EVALUATION OF BIOSORPTION PROCESS IN THE REMOVAL OF ARSENIC FROM WATER

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EVALUATION OF BIOSORPTION PROCESS IN THE REMOVAL OF ARSENIC FROM WATER

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering

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May 2022

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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ABSTRACT

Arsenic water pollution is a growing concern these days, as arsenic is a highly toxic compound that can have serious consequences for both human health and the environment. The World Health Organization (WHO) claims that the arsenic concentration in drinking water should not exceed 10 µg/L. To mitigate these issues, different methods were proposed to remove arsenic from the wastewater, includingoxidation, ion exchange, chemical precipitation, membrane filtration, and adsorption. Among all the proposed techniques, adsorption displayed the greatest ability to remove arsenic from wastewater, but the high prices of adsorbents were an obstacle that urged the development of alternative adsorbents such as natural biomass. This study was conducted based on three main objectives: to evaluate the effects of various types of biosorbents in the arsenic removal process; to study the effects of different operating parameters on the removal efficiency; and to study the removal mechanisms of arsenic using the biosorption process. The pH of the wastewater, the initial arsenic concentration, and the dosage of biosorbents were the operating parameters highlighted in this study. The outcomes of the results and discussions concluded that industrial by-products and microorganism were highly suitable for arsenic removal, supported by the high arsenic removal efficiency obtained. The optimum pH that should be applied for the removal of arsenite and arsenate is under neutral (pH 6-8) or nearly acidic conditions (pH 4), respectively. Additionally, a lower initial arsenic concentration is favoured to optimise the arsenic removal efficiency. Moreover, an optimum dosage of biosorbents should be determined rather than introducing a large amount of biosorbents as it was greatly dependent on the initial arsenic concentration. To wrap up, biosorbents were encouraged to replace the use of commercial adsorbents as biosorbents are readily available, cheaper, and environmentally friendly.

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LIST OF SYMBOLS / ABBREVIATIONS

b	Modal constant related to the free energy of adsorption,
	L/mg
C_i	Initial concentration of arsenic, mg/L
C _e	Equilibrium concentration of arsenic, mg/L
Κ	Constants of the relative adsorption capacity of the adsorbent,
	mg/g
т	Weight of biosorbent, g
Ν	Intensity of adsorption
q_e	Amount of solute adsorbed per unit weight of the adsorbent
	at equilibrium, mg/g
q_m	Maximum adsorption capacity, mg/g
V	Volume of arsenic solution,L
ASTDR	Agency for Toxic Substances and Disease Registry
As	Arsenic
DNA	Deoxyribonucleic Acid
Fe(III)	Ferric Oxide
HFO	Hydrous Ferric Oxide
ROS	Reactive Oxygen Species
UV	Ultraviolet

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Water is a crucial substance because it is used for a wide range of purposes, including domestic, commercial, and industrial. Moreover, water is a basic requirement component for all living organisms to sustain vital functions such as nutrition, respiration, circulation, excretion and reproduction(K1lıç, 2020). Due to population growth over the years, the global demand for drinking water has been rapidly rising. However, water scarcity has become a major concern in recent decades, owing to the negative effects of industrialization, which have polluted water sources. Water contamination has resulted in a wide range of social consequences, particularly in terms of human health and the environment.

In recent decades, the industrial revolution boosted anthropogenic activities, which resulted in increased heavy metal release into the environment. One of the dispersion pathways of heavy metals into the environment is through water bodies. Due to the extreme pressure on water bodies, both groundwater and surface water are severely polluted(Ramírez Calderón et al., 2020). Heavy metals can also disperse into water through natural sources like weathering of rocks and minerals. Long term exposure to heavy metals in concentrations that exceed permissible limits can lead to health problems in humans.Besides that, these heavy metals will also harm the fauna and flora in the ecosystem. These heavy metals consist of arsenic, zinc, copper, nickel, mercury, lead, and chromium (Dodbiba, Ponou and Fujita, 2015).

Contamination of groundwater and surface water with hazardous arsenic has now become a serious environmental issue in various countries around the world. In 2019, the Agency for Toxic Substances and Disease Registry (ASTDR) declared arsenic was ranked first on the hazardous substance priority list. This is because chronic ingestion of arsenic-rich drinking water causes arsenicosis. Groundwater and surface water containing arsenic is the primary source of drinking water for several countries, which poses a threat to millions of people.

The removal and recovery of arsenic from water sources is essential from a health and environmental perspective. Over the years, wastewater treatment specialists have been focused on developing effective methods to remove arsenic from water. As a result, several remedial technologies have been established, including oxidation, ion exchange, adsorption, membrane filtration and membrane filtration. Among these technologies, adsorption is regarded as the most promising technology because of its simple design and ease of operation. Additionally, the adsorption process is capable of effectively removing arsenic from water compared with other conventional technologies (Ramírez Calderón et al., 2020). However, the high cost of synthetic adsorbents such as iron oxides and activated carbon hindered the application of the adsorption process.

Researchers are looking for innovative, low-cost, and efficient methods to eliminate arsenic while also updating conventional treatment technologies in order to keep arsenic concentrations below the maximum allowable limit(Shakoor et al., 2019a). Consequently, the idea of replacing expensive synthetic adsorbents with low-cost, readily available sorbents has gained traction.

1.2 Problem Statement

It was found that the conventional arsenic removal methods have several shortages such as the high operating costs, low removal efficiency, complexity of the operation and results in the large volume of sludge formation. Therefore, a possible mitigation is needed to replace the inefficient conventional arsenic removal methods with a better technique. To cope with this issue, biosorption process could be applied in removing arsenic from the water by utilizing a more eco-friendly, simple and cheaper approach. This is because solid biowastes which can be derived from food wastes and agricultural wastes can be used as biosorbents (Shakoor et al., 2019a). This approach helps in valorise the wastes generated as well as save the operating costs of the process

The rapid development of technology has accelerated the human infrastructure activities and industrial processes. It was reported that several industries activities such as mining process and combustion of fossil fuel will generate and release arsenic into the environment through water bodies (Ramírez Calderón et al., 2020). The water containing arsenic is required to undergo a sequence of treatment process before the being consumed by people. Therefore, a sustainable technology should be introduced to solve this issue. In terms of sustainability, biosorption is the best candidate as the adsorbents used in the process can be derived continuously from abundant biological wastes.

1.3 Aim and Objectives

The goal of this study is to evaluate the biosorption process for eliminating arsenic from water in order to modernise the traditional remedial method. The following are the specific goals of this study:

- 1. To evaluate the effect of various types of biosorbents in the removal of arsenic from water.
- 2. To study the effect of operating parameters on the removal efficiency.
- 3. To evaluate the removal mechanisms of arsenic using biosorption process.

1.4 Importance of the Study

This study presented the importance to remove arsenic from the water before consumption as the presence of arsenic in the water supply will adversely affect human health. This is because arsenic is found to be carcinogenic in nature. Therefore, removal of arsenic should gain attention to raise the awareness of public on the hazardous impacts triggered by consuming water containing arsenic. Apart from that, this study attempts to reduce the treatment costs involved in the removal of arsenic by using biosorbents. Biosorbents are normally derived from food wastes and agricultural wastes. This approach is able to valorise the biomass wastes instead of using landfilling options. Furthermore, microorganisms such as bacteria and fungi can also be utilizing as biosorbents. This offers attractive and economically viable methods as the biological materials that readily available and relatively cheap whereas the conventional adsorption process tends to utilize activated carbon which are comparatively expensive compared to the biosorbents. This in turns helps to save the operational cost as well as increase the efficiency of the treatment process.

1.5 Scope and Limitation of the Study

The first scope of this study is to evaluate and compare effectiveness of various types of biosorbents in removing arsenic from the water in order to determine their capability to eliminate arsenic from water. The second scope of this study attempts to investigate the performance of biosorbents on arsenic removal under a wide range of operating parameters in order to identify the effect of aqueous environment on removal efficiency. The last scope involved is to evaluate the mechanisms of the interaction between biosorbents and arsenic.

However, this study has several limitations that need to take into considerations. This is a review-based study which all the information and data are obtained from published literature. Hence, some of the data might be outdated and not accurate.

CHAPTER 2

LITERATURE REVIEW

2.1 General Introduction to Arsenic

Arsenic (As) is the 33^{rd} element in the periodic table and it is a naturally formed crystalline metalloid that is extensively distributed throughout the Earth's crust. Metallic grey, yellow, and black are the three allotropic forms of arsenic. Grey arsenic is the most stable allotrope and it is the only form of arsenic that is applied in the industry. Arsenic is carcinogenic and it is regarded as one of the most hazardous chemical substances in the world. It is usually found in oxidation states of -3, 0, +3 and +5. Table 2.1 shows the chemical and physical properties of arsenic.

