APPLICATION OF MODIFIED WALNUT SHELL ADSORBENTS IN OILY WASTEWATER TREATMENT

by

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Abstract

Oil spills are of great concern because oily wastewater disrupts the aquatic ecosystem, causes animal mutations, contaminates surface water resources, and causes diseases such as human cancer. Current efforts are geared towards recovering spilled oil from marine environments and ensuring the effective separation of oil and water in the collected emulsion. After oil separation from the emulsion, a polishing step is required to treat the residual oil in the water before discharging the effluent into the aquatic environment. Adsorption using natural materials as adsorbents is seen as an attractive option due to its simplicity, cost-effectiveness, accessibility, and eco-friendliness. Recent adsorption studies have focused on modifying eco-friendly materials to enhance their adsorption potential. This study investigated a two-step modification of walnut shells (WS) to treat oily wastewater. Firstly, WS was modified with sodium hydroxide (NaOH) via the wet impregnation method to attain WS/NaOH. Then, tetrabutylammonium bromide (TBAB) was introduced as a co-adsorbent to enhance the oil removal potential of WS/NaOH. The surface morphologies and chemical composition of the WS and WS/NaOH were characterized by scanning electron microscopy and Fourier transform infrared spectroscopy, respectively. A one-factor-at-a-time experimental design was employed in this study. Findings from this research project indicated that raw WS and WS/NaOH are excellent adsorbents for the treatment of oily wastewater, with a removal efficiency of 81 % and 88 %, respectively. They generated adsorption capacities of 201 mg/g and 220 mg/g, respectively. However, with the introduction of TBAB as a co-adsorbent, an efficiency and capacity of 91 % and 226 mg/g, respectively, were achieved, proving the effectiveness of TBAB. Adsorption isotherm and kinetic studies were conducted to understand the adsorption mechanism of the proposed adsorbent. It was concluded that the Freundlich and Pseudo second-order model best represents the experimental results, as they show higher R^2 values of

0.9695 and 0.9998, respectively. This research project presents an eco-friendly and highly efficient adsorbent from modified WS to treat oily wastewater, offering a sustainable, scalable alternative to traditional methods by utilizing agricultural waste to remove oil pollutants in petrochemical wastewater treatment efficiently.

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Acronyms and abbreviations

AC	activated carbon
AD	adsorbent dosage
ANOVA	analysis of variance
ASTM	American Society for Testing and Materials
BOD	biochemical oxygen demand
CNTs	carbon nanotubes
COD	chemical oxygen demand
CPC	chloride monohydrate
CT	contact time
DAF	dissolved air flotation
FTIR	Fourier transform infrared spectroscopy
GO	graphene oxide
IC	initial oil concentration
PAHs	polycyclic aromatic hydrocarbons
PC	principal components
PCA	principal component analysis
pH	potential of hydrogen
RPM	revolution per minute

RT	reaction time
SEM	scanning electron microscopy
TBAB	tetrabutylammonium bromide
SS	suspended solids
TDS	total dissolved solids
TSS	total suspended solids
WS	walnut shells
WS/NaOH	walnut shells modified with sodium hydroxide
WS/NaOH/TB	walnut shells modified with sodium hydroxide and tetrabutylammonium bromide

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Chapter 1 Introduction

1.1. Background

Freshwater streams are increasingly contaminated because of rising industrialization and urbanization. Significant contributors to the rise in water contamination include sewage treatment facilities, industrial discharges, agriculture, and other anthropogenic activities. These industries discharge both organic and inorganic contaminants into water bodies [1], including pesticides, plasticizers, fertilizers, hydrocarbons, biphenyls, phenols, detergents, oils, greases, medications, plant and animal tissues, etc [2]. Even in small concentrations, these pollutants are hazardous.

One of today's most crucial strategic resources and a critical factor in the growth of modern economies is oil [3, 4]. Oil demand has increased due to the rapid expansion of the world economy, which has also increased the amount of oil trade. This has led to the extraordinary growth of the marine oil exploitation business. Crude oil is extracted, transported, and stored during the upstream process and refined during the downstream phase [5-7]. The oil sector generates significant oily waste from upstream and downstream operations, encompassing solid and liquid forms [8]. Since the Torrey Canyon supertanker sank in the British seas in the 20th century, the transportation of oil worldwide and the response to oil spills have experienced significant changes [9].

