REMOVAL OF ARSENIC FROM AQUEOUS SOLUTION BY VARIOUS NATURAL SOIL-BASED ADSORBENTS

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by

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LIST OF SYMBOLS AND ABBREVIATIONS

<	Lower Than
>	Higher Than
°C	Degree Celsius
%	Percentage
θ	Theta degree
µL	microliter
µg/L	Microgram per litre
AAS	Atomic Absorption Spectroscopy
As	Arsenic
Au	Gold
BET	Brunauer Emmett Teller
Ca	Calcium
CO	Carbon Monoxide
Cd	Cadmium
cm	Centimetre
Co	Cobalt
Cr	Chromium
Cu	Copper
et al	And Other
EDX	Energy Dispersive X-Ray

ETAAS	Electrothermal Atomic Absorption Spectroscopy
EU	European United
FAAS	Flame Atomic Absorption Spectroscopy
Fe	Iron
FTIR	Fourier-transform Infrared
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
HNO_3	Nitric Acid
Hg	Mercury
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
K	Potassium
K	Kelvin
L	litre
M	meter
Mg	Magnesium
mg/L	milligram per litre
Ni	Nickel
Pb	Lead
ppm	parts-per million
SEM	Scanning Electron Microscope
WHO	World Health Organization
XRD	X-Ray Diffraction
Zn	Zinc

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PENYINGKIRAN ARSENIK DARI LARUTAN AKUEUS OLEH PELBAGAI PENJERAP BERASASKAN TANAH SEMULAJADI

ABSTRAK

Aktiviti perindustrian, perlombongan dan pertanian yang pesat membawa kepada pembuangan bahan cemar seperti arsenik (As) ke dalam sumber air yang menyebabkan kesan buruk kepada organisma hidup. Oleh itu, penggunaan kaedah penyingkiran yang berkesan dan cekap adalah penting. Objektif kajian adalah untuk mengaplikasikan kaedah penjerapan dengan menggunakan bahan penjerap berasaskan tanah semulajadi termasuk tanah merah, tanah liat, berpasir dan hitam untuk penyingkiran arsenik daripada larutan akueus. Kajian ini melibatkan pencirian kandungan logam berat dan ciri fizikokimia penjerap tanah, diikuti dengan proses penjerapan kelompok dan kajian model dan mekanisme penjerapan. Keputusan untuk kepekatan arsenik dalam semua penjerap tanah adalah lebih rendah daripada had yang dibenarkan oleh European United (EU) dan purata kepekatan ferum (Fe) diperhatikan lebih tinggi dalam tanah merah berbanding dengan sampel tanah lain. Bagi analisis pencirian fizikokimia, tanah merah mempunyai bilangan kumpulan berfungsi tertinggi, kandungan mineral berasaskan Fe, luas permukaan dan isipadu liang dengan saiz zarah terkecil. Daripada kajian ini, keadaan optimum penyingkiran arsenik daripada larutan akueus ialah 2.2g/50 mL dos penjerap selama 60 minit masa sentuhan pada pH 5.5±0.5 dan suhu 40°C. Keupayaan dan kecekapan penjerap tanah dalam menyingkirkan arsenik daripada larutan akueus ialah tanah merah> tanah liat> tanah berpasir> tanah hitam. Model kinetik, isoterma dan termodinamik menunjukkan

mekanisme penjerapan arsenik adalah proses penjerapan kimia, bukan spontan dan endotermik.

REMOVAL OF ARSENIC FROM AQUEOUS SOLUTION BY VARIOUS NATURAL SOIL-BASED ADSORBENTS

ABSTRACT

Rapid industrialization, mining and agricultural activities lead to the release of contaminants such as arsenic (As) into the water sources that causes adverse effect to living organism. Thus, the application of effective and efficient removal method is crucial. The objective of the study is to apply the adsorption method by utilizing natural soil-based adsorbents including red, clay, sandy and black soil for removal of arsenic from aqueous solution. This study involved the characterisation of heavy metal content and physicochemical characteristic of soil adsorbents, followed by batch adsorption process and the study of adsorption model and mechanism. The results for concentration of arsenic in all soil adsorbents were lower than the permissible limit stated by European United (EU) and mean concentration of iron (Fe) observed to be higher in red soil compared to in other soil samples. For the physicochemical characterisation analysis, red soil has highest number of functional group, content of Fe based minerals, surface area and pore volume with the smallest particle size. From this study, the optimum removal conditions of arsenic from aqueous solution were 2.2 g/50 mL dosage of adsorbents for 60 minutes of contact time at pH of 5.5±0.5 and temperature of 40°C. The adsorption capability and efficiency of soil adsorbent in removing arsenic from aqueous solution were red soil> clay soil> sandy soil> black soil. The kinetic, isotherm and thermodynamic model showed that the mechanism of adsorption of arsenic was a chemisorption, non-spontaneous and endothermic process.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Water sources are considered as the fundamental resources of all living organism especially human, specifically for household, commercial, and agricultural purposes. However, throughout all these activities, waste specifically heavy metal pollutants were released into the water sources lead to contamination of water supplies. The occurrence of water pollution, particularly with heavy metals pollutants, poses serious hazards to the human population as well as animals and flora (Gunatilake, 2015).

