UNIVERSIDADE EDUARDO MONDLANE
Faculty of Engineering
Master in Hydrocarbon Processing Engineering

SYNTHESIS AND CHARACTERIZATION OF RICE HUSKS AS A NATURALLY OCCURRING ADSORBENT FOR THE TREATMENT OF PRODUCED WATER FROM OIL AND GAS INDUSTRY

A Dissertation by

Yvonne UWINEZA

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DECLARATION OF DOCUMENT ORIGINALITY

"I declare that this dissertation has never been submitted to obtain any degree or in any other context and is the result of my own individual work. This dissertation is presented in partial fulfillment of the requirements for the degree of Master of Science in Hydrocarbon Processing Engineering, from the Universidade Eduardo Mondlane".

Submitted by:

Yvonne UWINEZA

ABSTRACT

This research explores the potential of rice husks (RH) as a naturally available adsorbent for the remediation of produced water (PW), which is a significant byproduct of the oil and natural gas industry, characterized by the presence of hydrocarbons, heavy metals, and dissolved solids. The study involved the preparation of RH under controlled laboratory conditions, followed by an assessment of its efficacy in adsorbing copper and phenol from simulated PW. Various experimental parameters, including contact time, adsorbent dosage, and temperature, were meticulously optimized. The optimal conditions identified were 1 g of RH for copper, 0.8 g for phenol, a temperature of 333 K for both contaminants, and contact times of 45 minutes for copper and 60 minutes for phenol. The results demonstrated a removal efficiency of practically 98% for both copper and phenol. The adsorption kinetics conformed to a pseudo-second-order model, with copper adsorption aligning with the Langmuir isotherm, indicative of monolayer adsorption, while phenol adsorption corresponded to the Freundlich isotherm, suggesting multilayer adsorption on heterogeneous surfaces. Compared to the existing technology, such as advanced oxidation processes, electrocoagulation, and membrane filtration, which are costly, energy consumption, and secondary waste production, the obtained results position RH as a viable, cost-effective, and sustainable option for the treatment of PW, contributing to the resolution of environmental issues associated with wastewater management.

Keywords: Rice Husks, Produced Water, Adsorption, Copper Removal, Phenol Removal, Kinetics Models, Isotherms.

RESUMO

Esta pesquisa explora o potencial das cascas de arroz (CA) como um adsorvente naturalmente disponível para a remediação de água produzida (AP), que é um subproduto significativo da indústria de petróleo e gás natural, caracterizado pela presença de hidrocarbonetos, metais pesados e sólidos dissolvidos. O estudo envolveu a preparação de CA sob condições controladas de laboratório, seguidas por uma avaliação de sua eficácia na adsorção de cobre e fenol de AP simulado. Vários parâmetros experimentais, incluindo tempo de contato, dosagem de adsorvente e temperatura, foram meticulosamente otimizados. As condições ótimas identificadas foram 1 g de CA para cobre, 0,8 g para fenol, uma temperatura de 333 K para ambos os contaminantes e tempos de contato de 45 minutos para cobre e 60 minutos para fenol. Os resultados demonstraram uma eficiência de remoção de praticamente 98% para cobre e fenol. A cinética de adsorção obedeceu a um modelo de pseudo-segunda ordem, com adsorção de cobre alinhando-se com a isoterma de Langmuir, indicativa de adsorção de monocamada, enquanto a adsorção de fenol correspondeu à isoterma de Freundlich, sugerindo adsorção multicamadas em superfícies heterogêneas. Comparado à tecnologia existente, como processos de oxidação avançados, eletrocoagulação e filtração por membrana, que são caros, consomem energia e produzem resíduos secundários, os resultados obtidos posicionam a CA como uma opção viável, econômica e sustentável para o tratamento de AP, contribuindo para a resolução de problemas ambientais associados ao gerenciamento de águas residuais.

Palavras-chave: Casca de arroz, Água produzida, Adsorção, Remoção de cobre, Remoção de fenol, Modelos cinéticos, Isotermas.

DEDICATION

To God, the Almighty Father, for His boundless grace and guidance throughout this journey.

To my beloved parents, whose unwavering love, support, and encouragement have been the foundation of my success.

To my siblings, and all my relatives and friends, for their constant motivation and belief in me, which have been a source of strength and inspiration.

ACKNOWLEDGEMENTS

Above all, I offer my heartfelt gratitude to the Almighty for showering me with boundless blessings, strength, knowledge, and opportunities that have enabled me to conclude my studies and research successfully. This journey has been marked by His divine guidance and unwavering support, without which none of this would have been possible.

I sincerely appreciate Eduardo Mondlane University for providing an enriching academic environment that fostered my intellectual and professional growth. My heartfelt thanks go to the Center of Excellence in Studies of Oil and Gas Engineering and Technology (CS-OGET) for its pivotal role in facilitating my study and research. I am equally grateful to the Department of Chemical Engineering staff members, whose expertise and commitment have greatly contributed to my academic development.

I would also like to express my deep gratitude to the World Bank for sponsoring my studies and enabling me to pursue my academic aspirations with the necessary financial support.

I especially acknowledge my supervisor, Prof. Afonso Daniel Macheca, for his invaluable guidance, encouragement, constructive feedback, and continuous support throughout my research. His mentorship was crucial to the successful completion of this thesis. I also extend my appreciation to the laboratory technicians, especially Asmina Sulemane, for providing the essential resources and facilities that were crucial for conducting my experiments.

Lastly, I am immensely grateful to my family, friends, and classmates for their unwavering encouragement, support, and companionship, which have been crucial to my perseverance and success.

LIST OF ABBREVIATION, ACRONYMS, AND INITIALISM

AC: Activated Carbon

Acetyl-RH-NaOH: Acetylated-Rice Husks-NaOH

Acetyl-RH-H_3PO_4: Acetylated-Rice Husks-H_3PO_4

AOPs: Advanced Oxidation Processes

APs: Alkyl Phenols

BET: Brunauer-Emmett-Teller

BTEX: Benzene, Toluene, Ethylbenzene, and Xylene

BOD: Biochemical Oxygen Demand

COD: Chemical Oxygen Demand

ED: Electrodialysis

EOR: Enhanced Oil Recovery

FMA: Iron, Magnesium, and Aluminum

FTE: Freeze-Thaw Evaporation

IWM: Industrial Water Management

MF: Micro Filtration

NPD: Naphthalene, Phenanthrene, Dibenzothiophene

NORM: Naturally Occurring Radioactive Materials

NF: Nano Filtration

O&G: Oil and Gas

PAHs: Polyaromatics Hydrocarbons

PPM: Parts Per Million

PW: Produced Water

RH: Rice Husks

RO: Reverse Osmosis

SS: Suspended Solids

TDS: Total Dissolved Solids

UEM: Universidade Eduardo Mondlane

UF: Ultra Filtration

VOCs: Volatile Organic Compounds

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CHAPTER 1

INTRODUCTION

1.1. Background

The oil and gas (O&G) sector serves as the principal energy source globally, characterized by a multifaceted production and distribution process. This industry has significantly contributed to the economic evolution of nations by fulfilling the essential needs for heating, electricity, transportation, and various petrochemical products required by the global population. The production and distribution processes are facilitated by advanced technologies across three distinct segments: upstream, midstream, and downstream. The upstream segment encompasses exploration and production activities, including geological assessments and both onshore and offshore drilling operations. The midstream segment focuses on the transportation process that primarily involves moving raw or partially processed materials (such as crude oil, natural gas, or biomass-derived products) from upstream production sites (where raw materials are extracted) to downstream facilities (where refining, processing, or distribution occurs) and the storage and trading of crude oil, natural gas, and their refined derivatives. Finally, the downstream segment is responsible for refining processes and marketing activities. The upstream sector is particularly vital to the overall functioning of the O&G industry (Elijah et al., 2021, Mojarad et al., 2018, Cabrera et al., 2021).

O&G has gained global recognition due to its widespread use and importance in various industries. However, the extraction and exploration processes of these resources have resulted in the O&G industry facing a considerable challenge in managing the substantial volume of wastewater generated as a byproduct, the so-called produced or production water (PW) (Gulistan, 2014). PW is the water that naturally exists in underground formations and is brought to the surface along with crude oil and natural gas during production. It can also include water injected into the reservoir to enhance recovery. The volume of PW has witnessed a significant surge over the years, with its output escalating from less than 30 million barrels per day in 1990 to an estimated 100 million barrels per day in 2015. This substantial increase highlights the growing magnitude of this byproduct in the O&G industry.

Looking towards the future, the global demand for fuel is projected to experience a notable upswing. This forecast underscores the mounting reliance on energy resources and the need for sustainable strategies to meet the escalating energy demands of our modern society (Gul Zaman et al., 2021).

PW, also known as wastewater, consists of a diverse range of hydrocarbons present in free, dispersed, and dissolved states. It consists of various components, including organics, inorganics, production chemicals, and transformation compounds, along with heavy metals. Among the organic compounds present in PW are oil and grease, as well as aromatic compounds like Benzene, Toluene, Ethylbenzene, and Xylene (BTEX). Additionally, PW may contain halogenated aromatic compounds, chloroform, Naphthalene, Phenanthrene, Dibenzothiophene (NPD), Polyaromatics Hydrocarbons (PAHs), phenols, and trichloroethylene, which are considered significant organic pollutants (Varjani et al., 2020, Aljuboury et al., 2017, Gul Zaman et al., 2021). The discharge of PW has the potential to result in significant pollution of various environmental components such as surfaces, soil, and underground water. This pollution poses a serious threat due to the absence of adequate treatment measures to mitigate its harmful effects (Khader et al., 2022, Szép & Kohlheb, 2010).

At present, the predominant method of handling the wastewater produced at onshore oil and gas facilities involves injecting it back into the ground for disposal or to enhance oil recovery. This approach is widely considered to be the most environmentally friendly option due to its significant reduction in the consumption of freshwater or seawater (Yousef et al., 2020, Fakhru’l-Razi et al., 2009). The treatment facilities employed in this process are primarily designed to eliminate dispersed oil and grease as well as suspended solids to prevent blockages. Conversely, the wastewater generated from offshore oil and gas production is typically released into the ocean. This practice can disrupt the natural ecosystem, expose living organisms to harmful substances, and have detrimental effects on the aquatic environment. The primary objective of treating this wastewater is to reduce the levels of oil and grease to meet the required discharge regulations and environmental standards, often resulting in direct discharge into the ocean (Yousef et al., 2020, Gul Zaman et al., 2021, Adham et al., 2013). The effective handling and control of PW pose considerable technical and economic obstacles for oil and gas corporations.

The key differentiating factors between offshore and onshore PW management lie in the limitations of weight and space, which ultimately affect the overall efficiency of treatment processes. Besides reinjection and disposal into the ocean, another destination for PW after treatment is its use for auxiliary services in the facilities, such as cleaning services, irrigation of green areas such as gardens, etc. The expenses associated with managing PW vary depending on the operational methods employed and technologies. Across all sectors, the most ideal approach to PW management would be a solution that is both cost-effective and environmentally sustainable (Gul Zaman et al., 2021).

A wide range of treatment technologies have been suggested for the treatment of PW due to its diverse contaminants and their varying concentrations. These treatment methods typically require energy inputs to effectively eliminate the contaminants present in the PW. By treating PW, it becomes possible to explore additional water management options, including its reuse for agricultural and industrial purposes. However, selecting the most suitable treatment system to remove the majority of contaminants from PW can be a challenging task. Different treatment approaches, such as physical, chemical, or biological processes, or a combination of these methods, can be employed to achieve specific treatment objectives (Khader et al., 2022, Al-Ghouti et al., 2019).

Numerous methods for treating PW have been investigated in various studies. The literature extensively covers the examination of adsorption, membrane filtration, and chemical precipitation, all of which have demonstrated removal efficiencies exceeding 90% for different constituents found in PW. Among these techniques, adsorption stands out as a highly effective approach for enhancing water quality, as it can significantly decrease contaminant concentrations to extremely low levels. Due to its remarkable ability to treat PW in compliance with environmental regulations while keeping costs at a minimum, the adsorption-filtration method has been introduced as an environmentally sustainable, cost-efficient, and economically viable solution (Al-Ghouti et al., 2019).

1.2. Problem statement

As the energy demand continues to increase globally, the O&G industry plays a crucial role in converting crude oil into valuable products through various processes. However, the O&G sector is responsible for the generation of substantial quantities of PW, which represents the most significant waste stream linked to the extraction of hydrocarbons. This PW frequently exhibits elevated levels of contaminants, such as hydrocarbons, heavy metals, salts, and various organic substances, thereby presenting considerable environmental hazards and complicating water management efforts. If this wastewater is discharged without proper treatment, it can pose a threat to the environment due to the presence of hazardous contaminants. Therefore, it is essential to treat PW before its discharge. The most advanced treatment technologies, such as membrane separation, adsorption, advanced oxidation process, etc., are employed to meet the discharge requirements. Numerous countries are currently researching the treatment of PW, which contains high concentrations of metals, organic compounds, and inorganic toxic substances. Previous studies have explored the use of cellulose for treating these effluents, and it has demonstrated promising results, but one drawback is that the cost of preparing cellulose from bacteria is relatively high (Peng et al., 2020). In addition to this, the research conducted by Varjani et al. (2020) demonstrated significant advancements in the treatment of this wastewater through the utilization of various technologies, including membrane separation, advanced oxidation processes, electrochemical catalysis, and photocatalytic degradation. These innovative approaches have proven to be highly effective in enhancing the treatment efficiency of wastewater. The objective of this study is to explore the utilization of adsorbent derived from rice husks as a means to effectively treat PW.

The primary aim is to ensure that the treated water adheres to the prescribed limits for safe disposal or reuse in industrial or agricultural applications. Additionally, this approach aims to mitigate potential environmental hazards associated with oil-contaminated water. RH has been selected for this study due to its numerous benefits in the treatment process. Firstly, they serve as an attractive bio-based adsorbent material for removing pollutants. Secondly, they are cost-effective as they can be locally disposed of as waste. Lastly, RH are renewable resources, making them a sustainable choice.

Moreover, their abundance, easy availability, granular structure, insolubility in water, high chemical stability, and mechanical strength make them a potential biosorbent. Additionally, RH can effectively eliminate various pollutants, making them suitable for wastewater treatment (Shamsollahi & Partovinia, 2019, Chuah et al., 2005).

1.3. Research Objectives

1.3.1. General objective

The main objective of this study is to assess the efficiency of rice husks as a naturally existing adsorbent in the process of treating PW; however, emphasis was placed on phenol and copper.

1.3.2. Specific Objectives

- To prepare the adsorbent from rice husks under favorable conditions so that it will treat PW effectively.
- To characterize the produced adsorbent to understand their physicochemical behaviors fully.
- To evaluate the performance of prepared materials in the treatment of PW through adsorption studies.
- Optimize the results obtained considering the process parameters such as contact time, adsorbent dosage, initial concentration, and temperature.

1.4. Motivation, contribution, and significance

The management of PW is a significant environmental concern in the O&G industry. The management and disposal of PW, a notable byproduct of various O&G industries, presents complex challenges that are crucial for maintaining environmental sustainability. Traditional treatment methods for PW frequently require considerable financial resources and face significant technical obstacles, which can hinder their overall effectiveness and feasibility in numerous situations. Traditional methods for treating PW, such as physical or chemical methods, often involve expensive technologies or generate secondary waste that requires further treatment. This leads to increased treatment costs, highlighting the need to explore sustainable and cost-effective solutions (Gul Zaman et al., 2021). Physical adsorption methods, particularly those using activated carbon (AC), have proven to be highly effective in removing contaminants from PW due to their unique characteristics. However, the regeneration of AC results in the generation of liquid waste, further increasing treatment costs (Mandal et al., 2019, Al-Ghouti et al., 2019).

To address this issue, some researchers propose the use of inexpensive and locally abundant adsorbents derived from agricultural waste during PW treatment. These adsorbents offer good adsorption capacity, low cost, easy availability, and simple regeneration, making them a promising alternative for PW treatment (Acharya et al., 2018, Abdel-Ghani et al., 2016, Mandal et al., 2019). RH, a common byproduct of rice dehusking, is often seen as low-value agricultural waste. However, its unique properties, such as high surface area and porosity, make it a promising natural adsorbent. Converting this waste into useful materials reduces environmental impact and promotes a circular economy by increasing the value of byproducts that would otherwise contribute to waste. The exploration of rice husks' adsorption capabilities in treating PW aligns with the industry's increasing emphasis on sustainable practices and the need for innovative nature-based solutions.

The primary objective of this study is to investigate the capacity of RH as adsorbents and evaluate their effectiveness in the treatment of PW. The underlying motivation for conducting this research stems from the prospect of introducing a groundbreaking and eco-friendly technique that could revolutionize the treatment of PW in the O&G industry. By offering a sustainable alternative to conventional practices, this research tackles the critical demand for innovative and economically viable methods of treating PW while simultaneously promoting environmentally sustainable practices. Through a comprehensive examination of the characteristics and potential applications of RH, this study seeks to enhance the existing knowledge within the field of sustainable materials science and provide a pragmatic approach to addressing significant environmental challenges. Furthermore, it emphasizes the significance of exploring the potential of RH as a viable solution for PW treatment, highlighting the necessity for innovative approaches to overcome these challenges and the potential advantages of pursuing this avenue of investigation.