In recent years, terrestrial and marine hydrocarbon contamination in temperate regions, including northern Russia, Canada, Alaska, and the Qinghai-Tibet Plateau, has grown to be a severe environmental issue as it endangers human health, depletes natural resources and disrupts the economy [10-12]. Annually, 3.2 million tonnes of oil are emitted into the environment from all sectors [13]. The vast bulk of this oil results from commercial and industrial activity. The Gulf War of 1991 saw the most significant oil spill in history, with 4 and 8 million barrels of oil spilling into the Gulf and the Kuwaiti Desert, respectively [14]. In oil production projects in

Newfoundland, Canada, 381 spills from production platforms occurred between 1997 and 2010 [15]. Oil may spill into the ocean when tankers fill or empty their cargo or during any oil industry activity or accident. Natural disasters may also trigger spills that cause oil to percolate into the oceans [16].

The petroleum refining sector is at the forefront of the fight to implement practical and ecologically friendly methods for environmental preservation because it is considered one of the significant sources of pollution, both directly and indirectly, through oil exploitation and automobile exhaust gases [17]. Therefore, oil and gas operators are responsible for treating the wastewater from oilfield reservoirs using proper technological methods, and they can gain financially from increased oil production through water flooding. In addition, water from processed oil can be released into the environment or utilized for other projects because of its acceptable quality.

1.2. Objectives and significance of the study

To date, a variety of techniques have been employed to contain the spread of oil leakage and to treat oily wastewater, including in situ burning [18], mechanical collection [19], biodegradation [20], use of an electric field [21], and chemical dispersants [4]. Nevertheless, conventional methods suffer from drawbacks, including insufficient separation, limited selectivity, high toxicity, reduced recyclability, high operational expenses, lengthy time requirements, and the potential for reintroducing pollutants [22].

Adsorption has lately emerged as the primary technology for treating oily wastewater owing to its simplicity, cost-effectiveness, accessibility, and environmentally friendly attributes [23]. Recently, many studies have focused on the conventional and modern adsorption approaches used in treating oily wastewater. For example, Medeiros et al. [24] compared various methods for treating oily waste streams employed by industries. These methods include membrane separation technology, advanced oxidation techniques, and the utilization of microorganisms. The pros and cons of emerging approaches in treating oil-contaminated effluents were also discussed. Tian et al. [25] thoroughly examined and compared cutting-edge pretreatment and advanced treatment methods for petrochemical wastewater. They discussed the mechanisms to remove organic pollutants from petrochemical wastewater through these treatment systems. Additionally, the study explored harnessing bioenergy from petrochemical wastewater to reduce pollutants while facilitating bioenergy generation. Challenges such as slower processing times and high operational costs make these technologies undesirable.

Cost-effective and environmentally friendly adsorbents have recently been the focus of research to cut costs and minimize negative environmental impacts. Employing these adsorbents for treating oily wastewater provides economic advantages, diminishes environmental harm, guarantees adherence to regulations, and boosts sustainability efforts. Therefore, the aim of this research project was to develop a cost-effective, eco-friendly adsorbent that will overcome the drawbacks of the abovementioned techniques in treating petrochemical wastewater.

To achieve the aim, the specific objectives of this work were:

(1) To determine the treatability of oily wastewater using an adsorbent based on walnut shells (WS);

(2) To modify WS as adsorbents and determine their adsorption potential; and

(3) To identify the adsorption mechanism by examining the appropriate model.

The study focuses on a two-step modification of WS to create an effective adsorbent. By optimizing the modification process, the study aims to enhance the oil removal efficiency of WS, offering a sustainable and eco-friendly remedy for wastewater management. The various experimental parameters for the study were (1) adsorbent dosage (AD), (2) initial oil concentration (IC), (3) reaction time (RT), and (4) salinity. Some crucial questions the study seeks to answer are (1) What modifications to WS most effectively boost their oil adsorption capability in wastewater treatment, (2) What are the comparative advantages of modified WS compared to other adsorbents in the treatment of oily wastewater, and (3) What are the environmental and economic advantages of utilizing WS-based adsorbents for wastewater treatment in the oil and gas sectors. The study is crucial for developing a cost-efficient, environmentally sustainable adsorbent derived from WS to treat oily wastewater. It enhances resource optimization by converting agricultural waste into a practical solution and fosters advances in sustainable water treatment.