Properties Value **Atomic Number** 33 Appearance Grey/Yellow/Black Crystalline **Odor O**dorless **Atomic Mass** 74.9216 g/mol 5.724 g/cm³ at 20 °C Density **Melting point** 814 °C (36 atm) **Boiling point** 615 °C (sublimation) **Vapor Pressure** 279 mmHg at 267 °C Solubility in Water Insoluble

Table 2.1: Chemical and Physical Properties of Arsenic

Arsenic is applied in the production of silicon-based computer chips as it can cool down computer chips effectively. Besides that, it is also applied in the glass manufacturing industries in order to control color(Niagu et al., 2007). Although inorganic arsenic is no longer utilized as a pesticide in plantations, organic arsenic are still in use. Moreover, arsenic-containing wood preservative is also used to prevent deterioration or insect damage. Nevertheless, the application and production of arsenic has reported to be declined dramatically nowadays due to awareness of its toxicity. This can be proven by the fact that the arsenic that has been imported into the United States (US) has dropped from 20000 metric tons in 2002 and 2003 to less than 8000 metric tons in 2007(Gilbert, 2011).

2.1.1 Arsenite and Arsenate

In water, soluble arsenic exists in two major forms, which are arsenite (As(III)) and arsenate (As(V)). Figure 2.1 shows the molecular structure of arsenite and arsenate. Arsenic in water is tasteless, odorless, and colorless, therefore it is difficult to detect. The dominant types of arsenic present in water sources is affected by the geology and environment. Trivalent arsenite normally prevails in reduced/anaerobic conditions such as deep-rooted groundwater, whereas pentavalent arsenate prevails and is stable under oxidizing/aerobic environments, including surface water and shallow groundwater (Shakoor et al., 2019a). However, it is reported that arsenite and arsenate may coexist in both water sources. The pH of both arsenite and arsenate are within the range of 6-9. Arsenious acid, H₃AsO₃, is the primary species of arsenite, while arsenic acid, H₃AsO₄, is the dominant species of arsenate (Höll, 2010). The toxicity of arsenite is considered 60 times higher than arsenate. In addition, the solubility and mobility of arsenite is higher than arsenate, which indicate that arsenate is easier to remove from water than arsenite.



Figure 2.1: Molecular Structure of Arsenite and Arsenate

2.1.2 Health Hazard of Arsenic

Figure 2.2 summarizes the toxicity and health risks of long-term arsenic exposure. Chronic exposure to arsenic-contaminated drinking water poses a serious threat to human health. Long-term intake of arsenic-rich water will cause epidemiological toxicity. Arsenic generates an excessive amount of reactive oxygen species (ROS) that are harmful to organisms. As an example, arsenic may lead to fatal diseases including skin, liver, lung and bladder cancers due to its carcinogenic properties. Besides that, arsenic is also known to cause arsenicosis, a general term that is used to describe a group of diseases that are related to arsenic, for example, skin lesions, cardiovascular disease, possibly diabetes, and peripheral vascular disease(Siddique, Dutta and Choudhury, 2020).

As in epidemiology, arsenic tends to cause cytotoxicity and genotoxicity by generating excess ROS. Cytotoxicity occurs when excessive ROS damages lipids, proteins, and mitochondrial. This will affect the cell functions such as cell proliferation, differentiation, apoptosis, as well as induce autophagy. In genotoxicity cases, ROS induces base lesions and strand breaks when it reacts with both deoxyribose and bases in deoxyribonucleic acid(DNA) (Xie et al., 2014). Furthermore, ROS also results in oxidative DNA damage, alteration of DNA pairs, gene regulation mechanisms as well as affects gene stability(Shankar, Shanker and Shikha, 2014). When the genetic information within the cell is damaged, it will eventually result in mutation. In short, arsenic contamination in drinking water will cause a serious public health issue.



Figure 2.2: Arsenic toxicity in human

2.2 Arsenic Contamination in Groundwater and Surface Water

Arsenic contamination of water sources has become a global health and environmental issue. More than 70 countries have been affected by this problem, including USA, India, Bangladesh, and others (Shakoor et al., 2019a). Table 2.2 shows the arsenic level in water and the allowable limit of arsenic in water in various countries. Groundwater extracted from millions of wells serves as the main source of drinking water for citizens in these countries. However, all this groundwaters are heavily polluted with arsenic, with a concentration ranging from 0.15-5000 μ g/L.

Arsenic contamination in groundwater and surface water is attributed to several natural and anthropogenic causes. The weathering of arsenic-rich minerals is the main natural source of arsenic release into groundwater. Arsenic is the main component of more than 200 naturally occurring minerals, and it is also present in alluvial sediments. Desorption and dissolution of these minerals and alluvial sediments will release a high concentration of arsenic into groundwater (Arnous and Hassan, 2015). Besides that, the anthropogenic sources of arsenic are attributed to poorly managed industrial activities, for example, waste generated by the metallurgical and mining industries, combustion of fossil fuels, agricultural use of arsenic-containing herbicides, insecticides, and wood preservatives (Niagu et al., 2007). The degree of groundwater contamination caused by anthropogenic sources is significantly lower than natural sources, but their impact cannot be ignored.

The cases of arsenic contamination in surface water are much less as compared with groundwater as well as lower concentrations. This is because arsenic contamination of surface water is mainly caused by mining activities. Thus, the majority of surface water polluted with arsenic occurs in the ponds, lakes, and rivers that are in proximity to the mining industries.

As mentioned, the intake of arsenic-rich drinking water has emerged as a critical public health risk, and it has affected millions of people worldwide. In most countries, the provisional allowable limit for arsenic content in drinking water has been lowered from 50 μ g/L to 10 μ g/L. However, in some countries, such as Bangladesh, India, and China, the allowable guideline level for arsenic concentration in drinking water is still 50 μ g/L (Niagu et al., 2007).

Table 2.2. Arsenic Contamination in various Countries				
Country/Region	Arsenic level in	Permissible limit	References	
	groundwater (µg/L)	decided by WHO		
		(µg/L)		
China	50-4400	50	(Rahman, Naidu and Bhattacharya, 2009)	
Noakhali, Bangladesh	<1-4730	50	(Shankar, Shanker and Shikha, 2014)	
Ron Phibun, Thailand	1->5000	10	(Shankar, Shanker and Shikha, 2014)	
Taiwan	0.15–3590	10	(Rahman, Naidu and Bhattacharya, 2009)	
Tulare Basin, San Joaquin Valley,	<1-2600	10	(Arnous and Hassan, 2015)	
California				
West Bengal, India	<10 to 3200	50	(Nordstrom, 2002)	
Brazil ^{*sw}	0.4 to 350	10	(Nordstrom, 2002)	
Northern Bavaria, Germany	<10–150	10	(Arnous and Hassan, 2015)	
Mexico, Zimapan, Lagunera	300-1100	25	(Niagu et al., 2007)	
Nova Scotia,Canada	18–146	10	(Niagu et al., 2007)	

Table 2.2: Arsenic Contamination in Various Countries

*sw = surface water

2.3 Common Treatment Technologies

In order to effectively remove arsenic from water, the scientific community has developed and improved several treatment technologies, including oxidation, filtration, precipitation, ion exchange, and adsorption. Most of these methods are carried out through a combination of chemical and physical processes, which is known as physicochemical technology.

2.3.1 Oxidation

Oxidation is defined as the reaction of losing electrons from an atom, ion or molecule (Massachusetts Institute of Technology, 2008). The method involves the oxidative conversion of soluble arsenite to arsenate. Arsenic cannot be removed from aqueous solution by oxidation alone, so it must be followed by other removal technologies like precipitation, adsorption or ion exchange. Oxidation of arsenite is considered as an essential step before other treatment technologies to effectively remove arsenic from water. This is because arsenate adsorbs more freely onto the solid surface of sorbents than arsenite, which indicates that arsenate is easier to remove through precipitation or adsorption process.

2.3.1.1 Process Description

In general, oxidation of arsenite can be carried out with air or pure oxygen. However, air oxidation of arsenite is slow and inefficient. Thus, oxidizing agent can be applied to increase the oxidation rate. Ozone (O₃), hydrogen peroxide (H₂O₂), chlorine (Cl₂), chloramine (NH₂Cl) and ferrate can be used in the process as a strong oxidant for arsenite (Shankar, Shanker and Shikha, 2014). The oxidizing agents converts arsenite to arsenate, which is then removed from water via precipitation or adsorption technique. A typical schematic diagram showing the application of an oxidation process in wastewater treatment is portrayed as Figure 2.3.

Aside from that, photochemical and photocatalytic oxidation of arsenite have also been studied. It was discovered that the oxidation rate of arsenite can be further increased by the ultraviolet (UV) irradiation of water in the presence of oxidants. The application of combined UV and H_2O_2 in the oxidation process is proven to be more effective than using UV radiation or H_2O_2 separately (Dadwal and Mishra, 2017). Moreover, an advanced technique which is titanium dioxide-based photocatalysis, has been established for the oxidation of arsenite as well as removal of arsenate from water via adsorption.