1.5. Hypothesis

Utilizing RH as naturally occurring adsorbents in the O&G industry can effectively remove hydrocarbons from PW, demonstrating comparable or superior efficiency compared to conventional treatment methods. The adsorption capacity of RH will be influenced by varying factors, such as particle size, surface modification, contact time, and initial concentration of hydrocarbons, ultimately providing an eco-friendly solution for PW treatment. This hypothesis sets the stage for investigating the efficacy of RH as an adsorbent in treating PW in the O&G industry. It also highlights its potential advantages over traditional methods and indicates the various parameters that might affect its efficiency in the adsorption process, guiding the research methodology and potential areas of experimentation.

CHAPTER 2

LITERATURE REVIEW

2.1. Source of produced water

A significant quantity of water is required for the exploration and production of oil and gas. Regardless of whether the fuel is obtained from conventional or unconventional sources like coal bed methane, tight sands, and gas shale, the extraction process from onshore and offshore wells results in the generation of PW (Jiménez et al., 2018). Subsurface formations contain a range of underground fluids, including oil, gas, and saline water, which naturally permeate through rocks. These rocks were initially saturated with saline water, which later trapped hydrocarbon compounds. As the process continued, lower-density hydrocarbons moved toward trap locations, displacing some of the saline water within the formation. Ultimately, the reservoir rocks absorbed both saline water and hydrocarbons, such as oil and gas (Fakhru'l-Razi et al., 2009). When hydrocarbons mix with saline water and rise to the surface, they are commonly referred to as "connote water" or "formation water." To maintain hydraulic pressure and maximize oil recovery, additional water needs to be injected into the reservoir as the extraction of oil and gas reduces the reservoir pressure. During the later stages of hydrocarbon exploration, both the formation water and the injected water reach the production well and are collectively referred to as PW. As the production of oil and gas continues, the formation of water eventually reaches the production well, resulting in the simultaneous production of water and hydrocarbons. This water, known as PW or oilfield brine, is the most significant byproduct of oil and gas recovery operations. This type of petroleum wastewater primarily consists of a mixture of hydrocarbons and chemical additives. At the surface, processes are employed to separate the hydrocarbons from the PW. The quality of the PW deteriorates due to the presence of various components, including microbes and dissolved organic and inorganic substances, within the generated water (Igunnu & Chen, 2014, Fakhru'l-Razi et al., 2009, Bakke et al., 2013).

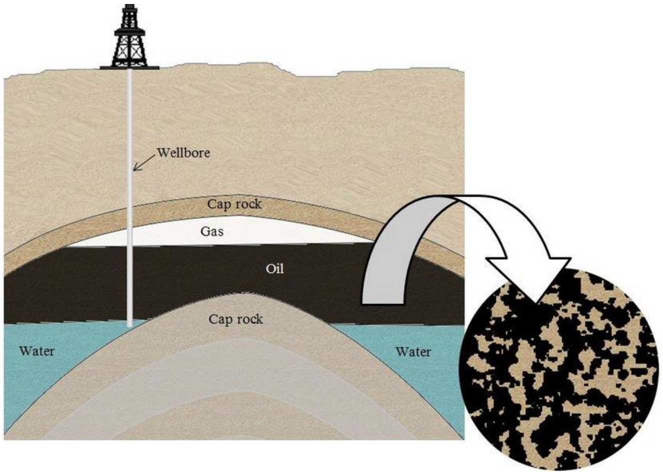

Figure 1. A typical oil and gas reservoir(adapted from Ramon & Fernandes, 2018).

The volume of water extracted from oil and gas wells is not static and tends to change over the lifespan of the well. In the early stages, water constitutes a minor fraction of the total fluids produced; however, as the well ages, the proportion of water increases while the proportion of hydrocarbons diminishes. Current estimates indicate that global PW reaches approximately 250 million barrels per day, in contrast to about 85 million barrels per day of oil. Consequently, the water-to-oil ratio stands at roughly 3:1, indicating a water cut of 70%. This global water cut has seen an upward trend over the past decade and continues to escalate. The increase in PW is primarily attributed to the aging of existing fields, although advancements in management practices and the development of new oil fields serve to mitigate this rising (Wang et al., 2012, Fakhru'l-Razi et al., 2009).

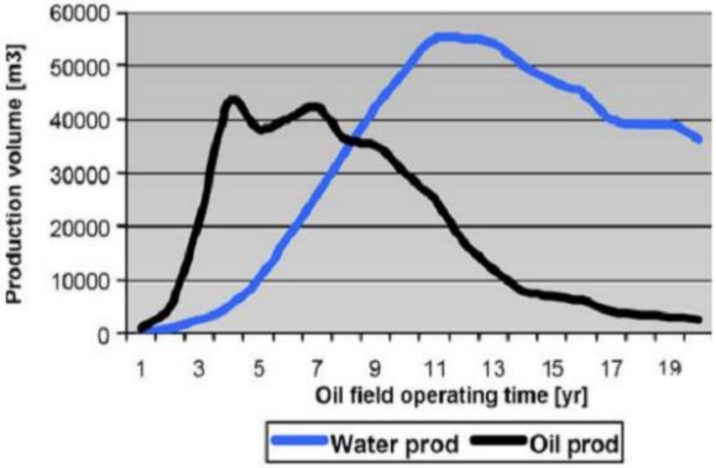

Figure 2. Production profile of PW and oil from a typical oilfield(adapted from Abbas et al., 2021)

2.2. Properties of produced water

PW is a complex mixture consisting of various components, such as organics, inorganics, production chemicals, and transformation compounds, as shown in Table 1. The composition of PW exhibits considerable variability influenced by multiple factors, such as the geographical setting of the extraction site, the underlying geological formations, the operational lifespan of the reservoir, the methods utilized for extraction, and the specific type of hydrocarbons being produced. Despite these variations, the qualitative makeup of PW generally mirrors that associated with oil and gas extraction processes. It primarily consists of the water that is naturally found within the geological formation, combined with any additional water that may be injected to enhance the recovery of oil and gas. Furthermore, the characteristics and volume of PW can fluctuate throughout the reservoir's operational life. In both onshore and offshore contexts, oil and grease are the most scrutinized components of PW, while salt content—measured in terms of salinity, conductivity, or total dissolved solids (TDS)—is particularly significant in onshore settings. Additionally, PW encompasses a variety of organic and inorganic substances that may pose toxicity risks, with some being naturally present and others resulting from chemical additives used for well management. These constituents can differ markedly across various locations and may also change over time within the same well (Yousef et al., 2020, Fakhru'l-Razi et al., 2009, Nasiri et al., 2017, Hollanda et al., 2021, Nasiri & Jafari, 2017, Amakiri et al., 2022).

The nature of the rock formations from which it is extracted, as well as the operational conditions and chemicals used in process facilities, define the characteristics of PW (Gulistan, 2014). The following are the major constituents of PW: Dissolved and dispersed oil compounds, Dissolved formation minerals, Production chemical compounds, Production solids (including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes), and Dissolved gases (Fakhru'l-Razi et al., 2009, Liang et al., 2018, Amakiri et al., 2022, Drioli et al., 2016).

2.2.1. Inorganic compounds/minerals

Anions and cations, heavy metals, and radioactive materials are among the inorganic dissolved compounds in PW.

❖ Heavy metals

Several metals, either dissolved or microparticulate, may be present in the PW (Veil, 2011). The concentrations of heavy metals found in PW are subject to variation based on the age of the well and the geological composition of the formation. Metals such as iron (Fe), chromium (Cr), barium (Ba), zinc (Zn), and various others have the potential to be present in the PW. It is important to note that while certain metals may be present in significant quantities, other metals such as cadmium (Cd), nickel (Ni), copper (Cu), chromium (Cr), and mercury (Hg) may only be found in trace amounts in petroleum effluents (Eldos et al., 2022, Al-Ghouti et al., 2019). Mercury, zinc, barium, manganese, and iron are frequently found in higher concentrations in PW than in seawater (Al-Ghouti et al., 2019). PW typically contains higher concentrations of heavy metals compared to receiving water for oil recovery and seawater (Igunnu & Chen, 2014).

❖ Anions and cations

PW contains a diverse range of cations and anions. Cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, and Fe^{2+}, and anions such as Cl^-, SO_4^{2-}, CO_3^{2-}, and HCO_3^- influence the chemistry of PW in terms of buffering capacity, salinity, and scale potential (Fakhru'l-Razi et al., 2009, Liang et al., 2018). Many of these ions are found in various concentration ratios in seawater and PW, which may contribute to the produced water's environmental toxicity (Veil, 2011). Salinity is caused by dissolved sodium and chloride, with calcium, magnesium, and potassium contributing less (Fakhru'l-Razi et al., 2009).

The salinity (salt concentration) of PW can range from 1000 mg/L to over 300,000 mg/L, whereas seawater salinity ranges from 32,000 mg/L to 36,000 mg/L. The anion and cation with the highest concentrations in PW, similar to those found in seawater, are chloride and sodium (Gul Zaman et al., 2021), consequently, this is why PW is generally denser than seawater (Al-Ghouti et al., 2019).

Table 1. Summary of oilfield-produced water(Fakhru'l-Razi et al., 2009, Al-Ghouti et al., 2019, Jiménez et al., 2018, Nasiri & Jafari, 2017, Al-Kindi et al., 2022)

Parameter	Values	Metals/Heavy metals	Values (mg/l)
Density (kg/m³)	1014 – 1140	Calcium	13 -25800
Surface tension (dynes/cm)	43 – 78	Sodium	132 – 97000
TOC (mg/l)	0 – 1500	Potassium	24 – 4300
COD (mg/l)	1220	Magnesium	8 – 6000
TSS (mg/l)	1.2 – 1000	Iron	< 0.1 – 100
pH	4.3 – 10	Aluminum	310 – 410
Total oil (IR; mg/l)	2 – 565	Boron	5 – 95
Volatile (BTX, mg/l)	0.39 – 35	Barium	1.3 – 650
Base/neutrals (mg/l)	< 140	Cadmium	< 0.005 – 0.2
Total non-volatile oil and grease by GLC/MS base (μg/L)	275	Chromium	0.02 – 1.1
Chloride (mg/l)	80 – 200000	Copper	< 0.002 – 1.5
Bicarbonate (mg/l)	77 – 3990	Lithium	3 – 50
Sulfate (mg/l)	< 2 – 1650	Manganese	< 0.004 – 175
Ammoniacal nitrogen (mg/l)	10 – 300	Lead	0.002 – 8.8
Sulfite (mg/l)	10	Strontium	0.02 – 1000
Total polar (mg/l)	9.7 – 600	Titanium	< 0.01 – 0.7
Higher acids (mg/l)	< 1 – 63	Zinc	0.01 – 35
Phenols (mg/l)	0.009 – 23	Arsenic	< 0.005 – 0.3
VFA's (volatile fatty acids) (mg/l)	2 – 4900	Mercury	< 0.001 – 0.002
		Silver	< 0.001 – 0.15
		Beryllium	< 0.001 – 0.004

- **Naturally occurring radioactive materials (NORM)**

Radioactivity in scale is caused by radioactive ions, primarily radium, which are co-precipitated from PW along with other types of scale (Fakhru'l-Razi et al., 2009). The quantity and types of radioactive substances are determined by their geologic formations (Zheng et al., 2016).

^{226}Ra and ^{228}Ra are the naturally occurring radioactive nuclides of primary concern in oil and gas production. Before becoming stable lead, these decay into various radioactive progeny (Ahmad et al., 2021). If seawater with a high sulfate concentration (2,712 mg/L) is injected into the reservoir to maintain pressure in the formation to improve oil and gas recovery and mixes, resulting in the formation water having a higher salt concentration and a lower pH than seawater, and the chemical equilibrium is disrupted, resulting in the precipitation of sulfates (primarily $BaSO_4$ and $SrSO_4$) as scale in the production pipes, lowering the concentration of dissolved barium in the PW (Veil, 2011). The most common scale co-precipitate is barium sulfate. The level of NORM accumulation in oil and gas waste can vary significantly between facilities, depending on reservoir source geology and operational conditions, and it will also change over the life of an oil-producing well (Ahmad et al., 2021).

2.2.2. Dissolved and dispersed oil compounds

Oil is a hydrocarbon mixture that contains BTEX, NPD, PAHs, and phenols. Due to the fact that the majority of hydrocarbons do not dissolve in water, most oil is dispersed in water as an emulsion or clearly separated into two phases (Fakhru'l-Razi et al., 2009).

- **Dissolved oil:** The main polar constituents of the hydrocarbon mixture present in PW are water-soluble compounds. BTEX, phenols, aliphatic hydrocarbons, carboxylic acid, and low-molecular-weight aromatic compounds are among the water-soluble organic species. The solubility of organic compounds in PW are influenced by pH, temperature (Jiménez et al., 2018) , and Pressure slightly increases the concentration of dissolved organic compounds (in the reservoir or during extraction). The dissolved organics in PW are unaffected by salinity. Total dissolved organics in PW are not increased by soluble compounds (Fakhru'l-Razi et al., 2009). The type of oil, volume of water produced, artificial technique, and age of production all influence oil solubility in PW (Jiménez et al., 2018).

  There is still a significant amount of toxic organic petroleum hydrocarbons in the dissolved oil, such as BTEX, PAHs, and APs, and among these dissolved compounds, PAHs are thought to be the most toxic to offshore-produced water. The concentration of these compound groups in offshore-produced water is also affected by factors such as production volume, technique, and age (Zheng et al., 2016).

The removal of toxic compounds such as aromatics, which are the most important chemicals contributing to the toxicity of natural environments, from water using oil/water separation techniques is extremely inefficient, Furthermore, the concentration of naphthalene, phenanthrene, dibenzothiophene, and their C1-C3 alkyl homologous and alkylated phenols decreases as the alkylation of components increases (Fakhru'l-Razi et al., 2009).

- **Dispersed oil:** Typically, it refers to oil in PW in the form of small droplets ranging in size from sub-microns to hundreds of microns. Both aliphatic and aromatic hydrocarbons will be present in dispersed oil. The amount of oil dispersed in PW is determined by the density of the oil, the droplet's shear history, the amount of oil precipitation, and the interfacial tension between the water and the oil (Fakhru'l-Razi et al., 2009, Gulistan, 2014).

2.2.3. Dissolved gases

PW contains considerable quantities of dissolved gases, predominantly volatile hydrocarbons, alongside other gases such as carbon dioxide (CO_2), oxygen (O_2), and hydrogen sulfide (H_2S). The solubility of these gases in aqueous solutions is influenced by various factors, notably decreasing with increasing salinity and temperature of the water while rising with elevated pressure conditions. When present in substantial concentrations, these gases pose significant toxic and corrosive risks (Costa et al., 2022, Amakiri et al., 2022). Carbon dioxide, oxygen, and hydrogen sulfide are gases that occur naturally as a result of bacterial activity or through chemical reactions occurring in water (Igunnu & Chen, 2014).

2.2.4. Production chemical compounds

Production chemicals are typically added to the oil and gas production system to prevent and treat operational problems, such as facilitating oil, gas, and water separation, preventing pipeline corrosion, and methane hydrate formation in the gas production system (Al-Ghouti et al., 2019, Costa et al., 2022). The chemicals required for the production process are unique and vary with the various production systems, and they can be classified into three broad groups: gas processing chemicals, simulation and work over chemicals, and production treating chemicals such as scale, corrosion, hydration inhibitors, biocides, water treating chemicals such as flocculants and anti-foams, emulsion breakers, reverse emulsion breakers, and coagulants, which are used in hydrocarbons' production (Al-Ghouti et al., 2019).

Corrosion inhibitors and reverse emulsion breakers, commonly employed as treatment chemicals, have the potential to exhibit high toxicity levels even at minimal concentrations, such as 0.1 parts per million (ppm). It is important to note that these chemicals, including biocides and other additives, can pose significant health risks. Conversely, certain corrosion inhibitors have the ability to create stable emulsions that present challenges in terms of separation (Nasiri et al., 2017).

2.2.5. Production solids

Production solids are a diverse group of materials that include formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes. Sulfides (polysulfides and hydrogen sulfide) are created in anoxic-produced water by the bacterial reduction of sulfate. Few microorganisms can survive in PW due to the presence of various toxic chemicals. Bacteria can clog or corrode equipment and pipelines. The suspended solids (SS) in PW contain some inorganic crystalline substances such as SiO_2, Fe_2O_3, Fe_3O_4, and $BaSO_4$ (Fakhru'l-Razi et al., 2009). Their concentration varies depending on the platform. The solids generated during oil production could cause serious problems. Common scales and bacteria, for example, can clog flow lines, resulting in oily sludge and emulsions that must be removed (Igunnu & Chen, 2014). The quantities of solid substances present in PW exhibit considerable variation across different sites, primarily influenced by the condition of the wellbore and formation. The presence of solids in PW plays a crucial role in determining its overall characteristics and properties (Liang et al., 2018).

It is crucial to thoroughly examine various factors that influence the production volume of PW to enhance global PW management. These factors include the technique employed for well drilling, the geographical placement of the well, the diverse types of completion methods, the water separation technologies utilized, the implementation of water injection or water flooding for improved oil recovery (EOR), the presence of inadequate mechanical integrity, underground communication, and other related aspects. By investigating these factors, a comprehensive understanding can be gained, leading to more effective management strategies for PW on a global scale (Nasiri et al., 2017, Liang et al., 2018).

2.3. Produced water management

PW is regarded as oilfield waste. PW management, whether waste or commodity, comes at a cost (Fakhru'l-Razi et al., 2009).