1.3. Organization of thesis

This thesis is structured into five chapters. Chapter 1, the current chapter, introduces the background of marine oil spills, detailing their major contributors and the conventional methods used to manage these spills, along with the limitations of these techniques. An overview of adsorption is provided, followed by the problem definition and the research objectives. Additionally, the chapter outlines the overall structure of the thesis.

Chapter 2 delivers an in-depth literature review of recent advancements in wastewater treatment technologies, with a particular focus on oily wastewater treatment through adsorption. The chapter discusses various adsorbents, the key factors influencing the adsorption process, and identifies research gaps requiring further exploration.

Chapter 3 describes the experimental setup, including the procedures for adsorbent development, oily wastewater preparation, and the materials and equipment used. It also details the experimental design and explains the rationale behind the chosen methodology.

Chapter 4 presents the results related to adsorbent development and evaluates the removal efficiencies of the adsorbents. It includes a characterization of the surface morphology and chemical composition of the materials, as well as findings on the optimal adsorbent dosage and the outcomes of adsorption isotherm studies.

Chapter 5 summarizes the research findings, emphasizing the potential advantages of developing environmentally friendly adsorbents. It concludes with recommendations for future research directions. The references supporting this thesis are listed at the end.

Chapter 2 Literature Review

2.1. Characteristics of petroleum wastewater

Oil has elevated concentrations of biochemical oxygen demand (BOD) and chemical oxygen demand (COD), hydrocarbons, heavy metals, volatile organic compounds, oil and grease constituents, total dissolved salts, ammonia, nitrates, sulfides, waste catalysts, greasy sludge, and other unwanted substances [26]. Petroleum effluent is a harmful pollutant to the environment since it contains large quantities of polycyclic aromatics, which are highly poisonous and act as contaminants in different quantities [27, 28]. Petroleum aliphatic hydrocarbons (up to C_{10}) and well-known aromatic compounds, including benzene, toluene, and ethylbenzene, were found to be the primary constituents of the organic contaminants in petroleum refinery effluent [29]. Asphaltenes and substances with oxygen, nitrogen, and sulfur are other forms of hydrocarbons that can be found in petroleum wastes. Generally, aromatic and aliphatic molecules in oily wastewater often account for up to 75% of petroleum hydrocarbons, with trace metals, oxygenated compounds, heterocyclic compounds, halogenated compounds, etc., making up the remaining 25% [26, 30, 31]. Table 2.1 below presents the characteristics of petroleum wastewater.

Table 2.1: Characteristics of petroleum wastewater

Parameters	**References**							
	[32]	[33]	[34]	[35]	[36]	[37]	[38]	[39]
COD (mg/L)	500-1000	21000	7896	1343	450	80-120	364	800
Sources	Industrial processes (spills, leaks, runoff from roads), Surfactants from cleaning operations, Chemical additives and emulsifiers from industrial processes, Textile industries (chemicals and dyes)							
BOD (mg/L)	-	8000	3378	846	174	40.25	-	350

Sources	Agricultural runoff (from plant debris and organic fertilizers), Biodegradable lubricants, Organic residues from food processing (sugars, starches, proteins), Waste from biological treatment processes, Organic compounds (alcohols, phenols, ketones)							
Total suspended solids (TSS)	90-300	2580	-	74	150	22.8	105	100
Sources	Oil and grease in particulate form, Industrial processes (particles from machining, grinding, cutting), Urban runoff (including debris, litter, and sediment from roads and construction sites), Natural sources (erosion, organic matter decomposition, sedimentation)							
pH	6.5-6.8	2.5	8.48	7.0	6.7	8.0	7.6	6.5-8.5
Sources	Chemical reactions (organic matter oxidation, hydrolysis of compounds), Corrosion and leaching, Cleaning agents and detergents, Industrial processes (metal cleaning, plating, processing operations), Atmospheric deposition							
Oil & Grease (mg/L)	400-1000	1140	-	240	870	-	946	3000
Sources	Oil and gas production (oil drilling, extraction and refining operations), Industrial processes (manufacturing, metalworking, food processing, and chemical production), Agricultural activities (the use of lubricants, hydraulic fluids, and machinery that can leak or spill oil), Marine activities (Ships, boats, and offshore platforms can release oil and grease into water bodies), Vehicle maintenance (Auto repair shops, car wash facilities, and gas stations can produce oily wastewater from vehicle maintenance activities, including oil changes, engine cleaning, and fuel spills)							
Total dissolved solids (TDS) (mg/L)	3000-5000	37000	-	-	-	-	-	-

