



Faculty of Resource Science and Technology

**Adsorption of Uranyl Ions from Seawater Using Chemically Modified
Sago Hampas**

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Adsorption of Uranyl Ions from Seawater Using Chemically Modified Sago Hampas

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

A handwritten signature in black ink, appearing to read 'Firdaus', written over a dotted line.

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ABSTRACT

Uranium is a crucial resource for nuclear energy; however, its terrestrial reserves are limited, and conventional mining methods pose significant environmental risks. Extracting uranium from seawater presents a sustainable alternative, but the low concentration of uranyl ions and competing ions in seawater create challenges. Raw sago hampas (RSH) was grafted with oxygen-containing functional group through a functionalization process to form esterified sago hampas (ESH) for U(VI) adsorption and evaluated using adsorption kinetics, isotherm, and thermodynamics studies. Adsorption kinetics studies show that both adsorbents follow pseudo-second-order model while isotherm studies conclude that both adsorption processes fitted Sips isotherm model. Thermodynamic studies indicate both adsorption processes exhibited by the RSH and ESH were endothermic but spontaneous and non-spontaneous respectively. Strong acids are tested to be the best desorption agents to release U(VI) from surfaces of RSH and ESH. The findings of this study contribute to the development of sustainable uranium extraction methods and offer an environmentally friendly approach for biosorption in nuclear resource management.

Keywords: Uranyl ions, sago hampas, adsorption, FTIR, SEM, ICP-OES

Penjerapan Ion Uranil Dari Air Laut Menggunakan Hampas Sagu Yang Diubah Suai Secara Kimia

ABSTRAK

Hampas sagu mentah (RSH) telah dicantumkan dengan kumpulan berfungsi yang mengandung oksigen melalui proses pefungsian untuk membentuk hampas sagu pengesteran (ESH) bagi penjerapan U(VI) dan dinilai menggunakan kajian kinetik penjerapan, isoterma, dan termodinamik. Kajian kinetik penjerapan menunjukkan bahawa kedua-dua penyerap mengikuti model pseudo-peringkat kedua manakala kajian isoterma menyimpulkan bahawa kedua-dua proses penjerapan mematuhi model isoterma Sips. Kajian termodinamik menunjukkan bahawa kedua-dua proses penjerapan yang dipamerkan oleh RSH dan ESH adalah endotermik tetapi kespontanan yang berbeza. Asid kuat didapati menjadi agen penyahjerapan terbaik untuk melepaskan U(VI) dari permukaan RSH dan ESH.

Kata kunci: *Ion uranil, hampas sagu, penjerapan, FTIR, SEM, ICP-OES*

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LIST OF ABBREVIATIONS

BSG	Brewer's Spent Grain
CEC	Cation-Exchange Capacity
FTIR	Fourier Transformed Infrared Spectroscopy
ESH	Esterified Sago Hampas
HYBRID	Hybrid Fractional Error Function
ICAN	International Campaign to Abolish Nuclear Weapons
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
PFO	Pseudo-First-Order
PSO	Pseudo-Second-Order
RMSE	Root Mean Square Error
RSH	Raw Sago Hampas
SEM-EDX	Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy
SSE	Sum of Squares Error

CHAPTER 1

INTRODUCTION

1.1 Study Background

Nuclear power, known for its high energy yield and low emissions, is crucial for addressing the energy crisis. However, uranium reserves are depleting, making seawater—a vast reservoir of approximately 4.5 billion tons of uranium—a viable alternative (Abney et al., 2017; Guo et al., 2021). While seawater uranium extraction is a groundbreaking technology (Sholl & Lively, 2016), it faces challenges due to low uranium concentration (~3 ppb) and competing metal ions (Zhang et al., 2016). A study in Kuala Langat further highlights uranium variability, with concentrations ranging between 0.67 and 139.09 $\mu\text{g L}^{-1}$ (Md Yunus & Hamzah, 2015). In Malaysia, natural processes such as rock erosion and mineral dissolution contribute more significantly to uranium levels than anthropogenic sources like nuclear wastewater and mining (Szlachta et al., 2020).

Given the increasing demand for nuclear energy, efficient and sustainable uranium extraction technologies are imperative. Conventional methods like ion exchange and precipitation are costly and generate hazardous waste (Younes et al., 2020). Recent innovations in synthetic adsorbents, including carbon nanotubes (Liu et al., 2022; Yan et al., 2024), amidoximated fibrous adsorbents (Im et al., 2023), inorganic adsorbents (Liu et al., 2023), and resin microcapsules (Wang et al., 2023), demonstrate high efficiency but remain expensive and complex to produce.

As an alternative, plant-based biosorbents derived from agricultural waste have shown promising uranium adsorption capacities (Anagnostopoulos et al., 2015; Wang et al., 2015; Anagnostopoulos et al., 2016; Zhang et al., 2016; Jiménez-Reyes et al., 2020). Their

performance can be further improved through chemical modifications such as esterification, graft polymerization, surface coating, and acid/alkali treatments to enhance functional groups for uranium binding (Torres, 2020).

Malaysia generates approximately 32,250 tonnes of sago hampas annually, a fibrous by-product from starch extraction (Rasyid & Kusumawaty, 2020). Despite its effectiveness in removing other pollutants, sago hampas has never been studied for uranium adsorption. Its cellulose, hemicellulose, lignin, and pectin composition provide active sites for uranium binding. This study aims to evaluate the adsorption capabilities of raw and esterified sago hampas (RSH and ESH) under varying U(VI) concentrations, pH, contact time, and temperature to determine optimal conditions for uranium removal. Adsorption kinetics, isotherms, and thermodynamics will be analysed, while FTIR and SEM-EDX will be used to characterize material modifications and adsorption behaviour.

1.2 Problem Statement

While the sago industry generates a massive quantity of sago waste, there's currently a lack of efficient disposal methods. However, there's growing interest in transforming this waste into valuable resources (Amin et al., 2019). Sago waste like sago hampas, mainly composed of cellulose and lignin with oxygen-containing functional groups, shows promise as a biosorbent for heavy metals like uranium. While sago hampas has been used to remove other contaminants like heavy metals, dyes, and organic pollutants, its application in adsorbing natural radionuclides such as uranium remains unexplored in literature. Additionally, most research focuses on converting sago hampas into biochar to enhance its adsorption capacity, leaving chemical modifications of raw sago hampas, particularly for uranium ion adsorption, relatively under-researched. Uranium's ability to rapidly disperse in the environment, particularly in aquatic systems, is well-documented, with concentrations

typically ranging from 0.01 to 1500 $\mu\text{g L}^{-1}$ (Szlachta et al., 2020). Moreover, it's uncertain whether uranium levels in seawater near Sarawak's shores fall within safe limits. This poses a potential public health risk from ingesting contaminated water. Recovering uranium from seawater could not only decrease the need for uranium ore mining but also help prevent environmental damage.

1.3 Objectives

Based on the problem statements stated, this study was intended to achieve the following objectives:

- i. To characterize physicochemical properties of sago *hampas* as a biosorbent by using analytical techniques such as FTIR and SEM-EDX
- ii. To chemically modify sago *hampas* to graft specific functional groups
- iii. To investigate the uranyl ions adsorption capability of untreated and esterified *sago hampas* in aqueous solutions and seawater

1.4 Chapter Summary

This thesis is structured into five key chapters, systematically exploring uranium adsorption from seawater using chemically modified sago *hampas* as a biosorbent. Chapter 1 (Introduction) outlines the significance of uranium in nuclear energy, challenges in its seawater extraction, and the potential of sago *hampas* as an eco-friendly and cost-effective biosorbent. The research objectives, problem statement, and study significance are also highlighted. Chapter 2 (Literature Review) examines uranium properties, biosorption mechanisms, agricultural waste-based biosorbents, and chemical modification techniques to enhance adsorption efficiency. Chapter 3 (Materials and Methods) details the experimental methodology, including sago *hampas* preparation, esterification, batch adsorption studies,

and characterization techniques such as FTIR, SEM-EDX, kinetic, isotherm, and thermodynamic analyses. Chapter 4 (Results and Discussion) presents findings on the successful modification of sago hampas, improved uranium adsorption performance, adsorption kinetics (pseudo-second-order), isotherm modeling (Sips model), and thermodynamic behavior (spontaneous and endothermic). The influence of pH, simulated seawater performance, and desorption efficiency using HNO_3 and HCl are also analyzed. Chapter 5 (Conclusion and Recommendations) summarizes key findings, emphasizing the enhanced adsorption capacity of esterified sago hampas and its potential for large-scale uranium recovery. Recommendations include further optimization, scale-up studies, and real seawater testing to assess industrial feasibility. This structured organization ensures a logical progression from problem identification to experimental validation and practical applications.

CHAPTER 2

LITERATURE REVIEW

2.1 History And Properties Of Uranium

In the late 18th century, German chemist Martin Klaproth (1743-1817) stumbled upon a new element while examining pitchblende, a mineral with properties distinct from known metals. He named it after the recently discovered planet Uranus. However, further investigation revealed he had isolated uranium oxide, not the pure element itself. This feat of isolating the element would not occur until 1841, thanks to French chemist Eugene Melchior Peligot (1811-1890). Uranium remained a scientific curiosity for much of the 19th century. In 1896, a serendipitous discovery by Henri Becquerel revealed uranium's ability to darken photographic plates, laying the groundwork for the field of radioactivity. Initially, the early 20th century saw increased interest in uranium due to its association with radium, a sought-after element for its perceived medicinal properties. Uranium also found use in specialized applications like coatings, dyes, and steels. However, the true significance of uranium wouldn't be realized until the dawn of World War II. Its potential for nuclear weapons, specifically enriched uranium and plutonium, became evident. Additionally, its density and hardness made it valuable for armour-piercing projectiles. This newfound strategic importance propelled uranium exploration and processing into a national priority for many countries.

By the mid-20th century, the growing demand for uranium fuelled by the expansion of nuclear power had firmly established it as an essential global commodity, a stark contrast from its previous status as a mere scientific curiosity. Currently, Australia, Canada, and Kazakhstan collectively contribute to approximately 52% of the world's uranium extraction.

Australia stands as the global leader in uranium resources, boasting 28% of the world's total, with Kazakhstan and Canada trailing behind at 15% and 9%, respectively. Figure 2.1 summarises the world's uranium resources by country.

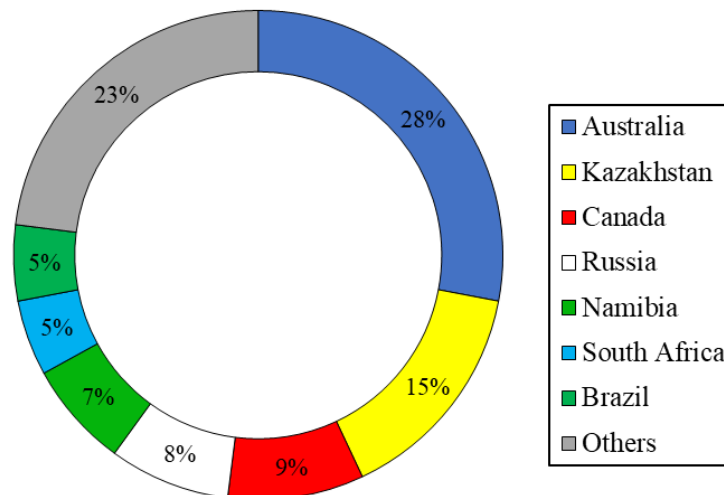


Figure 2.1: The world's uranium resources by countries (Lu, 2024)

As of 2020, approximately 445 nuclear reactors were operational worldwide, with an additional 55 under construction – a significant portion (11) being built in China. However, a concerning disparity exists between the number of reactors and the number of active nuclear warheads. Current estimates suggest a staggering 13,400 nuclear weapons stockpiled across nine countries: the United States, Russia, China, the United Kingdom, France, India, Israel, Pakistan, and North Korea. Notably, the US and Russia hold the most significant arsenals (Armstrong, 2023). This alarming number of warheads far outstrips the number of operational reactors, raising serious concerns about global nuclear security. The International Campaign to Abolish Nuclear Weapons (ICAN) has expressed deep anxieties about the current nuclear threat, highlighting that it may even surpass the dangers posed during the Cold War. Figure 2.2 highlights number of operational nuclear reactors and their country of origin.

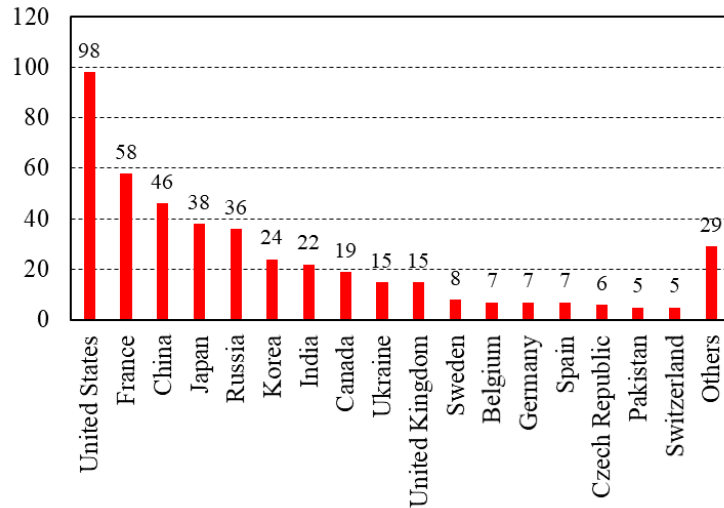


Figure 2.2: Number of operable nuclear reactors owned by countries in 2020 (World Nuclear Association, 2024).

2.2 Properties Of Uranium

Uranium, a dense, silvery-white, amphoteric heavy metal, is naturally abundant, averaging 2.4 mg per kilogram in the Earth's crust and 3.1 mg per litre in seawater (Waseem et al., 2015). Recognized as the heaviest naturally occurring radioactive element, uranium is dispersed throughout the environment, with concentrations varying based on the surrounding medium. Anthropogenic activities, such as uranium mining, nuclear weapons production, and nuclear power generation, are primary contributors to its presence.

In its elemental state, uranium remains stable in various isotopic forms, primarily U-238, U-235, and U-234. It exhibits multiple valence states, ranging from U^{2+} to U^{6+} . The U^{6+} state, often bonded with oxygen to form the uranyl ion (UO_2^{2+}), is highly mobile and soluble, commonly precipitating as black uraninite (UO_2). Natural uranium, the heaviest naturally occurring element, typically isn't enriched or depleted. Its geochemical cycle initiates with the weathering of oxidized uranium ores on the Earth's surface, releasing uranium into nearby water sources at a consistent isotopic ratio of 137.88:1 for U-238 and U-235. With a high density of 19.05 g/cm³, uranium is moderately paramagnetic, melting at 1132 °C and

boiling at 3818 °C. Its ductile and malleable nature allows it to be easily shaped. The metal can also form various crystallographic phases, including alpha, beta, and gamma.

Currently, 25 different uranium isotopes exist, ranging from atomic number 217 to 241. However, only three occur naturally: U-238, U-235, and U-234, with abundances of 99.274%, 0.720%, and 0.005%, respectively (Deshmukh et al., 2022). Of these, only U-235 and the artificially produced U-233 are fissile.

2.3 Uranium In Seawater As A Source Of Mining And Its Challenges

Since the mid-20th century, the prevalence of radioactive elements in the environment has escalated due to multiple factors. Uranium, a naturally existing element, is present in diverse biological samples, including soil, flora, and aquatic organisms in both marine and freshwater ecosystems. The level of uranium in soil and vegetation varies according to the geological composition of the region and the natural water sources, generally ranging from a few parts per million. In addition to these natural sources, anthropogenic activities, particularly those associated with the uranium nuclear fuel cycle, further augment the levels of uranium in the ecosystem (Banerjee et al., 2022). Numerous human activities necessitate the disposal of uranium compounds, such as uranium mining, uranium-rich deposits from phosphorus and gold mining operations, isotope enrichment facilities, nuclear fuel production, nuclear power stations, nuclear processing plants, and nuclear waste treatment facilities and repositories (Zhang et al., 2023). Severe natural and manmade catastrophes, such as failures in waste management procedures, have been associated with substantial environmental consequences. Prominent anthropogenic disasters include the Chernobyl and Fukushima Daiichi nuclear disasters.

The geochemical mobility of uranium remains complex owing to its capacity to produce many soluble compounds across a wide pH range. Under reducing conditions, hexavalent uranium ions (U^{6+}) convert to tetravalent ions (U^{4+}), leading to insoluble oxide deposition (Singh et al., 2020). This process can be reversed by exposure to atmospheric oxygen or co-precipitation (Karpas, 2014). Typical gold mine excavation can contaminate the soil with uranium, often called uraniferous tailings which are usually pumped into natural caves, sinkholes and accumulate in tailing dams (Balaram et al., 2022; Karpas, 2014). These tailings deposits face erosion and thus transported by the wind that can get into various water sources then into the soil and finally up the food chain (Chen et al., 2022). Figure 2.3 shows pathways of uranium from uraniferous tailings to water sources.