Figure 2.3: Schematic Diagram of Oxidation Process in Wastewater Treatment (EPA, 2015)

2.3.1.2 Advantages and Disadvantages

The main benefit of utilizing the oxidation process as a removal technique for arsenic in water is that it can improve the removal efficiency, as arsenate is easier to remove from water as compared to arsenite. Furthermore, air oxidation is a simple and low-cost operation. Moreover, the advanced photochemical and photocatalytic process is extremely stable and effective in removing arsenic from water.

One major disadvantage of air oxidation is that it is a slow and inefficient process. The oxidation process using chemical oxidants increases the oxidation rate, but it also increases the capital cost. As an example, the use of ozone (O_3) is too costly for developing countries because of the significant high energy input. Moreover, chemical oxidation highly depends on pH and the amount of interfering substances present in the water (Nicomel et al., 2015). For instance, this technique is inefficient in iron-rich water, because the oxidants oxidise both iron and arsenic at the same times (EPA, 2015). Thus, in order to achieve high arsenic removal efficiency, studies on the substance that occurs in water must be carried out prior to the selection of oxidizing agents.

2.3.2 Ion exchange

Ion exchange is a reversible chemical reaction that involves the interchange of ions between a solid and a liquid. Ion exchange resins are used to remove hazardous contaminants from water and replace them with desired ions (Dupont Water Solution, n.d.).

2.3.2.1 Process Description

An ion exchanger is typically a down-flow, packed bed column filled with immobile strong base-anion exchange resin (Massachusetts Institute of Technology, 2008). When the arsenic contaminated water flows through the column, the charged arsenate is attached to the resins through covalent bonding while beneficial ions belonging to the resin are released to the water. After that, the exhausted resin is required to be regenerated in three steps, which are backwash, regeneration with brine and water rinse to discharge arsenic and maintain the exchange capacity of the resin. Sodium chloride (NaCl) or hydrochloric acid (HCl) is used as regenerant solution in order to reactivate the resin for another treatment cycle (Bissen and Frimmel, 2003). The operating process of anion exchange is depicted at Figure 2.4. Arsenite is unable to be removed through the ion exchange process. Hence, oxidation of arsenite to arsenate is needed before the ion exchange process. However, the excess oxidant presence in the water requires to be removed prior to the ion exchange process in order to prevent damaging sensitive resins.



Figure 2.4: Scheme of Anion Exchange Process in Treatment of Raw Water

2.3.2.2 Advantages and Disadvantages

According to Baigorria et al (2020), the removal rate of arsenic from aqueous solution can be more than 95% by using an ion exchange technique. Furthermore, this method can be used to remedy water containing high arsenic concentrations at high pHbecause it is unaffected by water pH.

The ion exchange process involves high operating and capital costs. This is due to the resin regeneration process and the requirement to change exchange resins after a certain period of time. Besides, the treatment of disposed solutions is needed due to the hazardous of arsenic. In addition, when there is a high level of dissolved solid present in the water, the ion exchange process is not suitable for removing arsenic, because the dissolved solid will adversely affect the efficiency (Chiavola et al., 2015). Furthermore, the exchange availability of the resin decreases over time because the suspended or precipitated materials form a thin film on the resin and cause fouling.

2.3.3 Chemical Percipitation

Chemical precipitation is one of the commonly used arsenic treatment methods. It is a physicochemical process in which anions in the aqueous solution react with cations to form insoluble compounds.

2.3.3.1 Process Description

As with other treatment technologies, arsenite is required to be oxidized to arsenate in order to improve the removal efficiency. Next, the reagent is added into the reactor and further mixed with arsenic contaminated water. Precipitation typically happens in a 1 to 1 mole ratio, which means that one molecule of dissolved ions coupled with one molecule of reagent results in a precipitate that is insoluble in water (EMIS, 2020). However, excess reagent is required in order to completely remove arsenic. After the process, the precipitates are removed from the mainstream through solid separation technologies, such as filtration and sedimentation processes. A typical scheme for the precipitation process for raw water treatment is shown in Figure 2.5



Figure 2.5: Diagram of Precipitation Process in Raw Water Treatment (EMIS, 2020)

2.3.3.2 Advanatges and Disadvantages

Chemical precipitation is one of the most promising arsenic removal technologies due to its low capital cost and ease of operation. This technology is generally used for large-scale treatment of arsenic contaminated groundwater in developing countries, especially in arsenic-affected areas that are far away from rivers (Pal et al., 2007).

However, the operational cost of the chemical precipitation process is high because a 1:1 reagent to anion ratio is required in the process, thus it needs a large amount of reagent. Besides that, the produced precipitates such as arsenic (III) sulfide, calcium arsenate, and ferric arsenate are unstable under some situations, thus it is not suitable for directly discharging the precipitates to uncontained tailings as this will form arsenic-containing leachate. (Robins et al., 2001).

2.3.4 Membrane Filtration

A wide range of dissolved solids, including arsenic, can be removed easily through the membrane filtration process. The membrane filtration processis classified into four types: microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Each of these methods has its own set of advantages and limitations. Arsenic removal efficiency is highly affected by the membrane's pore size, as the contaminant larger than the pore size will be blocked by the membrane. According to Oakes (2005), nanofiltration with a 0.5-2 nm pore size is ideal for arsenic removal.

2.3.4.1 Process Description

Arsenite requires oxidative treatment prior to the membrane filtration process. This is due to the fact that, without oxidative conversion of arsenite to arsenate, the nanofiltration process cannot provide water quality below the maximum allowable concentration level of arsenic in water (Dadwal and Mishra, 2017). Membrane filtration is a technology that uses driving force to remove impurities from water through semi-permeable membranes which can selectively permeate water and retain specific solutes. As shown in Figure 2.6, the driving force is the pressure difference between the feed stream and the permeate side, which allows the water to pass through the membrane. In general, membranes are composed of synthetic materials containing billions of pores that serve as selective obstacles which block arsenic from passing through and permit water to pass through (Nicomel et al., 2015).



Figure 2.6: Method Diagram of Membrane Filtration Process(Díaz-Reinoso, 2020)

2.3.4.2 Advantages and Disasvantages

One of the main advantages of membrane filtration is that it can achieve high arsenic removal capacity. Furthermore, membrane filtration is also a well-defined process that can reduce inherent flaws while also being simple to implement(Ashraf et al., 2019).

Membrane filtration process is one of the most expensive treatment technologies. This is because high pressure is required for efficient operation. Besides that, the membrane filtration process is ineffective for treating highly arsenic-contaminated groundwater because it easily fouls the membrane, resulting in high capital and operational costs.

2.3.5 Adsorption

Adsorption is a method of removing substances from the gas or liquid phase using a solid as a medium. As adsorption is a surface phenomenon, the capacity of separation rate will be affected by the properties of the solid medium like surface area and polarity (Massachusetts Institute of Technology, 2008). Therefore, it is critical to identify the properties, performance and price of the adsorbent used prior to the adsorption process.

2.3.5.1 Process Description

In general, adsorption is a mass transfer process where molecules ions are transferred from the aqueous phase to the solid phase and then accumulated at the surface of the solid by van der Waals and electrostatic force (Nicomel et al., 2015). Figure 2.7 depicts the working principle of adsorption process. The adsorption process involves four sequential elementary steps, which are bulk transport, film transport, intra-particle diffusions, and adsorption.

- 1. Bulk transport: molecules in the bulk fluid are transported to the liquid film surrounding the adsorbents.
- Film transport: solute transfer from the liquid film to the external surface of the adsorbent particle by diffusing through a hydrodynamic boundary film.
- Intra-particle diffusions: internal diffusion of adsorbate molecules from the exterior of adsorbents into the pores of the adsorbent where the active site is located.
- 4. Adsorption: molecules interact with active binding sites of adsorbents



Figure 2.7: Working Principle of Adsorption Process(Peng and Guo, 2020)

2.3.5.2 Advantages and Disadvantages

The main advantage of the adsorption process is its considerably high arsenic removal efficiency. Besides that, the adsorption technology is easy to operate and handle, as well as no sludge production (Ashraf et al., 2019). Moreover, it does not require pre-oxidation of arsenite, which leads to cost effectiveness.

One of the disadvantages of adsorption is that it is limited to smallscale water treatment. Besides that, arsenic adsorption is strongly influenced by the characteristics of water, such as pH (Chiavola et al., 2015). Moreover, other ions present in contaminated water, such as phosphate and silicate, will also compete for the active site of the adsorbent. Furthermore, commercial activated carbon is typically costly due to the strenuous production process of activated carbon that involves high temperatures (Ceyhan et al., 2013). In addition, the exhausted activated carbon needs to be regenerated in order to maintain its adsorption capacity. However, the cost of the regeneration process for activated carbon is high and may cause material loss.

2.3.6 Summary of Common Treatment Technologies

The working principle, advantages and disadvantages of the conventional arsenic treatment methods is tabulated in Table 2.3. When deciding on strategies to reduce arsenic contamination in groundwater, both technological and socioeconomic factors should be taken into consideration. Besides that, the composition and environment of the contaminated water are also the affect that will affect the arsenic removal efficiency.