Sources	Agricultural runoff (use of Fertilizers, pesticides, and herbicides), Mining operations (dissolution of minerals and metals from ore processing and waste rock disposal), Industrial processes (use of chemicals and solvents), Oil and gas production (oil and gas exploration, drilling, and production), Municipal sources (use of detergents, cleaning agents, and personal care products in households)

2.2. Human and environmental health impacts of petroleum wastewater

There are various possible entry points for oily wastewater into surface and groundwater, including pipeline or tanker truck accidents, wastewater storage pond or tank leaks at well pads or dumpsites, and subsurface fluid migration through damaged well casings [40]. The petroleum industry discharges substantial volumes of pollutants into the environment, including hydrocarbons, heavy metals, phenols, and other hazardous compounds, through wastewater [30]. Small or large amounts of crude oil or refined oils, such as gasoline or diesel, have the potential to contaminate water bodies and coastal regions, leading to an oil spill, a form of pollution. This occurs due to harmful compounds in the leaked oil, posing significant health risks to oil workers, residents, marine life, animals, and the overall habitat in both the short and long term.

Oil pollution rapidly spreads across the water's surface, covering extensive areas and forming an air barrier threatening aquatic life. Oily wastewater further damages marine habitats due to substances such as `ammonia and hydrogen sulfide, which reduce dissolved oxygen levels in water bodies to levels insufficient for the survival of aquatic life. [41, 42]. The inevitable outcome is the wide-ranging death of aquatic organisms when the dissolved oxygen threshold limit falls below 2 mg/L [43]. Oil spills in marine environments could hinder the exchange of gases between phytoplankton and the ocean, reducing dissolved oxygen levels. This, in turn, could trigger significant fluctuations in oxygen levels and temperatures across various components of the sea, potentially resulting in the death of phytoplankton and weakening the aquatic food chain

[44]. The aromatic substances released during oil spills can modify hatched fish, accumulating carcinogens in fish or shellfish. This diminishes aquatic organisms' economic value and threatens human health [45]. Moreover, wetlands and mangroves suffer harm when spilled oil infiltrates coastal wetlands and protected marine life zones, reducing biodiversity [46]. In addition to inflicting severe damage on the natural aquatic environment and ecosystems in coastal regions, oil spills threaten crew members' lives and result in substantial economic losses and the destruction of resources [47, 48]. Furthermore, hydrocarbon contamination in marine environments leads to the extinction of fish, birds, and various marine species, resulting in a dramatic decline in aquatic resources. The consequences of the spills become notably more severe for operators if the oil leak results in flames or explosions [49]. Oil spills, therefore, need to be cleaned up immediately after the spill [50].

2.3. Treatment technologies

Different physical, chemical, and biological technologies have been employed for oily wastewater treatment. These technologies are discussed below.

2.3.1. Physical treatment methods

Physical techniques for treating oily wastewater include gravity separation, dissolved air flotation (DAF), and centrifugation. Physical separation is the primary technology for oily wastewater treatment in petroleum refineries [51]. Gravity separation, which uses the density difference between oil and water, is the most fundamental technique for treatment. A higher contrast improves the separation effect in density between the oil and water [52]. Gravity separation is the first separation step for dispersed and floating oil. In the initial treatment stages, gravity separation is effective in separating oil and water for compliance with environmental regulations. Widely employed in extensive facilities, the gravity separation approach is flexible and is frequently integrated with other treatments to attain optimal outcomes in the oil and gas sector. However, it is unsuitable for separating emulsified oil because it has several disadvantages: it requires ample space, has limited separation capacity, is challenging to operate and manage, and provides poor treatment results [53, 54].