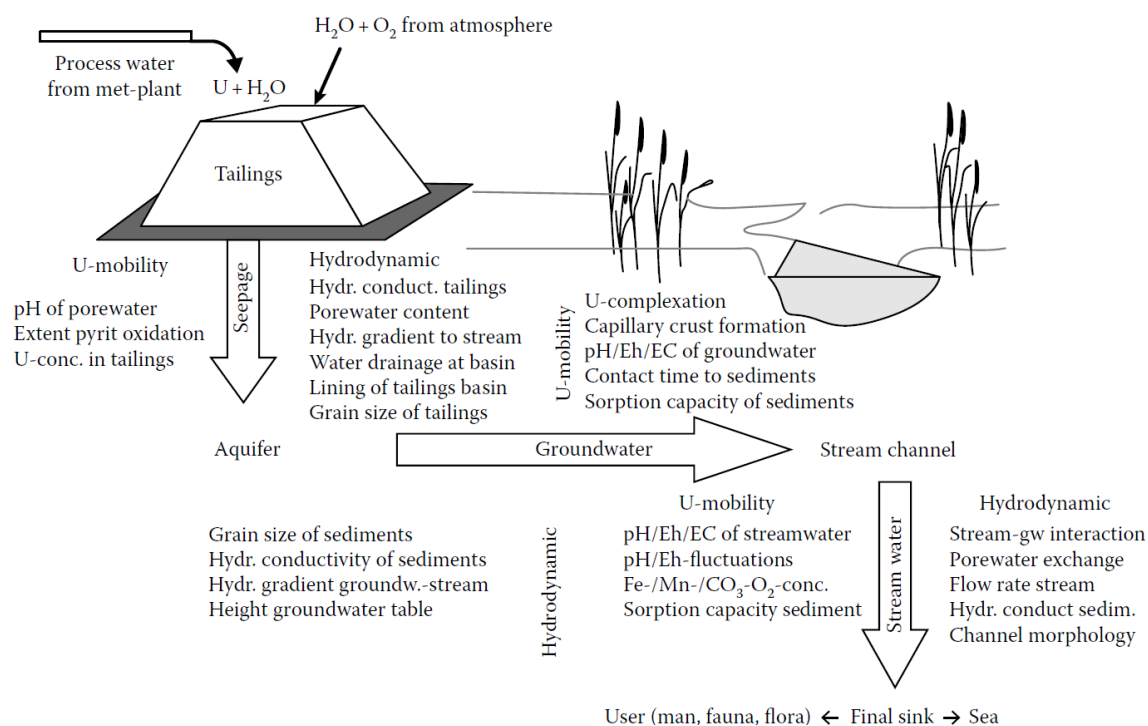


Figure 2.3: Dispersion of uranium from accumulation of gold mine tailings that gets into soils and various water sources (Karpas, 2014)

Uranium exists as a stable, linear polyatomic cation with oxygen, UO_2^{2+} with in hexavalent form called uranyl. Uranyl ions such as UO_2^{2+} in aqueous solutions have been the focus of study experimentally and computationally. In seawater, the uranyl exists as

anionic uranyl-carbonate complex, $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and it is inferred through experimentation that the anion forms neutral complex with Ca as $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3]$. Recent experimental methods only Ca and Mg form coordination bonds with the uranyl-carbonate complexes, where 90% of dissolved uranium is made up of $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3]$, followed by Mg.

Current and future global energy demands nuclear energy to be sustainable in which alternative sources of uranium needs to be looked upon. One viable option is to extract or mine uranium from the sea, a reserve which accounts for 3.3 ppb in seawater composition and equivalent to 4.4 billion tonnes of uranium (Qiao & Xu, 2018). The idea of mining uranium from the sea is not new and its research has been going on since the 1960s. According to Department of Energy's Office of Nuclear Energy, developing adsorbent technology capable of extracting uranium from seawater is one way to provide sustainable and economical supply of uranium for nuclear reactors for next century (Wood et al., 2016).

2.4 Biosorption

Biosorption is a physicochemical process of sorption of analytes biological material termed biosorbents. They are frequently made of biopolymers which can interact with pollutants through a range of processes, including chemical bonding, electrostatic interactions, and hydrophobic interactions (Torres, 2020; Mahmood-ul-Hassan et al., 2018). Biosorbents have gained attention as potential alternatives to synthetic adsorbents due to their low cost, availability, and eco-friendliness (Singh et al., 2020; Lin et al., 2021). They can be obtained from a range of sources, including agricultural by-products, algae, fungi, and bacteria (Redha, 2020; Escudero et al., 2018). Biosorbents undergo chemically modification to introduce nucleophilic functional groups that can enhance their affinity to adsorb contaminants such as positively charged uranyl ions (Noli et al., 2022; Hao et al., 2023).

2.4.1 Type Of Biosorbents

Crustacean shells are made of biopolymers called chitin and chitosan. It is famously known as the second most exploited biopolymer after cellulose (Singh et al., 2018). Chitin and chitosan can be labelled as rigid, white, inflexible nitrogenous polysaccharide (Gupta et al., 2018). Chitin and chitosan can be differentiated by numbers of N-acetyl-glucosamine units appear in the long chain of the biopolymer. If the number of N-acetyl-glucosamine units are less than 50%, then it is referred as chitin, whilst chitosan is vice versa (Escudero et al., 2018). Most of chitin and chitosan are widely obtainable from crustacean for instance crab and crayfish (Lin et al., 2021). Several studies have utilized chitin and chitosan biosorbents for uranyl adsorption. Poly(amidoxime)-graft-magnetic chitosan (P(AO)-g-MC) quickly and easily separates uranium from natural seawater, achieving an adsorption capacity of 5.14 mg/g in 7 days, thanks to its strong amidoxime groups and magnetic properties (Zhang et al., 2023). In another study by Lin et al. (2021), a film-like chitin/polyethyleneimine biosorbent with high nitrogen content and a porous structure achieved a uranium adsorption capacity of 950.49 mg g⁻¹, maintained integrity after 5 regeneration cycles, and utilized anion exchange and electrostatic attraction for adsorption.

Alginate is a natural highly soluble, anionic biopolymer that can be extracted from brown seaweed (Nathan et al., 2022) s. Alginate is not suitable for extraction of radionuclides and heavy metals due to its high solubility in solutions. However, they can be made as adsorbent by reacting with polyvalent metal ions through ion exchange. Besides, it can also be made as an adsorbent by calcinating it into hydrogel . Hybrid of alginate can be used to adsorb uranium from aqueous solutions. A hybrid of calcium alginate beads integrated with graphene oxide was able to adsorb 29.4 mg g⁻¹ of uranium in various freshwater sources (Basu et al., 2018). In addition, alginate aerogel cross linked with polyurea also shows uranyl

removal as high as 2023 mg g⁻¹ (Georgiou et al., 2023). A study by Jiang et al. (2020) developed new adsorbent of amino functionalized mesoporous silica into sodium alginate that effectively removes trace amount of U(VI) with adsorption capacity of 210 mg g⁻¹ in optimal conditions.

Microbial-based biomass can be used to adsorb uranium as well. These microbes can be obtained in large quantity from process like fermentation. Photosynthetic microbes, for instance algae, are commonly available and popular due to its biodegradable and can perform adsorption. The adsorption means of an alga is based on chromophore. Chromophores are as atoms or molecules that gives colour to the algae. Fresh water alga such as *Ulva latuca* and *Cladophora glomera* are reported to have maximum biosorption capacity of 147.5 mg g⁻¹ and 287.7 mg g⁻¹ respectively under optimal conditions (Mansour et al., 2020). Better biosorption capacities is exhibited by green alga *Ankistrodesmus* sp at maximum biosorption capacity of 601.2 mg g⁻¹ and shows removal efficiency of 95.6 % in simulated mine effluent (Cheng et al., 2021).

Waste material or by-products have been receiving great attention in bioremediation. These wastes are thrown away as a by-product from agricultural process or solid waste. High availability of these materials is what makes them useful as an adsorbent. In addition, exploitation of agricultural waste can reduce their accumulation in the environment and creating sustainable agriculture. Table 2.1 list out studies that have utilized agricultural waste as preferable biosorbent for sorption uranium.

Most of this agricultural waste can be made into activated carbon know as biochar. Biochar is produced when biomass undergoes the process of pyrolysis without oxygen (Hu et al., 2018). Any material that is rich in carbon can be made into a biochar and typically agricultural and animal wastes are the major sources of biochar. Biochar is high in carbon

and exhibits amorphous, random structure which makes biosorption uranium possible (Jiang et al., 2020). A recent study by utilized horse manure and turned it into biochar (Liao et al., 2023). The study obtained biosorption capacities of 516.5 mg g⁻¹ and removal efficiency of 93.9 %. Another study used biochar derived from macauba endocarp, which shows high removal efficiency of 80 to 86% as well as achieving high biosorption capacities of ranging from 52 to 417 mg g⁻¹, depending on pyrolytic temperatures (Guilhen et al., 2019).

Table 2.1: List of agricultural wastes and their biosorption capacities

Agricultural waste	Biosorption capacity (mg g ⁻¹)	References
Oakmoss	64.3	(Gül et al., 2019)
Sacred fir leaves	44.7	(Jiménez-Reyes et al., 2020)
Sago pondweed	268.8	(Yi et al., 2020)
Coconut leaf	184	(Hashmi et al., 2021)
Tea leaf	168	(Hashmi et al., 2021)
Coffee powder	152	(Hashmi et al., 2021)
Tea waste	97.7	(Yang et al., 2021)
Brewer's spent grain	297.3	(Su et al., 2022)
Rice Husk	21	(Su et al., 2022)
Sugarcane bagasse	29	(Abou-Hadid et al., 2022)

2.4.2 Biosorption Mechanism Of Uranyl Ions

Broadly utilized as an adsorbent, biomass possesses multiple functional groups, low cost, high uptake capacity, and extensive sources. There has been much research done on the relationship between uranium and biomass-based adsorbents. The uranium adsorption processes in biosorbents are diverse due to the large number of functional groups and

complex pore structures that are present on the surface (Torres, 2020; Lei et al., 2023). The biosorption can be categorised into 2: chemisorption and physisorption. Chemisorption, also known as chemical adsorption, occurs through the formation of chemical bonds between the adsorbate and the adsorbent (Abegunde et al., 2020). This type of adsorption is usually characterized by a high degree of specificity and selectivity, and it is often used for the separation of chemical species. Physisorption, also known as physical adsorption, occurs through weak van der Waals forces and is generally characterized by a low degree of specificity and selectivity (Deshmukh et al., 2022).

Chemisorption, a kind of adsorption, entails the formation of chemical interactions between the adsorbate and the adsorbent surface. This mechanism is generally more durable than physical adsorption, which relies on weaker forces such as van der Waals interactions. Chemisorption has superior selectivity compared to physical adsorption, indicating that certain adsorbates preferentially chemisorb onto certain adsorbents due to the distinct properties of the chemical interactions established. Chemisorption occurs when a substance with high oxygen affinity prefers to adsorb onto adsorbents with oxygen-containing functional groups, forming a monolayer of uranyl ions. This irreversible process, starting with activation energy, can be exothermic or endothermic. The mechanism of chemisorption includes ion exchange, electrostatic interaction, surface complexation and precipitation. Ion exchange mechanism can be simplified as metal ions that are loaded onto oxygenated functional group that are on the surface of a biosorbent (Dong et al., 2018). The efficiency of this functional group depends on the speciation of uranyl ions which are heavily influenced by pH and the cation-exchange capacity (CEC) on the biosorbent (Dubey et al., 2021). Electrostatic interaction on the hand involves the interaction between positively charged species of uranyl ions and negatively charged surface of a biosorbent. It is typically

a weak process that is dependent on the pH of solution and net charge of biosorbent (pH_{pzc}) (Chen et al., 2022; Nathan et al., 2022). Surface complexation forms complexes, inner or outer sphere when uranyl ions interacted with functional groups that are on biosorbent surface. The mechanism of surface complexation usually explains the biosorption process of most biosorbents. Precipitation mechanism forms deposit of metals in the solution during biosorption process (Wang et al., 2018). This mechanism usually works together with aforementioned mechanism whereby the functional group has no significant effect on the precipitation but to promote precipitation itself via other means of mechanism (Yang et al., 2019).

Most studies of biosorption mechanism of uranium determined through kinetic, isotherm and thermodynamics studies pointed chemisorption as the most prevalent mechanism. For example, chitosan and chitin derived or modified biosorbents from several studies follows pseudo-second order kinetic model which implies that the rate limiting step is chemisorption (Christou et al., 2019; Szlachta et al., 2020; Lin et al., 2021; Rostamian & Firouzzare, 2021). Agricultural wastes are made up of variation of inorganic and organic moiety such as hemicellulose, cellulose, lignin, protein, carbohydrates, pectin in their cell wall. Agricultural wastes that are rich with inorganic and organic moiety can effectively chemisorb uranyl ions due to large abundancy of carboxyl, amine, hydroxyl, keto, and aldehyde groups (Chakraborty et al., 2022). For instance, carbonized fibres derived from arecanut shells involve functional groups, particularly C=O and C-O, which exhibit selective affinity towards uranyl ions. Measuring the zeta potential values of its surface suggests an electrostatic interaction between positively charged uranyl ions and a negatively charged surface, in addition to adherence to pseudo-second-order kinetics model (Dhanya & Rajesh, 2023). A study by Nuhanović et al. (2019) decided that biosorption mechanism of sugar

beet pulp to be controlled by chemisorption with other mechanism including physisorption happening simultaneously. Chemisorption also dominated biosorption process of uranyl ions via rice and coffee husks (Ferreira et al., 2020).

Physisorption, an abbreviation for physical adsorption, is commonly defined as a van der Waals contact that occurs between the adsorbate and the adsorbent. This van der Waals interaction is weak but long-lasting and releases energy equal to the enthalpy of condensation. The interaction is considered weak because the energy must always be dissipated so that the adsorbate remains on the surface. Otherwise, the adsorbate leaves the surface. The energy expenditure in this type of adsorption is so low because of the accommodation process. Analogous to chemisorption, investigations on kinetics, isotherms, and thermodynamics have been employed to ascertain if the biosorption of a specific biosorbent constitutes physisorption. Although many studies conclude that chemisorption is the main mechanism of sorption process, many come into conclusion that physisorption were the main or large involved as well. Biochar derived from macauba endocarp exhibited physisorption on uranyl ions as observed via FTIR analysis and hybrid adsorption as the biosorption process fits with Redlich-Peterson isotherm model (Guilhen et al., 2021). Red beet peel biosorption mechanisms were determined to be both chemisorption and physisorption based on data obtained through data fittings and characterisation (Smječanin et al., 2022). Table 2.2 highlights how chemisorption relies on stronger, specific chemical interactions with higher energy requirements as opposed to physisorption which is governed by weaker, less selective physical interactions.

Table 2.2: Summary of the main differences between chemisorption and physisorption

Aspect	Chemisorption	Physisorption
Interaction type	Formation of chemical bonds (e.g. ion exchange, electrostatic interactions, surface complexation, precipitation).	Occurs via weak van der Waals forces.
Selectivity	High specificity and selectivity, as it relies on chemical interactions between specific functional groups and adsorbates.	Generally lower specificity and selectivity due to non-specific, physical interactions.
Energy requirements	Involves activation energy and can be either exothermic or endothermic; the process is generally more energetically demanding due to bond formation.	Requires very low energy (comparable to the enthalpy of condensation) and is less energy-intensive overall.
Kinetic behaviour	Often follows pseudo-second order kinetics, indicating that the rate-limiting step is associated with chemical interactions.	Kinetic, isotherm, and thermodynamic studies are used to characterize the process, but no single kinetic model dominates.
Functional groups involved	Involves oxygen-containing groups such as carboxyl, amine, hydroxyl, keto, and aldehyde groups present on biosorbents.	Less dependent on specific functional groups; relies on the general surface properties and long-lasting physical contacts.
Reversibility	Typically irreversible once the strong chemical bonds are formed.	More reversible as the weak interactions allow the adsorbate to be more easily released from the surface.

2.4.3 Effect Of Functionalisation Of Biosorbent For Uranyl Ions Removal

The adsorption capacity of biosorbents may be lower than other types of adsorbent due to low mechanical strength or lack of suitable adsorptive sites which are dependent on their composition. Besides, untreated, or raw biosorbents contains substances that mask functional groups on its surface and prevents the process of adsorption thus minimising its adsorption capacity. Prior to functionalisation, biosorbents usually goes through steps of physical treatment such as washing, drying, crushing, grinding, and sieving to obtain optimal form for biosorption (Syeda et al., 2022). Chemical modification is a technique that can be used to improve the performance of adsorbent for contaminant removal. It involves the introduction of functional groups onto the surface of the adsorbent that can interact with the contaminant, such as carboxyl, hydroxyl, aldehydes, ketones, alcohols, and phenolic groups (Turanov et al., 2020). After modification, surface energy, area, roughness, hydrophobicity, and reactivity also improved (Lingamdinne et al., 2022).

Several techniques can be used to chemically modified adsorbents such as mechanical, thermal, or chemical processes. The thermal process mainly develops the porosity of the adsorbent, chemical process makes use of acid, alkali, or salts to graft new functional groups onto the surface of adsorbent, while in physical process the density and solubility of adsorbent increases (Abdelhakim et al., 2021). These methods can also be combined such as thermochemical or mechanochemical. However, only chemical modification is far better than the other methods of modification due to lesser time consumption and direct changes can be applied to the surface of biosorbents as well as introduction of additional surface properties.

The selection of chemical modification as the best way to improve biosorption capacity is evidently proven by Noli et al. (2022) using grape peels. The study employed

five different forms of grape peels for uranyl adsorption which are untreated, NaOH treated, Na₂CO₃ treated, biochar and HNO₃ treated biochar. The study concluded that alkali treated had the highest biosorption capacity and the lowest was the biochar grape peel.

2.5 Factors Influencing Biosorption Of Uranyl Ions

The biosorption of biosorbents is subject to several influencing parameters, including the pH value, the temperature, the initial concentration of uranyl ions and the contact time between biosorbent and uranyl ions. These variables have a direct influence on both the adsorption capacity and the determination of optimal operating parameters within the adsorption process (Ji et al., 2022).

2.5.1 Contact Time

The contact time in connection with biosorption refers to the duration during which the biosorbent material is in contact with the solution containing uranyl ions. It is a critical parameter that affects the efficiency of uranyl removal from the solution. Biosorption capacity does not affect by contact time between biosorbent and sorbate directly but act as a limiting factor (Fan et al., 2021). Studies have shown that the biosorption of uranium occurs very quickly in the initial phase of the process because there are many active sites to which the heavy metals can bind (Fang et al., 2022). This rapid biosorption is attributed to the large surface area available for adsorption of heavy metals in the early stages of the process (Nuhanović et al., 2021; Smječanin et al., 2022; Orabi et al., 2021). However, it is important to note that the biosorption process reaches equilibrium when all the available active sites are saturated by the metal ions thus further increase in contact time will not increase biosorption capacity (Banerjee et al., 2022). The typical contact time for a biosorption process to reach equilibrium is 30-240 minutes, but for some studies the equilibrium may

take up to hours (Hu et al., 2018; Ferreira et al., 2020). For example, equilibrium was reached in 30 min for rice straw due to the larger number of available active sites during the initial stages of biosorption of uranyl ions (Hussein et al., 2019).

