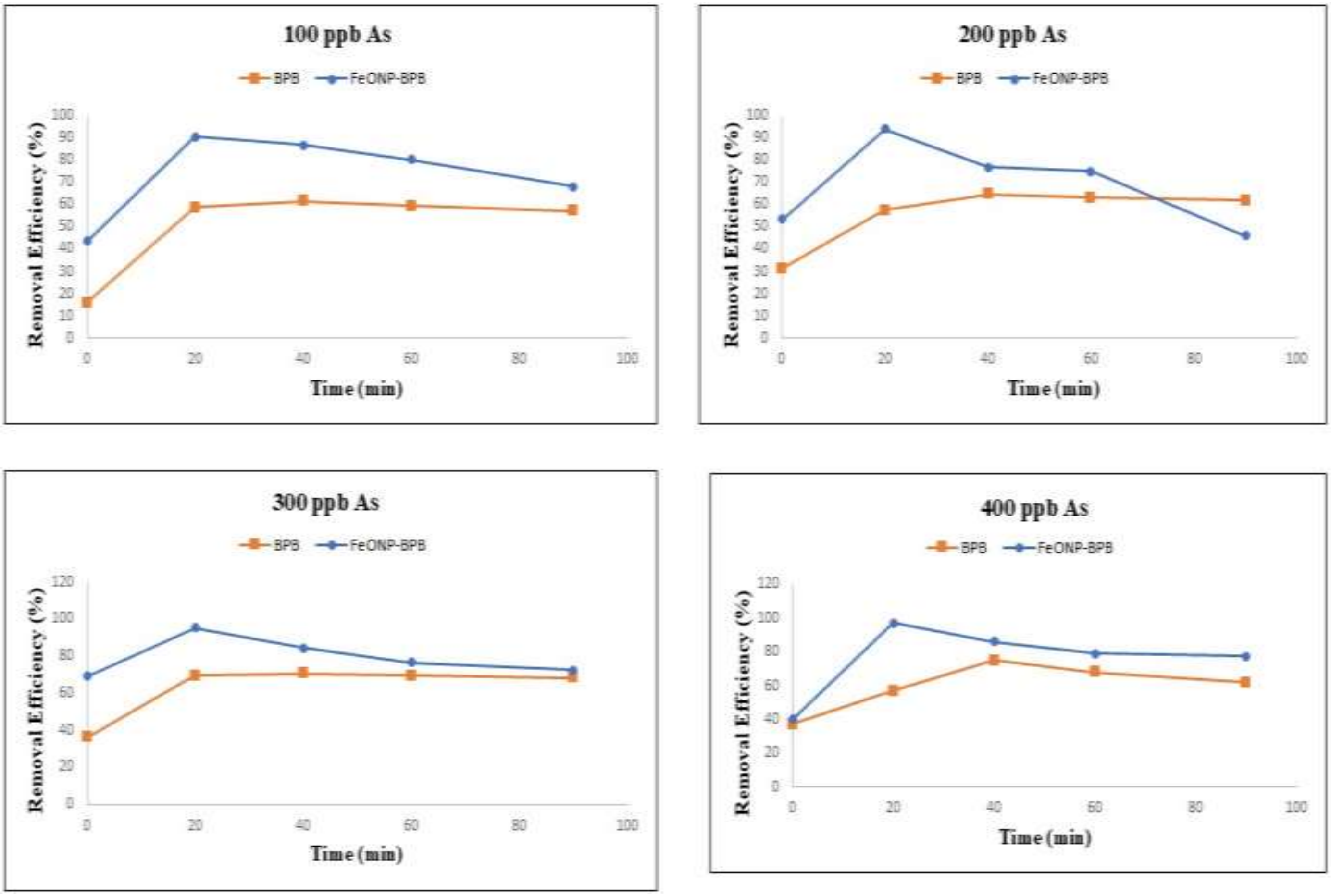


Figure 6.2 : Removal efficiencies of As by BPB and FeONP-BPB

6.3 Adsorption Isotherm

The properties of the adsorbent and the adsorbate, as well as the chemistry between them, all have an impact on adsorption, as is shown by isotherm studies. Three isotherm models the Langmuir, Freundlich, and Temkin adsorption isotherms helped to understand the adsorption mechanism at play. Freundlich isotherm depicts the formation of heterogeneous layers on the adsorbent surface as a result of adsorption, whereas Langmuir isotherm defines monolayer adsorption.