Additionally, because microorganism are unable to digest heavy metals after they are introduced into the environment, they potentially causes adverse effect on the ecosystem and other ecological receptors and accumulate throughout the food chain (Yang et al., 2019). The common heavy metals that contaminate the water sources are arsenic (As), cadmium (Cd), mercury (Hg), nickel (Ni), and lead (Pb) (Muhammad et al., 2018). These elements are carcinogenic agents, well-known toxics and highly water-soluble.

Arsenic is an element that abundant in the earth's crust and occurs naturally in geological formations (Baker et al., 2018). This element, which is primarily inorganic form, can be found in soil, water and air which considered as a toxic elements. The used of arsenic primarily found in herbicide, pesticide and in preservation of wood (Zaynab et al., 2022). Since arsenic can easily dissolve in water, there were some of the significant potentials of arsenic exposure sources. Human activity, including smelting, mining, coal ash disposal and pesticide use that lead to soil and water contamination. Contaminated of arsenic in water due to agricultural irrigation linked to exposure pathway to food crops and soil (Baker et al., 2018).

Moreover, in comparison to other heavy metals, arsenic is highly toxic as the exposure of arsenic will cause adverse health effects especially in human populations. The exposure from contaminated drinking water was linking to chronic ingestion of arsenic which lead to both non-cancer and cancer health problems for example skin lesions and skin cancer (Baker et al., 2018). Arsenic element are non-degradable, and exposure may cause several adverse health problems such as dermal cancer and also other carcinogenic cardiovascular and gastrointestinal effects (Nicolopoulou-Stamati et al., 2016).

Since the exposure of arsenic lead to several adverse effect, removal method of arsenic especially from water sources has received interest among researchers. Therefore, efficient and effective methods are needed for the elimination of arsenic pollutants from water sources. The removal process can be utilized through several technique including chemical precipitation, membrane operations, coagulation, complexion, adsorption, foam flotation, ion exchange, electro-deposition and solvent extraction (Gunatilake, 2015).

Some of these methods have inherent limitations of generating sludge, costly disposal, sensitive operating conditions and low efficiency methods. However, adsorption is the most efficient method compared to others (Ugwu & Igbokwe, 2019). The adsorption technique is an emerging and newly process that has a great potential in removing heavy metals in different samples. This technique provides simple operation, high-quality, flexibility in design, the adsorbent can be regenerated and reversible (Yao et al., 2020). Natural soil, clay and zeolite are the potential natural adsorbent material in which they have cation exchange capacity, high efficiency for adsorption and also large specific surface area (Rafati et al., 2016).

Soil is one of the natural adsorbents which is utilized in the treatment or removal process of heavy metal. Iron oxide in the soil is one of the oxide compounds that initially occur in soil that can be used as a heavy metal removal agent. The existence of oxide in soil has a distinct relatively high surface energy, electrochemical properties, provide the structural cementation in the ground and specifically has a strong ability to adsorb.

Thus, soil properties are influenced by the occurrence of free Fe oxides, characteristics and especially its overall content (Zhang et al., 2016). To date, there is scarce information regarding the previous methods that concurrently detects and removes arsenic compound since previous researchers focused solely only on whether the detection or removal of arsenic compound from various types of samples. Thus, this study were focus on the removal of arsenic using adsorption techniques with utilizing natural soil adsorbent of red, clay, sandy and black soil.

1.2 Problem Statement

Industrialization, cleaning, and marketplace activities contribute to the contamination of water sources which drawn by the unethical removal and disposal of waste materials into water sources. The significant component of a pollutant that will cause water pollution is heavy metal. Water sources, which are contaminated with heavy metals, can produce a severe effect on human health.

Arsenic contamination especially in groundwater lead to massive epidemic of arsenic related toxicities in several countries Bangladesh, China, Cambodia, Taiwan China and India (Riaz et al., 2022). This is occurred due to rapid metropolitan development and industrialization which increased the exploitation of the natural resource and pollution. Recently, some studies had reported the detectable value of arsenic concentration in several river and reservoir around Malaysia including Langat River, Linggi River and Bukit Merah Reservoir (Abdullah et al., 2020; Ahmed et al., 2021; Razak et al., 2021). Similarly, along with the growth of development of technology and industries, the exposure and contamination of arsenic especially in Malaysia has a great potential to be occurred in future.