2.5.2 Initial Concentration Of Uranyl Ions, U(VI)

Research on the impact of initial U(VI) concentration on biosorption processes is crucial for understanding the efficiency and capacity of U(VI) removal from aqueous solutions. Smječanin et al. (2022) study explores the impact of initial U(VI) concentration on red beet peel biosorption, revealing a complex process involving surface chemisorption and intraparticle diffusion, highlighting mixed control in uranium biosorption kinetics. Furthermore, the study by Nuhanović et al. (2021b) explored a biocomposite made from sugar beet pulp and pomelo peel, highlighting the impact of the initial concentration of U(VI) on sorption capacity and efficiency. Their research highlighted the importance of understanding the relationship between the initial U(VI) concentration and the adsorption capacity of biomass-based adsorbents, providing essential insights for improving U(VI) removal methods.

The variations in initial U(VI) levels in solutions have significant environmental implications, particularly regarding the cleanup of uranyl ions in solution. Understanding the influence of initial U(VI) concentration on biosorption processes is crucial for creating efficient and sustainable treatment methods. While existing studies have illuminated the impact of initial U(VI) concentration on biosorption, additional research is essential to explore the dynamics of U(VI) uptake across different concentration ranges (Nathan et al., 2022).

To sum up, the initial concentration of U(VI) plays a significant role in biosorption processes with biomass-based adsorbents, impacting the effectiveness, capability, and

processes involved in the removal of U(VI). The findings from these studies contribute to the advancement of sustainable and effective strategies for mitigating uranium contamination in aqueous environments.

2.5.3 Initial pH Of Uranyl Solutions

The initial pH of uranyl solutions plays a crucial role in biosorption processes, significantly influencing the efficiency and mechanisms of uranyl ion uptake by biomass-based adsorbents. Several studies have investigated the impact of initial pH on the biosorption of uranyl ions, providing valuable insights into the optimization and understanding of the biosorption process. The starting pH of the solution influences the surface charge of the adsorbent material (Chen et al., 2022). When the pH values is lower than the point of zero charge (pH_{zpc}), the adsorbent carries a positive charge. Conversely, when pH exceeds the pH_{zpc} , the surface shifts to negative charge (Syeda et al., 2022). This affects the electrostatic interaction that binds the adsorbent and adsorbate. At pH values below pH_{zpc} , the electrostatic interaction is repulsive, which can hinder the adsorption process (Liu & Zhang, 2022). Conversely, at pH values above pH_{zpc} , the electrostatic interaction becomes favourable, promoting the adsorption of U(VI) ions (Gupta et al., 2018).

The speciation of U(VI) in solution is strongly pH dependent. At lower pH values, U(VI) ions tend to be more mobile and are predominantly present as positively charged species (Hossain et al., 2020). As the pH increases, the uranyl species become neutral or negatively charged (Jun et al., 2021). This change in speciation affects the interaction between U(VI) ions and the adsorbent surface, influencing the adsorption capacity and mechanisms. The acidity or alkalinity of the solution influences the protonation and deprotonation processes of functional groups present on the surface of the adsorbent (Nathan et al., 2022). The activity of oxygen containing functional groups is affected by the pH level

of the solution. This subsequently influences the accessibility and charge of binding sites on the adsorbent surface, which are essential for the adsorption of U(VI) ions (Nuhanović et al., 2021).

The ability of the adsorbent to capture U(VI) ions is significantly affected by the pH of the solution, which determines the species of U(VI), the state of functional groups, and the surface charge of the adsorbent. Understanding the ideal pH levels for effective biosorption is crucial for enhancing the elimination of U(VI) from aqueous solutions (Wang & Guo, 2023). Zheng et al. (2018) carried out research to explore how pH influences the biosorption and biomineralization of uranium (VI) by *Saccharomyces cerevisiae*. The research demonstrated that the initial pH significantly influenced the biosorption efficiency, with specific biochemical interactions being facilitated at different pH levels. This study highlights the importance of considering the initial pH of uranyl solutions in selecting efficient biosorbents for uranium biosorption.

2.5.4 Temperature

Temperature is a critical factor that significantly influences the adsorption process of various adsorbents. Several studies have investigated the impact of temperature on adsorption capacity, efficiency, and mechanisms using different types of adsorbents. Temperature influences adsorption capacity by affecting the solubility and molecular interactions between adsorbent and adsorbate (Chen et al., 2022). Generally, an increase in temperature enhances adsorption capacity by providing more energy for adsorption processes to occur effectively (Torres, 2020; Liu & Zhang, 2022). This elevated energy can lead to improved number of active sites that increases adsorption capacity (Banerjee et al., 2022). Adsorption that involves the use of microorganisms prefers lower temperature rather

than higher ones because of decreased metabolic activity of microorganisms once higher temperature is applied (Sharma & Shukla, 2021).

2.6 Determination Of Biosorption Mechanisms Of Uranyl Ions

Experimental data obtained through adsorption studies of varying adsorption conditions can be used to determine the means of adsorption of uranyl ions on an adsorbent. Conditions such as temperature and time are crucial as they determine the interaction of uranyl ions and adsorbent surfaces during adsorption processes. The precise determination of adsorption mechanism can be made through modelling of adsorption processes by employing adsorption modelling (Sun & Li, 2021). Adsorption isotherm for example can be used to predict the maximum amount of solute that can be adsorbed on an adsorbent. In the scenario of environmental condition such as seawater, a solution can contained more than a single sorbate where one single sorbate is preferred. Besides, the existence of other type of adsorbent (typically microorganisms) may affect adsorption capacity of adsorbent (Zhang et al., 2023). These other sorbates are considered as competitive ions and may affect the adsorption capacity of a single, targeted sorbate. Isotherm models such as Freundlich, Langmuir and Sips models are typical isotherm models used for adsorption processes.

2.6.1 Kinetics Study

Kinetics study plays an essential role in understanding the dynamics and efficiency of adsorption processes (Islam et al., 2021). They influence the development and optimization of treatments for various pollutants, including heavy metals such as uranium (VI) ions (Inglezakis et al., 2020). These studies provide insight into the rate at which adsorbate molecules interact and attach to the surface of adsorbents, providing important data for the design of effective environmental remediation systems.

The process of adsorption mass transfer involves three fundamental steps. The initial phase is referred to as external diffusion, during which the adsorbate moves from the liquid phase into the liquid film surrounding the adsorbent. The difference in concentration levels between the bulk solution and the adsorbent's surface drives the process of external diffusion (Inglezakis et al., 2020). In the second stage, referred to as internal diffusion, the adsorbate moves into the pores of the adsorbent. The third step involves the adsorption of the adsorbate onto the active sites of the adsorbent. Kinetic models like the pseudo-first order and pseudo-second order are frequently used to characterize the adsorption process.

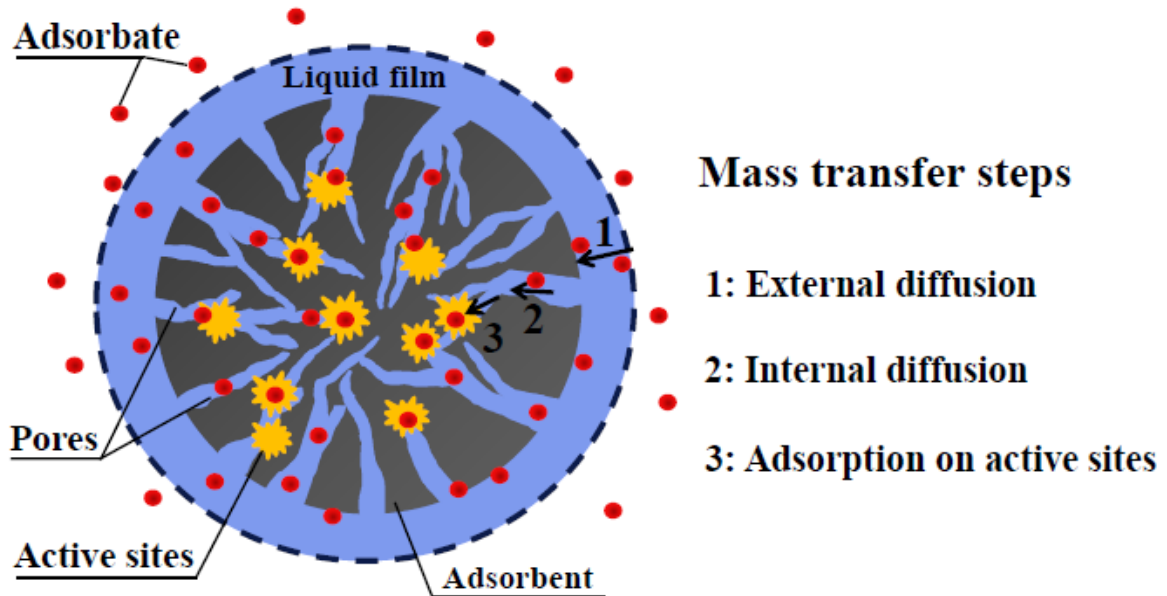


Figure 2.4: Steps of adsorption mass transfer (Wang and Guo, 2020)

The pseudo-first-order (PFO) is one of the most used adsorption kinetics models that originates from chemical-reaction model. The adsorption process that follows PFO usually represented as having high initial concentration of adsorbates and low active sites, where it fits the description of internal diffusion or physical adsorption (physisorption). Pseudo-second-order (PSO) model on the other hand describes adsorption kinetics where the number of active sites complement with number of adsorbates (Haryanto et al., 2017). PSO basically describe adsorption on active sites or chemical adsorption (chemisorption).

2.6.2 Isotherm Study

Isotherm study uses adsorption isothermal models to describe interaction between adsorbate and adsorbent. Information that can be gathered from this study are adsorption capacity and surface properties. Adsorption experiments are performed with different initial concentrations to fit isotherm models that describes it. Typically, Langmuir, Freundlich and Sips isotherm model are used to describe the adsorption of uranium ions on low-cost adsorbents such as sago hampas (Chakraborty et al., 2022).

Langmuir isotherm models basically assume that monolayer adsorption happens on an identical surface with no interaction between adsorbate closest to it and have constant binding energy. The separation factor (R_L) is used to determine whether the adsorption process is favourable or non-favourable. An altered brewer's spent grain (BSG) exhibit adsorption processes that fits with Langmuir isotherm model with maximum adsorption capacity of 221 mg g^{-1} of uranyl ions (Su et al., 2020) . Another similar isotherm study on adsorption of U(VI) using carbon fibres made from rice husk and sugarcane bagasse adhere to Langmuir isotherm models with maximum adsorption capacities of 21.0 mg g^{-1} and 29.0 mg g^{-1} respectively (Abou-Hadid et al., 2022).

Freundlich isotherm model assume that the adsorption of uranyl ions occurs on a heterogeneous surface and exist interaction between adsorbed ions. In simple terms, Freundlich isotherm model describes multilayer adsorption. An adsorption process that fits with Freundlich model also indicate physisorption as the major adsorption mechanism (Chen et al., 2022). Isotherm study on adsorption of U(VI) using pistachio shells conclude that the adsorption process fits with Freundlich isotherm model with coefficient of determination (R^2) near to 0.99 and in line with multilayered structure of pistachio shells as seen using

TEM (Younes et al., 2020). Similar study by Nuhanović et al. (2021b) using pomegranate peel waste also found that the adsorption process fitted well with Freundlich model.

Sips isotherm model is a hybrid model that combines both Langmuir and Freundlich isotherm models. This model is used to predict monolayer adsorption in homogenous and heterogeneous surface as it avoids the restriction of increase number of adsorbate that is assumed by Freundlich model (Chen et al., 2022). The Sips model is heavily influenced by adsorption conditions such as temperature, pH, and initial adsorbate concentrations (Majd et al., 2020). A surface ion-imprinted brewer's spent grain was used by Su et al. (2022) to remove U(VI) from simulated wastewater. Out of all isotherm model tested, Sips model fitted the study well with $R^2 > 0.99$ while Langmuir and Freundlich model obtained $R^2 < 0.99$ (Su et al., 2022). Magnetically modified pig manure biochar adsorption with U(VI) also fitted to Sips isotherm models to signify monolayer adsorption (Liao et al., 2023).

2.6.3 Thermodynamic Study

The fact that adsorption is a temperature-dependent process facilitates the evaluation of the thermodynamic parameters of these processes. Thermodynamic considerations are necessary for adsorption experiments to determine the spontaneity and feasibility of such processes. Experimental data that can be obtained from adsorption experiments can determine the Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°).

A chemical reaction's spontaneity can be gauged using the Gibbs free energy change (ΔG°). Two types of adsorption processes are indicated by positive or negative ΔG° values: spontaneous and non-spontaneous. A negative value indicates spontaneous adsorption, while a positive value indicates non-spontaneous adsorption. Most of U(VI) adsorption studies using agricultural waste reported spontaneous adsorption (Gül et al., 2019; Hashmi et al.,

2021; Deshmukh et al., 2022) . For example, Jiménez-Reyes et al. (2020) reported spontaneous adsorption for U(VI) as indicated by negative ΔG° when using *Abies religiosa* leaf. However, Nuhanović et al. (2021b) reported otherwise when using acid modified pomegranate peel.

Positive or negative values of enthalpy change (ΔH°) are one way to determine whether the adsorption processes are either endothermic and exothermic, respectively. Enthalpy change for U(VI) adsorption are either positive (endothermic) and negative (exothermic). For example, adsorption of U(VI) using rice straw showed enthalpy change $\Delta H^\circ = -151.2 \text{ kJ mol}^{-1}$ that indicate exothermic process (Abou-Hadid et al., 2022). However, a study by Deshmukh et al. (2022) via *Phyllanthus emblica* bark showed positive enthalpy change that of endothermic phenomena. The magnitude of enthalpy change can also determine the strength of adsorption process and as an indicator of what mechanism dictates the adsorption process (Dubey et al., 2021). Figure 2.5 summarise the enthalpy values and its corresponding mechanism of adsorption.

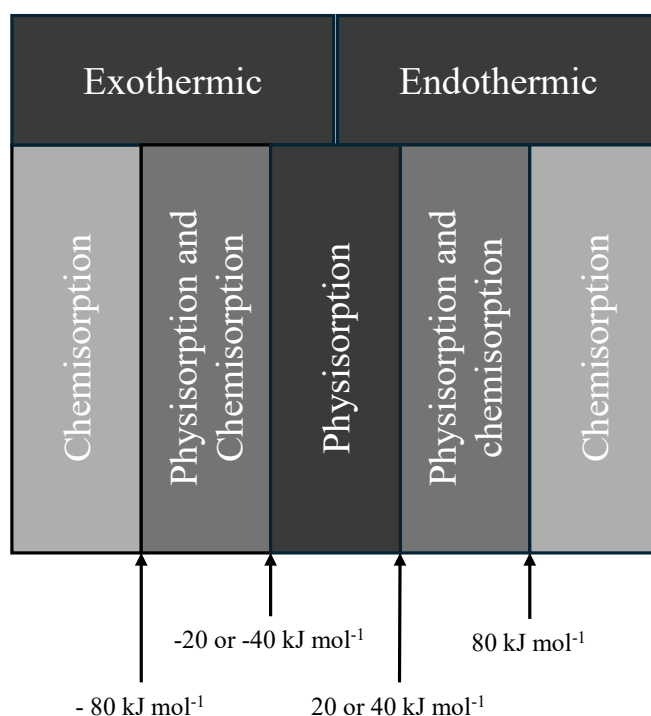


Figure 2.5: Enthalpy values to indicate either chemisorption or physisorption

CHAPTER 3

MATERIALS AND METHODS

3.1 Sample Preparation

The sago hampas were gathered in large quantities from the nearby Pusa, Sarawak sago processing business. The sago hampas were properly cleaned using tap water before being used, and then they were again rinsed with deionised water to get rid of any contaminants like dirt. The cleaned sago hampas were completely dry underwent a process of sun and air drying for a duration of 2 weeks, followed by additional drying in an oven at 70 °C. The dehydrated sago hampas was grounded into a powder form and sieved using 500 µm, 2000 µm, and 3000 µm particle sizes. The fine samples were then kept in airtight plastic container based on the size of the particles to avoid any additional microbial or moisture contamination.

3.2 Functionalization Of Sago Hampas

With minor modifications, the functionalization of sago hampas was carried out in accordance with Zhang et al. (2016) methodology. Esterification introduces oxygen containing functional groups such as carboxyl and hydroxyl groups to improve the adsorptive capacity of sago hampas. Three processes were used in the procedure to functionalise sago hampas: esterification, acidification, and alkalisation. For one hour at 45 °C, around 25 g of samples were submerged and swirled in 300 mL of concentration 10 % potassium hydroxide solution. Whatman No. 42 filter paper was used to filter the alkalisated sago hampas after they had been cleaned to a pH of 8. Afterward, the samples underwent drying for one hour at a temperature of 105 °C in an oven. The process of acidification came

next. For one hour at 45 °C, 20 g of alkalis samples were submerged in 200 mL of 15% succinic acid. Subsequently, the sago hampas underwent acidification, followed by filtration, and were then dried at 105 °C for one hour. The esterification process was the last stage. The acidified sago hampas were combined with 300 ml of acetone, 30 g of succinic acid, and 5 g of p-toluene sulfonic acid. For three and a half hours, the mixture was allowed to reflux at 75 °C. The solution was adjusted to a pH of 4, after which the sago hampas were filtered and dehydrated at 105 °C for two hours. The three processes' underlying reactions are depicted in Figure 3.1.