The DAF technique is well-recognized for treating oily wastewater. In DAF, pressurized air is applied to the bottom of an open basin, where the air bubbles rise to the top, carrying contaminants [55]. The treatment of oily wastewater has considerable potential since flotation devices have a high processing capacity, produce less sludge, and enhance separation efficiency [56]. Chemicals that encourage coagulation and enhance floc size for simple separation are commonly used in DAF units. At this stage, heterogeneous components of the effluent, such as suspended solids, colloids, dispersion, and immiscible liquids, are eliminated [53, 57]. Conventional DAF produces microbubbles between 20 and 100 microns in size. Oil droplets are attracted to the microbubbles, which increase the buoyant properties of the droplet and cause it to rise. Pressure and air saturation in the wastewater control the DAF process. The pressure must be brought down to atmospheric levels with excess dissolved gas for the microbubbles to form and float to the system’s surface [54]. The DAF method can remove emulsified oil and produce treated water of higher quality than the gravity separation method [58]. The technology requires fewer, shallower treatment facilities and operates with improved surface loading [59]. However, the DAF technology has a few drawbacks, including high operational costs (bubbles must be produced continuously).

Centrifugation relies on centrifugal force to partition oil from water. Wastewater is subjected to spinning within a centrifuge, prompting the denser oil to migrate outward, facilitating its collection [24]. The primary benefits of centrifugation include less space and operation time demands, making it well-suited for small workshops [60]. This approach excels at removing minute oil droplets effectively. Contemporary centrifugation technology enables processing substantial wastewater volumes at minimal operational expenses and with lower capital investment than gravity settling requirements. Centrifugation has been extensively employed for separating oil, water, and solids within oil sludge on a large scale. However, due to limitations in efficiently separating highly viscous oil sludge, Li et al. [61] investigated a physical approach utilizing froth flotation and centrifugation to improve oil and solid material separation at moderate temperatures. The findings indicated that, under specific conditions (flotation duration of 25 min, an impeller speed of 1580 rotations per min, sludge to flotation liquid ratio of 1:12, tap water as the flotation liquid at 33°C), the oil recovery and the oil content of residue were 93.7% and 3.1%, respectively.

2.3.2. Chemical treatment methods

Chemical technologies have been commonly employed for the treatment of oily wastewater. In chemical treatment, reactions involve oil particles, suspended sediments, COD, and various contaminants. Coagulation (followed by flocculation, a physical method), adsorption, and electrochemical technology are frequently used to treat oily wastewater [62, 63].

Coagulation and flocculation have also been applied for oily wastewater treatment. Coagulation/flocculation is cost-effective and eco-friendly due to its simplicity, affordability, and consistent effectiveness [64]. In oily wastewater treatment, coagulants initially work to counteract the negative charges on oil particles, diminishing the electrostatic repulsion within the electric double-layer, a process known as destabilization. Subsequently, these destabilized particles undergo development and gradually combine into larger clusters known as flocs. These flocs are then separated from the water phase through free precipitation or air flotation [65]. Coagulants commonly utilized in treating oily wastewater include inorganic flocculants such as aluminum sulfate, poly aluminum chloride, and polymeric ferric sulfate, as well as organic polymeric coagulants such as polyacrylamide, polyethylene oxide, and polyvinyl alcohol [66]. Daud et al. [67] utilized aluminum sulfate, poly aluminum chloride, ferric chloride, and ferric sulfate as coagulants to determine the effectiveness of coagulation and flocculation for the removal of suspended solids (SS), color, COD, and oil and grease from biodiesel wastewater, employing a conventional jar test setup. The results showed that the effect of coagulant dosage on SS, color, COD, and oil and grease removal showed a similar trend, and poly aluminum chloride was found to be superior and was observed at a reasonably lower amount of coagulant (300 mg/L). The effectiveness of oil removal was enhanced by as much as 99% by applying zinc silicate and anionic polyacrylamide, with suspended particle concentrations reduced to below 5 mg/L [32]. These results indicate that coagulation and flocculation is effective as a pre-treatment for treating biodiesel wastewater.