The Langmuir adsorption model can be represented in linear form as follows:

$$1/qe = (1/KLq\ max) \times (1/Ce\ ) + (1/qmax) \tag{2}$$

Where, qe represents adsorbent equilibrium As concentration (mg/g); C_e is the As concentration in the solution at equilibrium (mg/g); q_{max} indicates the maximum quantity of As adsorbed per unit weight of adsorbent, sufficient to establish a fully saturated monolayer on the surface at high C_e (mg/g); and K_L is Langmuir adsorption constant. The parameters for Langmuir isotherm were obtained by plotting $1/C_e$ vs $1/q_e$ as shown in **Fig. 6.3.**

The Freundlich isotherm model is derived from Langmuir isotherm model which assumes the existence of sites on the adsorbent with different affinities for each specific adsorbent. The model further elucidates the individual site behaviour in accordance with the principles outlined in the Langmuir isotherm. The Freundlich adsorption model can be represented as:

$$log\ qe = log\ Kf + (1/n)log\ Ce \qquad (3)$$

Where, K_f indicates the ability of the adsorbent referred as the Freundlich adsorption capacity and n indicates the heterogeneous nature of the system which reflects the variation in the attraction towards the adsorbate with changes in the biosorption density. The parameters for Freundlich adsorption isotherm were obtained by plotting log C_e vs log q_e as shown in **Fig. 6.3.**

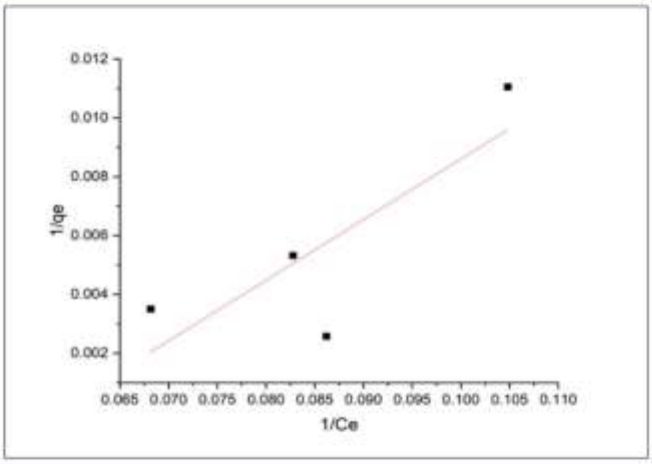
The adsorbent-adsorbate interaction is explained by the Temkin isotherm:

$$qe = (RT/bT\ )lnAT + (RT/bT\ )lnCe \qquad (4)$$

Where, A_T refers to Temkin isotherm equilibrium binding constant (L/g), b_T indicates Temkin adsorption isotherm constant, R represents universal gas constant (8.314J/mol/K) and T is the temperature at 298K. The parameters for Temkin isotherm were obtained by plotting ln C_e vs q_e as shown in **Fig. 6.3.**

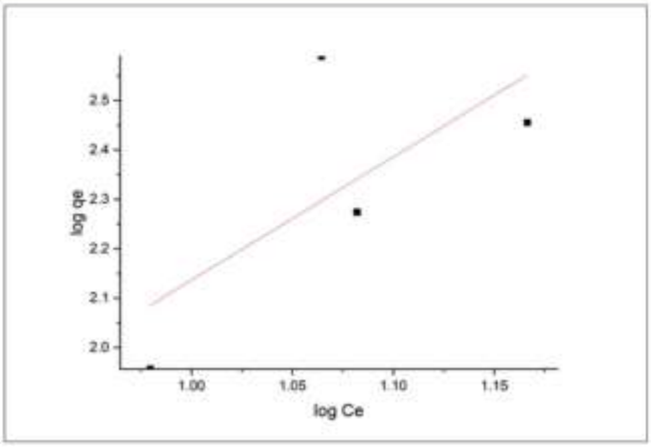
a.

Equation	Y= a + b*x
Plot	B
Weight	No weighting
Intercept	-0.1199±0.00819
Slope	0.20586±0.10307
Residual Sum of Squares	1.4483.8E-5
Pearson's r	0.81612
R-Squares (COD)	0.66606
Adj. R- Squares	0.49909



b.