Treatment	Description	Advantages	Disadvantages
Technologies			
Oxidation	Oxidative converts soluble	Improved removal efficiency	• Air oxidation is slow and inefficient
	arsenite to arsenate	• Simple design	• Highly dependent on pH and the amount
		• Low operating cost	of interfering substances present in water.
Ion Exchange	Interchange of ions between	• High removal rate	• High operating and capital costs
	the resins and arsenic	• Non-depend on water pH	• Inefficient when a high level of dissolved
			solids is present
			• Fouling of resin affects exchange capacity

Table 2.3: Description, Advantages and Disadvantages of the Conventional Arsenic Treatment Technologies

		Table 2.3: Continued	
Chemical	Arsenic ions react with cation	Low capital costs	High operational costs
Precipitation	reagents and form an insoluble	• Ease of operation	• Required treatment for disposed
	precipitate	• Suitable for large-scale	precipitate
		treatment	
Membrane	Using driving force to remove	High removal efficiency	• High operating costs due to high pressure
Filtration	impurities from water through	Well-defined process	is required
	semi-permeable membranes		• Inefficiency for water contains high
			concentration of arsenic
Adsorption	Arsenic transfer from the liquid	• High arsenic removal	• Limited to small-scale water treatment
	phase and accumulates on the	efficiency	• Highly dependent on concentration and
	surface of sorbents	• Ease of operation	pH of the environment
		• No sludge production	• Inefficiency when high levels of
		• Not required peroxidation of	interfering substances are present in water
		arsenite	• High cost activated carbon

Table 2.3. Continued

2.4 Biosorption

The biosorption process is characterized as the removal of specified substances from aqueous medium by biological materials (Michalak, Chojnacka and Witek-Krowiak, 2013). The substances to be removed may be present in organic or inorganic as well as soluble or insoluble forms. Sorption encompasses two types of mechanisms: absorption and adsorption, which are frequently confused. Table 2.4 shows the mechanisms, phenomena and definition of absorption and adsorption.



Table 2.4: Mechanisms, Phenomena and Definition of Sorption

In the absorption process, the substances are completely diffused into the absorbent, and it is difficult to separate them from the absorbent. As stated, the adsorption technology is propelled by van der Waals forces and electrostatic attraction. Thus, the molecule ions are easily removed from the surface of the adsorbent as it is loosely adhered (Diffen, 2021).

2.4.1 **Process Description**

Due to the complicated structure of the biomass, there are numerous ways for the biosorbents to remove pollutants from the aqueous solution. The biosorption mechanisms are considered a complex process as it is not yet completely exploited. The mechanisms of the biosorption process can be divided into two criteria, which are metabolism-based and the position where biosorption occurs. For the first criteria, it can be classified as metabolism dependent and non-metabolism dependent based on their reliance on the cell's metabolic activity (Rahimizadeh and Liaghat, 2015).The second criteria can be divided into three subdivisions according to the location where the biosorption process happens, which are intracellular accumulation, extracellular precipitation, and cell surface sorption. Figure 2.8 summarizes the classifications of biosorption mechanisms.



Figure 2.8: The Mechanisms of Biosorption Process According to Criteria

The biosorbents contain different functional groups, including hydroxyl, carboxyl, amino, ester and sulfhydryl, which play an important role in binding pollutants from aqueous media (Ramírez Calderón et al., 2020). Biosorption is primarily occurs through various interactions between functional groups and ions, including precipitation, adsorption, ion exchange, complexation, chelation, and entrapment in the inner space of cells. The biosorption process can take place in a single mechanism, but it is more likely to occur in a series of biosorption pathways due to its complexity. The biomass used in the process can be living cells like microalgal and fungal or dead cells such as agricultural waste. Metabolism dependent is refers to the use of living biomass in the process, whereas non-metabolism dependent uses dead biomass. The biosorption process using dead biomass is defined as a passive mode which is independent of cell metabolism. The molecules ions will bind to the surface of biomass and extracellular materials (Ismail and Moustafa, 2016). This process is rapid and reversible. On the other hand, the biosorption process using living biomass refers to intracellular uptake, where the molecule ions will be transported across the cell membrane. The process is relatively slow due to the reaction of the living biomass. The biosorption mechanism using living biomass can be divided into two steps:

- 1. The molecule ions bound to the surface of biomass by interacting with functional groups on the cell's surface.
- 2. Active biosorption allows molecule ions to pass through the cell membrane and into the cells.

2.4.2 Advantages

Biosorption has several advantages, the most important is that it is a costeffective alternative technology with low capital and operating costs. This is due to the fact that the adsorbent used in the process is made from low-cost, naturally occurring, and renewable biological materials. In the biosorption process, fewer expensive reagents are required, which reduces disposal and storage issues. Besides that, due to its rapid kinetics of adsorption and desorption, the biosorption process is able to remedy large volumes of wastewater as well as highly selectivity in the removal of desired heavy metals. Moreover, biosorption has a high affinity for metals and can often mitigate residual metal levels to less than 1 μ g/L(Ismail and Moustafa, 2016).By applying biosorption to the removal of heavy metals, it can significantly minimize the formation of disposed sludge and hazardous waste. Furthermore, biosorption works under a wide range of operating conditions, including pH, temperature, and interfering substances present in water (Dodbiba, Ponou and Fujita, 2015).

2.4.3 General Application

Although many studies on biosorption have been published in journals and conducted on a laboratory scale, the process is rarely implemented on an industrial scale. This is because the mechanisms for the regeneration of biomass and removal of pollutants are too complicated (Michalak, Chojnacka and Witek-Krowiak, 2013). Besides that, the process of transferring from lab-scale to industrial application is slow.

Several publications have emerged that cover a variety of biosorption applications, including the removal of toxic pollutants from water, feed additives, and fertilizers(Michalak, Chojnacka and Witek-Krowiak, 2013).Biosorption is commonly applied in the removal and retrieval of soluble toxic pollutants in water or sewage. This is due to their effectiveness in removing diluted but extremely hazardous substances such as heavy metals and organic compounds from industrial sewage.Another beneficial application of biosorption process is the fertilizer and feed component industry. Biosorption technology can be used to manufacture biological fertilizer and feed components at a low cost by utilising biomass as a nutrient carrier in plant and animal nutrition (Michalak, Chojnacka and Witek-Krowiak, 2013).

Moreover, this technique is also applied in the metal recovery industry. The operating costs and amount of chemicals required for the operation of precious metals like gold, silver and platinum can be reduced by applying the low-cost biosorption technique. Even though biosorption is a potential technique in this field, further research is needed to develop a selective metal bio-recovery strategy in multi-metal systems (Rene et al., 2017).

To wrap out, biosorption process is an eco-friendly and cost-effective alternative technology in water and wastewater treatment plants. Hence, it become one of the most promising technology for elimination of arsenic from water sources. However, several scientific aspects need to be analyzed before the technology can be commercialized and wide adopted in industrial scale. This study is conducted in order to evaluate the biosorption process in removal of arsenic from water in terms of biosorbent types, operating conditions, and the main mechanisms involved.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Framework for the Methodology of Literature Review

A framework for literature review was developed in the attempts to enclose all the big ideas, empirical studies, primary studies, and secondary studies before the commencement of a review work (Bolderston, 2008). Literature review were viewed as a tool to connect all the empirical studies such as qualitative, quantitative, or other available mixed methods with the literature claims or concepts that used to support a specific study (Rocco and Plakhotnik, 2009). Therefore, a systematic approach was used to develop the methodology of literature review, as shown in Figure 3.1. Based on the figure, it shows that there were six main steps involved in the methodology of literature review.



Figure 3.1: Systematic approach used to develop the methodology of literature review (Templier and Paré, 2015).

It was reported that there are several types of literature review, which are narrative analysis, grounded theory, meta-ethnography, frequency analysis and meta-analysis. In this study, narrative analysis was employed to provide a narrative summary for the biosorption process involved in removing arsenic from water by gathering different literature, data and information from previous studies.

3.2 Formulate Problem Statement and Objectives

The first kick-off step in literature review was to formulate the problem for the review. This step included choosing a relevant topic of interest which covered the title of the project. Next, defined a focus of the study (Bolderston, 2008). For example, developing aims, objectives, and problem statements for the study. In this step, discussions with the project supervisor played an important role as the guidance from project supervisor is useful to provide a clear picture and direction in formulating all the necessary elements required to define the focus of this study. This was completed by having virtual meetings and discussions with the project supervisor, Dr. Ng Yee Sern to develop aims, objectives, and the problem statements for this study.

To summarise, the objective of this reviewwas to assess the impact of different biosorbents and operating parameters on arsenic removal efficiency in water. Furthermore, this study also investigated the removal mechanisms of arsenic using biosorption process.