Due to the adverse effect of arsenic, some methods for treatment of arsenic in wastewater had been introduced including ultrafiltration, coagulation, flocculation and ion exchange. Unfortunately, those techniques were no longer attractive to be applied due to higher in cost of production, toxic, and cause incomplete removal. Regarding on that issues, the research interest into the production of alternative adsorbents to replace the costly method of treatment has increased. Attention has been focused on the natural adsorbents, such as soil, chitosan, clay or agricultural and food bio-waste that were known as low-cost adsorbents (Abebe et al., 2018). Hence, this study was conducted to study the physicochemical characteristic of natural soil adsorbents prior to be used as the potential adsorbent in the removal process of arsenic from aqueous solution.

1.3 Objectives

1.3.1 General Objective

The general aim of this research is to perform the removal process of arsenic from aqueous solution by using various natural soil-based adsorbents.

1.3.2 Specific Objectives

1. To characterize the heavy metal content and physicochemical characteristic of potential soil-based adsorbent.
2. To investigate the optimum condition for the removal of arsenic using different types of natural soil adsorbent.
3. To determine the kinetic, isotherm, thermodynamic adsorption models and mechanism for removal of arsenic using the soil adsorbents.

1.4 Significance of Study

This study introduces a simple and effective method for the removal of arsenic from aqueous solution. The adsorption method of arsenic using soil as the adsorbent is a simple, low cost and non-toxic. This study also ~~will~~ provides some information regarding the application and mechanism of adsorption of arsenic on the surface of soil adsorbent. Other than that, this study also will demonstrate the influence of physicochemical characteristic of soil in the adsorption of arsenic. Consequently, in future, this study will help to provide some information to government, responsible authority and industries regarding on the development of efficient treatment or removal methods of arsenic from water sources.

1.5 Scope of Study

With a great potential of utilising natural adsorbents such as soil for the treatment of contaminated water, there has been a corresponding interest in its application to remove arsenic from water sources. From the observation of current scenario, the present study analyses the application of natural soil adsorbents in removal process of arsenic from aqueous solution. To this end, the study will also determine the optimal condition for the removal of arsenic. The scope of the study was restricted to select four different type of soil adsorbents including red, clay, black and sandy soil collected in Malaysia, and more specifically in geographical area of Machang, Kelantan. The study also limited to the collection of soils based on the colour of the soil. Further, the study also involved an analysis of physicochemical characteristic of the soil samples prior to be used as the adsorbents.

CHAPTER 2

LITERATURE REVIEW

2.1 Nature of Arsenic

Arsenic is an element which can be found in the Earth's crust (Jasudkar et al., 2019). Arsenic is an element which formed in combination with metals and sulphur. In the combination with oxygen, arsenic can be formed as secondary minerals (Rae, 2020). Arsenic usually appears in yellow, black and grey (Shaji et al., 2021). As stated by WHO, the allowable limit for concentration of arsenic in drinking water was 10 μg/L. Among from the other metal pollutants, arsenic can be described as highly toxic metal and was classified as carcinogen, teratogen and mutagens element (Shaji et al., 2021).

Arsenic primarily occur in organic form (Baker et al., 2018). Inorganic As compounds including arsenite, As(III) and arsenate, As(V) are found naturally and produced as result of mining and ore smelting. The interaction between inorganic with sulphur and oxygen result in the production of inorganic derivatives, while interaction with hydrogen and carbon will yield the organic compounds (ATSDR, 2013). Organic arsenic can be found in seafood especially in fish (Shaji et al., 2021). The different formation of arsenic is due to its atomic structure and this lead arsenic to be classified as a metalloid in the periodic classification.

Arsenite can be found from the smelting of metal sulphide ores. Arsenic from mineral deposits were dissolved and will accumulate in groundwater, resulting to the environmental pollution and exposure to the living organism. Due to the similarities in chemistry or chemical properties, arsenate have a tendency to be transport along with phosphate within the living systems.

The two formation of arsenic have different level of toxicity. The toxicity level of arsenite is higher in comparison to arsenate (Shaji et al., 2021). In the presence of oxidant for example free chlorine, arsenite can be converted to arsenate which is less toxic form of arsenic. The toxicity level of arsenic depend on the ability to bind with thiol groups, which likely the residues of cysteine in peptides and proteins (Doerge et al., 2020). Arsenite species has the ability to bind to thiol group while arsenate species has less tendency to bind to thiol groups. Methylated arsenite species for example dimethylarsenic acids is more toxic as it retain the toxic properties of arsenite. The binding and interaction of arsenic is influenced by the chelation with to two atoms of sulphur in bis-thiols, in which the produced complexes responsible to arsenic toxicity (Rae, 2020).