Several factors drive the need for effective management techniques when it comes to PW. These factors include the scarcity of local water resources, the presence of legislation governing water management practices, the potential risk of formation plugging, the expensive nature of disposing of PW, the quality of water used in enhanced oil recovery processes, and the growing demand for water in production operations. In order to safely and responsibly dispose of PW through deep well injection or discharge into surface water, it is necessary to treat the water to remove any dispersed and dissolved oil, solids, and toxic compounds that may be present (Dores et al., 2012, Hussain et al., 2014). The PW was managed in the most convenient or least expensive way possible. the selection of a management option for PW is influenced by a variety of factors, including (Jiménez et al., 2018):

- the water's chemical and physical properties,
- flowrate
- end-use
- regulations
- technical feasibility
- Economic feasibility.

A pollution prevention hierarchy with three tiers is implemented to manage the PW. The first tier focuses on minimizing the amount of water produced by utilizing technologies that adapt, modify processes, or substitute products to generate less water. This approach not only has the potential to save operators money but also safeguards the environment. The second tier involves the effective recycling or reuse of water. Once treated, the PW can be reused or recycled through methods such as injection for enhanced recovery, injection for future use, agricultural use, industrial use, or even for drinking water purposes. If neither of these tiers is feasible, the third tier involves disposal as the only remaining option. Discharge, injection, evaporation, and off-site commercial disposal are among the methods used for disposing of PW. Some of these methods require treatment of the PW, while others do not (Fakhru’l-Razi et al., 2009, Jiménez et al., 2018, Onyems Igwe & AL Saadi, 2013, Veil, 2011).

Some of the potential options for managing PW include (Gulistan, 2014):

- Discharge
- Injection (into the same formation from which oil has been extracted or another formation)
- Reuse in oil and gas operations
- Consume for beneficial purposes.

2.4. Effect of PW on the environment

The recent discharge of untreated PW has emerged as a critical environmental concern, primarily due to the diverse array of chemical constituents that may be present in such water. These chemicals, whether acting independently or in combination, can exert profound effects on the environment, leading to disruptions in the physiological and behavioral patterns of aquatic organisms, bioaccumulation of harmful substances, and the degradation of physical habitats. Historically, PW from oil extraction was often disposed of in expansive evaporation ponds, a practice that resulted in the release of VOCs into the atmosphere, including compounds that contribute to ozone formation. Elevated ozone levels, exceeding established air quality standards, are linked to various respiratory ailments in humans. The ecological consequences of PW on marine life are contingent upon the specific chemical constituents and their concentrations, as well as the characteristics of the discharge point and the hydrological conditions of the receiving environment. Furthermore, the application of PW with high concentrations of salts and hydrocarbons for soil irrigation adversely impacts soil health by clogging pores and destabilizing the soil ecosystem. Additionally, the presence of hydrocarbons in PW released into streams significantly affects the biodiversity of marine communities, as such discharges often create a surface oil layer that impedes oxygen transfer within aquatic ecosystems (Wang et al., 2012, Fakhru’l-Razi et al., 2009, Li et al., 2021, Al-Kindi et al., 2022, Onyems Igwe & AL Saadi, 2013).

Industries such as petroleum refineries consistently produce substantial quantities of wastewater laden with high concentrations of phenolic compounds and other hydrocarbons. These phenolic substances represent a major category of pollutants found in refinery effluents and are recognized for their resistance to biological degradation.

In the context of offshore drilling, PW is frequently discharged directly into the surrounding aquatic environment. The organic and inorganic constituents present in PW exhibit greater toxicity than crude oil itself. The introduction of these hazardous substances into aquatic ecosystems threatens both marine life and agricultural resources by disrupting the natural balance of these environments. Numerous studies have indicated that oil field-produced wastewater can adversely affect the environment in various ways, including the deflection of clay due to excessive sodicity, harm to plant life resulting from dehydration and increased soluble salts, damage to aquatic ecosystems through reduced oxygen levels, plugging of deep formations caused by suspended solids leading to elevated injection pressures and decreased flow rates of injected PW, and the negative effects of chemical additives such as corrosion inhibitors and hydrogen sulfide scavengers**.** Improving the environmental sustainability and friendliness of processing industries requires implementing wastewater treatment methods that aim to eliminate phenolic compounds and other pollutants. This approach is crucial for reducing the ecological harm associated with the release of wastewater generated by various processing sectors, including petroleum refineries (College et al., 2014, Gazali et al., 2017, Abbas et al., 2021).

2.5. Produced water treatment technology

Treatment of PW has been tried and proven to be an effective method of handling PW. Studies to identify, validate, and compile existing and newly developed techniques demonstrate the cost-effectiveness of PW treatment. PW treatment is a viable option for managing PW. Instead of being a waste, treated PW has the potential to be a valuable product (Arthur et al., 2005). The treatment options are primarily determined by the water's quality and ability to meet the regulatory limits established for the purposes for which it is reused. The standards, regulatory constraints, and volume generated will determine the treatment objectives (Hameed & Abbas, 2021).

The following are the general goals for operators when planning production water treatment (Arthur et al., 2005, Fakhru’l-Razi et al., 2009):

- De-oiling entails removing free and dispersed oil and grease from PW.
- Removal of dissolved organics (soluble).
- Disinfection: the removal of bacteria, microorganisms, algae, …

- Removal of suspended solids: involves the removal of suspended particles, sand, turbidity, …
- Dissolved gas removal entails the removal of light hydrocarbon gases, carbon dioxide, hydrogen sulfide, and other dissolved gases.
- Desalination or demineralization involves removing dissolved salts, sulfates, nitrates, contaminants, scaling agents, and other impurities.
- Softening: removal of excess hardness from water
- Removal of NORM

The selection of the treatment method for PW is often a complex issue that is influenced by the overall treatment goal. The primary objective is to choose a method that is both cost-effective and efficient. In order to achieve these objectives, operators have traditionally employed a stand-alone or combination of physical, biological, and chemical treatment methods for PW management and treatment. These combined treatments, which involve less energy-intensive processes, have been utilized to enhance the quality of water in accordance with regulatory standards. In the oil and gas industry, a variety of treatment methods are currently being employed with the aim of removing significant amounts of pollutants from PW before it is either disposed of in the sea or reused for purposes such as re-injection, irrigation, wildlife consumption and habitat, and industrial water (Nasiri et al., 2017, Olajire, 2020).

2.5.1. Chemical treatment

2.5.1.1. Precipitation

PW often undergoes precipitation, which is a widely employed chemical treatment technique. This particular method can remove a significant portion of suspended and colloidal particles, with the potential to remove as much as 97% of them (Al-Ghouti et al., 2019, Abbas et al., 2021). Coagulation and flocculation were used to remove the suspended solids and colloidal particles (Duraisamy et al., 2013). Various substances were employed in the treatment of the PW, including modified hot lime, FMA (a mixed metal polymer), Spillsorb, calcite, and ferric ions. FMA, which is composed of inorganic mixed metals such as iron, magnesium, and aluminum, proved to be particularly advantageous due to its ability to remove oil, promote coagulation, and inhibit scale formation. This compound exhibited significant efficacy in treating PW with elevated levels of suspended solids, achieving a remarkable 92% removal of SS and 97% removal of oil (Jiménez et al., 2018).

Lime exhibits superior capability in removing suspended solids compared to alternative chemicals, making it a highly efficient option. Additionally, lime proves to be a cost-effective chemical solution. In the treatment of PW from oil and gas fields, the removal of contaminants such as arsenic, hydrocarbons, and mercury has been successfully achieved through the utilization of flocculants, oxidants, and ferric ions. These substances play a crucial role in the effective purification of the water, ensuring the removal of harmful substances and promoting environmental sustainability (Gulistan, 2014).

2.5.1.2. Chemical oxidation

The process involves the utilization of potent oxidizing agents, exposure to radiation, and the presence of a catalyst to achieve the conversion of organic constituents into their most stable oxidation states through oxidation (Duraisamy et al., 2013). The application of this technology is commonly employed for the removal of COD, BOD, odor, color, organic compounds, and certain inorganic substances from PW, resulting in an almost perfect water recovery rate. Moreover, various factors play a significant role in determining the rate of oxidation in this technology, such as the dosage of chemicals, the type of oxidant utilized, the quality of the raw water, and the duration of contact between the water and the employed oxidant (Al-Ghouti et al., 2019, Abbas et al., 2021).

The primary benefits of this treatment method include a minimal need for equipment, the absence of waste generation, no necessity for pretreatment processes, and the capability to attain nearly a complete water recovery rate. Conversely, the significant disadvantages encompass elevated chemical costs, the requirement for regular maintenance and calibration of the chemical pump, and the generation of byproducts during the process that are challenging to eliminate. AOP represents a significant advancement in the domain of water treatment, offering an efficient method for the rapid oxidation of organic contaminants through the incorporation of various oxidants or their combinations. This technique employs chemical oxidizers such as ozone, iron, and hydrogen peroxide to facilitate the degradation of pollutants. Additionally, the treatment process incorporates hydroxyl radicals, utilizing compounds like zinc oxide, titanium dioxide, and iron oxide to enhance its effectiveness (Al-Ghouti et al., 2019).

2.5.1.3. Photocatalytical treatment

Advanced oxidation processes (AOPs) are increasingly employed in wastewater management due to their cost-effectiveness and superior efficiency in eliminating hazardous contaminants. Titanium dioxide (TiO2) is frequently utilized in the treatment of wastewater from the printing and dyeing industries, owing to its exceptional photocatalytic properties and its environmentally benign nature. Research has demonstrated that semiconductor photocatalysis utilizing TiO2 represents a viable and effective approach for the treatment of wastewater generated from oil and gas operations, ensuring compliance with regulatory standards (Liu et al., 2021). Pollutant removal is accomplished through the photocatalytic decomposition of water on TiO2 electrodes. The following is the general procedure for the photocatalytic treatment of organic pollutants:

$$\text{Organic pollutants} + O_2 \xrightarrow{\text{semiconductor, hv}} H_2O + CO_2 + \text{minerals acids}$$

Soda addition was used to raise the pH of oilfield-produced water before a photocatalytic reaction in a proposed process. The supernatant was filtered after flocculation and settling (Fakhru’l-Razi et al., 2009). Photoelectrocatalysis was found to be more efficient at COD removal and toxicity reduction than photocatalysis (Duraisamy et al., 2013).

2.5.1.4. Electrochemical process

While this method has been extensively applied in the treatment of various types of wastewater, its application in the treatment of PW remains limited. Nevertheless, this approach is increasingly being proposed as a promising technology for future PW treatment. The primary benefits of this technology, in comparison to other treatment methods, include its cost-effectiveness and environmentally friendly nature, as it does not require additional chemicals and does not produce secondary waste. Moreover, it demonstrates high efficiency in the removal of organic compounds, contributes to energy production and conservation, and facilitates the recovery of valuable resources from PW without causing environmental harm. In a study focused on the removal of organics from oilfield-produced water, a catalytic electrochemical pilot-scale plant was established, utilizing iron as the cathode material, double anodes composed of graphite and active metals, along with a noble metal catalyst featuring a large surface area. The findings indicated a significant reduction in COD and BOD, exceeding 90% within a mere six minutes.

As a byproduct of the process, Mn^{2+} is generated, which aids in the oxidation and coagulation of the organic contaminants (Duraisamy et al., 2013, Al-Ghouti et al., 2019, Fakhru'l-Razi et al., 2009). Electrochemistry, a field that focuses on enhancing chemical reactions through the utilization or production of electricity, presents itself as a cost-effective and environmentally friendly technology in comparison to alternative methods of treating PW. This approach eliminates the generation of secondary waste, eliminates the need for supplementary chemicals, and enhances the advantageous applications of the treated water (Jiménez et al., 2018, Al-Ghouti et al., 2019).

2.5.1.5. Treatment with Ozone

The process of ozonolysis involves the treatment of PW through the breakdown of dissolved organic compounds using ozone. While certain compounds like BTEX can be effectively destroyed through sonochemical oxidation, the combination of ozone and hydrogen peroxide does not enhance the oxidation of organic substances into CO_2 (Fakhru'l-Razi et al., 2009). The ozonation process involves the occurrence of both direct and indirect oxidation reactions. Ozone (O_3) can engage in slow, direct reactions with organic substrates owing to its significant reduction potential. Additionally, it can be classified as an AOP when it decomposes to produce hydroxyl radicals. However, a notable drawback of utilizing O_3 in wastewater treatment is its cost; the generation of O_3 necessitates considerable energy input, rendering it an expensive oxidant (Jiménez et al., 2018).

2.5.1.6. Fenton process

The Fenton oxidation adsorption process encompasses two distinct stages, namely, flocculation and settlement. Through this process, the COD of the PW was effectively reduced from an initial concentration of 93.1 mg/L to only 5 mg/L. Similarly, the oil content was significantly diminished from 2634 mg/L to trace amounts of 100 mg/L. To achieve this, poly-ferric sulfate was employed as the flocculent, with a settling time of 30 minutes. The process was conducted under specific operational conditions, including a pH range of 3–4, utilization of 30% H_2O_2 at a volume of mL/L, a Fe^{3+} to H_2O mass ratio of 4%, an oxidation time of 120 minutes, and an active carbon dose of 4000–5000 mg/L with an adsorption time of 120 minutes (Fakhru'l-Razi et al., 2009). The integration of flocculation with the Fenton oxidation adsorption technique enables a significant reduction of approximately 95% in both COD and dispersed oil content.

This innovative approach effectively combines the benefits of flocculation, which promotes the aggregation of particles, with the Fenton oxidation adsorption process, which utilizes the powerful oxidizing properties of Fenton's reagent to degrade organic pollutants. The synergistic effect of these two processes results in a highly efficient treatment method for reducing COD and dispersed oil content, thereby enhancing the overall water quality (Duraisamy et al., 2013).

2.5.1.7. Demulsifies

The alkali/surfactant/polymer (ASP) flooding process involves the utilization of significant quantities of alkali, surfactants, and polymer chemicals. These substances play a crucial role in enhancing the stability of oil droplets, reducing the interfacial tension between oil and water, and modifying the zeta potential on the surfaces of oil droplets (Fakhru’l-Razi et al., 2009). The presence of a protective layer, known as the skin, around small droplets in an emulsion of oil and water plays a crucial role in preventing the coalescence of water droplets and maintaining the stability of the emulsion. Demulsifiers, which are surface-active agents, work by interfering with the effects of surfactants. However, the presence of various solid particles in crude oil, including silts, iron sulfide, and paraffin, adds complexity to the demulsification process and can be utilized to separate emulsions found in PW (Duraisamy et al., 2013, Jiménez et al., 2018).

2.5.1.8. Ionic liquids

Hydrophobic room-temperature ionic liquids efficiently remove certain soluble organic components while being ineffective against other contaminants (Duraisamy et al., 2013). Yet, the low solubility of ionic liquids in the aqueous phase, as well as the difficulty of solvent regeneration, limits the extended use of the ionic liquids tested for the removal of water-soluble organic compounds from an aqueous waste stream (Fakhru’l-Razi et al., 2009).

2.5.2. Physical treatment

2.5.2.1. Filtration

One effective approach to treating wastewater and water involves the utilization of a porous filter within a media system. This filter selectively permits the passage of water while obstructing the flow of impurities. Various porous substances, such as crushed stone, activated carbon, and sand, can serve as suitable filter media. Among these options, sand stands out as the most commonly employed material due to its widespread availability, efficiency, and affordability (Hameed & Abbas, 2021, Al-Ghouti et al., 2019).

To efficiently eliminate metals from PW, various pre-treatment processes may be utilized before the implementation of sand filtration. The pretreatment process consists of three stages: pH adjustment to initiate oxidation-reduction, an aeration unit to enhance the oxygen concentration in the reaction, and a solid separation unit to allow enough time for the settling of precipitated solids. To further remove any remaining fine solids that were not removed during the pretreatment stages, sand filtration will be employed. The application of sand filtration has demonstrated a significant capacity for the removal of COD and nitrogen, resulting in filtered water that is devoid of ammonia and phosphorus. In a novel approach, researchers have integrated a sand filtration method with ozone treatment to enhance the purification of PW. This innovative strategy effectively reduced the oil concentration to 20 mg/l and decreased the COD from 320 mg/l to 102 mg/l. Additionally, sand filtration proved effective in eliminating oil and grease from PW, achieving an impressive removal rate of 95.8 percent (Al-Ghouti et al., 2019, Hameed & Abbas, 2021, Duraisamy et al., 2013).

2.5.2.2. Flotation

Gas bubbles are effectively employed in this technique to separate suspended particles that are resistant to removal through sedimentation. The procedure involves introducing gas into the treated water, causing the suspended particulates and oil droplets to adhere to the air bubbles and ascend to the water's surface, forming a foam layer. This foam layer is subsequently eliminated through skimming. The process can be conducted using various gases such as air, nitrogen, or other inert gases. It is particularly useful for removing volatile organics, oil, and grease from PW. Remarkably, the flotation process has demonstrated an impressive oil removal efficiency of up to 93% (Al-Ghouti et al., 2019, Hameed & Abbas, 2021, Igunnu & Chen, 2014). Gas flotation technology is capable of eliminating particles as small as 25 micrometers and can achieve the removal of contaminants down to 3 micrometers in size when coagulation is employed as a pre-treatment method. However, it is important to note that this process is ineffective in removing soluble oil components from water. The efficiency of flotation is maximized when the size of the gas bubbles is smaller than that of the oil droplets, and it is anticipated to perform optimally at lower temperatures due to the requirement of gas dissolution into the water stream (Igunnu & Chen, 2014).