3.3 Search the Relevant Literature

The following step was to collect and track all the literature that are related to the topics of focus that were defined in the first step. The collection of relevant literature was time consuming as there are a large number of published literatures including articles, journals, or e-books that covered the topic of interest (Levy and Ellis, 2006). Therefore, employing useful techniques such as identification of keywords and uses of interchangeable terms or synonyms in the searching job were extremely important. The title for this project was "Evaluation of biosorption process in the removal of arsenic from water". The identified keywords for this project were "biosorption of arsenic", "removal of arsenic from water", "water pollution caused by arsenic" whereas the synonyms wereused to track the relevant literature including "bio-adsorption" and "arsenic purification". The channels used for the searching job include:

- ScienceDirect (https://www.sciencedirect.com/)
- ResearchGate (https://www.researchgate.net/)
- National Center for Biotechnology Information (https://www.ncbi.nlm.nih.gov/)
- SpringerLink (https://link.springer.com/)
- UTAR Library E-Journals Website (https://library.utar.edu.my)
- Hindawi (http://www.hindawi.com/)

Besides that, the publication years of the relevant literature were limited to the last 20 years in order to eliminate data that is antiquated from this study.

3.4 Screening for Inclusion and Evaluating the Quality of Primary Studies

The searching for literature was followed by the appraising the collected literature, which is commonly known as screening for inclusion. This action included to sort and screen the collected literature according to the level of relevance to the title (Templier and Paré, 2015). Besides that, the data for the specific topic was collected from reliable sources as stated in step 2. As the sorting of collected literature involves tedious steps such as screening the authors' names, publication year and the abstract of the literature, the help of software such as Mendeley efficiently save the time spent for screening process. Figure 3.2 shows the use of Mendeley software in the screening process. Based on Figure 3.2, it can be seen that all the collected literature were classified by folders, and the screening process was conducted based on the folders and the categories of the literature to filter the irrelevant literature for this study.



Figure 3.2: The application of Mendeley software in screening for inclusion

3.5 Extract and Analyse Data

After the screening process, relevant and useful data like figures or tables was extracted from the screened literature. The extraction of data was planned wisely as this outcome for the step will be served as the primary materials for the following analysis step. Therefore, the extracted data were precise, accurate and appropriate to the topic of interest. Generally, there are two approaches used in extracting the data, which include specifying the types of information to be extracted and applying a structured procedure for the data extraction process (Templier and Paré, 2015). This helped to eliminate those invalid data and extract only those appropriate data that can be linked and connected to the aims and objectives of the study.

After extracting the useful data, the primary materials which are composed by the extracted data and information was analysed. In the analysing step, comprehension was applied to summarise, differentiate, interpret and contrast the extracted data (Levy and Ellis, 2006). This made use of the gathered information to report the review results.

3.6 Presentation of Report

The last step involved in the methodology of this studywas to write the final report as the step to present the results. At this stage, the analysed and

synthesized data was compiled and put together to present as the results for the report(Bolderston, 2008). In this study, narrative analysis was conducted to review the biosorption process in the removal of arsenic from water sources. In the narrative analysis, qualitative inferences were presented as part of the synthesizing step, and the conclusions of the study were as transparent as possible followed by the explanation of the conflicting results encountered in the study (Templier and Paré, 2015). Besides that, the objective of narrative analysis was to summarize or synthesise the published information of specific topic, rather than to derive generalisations or cumulative knowledge from the data reviewed. In this study, the extracted data such as the definition and mechanisms of biosorption, the common treatment technologies for the arsenic removal from water and the properties of arsenic pollution were analysed accordingly to meet the requirements for the aims and objectives of this study.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Types of Biosorbents

In recent years, the field of biosorption has exploded in popularity due to the limitations of synthetic adsorbents, such as high cost and low availability. Several studies have found that a wide range of natural materials are able to be used as biosorbents to remove metal ions from contaminated water sources(Tajernia et al., 2014; Sari and Tuzen, 2009; Prasad et al., 2011; Prasad et al., 2013; Pehlivan et al., 2013b; Pehlivan et al., 2013a; Maheswari and Murugesan, 2009; Khaskheli et al., 2011; Kamsonlian et al., 2013; Kamsonlian, Balomajumder and Chand, 2012; Kamsonlian et al., 2012; Aryal, Ziagova and Liakopoulou-Kyriakides, 2010; Ali et al., 2014; Shakoor et al., 2019b). Microbial and industrial by-products can all be recognized as effective biosorbents. Thus, the researchers conducted experiments to investigate the capacity of various biosorbent materials to remove arsenic and arsenate from wastewater. However, the determination of optimum biosorbents for the arsenic removal process is a challenge as biosorbents with the ability to bind arsenic ions with greater affinities are desirable to discover. Therefore, it is critical to choose a biosorbent from the wide range of materials available. The ideal biosorbent should have the following characteristics(Kanamarlapudi, Chintalpudi and Muddada, 2018):

- High biosorption capacity
- Economic feasibility (low cost)
- Large-scale availability
- Reusable and with a high desorption capacity

4.1.1 Industrial- by Product as Biosorbent

The use of low-cost by-products from different industries as biosorbents has sparked a lot of interest in the removal of variousheavy metals from wastewater. Many industries, particularly agricultural and food industries, generate large amounts of waste and by-products, resulting in high disposal costs. By utilizing these low-cost industrial wastes as biosorbents for removing arsenic ions from effluent, the dual problem of waste disposal and wastewater treatment can be solved(Kim, 2013).In addition, agricultural and food industrial wastes appear to be a viable option for wastewater treatment due to their unique chemical composition and widespread availability. Food industrial and agricultural wastes are typically made up of lignin and cellulose that contain different functional groups, including carboxyl, hydroxyl, carbonyl, aldehydic, phenolic, and ether groups that act for metal binding (Dadwal et al., 2017; Sahmoune, 2016). Several research studies have been carried out to evaluate the removal of arsenic from wastewater using a number of industrial wastes such as sugarcane bagasse, rice husk, fruit peels, and eggshell(Tajernia et al., 2013; Khaskheli et al., 2011; Shakoor et al., 2019b).

4.1.2 Microorganism as Biosorbents

The microbial biosorbent can be categorized into two main categories, which are bacteria and fungi. A variety of microbes have been studied for arsenic ion adsorption. It was discovered that a variety of functional groups found on microbial cell walls, such as carboxyl, phosphate, amine, and hydroxyl, play an important role in metal adsorption (Sahmoune, 2016). Bacteria and fungi were mainly isolated from natural sources such as soil, water, and mining environments, and then grown on a low-cost growth medium.

4.1.2.1 Bacteria

The application of bacteria as biosorbents is currently a rapidly expanding field in environmental remediation. It was discovered that numerous functional groups found on the surface of the cells, such as carboxyl, phosphate, anime, hydroxyl, and sulfhydryl groups, play an significant role in arsenic adsorption(Sahmoune, 2016). Metal sorption by bacterial involves physical adsorption, ion exchange, chelation, coordination, or a series of these methods, which will be discussed in section 4.3.

4.1.2.2 Fungi

Fungal biomass as a biosorbent has increased in trend as it contains a high percentage of cell wall material that is able to participate in metal binding and further increase fungi's heavy metal adsorption ability. The fungal cell wall is made up of carbohydrates, chitin, chitosan, polyuronide, polyphosphates, lipids, and protein. These compositions offer various functional groups, including amine, imidazole, phosphate, sulfate, sulfhydryl, and hydroxyl groups that are responsible for metal binding(Dadwal, Mishra and Technology, 2017). Different fungal specieshave distinct functional groups and cell wall compositions.

4.1.3 Modification of Biosorbents

Although raw biosorbent materials are capable of remediating heavy metalcontaminated water, they also have several limitations like decreased sorption capacity, coloration as well as release of soluble organic matter into the water sources(Shakoor et al., 2016). Pretreatment or modification of biosorbents appears to be a viable solution to these drawbacks. Modification of biosorbent is able to improve arsenic removal efficiency by altering their surface properties and increasing the number of metal binding sites (Kanamarlapudi, Chintalpudi and Muddada, 2018). Additionally, modified biosorbents may be useful in solving coloration problems and reducing the discharge of soluble organic compounds into the water.

There are two types of pretreatments for biosorbents: physical and chemical. Physical pretreatments such as drying, autoclaving, and heating are simple and relatively cheap, but they are rarely used due to their ineffectiveness in improving sorption capacity. Chemical pretreatment, on the other hand, is prioritised because it is effective at increasing biosorbent stability and sorption capacity. Chemical treatment can be divided into three types: acid treatment, alkali treatment, and iron oxide mineral coating. In particular, iron coating is a common method for modifying biosorbents due to its natural affinity for arsenic species and the ability to achieve excellent removal efficiencies (Aryal, Ziagova and Liakopoulou-Kyriakides, 2010). Several pretreated biosorbents are discussed in this study, including hydrous ferric oxide (HFO) coated sugarcane bagasse, ferric oxide (Fe(III)) coated rice husk, and ferric oxide (Fe(III)) treated Staphylococcus xylosus(Pehlivanet al., 2013; Pehlivanet al., 2013; Aryal et al., 2010).