Chemical oxidation is one of the most effective ways to remove COD and petroleum hydrocarbons from oily wastewater. Chemical oxidation uses redox reactions to convert organic molecules into readily biodegradable substances directly or indirectly. This intricate process, called electrochemical oxidation, involves producing oxidants that oxidize the contaminants found in oily wastewater after introducing an electric current [68]. This process results in the mineralization of pollutants, decomposition, and the ease of creating airtight circulation without secondary pollution [62, 69]. The successful application of chemical oxidation in oil treatment involves using reactive substances to decompose contaminants. This approach efficiently treats intricate mixtures, decreases organic content, and improves water quality. Nevertheless, challenges arise, such as the costs associated with chemicals and the need for meticulous management to avert environmental repercussions and guarantee safety.

The electrolysis method is another approach for treating oily wastewater, leading to a time-dependent reduction in COD. This process involves three key stages: efficiently reducing contaminants in the oily wastewater and cleaning. Initially, oil components are directly oxidized at the electrode, facilitated by either the metal oxide or hydroxyl radicals at the electrode surface. Subsequently, oil components are indirectly oxidized by newly generated intermediate oxidizing agents. Finally, electro-flotation induces the aggregation of suspended oil droplets in the third step [70-72]. Electrochemical catalysis offers an efficient method for treating oily wastewater [73]. Ma and Wang designed a treatment technique for treating oily waste based on a pilot-scale system with multiple cathodes and anodes [73]. The cathode contained iron and a catalyst with a large surface area that contained noble metals, and the anode comprised active metal and graphite. By adopting the electrochemical technique, they recorded a reduction in BOD and COD of about 90% and a reduction in suspended solids of 99% [74]. The successful application of electrolysis in oil treatment involves utilizing electric currents to degrade contaminants and improve oil and water separation. This electrolysis method proves effective for emulsified oils, decreasing reliance on chemicals and enabling precise control. Although there are challenges like energy consumption and equipment maintenance, ongoing advancements are making these systems increasingly practical.

One of the traditional methods available for marine oil spill clean-up is dispersant application, a chemical agent introduced into the spill to break the oil into many tiny droplets using sea energy [75]. These abundant tiny oil droplets typically persist within the water column and disperse naturally. Once in the water column, processes such as biodegradation, dissolution, and potential sedimentation act upon these minute oil droplets. Of these processes, biodegradation, also called microbial degradation, is predominant [75]. Due to wave actions, Chemical dispersants accelerate the speed and extent of oil dispersion and dilution [76]. These dispersants encompass surfactants and active agents that reduce the interfacial tension between oil and water, breaking down oil slicks into minuscule droplets, solvents, and other compounds. Dispersants facilitate the formation of tiny oil droplets, enabling swift entrainment into the water column without resurfacing, coalescing, or reaching coastal regions [77]. Surface dispersant applications are considered particularly effective in eliminating floating oils, mainly when deployed in remote areas, addressing significant spill incidents, and minimizing health risks to at-sea responders compared to alternative response techniques. During the early 1960s, dispersants saw widespread use in numerous countries. However, following the Torrey Canyon incident in 1967, where the application of dispersants led to significant environmental harm, several nations have imposed restrictions on their usage. Subsequently, researchers developed less hazardous chemical dispersants, safer than those employed during the Torrey Canyon spill [78].

2.3.3. Biological treatment

Biological treatment, also known as bioremediation, is the process by which biological agents such as microbes, biosurfactants, and enzymes convert complex organic pollutants into simpler organic molecules [79]. Bacteria are the most active agents for degrading critical petroleum hydrocarbon components, contributing significantly to the ability of the environment to break down oil spills while producing the useful byproduct lipase [80]. Microbial degradation is the foremost and highly efficient natural approach for treating petroleum hydrocarbon contaminants from the environment [81, 82]. Their research delved into the substantial biodegradation of alkyl aromatics within marine sediments before the noticeable biodegradation of the crude oil's n-alkane profile [83]. They identified microorganisms as the agents behind the degradation of alkyl aromatics. One of the crucial limitations to the biodegradation of oil pollutants in the environment is the low accessibility of these pollutants to microorganisms.