2.2 Transformation and Transportation of Arsenic

2.2.1 Transformation and Transportation of Arsenic in Water

Arsenic be able to transform into another arsenic compounds when present in water, soil, and atmosphere (Jang et al., 2016). The important factor controlling arsenic speciation and transformation are pH and redox potential. In water, arsenic mainly found arsenite in reducing anaerobic environment and as arsenate in aerobic conditions (Jha et al., 2017). The processes controlling arsenic between solid and aqueous phases may due to action of adsorption, redox reaction or biological transformation between mineral surface and arsenic (Cullen, 2014).

The released of arsenic to the ground or well-water due to natural occurrence or phenomenon, affected by geothermal systems, regional hydro-geological conditions and also water-rock interactions (Mosaferi et al., 2017). The oxidation of sulfide minerals and reductive dissolution and desorption of Fe oxides also contribute to the contamination of arsenic in groundwater (Gosh, 2019). The reduction and oxidation of arsenic minerals can be considered as an important mechanism for the release of arsenic in groundwater (Masuda, 2018). Anthropogenic activities of mining operations, geothermal, as well as disperse arsenic in the environment and excess pumping of shallow groundwaters, thereby expanding arsenic contamination.

Several studies were conducted which focused on the contamination of arsenic in groundwater. It was reported that millions people were exposed to contamination of arsenic in several countries including in India and Bangladesh (Jasudkar et al., 2019). The arsenic-contaminated groundwater recorded to be at levels above 10 µg/L in those countries. The consumption of high arsenic concentration of groundwater heighten the vulnerability of arsenic exposure in India and also several geographical regions in mainland China (Sanjrani, 2019).

The anthropogenic activities may also contribute to the arsenic contamination in the water sources especially sea, river and lake (Arif et al., 2020). The anthropogenic impact includes releases from phosphate fertilizer plants, metallurgical plants and mining activities (Vareda et al., 2019). The industrialisation of manufacturing metal alloys, glass, battery grids, electronics and telecommunications products may lead to the released of arsenic in their effluent into the water sources without the proper treatment (Baker, 2018). Once the untreated wastewater which contained arsenic released, it will contaminate and react with the organism in the water sources.

2.2.2 Transformation and Transportation of Arsenic in Soil

In soil, arsenic can be chemically transformed though several mechanisms include redox reaction, adsorption, precipitation, volatilization and dissolution. Arsenite is easily absorbed to Fe, aluminium (Al) and manganese (Mn) oxides in the soil environment and oxidized to the arsenate form (Caporale & Violante, 2016). Under aerobic environment, the inorganic form of arsenic can easily bind to organic and inorganic materials in soil such as Fe, Al, and Mn oxide, which exists in the pentavalent state.

Naturally, the oxidation as well as hydrolysis that occurred in process of weathering and also erosion of minerals lead to the release of arsenic species. In the soil environment, Fe oxy-hydroxide will adsorb the released arsenic species (Jang et al., 2016). The arsenic contamination of soil influenced by the rapid increase in the injudicious application of pesticides and fertilizers, faulty methods of disposal of contaminated wastes, mining and industrialization activities, spillage of coal combustion and petro-chemicals residues deposition on the soil (Jha, 2015). According to recent study, the presence of arsenic in soil sample were reported due to the activities of smelting and mining (Akopyan et al., 2018). Past research also reported the contamination of arsenic in the waste sediments, forest soil and rock soil near the mining area in Korea (Kim et al., 2020).

The application of arsenic-based fertilizers, herbicides, insecticides and pesticides also lead to the contamination of arsenic within soil (Hebbar et al., 2018). In United States, it was reported that the use of arsenic-based pesticides as well as herbicides contribute the transport of arsenic into agricultural soils which lead to the presence of higher levels of total arsenic in rice grown compared to the other country (Punshon et al., 2017). Recent study in Nigeria indicated that higher content of arsenic in agricultural soil of some area within the farm which exceed the allowable standard limit recommended by WHO in agricultural soils (Kayode et al., 2021).