2.5.2.3. Cyclones separators

Hydrocyclones utilize physical techniques to separate solids from liquids based on the density of the solids being separated. These devices are typically constructed from metal, plastic, or ceramic materials and are characterized by a cylindrical top and a conical base, devoid of any moving components. The liquid is introduced tangentially onto the conical base through a cylindrical section located at the top. The effectiveness and separation capacity of hydrocyclones can be determined by the angle of the conical section.

This system consists of two distinct parts: the underflow or reject stream at the bottom and the overflow or product stream at the top, which is derived from the original stream. Depending on the specific model of hydrocyclone employed, particles within the range of 5 to 15 μm can be effectively removed. Generally, hydrocyclones boast a lengthy operational lifespan and do not necessitate the use of chemical additives in the feedwater. However, they do generate a significant quantity of concentrated solids, which are considered oil field waste. Hydrocyclone systems are compact in design and capable of treating influents at high concentrations. Nonetheless, they are susceptible to issues such as clogging and fouling. Hydrocyclones have been extensively utilized for the treatment of PW and are commercially available from various companies specializing in PW treatment (Nasiri et al., 2017, Igunnu & Chen, 2014, Liang et al., 2018, Veil, 2011).

An Epcon (compact floatation unit) is a three-phase separator that can separate water, oil, and gas. This separation is based on centrifugal force and gas floatation. Treated water drains from the vessel's bottom, and a pipe suspended from the top extract’s gas, oil, and some water. The removal efficiency of the Epcon unit for dispersed oil was only 50–70%. Compact systems with small and light characteristics are preferred in offshore installations due to space constraints (Fakhru’l-Razi et al., 2009, Nasiri et al., 2017).

2.5.2.4. Electrodialysis

Salts that exist in the form of cations and anions can be dissolved in water. These ions possess the capability to adhere to electrodes that possess opposite charges. In the process of electrodialysis, membranes are placed between a set of electrodes, enabling the passage of cations and anions. This technique is particularly suitable for the reclamation of water that has been produced and contains low concentrations of TDS (Fakhru’l-Razi et al., 2009).

The lack of economic competitiveness in ED can be attributed to the exorbitant expenses associated with electrodes and ion exchange membranes. Although ED is primarily used for eliminating inorganic minerals, TDS, and heavy metals, its effectiveness is hindered by various factors. These include fouling and the limited lifespan of the membrane caused by the precipitation of poorly soluble salts consisting of highly insoluble anions (Amakiri et al., 2022).

2.5.2.5. Membrane filtration technology

Membrane technology has been extensively utilized by researchers for various separation processes in PW treatment, employing microporous films characterized by specific pore sizes that facilitate the selective separation of fluids from their constituents. This technology encompasses a spectrum of treatment methods, ranging from basic processes aimed at the removal of suspended solids to advanced desalination techniques, ultimately yielding higher-quality water with reduced sludge production. The membrane separation techniques, which include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), are capable of treating PW to achieve stringent regulatory standards, with membrane pore sizes decreasing in the order of MF (0.1 microns), UF (0.01 micron), NF (0.001 microns), and RO (0.0001 microns). The operational principle of these membrane processes is primarily driven by a pressure gradient, where RO effectively separates dissolved and ionic substances, MF targets suspended particles, UF focuses on macromolecules, and NF selectively filters multivalent ions. While MF and UF can function independently for industrial wastewater treatment, RO and NF are predominantly utilized in desalination applications. The membrane technology employs two distinct filtration methodologies: dead-end filtration, where liquid movement is perpendicular to the filter surface, leading to the accumulation of contaminants that can impair filter performance, and cross-flow filtration, where liquid flows parallel to the filter surface, allowing for a more consistent flow while maintaining a layer of trapped particles. Nonetheless, a significant challenge associated with this technology is fouling, which necessitates increased pressure during operation and periodic chemical cleaning to mitigate its effects. A fouled membrane can exhibit diminished productivity, selectivity, and flux, potentially resulting in a substantially reduced operational lifespan (Igunnu & Chen, 2014, Jiménez et al., 2018, Duraisamy et al., 2013, Hameed & Abbas, 2021, Abbas et al., 2021, Olajire, 2020, Salem & Thiemann, 2022).

2.5.2.6. Adsorption

Adsorption is a highly effective method for improving water quality, as it can retain pollutants in the final effluents at concentrations as low as parts per billion (ppb) and even lower. Various adsorbents, such as organoclays, zeolites, chitosan, and activated carbon, can be employed to achieve adsorption. However, the performance of these adsorbents is influenced by several factors, including pH, temperature, suspended oil levels, metal concentrations, salinity, and dissolved contaminants.

Adsorption technology is particularly useful for removing manganese, iron, total organic carbon (TOC), BTEX, and heavy metals from PW while simultaneously achieving almost complete water recovery. It is important to note that adsorption is typically employed as a polishing step in the overall treatment process rather than as a standalone technology due to the potential for adsorbents to become overloaded with organic compounds. Depending on the quality of the feed water and the type of media used, the replacement or regeneration of the adsorbent media may be necessary. Regeneration involves the use of chemicals to unblock the active sites on the media, which often leads to the generation of liquid waste. On the other hand, media replacement results in the management of solid waste (Igunnu & Chen, 2014, Nasiri et al., 2017, Liang et al., 2018, Jiménez et al., 2018).

AC is widely recognized as the most potent adsorbent available. Essentially composed of pure carbon, these solid materials exhibit exceptional capabilities for eliminating various pollutants from contaminated water. This efficacy can be attributed to their distinctive properties, such as high surface reactivity, thermal stability, adsorption ability, extensive surface area, and microporous structure. Despite these advantageous characteristics, the cost of activated carbon hinders its widespread use as an adsorbent on a large scale. Nevertheless, employing activated carbon as an adsorbent remains preferable to alternative techniques for water decontamination due to its cost-effectiveness, simplicity, and efficiency. Moreover, activated carbon can effectively remove not only suspended particles and insoluble free hydrocarbons but also dissolved organic compounds, heavy metals, and radioactive materials (Khader et al., 2022, Al-Ghouti et al., 2019, Gamwo et al., n.d., Agrawal et al., 2017, Ahmaruzzaman & Gupta, 2011, Kumar et al., 2023).

Similar to other adsorption processes, the restoration of activated carbon is imperative after several treatment cycles to restore its pollutant removal effectiveness, which diminishes significantly over time. To achieve this, a range of chemicals, including acids, bases, redox agents, and organic solvents, can be employed for the regeneration of activated carbon. However, this approach leads to the generation of liquid waste and subsequently escalates the overall treatment expenses (Gamwo et al., n.d., Al-Ghouti et al., 2019). Aside from commercial activated carbons, various agricultural wastes such as coconut shells, RH, barley straw, banana peels, etc., have been used as adsorbents to remove oil and organic and inorganic contaminants from various industrial wastewater, such as textile and petroleum industry effluent (Sakhile et al., 2023).

The synthesis of organoclay involves the combination of sodium montmorillonite clay with a cationic quaternary amine salt, resulting in the formation of a modified clay material. When this organoclay is utilized alongside activated carbon, it effectively lowers the concentration of hydrocarbons in water, ensuring compliance with water quality standards. Copolymer beads, on the other hand, are prepared through suspension polymerization using methylmethacrylate (MMA) and divinylbenzene (DVB) as the primary monomers. These copolymers exhibit the ability to significantly reduce the oil content present in PW, achieving a reduction of approximately 85%. This demonstrates their potential as effective agents for oil removal in water treatment processes (Fakhru’l-Razi et al., 2009). Researchers have studied the use of eggshells as a biosorbent to remove oil from PW. The eggshell was prepared in a manner that enhanced its ability to effectively absorb oil in its original state. Experimental studies on biosorption using the eggshell biosorbent demonstrated its potential for removing crude oil from PW, achieving an impressive removal efficiency of nearly 100% when a concentration of 1.8 g eggshell per liter of PW was employed, even at high oil concentrations of up to 194 mg/l (Muhammad et al., 2012).

Barley straw, an agricultural byproduct, underwent modification through the addition of a cationic surfactant and hexadecylpyridinium chloride monohydrate (CPC). This modified barley straw was then employed as an adsorbent to eliminate oil from oily wastewater. In contrast, a different adsorbent derived from dry banana peels was utilized to remove 194 mg/L of oil within a 35-minute timeframe. Notably, the maximum dosage of banana peels required per liter of PW was determined to be 267 mg (Gulistan, 2014).

Zeolites have a wide range of applications, including their use as ion-exchange resins. In this study, the researchers propose the use of hydrophobic zeolite pellets in a fixed bed to effectively adsorb dissolved organic compounds in the PW. Additionally, they suggest the use of a resin-filled adsorption column as an alternative method for removing soluble organic compounds.

However, it is important to note that the presence of suspended particles in the raw PW can hinder the efficiency of the media in removing these compounds. Furthermore, the regeneration of adsorbers can lead to the generation of chemical waste, which presents a new challenge associated with these methods (Fakhru'l-Razi et al., 2009, Gulistan, 2014). The efficacy of "tailored" zeolites, which are created by adsorbing neutralized amines onto natural zeolites, was investigated as a means of adsorbing BTEX from saline-PW. Following the treatment with ethyleneamine and methylamine zeolites, the levels of BTEX in the PW were significantly reduced, with a minimum reduction of 70% to 85% (Janks & Cadena, 1992).

Offshore-PW underwent a series of adsorption processes utilizing Crudersorb technology and polymeric resins to effectively reduce the concentration levels of oil and grease to less than 29 parts per million (ppm). Crudersorb was responsible for removing suspended and dispersed oil droplets, while the resin effectively eliminated dissolved hydrocarbons, aliphatic carboxylic acids, aromatic carboxylic acids, and phenolic compounds. In a separate process, the surfaces of PET fibers were modified from oleophilic to hydrophilic through grafting with COOH, NH, and OH groups. These modified fibers were then employed to treat oilfield-produced water. The resulting treated effluent exhibited the following characteristics: an oil and grease concentration below 2.4 milligrams per liter (mg/L) and an SS concentration below 2 mg/L (Fakhru'l-Razi et al., 2009, Gulistan, 2014).

2.5.2.7. C-TOUR

C-TOUR, a patented technology, utilizes liquid condensate as an extraction medium to separate dissolved components in PW. This innovative process employs solvent extraction by injecting gas condensate into the PW, effectively extracting hydrocarbons and water-soluble organics. The condensate acts as a solvent, facilitating the extraction of hydrocarbon pollutants from the PW stream. Furthermore, the condensate aids in the coalescence of these pollutants, resulting in the formation of larger and lighter oil droplets.

These oil droplets are then separated from the PW stream either hydraulically or mechanically and can be reused in the oil process streams. The C-TOUR process involves several steps to achieve its objectives. Firstly, a condensate stream from the production process is injected into the PW. This allows for contact between the condensate and water, enabling the extraction process to take place. Subsequently, the contaminated condensate is removed from the water, ensuring the separation of the extracted pollutants. Finally, the contaminant condensate is recycled back into the original production streams, completing the cycle of the C-TOUR process. Field trials conducted with the C-TOUR process have demonstrated its effectiveness in removing various dissolved organics from PW. The removal efficiency for dispersed oil, 2-3 ring PAHs, and NPD was found to be approximately 70%. For C6 phenols, the removal efficiency was around 60%, while for C4-C5 phenols, it was 20%. These results highlight the capability of the C-TOUR process in significantly reducing the presence of these contaminants in PW (Fakhru'l-Razi et al., 2009, Jiménez et al., 2018,Veil, 2011).

The C-Tour technique has proven to be highly effective in eliminating dispersed oil from PW, achieving removal rates between 50% and 70%. Furthermore, it possesses the ability to disperse dissolved organic substances. In comparison to alternative cleaning methods, such as Epcon, C-Tour exhibits superior efficiency in extracting PAHs and BTEX compounds that are present in aqueous solutions. Notably, it has been observed to enhance the discharge of BTEX by 17% relative to other treatment approaches (Ibrahim et al., 2023).

2.5.2.8. Freeze-thaw / Evaporation

The Energy and Environmental Research Centre (EERC) and B.C. Technologies Ltd. (BCT) developed the freeze-thaw-evaporation (FTE) process in 1992 as a reliable and well-established technology for water treatment and disposal. This innovative approach utilizes the principle of temperature-dependent solubility. By employing freezing, thawing, and conventional evaporation, the FTE process effectively manages water resources. The freezing point of salts and other dissolved constituents in PW is lower than that of pure water. Consequently, when the PW is cooled below 32°F without reaching its freezing point, it forms relatively pure ice crystals and an unfrozen solution. The unfrozen solution, which contains a high concentration of dissolved constituents, is separated from the ice.

The ice can then be collected and melted to obtain clean water. The combination of freezing and evaporation in this technology makes it both efficient and cost-effective. However, it does have certain limitations, such as the need for sub-zero ambient temperatures and a large physical space. Despite these limitations, the FTE process is capable of removing more than 90% of heavy metals, total dissolved solids (TDS), volatile and semi-volatile organics, total suspended solids, and total recoverable petroleum hydrocarbons from PW. Moreover, FTE does not require the use of chemicals, infrastructure, or supplies that may restrict its application. It is user-friendly, easy to monitor, and has a lifespan of 20 years. By integrating conventional evaporation into this process, significant quantities of clean solvent can be obtained (Igunnu & Chen, 2014, Jiménez et al., 2018, Duraisamy et al., 2013).

2.5.3. Biological treatment

The biological treatment process is widely recognized as a cost-effective method for eliminating pollutants from wastewater. This process can be carried out under either aerobic or anaerobic conditions, making it an economical choice for bioremediation. Additionally, it is worth noting that PW typically contains microorganisms such as algae, fungi, and bacteria, which can be harnessed for the treatment process. These microorganisms utilize the pollutants present in the water as a source of nutrients for their growth. Several approaches can be employed for the biological treatment of PW, including the use of series reactor tanks and aerobic biological filters. In terms of microorganism sources, researchers have explored microorganisms found in nature, commercially available microorganisms, specific microorganism communities, and biodegradable sewage sludge. Among these, the activated sludge method is the most commonly used for wastewater treatment. In a pilot plant, an oil skimmer was employed to remove oil from the water before it underwent treatment in an activated sludge system. The treatment unit, utilizing naturally occurring microbial growth in an aeration tank, achieved an impressive removal efficiency of 98–99% for total petroleum hydrocarbons (TPH) at a solids retention time (SRT) of 20 days. Furthermore, the use of Basillus sp. under aerobic conditions resulted in a 90% removal efficiency for COD at a concentration of 2600 mg/l in PW.In anaerobic conditions, the microbial group consisting of Rhodopseudomonas, Clostridia, and Methanosarcina was effective in removing COD from PW, achieving a removal rate of 65% (Fakhru’l-Razi et al., 2009, Al-Ghouti et al., 2019, Hameed & Abbas, 2021, Golestanbagh et al., 2016).

2.5.4. Combined system

Various treatments have been described previously for the treatment of PW, but not all of them are suitable for every component. Some treatments may be ineffective or inconvenient for certain groups of components. Therefore, it is often necessary to combine different types of treatments to achieve optimal efficiency in the treatment of PW. For example, a pilot plant was used to treat PW using flotation, sand filtration, and a UF membrane. This combination of treatments successfully reduced the content of suspended solids and oil to less than 1.0 mg/L and 0.5 mg/L, respectively. Additionally, the concentrations of Fe and bacteria met the required standards for discharge or injection into an oil well. In another study, a method involving water softening and RO membranes was used to treat oilfield-produced waters containing boron and solubilized hydrocarbon compounds. This method effectively reduced the boron concentration to less than 2 mg/L. Furthermore, in a process aimed at meeting drinking water quality standards from oilfield-produced water, various physical and chemical pretreatments were proposed, including air flotation, clarification, softening, filtration, and RO. Lastly, a pilot-scale hybrid reverse osmosis process was employed to treat PW for irrigation or discharge to surface waters. This process successfully reduced the conductivity by 98% and TDS by 96%, reaching acceptable levels for irrigation or discharge to surface waters (Fakhru'l-Razi et al., 2009, Jiménez et al., 2018, Duraisamy et al., 2013).

Traditional and biological methods have been widely employed for the treatment of wastewater; however, these methods frequently fall short of the rigorous discharge standards set for the diverse array of organic and inorganic pollutants present. Consequently, there is a pressing need for advanced tertiary treatment methods to effectively meet the specified limits for these contaminants. Techniques such as electrocoagulation, membrane filtration, AOPs, and various electrolytic methods have been utilized in wastewater treatment. Despite their application, these methods exhibit certain drawbacks: electrocoagulation suffers from electrode corrosion and the necessity for continuous chemical and electrical input; membrane processes are hindered by issues of clogging and fouling; AOPs are characterized by high energy consumption and the production of transformation by-products; and electrochemical methods, including anodic processes and electro-Fenton, are often associated with elevated operational costs and the leaching of electrode materials.

In contrast, adsorption stands out as an effective tertiary treatment option, recognized for its operational simplicity, cost efficiency, lower energy demands, versatility in application, and potential for material recycling (Srivastava et al., 2021).

2.6. Adsorption

Adsorption is a well-established and cost-effective technique that has undergone significant advancements in recent years, making it an effective method for enhancing water quality. This process involves the attachment of various substances, such as gases, liquids, dissolved solids, molecules, atoms, or ions, onto the surface of another substance known as the adsorbent. The mechanism of adsorption is governed by attractive forces that bring together a solute, referred to as the adsorbate, and a solid surface, known as the adsorbent. Physisorption and chemisorption are the two main categories into which adsorption is typically divided, based on the strength of the interaction between the adsorbate and the substrate. This interaction has been extensively studied during isotherm and kinetic investigations. The adsorbent material used in this process is typically a porous medium with a large internal surface area, allowing for the formation of a thin film of adsorbate on its surface. The adsorption sites, which are available for the adsorbate to bind to, can be found either on the surface of the adsorbent or within its pores. Consequently, the micro-pore surface area exhibits a significantly higher adsorption capacity compared to the meso-pore and macro-pore surface areas (Yousef et al., 2020, Gulistan, 2014, Gul Zaman et al., 2021).