Removing or breaking down petroleum hydrocarbon molecules from soil presents challenges due to their capacity to adhere to soil components [84]. Microbial metabolism entails harnessing the microbial decomposition of crude oil to convert organic substances into nutrients for the microbial organic components or to propagate into additional microorganisms, thereby eliminating organic matter from wastewater [85]. Ma et al. [86] isolated eight strains displaying significant petroleum-degrading capabilities from surface water and mud of an oil terminal, employing crude oil as a carbon source. Subsequently, they selected two highly effective petroleum-degrading yeasts through enrichment culture. Following five days of mixed culture, the petroleum degradation rate escalated to 51%. Using the activated sludge process, organic matter is broken down by microorganisms using dissolved oxygen in the aeration tank [87]. In a recent study, Uma et al. [88], explored distinct soil bacteria sourced from a hydrocarbon-contaminated area, aiming to treat synthetic oily bilge water and produce biopolymer using the activated sludge process. Their experiments revealed optimal organic removal (81%) and the highest polyhydroxyalkanoate yields from cell dry mass (81%) when the substrate concentration reached 5000 mg/L of soluble COD.

Biofilm technology has also been applied for oily wastewater treatment. Due to its cost-effectiveness, capability to handle high volume loads, absence of sludge, biological detoxification, enhancement of wastewater biodegradability, generation of methane as a clean energy source, and other advantages, the anaerobic biofilm reactor has been widely used [89, 90]. The moving bed biofilm reactor (MBBR), sequential batch biofilm reactor (SBBR), up-flow anaerobic sludge bed-anaerobic biological filter (UASB-BF), and microporous membrane bioreactor (MBR) have been identified as some of the most popular technologies [91, 92]. Emadian et al [93] treated diluted bilge water using a hybrid up-flow anaerobic sludge blanket bioreactor. Their findings demonstrated that with 8 h of hydraulic retention time and a 0.6 g COD/d organic load rate, the COD elimination rate was 75%.

Table 2.2: Oily wastewater treatment technologies

Technique	Source of oily wastewater	Treatment effect	References
Dissolved air floatation	Synthetic industrial effluent	>90% oil removal	[57]
Microfiltration	Prepared oily wastewater	99% oil removal	[94]
Dynamic membrane	Prepared oily wastewater	99% oil removal	[95]
***Graphene oxide alginate aerogel**	Synthetic oil-seawater mixtures	90% oil removal	[96]
***Sodium alginate – nano fibrillated cellulose**	Synthetic oil-seawater mixtures	99.65% oil removal	[97]
Electroflotation	Industrial oily wastewater	99.71% oil removal	[98]
Electrocoagulation	Biodiesel wastewater	98.42% oil and grease removal	[99]
Electrocoagulation	Biodiesel wastewater	97.8% oil and grease removal	[100]
Electrochemical reactor	Oily bilge wastewater	93.2% oil and grease removal	[101]
Electrocoagulation	Oily bilge wastewater	95.6 ± 0.2% oil and grease removal	[102]
Biological aerated filter	Oilfield wastewater before desalination	84-90% *PAHs removal	[103]
Batch stirred tank Bioreactor	Oilfield produced Water	>60% crude oil removal	[104]
Membrane sequential batch reactor	Synthetic petroleum Wastewater	>97% hydrocarbon removal	[105]

MBR and MBBR	Shipboard slop wastewater	70-85% of total petroleum hydrocarbon removal	[106]
***Pseudomonas* strain**	Synthetic oily wastewater	95 ± 1.5% oil removal	[107]
AGR	Brewery wastewater	67.39% oil removal	[108]
Anoxic-oxic MBR	Refinery wastewater	96.6% oil removal	[109]
Aerobic granular reactors	Emulsified diesel wastewater	90.31% oil removal	[110]
Microelectrolysis using Fe-C fillers	Synthetic wastewater containing diesel	81.4% oil removal	[111]
Microelectrolysis using Fe-C fillers	Ship sewage	80.1% oil removal	[112]
Halomonas venusta	Span-Twen-kerosene/water	92% oil removal	[113]
Bacillus subtilis	Waste crude oil	95% oil removal	[114]
Pseudomonas aeruginosa	Distilled water	85% oil removal	[115]
Membrane technology	Synthetic oil-water emulsions	98.8% oil and grease removal	[116]
Membrane technology	Synthetic oil-water emulsion	> 98% oil	[117]

*PAHs = polycyclic aromatic hydrocarbons

2.4. Adsorption

Adsorption is a process of mass transfer wherein solutes or removable substances are transferred from a fluid phase to the surface of a solid phase. It represents a primary mechanism whereby molecules or ions adhere to a solid surface. This phenomenon allows for the accumulation and concentration of substances through intermolecular interactions. Understanding the intricacies of adsorption is crucial in various fields, from catalysis and environmental remediation to drug delivery and gas separation.