4.1.4 Performance of Biosorbents in Removing Arsenic From Water

The arsenic removal efficiency can be assessed using one of two methods: batch or column.In the batch mode, a predefined amount of biosorbents is mixed with a solution that consists of a constant arsenic concentration for a specific contact time.After that, the removal efficiency is calculated by using Equation (4.1)(Pehlivanet al., 2013):

$$Q_e = \frac{(C_i - C_e)V}{m} \tag{4.1}$$

Where,

 Q_e = removal efficiency (mg/g) C_i = initial concentration of arsenic (mg/L) C_e = equilibrium concentration of arsenic (mg/L) V= volume of arsenic solution (L) m=mass of biosorbent (g)

Batch sorption is a popular method for determining the maximum adsorption capacity of different biosorbents because it is simple to conduct and provides data regarding the impact of different solution parameters on the biosorption process by running numerous batch experiments at the same time. Although batch systems have been widely used to assess the sorption potential of biosorbents, they still have some drawbacks. As the batch system is static in operation, it may lead to arsenic saturation on the biosorbent surface because of binding sites obstruction, leading to lower arsenic removal efficiency(Shakoor et al., 2016). Furthermore, the repeated adsorptiondesorption process potentially leads to the desorption of sorbed arsenic ions, resulting in an inaccurate adsorption capacity of biosorbents.

In a column system, arsenic-contaminated water is flowed through a column filled with packed biosorbent where a large-scale sorption process occurs. The column system, on the other hand, prevents the desorption or resorption of arsenic ions bound to the biosorbent surface as the arseniccontaminated water only flows through the packed biosorbent once and does not interact with biosorbent for an extended period of time(Sahmoune, 2016).

In this study, biosorbents from different categories along with different experimental methods were evaluated and is tabulated in Table 4.1. The arsenic uptake capacities (Q_e) of various biosorbents studied in previous research are listed in Table 4.2, along with their respective optimal operating conditions including pH, contact time, temperature (T), initial arsenic concentration (C_i), and biosorbent dosage (m).

Category	Biosorbents	Experimental Method
Industrial by-Product	Raw sugarcane bagasse	Batch
	HFO coated sugarcane	Batch
	bagasse	
	Bagasse fly ash	Column
	Raw rice husk	Batch
	Fe(III) coated rice husk	Batch
	Banana peel	Batch
	Mosambi peel	Batch
	Orange peel	Batch
	Egg shell	Batch
Bacteria	Staphylococusxylosus	Batch
	Rhodococcussp WB-12	Batch
	Arthrobacter sp.	Batch
Fungi	Aspergillus fumigatus	Batch
	Inonotushispidus (4g/L)	Batch

Table 4.1: Category of Each Biosorbents

Biosorbents	m (g/L)	C _i (mg/L)	рН	Т (°С)	Time (min)	Q _e (n	ng/g)	Maxin Rem Efficien	mum oval cy (%)	Reference
						As(III)	As(V)	As(III)	As(V)	
Raw sugarcane bagasse	25.0	65.00	9	24	120	11.90	-	98.00	-	(Tajernia et al., 2014)
HFO coated sugarcane bagasse	4.0	300.00	4	22	180	-	22.10	-	98.00	(Pehlivan et al., 2013)
Bagasse fly ash	3.0	0.08 As(III); 0.07 As(V)	7	20	-	-	-	98.90	95.90	(Ali et al., 2014)
Raw rice husk	6.0	-	6	30	300	-	-	93.60	-	(Kamsonlian et al., 2012)
Fe(III) coated rice husk	4.0	1.00-75.00	4	22	360	-	2.50	-	94.00	(Pehlivan et al., 2013)
Banana peel	8.0	10.00	7	35	90	-	-	82.23	-	(Kamsonlian et al., 2012)
Mosambi peel	40.0	100.00	6 As(III); 4 As(V)	40	240	2.12	3.32	84.90	89.10	(Kamsonlian et al., 2013)
Orange peel	0.2	0.01-50.00	7	25	120	-	-	-	85.00	(Khaskheli et al., 2011)

Table 4.2: Arsenic Removal Efficiency of Biosorbents Under Optimal Experimental Conditions

Table 4.2: Continued										
Egg shell	1.0	4.00	7 As(III); 4.1 As(V)	20	120	3.38	2.69	87.00	71.00	(Shakoor et al., 2019b)
Fe(III)coatedStaphylococusxylosus	1.0 As(III); 2.0 As(V)	10.00-300.00	7 As(III); 3 As(V)	-	30 As(III); 150As(V);	54.35	61.36	49.00	83.00	(Aryal, Ziagova and Liakopoulou- Kyriakides, 2010)
Rhodococcussp WB-12	1.0	100.00	7	30	30	77.30	-	88.40	-	(Prasad et al., 2011)
Arthrobacter sp.	1.0	100.00	7 As(III); 3 As(V)	28	30	74.91	81.63	88.00	91.00	(Prasad et al., 2011)
Aspergillus fumigatus	-	180.00	5	35	-	175	-	97.20	-	(Maheswari and Murugesan, 2009)
Inonotushispidus	4.0	10.00	6 As(III); 2 As(V)	20	30	51.9	59.6	90.00	91.00	(Sari and Tuzen, 2009)

Table 4.2: Continued

Table 4.2 shows that the majority of biosorbents eliminated more than 80.00% of arsenic, indicating that industrial by-products, bacteria, and fungi have a high ability to be used in the arsenic removal process.Sugarcane bagasse, rice husk, aspergillus fumigatuas, and inonotushispidus, in particular, had a removal efficiency of over 90.00%. This suggests that both agricultural waste and fungi have a higher potential for removing arsenic than bacteria. However, feasibility studies for arsenic removal involving non-living biosorbents are more likely to apply than biosorption processes using living microbes need a nutrient supply and a complex bioreactor system.Furthermore, due to the toxicity of the arsenic being extracted as well as other unsuitable conditions such as temperature and pH of the aqueous solution being optimised, maintaining a healthy microbial population is challenging(Ismail and Moustafa, 2016).As a result of these factors, the use of non-living biomass as biosorbents has been prioritised at this point.

Table 4.2 reveals that the optimum operating temperature for biosorbents to effectively remove arsenic falls in between 20.00 °C and 40.00 °C. According to Ismail and Moustafa (2016), a temperature range of 20.00 °C to 35.00 °C is the most suitable temperature for most biosorbents to achieve maximum biosorption efficiency. Even though some biosorbents can reach a higher efficiency at temperatures higher than 45.00 °C, these high temperatures might permanently damage the proteins of microbial living cells, reducing metal uptake(Dodbiba, Ponou and Fujita, 2015). This proves that the removal of arsenic from wastewater can be conducted under ambient temperature or elevated temperature conditions with a slight temperature increment.

In addition, another useful piece of information that could be extracted from Table 4.2 was that the optimum pH for most of the biosorbents used to remove arsenite and arsenate was neutral (pH 6-7) and acidic environment (pH 3-4), respectively. Dodbiba et al. (2015) claimed that the typical range of pH for removing the metal is between 2.5 and 6, which corresponds to data gathered from various sources.

Table 4.2 also shows that the contact time for raw rice husk and Fe(III)-coated rice husk to reach equilibrium was longer than that for other types of biosorbents, with contact times of 300 mniutes and 360 mniutes, respectively. The longer contact time might be attributed to the lower availability of sorption sites as well as lower sticking probability onto the sorption sites of the rick husk compared with other biosorbents (Kamsonlian et al., 2012). Shorter equilibration time is one of the characteristics of highly favourable sorptive interactions, thus biosorbents that require a shorter time to reach equilibrium are preferred for use in adsorption processes.

Another obvious observation that could be drawn from Table 4.1 was that most of the biosorption experiments were conducted in batch operation mode. This might be due to the complexity of column operation inarsenic removal. Aside from that, the transition from batch-scale to column mode is time-consuming(Michalak, Chojnacka and Witek-Krowiak, 2013).

To come to the point, it was discovered that industrial by-products and bacteria and fungi have the potential to replace the use of synthetic biosorbents due to the high removal efficiency achieved by using these biosorbents, with an average removal efficiency of 80.00%. However, nonliving biomoss is preferable to living micobesat this point due to its ease of handling and lack of requirement for growth. Moreover, biosorbents require shorter contact times than is feasible in the biosorption process. Apart from that, it was found that the optimum temperature and pH allocated for the arsenic removal process fell in the range of 20.00 °C to 35.00 °C, and a neutral or acidic environment was preferable for these biosorbents.

4.2 Effect of Operating Parameters on the Removal Efficiency

Several factors influence the effectiveness of biosorption process which includes initial arsenic concentration, amount of biosorbent dosage and pH. The impact of these factors on arsenic biosorption has been discussed in the followingsections.

4.2.1 Effect of pH

Figure 4.1 depicts the effect of pH on the performance of various biosorbents in removing arsenic. One of the most important factors influencing arsenic sorption by biosorbent is the pH of the aqueous solution. This is due to the fact that pH can have a significant impact on the activity of functional groups present on the biosorbents, the speciation of arsenic in water, and the competition of sorbates for binding sites (Kamsonlian et al., 2012).