The effectiveness of the adsorption process is primarily attributed to the properties of the adsorbent, which include a large surface area, significant adsorption capacity, a microporous structure, and unique surface reactivity. However, despite these beneficial characteristics, the adsorption process incurs high costs due to the expensive nature of the adsorbents and the associated regeneration procedures. This has led to an increased interest in the development and application of various alternative adsorbents aimed at removing aromatic compounds from water. Researchers are actively seeking to create adsorbents that are not only effective but also cost-efficient and readily available, particularly those derived from waste materials. Significant research efforts have been directed toward identifying more affordable substitutes, such as bagasse pith, carbonized bark, peat, lignite, soil, chitin, rice husk, rice straw, wood, and fly ash, for the adsorption of phenolic compounds, with varying degrees of success.

The widespread availability of agricultural by-products positions them as promising sources of inexpensive raw materials for natural adsorbents, with rice husk, in particular, being recognized as an effective adsorbent for various metals and basic dyes (Daffalla et al., 2010).

2.6.1. Adsorption isotherm

The adsorption isotherm is a valuable tool for understanding the relationship between the mass of adsorbed adsorbate and the concentration of the sorbent under constant ambient conditions. Various mathematical models have been developed to describe adsorption isotherms, with some based on simplified physical descriptions of adsorption and desorption, while others are purely empirical and aim to correlate experimental data. The isotherm is particularly significant in predictive modeling procedures for the analysis and design of sorption systems. The most commonly used adsorption isotherm models are the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (DRK) models. Among them, the models available in the literature to describe experimental data on adsorption isotherms, the Langmuir and Freundlich models, are the most commonly employed and are the one employed in this study. Different adsorption isotherm models were used to manipulate the sorption capacity uniquely. The sorption capacities were determined by applying the following correlation equation:

$$q_e = \frac{(c_i - c_e)V}{m} \qquad (1)$$

Where-, C_i is the initial adsorbate concentration, C_e is the equilibrium adsorbate concentration, V is the volume of the PW solution used, and m is the mass of the adsorbent (Erhayem et al., 2015, Gulistan, 2014, Piccin et al., 2011).

2.6.1.1. The Langmuir isotherm

The Langmuir isotherm was initially formulated based on investigations into the adsorption of gases onto activated carbon. This model serves to evaluate the adsorption capacity of the adsorbent and posits that the adsorption process takes place on a uniform surface through monolayer sorption, with no interactions occurring between the adsorbed molecules. Furthermore, the model presumes that the energies associated with adsorption are consistent across the surface and that there is no movement of the adsorbate once it has been adsorbed.

Once these active sites become saturated with the sorbate, further adsorption is prevented. The Langmuir isotherm model can be succinctly described as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (2)$$

Where-, q_m is the maximum monolayer adsorption capacity (mol g^{-1}), K_L is the Langmuir constant (L mol^{-1}), q_e is the adsorption capacity (mol g^{-1}) (Tessema et al., 2020, Piccin et al., 2011, Erhayem et al., 2015, Saha & Orvig, 2010). The non-dimensional equilibrium parameter, R_L, is used to describe the fundamental characteristics of the Langmuir isotherm and is determined by a specific definition.

$$R_L = \frac{1}{1 + bC_O} \qquad (3)$$

Where, Co is the highest initial solute concentration, b the Langmuir's adsorption constant (L/mg). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L>1$), linear ($R_L =1$), favorable ($0< R_L <1$), or irreversible ($R_L = 0$) (El-Nafaty et al., 2013, Muhammad et al., 2012).

2.6.1.2. The Freundlich isotherm

The Freundlich isotherm is a practical equation that characterizes the adsorption of substances on heterogeneous surfaces. It is commonly employed to analyze energy systems with heterogeneous surfaces and to describe the process of multilayer adsorption, taking into account the interaction between the adsorbed molecules. The assumptions underlying this model include the occurrence of multilayer adsorption, the non-uniform distribution of adsorption heat and affinity, as well as the presence of a heterogeneous surface. The Freundlich isotherm can be mathematically represented by an equation:

$$\log \mathrm{qe} = \log K_f + \frac{1}{n} \log \mathrm{Ce} \qquad (4)$$

Where-, K_f and n are Freundlich constants, the K_f is adsorption capacity while n is biosorption intensity; qe is an adsorption capacity (mg/g); C_e is an equilibrium concentration (mg/L).

The log qe versus log Ce plot allows determining the Freundlich constants (Tessema et al., 2020, Piccin et al., 2011, Erhayem et al., 2015, Mandal et al., 2019).

2.7. Adsorbent

The process of adsorption is widely recognized as one of the most important traditional methods for purifying and reclaiming PW. Various types of adsorbents, including activated carbons, zeolites, activated alumina, or low-cost materials, can be utilized in the adsorption process. Among these, activated carbon stands out as the most commonly used adsorbent. However, a significant drawback of using activated carbon is its high initial and regeneration costs. In recent years, there has been a growing interest in developing natural adsorbents for the removal of oil from PW (Gulistan, 2014, Khader et al., 2022).

The increasing awareness of environmental pollution has catalyzed significant interest in the production of activated carbons from carbonaceous precursors, as shown in Figure 3, particularly those originating from agricultural waste, which are notably economical (Beker et al., 2010, Srivastava et al., 2021). These agricultural byproducts offer low-cost raw materials for activated carbon synthesis, exhibiting remarkable mechanical strength and significant adsorption capacities. A more advantageous strategy for increasing the value of these materials is to transform them into economical precursors for activated carbon production. This approach not only generates a valuable product for the remediation of contaminated environments but also helps reduce the accumulation of solid waste. One of the main benefits of natural sorbent materials is their cost-effectiveness, as they are easily accessible and can be obtained from agricultural waste and byproducts.

To improve their effectiveness, pretreatment methods are employed that optimize the presence of functional groups, such as hydrophobic properties, and increase pore volume (De Gisi et al., 201, Trinh Trong et al., 2023). These pretreatment techniques may involve physical or chemical modifications of the sorbent materials, where the chemical activation typically involves the impregnation of the precursor with various chemicals, including phosphoric acid, nitric acid, potassium hydroxide, sodium hydroxide, and zinc chloride, while physical activation employs gases such as nitrogen, steam, carbon dioxide, air, or their combinations (Trinh Trong et al., 2023, Beker et al., 2010).

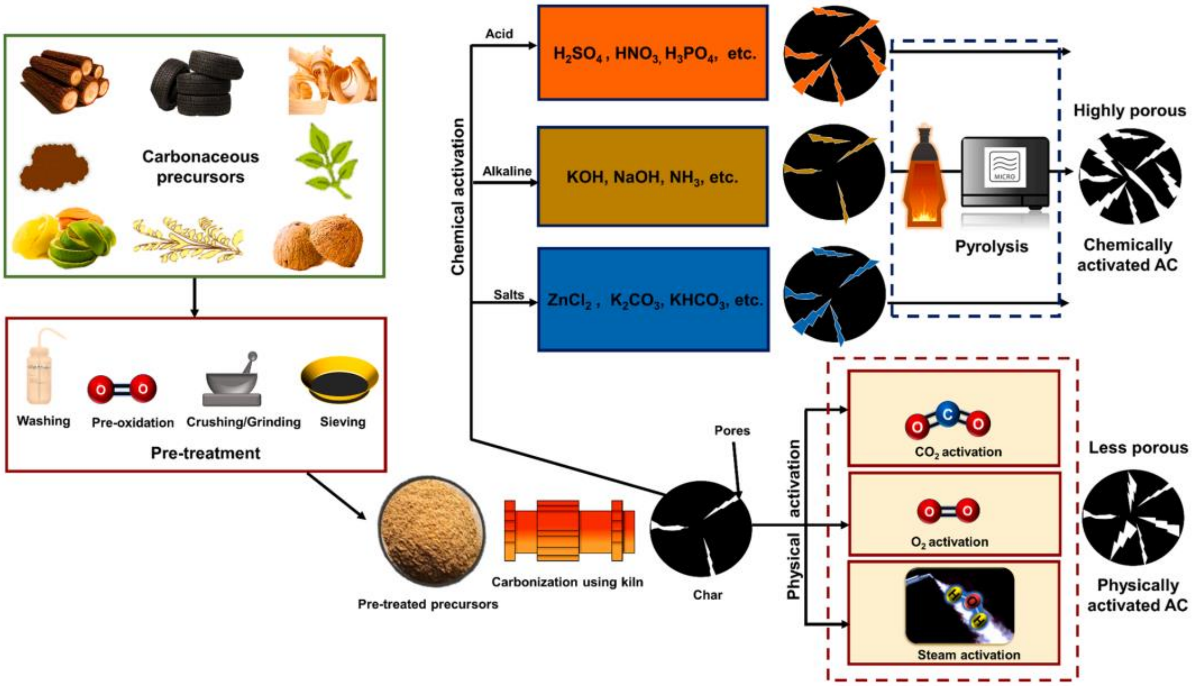

Figure 3. Schematic showing preparation of activated carbon from different carbonaceous precursors(adapted from Srivastava et al., 2021)

2.7.1. Rice husks as a low-cost adsorbent

Rice husk (RH) is a highly important agricultural byproduct, representing approximately 20% of the total weight of harvested rice, with an annual production reaching several tons. Historically, it has been used for landfill and as a source of fuel or biogas; however, recent advances have driven the search for innovative applications for this material. RH's inherent bio-based characteristics, coupled with its renewable and low-cost nature, make it an attractive option for contaminant removal. As a byproduct of the rice milling process, RH can be converted into activated carbon, which is recognized for its efficacy as an adsorbent in water purification and industrial wastewater treatment (Shamsollahi & Partovinia, 2019, Deiana et al., 2008).

The unique morphology of RH, characterized by its irregular surface, enhances its capacity to adsorb metals and other contaminants, allowing for effective adsorption across various regions of the material. Physical analyses have revealed the presence of functional groups, such as carboxyl and silanol, which facilitate adsorption processes, while understanding the chemical structure of RH is essential for comprehending its adsorption capabilities.

RH provides dual environmental benefits—reducing agricultural waste while offering a cost-effective wastewater and air pollution control solution. Its abundance, granular composition, chemical stability, and mechanical strength make it a promising candidate for biosorption applications. Primarily composed of cellulose, lignin, and minerals, RH's composition varies based on rice variety and environmental factors. Its high lignin and cellulose content make it ideal for producing activated carbon with a microporous structure and large surface area, predominantly featuring micropores. This production occurs through either physical (thermal) or chemical activation. The key components responsible for adsorption are carbon and silica (Ahmaruzzaman & Gupta, 2011, Shamsollahi & Partovinia, 2019, Deiana et al., 2008, Noor Syuhadah & Rohasliney, 2012)

Additionally, RH is characterized by a notably high ash content, with silica (SiO2) accounting for 76–99% of its total weight, while other metallic impurities are present in minimal amounts. Furthermore, the properties of RH ash can also differ based on the geographical conditions in which the rice is cultivated (Menya et al., 2018). The chemical composition and physicochemical properties of RH are presented in the table below.

Table 2. Typical composition of rice husks(Shamsollahi & Partovinia, 2019, Abdelwahab et al., 2005, Chuah et al., 2005, Lewoyehu, 2021)

Composition	percent
Cellulose	32.24
Hemicellulose	21.34
Lignin	21.44
Extractives	1.82
Water	8.11
Mineral ash	15.05
Chemical composition in mineral ash	

SiO_2	96.34
K_2O	2.31
MgO	0.45
Fe_2O_3	0.2
Al_2O_3	0.41
CaO	0.41
K_2O	0.08

Table 3. Physicochemical characteristics of rice husks(Chuah et al., 2005)

Characteristics	value
Bulk density (g/ml)	0.73
Solid density (g/ml)	1.5
Moisture content (%)	6.62
Ash content (%)	45.97
Particle size (mesh)	200-16
Surface area (m2/g)	272.5
Surface acidity (meq/gm)	0.1
Surface basicity (meq/gm)	0.45

2.8. Kinetics studies of adsorption

The field of adsorption dynamics focuses on understanding the rate at which solutes are taken up by a solid-solution interface, which in turn determines how long the adsorbate remains at that interface.

Chemical kinetics provides insights into the pathways and timeframes required to reach equilibrium in a reaction. The kinetics of sorption, on the other hand, are heavily influenced by the physical and chemical properties of the sorbent material. Among the various kinetic models, the most commonly observed ones in the context of PW adsorption are the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The pseudo-first-order model suggests that adsorption occurs primarily due to physical forces when it aligns with the experimental data. Conversely, the pseudo-second-order model indicates that the adsorption mechanism is predominantly driven by chemical means when it fits the experimental data well (Saha & Orvig, 2010, Yousef et al., 2020).

2.8.1. Pseudo-first order kinetics model

The Lagergen Model, also referred to as the pseudo-first-order model, can be used to explain the sorption phenomenon that takes place at the interface between a liquid and a solid. This expression is as follows:

$$\frac{d_q}{d_t} = k_1(q_e - q_t) \qquad (5)$$

The solved linear equation is as follows:

$$\ln(\mathrm{qe} - \mathrm{qt}) = \ln \mathrm{qe} - k_1 \mathrm{t} \qquad (6)$$

Where, qe and qt are the adsorption capacities at equilibrium and at time t, respectively, and k_1 is the rate constant of pseudo-first-order adsorption. The values of k_1 and the calculated qe can be obtained respectively from the slope and intercept of the linear plot of $\ln(\mathrm{qe} - \mathrm{qt})$ versus (t) (Saha & Orvig, 2010, Yousef et al., 2020, Abdel-Ghani et al., 2016, Mandal et al., 2019).

2.8.2. Pseudo-second order kinetics model

The assumption made by the second-order kinetic model is that the rate-limiting step primarily involves chemical interactions, which result in the binding of ions to the surface through a bonding mechanism as strong as covalent bonding. The pseudo-second-order equation, derived from the concept of equilibrium adsorption, can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

Where-, k_2 (g/mg min.) is the rate constant of second-order adsorption. Plots of (t/qt) versus (t) give $1/q_e$ as the slope and $1/K_2q_e^2$ as the intercept (Abdel-Ghani et al., 2016, Saha & Orvig, 2010, Mandal et al., 2019).

2.9. Thermodynamic study

Adsorption thermodynamic parameters, including the Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) are instrumental in clarifying the mechanisms and behaviors associated with adsorption at varying temperatures. This investigation was essential for evaluating whether the adsorption process is characterized as endothermic or exothermic, in addition to assessing its spontaneity. Through the analysis of these thermodynamic parameters, significant insights were obtained concerning the energy transformations and the spontaneous nature of the adsorption process across different thermal conditions. The Van't Hoff equation was used to calculate ΔH° and ΔS°:

$$\Delta G^{\circ} = -RTlnK_c \qquad (8)$$

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad (9) ,$$

Where ΔH° (kJ/mol) is the enthalpy change, ΔS° (kJ/mol) is the entropy change, R is the universal gas constant 8.314 kJ/kmolK, and T(K) is the absolute temperature, K_c is the equilibrium constant. The values of ΔH° and ΔS° were calculated from the plot of lnK_c against 1/T, in which a straight line with a slope and intercept of $\frac{\Delta H^{\circ}}{R}$ and $\frac{\Delta S^{\circ}}{R}$ can be obtained, respectively (Yusop et al., 2021, Lin et al., 2013, Hadi et al., 2020, Piccin et al., 2011, Zafar et al., 2020).

CHAPTER 3

RESEARCH METHODS AND STRATEGY

This research is an experimental study on the treatment of PW by using RH as a naturally occurring adsorbent. This chapter serves as a comprehensive summary of the research methodology, approaches, and techniques applied to tackle the research problem and achieve the objectives of this study.

3.1. Materials

RH was obtained from a rice milling company located in Gaza Province, Southern Mozambique, and all chemicals used were phosphoric acid and sodium hydroxide for the chemical activation process, acetic anhydride, pyridine, acetone, and ethanol for the acetylation process. The water used in all experiments was distilled water, and an oven was used for the drying process. Crucible and muffle furnaces were used during the carbonization process. A heating mantle and magnetic stirrer were used for mixing, and a pH meter was used for pH measurement. A sieving machine and a mesh of 75 µm were used to obtain the desired particle size of RH.

3.2. Pretreatment of rice husks

The initial treatment of the RH samples involved multiple washings with distilled water at 50°C to eliminate dust, dirt, and any soluble contaminants. This was followed by a drying process in an oven maintained at 60 °C for 24 hours (Wang et al., 2015). Once dried, the RH was processed using a Retsch ZM 200 mill, and subs passed through a sieve with a mesh size of 75 µm.

3.3. Rice husks activation

Activated carbon can be produced through two primary methods: physical activation and chemical activation. In physical activation, gases like nitrogen, steam, carbon dioxide, air, or their combinations are utilized without the need for a catalyst. On the other hand, chemical activation involves a pretreatment step where the material is combined with a chemical before the activation process. Commonly employed chemicals for this purpose include H_3PO_4, H_2SO_4, KOH, NaOH, and $ZnCl_2$. These methods offer distinct approaches to the production of activated carbon, each with its advantages and applications (Paraskeva et al., 2008).