2.2.3 Transformation and Transportation of Arsenic through Atmosphere

In the atmosphere, the dynamic physical and chemical transformation of arsenic can be depending on pH, oxydo-reduction and meteorological conditions (Rai et al., 2019). Arsenic mainly adsorbed on particles, which then deposited on land and water and dispersed by winds. Natural activities of exudates from wind-blown dusts and vegetation and also volcanic activity may contribute to the released of arsenic to the atmosphere (USEPA, 2017). At higher pH, the occurrence of oxidation of arsenite to arsenate in the presence of atmospheric oxygen were prominence. Atmospheric emissions of volatile arsenic released from natural and anthropogenic processes including smelting or fossil fuel combustion. Anthropogenic emission is higher than natural emission. The main naturally sources of arsenic emissions into the atmosphere were volatilization and volcano through biomethylation of arsenic (Jang et al., 2016).

Major anthropogenic emission of arsenic in South China was discovered to be from mineral ores including metals extraction, smelting processes, ore beneficiation and combusting coal (Sha et al., 2019). The study indicated that arsenic emission was contributed by the iron and steel industry, non-ferrous metal processing and smelting and combustion of coal with percentage of nearly 24, 48, and 25%, respectively (Sha et al., 2019).

Seasonal changes also influenced the transportation of arsenic atmosphere. The analysis of the composition of atmospheric fine particulate matter (PM2.5-bound) in Shandong Province of China observed the presence of arsenic species in PM during the winter season (Yin et al., 2017). Another study conducted in Upper Silesia, Poland showed that seasonal changes affected the arsenic mass percentages in water-soluble as well as environmental concentrations of inorganic arsenic in submicron atmospheric particles (PM1) (Nocon et al., 2019).

2.3 Exposure Pathways of Arsenic to Living Organism

The exposure of arsenic and its compounds are widely distributed in the environment. According to WHO, the released of arsenic to the environment may cause by activities of metal smelting, mining, industrialisation and combustion of fossil fuels result in mobilization of arsenic into groundwater or drinking-water sources influenced by the drilling of tube wells (Ayotte et al., 2017). The used of agricultural pesticide production also may contribute to the contamination of arsenic in food crops especially in paddy (rice) (Islam et al., 2016). The daily intake of arsenic is typically mostly derived from primary food sources include meat, fish, shellfish, poultry, grains and dairy products (Adeloju et al., 2021).

2.3.1 Environmental Exposure

The contamination of arsenic in atmosphere, water and soil causes the exposure of that toxic pollutant to the living organism and also environment. People who live around the mining sites were prone to the exposure of arsenic through environment including atmosphere, water and soil. The development of mining and industrialization activities associated with the distribution and extraction of mineral substances (Hoang et al., 2021). The significant pathway of arsenic contamination in environment was arsenic transportation through the vicinity of mining due to heavy rainfall and strong winds (Hoang et al., 2021).

The contaminated groundwater affected the daily activities especially for domestic purpose including drinking, cooking and also household chores (Saha et al., 2019). The usage of contaminated water sources may indirectly expose people to arsenic contamination. The contribution of waste product which released from smelting, hard rock mining and coal combustion will cause pollution of arsenic to the air (Martin et al., 2014). People will expose through the inhalation of the airborne arsenic. Arsenic accumulation in agricultural crops result from the utilisation of contaminated soils and irrigation water (Bhattacharyya et al., 2020). The poisioning effect of arsenic will be exposed to living organism as it will accumulate through vegetables, fruits, and crops.

2.3.2 Dietary Exposure

The contamination of arsenic in water and soil may lead to multiple dietary exposure pathways including drinking water and the consumption of food crops and seafood (Baker, 2018). Based on epidemiological studies in arsenic-endemic areas, drinking water is considered to be important exposure pathway of arsenic in human (Diaz et al., 2015). It can be explained that the common pathway for the exposure of inorganic arsenic was through the use of contaminated drinking water in cooking or preparation of food (FAO/WHO, 2011). A study conducted around Bangladesh found out that the main single drinking water sources contained higher level of arsenic (Saha et al., 2019). Most of the population in the study area facing harmful health risks by consuming contaminated water.

Ingestion of food contaminated with arsenic result in serious health effect to human and living organism. Plant crops are the main source of dietary exposure as they absorb arsenic via their roots and store considerable amounts of it in their edible sections (Mitra et al., 2020). Rice also absorbs inorganic arsenic from water and soil up to 10 times compared to other food crops (Upadhyay et al., 2020). The maximum allowable concentrations of arsenic in vegetables and food is 0.5 and 1 mg/kg (FOA/WHO, 2011).

It was also become a concerned as rice-based food may contribute to the exposure of arsenic. One of that is rice flour which used in majority of processed foods (Jackson et al., 2012). A study in Australia recorded the contamination of inorganic arsenic in rice-based food including puffed and baby rice as well as rice cakes and snacks with some of the samples were found to exceed the allowable limit stated by European Union (EU) recommended for both young children and adult (Chakraborti et al., 2018).