Figure 4.1:Effect of pH on Arsenic Removal Efficiency: (a) Arsenite (As(III)); (b) Arsenate (As(V))

Figure 4.1(a) shows that the removal efficiency of arsenite increased dramatically at pH greater than 2, peaking at pH 6-8. This is because hydrogen ions have a higher concentration and mobility at lower pH, and these hydrogen ions may compete with arsenic ions for binding sites, resulting in lower removal efficiency(Ramírez Calderón et al., 2020). However, for pH values greater than 7, there is a slight reduction in arsenite removal, which could be due to the limitation of arsenite ion mobility at higher pH values, as well as fewer electrostatic attractions(Kamsonlian et al., 2012).Furthermore, in an alkaline environment, the functional groups responsible for arsenic removal, such as carboxyl, hydroxyl, and amide groups on biosorbents will be negatively charged. This will create a repulsion environment between anionic arsenic ions and negatively charged biosorbents, resulting in a low removal efficiency(Prasad et al., 2011). According to Figure 4.1(b), it shows that the maximum sorption of arsenate was occurred at pH 4. Arsenate removal efficiency was reduced at pH levels higher than 4 because of the electrostatic repulsion between negatively charged functional groups present on the biosorbent surface and arsenate species (Kamsonlian et al., 2013).

In short, based on Figure 4.1, pH 6-8 and pH 4 were determined to be the optimum pH for removing arsenite and arsenatefrom wastewater through the biosorption process.According to Kamsonlian et al. (2013),neutral environments (pH of around 6-8) resulted in the greatest uptake of arsenite, whereas acidic environments (pH of nearly 4) were favourable for arsenate. Thus, the findings are consistent with the review of literature.

4.2.2 Effect of Initial Arsenic Concentration

The initial arsenic concentration serves as a significant driving force in conquering mass transfer resistanceoccured between the liquid and solid phases(Ismail and Moustafa, 2016). According to Figure 4.2, the removal efficiency of various biosorbents decreases as the initial concentration of arsenic ions increases. This is because at high arsenic concentration, the available binding sites of biosorbents are saturated at short time, resulting in a high concentration of arsenic ions that remain unbound in the aqueous solution(Kanamarlapudi, Chintalpudi and Muddada, 2018). In contrast, an

approximate 100% arsenic removal efficiency able toobtain when the initial arsenic concentration is lower due to complete ion interaction with the available binding sites.Dodbiba et al. (2015) claimed that optimum arsenic removal efficiency can be achieved with a low arsenic ion concentration. In brief, this evidences that a low initial arsenic concentration in aqueous solution is ideal for arsenic removal.



Figure 4.2: Effect of Initial Arsenic Concentration on Removal Efficiency: (a) Arsenite (As(III)); (b) Arsenate (As(V))

4.2.3 Effect of Biosorbent Dosage

Biosorbent dosage strongly affects the arsenic removal efficiency as the available binding sites for arsenic ions' sorption depend on the amount of biosorbents(Kanamarlapudi, Chintalpudi and Muddada, 2018). According to Figure 4.3, the arsenic removal efficiency initially increases as the biosorbent dose is increased due to the increased number of available binding sites. After the biosorbents had reached their maximum removal efficiency, increasing the biosorbent concentration had no discernible effect on removal efficiency because ahigh biosorbent concentration might restrict the transfer of arsenic ions to the sorption sites, resulting in lower uptake (Ismail and Moustafa, 2016). In short, increasing biosorbent concentration improves arsenic removal efficiency but too high biosorbent concentration might decreases arsenic uptake due to a lower adsorbate to biosorbent ratio that interferes with binding sites.



Figure 4.3: Effect of Biosorbent Dosage on Arsenic Removal Efficiency: (a) Arsenite (As(III)); (b) Arsenate (As(V))

4.3 Mechanisms of Biosorption

Table 4.3 summarises the functional groups of the biosorbents that are responsible for removing arsenic, along with mechanisms and isotherm models. The binding of arsenic ions occurs through physical adsorption, ion exchange, chelation, coordination, and electrostatic interaction, which is depicted in Figure 4.4.Table 4.3 shows that the functional groups present on raw biosorbents and iron coated biosorbents, as well as the mechanisms involved, are vastly different. In this section, the mechanism and functional groups responsible for arsenic removal in each biosorbent will be discussed.



Figure 4.4: Mechanisms Involved in Biosorption Process

Biosorbent	Mechanism	Functional groups involved	Isotherm model	Reference	
Raw sugarcane bagasse	physical adsorption	-СООН, -ОН, -С=О	Langmuir and	(Tajernia et al., 2014)	
			Freundlich		
Egg shell	physical adsorption	-СООН, -ОН, -NH ₂ ,	Langmuir	(Shakoor et al., 2019b)	
Orange peel	Coordination	-ОН, -СН,-С=О,-СО	Langmuir and	(Shakoor et al., 2019b)	
			Freundlich		
Raw rice husk	Coordination	-СООН, -ОН, -СН	Freundlich	(Kamsonlian et al., 2012)	
Banana peel	Coordination	-NH, -OH, -C-H, -SiO	Freundlich	(Kamsonlian et al., 2012)	
Mosambi peel	Coordination	-COOH, -OH, -NH ₂ , -NH	Freundlich	(Kamsonlian et al., 2013)	
Bagasse fly ash	Ion exchange	-СООН, -ОН, -NH,-С=О	Langmuir and	(Ali et al., 2014)	
			Freundlich		
Rhodococcussp WB-12	Ion exchange	-СООН, -ОН, -NH,-C=О	Langmiur	(Prasad et al., 2011)	
Arthrobacter sp.	Ion exchange	-СООН, -ОН, -NH,-C=О	Langmuir	(Prasad et al., 2011)	
Inonotushispidus	Ion exchange	-COOH, -OH, -NH,-C=O	Langmuir	(Sari and Tuzen, 2009)	
Aspergillus fumigatus	Ion exchange	-COOH, -OH, -NH ₂ , -SH, PO ₄ ^{3–}	Freundlich	(Maheswari and	
				Murugesan, 2009)	

 Table 4.3:
 Mechanism, Functinal Groups and Isotherm Model for Each Biosorbent

Table 4.3: Continued						
Fe(III) coated rice husk	Electrostatic interactions, ion	\equiv FeOH ₂ ⁺	Langmiur	(Pehlivan et al., 2013)		
	exchange, and chelation					
HFO coated sugarcane	Electrostatic interactions, ion	\equiv FeOH ₂ ⁺	Langmiur	(Pehlivan et al., 2013)		
bagasse	exchange, and chelation					
Fe(III) coated	Electrostatic interactions, ion	\equiv FeOH ₂ ⁺	Langmiur	(Aryal, Ziagova and		
Staphylococusxylosus	exchange, and chelation			Liakopoulou-Kyriakides,		
				2010)		

4.3.1 Raw Biosorbent

According to Table 4.3, the three most active functional groups found on biosorbents involved in the biosorption process were hydroxyl (-OH), carboxyl (-COOH), and amide (-NH),which play an important role in removing arsenic from water. Besides, other functional groups such as carbonyl (-C=O). amide (-NH₂), aliphatic stretching(-C-H), siloxane (-SiO), thiol (-SH) and phosphate (PO_4^{3-}) also responsible for arsenic removal. The raw biosorbents remove arsenic ions from aqueous solution via three mechanisms: physical adsorption, ion exchange, and coordination.

As shown in Table 4.3, arsenic ions physically adsorb onto raw sugarcane bagasse and eggshell. Unlike chemical bonding, physical adsorption is non-specific and has weak interaction forces, with arsenic ions trapped on the surface of biosorbents by Van der Waals forces(Ramírez Calderón et al., 2020).

Besides, arsenic ion was adsorbed by fruit peels and raw rice husk via coordination mechanisms, as shown in Table 4.3. To form a coordinate covalent bond with functional groups, the arsenic atom in the complex accepts a lone pair of electrons from the biosorbents (Kanamarlapudi, Chintalpudi and Muddada, 2018). Compounds with these types of bonds are referred to as coordinate compounds.The coordinating groups in the biosorption process are -OH, -CH, -C=O, -CO, -COOH, -NH, and -SiO.

Based on Table 4.3, it indicates that the majority of microorganisms adsorbed arsenic ions through a mechanism of ion exchange, which involves the exchange of binary arsenic ions during biosorption with the counter-ions present on the surface of the biosorbent (Kanamarlapudi, Chintalpudi and Muddada, 2018). The attraction force formed between arsenic and biosorbent is electrostatic or columbic. The biosorption of arsenite is attributed to the dominant monoanionic ($H_2AsO_3^-$) species, which substitute functional groups or water molecules(Prasad et al., 2013). On the other hand , the dominant species of arsenate ($H_2AsO_4^-$) sorbed onto the sorbent by substituting functional groups.

4.3.2 Iron Coated Biosorbent

Iron oxyhydroxide (\equiv FeOH₂⁺) is the main functional group of iron-coated biosorbents that responsible for arsenic removal. Iron-coated biosorbents can remove arsenic from the solution phase through a variety of mechanisms, including electrostatic interaction, ion exchange, and chelation.