The process of chemical activation presents numerous benefits in comparison to physical activation, primarily characterized by a reduced activation temperature of less than 500°C, as opposed to the 500–900°C range required for physical activation.

Additionally, chemical activation typically involves a singular activation step, resulting in higher yields, enhanced porous properties, and decreased activation durations (Lewoyehu, 2021). In the context of chemical activation, the use of dehydrating agents promotes the removal of hydrogen and oxygen in the form of water rather than facilitating the release of carbon oxides (COx) and hydrocarbons. This mechanism effectively curtails the loss of volatile substances and tars, resulting in a greater retention of fixed carbon and an enhanced carbon yield relative to physical activation processes. Additionally, the Brunauer–Emmet–Teller (BET) surface area of activated carbon produced through chemical activation surpasses that achieved via physical activation. For example, when RH is subjected to the same activation temperature, the BET surface areas resulting from chemical and physical activation are measured at 750 and 166 m^2/g, respectively (Menya et al., 2018, Alam et al., 2020).

Chemical activation proves to be more effective than physical activation in generating a high surface area, which subsequently enhances the adsorption capacity of agricultural waste materials. Based on these advantages, I chose to use chemical activation over physical activation during the activation of RH.

3.3.1. Chemical activation using sodium hydroxide

A sodium hydroxide solution with a molarity of three was prepared, and RH, which had been processed to a particle size of 75 micrometers, was immersed in this sodium hydroxide solution at a ratio of 1:4 (RH to sodium hydroxide) for 24 hours. Following this impregnation, the mixture was filtered, and the resulting material was thoroughly washed with distilled water before being dried at 105°C overnight. Subsequently, the dried material underwent carbonization in a muffle furnace at a temperature of 450°C for 2 hours (Saad et al., 2020).

3.3.2. Chemical activation using phosphoric acid

A 3M phosphoric acid solution was prepared, into which 100 grams of RH, previously sieved to a particle size of 75 micrometers, were submerged in $1dm^3$. This mixture was subjected to heating on a magnetic stirrer at a temperature of 80°C for three hours. Following the impregnation process, the sample underwent filtration, was rinsed with distilled water, and was subsequently dried at 100°C for 24 hours. The resulting dried sample was then carbonized in a muffle furnace at 450°C for two hours (Cheenmatchaya & Kungwankunakorn, 2014).

3.3.3. Acetylation of rice husk

In a round-bottom flask, a sample of carbonized RH was combined with pure acetic anhydride and a pyridine catalyst at a concentration of 5% w/w. The solid-to-liquid ratio was maintained at 1 g per 20 mL, and the apparatus was operated under atmospheric pressure. The mixture was heated to 100 °C and refluxed for three hours. Upon completion of the reaction, the hot reagent was decanted, and the acetylated carbonized rice husks were thoroughly washed with ethanol and acetone to eliminate any unreacted acetic anhydride and the byproduct acetic acid. Following this, the acetylated carbonized rice husks underwent a drying process in an oven at 60 °C for 16 hours (Sun et al., 2002, Wang et al., 2020, Teli & Valia, 2013, Sun et al., 2004)**.** Figure 4 summarizes all the processes of preparing the adsorbent from raw rice husks.

Figure 4. Schematic of adsorbent preparation

3.3.4. Characterization of adsorbent

3.3.4.1. The Proximate Analysis

3.3.4.1.1. Ash content determination

The assessment was conducted by the ASTM standard protocol E-1755-01. A mass of 1 gram of dry biomass was accurately measured and placed into a crucible, which was subsequently positioned in a muffle furnace (specifically, the Termolab—Electric Ovens, MLM model). Following the established procedure, the sample was initially subjected to a temperature of 250ºC, with a controlled heating rate of 10ºC per minute, and this temperature was sustained for 30 minutes. Thereafter, the temperature was elevated to 575ºC, where it was maintained for approximately 15 hours to ensure complete combustion of the carbon content. Upon completion of the heating process, the samples were allowed to cool before being weighed, and the ash content was calculated using the designated Equation (10).

$$Ash\ content\ \% = \frac{m_2 - m_1}{m_o} \times 100 \tag{10}$$

Where, m_2 represent the mass of the crucible containing ash after burning (g), m_1 is the mass of the empty crucible (g), and m_0 stands for the mass of the sample at the beginning (g).

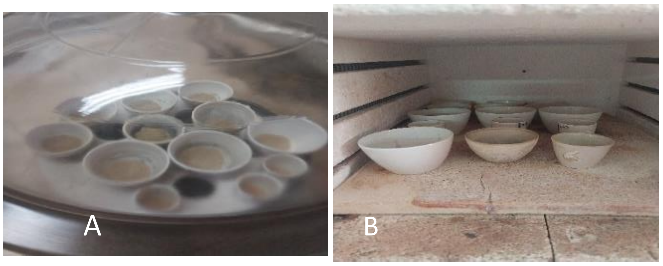

Figure 5: Ash content: (A) Crucible holding sample in a desiccator, (B) Crucible in the muffle

3.3.4.1.2. Volatile content

The assessment of volatile content was conducted by the ASTM E-872 standard, which involves the burning of biomass at a specified temperature of 950ºC within a muffle furnace (Termolab brand—Electric Ovens, MLM model). In this procedure, a biomass sample weighing precisely 1 g is placed in each crucible, which is subsequently introduced into the muffle furnace. The process is maintained at a stable temperature of 950ºC for a duration of 7 minutes. The calculation of the volatile content was performed using equation (11).

$$Volatile\ content(\%) = \left(\frac{m_0 - m_f}{m_0}\right) \times 100 \qquad (11)$$

Where, m_f stands for a mass of residual after burning (g) (mass of crucible with the sample after burning minus the mass of empty crucible), and m_0 is the mass of the sample at the beginning (g).

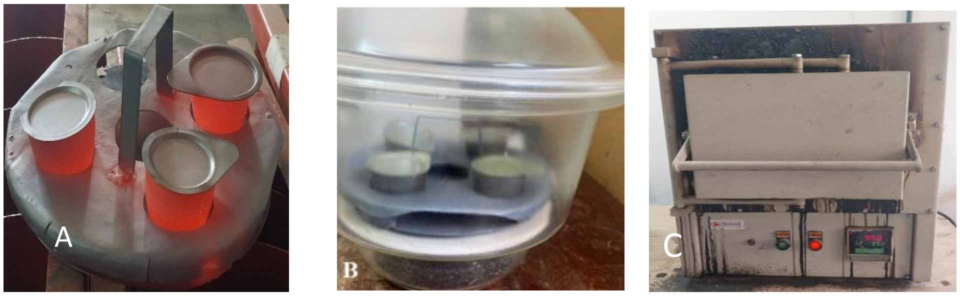

Figure 6: Volatile content: (A) Nickel crucible after being removed from the muffle, (B) Nickel crucible in the desiccator, (C) Muffle

3.3.4.1.3. Moisture content

Moisture content, defined as the mass of water present in biomass, can be quantified on both wet and dry bases. In this study, the moisture analyser Sartorius model MA 35 was employed to assess the moisture content of the samples in their unaltered condition. This apparatus features a weighing unit where 2 grams of the sample are placed alongside a halogen heating unit, which facilitates the drying of the sample at a temperature of 105ºC. The determination of moisture content is achieved through the method of loss by drying, which involves measuring the mass of moisture in the sample and relating it to the overall weight of the sample, thereby calculating the percentage of moisture contained within it.

Figure 7: Moisture analyser

3.3.5. Adsorption study

An experiment was conducted to investigate the adsorption of copper and phenol using rice husks as the adsorbent material. This study focused on phenol and copper, among other contaminants of PW, because they are among the toxic ones, and they were available in the laboratory. According to Aksu & Işoğlu, (2005) and Zhang, (2021), a simulated PW solution was created, which involved the preparation of a 1000 ppm copper stock solution by dissolving 3.93 grams of $CuSO_4 \cdot 5H_2O$ in one liter of distilled water, alongside a 1000 ppm of phenol stock solution. Standard solutions for both copper and phenol were subsequently prepared through the dilution of these stock solutions. The adsorption experiments for phenol and copper were performed utilizing a UV-vis spectrophotometer with measurements taken at wavelengths of 270 nm for phenol and 610 nm for copper. Calibration curves, illustrated in the accompanying Figure 8, serve to elucidate the correlation between pollutant concentration and absorbance. These curves facilitate the transformation of recorded signals into accurate measurements of pollutant concentrations.

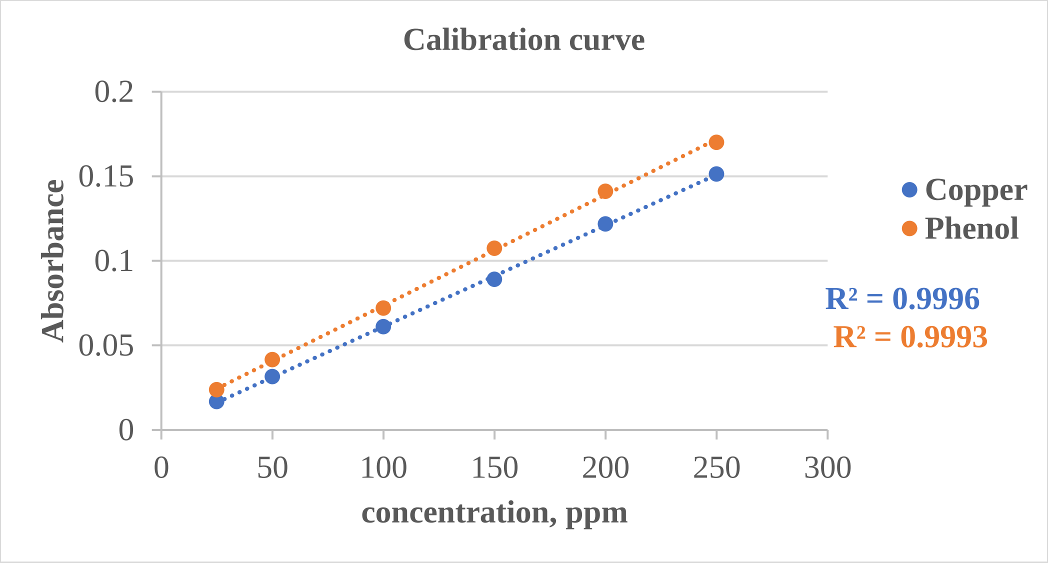

Figure 8: Calibration curve of phenol and copper

In this study, a 250-ml beaker was employed, which was subsequently filled with PW. The concentration of the prepared adsorbent to PW was systematically varied, and the beaker was positioned on a magnetic stirrer. The temperature for the experiment was consistently maintained at room temperature.

The effect of operating parameters, including contact time, temperature, initial concentration of pollutants, and adsorbent dosage, was investigated by varying one parameter and keeping the other parameters constant at the same time, which aimed to evaluate the effectiveness of RH adsorbents in the treatment of PW (Al-Zuhairi et al., 2019). The amount of copper and phenol absorbed and the percentage removal of copper and phenol were measured by the following equation:

$$\%\ \mathrm{R} = \frac{(C_0 - C_t) \times 100}{C_0} \tag{12}$$

$$Q_t = \frac{(c_i - c_t)V}{m} \tag{13}$$

where C_o is the initial concentration (mg/L), C_t is the concentration at time t (mg/L), %R is the removal percentage of pollutants, Qt is copper and phenol absorbed at a given time, V is a Volume of sample solution (L), and m is mass of adsorbent (g).

CHAPTER 4.

RESULTS AND DISCUSSION

This chapter provides a comprehensive overview of the outcomes derived from the experimental investigations undertaken. It details the presentation and analysis of the findings obtained during the research process, emphasizing the characterization of the prepared adsorbent. Additionally, the chapter examines the impact of various operating parameters, aiming to elucidate how alterations in these parameters influence adsorption efficiency.

4.1. Characterization of adsorbents

4.1.1. The Proximate Analysis

In this study, the rice husk sample underwent characterization through proximate analysis, which assessed its ash content, moisture content, and volatile matter. The results of the proximate analysis indicated a moisture content of 6.29%, an ash content of 32.78%, and a volatile matter percentage of 53.88%. Previous studies have reported varying results; for instance, (Braga et al., 2014) found a moisture content of 8.09±0.04%, an ash content of 34.6±0.06%, and a volatile matter percentage of 52±2% in rice husk. Additionally, (Bari et al., 2022) conducted proximate analysis at different temperatures, revealing an ash content of 21.82% at 500°C and 21.91% at 700°C, while the volatile matter was measured at 63.22% at 500°C and 63.81% at 700°C. Furthermore, (Rhaman et al., 2015) reported an ash content of 22.3%, a moisture content of 11.2%, and a volatile matter percentage of 51.9% in their analysis. The obtained results and the ones from the literature show a slight difference, which may be due to RH composition, which varies based on paddy type, rice variety, fertilizer type, soil chemistry, climate, and geographical location (Shamsollahi & Partovinia, 2019).

4.2. Adsorption studies

4.2.1. Effect of raw RH and modified RH on phenol and copper removal.

Figure 9 illustrates that unmodified RH exhibited the lowest efficiency in removing copper and phenol, with respective efficiencies of 29.56% and 17.91%. Notably, the performance of unmodified RH was superior in removing copper compared to phenol, attributed to the stronger electrostatic forces, ion exchange capabilities, and enhanced pore penetration that facilitate copper adsorption. In contrast, the weaker interactions and higher solubility of phenol hinder its effective adsorption.

Conversely, the modified forms of RH, specifically acetyl-RH-H_3PO_4 and acetyl-RH-NaOH, showed significantly improved performance in removing both contaminants, achieving efficiencies of 77.11% for copper and 80.7% for phenol. The marked increase in phenol and copper removal efficiencies following the modification of RH can be linked to enhanced basicity and hydrophobicity, which favorably influence phenol adsorption due to its polar hydroxyl groups, despite the lack of strong chelation mechanisms that are effective for copper.

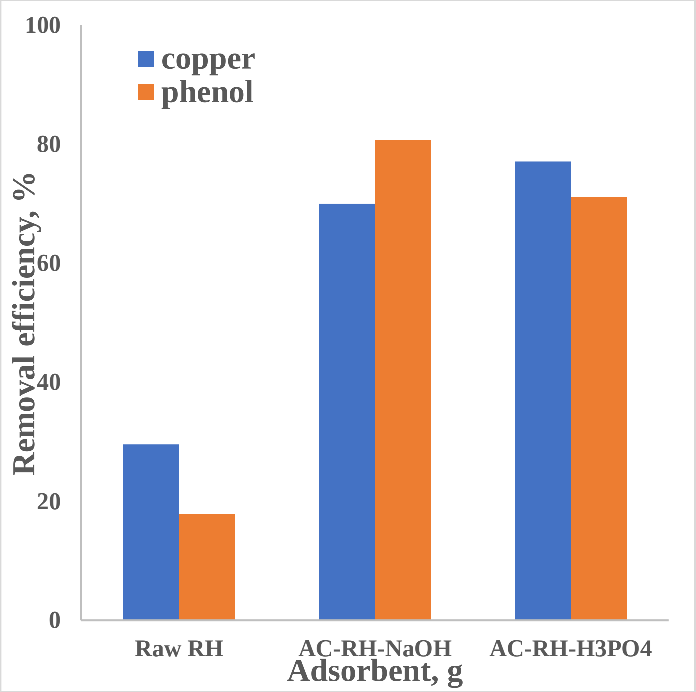

Figure 9: Effect of raw RH and modified RH in the removal of phenol and copper

4.2.2. Effect of adsorbent dosage

The adsorbent dosage is a critical factor that significantly affects the adsorption process by influencing the adsorbent's capacity to capture contaminants. An increase in the adsorbent quantity enhances the efficiency of contaminant removal as it provides more active sites for the sorbate to adhere to. Nevertheless, beyond a certain threshold, the addition of more adsorbent leads to the establishment of adsorption equilibrium, where any further increase may not enhance removal efficiency and could potentially diminish it due to interactions among the adsorbent's active sites. Once the optimal dosage of the sorbent is achieved, a balance between the sorbate and sorbent is established under the given operational conditions (Chakraborty et al., 2011, Razavi et al., 2015, Montalvo-Andía et al., 2022).

As shown in Figure 10, this study demonstrated that the removal efficiency for copper and phenol improved significantly with increasing adsorbent dosage. At a constant initial concentration (50 ppm for copper and 40 ppm for phenol) and room temperature, maximum removal efficiencies were observed at 1 g for copper (91.33%) and 0.8 g for phenol (93.57%). Beyond these optimal dosages, additional adsorbent led to minimal changes in efficiency, likely due to the aggregation of adsorbent particles, which reduced the available active surface area. These findings align with the broader literature. (Tabana et al., 2020), a sharp increase in phenol removal efficiency was observed with increasing the clay loading from 5 g/L (68%) to 10 g/L (83%). Similarly, Ozsoy and Kumbur, (2006) found that copper removal efficiencies increased from 29.4% to 78.3% as adsorbent dosage rose from 1 to 10 g/L, highlighting the importance of optimizing dosage for specific conditions. Meena et al. (2005) reported similar trends for heavy metals, emphasizing the balance between maximizing adsorption efficiency and minimizing material usage. The rapid initial increase in removal efficiency with dosage reflects the availability of abundant active sites. However, as saturation approaches, additional adsorbent fails to significantly contribute to adsorption due to limited adsorbate molecules available for interaction. This trend is consistent with equilibrium conditions observed in isotherm studies, as reported by Mandal et al. (2019). This underlines the importance of careful dosage optimization to ensure cost-effective treatment while minimizing resource wastage.