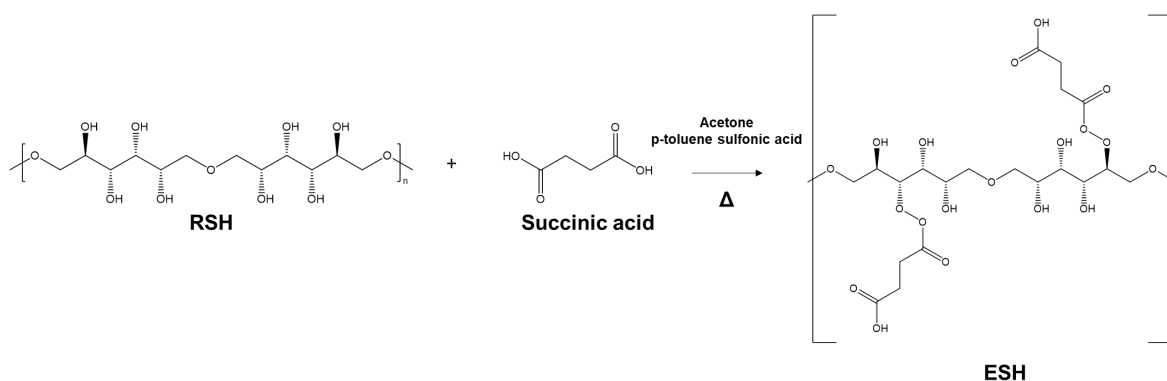


Figure 3.1: Chemical equation for esterification process of RSH into ESH

3.3 Batch Adsorption Experiments

Solutions containing 100 mg L⁻¹ of uranyl ions were prepared by diluting a standard solution of 1000 mg L⁻¹ uranyl nitrate hexahydrate (N₂O₈U.6H₂O) solution with deionised water. This solution is known as stock solution. For batch experiment, low U(VI) concentrations (specifically 1 to 5 ppm) U(VI) solutions were subsequently made using the stock solution. With the sole exception of those carried out for thermodynamics studies, all experiments were conducted at room temperature (25 °C). The pH of each sample had been adjusted using NaOH and HNO₃ in advance and then obtained with pH meter. Each experiment was conducted in triplicate. In a conical flask, sago hampas and U(VI) solution were combined at a ratio of around 1 g L⁻¹. A wrist shaker set to 450 rpm was used to shake

the samples. 10 ml aliquots were drawn from the solution every 20 to 200 minutes. Membrane filter featuring a 0.45 µm pore was used to filter the aliquots. Solid samples were dried at 80°C using oven for an entire night. Whatman 42 filter paper was used for the filtering step. The PerkinElmer Optima 8000 brand of Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used to evaluate the samples, while SEM and FTIR were used for further analysing the surface of sago hampas. To establish a linear calibration curve, the ICP-OES was calibrated using uranyl standard solutions at calibration points between 0.2 and 5.0 mg L⁻¹. Equation 3.1 was used to calculate adsorption capacity (Q).

$$\text{Adsorption Capacity (Q)} = \frac{(C_i - C_f) \times V}{m} \quad \text{Equation 3.1}$$

In this context, C_i and C_f represent the concentrations of uranyl ions (in mg L⁻¹) prior to and following the adsorption process, while V denotes the volume of the solution (in litres), and m indicates the mass of adsorbent utilized (in grams). The batch experiment was carried out again to examine additional parameters as outlined in Table 3.1.

Table 3.1: Parameters tested to ensure optimum performance of sago hampas

Parameters	Conditions
Initial U(VI) concentrations (mg L ⁻¹)	1.0, 2.0, 3.0, 4.0, 5.0
pH	2.0, 3.0, 4.0, 5.0, 6.0, 7.0
Contact time (min)	5.0, 10.0, 20.0, 40.0, 80.0, 120.0, 140.0, 160.0, 180.0, 200.0
Temperature (°C)	25.0, 35.0, 45.0

3.4 Characterisation Of Sago Hampas

To investigate sago hampas samples' surface, Scanning Electron Microscopy with Electronic Dispersive X-Ray (SEM-EDX) and Fourier-transform infrared spectroscopy (FTIR) were utilized. A JEOL JSM-6390 LA, an SEM-EDX instrument from Japan was

employed to capture surface morphology, revealing detailed structure of sago hampas as well as its elemental composition. For FTIR analysis, a Thermo Scientific Nicolet iS10 instrument was used. This allowed for the collection of spectral data in the 400 – 4000 cm⁻¹ wavenumber range, both prior to and following adsorption experiments and functionalization processes.

3.5 Evaluation Of Adsorption Data

Table 3.2 shows the formulas for the kinetic and isotherm models used for interpreting the experimental data. The error functions described in Table 3.3 were used for deciding which kinetics and isotherms models corresponded to the adsorption data acquired. Every calculation and illustrations were created using Microsoft Excel.

Table 3.2: Kinetic and isotherm models together with their corresponding equations

Models	Type of models	Formula
Pseudo-first-order model (PFO)	Kinetic	$q_t = q_e (1 - e^{-k_1 t})$
Pseudo-second-order model (PSO)	Kinetic	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$
Langmuir isotherm model	Isotherm	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$
Freundlich isotherm model	Isotherm	$q_e = K_F C_e^{\frac{1}{n}}$
Sips isotherm model	Isotherm	$q_e = \frac{K_T C_e}{1 + K_S C_e^{n_s}}$

Table 3.3: Functions of error and their corresponding formulae

Statistical parameters	Formula
Coefficient of Determination (R^2)	$R^2 = \frac{\Sigma(q_{\text{mean}} - q_{\text{cal}})^2}{\Sigma(q_{\text{cal}} - q_{\text{mean}})^2 + \Sigma(q_{\text{cal}} - q_{\text{exp}})^2}$
Chi-square test (X^2)	$X^2 = \Sigma \left(\frac{(q_{\text{exp}} - q_{\text{cal}})^2}{q_{\text{cal}}^2} \right)$
Sum of squares error (SSE)	$\text{SSE} = \Sigma (q_{\text{exp}} - q_{\text{cal}})^2$
Root mean square error (RMSE)	$\text{RMSE} = \sqrt{\frac{1}{N_{\text{exp}}} \Sigma (q_{\text{exp}} - q_{\text{cal}})^2}$
Hybrid fractional error function (HYBRID)	$\text{HYBRID} = \frac{100}{N_{\text{exp}} - N_{\text{para}}} \Sigma \frac{q_{\text{exp}} - q_{\text{cal}}}{q_{\text{exp}}}$

3.6 Simulated Seawater And Desorption Studies

To simulate seawater conditions, 25.6 g L⁻¹ NaCl, 193 mg L⁻¹ NaHCO₃, and 3 mg L⁻¹ U(VI) were used (Su et al., 2022b). A proportion of 1 g L⁻¹ of sago hampas/simulated seawater was agitated in 50 mL centrifuge tubes at 300 rpm, room temperature, and pH 7.05. The experiments were run in triplicates. Following seawater adsorption studies, the samples were filtered, rinsed with deionized water, and dried in an oven at 105 °C for 12 hours. Desorption studies were performed with two desorption agents: 1.0 M HNO₃ and 1.0 M HCl. The dried samples were mixed with desorption agents in 0.5 g L⁻¹ ratio of sago hampas/acid for a day. The regenerated sago hampas were collected through filtration, and the filtrate was analysed with ICP-OES. Equation 3.2 contains the formula for calculating the desorption ratio.

$$D_e (\%) = \frac{c_d * V_d}{m_d * q_e} \times 100 \quad \text{Equation 3.2}$$

Where D_e (%) is the desorption ratio, c_d (mg L⁻¹) is the uranyl ion concentration after desorption, m_d (g) is the mass of sago hampas loaded with uranyl ions after adsorption, V_d (L) is the volume of desorption agents used, and q_e (mg g⁻¹) is the biosorption capacity of sago hampas after simulated seawater adsorption studies.

CHAPTER 4

RESULTS

4.1 FTIR Analysis on RSH And ESH

Figure 4.1 displays the superimposed FTIR spectra of sago hampas before and after functionalization. Notable bands at 3332 cm^{-1} and peaks between 1422 and 1455 cm^{-1} indicate the presence of hydroxyl groups (O-H). The peak at 2891 cm^{-1} corresponds to the stretching and bending of saturated aliphatic C-H bonds. The region between 1606 cm^{-1} and 1715 cm^{-1} suggests symmetrical stretching of C=O bonds in carboxylic acids. Additionally, small peaks in the fingerprint region ($1500\text{--}500\text{ cm}^{-1}$) are observed, with symmetrical stretching of COO^- at 1422 cm^{-1} and 1430 cm^{-1} , and sharp peaks for C-O single bonds in carbohydrates at $1019\text{--}1027\text{ cm}^{-1}$ and between $1158\text{--}1316\text{ cm}^{-1}$. Table 4.1 summarizes responsible grafted functional groups onto ESH.

Table 4.1: Summary of responsible oxygen-containing functional group for uranyl adsorption

Functional groups	Wavenumber (cm^{-1})
Hydroxyl (-OH)	3332
	1422-1455
Aliphatic C-H	2891
Carbonyl (C=O)	1606-1715
Carboxylate (COO^-)	1422-1455
Carbohydrate (C-O)	1019-1027
	1158-1316

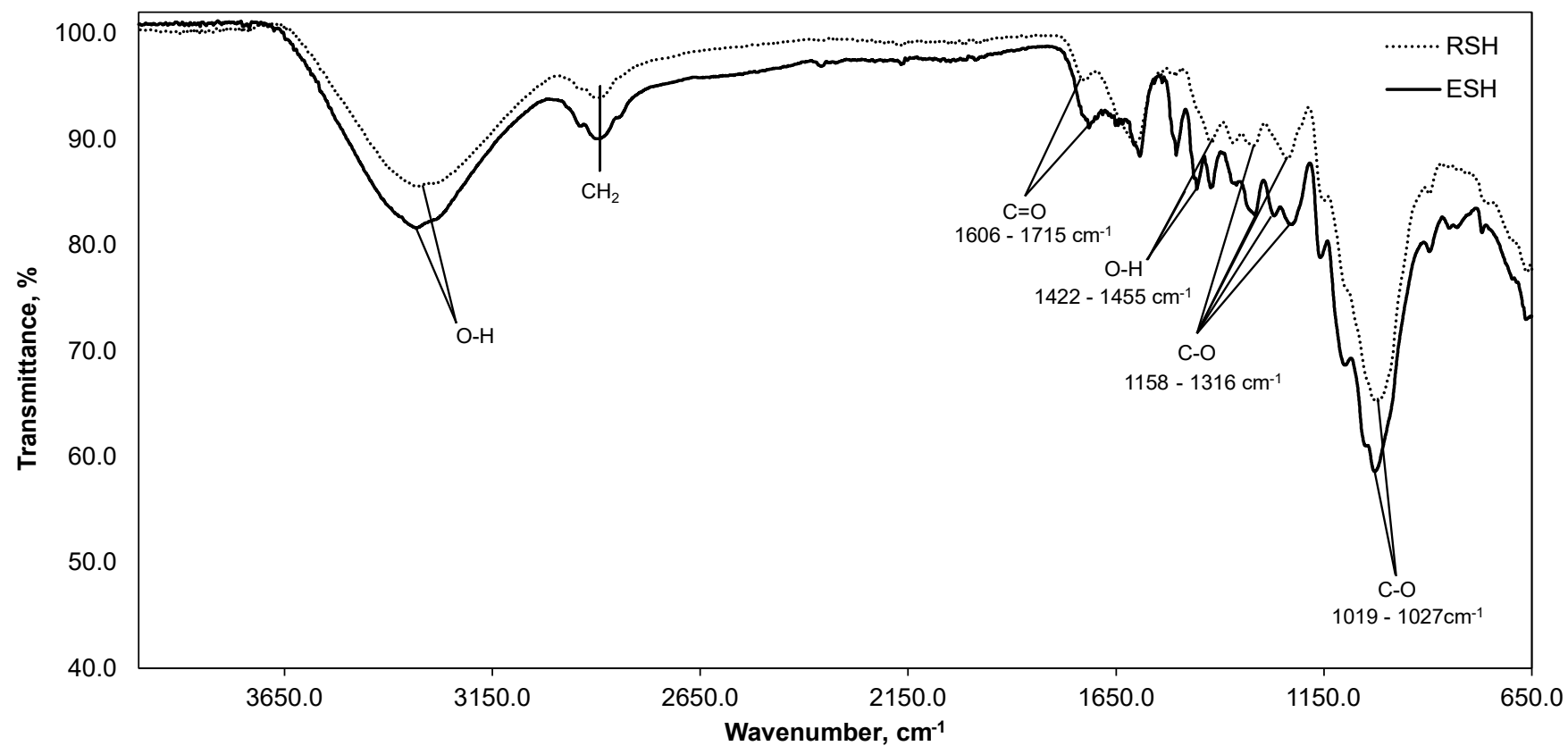


Figure 4.1: FTIR spectra of (a) RSH and (b) ESH

4.2 FTIR Analysis of ESH Prior And After Uranyl Adsorption

Following functionalization, Figure 4.2 reveals shifts, decreased peak intensities, and the disappearance of peaks associated with oxygen-containing functional groups after exposure to UO_2^{2+} ions, indicating successful uranium adsorption onto ESH. Notably, the elimination of peaks in the $1422\text{--}1593\text{ cm}^{-1}$ range suggests effective binding sites for uranyl ions. Furthermore, an increased intensity at the UO_2^{2+} fingerprint peak at 915 cm^{-1} and peak shifts post-adsorption are observed.

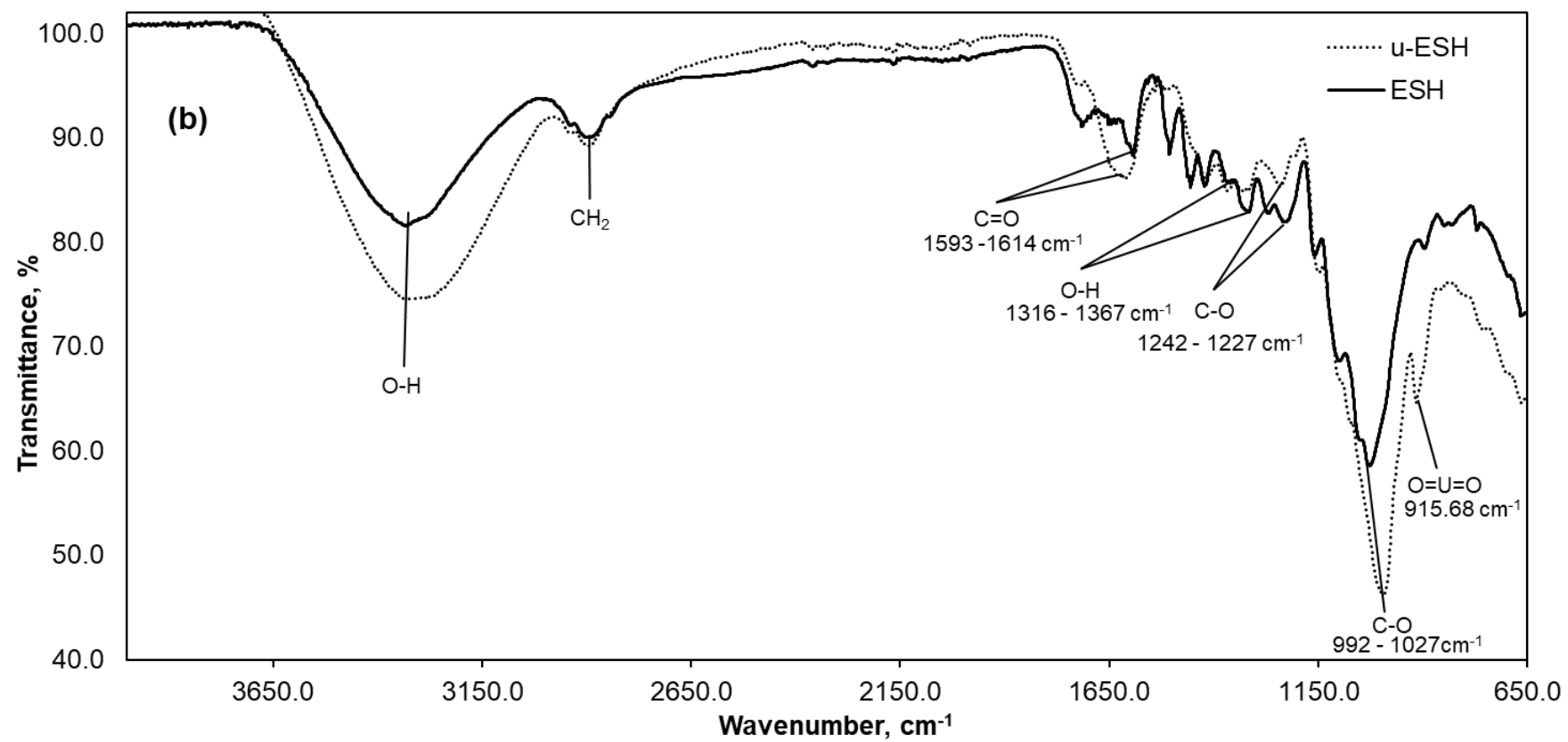


Figure 4.2: FTIR spectra of ESH and u-ESH

4.3 SEM-EDX Analysis Of RSH, ESH & U-ESH

The surface morphology of raw sago hampas (RSH) and esterified sago hampas (ESH), both before and after uranium adsorption, was analysed using Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDX). In Figure 4.3(a), the SEM micrograph of RSH reveals a dense, irregularly shaped, rough, and elongated surface lacking visible pores. White, spiky, spherical structures, indicative of lignocellulose and pectic components, are prominently observed. Additionally, small quantities of elliptical-shaped sago starch granules are present.

Upon functionalization, as shown in Figure 4.3(b), the ESH surface exhibits a smoother texture, suggesting the removal of surface contaminants such as lignin, hemicelluloses, and wax during the hydrolysis process. This smoother surface exposes underlying pores, potentially increasing the number of active sites available for adsorption.

Figure 4.3(c) presents the SEM micrograph and corresponding EDX analysis of ESH after U(VI) adsorption. The surface appears smoother and whiter, likely due to the deposition of uranium particles. EDX data confirm the presence of uranium, accounting for 1.81 wt% of the sample, as indicated by distinct signals corresponding to uranium elements.