Equation	Y= a + b*x
Plot	log qe
Weight	No weighting
Intercept	-0.35544 ± 1.94834
Slope	0.249197 ± 1.81211
Residual Sum of Squares	0.1157
Pearson's r	0.69714
R-Squares (COD)	0.48601
Adj. R- Squares	0.22901



c.

Equation	Y= a + b*x
Plot	qe
Weight	No weighting
Intercept	-765.26777 ± 1052.07325
Slope	406.03401 ± 424.96261
Residual Sum of Squares	33737.05745
Pearson's r	0.55982
R-Squares (COD)	0.3134
Adj. R- Squares	-0.0299

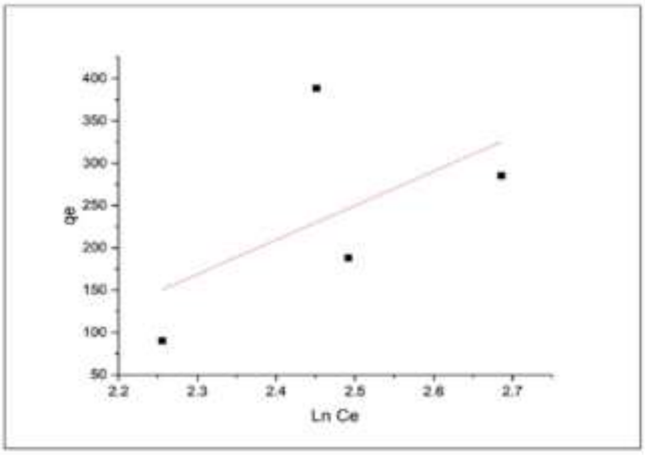


Figure 6.3 : Different isotherms for FeONP-BPB: a.Langmuir isotherm, b.Freundlich isotherm, c. Temkin isotherm

The fitting parameters for the Langmuir, Freundlich, and Temkin adsorption isotherms were showed in **Table 6.1**. Considering the best dearsenification capacity shown in pH 7, the study results fit the Langmuir model best. Overall, Langmuir isotherm show better fit than the other isotherms as per the batch adsorption study. FeONP-BPB has a comparatively higher adsorption capacity when compared to BPB. The adsorption may further be explained by different types of van der Waals contact and the electrostatic attraction force between the sites of the adsorbent and the adsorbate respectively.

Table 6.1: Adsorption isotherm parameters for F^- adsorption by CTR and FeONP-TR

	Langmuir isotherm	**q_{max} (mg g^{-1})**	**K_L (L mg^{-1})**	**R^2**
FeONP-BPB	pH 7	83.4028	0.05824	0.5
	Freundlich isotherm	***n***	**K_F (L mg^{-1})**	**R^2**
	pH 7	2.49197	0.441123	0.3
	Temkin isotherm	**B_T (J mol^{-1})**	**K_T (L mg^{-1})**	**R^2**
	pH 7	406.034	0.151869	0.03

6.4 Arsenic removal mechanism

The removal of As from the As-contaminated water may be attributed to adsorption and co-precipitation. The high surface area of nanoparticles and biochar aid to adsorption of As. Arsenic ions are attracted to and bind with the surface of the iron oxide nanoparticles due to electrostatic forces and chemical interactions. Arsenic can be also be co-precipitated with iron oxides as part of a larger iron-arsenic compound. The interaction of iron oxide nanoparticles which can form strong surface complexes. The reaction between iron oxide nanoparticles (Fe_2O_3) with As (V) may result to the formation of ferric arsenate ($FeAsO_4$). Similarly, As (III) may be oxidised to As (V) and follow the similar reaction.

CHAPTER-VII

7. Conclusion

The removal efficiency by FeONP-BPB was evidently higher compared to that of BPB. For 100, 200, 300 and 400 µg/L As contaminated water at pH 7, BPB showed dearsenification capacity of 61.45%, 64.71%, 70.68% and 75.02% respectively while FeONP-BPB showed 90.46%, 93.96%, 95.31% and 97.1% for the same. FeONP-BPB showed maximum As removal efficiency of 97.1% under pH 7 with an initial As concentration of 400 µg/L compared to 75.02% shown by BPB under same condition. It can be said that modification of tea waste by iron oxide nanoparticles and banana peel biochar aided in enhancing dearsenification of water. The present study demonstrates an effective way to utilise tea residue, banana peel waste which are generally discarded, in removal of As from water. Application of waste materials promises as a sustainable method to remove As from As contaminated water.

CHAPTER-VIII

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