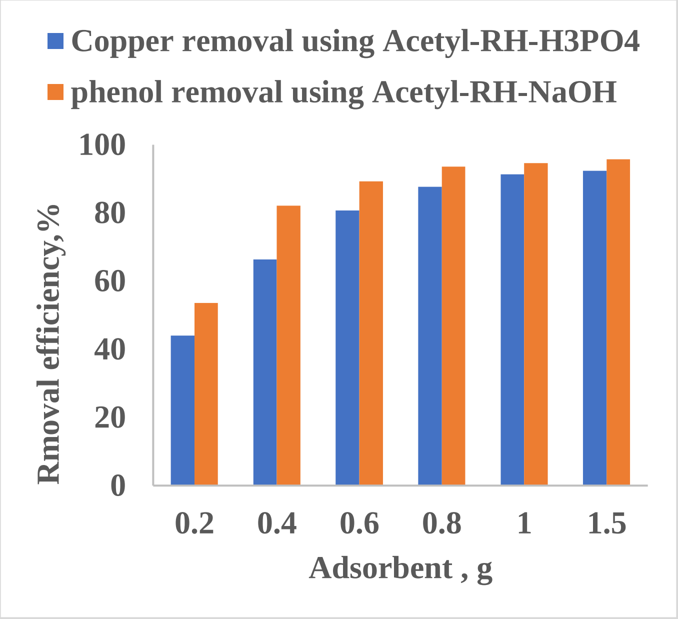

Figure 10: Effect of adsorbent dosage

4.2.3. Effect of temperature

As shown in Figure 11, the effect of temperature on adsorption was evident, with removal efficiencies of phenol and copper improving as the temperature increased from 303K to 393K. The optimum point for the removal efficiencies of phenol and copper were achieved at 333K, indicating the endothermic nature of the adsorption process. This trend suggests that higher temperatures enhance the kinetic energy of adsorbate molecules, promoting their interaction with the adsorbent surface and potentially activating additional adsorption sites. The observed temperature dependence corroborates previous studies. Mandal et al. (2019) reported improved phenol removal at higher temperatures due to increased chemical interaction between the adsorbate and the adsorbent. Similarly, Meena et al. (2005) and Zafar et al. (2020) noted improved adsorption capacities for heavy metals and copper at elevated temperatures, suggesting that increased kinetic energy facilitates faster adsorption rates and potentially creates new active sites. Temperature-sensitive processes, such as this one, offer opportunities for optimization in industrial applications. Controlled heating can enhance adsorption performance, particularly when integrated with energy recovery systems to offset operational costs.

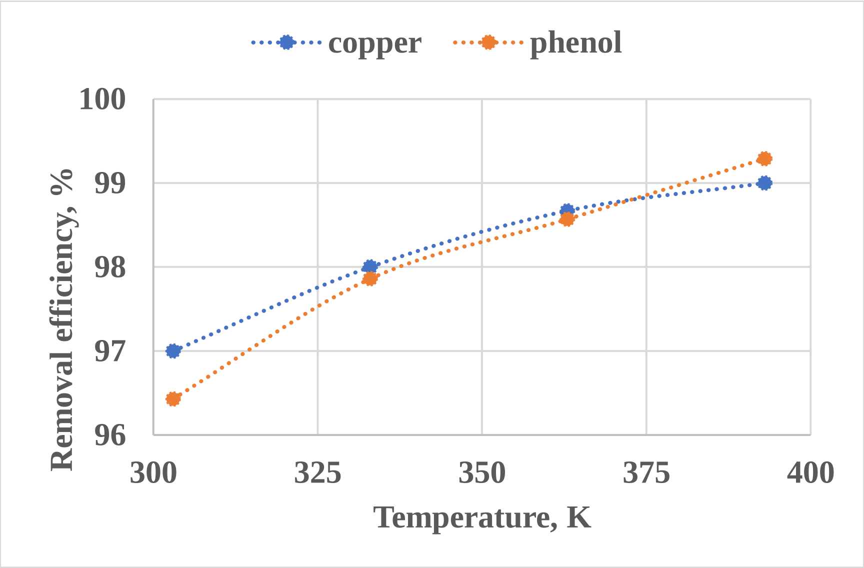

Figure 11: Effect of temperature

4.2.4. Effect of initial concentration

The study revealed an inverse relationship between removal efficiency and initial adsorbate concentration. While the adsorption capacity increased with higher concentrations (50-150 ppm for copper, 40-150 ppm for phenol), removal efficiency declined, as illustrated in Figure 12. This is because, at higher concentrations, the fixed number of active sites on the adsorbent becomes saturated, leading to competition among adsorbate molecules and incomplete removal. This behavior is corroborated by studies such as Aksu & Işoğlu (2005), who reported a decrease in copper biosorption yield from 45.9% to 11.0% as the initial concentration rose. Mandal et al. (2019) observed similar trends for phenol, attributing the reduced efficiency to limited adsorption sites and surface saturation. Ozsoy and Kumbur (2006) noted that while copper adsorption capacity increased with concentration, the overall percentage removal decreased as saturation was reached.

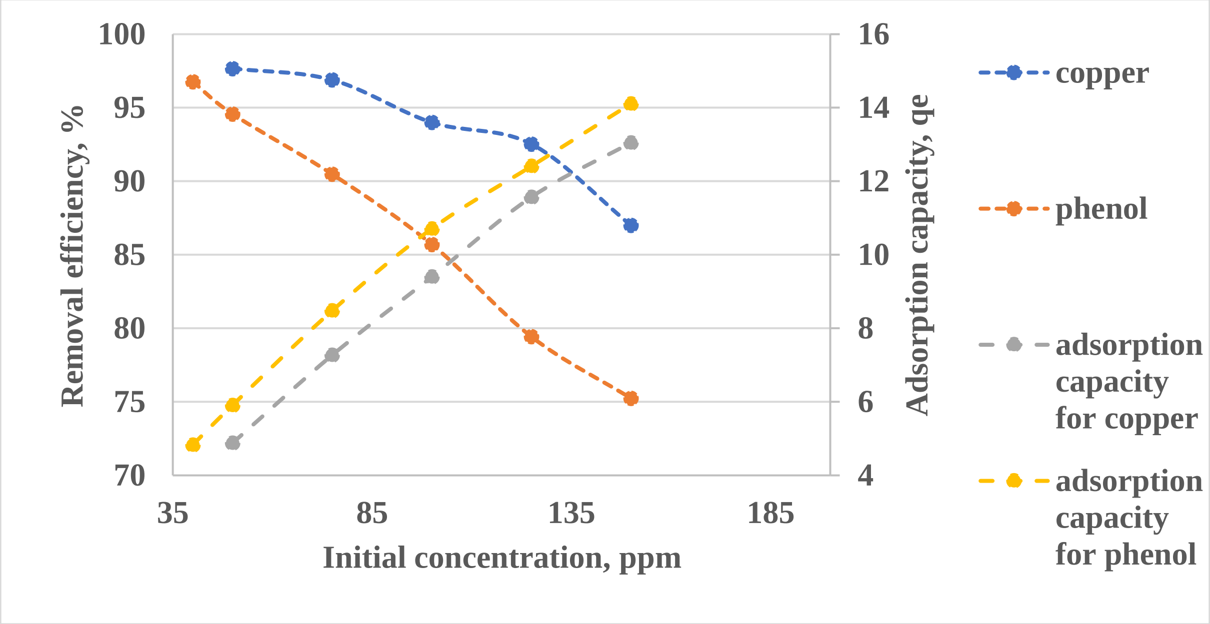

Figure 12: Effect of initial concentration

4.2.5. Effect of contact time

Analyzing the removal percentage over time yielded valuable insights into the treatment duration and the point at which adsorption equilibrium is achieved. The findings indicated that extending the contact time enhances the absorption of contaminants, including metals, from the solution. As contact time increases, the adsorption rate diminishes, ultimately approaching equilibrium.

This reduction can be attributed to a decrease in the overall surface area of the adsorbent and a corresponding reduction in the number of accessible binding sites. These results likely highlight the initial availability of the adsorbent's surface area, the presence of numerous void binding sites, and the effectiveness of functional groups on the adsorbent during the early phases of the process (Chakraborty et al., 2011, Akhbarizadeh et al., 2018).

The adsorption of copper and phenol showed a time-dependent increase in removal efficiency, reaching equilibrium at 45 minutes for copper (97%) and 60 minutes for phenol (96.43%), as illustrated in Figure 13. The initial phase of rapid adsorption reflects the abundant availability of active sites on the adsorbent surface, which allows for fast interaction with adsorbate molecules. As expected, as these sites become occupied, the adsorption rate slows until equilibrium is achieved. This trend aligns with observations by Teker et al. (1999), who reported equilibrium for copper adsorption at 60 minutes. The rapid initial adsorption occurs due to abundant vacant active sites on the adsorbent surface. As these sites become occupied, the process slows due to diffusion resistance and reduced accessibility to deeper adsorption sites. Mandal et al. (2019) emphasized that this behavior is common in adsorption processes, with faster adsorption at the beginning and slower rates as equilibrium approaches. Interestingly, studies by Thakur and Parmar (2013) demonstrated that prolonged contact times beyond equilibrium could lead to desorption, slightly reducing removal efficiency. This phenomenon underscores the necessity of identifying the optimal contact time to prevent unnecessary energy usage and potential loss of adsorbate. Optimizing contact time is crucial in practical applications. Prolonged treatment beyond equilibrium can result in minimal efficiency gains but increased operational costs. Furthermore, desorption or re-equilibration processes may occur at extended durations, as highlighted by some studies, reducing overall effectiveness.

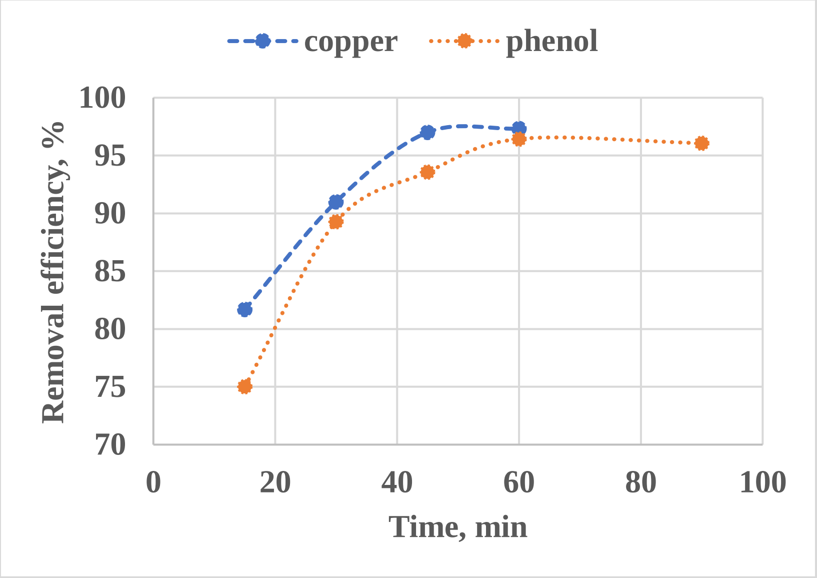

Figure 13: Effect of contact time

4.3. Adsorption kinetics

Analyzing experimental data associated with kinetic models allows for exploring the adsorption rate. It offers insights into the interactions between the adsorbent and adsorbate, helping to differentiate between physisorption and chemisorption. In this research, both pseudo-first-order and pseudo-second-order kinetic models were assessed. The validation of the pseudo-first-order model indicates that the adsorption process is primarily characterized by physisorption, suggesting a uniform nature of the adsorbent particles. In contrast, the validation of the pseudo-second-order model points to chemisorption, highlighting a heterogeneous composition of the adsorbent particles.

4.3.1. Pseudo-first-order kinetics

The experimental data about pseudo-first-order kinetics were analyzed using the models delineated in Equation 6 and shown in Figure 14. A linear representation of Equation 6, specifically ln (Qe - Qt) plotted against time (t), illustrates the characteristics of pseudo-first-order kinetics. In this context, the rate constant K_1 and the calculated equilibrium adsorption capacity (qe) can be derived from the slope and intercept of the linear plot, respectively.

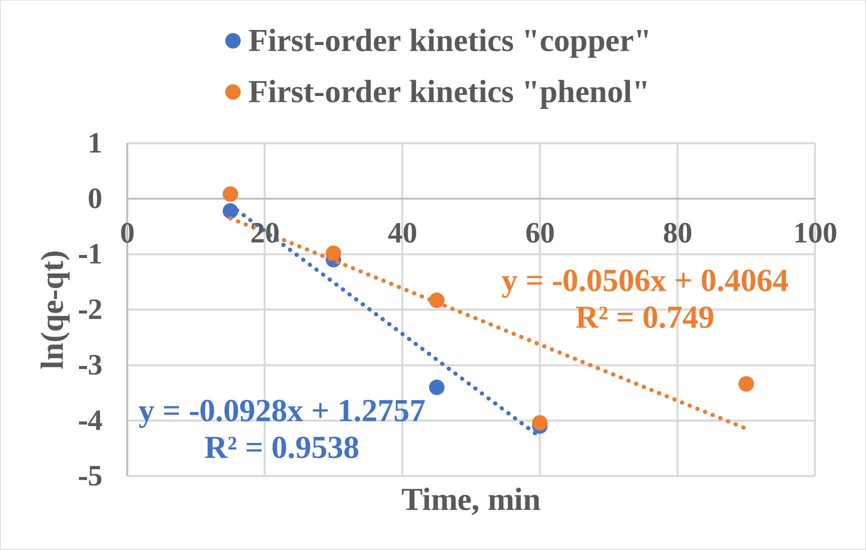

Figure 14: Pseudo-first-order kinetics for copper and phenol

4.3.2. Pseudo-second-order kinetics

The experimental data about pseudo-second-order kinetics were analyzed using the models outlined in Equation 7. By plotting (t/qt) against time (t), which corresponds to the pseudo-second-order kinetics, the slope of the resulting graph yields 1/qe, while the intercept provides $1/K_2qe^2$. This graphical representation serves as a method for extracting the parameters associated with pseudo-second-order kinetics.

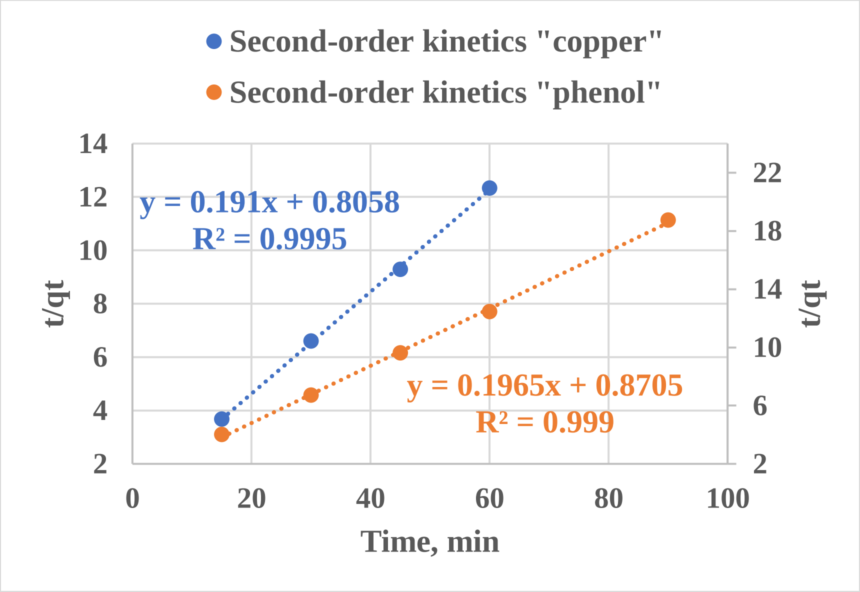

Figure 15: Pseudo-second-order kinetics for copper and phenol

Figure 15 illustrates the relationship between t/Qt and t. The regression coefficient, denoted as R^2, indicates that the sorption processes of phenol and copper on modified RH adhere to pseudo-second-order kinetics models. The results derived from the linear relationship and subsequent calculations have been organized in Table 4. Analyzing the regression coefficients alongside the calculated Qe values from the graphs for both pseudo-first-order and pseudo-second-order kinetic models reveals that the pseudo-second-order model provides a significantly better fit for the data than the pseudo-first-order model.

Table 4. Kinetics models for adsorption of copper and phenol.

Kinetics models	**Parameters**	**Values**	
		Copper	**Phenol**
Pseudo-second-order	k_2	0.04527	0.0443564
	Qe	5.2356	5.0890585
	R^2	0.9995	0.999
Pseudo-first-order	Qe	3.58121	1.501403
	k_1	-0.00155	-0.0005622
	R^2	0.9538	0.749

4.4. Adsorption isotherm

The examination of the experimental isotherm data proved to be crucial, as it facilitated the formulation of an equation that was subsequently utilized for design objectives. A range of isotherm models exists in the literature for the analysis of experimental isotherm data, among which the Langmuir and Freundlich models were employed in this study.

4.4.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm for copper and phenol is illustrated in Figure 16. As the equation (2) states, the Langmuir isotherm model can be succinctly described as follows:

$$\frac{1}{q_e} = \frac{1}{K_L q_m}\frac{1}{C_e} + \frac{1}{q_m} \tag{14}$$

Where-, q_m is the maximum monolayer adsorption capacity (mol g^{-1}), K_L is the Langmuir constant (L mol^{-1}), and q_e is the adsorption capacity (mol g^{-1}). The $1/q_e$ versus $1/C_e$ plot allows for determining the Langmuir constants. Following the calculations, all Langmuir isotherm parameters have been compiled in Table 5.