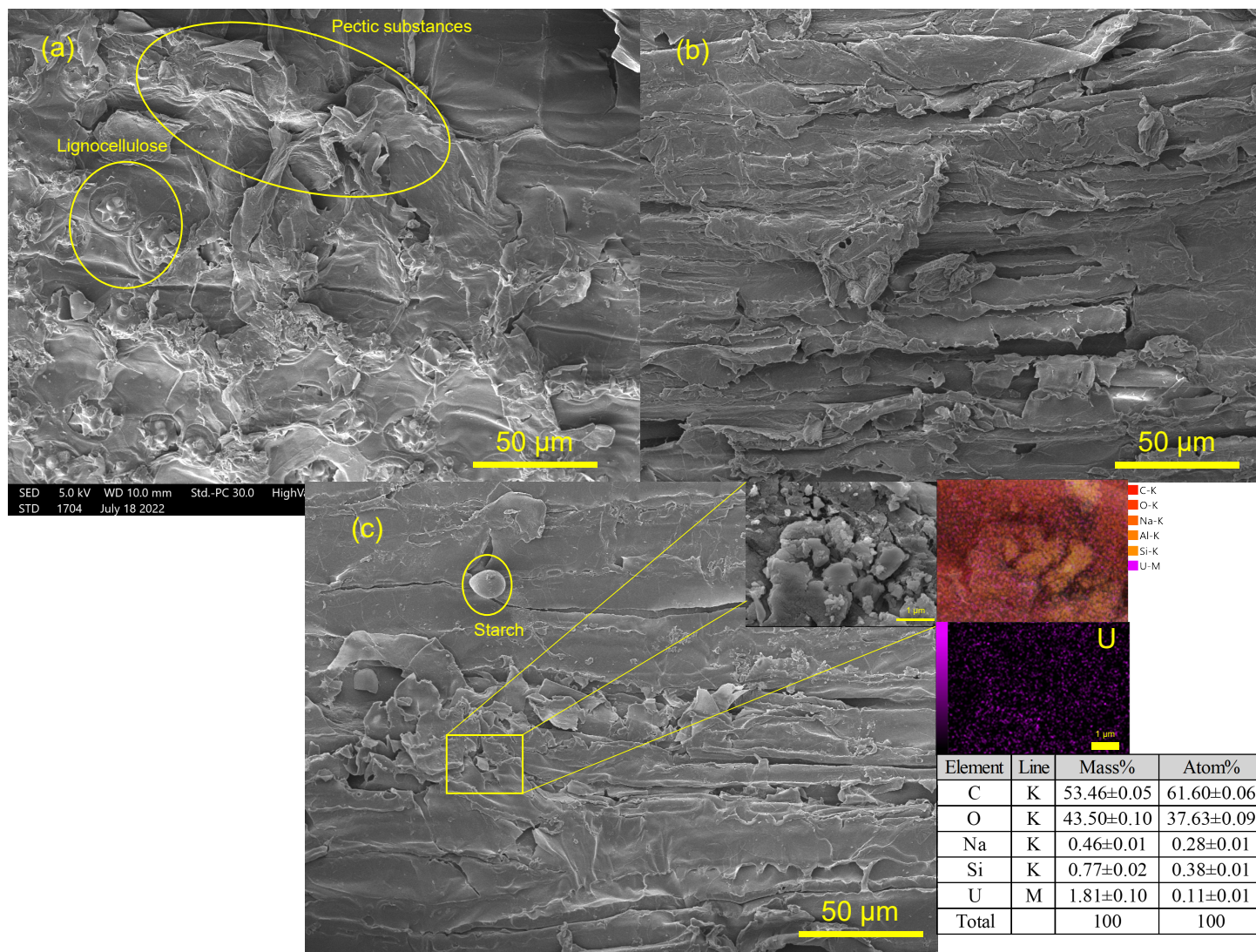


Figure 4.3: 500x magnification SEM micrographs of (a) RSH, (b) ESH, and (c) u-ESH. Effect of time and kinetic studies

4.4 The Effect Of Time And Kinetic Studies Of Rsh And Esh

The study evaluated the impact of adsorption duration on uranium removal using raw sago hampas (RSH) and esterified sago hampas (ESH) to determine their effectiveness in treating uranium-contaminated seawater. As depicted in Figures 4.4(a) and 4.4(b), both adsorbents exhibited rapid uranium uptake within the initial 80 minutes, followed by a more gradual adsorption rate from 100 to 200 minutes. To model the adsorption kinetics, pseudo-first-order (PFO) and pseudo-second-order (PSO) models were applied to the experimental data. The calculated parameters are presented in Table 4.2, with non-linear fittings illustrated in Figures 4.4(a) and 4.4(b). Among the models evaluated, the PSO model demonstrated the best fit for both adsorbents, evidenced by an R^2 value of 1 and minimal error function values.

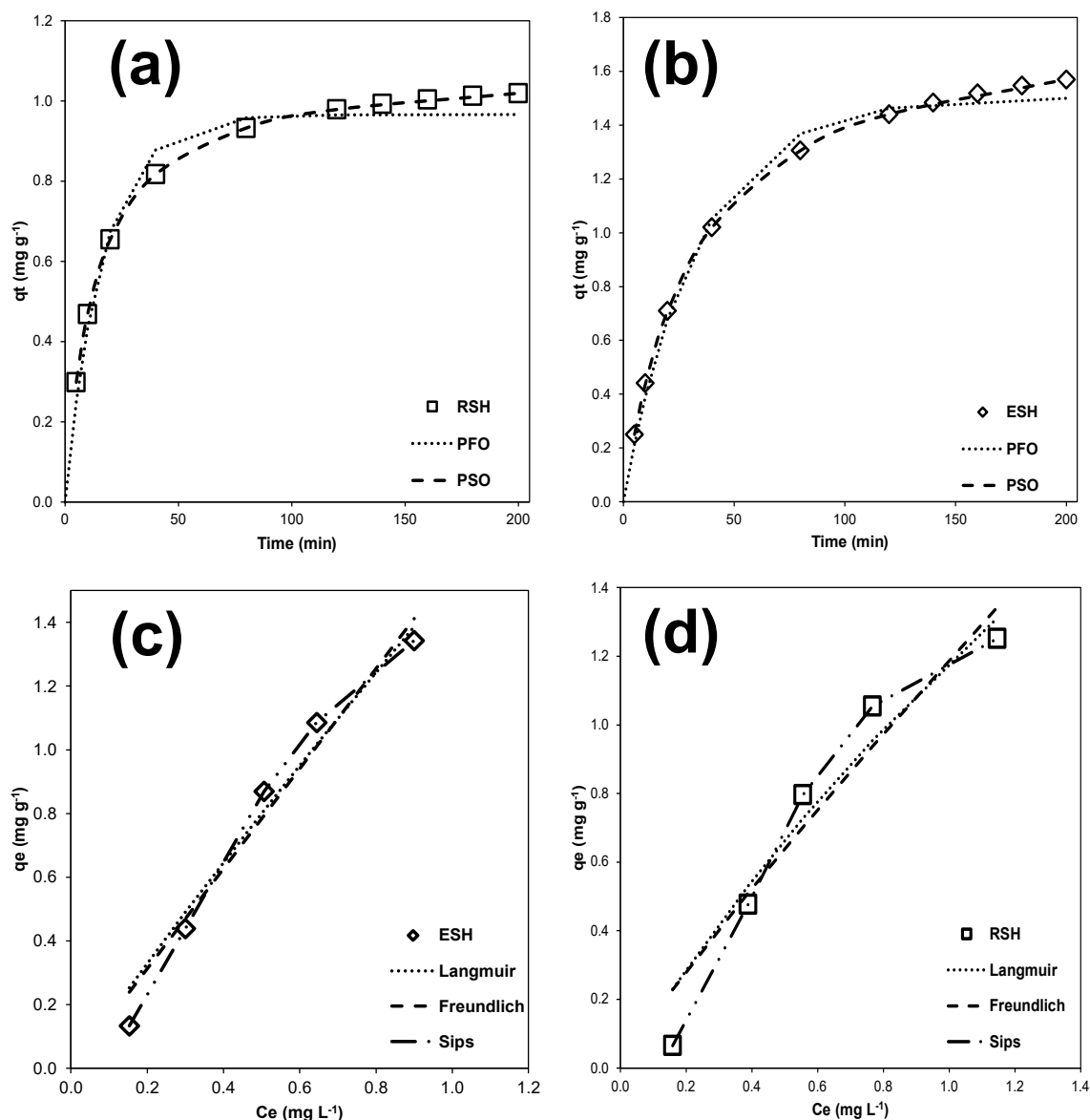


Figure 4.4: (a) Kinetics models fitted nonlinearly on RSH, (b) Kinetics models with nonlinear fittings on ESH, (c) Fitting of non-linear isotherm models on RSH., (d) Fittings of isotherm models on ESH that are not linear. Constant variables were used in kinetics studies such as 1.0 g L⁻¹ of adsorbent/adsorbate, initial U(VI) concentration = 1.0 mg L⁻¹, room temperature. Constant variables were used in adsorption isotherm studies: 1 g L⁻¹ adsorbent/adsorbate, pH = 4.0, contact time = 40 min, room temperature

Table 4.2: The values of kinetic parameters of RSH and ESH determined using three kinetic models from contact time adsorption experiments

Kinetic model	Parameters	RSH	ESH
Pseudo-first-order	k_1 (min^{-1})	0.060	0.030
	$qt_{200\text{min, exp}}$ (mg g^{-1})	1.020	1.570
	$qt_{200\text{min, theo}}$ (mg g^{-1})	0.966	1.504
	R^2	0.978	0.998
	RMSE	0.041	0.047
	SSE	0.012	0.015
	χ^2	0.003	0.002
	HYBRID	0.265	0.286
Pseudo-second-order	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.070	0.018
	$qt_{200\text{min, exp}}$ (mg g^{-1})	1.020	1.570
	$qt_{200\text{min, theo}}$ (mg g^{-1})	1.019	1.570
	R^2	1	1
	RMSE	0.003	2.47×10^{-4}
	SSE	4.38×10^{-5}	4.27×10^{-7}
	χ^2	1.03×10^{-5}	5.30×10^{-8}
	HYBRID	0.001	5.26×10^{-6}

4.5 Effect Of Initial Concentration And Isotherm Studies

Batch experiments were conducted to assess the effect of initial uranium concentration on adsorption by raw sago hampas (RSH) and esterified sago hampas (ESH) under the following conditions: initial uranium concentration (C_0) ranging from 1.0 to 5.0 mg L^{-1} , pH 4.0, temperature 25 °C, and adsorbent dosage of 1.0 g L^{-1} . The adsorption capacity increased with the initial uranium concentration up to 5.0 mg L^{-1} , with no saturation observed, as illustrated in Figures 4.4(c) and 4.4(d).

To model the adsorption process, the Langmuir, Freundlich, and Sips isotherm models were applied. The resulting plots and parameters are presented in Figures 4.4(c) and 4.4(d), and Table 4.3. Error functions were employed to determine the best-fitting model, similar to the approach used in kinetic studies. The Sips isotherm model exhibited the highest correlation values and the lowest statistical parameters, indicating it as the most suitable model for describing the adsorption processes of both RSH and ESH. The parameter n_s was

not equal to 1, suggesting that the Sips model behaves similarly to the Freundlich model at low initial U(VI) concentrations, indicating multilayer adsorption, while monolayer adsorption occurs at $1/n_s$ active sites. Furthermore, the maximum adsorption capacity q_{ms} was higher for ESH than for RSH, implying that the functionalization process enhanced the number of active sites in ESH.

Table 4.3: Parameters calculated using respective isotherm models

Isotherm models	Parameters	RSH	ESH
Langmuir	$q_{\max}$ (mg g ⁻¹)	5.359	16.202
	K_L (L mg ⁻¹)	0.283	0.104
	R_L	0.630	0.808
	R^2	0.934	0.993
	RMSE	0.098	0.074
	SSE	0.048	0.027
	χ^2	0.014	0.007
	HYBRID	2.571	1.297
	n	0.895	1.002
	K_F (L ^{1/n} mg ^{1-1/n} g ⁻¹)	1.188	1.569
Freundlich	R^2	0.925	0.993
	RMSE	0.108	0.075
	SSE	0.059	0.028
	χ^2	0.017	0.007
	HYBRID	2.742	1.164
	q_{ms} (mg g ⁻¹)	1.391	1.763
	K_s (L ^{ns} mg ^{-ns})	6.301	3.971
Sips	n_s	2.633	2.064
	R^2	1	1
	RMSE	8.41 x 10 ⁻⁵	1.58 x 10 ⁻⁴
	SSE	3.54 x 10 ⁻⁸	1.25 x 10 ⁻⁷
	χ^2	9.98 x 10 ⁻⁹	3.17 x 10 ⁻⁸
	HYBRID	5.93 x 10 ⁻⁶	2.81 x 10 ⁻⁶

4.6 Influence Of Temperature And Thermodynamic Studies

The study investigated the effect of temperature on the thermodynamic properties of raw sago hampas (RSH) and esterified sago hampas (ESH) by conducting batch adsorption experiments at 25 °C, 35 °C, and 45 °C. The initial uranium concentration was set at 1.0 mg/L, with a pH of 7.0. As illustrated in Figure 4.6, both adsorbents exhibited a slight decrease in adsorption capacity with increasing temperature. Thermodynamic parameters calculated from the data are presented in Table 4.4. The enthalpy change (ΔH°) was determined to be -10.72 kJ/mol for RSH and -99.30 kJ/mol for ESH. Both adsorbents also displayed negative entropy change (ΔS°) values. Additionally, the Gibbs free energy change (ΔG°) was negative for ESH across the tested temperatures.

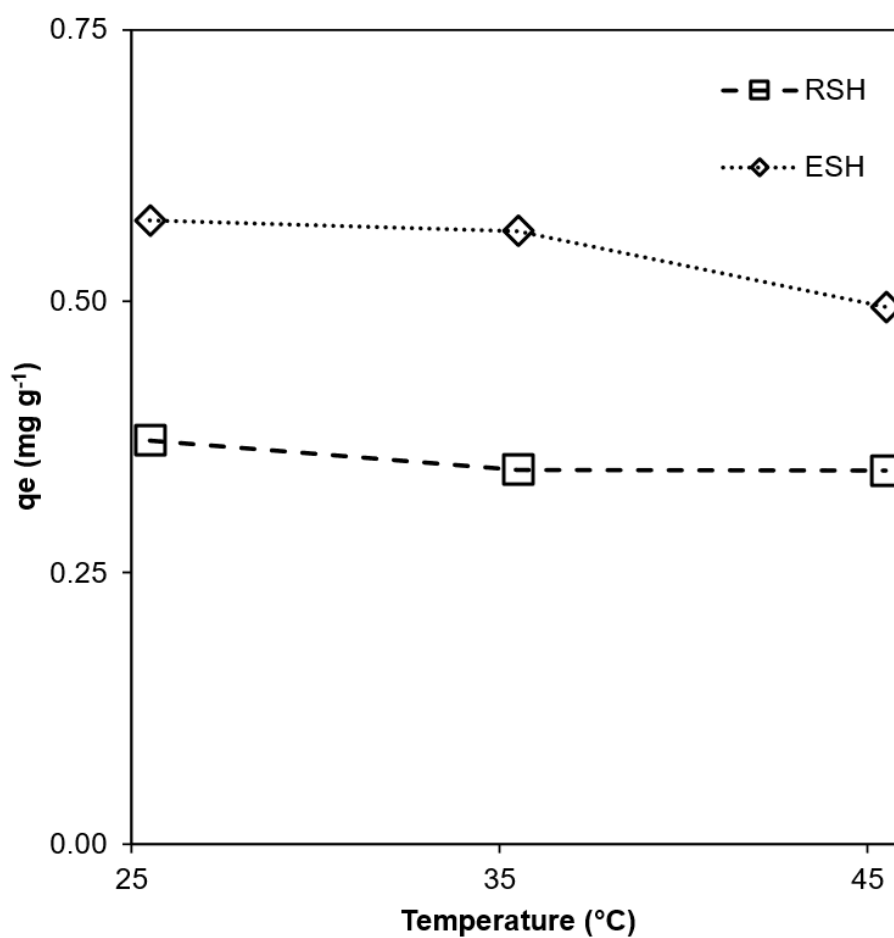


Figure 4.6: Effect of temperature against adsorption capacities of RSH and ESH. For adsorption thermodynamics studies, constant factors were 1.0 g L⁻¹ adsorbent/adsorbate, pH = 4.0, t = 40 min, initial U(VI) concentration = 1.0 mg L⁻¹

Table 4.4: Thermodynamic parameters of RSH and ESH

Thermodynamic parameters	RSH	ESH
ΔH° (kJ mol ⁻¹)	-10.72	-99.3
ΔS° (J mol ⁻¹ K ⁻¹)	-0.04	-0.30
25 °C ΔG° (kJ mol ⁻¹)	2.01	-8.89
35 °C ΔG° (kJ mol ⁻¹)	2.43	-5.86
45 °C ΔG° (kJ mol ⁻¹)	2.86	-2.82

4.8 Effect of pH

The adsorption capacities of raw sago hampas (RSH) and esterified sago hampas (ESH) were evaluated across a pH range of 2.0 to 7.0, with the findings presented in Figure 4.7. For RSH, the adsorption capacity decreased until pH 7.0 and then significantly improved from pH 2.0 to 4.0. In the case of ESH, the adsorption capacity was higher than that of RSH between pH 2.0 and 3.0 but gradually declined until pH 7.0.

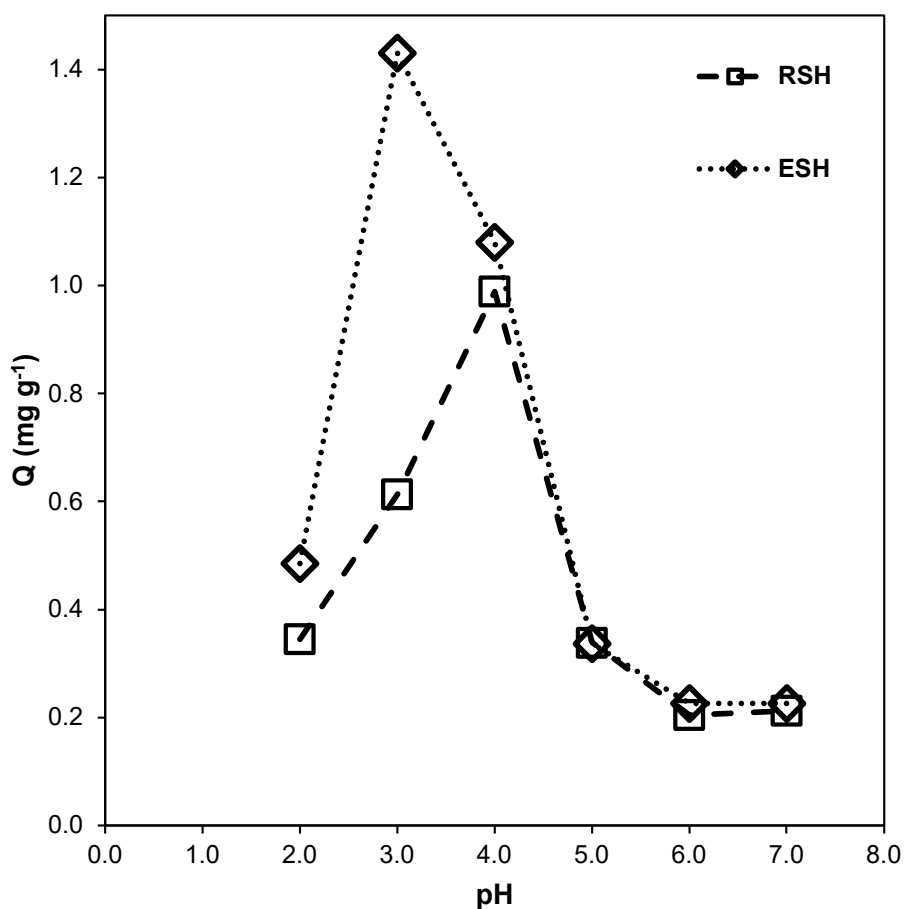


Figure 4.7: Effect of pH on U(VI) ions adsorption by RSH and ESH. For pH study, the constant factors were 1 g L⁻¹ adsorbent/adsorbate ratio, $t = 40$ min, room temperature, initial U(VI) concentration = 1.0 mg L⁻¹

4.9 Simulated Seawater And Desorption Studies

Simulated seawater and desorption experiments were conducted to assess the efficacy and reusability of raw sago hampas (RSH) and esterified sago hampas (ESH) as biosorbents for uranium removal. The simulated seawater comprised 25.6 g/L NaCl, 193 mg/L NaHCO₃, and 3 mg/L U(VI) ions. Both RSH and ESH samples were equilibrated in this solution for 24 hours. Subsequent desorption studies employed acidic eluents, specifically 1.0 M HNO₃ and 1.0 M HCl.