The ingestion of other crops for example grains, fruit and vegetable also contribute to the exposure of arsenic. According to Islam (2017), some of the staple food samples, including cereals, fruits (banana) and vegetables (tomato) showed highest concentration of arsenic which exceed the safe limit. In Pakistan, higher concentration of were observed in crops and vegetables samples such as wheat, maize, sprout were 2.31, 3.73 and 1.78 mg/kg, respectively (Natasha et al., 2022). It was become a concern as vegetable and fruit which classified as healthy food may also be contaminated with arsenic.

The consumption of seafood including fish and shellfish by a number of human populations were known as another source of arsenic exposure especially in industrialized nation. Several type of seafood contain high levels of arsenobetaine, an organic arsenic that is relatively nontoxic (FAO/WHO, 2011). The presence of higher levels of arsenic was observed in sole, sardine and cephalopods samples collected around market in Nothern Italy (Fillipini et al., 2018).

2.4 Effect of Arsenic Exposure

The direct effect on the acute exposure to a high arsenic concentrations can be observed through the abdominal pain, vomiting, and somehow in extreme case can lead to fatality (WHO, 2016). The exposure and intake of inorganic arsenic over a long period is acutely toxic and can affect the human cardiovascular, renal, gastrointestinal, dermal, neurological, hepatic, pulmonary, respiratory and reproductive systems and carcinogenic effect (ATSDR, 2017). The effect of arsenic depend on the level of exposure, which can be elevated by the consumption of contaminated groundwater and food sources, inhalation as well as skin contact (Adeloju et al., 2021).

Arsenic exposure will also cause the cardiovascular disease, including cardiac arrhythmias, atherosclerotic cardiovascular, gangrene of extremities, thickening of blood vessels, peripheral arterial diseases, hypertension and even heart attack (Newman et al., 2016). Other than that, the exposure to arsenic will affect both peripheral and central nervous system by impairing the nerve and brain tissues which may lead to peripheral neuropathy, brain malfunction, hallucinations, memory loss, seizures, coma, depression and affects body coordination (Sharma and Kumar, 2019).

Pulmonary and respiratory diseases also associate with the effect of arsenic exposure since it can enter human body through inhalation process. Based on the research carried out in United States, a lower arsenic exposure was associated with lung disease such as stopping for breathing, lower lung function, airflow obstruction and self-reported emphysema (Powers et al., 2019). The additional effect of arsenic to pulmonary and respiratory system are chronic cough, tracheal bronchitis and shortness of breath (ATSDR, 2017).

Arsenic can cause adverse effect to other body system including haematological (anaemia and leucopoenia), hepatic (cirrhosis and fatty degeneration), renal system (haematuria and cortical necrosis) and reproductive system (ATSDR, 2017). According to WHO (2016), the clearest association of arsenic exposure can be seen in skin or dermal diseases including hyperpigmentation, skin lesions, abnormal skin thickening as well as skin cancer. It was noted that the exposure to low and moderate levels of arsenic will increase the possibility of getting skin diseases such as skin lesions (Karagas et al., 2015).

Chronic arsenic exposure also lead to various epigenetic and genotoxic alterations which resulting in an increased cancer risk (Minatel et al., 2018). Chronic arsenic exposure can lead to number of cancers which include skin, lung and kidney (Huy et al., 2014). The biotransformation of arsenic will lead to the deregulation of genome, gene expression changes and aberrant DNA methylation patterns (Palma-lara et al., 2020). Metabolism of arsenic produces derivatives that promote chromosomal instability and induce DNA damage. This can be said that both the carcinogenic and non-carcinogenic risks may associate with arsenic pollution or exposure (Mochizuki et al., 2019).

2.5 Analytical Method for Detection of Arsenic

The detection of heavy metals involved different analytical technique. For the detection of arsenic, the common analytical methods that being applied are Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and voltammetry technique (Thakkar et al., 2021). These instruments are highly selective techniques, require relatively complex instruments and operational procedures, and long detection times (Lu et al., 2018). Other than that, the application of another analytical method which is electrochemical method had attract interest in many researchers especially for the arsenic detection in aqueous or water samples.

2.5.1 Atomic Absorption Spectroscopy (AAS)

The AAS analytical technique is classified into two types which are the electrothermal and flame heating method of a sample cell (Hill & Fisher, 2017). The application of Flame Atomic Absorption Spectroscopy (FAAS) is generally related to simple and rapid identification of sufficient or few elements and analyte in the sample while in comparison with another detection techniques for example electrochemical technique. Electrothermal atomic absorption spectroscopy requires complex and sensitive operator skill and time consuming, but yields a lower limits of detection when compared with FAAS.