As mentioned, the arsenite existed as $H_2AsO_3^-$ at pH 7, which could interact with (\equiv FeOH₂⁺) through both physical sorption and ion exchange(Aryal, Ziagova and Liakopoulou-Kyriakides, 2010). Arsenic ions can be removed through ion exchange between the positive charge of active groups on the surface of biosorbents (\equiv FeOH₂⁺) and the anion arsenic ions, resulting in the formation of a bond between Fe(III) and arsenic ions. For example, the ion exchange occurred when the negatively charged arsenate species, $H_2AsO_4^-$ substituted the hydroxyl groups in \equiv FeOH₂⁺.

Further, the electrostatic forces between the negatively charged arsenate species, $H_2AsO_4^-$ and the positively charged iron oxyhydroxide surface \equiv FeOH₂⁺ in natural waters are strong enough to generate high adsorption efficiency(Pehlivanet al., 2013).Chelation is another possible reaction mechanism in which surface complexes are formed when positively charged surface groups (\equiv FeOH₂⁺) interact with negatively charged arsenic ions.

4.4 Adsorption Isotherm

The adsorption isotherm is widely used to evaluate the feasibility of adsorbents in a systematic and quantitative manner. The isotherm model can provide quantitative information about the interaction between adsorbate and adsorbent and the affinity of the adsorbents (Dadwal, Mishra and Technology, 2017). The two most commonly used adsorption isotherms to evaluate equilibrium sorption data between adsorbate ions and biosorbents are the Langmuir and Freundlich isotherm models.

4.4.1 Langmiur Isotherm Model

The performance of various adsorbents is widely quantified and compared using this model. This model describes the monolayer adsorption of an adsorbate with active sites. Furthermore, this model assumes that adsorption only takes placeon a limited quantity of localised binding sites that are equivalent in terms of energy(Dadwal, Mishra and Technology, 2017). Additionally, there is no interaction between the molecules that have been adsorbed at neighbouring sites.(Ismail and Moustafa, 2016). This empirical isotherm also takes into account the homogeneous surface on which adsorption occurs.The non-linear form of the Langmuir isotherm is shown as Equation (4.2)

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{4.2}$$

Where

 q_e = quantity of sorbate adsorbed per unit weight of the adsorbent at equilibrium (mg/g)

 C_e = equilibrium concentration of the sorbate in the bulk solution (mg/L)

 q_m = maximum adsorption capacity (mg/g)

b = modal constant related to the adsorption free energy (L/mg)

Various biosorbents mentioned in Table 4.3, such as raw sugarcane bagasse, eggshell, orange peel, bagasse fly ash, rhodococcussp WB-12, anthrobactersp, inonotushispidus, Fe(III) coated rice husk, HFO coated sugarcane bagasse and Fe(III) coated staphylococcus xylosuswere reported to be best match with the Langmuir isotherm model for the adsorption of arsenic.

4.4.2 Freundlich Isotherm Model

The Freundlich isotherm model characterises reversible and non-ideal adsorption. This isotherm is not limited to modelling monolayer formation; it is also used to simulate multilayer adsorption with non-uniform heat of adsorption and affinities distributed across a heterogeneous surface(Dadwal, Mishra and Technology, 2017). Moreover, the stronger binding sites were adhered first, with strength for the binding decreasing as thesite occupancy increased. (Rene et al., 2017). The non-linear form of the Freundlich isotherm is depicted in the Equation (4.3).

$$q_e = K C_e^{1/n} \tag{4.3}$$

Where

K = constants of the adsorbent's relative adsorption capacity (mg/g)

N = intensity of adsorption

According to Table 4.3, it shows that the biosorption behaviour of raw sugarcane bagasse, orange peel, raw rice husk, banana peel, mosambi peel, bagasse fly ash, and aspergillus fumigatus was well described by the Freundlich isotherm model. As a result of these findings, it was found that biosorption actually happened on the heterogeneous surface of these biosorbents.

4.5 Comparisons with Adsorbents

The feasibility of using natural biomass and microorganisms as a substitute for commercial adsorbents was investigated through comparison with adsorbents in terms of maximum arsenic removal efficiency. As stated, most of the biosorbents are capable of achieving more than 80.00 % of arsenic removal efficiency. On the other hand, the effectiveness of char carbon and activated carbon in removing arsenic was evaluated by Pattanayak et al. (2000) and Tajernia et al. (2014), respectively.Pattanayak et al. (2000)conducted a study on the removal of arsenite and arsenate ions from water samples by using char carbon. The ideal conditions for removing arsenic ions from water were as follows: pH 3 and temperature of 25.0 °C. The initial arsenite and arsenate concentrations were 0.0001 mg/L and 0.157-0.737 mg/L, respectively. The maximum arsenic removal efficiency of char carbon was found to be 88.00 % and 95.00 % for arsenite and arsenate respectively. Besides, the performance of activated carbon as an adsorbent to remove arsenite from aqueous solutions was evaluated by Tajernia et al. (2014). The batch experiment was carried out with 17.6 g/L of biomass dosage, an initial arsenic concentration of 67.15 mg/L, contact times of 150 minutes, and a temperature of 24 °C. At optimum conditions, the maximum arsenite removal efficiency of 89.00 % was obtained at pH 7.4.

The majority of biosorbents can achieve the same arsenic removal percentage as synthetic adsorbents, as evidenced by the comparison in terms of removal efficiency. As previously stated, in the adsorption interaction, a shorter equilibration time is beneficial. Several biosorbents, particularly for microorganisms, have demonstrated excellent performance as adsorbents in terms of removal efficiency while requiring less equilibration time. In brief, the use of industrial by-products and microorganisms in the arsenic removal process is feasible due to their ability to achieve high removal efficiencies as expensive adsorbents, as well as several biosorbents with shorter equilibration time. As a result, there is a greater likelihood of low-cost biosorbents being used to treat arsenic-contaminated water in the near future.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

To come to a point, industrial by-products and microorganisms were the suitable candidates to remove arsenic as these biosorbents manifested excellent performance in terms of arsenic removal efficiency. The best removal efficiency recorded were 98.90 % and 97.20 % for bagasse fly ash and *Aspergillus fumigatus*, respectively. The outcomes of the results and discussions demonstrated that pH of the wastewater, initial arsenic concentration in the wastewater, and dosage of biosorbents were the main factors that affected the arsenic removal efficiency.

Among the stated parameters, pH of the wastewater was found to be the critical factor that contributed to the decrement in arsenic removal efficiency, as the arsenic species and functional groups of the biosorbents will be altered according to the pH of the aqueous solution, which subsequently affects the arsenic removal efficiency. Besides, batch scale processes suggest that a lower initial arsenic concentration should be employed to optimize the arsenic removal efficiency. Furthermore, it was discovered that an optimum dosage of biosorbents should be figured out instead of introducing a large amount of biosorbents due to the fact that an excess dosage of biosorbents would induce mass transfer resistance during the biosorption process.

In attempts to determine the appropriate functional groups of untreated biosorbents that play an important role in arsenic removal, it was discovered that carboxyl (-COOH), hydroxyl (-OH), and amide (-NH) functional groups were the most active functional groups used in the biosorption process. The raw biosorbents showed three mechanisms during the biosorption process, including physical adsorption, coordination and ion exchange. On the other hand, the mechanism and functional groups of the modified biosorbents were discovered to be distinct from those of the untreated biosorbents. The functional group on the iron-coated biosorbents was iron oxyhydroxide (\equiv FeOH₂⁺), and the removal process involved three mechanisms: electrostatic interactions, ion exchange, and chelation.

Additionally, there were two adsorption isotherms, Langmuir and Freundlich, which will be applied to determine the quantitative information regarding the interactions between the arsenic ions and biosorbents as well as the affinity of biosorbents. The reviewed studies showed most of the biosorbents best fit the Langmuir isotherm model, which involved monolayer adsorption. On the other hand, it was found that industrial by-products and microorganism exhibited high potential to replace the existing synthetic adsorbent in arsenic wastewater treatment on the grounds that these biosorbents were relatively cheap, environmentally friendly, and highly abundant.

5.2 **Recommendations**

The feasibility of using industrial by-products, bacteria and fungi as low-cost biosorbents in arsenic removal has been proven through this study. Therefore, extensive research on these biosorbents in arsenic removal can be carried out. Several recommendations are provided which aims to enhance existing experimental findings while also providing more detail information and scope for other researchers:

- 1. Evaluating the performance of these biosorbents with real arseniccontaminated wastewater in a continuous flow of operation to better simulate the environments of a real wastewater treatment plant.
- 2. Additional parameter studies such as the effect of agitation speed, particle sizes, and coexistence of other metal ions can be performed to truly access the adsorption performance of these biosorbents.
- 3. Investigation of the potential health and environmental impacts of these biosorbents to determine the feasibility of these biosorbents used to treat wastewater.
- 4. The application of these biosorbents in the removal of other heavy metals can be investigated.
- 5. Desorption experiments can be carry out to identify the suitable desorption agent for assisting in biosorbent regeneration.

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