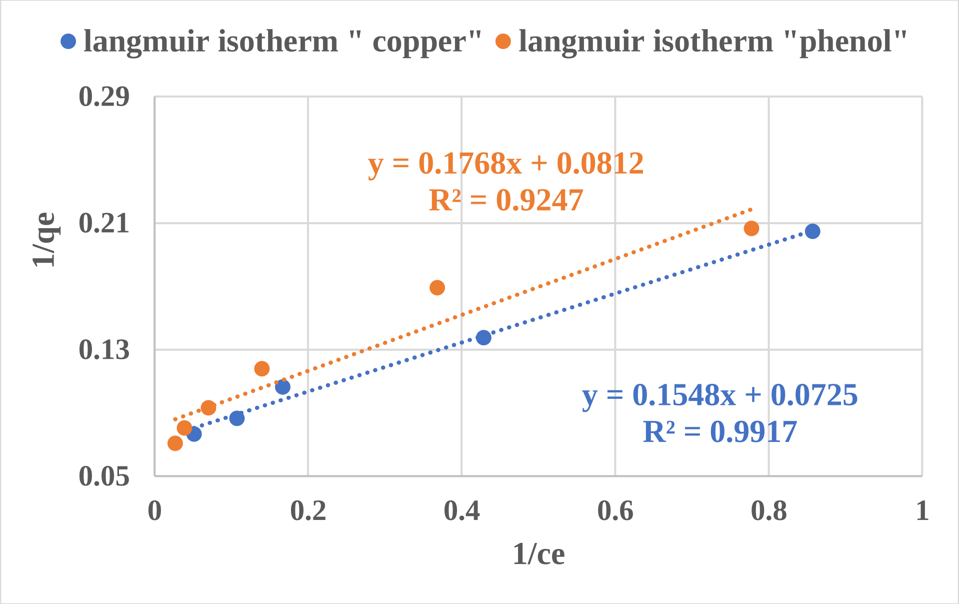

Figure 16: Langmuir isotherm for adsorption of copper and phenol on modified RH

4.4.2. Freundlich adsorption isotherm

The Freundlich adsorption isotherm for copper and phenol is illustrated in Figure 17. The experimental data about Freundlich adsorption isotherm were analyzed using Equation 4. By plotting log q_e versus log C_e, which corresponds to the Freundlich isotherm, the slope of the resulting graph yields 1/n, while the intercept provides $logK_F$. This graphical representation serves as a method for extracting the parameters associated with Freundlich adsorption isotherm. Following the calculations, all Freundlich isotherm parameters have been compiled in Table 5.

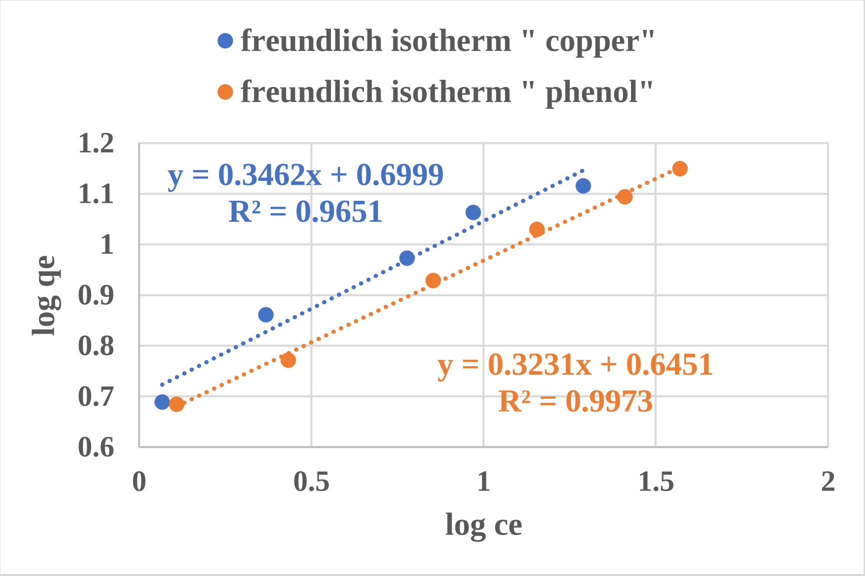

Figure 17: Freundlich isotherm for adsorption of copper and phenol on modified RH

As you can see from Figures 16 and 17, in the case of copper, the data aligns more closely with the Langmuir isotherm model compared to the Freundlich model, demonstrating monolayer adsorption on a homogeneous surface. Conversely, for phenol, the Freundlich isotherm model demonstrates a better fit than the Langmuir model, indicating multilayer adsorption on a heterogeneous surface.

Table 5. Adsorption isotherm parameters on the adsorption of copper and phenol on the RH adsorbent.

Adsorption isotherm	**parameters**	**Values**	
		Copper	**Phenol**
Langmuir isotherm	Qmax	13.7931	12.3153
	K_L	0.46835	0.45928
	R^2	0.9917	0.9247
Freundlich isotherm	n	2.8885	3.09502
	K_F	2.01355	1.90618
	R^2	0.9651	0.9973

4.5. Thermodynamic study

A thermodynamic analysis was conducted to evaluate the viability of the adsorption process by examining the variations in Gibbs free energy, enthalpy, and entropy. The Gibbs free energy change served as an indicator of the process's spontaneity, while the enthalpy changes provided insights into whether the process was endothermic or exothermic. Additionally, the entropy change offered information regarding the adsorption process, distinguishing between physical and chemical adsorption.

These thermodynamic parameters are the change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). These parameters are determined by equations 8 and 9. The enthalpy (ΔH°) and entropy (ΔS°) changes were derived from the slope ($\frac{\Delta H^{\circ}}{R}$) and intercept ($\frac{\Delta S^{\circ}}{R}$) of the plot correlating ln K_C with 1/T, as illustrated in the subsequent figure. Following the calculations, all thermodynamic parameters have been compiled in Table 6.

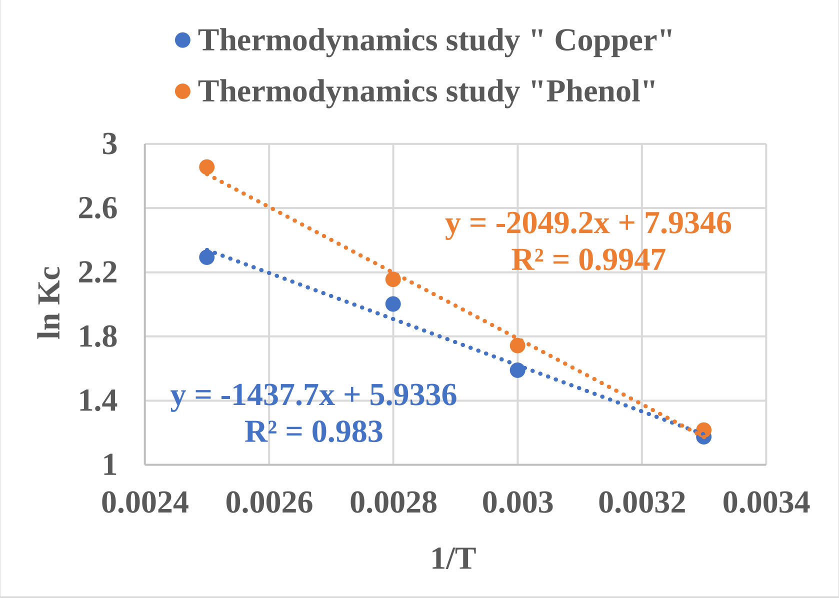

Figure 18: Thermodynamic study for adsorption of phenol and copper on modified RH.

Table 6. Thermodynamic parameters for adsorption of phenol and copper on RH adsorbent.

Thermodynamic parameters	**Values**	
	Copper	**Phenol**
Enthalpy, J/mol	11953.0378	17037.05
Entropy, J/mol	49.3319504	65.96826
R^2	0.983	0.9947
Gibbs Energy, J/mol	-4399.79873	-4822.558

The negative value of ΔG° suggests that the adsorption process is both feasible and spontaneous. In contrast, the positive values of ΔH° and ΔS° signify that the adsorption process is characterized as endothermic and exhibits randomness, reflecting an enhanced degree of freedom at the solid-liquid interface.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

The study aimed to explore the use of rice husks (RH) as an eco-friendly material for treating produced water (PW) generated by the oil and gas (O&G) industry. The research was motivated by the pressing need for sustainable solutions to mitigate the environmental challenges associated with PW, a complex waste stream characterized by hydrocarbons, heavy metals, salts, and various organic pollutants. Traditional methods for PW treatment often involve high costs, complex operations, and the generation of secondary waste. Against this backdrop, the use of RH offers a promising alternative due to its renewable nature, local availability, and effective adsorption properties.

The results of the study demonstrated the effectiveness of RH in significantly reducing contaminants in PW. Experimental findings revealed that RH achieved high removal efficiencies for phenol and copper. The results were compared favorably with the current literature and revealed an alignment, further supporting the viability of RH as an effective adsorbent. The adsorption kinetics indicated that the removal process followed a pseudo-second-order model, suggesting that chemisorption predominantly governs the adsorption mechanism. This implies a strong interaction between RH and the contaminants, enhancing the adsorption capacity. Additionally, the adsorption isotherm analysis revealed that the Langmuir model fits well for copper removal, demonstrating monolayer adsorption on a homogenous surface with a finite number of adsorption sites. In contrast, phenol removal was best described by the Freundlich model, indicating multilayer adsorption on a heterogeneous surface. These findings underscore the versatility and efficiency of RH as an adsorbent for PW treatment.

This study demonstrated RH’s potential to address environmental challenges associated with PW. Key operational parameters, including contact time, temperature, adsorbent dosage, and initial pollutant concentrations, were identified as crucial to optimizing adsorption efficiency. Moreover, this research supports global sustainability goals by promoting the reuse of agricultural waste and advocating for a circular economy approach.

The findings provide a foundation for further research into the scalability and optimization of RH-based adsorption systems, paving the way for their integration into large-scale IWM practices.

5.2. Recommendations

Future studies should explore the effects of physical treatments on RH, as the current research focused on chemical treatments. Given the potential differences in outcomes between chemical and physical methods, investigating physical treatment techniques such as mechanical processing, heat treatment, or compression could provide valuable insights. These studies would help broaden our understanding of RH's versatility and its potential applications, particularly in contexts where chemical treatments may not be as effective or desirable.

Additionally, comprehensive cost-benefit analyses should be conducted to evaluate the economic feasibility of using RH on an industrial scale. These studies should encompass all aspects, including the costs of raw materials, processing, regeneration, and waste disposal. A clear economic framework would aid in demonstrating the financial viability and practicality of implementing RH-based systems.

While RH is renewable and biodegradable, the long-term environmental impacts of their use and disposal require thorough assessment. Evaluating these impacts is crucial to ensure the sustainability of this approach. Such studies would provide insights into any potential ecological risks and inform strategies to mitigate them, aligning with global environmental standards.

Lastly, pilot-scale studies should be undertaken in collaboration with the O&G industry to validate the real-world applicability of RH as an adsorbent. These trials would bridge the gap between laboratory research and industrial deployment, offering valuable data on performance, scalability, and operational challenges. Successful implementation at this level would pave the way for widespread adoption of RH-based PW treatment solutions.

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APPENDIX

***Table A 1*: Calibration curve for phenol and copper**

Concentration, ppm	**Absorbance, Copper**	**Absorbance, Phenol**
25	0.0167	0.0238
50	0.0315	0.0416
100	0.0611	0.072
150	0.089	0.1074
200	0.1219	0.1412
250	0.1514	0.1701

***Table A 2*: Effect of raw RH and RH modified on phenol and copper removal**

Adsorbent, g	**Copper**	**Phenol**
Raw RH	29.56	17.91
AC-RH-NaOH	70	80.7
AC-RH-H3PO4	77.11	71.13

***Table A 3*: Effect of contact time**

Copper, dosage of 1g			
Time, minutes	**Adsorption Efficiency, %**	**t/qt**	**ln(qe-qt)**
15	81.67	3.6735	-0.2232
30	91	6.5934	-1.0987
45	97	9.2783	-3.4022
60	97.33	12.3288	-4.0964
Phenol, dosage of 0.8g			
Time, minutes	**Adsorption Efficiency, %**	**t/qt**	**ln(qe-qt)**
15	75	4	0.0853
30	89.28	6.72	-0.9816
45	93.57	9.6183	-1.8299
60	96.43	12.4444	-4.0415
90	96.07	18.7361	-3.3402

Table A 4: **Effect of adsorbent dosage**

Adsorbent, g	Copper	Phenol
	Adsorption Efficiency, %	Adsorption Efficiency, %
0.2	44	53.57
0.4	66.33	82.14
0.6	80.67	89.29
0.8	87.67	93.57
1	91.33	94.64
1.5	92.33	95.71

Table A 5: **Effect of initial concentration of pollutants (copper and phenol)**

Copper						
Concentration ci (ppm)	**Adsorption Efficiency, %**	**Adsorption Capacity, qe**	**1/ce**	**1/qe**	**log ce**	**log qe**
50	97.67	4.88	0.8571	0.2048	0.0669	0.6887
75	96.89	7.27	0.4286	0.1376	0.368	0.8613
100	94	9.4	0.1667	0.1064	0.7781	0.9731
125	92.53	11.57	0.1071	0.0865	0.97	1.0632
150	87	13.05	0.0513	0.0766	1.29	1.1156
Phenol						
Concentration, ci (ppm)	**Adsorption Efficiency, %**	**Adsorption Capacity, qe**	**1/ce**	**1/qe**	**log ce**	**log qe**
40	96.78	4.83	0.7778	0.2066	0.1091	0.6848
50	94.57	5.91	0.3684	0.1692	0.4337	0.7716
75	90.48	8.48	0.14	0.1179	0.8539	0.9285
100	85.71	10.71	0.07	0.0933	1.1549	1.03
125	79.43	12.41	0.0389	0.0806	1.4102	1.0938
150	75.24	14.11	0.0269	0.0709	1.5699	1.1494

***Table A 6*: Effect of temperature**

Effect of temperature			
Copper			
Temperature, K	**Adsorption Efficiency, %**	**1/T**	**ln Kc**
303	97	0.0033	1.1735
333	98	0.003	1.5892
363	98.67	0.0028	2.0015
393	99	0.0025	2.2925
Phenol			
Temperature, K	**Adsorption Efficiency, %**	**1/T**	**ln Kc**
303	96.43	0.0033	1.2164
333	97.86	0.003	1.7419
363	98.57	0.0028	2.1547
393	99.29	0.0025	2.855

CURRICULUM VITAE

PERSONAL DATA

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Full name: Yvonne UWINEZA

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PROFILE

Yvonne UWINEZA is a chemist in environmental chemistry by profession, with practical skills in the field of solution, standardization of solution and quality control. Besides, Yvonne acquired entrepreneurship skills in which she acquired either in University or High school and working with the community strengthen Yvonne in a good team working with positive attitude and good communication skills, strong people management skills and with detailed problem-solving approach.

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EDUCATION

MSc | Hydrocarbon Process Engineering (2022- 2024)

Eduardo Mondlane University – Maputo, Mozambique

- Courses: Fundamentals of Chemical Engineering and Thermodynamics; Global Energy Industry, Advanced Catalysis; Hydrocarbon Processing Technologies I and II; Process Instrumentation and Control System Development; Laboratory Analytical Techniques, Process Economics, project management, Engineering Design tool.

BSc Applied Chemistry | Environmental Chemistry (2014 – 2018)

University of Rwanda College of Sciences and Technology – Rwanda

- Courses: Inorganic Chemistry, Fundamentals of Chemistry, Fundamental Physics, Analytical Chemistry, Organic Chemistry, Physical Chemistry, Quantum Chemistry, Biochemistry, Probability and Statistics, Polymer and Organic Spectroscopy, Chemical Engineering, Earth Science, Entrepreneurship Development, Environmental Chemistry, Environmental Health and Toxicology, Fundamental of Waste Management, Environmental Impact Assessment and Law, GIS and Remote Sensing.

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EXPERIENCE

July 2017-August 2017: WASAC/ Cyunyu branch in Rusizi district

- **Position**: Research intern (Industrial attachment)

March 2024 – June 2024: Process Engineer | Sasol Petroleum Temane | Inhambane, Mozambique

- **Position:** Internship

Working in gas processing plant in process safety management

2020-2021: Rwanda Transport Development Agency (RTDA)

- **Position**: Enumerator (Data collector)
- **Project:** Base -Rukomo project (Road construction project)
- **Responsibilities:**

we work with Rwanda Transport Development Agency in data collection on the project of road construction (Base - Rukomo). The main duties of this project were to conduct interview with citizens to know the impacts (positive and negative) of road construction in different sectors such as agriculture and business in different areas of the country

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SOFTWARE SKILLS

- COCO Simulator
- SCILAB
- DWSIM
- Microsoft office: Word, Excel, PowerPoint

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LANGUAGES

Mother tongue: Kinyarwanda; listening, speaking, and writing at excellent level.

	listening	writing	speaking
French	fluent	fluent	fluent
English	Fluent	fluent	fluent
Swahili	good	good	Good

===

CERTIFICATES

1. English Proficiency certificate by the University of Rwanda Certificate

2. Itorero ry’igihugu certificate,

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I assure that the information provided above is genuine and true.

UWINEZA Yvonne