In the analysis of elements such as heavy metals, many researchers had applied this technique in their study. This analytical method is highly sensitive for elements that are difficult to excite, remarkably free from interferences involved and relatively simple and rapid method (Bisergaeva & Sirieva, 2020). Hence, it became clear that atomic spectroscopy had a great potential for both qualitative and quantitative investigations. The fundamental concept of ETAAS and FAAS can be explained as when the sample placed into the atom cell, where it is desolated and subsequently atomised (Hill & Fisher, 2017).

2.5.2 Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS)

In AAS, the most commonly applied method for determining arsenic are ET-AAS and GF-AAS (Lim et al., 2013). The technique can be an attractive techniques as these techniques able to perform rapid and accurate screening for arsenic content especially in water. In GF-AAS technique, the detection obtained as radiation from a certain excited element was transmitted through the vapour containing ground-state atoms of that element (Finsgar et al., 2019). By raising the temperature of the furnace, the targeted metal atoms were introduced into the radiation beam, resulting in volatilisation the injection specimen. The utilisation of matrix modifier in GF-AAS analysis was purposed for stabilisation, reducing matrix interference and increasing sensitivity of analyte (Forero-Mendieta et al., 2022). Table 2.1 shows the previous studies on detection of arsenic in various type of sample using GFAAS.

Table 2.1 The previous study on detection of arsenic using GFAAS

Author	Modifiers	Limit of Detection, LoD (µg/L)	Limit of Quantification, LoQ (µg/L)	Sample
Khalid et al., 2016	Palladium nitrate and magnesium nitrate	0.12	1.2	Medical Product
Finsgar et al., 2019	Palladium and magnesium nitrate	1.6	5.3	Pigment
Chansuvarn, 2019	Palladium nitrate	0.10	1.0	Spiked Soil
Irnawati et al., 2021	Palladium solution	0.009	0.027	Water, river and well
PerkinElmer Food Safety and Quality, 2021	Palladium and magnesium nitrate	0.003	-	Fruit juices

2.5.3 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The other analytical method for arsenic speciation analysis is the inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS is the most commonly used detector for arsenic analysis because it has high ionization efficiency, low matrix interference, high selectivity, and wide dynamic range for sensitive detection (Reid et al., 2020). This technique efficiently measures concentrations up to (µg/L) in samples through efficient ionization on plasma (Hwang et al., 2021). However, such systems are expensive and complicated, and hence they are not commonly equipped and used in many laboratories. Moreover, the operation requires skilled techniques and high running costs (Le et al., 2021).

Speciation analysis of arsenic involves three steps, including extraction, separation, and detection (Komorowicz et al., 2019). The most common extraction methods are mechanical stirring, Soxhlet extraction, ultrasound extraction, and microwave-assisted extraction that were used to release arsenic species in the analysed samples (Nawrocka et al., 2022). While ICP-MS are powerful detectors, their applications to chemical speciation analysis reach their full potential only when they are complemented with efficient separations (Reid et al., 2020). Methanol, water, a mixture of water/methanol in different ratios, and diluted acids are the most frequently used solvents. (Komorowicz et al., 2019).

The combination of analytical techniques must be used to obtain sufficient selectivity and sensitivity for speciation analysis by coupling of high-performance liquid chromatography (HPLC) and ICP–MS thus ensures a suitable separation of arsenic species, as well as good sensitivity and selectivity for quantification even at trace levels in samples (Reid et al., 2020). The HPLC system using a column for the separation of specific substances has also been reported to display excellent efficiency (Hwang et al., 2021). Coupled with ICP-MS for determination, as HPLC-ICP-MS system it is a method of choice for separation and measurements all arsenic species in water (Rajakovic & Ognjanovic, 2018). Table 2.2 shows the previous study on detection of arsenic using ICP-MS analysis.

Table 2.2 The previous study on detection of arsenic using ICP-MS technique

Author	Technique	Limit of Detection, LOD µg/kg	Limit of Quantification, LOQ µg/kg	Sample
Komorowicz et al., 2019	ICP-DRC-MS	0.05-0.15	0.17-0.45	Freshwater fish
Stetson et al., 2021	LC-ICP-MS	-	0.1	Surface & groundwater
Lee et al., 2021	Fs-LA-ICP-MS	0.028	-	Arsenic aqueous solution
Hwang et al., 2021	ICP-MS & HPLC-ICP-MS	0.221-7.94	1.40-3.37	Salted food & sea salt
Nawrocka et al., 2022	HPLC-ICP-MS	0.27-0.34	0.38-0.46	Seafood

2.5.4 Voltammetry Technique

The application of another analytical method which is electrochemical method had attracted many researchers especially for the detection of arsenic in water samples. The electrochemical system employs a setup having three electrodes, working electrode (WE), count electrode (CE) and reference electrode (RE) (Cui et al., 2015). Electrochemical methods have the advantages to be applied for the identification and detection of heavy metals due to its low cost, simplicity, high sensitivity, ease of operation, rapid analysis, portability and applicability for field monitoring of environmental samples (Lu et al, 2018).