As illustrated in Figure 4.6(a), the removal efficiencies of U(VI) after 24 hours were 66.0% for RSH and 91.4% for ESH. Desorption studies, depicted in Figure 4.6(b), revealed that the maximum desorption ratio for RSH was 76.6% using 1.0 M HNO₃, while for ESH, it was 72.8% with 1.0 M HCl.

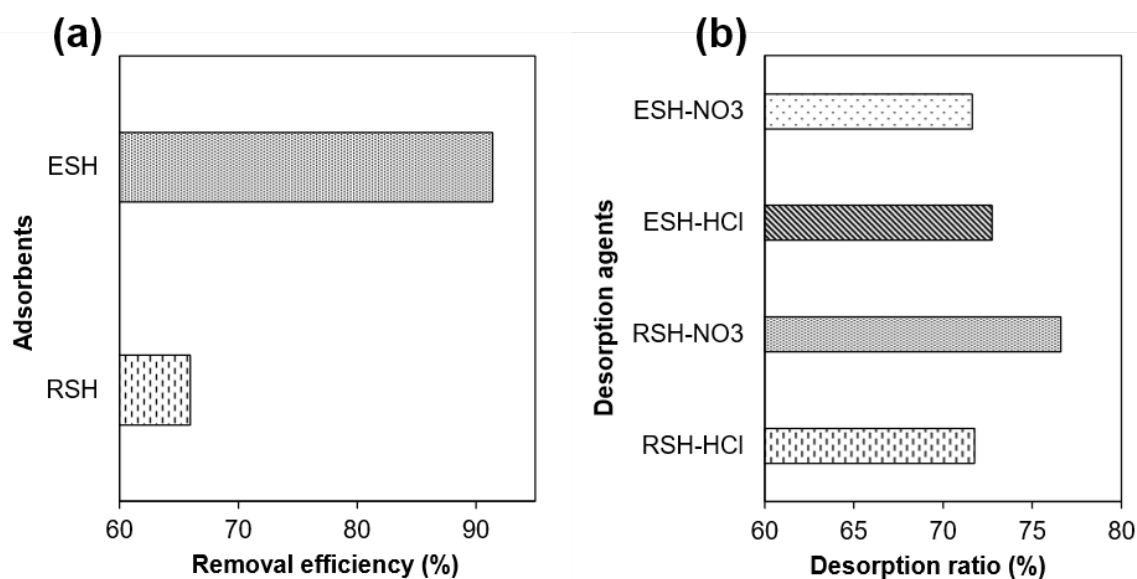


Figure 4.6: (a) Removal efficiency (%) of U(VI) in simulated seawater studies and (b) desorption ratio (%) of U(VI) using HNO₃ and HCl

CHAPTER 5

DISCUSSION

5.1 FTIR Spectral Analysis And Functional Group Identification

The FTIR analysis confirms the presence of functional groups such as hydroxyls, carboxylic acids, and carbohydrates in sago hampas, which are integral components of its molecular structure, including cellulose, lignin, and pectin. The observed bands align with findings from Nordin et al. (2020), who reported similar functional groups in sago-based materials. The peak at 2891 cm^{-1} , associated with aliphatic C-H bonds, is consistent with the results of Psyrillou and Noli (2021). The C=O stretching region between 1606 cm^{-1} and 1715 cm^{-1} corresponds with observations by Bağda et al. (2018) and Nuhanović et al. (2021).

The functionalization process, involving alkalization, neutralization, and esterification, effectively removes hemicellulose, pectic compounds, and other impurities, leading to an increased abundance of oxygen-containing functional groups like O-H and C-O moieties. This enhancement facilitates the grafting of these groups onto the sago hampas surface, as supported by studies from Su et al. (2022) and Sirry et al. (2019).

The shifts and reductions in peak intensities observed in Figure 4.1(b) after uranium exposure indicate complexation and ion exchange between the functional groups and UO_2^{2+} ions, confirming successful adsorption. The disappearance of peaks in the $1422\text{--}1593\text{ cm}^{-1}$ range suggests that these sites are effectively occupied by uranyl ions. Additionally, the increased intensity at the 915 cm^{-1} peak and observed shifts post-adsorption are attributed to the deprotonation of surface functional groups, facilitating binding with U(VI), as noted by Dai et al. (2020).

5.2 SEM-EDX Characterization Of Surface Morphology And Uranium Uptake

The initial SEM observations of RSH align with previous studies, indicating a complex surface morphology characterized by dense and irregular structures. The presence of lignocellulose and pectic components, observed as white, spiky, spherical formations, is consistent with findings by Bukhari et al. (2017). The detection of elliptical sago starch granules corroborates the observations reported by Hammado et al. (2020).

The transformation from RSH to ESH results in a smoother surface morphology, attributed to the removal of impurities such as lignin, hemicelluloses, and wax during the hydrolysis process. This observation is in agreement with studies by Abegunde et al. (2020) and Ye et al. (2023), who reported similar surface modifications post-functionalization. The exposure of inner pores enhances the material's adsorption capacity by increasing the availability of active sites, particularly those containing oxygen functional groups, as noted by Cheng et al. (2021).

Post-adsorption SEM images reveal a smoother and whiter surface on ESH, indicative of uranium particle deposition. This visual change aligns with observations by Yacob et al. (2017) and Deshmukh et al. (2022), who reported similar morphological alterations upon metal ion adsorption. The EDX analysis further substantiates the successful adsorption of uranium, with a measured concentration of 1.81 wt%, confirming the efficacy of the functionalized sago hampas in sequestering U(VI) ions.

5.3 Adsorption Kinetics U(VI) Adsorption

The initial rapid adsorption observed within the first 80 minutes can be attributed to a significant concentration gradient and an abundance of available adsorption sites on both RSH and ESH. This aligns with findings by Liao et al. (2023), who reported similar trends in adsorption studies. The subsequent plateau in adsorption rate between 100 and 200 minutes may result from the saturation of active sites and electrostatic repulsion among adsorbed U(VI) ions, as suggested by Celikbıcak et al. (2021) and Maurya et al. (2023). Notably, biomass-derived adsorbents typically reach equilibrium within 100 to 1500 minutes, as reported by Georgiou et al. (2023).

The superior fit of the PSO model indicates that chemisorption governs the adsorption process, involving mechanisms such as electrostatic interactions and ion exchange between UO_2^{2+} species and functional groups on the adsorbent surface. This observation is consistent with studies by Lin et al. (2021) and Banerjee et al. (2022). Furthermore, the enhanced adsorption capacity of ESH compared to RSH underscores the effectiveness of esterification in increasing active sites and improving uranium removal efficiency.

5.4 Adsorption Isotherm Modeling of U(VI) Adsorption

The observed increase in adsorption capacity with rising initial uranium concentrations up to 5.0 mg/L, without reaching saturation, suggests that both RSH and ESH possess a substantial number of available adsorption sites within this concentration range. The application of the Sips isotherm model, which combines elements of both Langmuir and Freundlich models, indicates that the adsorption process involves heterogeneous surface binding sites with varying affinities (Abu-Alsoud et al., 2020). The n_s parameter deviating

from 1 supports the presence of multilayer adsorption at lower uranium concentrations, transitioning to monolayer adsorption as site occupancy increases (Satpathy et al., 2021). This aligns with the heterogeneous surface morphology observed in sago hampas through SEM analysis.

The higher q_{ms} value for ESH compared to RSH underscores the effectiveness of the functionalization process in enhancing adsorption capacity. This improvement is likely due to the introduction of additional active sites and increased surface area, facilitating greater uranium ion uptake (Zhao et al., 2021). These findings are consistent with prior studies demonstrating that functionalized biomass materials exhibit enhanced adsorption properties due to increased heterogeneity and active site availability.

5.5 Thermodynamic Evaluation of U(VI) Adsorption

The observed decline in adsorption capacity with rising temperature suggests that the adsorption processes for both RSH and ESH are exothermic in nature. This is corroborated by the negative ΔH° values, indicating that the adsorption releases heat. Such behavior is consistent with findings in similar studies, where exothermic adsorption processes have been reported (Nuhanovic et al., 2019; Ma et al., 2020).

The negative ΔS° values imply a decrease in randomness at the solid-liquid interface during adsorption, suggesting a more ordered arrangement as uranium ions are immobilized onto the adsorbent surfaces. This decrease in entropy is characteristic of adsorption processes where the adsorbate molecules are more structured upon binding to the adsorbent (Ebelegi et al., 2020; Jimenez-Reyes et al., 2020).

The negative ΔG° values observed for ESH indicate that the adsorption process is spontaneous at the temperatures studied. The magnitude of ΔH° for ESH (-99.30 kJ/mol) suggests a chemisorption mechanism, as values exceeding 80 kJ/mol are typically associated

with chemical adsorption involving strong interactions between the adsorbate and adsorbent (Estes et al., 2020).

In contrast, the ΔH° value for RSH (-10.72 kJ/mol) falls within the range indicative of physisorption, which involves weaker, physical forces. These distinctions highlight the enhanced binding affinity and potential chemical interactions facilitated by the functional groups introduced during the esterification of sago hampas.

In summary, the thermodynamic analysis reveals that both RSH and ESH exhibit exothermic and spontaneous adsorption behaviors, with ESH demonstrating a chemisorption mechanism likely due to the increased availability of active sites resulting from the functionalization process.

5.6 Influence of pH on U(VI) Adsorption and Surface Interaction

The observed variations in adsorption capacities with pH can be attributed to the interplay between uranium speciation and the ionization state of functional groups on the adsorbents. At lower pH levels (2.0 to 4.0), uranium predominantly exists as the uranyl ion (UO_2^{2+}), which is more readily adsorbed due to favorable electrostatic interactions with negatively charged functional groups on the adsorbent surfaces (Lu et al., 2015). As the pH increases beyond this range, uranyl ions are less likely to undergo hydrolysis, which can lead to the formation of larger, less adsorbable complexes such as $(\text{UO}_2)_3(\text{OH})^{5+}$ and $(\text{UO}_2)_4(\text{OH})^{7+}$. Additionally, the acidic environment reduces the protonation of functional groups on the surfaces of the adsorbents, which increases the number of active sites that are available for binding (Pyrillou & Noli, 2021).

The superior adsorption performance of ESH compared to RSH at pH 2.0 to 3.0 suggests that the functionalization process enhances the availability of active sites, thereby improving uranium uptake. However, the gradual decrease in adsorption capacity for both

adsorbents as pH approaches 7.0 indicates that the formation of larger uranium complexes and the potential for surface charge repulsion diminish the effectiveness of the adsorption process at higher pH levels (Ye et al., 2023).

5.7 Evaluation of Seawater Adsorption & Desorption Performance

The higher U(VI) removal efficiency observed for ESH compared to RSH can be attributed to the functionalization process, which enhances the availability of active sites and introduces additional oxygen-containing functional groups, thereby increasing the heterogeneity of the ESH composition. This finding aligns with previous research indicating that functionalized biosorbents exhibit improved uranium adsorption capacities (Georgiou et al., 2023).

The desorption results indicate that both HNO_3 and HCl are effective eluents for recovering adsorbed uranium from the biosorbents. The slightly higher desorption ratio observed for RSH with HNO_3 suggests a difference in the interaction strength between uranium ions and the functional groups present on RSH and ESH. The increased saturation of U(VI) on ESH's surface may necessitate a higher concentration of eluent or extended desorption time to achieve comparable desorption efficiency. Similar observations have been reported in studies utilizing acidic eluents for uranium desorption (Mahmoud, 2021; Noli et al., 2019).

These findings underscore the potential of ESH as an effective and reusable biosorbent for uranium removal from seawater, highlighting the importance of functionalization in enhancing adsorption performance and the efficacy of acidic desorption agents in regenerating the biosorbents.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

The initial U(VI) batch adsorption studies utilizing RSH and ESH have effectively established the optimal settings as follows: pH 3.0 - 4.0, starting uranium concentration of 1 mg L⁻¹, over 200 minutes of contact time at ambient temperature (25 °C). The adsorption kinetics data conformed well to the pseudo-second-order model for both adsorbents, indicating that chemisorption was the rate-limiting phase. The adsorption capacity decreased with increasing temperature, and thermodynamic analyses indicated that the biosorption process is physical, exothermic, and spontaneous. The accurate fitting of the Sips isotherm models indicates that the biosorption process was multi-layered, aligning with the SEM observations of a heterogeneous surface. FTIR and EDX analyses validate the grafting of oxygen-containing functional groups by the observation of newly formed and intensified peaks, whereas the interaction of U(VI) with these functional groups is identifiable at 915 cm⁻¹. Simulated seawater investigations demonstrate that ESH exhibits superior removal efficiency of U(VI) in comparison to RSH, whereas strong acids like HNO₃ and HCl serve as effective desorption agents, resulting in a significant recovery percentage of U(VI) from biosorbents.

Based on the findings of this study, several recommendations are proposed to guide future research and potential applications of functionalized sago hampas (ESH) for uranium adsorption. Given ESH's superior performance in simulated seawater, further evaluation under real marine conditions is strongly recommended to validate its field applicability. Pilot-scale trials under continuous flow conditions are also recommended to assess the adsorbent's practical feasibility. Comparative studies with commercial adsorbents should be

carried out to benchmark ESH's performance in terms of capacity, cost-effectiveness, and selectivity. Finally, long-term stability and ecotoxicity assessments are crucial to ensure that ESH use poses no adverse environmental impact, particularly in marine ecosystems.

REFERENCES

- Abdelhakim, A. M., Awad, E. A. M., Mohamed, I. R., & El-Sheikh, E. M. (2021). Removal of uranium and associated elements from Sinai wells water using the dried and chemically modified orange peels. *Zagazig Journal of Agricultural Research*, 48(1), 137-159.
- Abegunde, S. M., Idowu, K., Adejuwon, O. M. & Adeyemi-Adejolu, T. (2020). A review on the influence of chemical modification on the performance of adsorbents. *Resources, Environment and Sustainability*, 1(1), 1-9.
- Abney, C. W., Mayes, R. T., Saito, T. & Dai, S. (2017). Materials for the recovery of uranium from seawater. *Chemical Review*, 117(23), 13935-14013.
- Abou-Hadid, A. F., El-Behairy, U. A., Elmalih, M. M., Amdeha, E., El Naggat, A. M. A., Taha, M. H., & Hussein, A. E. M. (2022). Production of efficient carbon fiber from different solid waste residuals for adsorption of hazardous metals from wastewater samples. *Biomass Conversion and Biorefinery*, 14(9), 10501-10516.
- Abu-Alsoud, G. F., Hawboldt, K. A., & Bottaro, C. S. (2020). Comparison of four adsorption isotherm models for characterizing molecular recognition of individual phenolic compounds in porous tailor-made molecularly imprinted polymer films. *ACS Applied Materials & Interfaces*, 12(10), 98-109.
- Amin, N., Sabli, N., Izhar, S., & Yoshida, H. (2019). Sago Wastes and Its Applications. *Pertanika Journal of Science & Technology*, 27(4), 1841-1862.

- Anagnostopoulos, V. A., Koutsoukos, P. G., & Symeopoulos, B. D. (2015). Removal of U (VI) from aquatic systems, using winery by-products as biosorbents: equilibrium, kinetic, and speciation studies. *Water, Air & Soil Pollution*, 226(1), 1-14.
- Anagnostopoulos, V., Symeopoulos, B. K., & Bekatorou, A. (2016). Biosorption of U (VI) from aqueous systems by malt spent rootlets. *International Journal of Environmental Science and Technology*, 13(1), 285-296.
- Bağda, E., Sarı, A., & Tuzen, M. (2018). Effective uranium biosorption by macrofungus (*Russula sanguinea*) from aqueous solution: equilibrium, thermodynamic and kinetic studies. *Journal of Radioanalytical and Nuclear Chemistry*, 317(1), 1387-1397.
- Balaram, V., Rani, A., & Rathore, D. P. S. (2022). Uranium in groundwater in parts of India and world: A comprehensive review of sources, impact to the environment and human health, analytical techniques, and mitigation technologies. *Geosystems and Geoenvironment*, 1(2), 1-21.
- Banerjee, S., Kundu, A., & Dhak, P. (2022). Bioremediation of uranium from waste effluents using novel biosorbents: a review. *Journal of Radioanalytical and Nuclear Chemistry*, 331(6), 2409-2435.
- Basu, H., Singhal, R. K., Pimple, M. V., & Saha, S. (2018). Graphene oxide encapsulated in alginate beads for enhanced sorption of uranium from different aquatic environments. *Journal of Environmental Chemical Engineering*, 6(2), 1625-1633.
- Bukhari, N. A., Loh, S. K., Bakar, N., & Ismail, M. (2017). Hydrolysis of Residual Starch from Sago Pith Residue and Its Fermentation to Bioethanol. *Sains Malaysiana*, 46(8), 1269-1278.

- Celikbıçak, O., Bayramoglu, G., Acikgoz Erkaya, I., & Arica, M. Y. (2021). Aggrandizement of uranium (VI) removal performance of *Lentinus concinnus* biomass by attachment of 2, 5-diaminobenzenesulfonic acid ligand. *Journal of Radioanalytical and Nuclear Chemistry*, 328(3), 1085-1098.
- Chakraborty, R., Asthana, A., Singh, A.K., Jain, B., & Susan A. B. H. (2022). Adsorption of heavy metal ions by various low-cost adsorbents: a review. *International Journal of Environmental Analytical Chemistry*, 102(2), 342-379.
- Chen, X., Hossain, M. F., Duan, C., Lu, J., Tsang, Y. F., Islam, M. S., & Zhou, Y. (2022). Isotherm models for adsorption of heavy metals from water - A review. *Chemosphere*, 307(1), 1-14.
- Cheng, Y., Li, F., Liu, N., Lan, T., Yang, Y., Zhang, T., & Qing, R. (2021). A novel freeze-dried natural microalga powder for highly efficient removal of uranium from wastewater. *Chemosphere*, 282(1), 1-9.
- Christou, C., Philippou, K., Krasia-Christoforou, T., & Pashalidis, I., (2019). Uranium adsorption by polyvinylpyrrolidone/chitosan blended nanofibers. *Carbohydrate Polymers*, 219(1), 298-305.
- Dai, Y., Zhou, L., Tang, X., Xi, J., Ouyang, J., Liu, Z., & Adesina, A. A. (2020). Macroporous ion-imprinted chitosan foams for the selective biosorption of U (VI) from aqueous solution. *International Journal of Biological Macromolecules*, 164(1), 4155-4164.
- Deshmukh, P., Sar, S. K., Smječanin, N., Nuhanović, M., & Lalwani, R. (2022). Magnetically Modified Waste Bark of *Aegle marmelos* Tree as a Promising Biosorbent for Uranium(VI) Sorption. *Radiochemistry*, 64(4), 532-542.

- Dhanya, V., & Rajesh, N., (2023). A cradle-to-cradle approach towards remediation of uranium from water using carbonized arecanut husk fiber. *RSC Advances*, 13(7), 4394-4406.
- Dong, L., Hou, L. A., Wang, Z., Gu, P., Chen, G., & Jiang, R. (2018). A new function of spent activated carbon in BAC process: Removing heavy metals by ion exchange mechanism. *Journal of Hazardous Materials*, 359(1), 76-84.
- Dubey, S., Gusain, D., Chandra Sharma, Y., & Bux, F. (2021). Adsorbents. In D. Gusain & F. Bux (Eds.), *Batch Adsorption Process of Metals and Anions for Remediation of Contaminated Water* (pp. 9-39). CRC Press.
- Ebelegi, A. N., Ayawei, N. & Wankasi, D., (2020). Interpretation of Adsorption Thermodynamics. *Open Journal of Physical Chemistry*, 10(1), 166-182.
- Escudero, L. B., Quintas, P. Y., Wuilloud, R. G., & Dotto, G. L. (2018). Recent advances on elemental biosorption. *Environmental Chemistry Letters*, 17(1), 409-427.
- Estes, S. L., & Powell, B. A. (2020). Enthalpy of uranium adsorption onto hematite. *Environmental Science & Technology*, 54(23), 4-12.
- Fan, M., Wang, X. E., Song, Q., Zhang, L., Ren, B., & Yang, X. (2021). Review of biomass-based materials for uranium adsorption. *Journal of Radioanalytical and Nuclear Chemistry*, 330(1), 589-602.
- Fang, Y., Liu, L., Xiang, H., Wang, Y., & Sun, X. (2022). Biomass-based carbon microspheres for removing heavy metals from the environment: A review. *Materials Today Sustainability*, 18(1), 1-16.
- Ferreira, R. V. D. P., de Araujo, L. G., Canevesi, R. L. S., da Silva, E. A., Ferreira, E. G. A., Palmieri, M. C., & Marumo, J. T. (2020). The use of rice and coffee husks for

- biosorption of U (total), ^{241}Am , and ^{137}Cs in radioactive liquid organic waste. *Environmental Science and Pollution Research*, 27(1), 36651-36663.
- Georgiou, E., Raptopoulos, G., Anastopoulos, I., Giannakoudakis, D. A., Arkas, M., Paraskevopoulou, P., & Pashalidis, I. (2023). Uranium removal from aqueous solutions by aerogel-based adsorbents - A critical review. *Nanomaterials*, 13(2), 1-20.
- Guilhen, S. N., Mašek, O., Ortiz, N., Izidoro, J. C., & Fungaro, D. A. (2019). Pyrolytic temperature evaluation of macauba biochar for uranium adsorption from aqueous solutions. *Biomass and Bioenergy*, 122(1), 381-390.
- Guilhen, S. N., Rovani, S., de Araujo, L. G., Tenório, J. A., & Mašek, O. (2021). Uranium removal from aqueous solution using macauba endocarp-derived biochar: Effect of physical activation. *Environmental Pollution*, 272(1), 1-42.
- Gül, Ü. D., Şenol, Z. M., Gürsoy, N., & Şimşek, S., (2019). Effective UO_2^{2+} removal from aqueous solutions using lichen biomass as a natural and low-cost biosorbent. *Journal of Environmental Radioactivity*, 205(1), 93-100.
- Guo, H., Mei, P., Xiao, J., Huang, X., Ishag, A., & Sun, Y. (2021). Carbon materials for extraction of uranium from seawater. *Chemosphere*, 278(1), 130411-130423.
- Gupta, N. K., Sengupta, A., Gupta, A., Sonawane, J. R., & Sahoo, H. (2018). Biosorption- an alternative method for nuclear waste management: a critical review. *Journal of Environmental Chemical Engineering*, 6(2), 2159-2175.
- Hammado, N., Utomo, S., & Budiyo, B. (2020). Characteristic lignocellulose of sago solid waste for biogas production. *Journal of Applied Engineering Science*, 18(2), 157-164.

- Hao, M., Liu, Y., Wu, W., Wang, S., Yang, X., Chen, Z., & Wang, X. (2023). Advances porous adsorbents for radionuclides elimination. *EnergyChem*, 5(4), 1-56.
- Haryanto, B., Singh, W. B., Barus, E. S., Ridho, A., & Rawa, M. R. (2017). Pseudo Order Kinetics Model to Predict the Adsorption Interaction of Corn-Stalk Adsorbent Surface with Metal Ion Adsorbate Cu (II) and Fe (II). Proceeding of *Journal of Physics: Conference Series*, 801, 1-7
- Hashmi, S., Sengupta, A., & Chauhan, R. S. (2021). Cost effective separation of uranium ion using exhausted household products and natural bio-sorbent. *Journal of Radioanalytical and Nuclear Chemistry*, 329(3), 1351-1373.
- Hossain, M. S., Ahmed, M. K., Sarker, S., & Rahman, M. S. (2020). Seasonal variations of trace metals from water and sediment samples in the northern Bay of Bengal. *Ecotoxicology and Environmental Safety*, 193(1), 1-12.
- Hu, H., Zhang, X., Wang, T., Sun, L., Wu, H., & Chen, X. (2018). Bamboo (*Acidosasa longiligula*) shoot shell biochar: its potential application to isolation of uranium(VI) from aqueous solution. *Journal of Radioanalytical and Nuclear Chemistry*, 316(1), 349-362.
- Hussein, G., Swafy, S., & Ebian, O. (2019). Adsorption of uranium from sulfate leach liquor using rice straw impregnated with chlorophenyl hydrazinyl pyrazoloquinazolinon. *Separation Science and Technology*, 54(11), 1764-1777.
- Im, J. G., Pak, H. S., Jon, U. C., Ri, S. B., Om, S. Y., & Jong, C. J. (2023). Study on the uranium adsorption and reusability characteristics of amidoximated polypropylene-acrylonitrile-acrylic acid fibrous adsorbent. *Journal of Radioanalytical and Nuclear Chemistry*, 332(10), 3911-3918.

- Inglezakis, V. J., Balsamo, M., & Montagnaro, F. (2020). Liquid–solid mass transfer in adsorption systems—an overlooked resistance? *Industrial & Engineering Chemistry Research*, 59(50), 7-16.
- Islam, M. A., Chowdhury, M. A., Mozumder, M. S. I., & Uddin, M. T. (2021). Langmuir adsorption kinetics in liquid media: interface reaction model. *ACS Omega*, 6(22), 14481-14492.
- Ji, Z., Zhang, Y., Wang, H., & Li, C. (2022). Research progress in the removal of heavy metals by modified chitosan. *Tenside Surfactants Detergents*, 59(4), 281-293.
- Jiang, X., Wang, H., Wang, Q., Hu, E., & Duan, Y. (2020). Immobilizing amino-functionalized mesoporous silica into sodium alginate for efficiently removing low concentrations of uranium. *Journal of Cleaner production*, 247(1), 1-11.
- Jiménez-Reyes, M., de M Ramírez De La Cruz, F., & Solache-Ríos, M. (2020). Physicochemical behavior of uranium and lanthanum in the presence of *Abies religiosa* leaf biomass. *Water, Air, & Soil Pollution*, 231(9), 1-20.
- Jun, B. M., Lee, H. K., Park, S., & Kim, T. J. (2021). Purification of uranium-contaminated radioactive water by adsorption: A review on adsorbent materials. *Separation and Purification Technology*, 278(1), 1-30.
- Karpas, Z. (2014). *Analytical Chemistry of Uranium: Environmental, Forensic, Nuclear, and Toxicological applications*. CRC Press.
- Kumari, G., Guleria, A., Singh, K., Kumar, N., Guleria, A., Kumar, D., & Lima, E. (2022). Lignocellulosic biopolymers as potential biosorbents. In T. Bhaskar, & A. Pandey (Eds.), *Biomass, Biofuels, Biochemicals* (pp. 391-429). Elsevier Applied Science Publication.

- Lei, J., Liu, H., Zhou, L., Wang, Y., Yu, K., Zhu, H., & Zhu, W. (2023). Progress and perspective in enrichment and separation of radionuclide uranium by biomass functional materials. *Chemical Engineering Journal*, 471(1), 1-24.
- Liao, J., Ding, L., Zhang, Y., & Zhu, W. (2023). Efficient removal of uranium from wastewater using pig manure biochar: understanding adsorption and binding mechanism. *Journal of Hazardous Materials*, 423(1), 1-12.
- Lin, Z., Chen, L., & Ye, Z. (2021). Film-like chitin/polyethylenimine biosorbent for highly efficient removal of uranyl-carboante compounds fromw water. *Journal of Environmental Chemical Engineering*, 9(4), 1-10.
- Lingamdinne, L. P., Choi, J. S., Angaru, G. K. R., Karri, R. R., Yang, J. K., Chang, Y. Y., & Koduru, J. R. (2022). Magnetic-watermelon rinds biochar for uranium-contaminated water treatment using an electromagnetic semi-batch column with removal mechanistic investigations. *Chemosphere*, 286(2), 1-11.
- Liu, C., & Zhang, H. X. (2022). Modified-biochar adsorbents (MBAs) for heavy-metal ions adsorption: A critical review. *Journal of Environmental Chemical Engineering*, 10(2), 1-35.
- Liu, C., Li, Y., Liu, D., Lei, M., Li, B., Fu, C., & Zhang, J. (2023). In suit establishment of Ti3C2 MXenes exchanger via Na⁺, K⁺ and NH₄⁺ intercalation: exceptionally UO₂²⁺ loading capability and hijacking mechanism. *Chemical Engineering Journal*, 468(1), 1-13 .
- Liu, C., Li, Y., Liu, S., Zhou, Y., Li, B., Liu, D., & Ye, L. (2022). Polyethylenimine embellished multiwalled carbon nanotube (MWC-NTs) for efficiently enhancing

- sequestration of uranium(VI) from seawater. *Journal of Environmental Chemical Engineering*, 10(5), 1-11.
- Lu, M. (2024, January 20). Cumulative uranium production, by country (1945–2022). Visual Capitalist. <https://www.visualcapitalist.com/cumulative-uranium-production-by-country-1945-2022/>
- Lu, S., Lu, S., Cui, X., Zhang, Y., & Liu, J. (2015). The effect of solution chemistry on the adsorption of uranium (VI) onto sericite. *Journal of Radioanalytical and Nuclear Chemistry*, 303, 761-769.
- Ma, F., Gui, Y. L. P., Xue, Y., & Song, W. (2020). Functional fibrous materials-based adsorbents for uranium adsorption and environmental remediation. *Chemical Engineering Journal*, 390(1), 1-20.
- Mahmood-ul-Hassan, M., Suthar, V., Ahmad, R., & M, Y. (2018). Biosorption of metal ions on lignocellulosic materials: batch and continuous-flow process studies. *Environmental Monitoring and Assessment*, 190(287), 1-13.
- Mahmoud, M. A. (2021). Sorption of U(VI) ions from aqueous solution by eggplant leaves: Isotherm, kinetics and thermodynamics studies. *Progress In Nuclear Energy*, 138(1), 1-7.
- Majd, M. M., Kordzadeh-Kermani, V., Ghalandari, V., Askari, A., & Sillanpää, M. (2022). Adsorption isotherm models: A comprehensive and systematic review (2010– 2020). *Science of The Total Environment*, 812(1), 1-28.
- Mansour, H., Mahmoud, K., Kamal, H., & Mahdy, H. (2020). Uranium Bio-sorption from its Processed Waste Solution by Green Algae. *Egyptian Journal of Chemistry*, 63(10), 4039-4054.

- Maurya, A., Marvaniya, K., Dobariya, P., Chudasama, N., Mane, M., Patel, K., & Kushwaha, S. (2023). Protocol for extraction, characterization, and computational analysis of uranium from seawater. *STAR Protocols*, 4(1), 1-24.
- Md Yunus, S., & Hamzah, S. (2015). Natural radionuclides and heavy metals pollution in seawater at Kuala Langat Coastal Area. *The Malaysian Journal of Analytical Sciences*, 4(2015), 766-774.
- Nathan, R. J., Jain, A. K., & Rosengren, R. J. (2022). Biosorption of heavy metals from water: mechanism, critical evaluation and translatability of methodology. *Environmental Technology Reviews*, 11(1), 91-117.
- Noli, F., Kapashi, E., & Kapnisti, M. (2019). Biosorption of Uranium and Cadmium using sorbents based on Aloe Vera wastes. *Journal of Environmental Chemical Engineering*, 7(2), 1-31.
- Noli, F., Kapashi, E., Pashalidis, I., Margellou, A., & Karfaridis, D. (2022). The effect of chemical and thermal modifications on the biosorption of uranium in aqueous solutions using winery wastes. *Journal of Molecular Liquids*, 351(1), 1-11.
- Nordin, N. A., Rahman, N. A., & Abdullah, A. H. (2020). Effective removal of Pb(II) Ions by Electrospun PAN/Sago Lignin-Based Activated Carbon Nanofibers. *Molecules*, 25(13), 1-21.
- Nuhanović, M., Grebo, M., Draganović, S., Memić, M., & Smječanin, N. (2019). Uranium (VI) biosorption by sugar beet pulp: equilibrium, kinetic and thermodynamic studies. *Journal of Radioanalytical and Nuclear Chemistry*, 322(1), 2065-2078.

- Nuhanović, M., Smječanin, N., Curić, N., & Vinković, A. (2021). Efficient removal of U(VI) from aqueous solution using a biocomposite based on sugar beet pulp and pomelo peel. *Journal of Radioanalytical and Nuclear Chemistry*, 328, 347-358.
- Nuhanović, M., Smječanin, N., Mulahusić, N., & Sulejmanović, J. (2021b). Pomegranate peel waste modified with H₃PO₄ as a promising sorbent for uranium(IV) removal. *Journal of Radioanalytical and Nuclear Chemistry*, 328, 617-626.
- Orabi, F. M. A., Khalillia, F. I., & Ismaila, L. S. (2021). Removal of uranium (VI) and thorium (IV) from aqueous solution by *Hedera helix* leaves: kinetics and thermodynamic studies. *Desalination and Water Treatment*, 237(2021), 202-213.
- Psyrillou, A., & Noli, F. (2021). Investigation of uranium biosorption using tomato peel in raw and modified form. *Journal of Radioanalytical and Nuclear Chemistry*, 330(1), 305-314.
- Qiao, J., & Xu, Y. (2018). Direct measurement of uranium in seawater by inductively coupled plasma mass spectrometry. *Talanta*, 183, 18-23.
- Rasyid, T. H., & Kusumawaty, Y. H. S., 2020. The utilization of sago waste: prospect and challenges. *Proceedings of International Conference on Forest Products (ICFP)*, 415, 1-8.
- Redha, A. A. (2020). Removal of heavy metals from aqueous media by biosorption. *Arab Journal of Basic and Applied Sciences*, 27(1), 1-12.
- Rostamian, R., & Firouzzare, M. (2021). Preparation of forcespun γ -irradiated chitin from shrimp shell wastes and its evaluation as uranyl ion adsorbent. *Journal of Radioanalytical and Nuclear Chemistry*, 329(2), 731-739.

- Šabanović, E., Muhić-Šarac, T., Nuhanović, M., & Memić, M. (2019). Biosorption of uranium (VI) from aqueous solution by Citrus limon peels: kinetics, equilibrium and batch studies. *Journal of Radioanalytical and Nuclear Chemistry*, 319, 425-435.
- Satpathy, A., Wang, Q., Giammar, D. E., & Wang, Z. (2021). Intercomparison and refinement of surface complexation models for U (VI) adsorption onto goethite based on a metadata analysis. *Environmental Science & Technology*, 55(13), 52-61.
- Sharma, B., & Shukla, P. (2021). Lead bioaccumulation mediated by *Bacillus cereus* BPS-9 from an industrial waste contaminated site encoding heavy metal resistant genes and their transporters. *Journal of Hazardous Materials*, 401(1), 1-44.
- Sholl, D. S., & Lively, R. P. (2016). Seven chemical separations to change the world. *Nature*, 532, 435-437.
- Singh, S., Kumar, V., Datta, S., Dhanjal, D. S., Sharma, K., Samuel, J., & Singh, J. (2020). Current advancement and future prospect of biosorbents for bioremediation. *Science of the Total Environment*, 709, 1-121.
- Sirry, S. M., Aldakhil, F., Alharbi, O. M., & Ali, I. (2019). Chemically treated date stones for uranium (VI) uptake and extraction in aqueous solutions. *Journal of Molecular Liquids*, 273, 192-202.
- Smječanin, N., Bužo, D., Mašić, E., Nuhanović, M., Sulejmanović, J., Azhar, O., & Sher, F. (2022). Algae based green biocomposites for uranium removal from wastewater: kinetic, equilibrium and thermodynamic studies. *Materials Chemistry and Physics*, 283, 1-9.