Voltammetry techniques which employ measuring current at various potential points in a current - voltage curve are most widely used in the determination and measurement of heavy metal ions due to its high accuracy and sensitivity (Bansod et al, 2017). The common voltammetry methods used to detect heavy metal specifically As are anodic stripping voltammetry (ASV), linear sweep anodic stripping voltammetry (LSASV), square wave anodic stripping voltammetry (SWASV), differential pulse anodic stripping voltammetry (DPASV), cathodic stripping voltammetry (CSV) and cyclic voltammetry (CV) (Guo et al, 2017). In the determination of the concentration of arsenite and arsenate. Table 2.3 shows the different voltammetry technique that being used for detection of arsenic species.

Table 2.3 The previous study on detection of arsenic using voltammetry technique

Author	**Technique**	**Electrode**	**Sample**
Magalona et al., 2018	DPSAV	A gold disk electrode	Raw groundwater
Tupitu et al., 2018	LSV	Gold electrode	Environment water samples
Dang et al., 2019	DPSAV	Gold disk electrode	The media of KCl 0.1 M + HCl 0.1 M
Babar et al., 2019	SWASV	Gold nanotextured electrode	Aqueous Solution of As
Sullivan et al., 2020	SWASV	Gold nanostar modified electrodes	Alkaline buffering system

2.6 Removal of Arsenic from Water Sources

The development of removal method for heavy metal especially arsenic has been carried in several previous studies. The method for arsenic removal or treatment can be classified into ion-exchange, adsorptive, membrane separation and precipitative, in which each method has their own advantages and limitations (Weerasundara et al., 2021). The comparison of the advantages and limitations of each method are shown in Table 2.4. From the comparison, adsorptive method is suitable to be applied with several advantage and a few limitations.

Table 2.4 The advantages and limitation of arsenic removal method

Technique	Advantages	Limitation	References
Ion Exchange -Anion exchange -Electro-dialysis	-Good removal of a wide range of heavy metals	-High raw materials cost	Bashir et al., 2019
Membrane Separation -filtration -Reverse osmosis	-Ecologically sustainable method -High efficiency and selectivity -Effective with a wide range of metals	-Concentrated sludge production -Expensive preparation cost -High requirement for additional complex agents	Zhu et al., 2019
Precipitative -coagulation -Lime softening	-Simple operation -Able to process various heavy metals	-Cause secondary pollution -High reagent costs -High sludge production	Eivaziho-llagh et al., 2019
Adsoprtive -Activated carbon -Sand/Soil minerals -Agricultural Waste Product -Nanoparticles	-Low costs -Simple operation a large adsorption capacity -Effective for a variety of metals having no secondary pollution -Usage of biodegradable biosorbent materials	-Adsorbents require regeneration	Qasem et al., 2021

2.6.1 Adsorption Method

Adsorption can be defined as a mass transfer process of substances bound by physicochemical interactions on the surface of solid (adsorbents) including natural occurring soil and mineral deposits, agricultural waste product such as rice husk, sugarcane, corncob and coir pith and also egg shells (Chaemiso & Nefo, 2019). Adsorbents are insoluble solid materials that commonly have high specific surface area. The ions in polluted water can adsorb onto adsorbent through the process of ion exchange, surface complexation as well as electrostatic attraction (Lata & Samadder, 2016). The performance of adsorbents can be measured with adsorption capability of an adsorbent to adsorb the ions (Yao & Yang, 2020).

For adsorption pathway of ion exchange, it was affected by the availability of competing ions and pH as well as temperature. Ion exchange can occur with the force of concentration gradient and affinity capacity (Chiavola et al., 2015). For surface complexation adsorption pathway, it incorporate the complexation of surface carboxyl or hydroxyl groups with metalloid or metal oxide under the influenced of concentration, pH and ionic strength (Wu et al., 2017). In electrostatic attraction, the forces involved are chemical bond and Van der Waals forces which influenced by properties of solution and adsorbent, including pH, the presence of functional groups and also the specific surface area (Wang et al., 2019).

The specific parameters will influence and enhance the adsorption technique including contact time, the characteristic of chemical and physical of the adsorbents, pH, adsorbate dosage, the concentration of adsorbate in liquid and temperature (Ariffin el al., 2017). The interaction or binding of ions in solution with the functional group