- Smječanin, N., Nuhanović, M., Sulejmanović, J., Grahek, Ž., & Odobašić, A. (2022). Study of uranium biosorption process in aqueous solution by red beet peel. *Journal of Radioanalytical and Nuclear Chemistry*, 331(3), 1459-1471.
- Su, Y., Böhm, W., Wenzel, M., Paasch, S., Acker, M., Doert, T., & Weigand, J. J. (2020). Mild hydrothermally treated brewer's spent grain for efficient removal of uranyl and rare earth metal ions. *RSC advances*, 10(73), 45116-45129.
- Su, Y., Wenzel, M., Paasch, S., Seifert, M., Doert, T., Brunner, E., & Weigand, J. J. (2022). One-pot synthesis of brewer's spent grain-supported superabsorbent polymer for highly efficient uranium adsorption from wastewater. *Environmental Research*, 212, 1-15.
- Su, Y., Wenzel, M., Seifert, M., & Weigand, J. J. (2022b). Surface ion-imprinted brewer's spent grain with low template loading for selective uranyl ions adsorption from simulated wastewater. *Journal of Hazardous Materials*, 440, 1-14.
- Sun, Y., & Li, Y. (2021). Application of surface complexation modeling on adsorption of uranium at water-solid interface: A review. *Environmental Pollution*, 278(1), 1-12.
- Syeda, H. I., Sultan, I., Razavi, K. S., & Yap, P. S. (2022). Biosorption of heavy metals from aqueous solution by various chemically modified agricultural wastes: A review. *Journal of Water Process Engineering*, 46, 1-42.
- Szlachta, M., Neitola, R., Peräniemi, S., & Vepsäläinen, J. (2020). Effective separation of uranium from mine process effluents using chitosan as a recyclable natural adsorbent. *Separation and Purification Technology*, 253, 1-11.
- Torres, E., (2020). Biosorption: A review of the latest advances. *Processes*, 8(12), 1-23.

- Turanov, A. N., Karandashev, V. K., Emel'chenko, G. A., Su, S., Liu, Q., & Wang, J. (2020). Sorption of U (VI) from Aqueous Solutions by Chemically Modified *Luffa cylindrica* Fibers. *Russian Journal of Physical Chemistry A*, 94, 1471-1475.
- Wang, F., Tan, L., Liu, Q., Li, R., Li, Z., Zhang, H., & Wang, J. (2015). Biosorption characteristics of uranium (VI) from aqueous solution by *pollen pini*. *Journal of Environmental Radioactivity*, 150, 93-98.
- Wang, H., Gao, B., Fang, J., Ok, Y. S., Xue, Y., Yang, K., & Cao, X. (2018). Engineered biochar derived from eggshell-treated biomass for removal of aqueous lead. *Ecological Engineering*, 121, 124-129.
- Wang, J., & Guo, X. (2023). Adsorption kinetics and isotherm models of heavy metals by various adsorbents: An overview. *Critical Reviews in Environmental Science and Technology*, 53(21), 1837-1865.
- Wang, Y., Li, H. & Lin, S. (2022). Advances in the study of heavy metal adsorption from water and soil by modified biochar. *Water*, 14(23), 1-11.
- Wang, Z., Huang, F. Y., Liu, Y., Yi, F. C., Feng, Y., Luo, Y., & Wang, Z. Y. (2022). Adsorption properties and mechanism of uranium by three biomass materials. *Radiochimica Acta*, 110(1), 23-35.
- Wang, Z., Meng, X., Du, Z., Wang, S., Qu, C., Mo, H., & Chen, S. (2023). Zinc loaded amidoxime polyacrylonitrile porous resin microcapsules for uranium extraction from seawater. *Journal of Radioanalytical and Nuclear Chemistry*, 332(4), 1225-1235.
- Waseem, A., Ullah, H., Rauf, M. K., & Ahmad, I. (2015). Distribution of Natural Uranium in Surface and Groundwater Resources: A Review. *Critical Reviews in Environmental Science and Technology*, 45(22), 2391-2423.

- Wood, J. R., Gill, G. A., Kuo, L. J., Strivens, J. E., & Choe, K. Y. (2016). Comparison of analytical methods for the determination of uranium in seawater using inductively coupled plasma mass spectrometry. *Industrial & Engineering Chemistry Research*, 55(15), 4344-4350.
- World Nuclear Association. (2024, May 7). Number of operable nuclear power reactors worldwide as of May 2024, by country [Graph]. In Statista. Retrieved January 23, 2025, from <https://www.statista.com/statistics/267158/number-of-nuclear-reactors-in-operation-by-country/>
- Yacob, N., Yusof, M. R., Ainun, Z. M. A., & Badri, K. H., 2017. Effect of cellulose fiber from sago waste on properties of starch-based films. *Proceedings of The Wood and Biofiber International Conference*, 368, 1-11.
- Yan, Z., Gao, Y., Pu, Y., Luo, Z., Zhang, M., Chen, X., & Duan, T. (2024). Ultrathin nickel hydroxide nanosheets decorated carbon nanotubes for electrochemical detection of uranyl ion. *Journal of Radioanalytical and Nuclear Chemistry*, 331(1), 117-123.
- Yang, A. L., Yang, S. Y., & Zhu, Y. K. (2021). Magnetic modification of used tea leaves for uranium adsorption. *New Carbon Materials*, 36(4), 821-826.
- Yang, J., Hou, B., Wang, J., Tian, B., Bi, J., Wang, N., & Huang, X. (2019). Nanomaterials for the Removal of Heavy Metals from Wastewater. *Nanomaterials*, 9(3), 1-12.
- Ye, X., Chi, R., Wu, Z., Chen, J., Lv, Y., Lin, C., & Luo, W. (2023). A biomass fiber adsorbent grafted with phosphate/amidoxime for efficient extraction of uranium from seawater by synergistic effect. *Journal of Environmental Management*, 337, 1-8.

- Yi, Z., Liu, J., Liu, X., Zeng, R., & Cui, Y., 2020. Uptake of uranyl (UO_2^{2+}) in water body by sago pondweed. *Proceedings of 2nd International Conference on Advances in Civil Engineering, Energy Resources and Environment Engineering*, 526, 1-6.
- Younes, A., Ali, J. S., Nur, M. T., Duda, A., Wang, J., Samson, J., & Drain, C. M. (2020). Pistachio shells as remediating agents for uranium in contaminated industrial seawater. *Journal of Environmental Radioactivity*, 217, 1-9.
- Zhang, D., Fang, L., Liu, L., Zhao, B., Hu, B., Yu, S., & Wang, X. (2023). Uranium extraction from seawater by novel materials: A review. *Separation and Purification Technology*, 320, 1-12.
- Zhang, X., Kong, L., Song, G., & Chen, D. (2016). Adsorption of uranium onto modified rice straw grafted with oxygen-containing groups. *Environmental Engineering Science*, 33(12), 942-950.
- Zhang, Y., Cai, T., Zhao, Z., & Han, B. (2023). Poly (amidoxime)-graft-magnetic chitosan for highly efficient and selective uranium extraction from seawater. *Carbohydrate Polymers*, 301, 1-8.
- Zhao, M., Cui, Z., Pan, D., Fan, F., Tang, J., Hu, Y., & Wu, W. (2021). An efficient uranium adsorption magnetic platform based on amidoxime-functionalized flower-like $\text{Fe}_3\text{O}_4@ \text{TiO}_2$ core-shell microspheres. *ACS Applied Materials & Interfaces*, 13(15), 31-39.
- Zheng, X. Y., Shen, Y. H., Wang, X. Y., & Wang, T. S. (2018). Effect of pH on uranium (VI) biosorption and biomineralization by *Saccharomyces cerevisiae*. *Chemosphere*, 203(1), 109-116.

APPENDICES

Appendix A: Journal Publications

1. Wee, B.S., **Maligan, M.F.**, Chin, S.F., Elias, M.S. and Shirai, N., 2024. Adsorption of U (VI) ions using functionalized sago hampas: kinetics, isotherms, and thermodynamics studies. *Journal of Radioanalytical and Nuclear Chemistry*, 333(6), pp.2679-2689.

Appendix B: ICP-OES data for adsorption studies

3/4/2023

9:57:40 AM

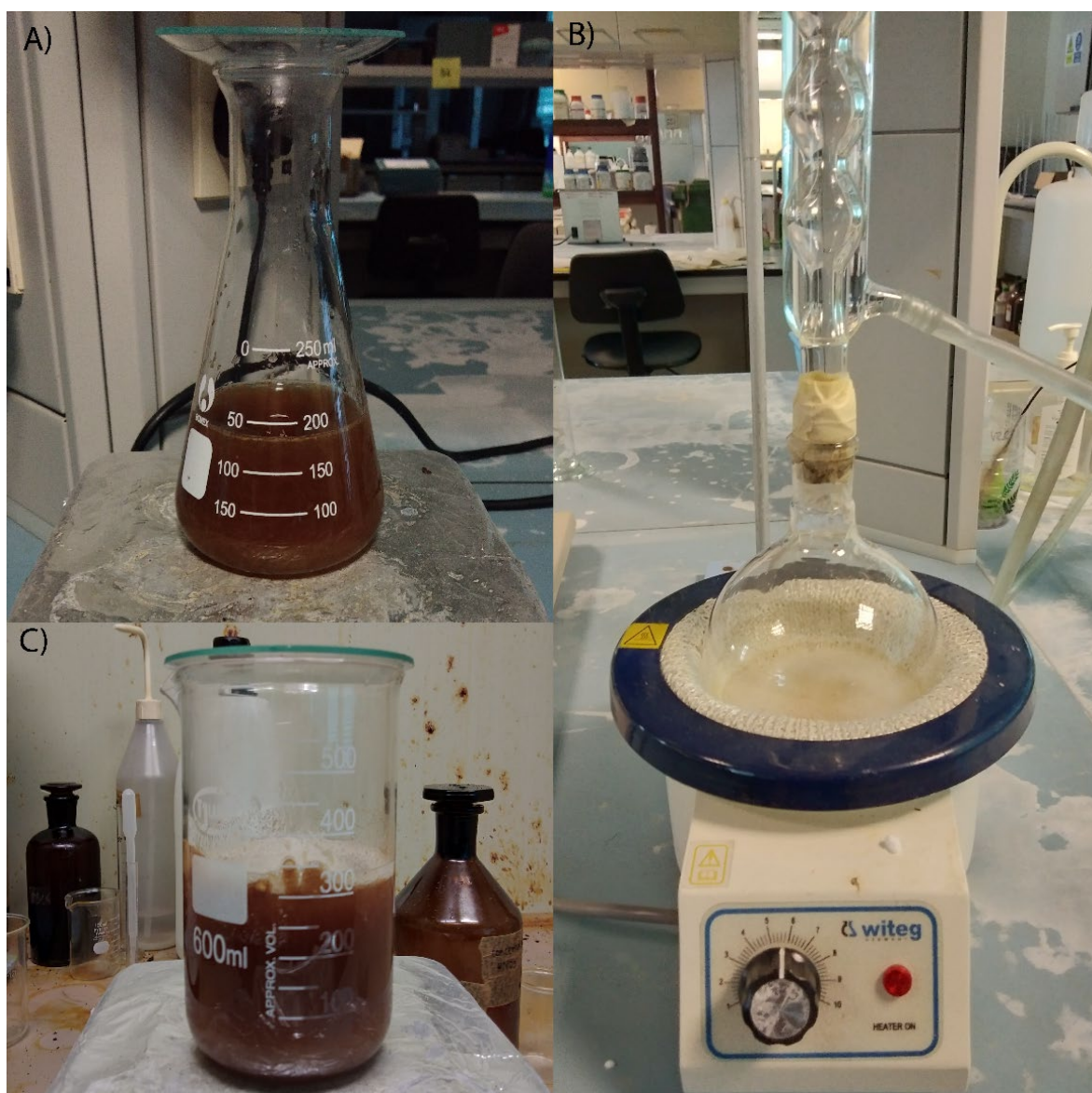
230403 04 21

Mean Data								
ID:	Calib Blank 1				Seq. No.:	1	A/S Pos:	1
Sample Qty:	g	Prep. Vol.:	Dilution:	:	Date:	3/4/2023 8:31:13AM		
Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
U 409.014	852.7	[0.00]	156.72	mg/L				18.38 %
Mean Data								
ID:	Std 0.2				Seq. No.:	2	A/S Pos:	2
Sample Qty:	g	Prep. Vol.:	Dilution:	:	Date:	3/4/2023 8:33:08AM		
Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
U 409.014	20,162.0	[0.2]	310.95	mg/L				1.54 %
Mean Data								
ID:	Std 0.5				Seq. No.:	3	A/S Pos:	3
Sample Qty:	g	Prep. Vol.:	Dilution:	:	Date:	3/4/2023 8:35:01AM		
Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
U 409.014	47,828.6	[0.5]	595.02	mg/L				1.24 %
Mean Data								
ID:	Std 1.0				Seq. No.:	4	A/S Pos:	4
Sample Qty:	g	Prep. Vol.:	Dilution:	:	Date:	3/4/2023 8:36:53AM		
Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
U 409.014	97,119.2	[1.0]	1,300.66	mg/L				1.34 %
Mean Data								
ID:	Std 3.0				Seq. No.:	5	A/S Pos:	5
Sample Qty:	g	Prep. Vol.:	Dilution:	:	Date:	3/4/2023 8:38:45AM		
Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
U 409.014	285,481.8	[3.0]	4,797.68	mg/L				1.68 %
Mean Data								
ID:	Std 5.0				Seq. No.:	6	A/S Pos:	6
Sample Qty:	g	Prep. Vol.:	Dilution:	:	Date:	3/4/2023 8:40:36AM		
Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
U 409.014	482,863.8	[5.0]	6,911.46	mg/L				1.43 %
Mean Data								
ID:	QC - 2.00 mg/L 3/4/2023 8:42:31AM All analyte(s) passed QC.				Seq. No.:	7	A/S Pos:	7
Sample Qty:	g	Prep. Vol.:	Dilution:	:	Date:	3/4/2023 8:42:27AM		
Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
U 409.014	194,424.5	2.020	0.0268	mg/L	2.020			1.33 %
3/4/2023 8:42:29AM QC value within limits for U 409.014 Recovery = 101.02%								
Mean Data								
ID:	21 - 1				Seq. No.:	8	A/S Pos:	11
Sample Qty:	g	Prep. Vol.:	Dilution:	:	Date:	3/4/2023 8:44:21AM		
Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD
U 409.014	1,375.0	0.014	0.0055	mg/L	0.014	0.0055	mg/L	38.24 %
Mean Data								
ID:	21 - 2				Seq. No.:	9	A/S Pos:	12
Sample Qty:	g	Prep. Vol.:	Dilution:	:	Date:	3/4/2023 8:46:15AM		
Analyte	Corr. Intensity	Conc (Calib)	Std. Dev.	Calib Units	Conc (Sample)	Std. Dev.	Sample Units	RSD

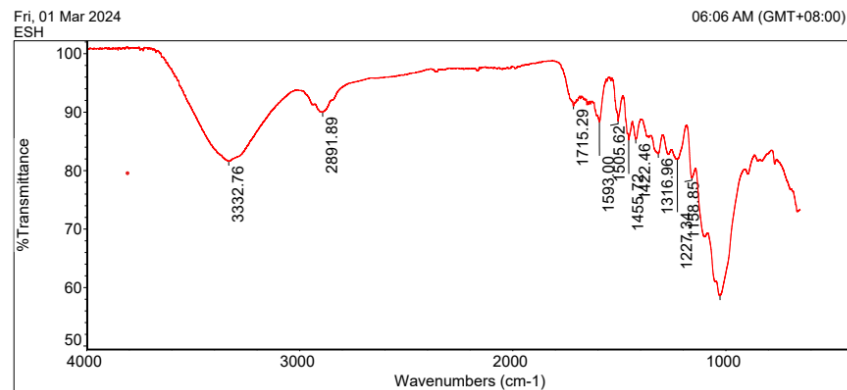
1

5

Appendix C: Experimental setup of functionalisation processes of sago hampas



Appendix D: Raw FTIR spectra of RSH and ESH



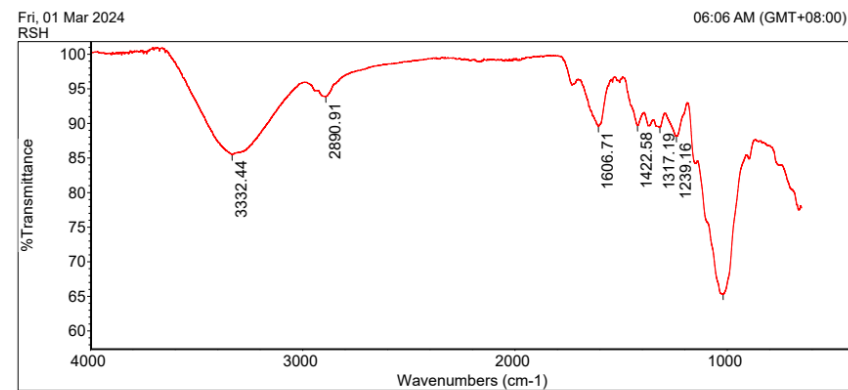
Wed Nov 17 14:33:29 2021 (GMT+08:00)

FIND PEAKS:

Spectrum: 500um ESH
Region: 3999.81 649.92
Absolute threshold: 97.971
Sensitivity: 50

Peak list:

Position:	Intensity:
1027.39	58.596
1158.85	78.790
1227.34	81.932
1316.96	82.880
1422.46	85.376
1455.72	85.241
1505.62	88.456
1593.00	88.356
1715.29	91.061
2891.89	90.031
3332.76	81.581



Wed Nov 17 14:33:41 2021 (GMT+08:00)

FIND PEAKS:

Spectrum: 500um RSH
Region: 3999.81 649.92
Absolute threshold: 99.806
Sensitivity: 50

Peak list:

Position:	Intensity:
1019.38	65.119
1239.16	87.931
1317.19	89.193
1422.58	89.523
1606.71	89.379
2890.91	93.654
3332.44	85.292