There exist two forms of adsorption: chemical, also known as chemisorption, which occurs due to chemical reactions between the adsorbent and the adsorbate, resulting in the formation of covalent or ionic bonds; and physical adsorption, wherein the rise in adsorbate concentration at the interface is driven by non-specific van der Waals forces, irrespective of the substance's nature. Chemisorption is selective, typically irreversible, and involves a considerable heat impact ranging from tens to hundreds of kJ/mol. On the other hand, physical adsorption is weakly specific and reversible [118, 119]. Adsorbate migration typically occurs in three stages: (1) movement of the adsorbate to the outer shell of the adsorbent, (2) diffusion within the pores of the adsorbent material, and (3) the process of solute adsorption and desorption [120]. The adsorbate, adsorbent, and matrix properties influence the speed at which these processes occur. Adsorption isotherms are utilized to determine the maximum adsorption capacity of the material. The shape of an adsorption isotherm is determined by plotting the number of molecules adsorbing per unit area of the interface against either the gas pressure or the equilibrium concentration of the liquid solution [121]. The most commonly utilized models for assessing pollutant adsorption include the Langmuir and Freundlich isotherms [122].

Desorption, or the transfer of adsorbate ions from the adsorbent surface to the solution, frequently occurs in conjunction with adsorption. One can assess the reversibility of adsorption based on the amount of adsorbate that is desorbed from the absorbent: the reversibility of the adsorption process increases with the amount of desorbed adsorbate. [123, 124].

Two main approaches to running the adsorptive processes are batch flow and continuous flow methods. Batch adsorption is frequently employed on a laboratory pilot size to treat minute quantities. These systems consist of a batch reactor with an adsorbent colloidally suspended in an adsorbate combined over a predetermined period. Until equilibrium is attained, the effects of variables such as temperature, adsorbate concentration, amount of adsorbent, agitation speed, and adsorbent particle size are also assessed [125]. In general, industrial-scale processes employ continuous adsorption systems. The fixed bed column of continuous flow is the most widely utilized approach for adsorbate and adsorbent interaction in this approach. Studies of continuous adsorption systems assess the effects of variables on column adsorptive processes, including initial adsorbate concentration, the flow of adsorbate, column bed height, pH, adsorbent particle size, system temperature, breaking points, and exhaustion [126].

2.4.1. Wastewater treatment by adsorption

Adsorption is considered a highly effective approach for wastewater treatment due to numerous qualities that render it more efficient than similar methods [127]. The United States Environmental Protection Agency (USEPA) acknowledges the adsorption process as one of the finest and most remarkable wastewater treatment methods, citing its remarkable removal efficiency, which can attain up to 99.9% [128]. Removing dye from aqueous solutions is an everyday use for this separation method. Adsorption is particularly useful in the textile, leather, dyeing, cosmetics, plastics, food, and paper industries since water recovery is crucial. To remove methylene blue dye from an aqueous solution, fly ash and red mud underwent chemical and heat treatment of 800 °C overnight [129]. The findings indicated that subjecting fly ash and red mud to heat treatment reduced their adsorption capacity. Conversely, acid treatment using HNO_3 had varying effects on both materials: it enhanced the adsorption capacity of the fly ash while diminishing that of red mud. In addition, Shi et al. [130] grafted sunflower stalks chemically with quaternary ammonium groups to enhance their adsorption capacity. The findings revealed that the maximum adsorption capacities for two dyes Congo red and direct blues on modified sunflower stalks were reported as 191 mg/g and 216 mg/g, respectively. These values were at least four times higher than those observed on the untreated sunflower stalks.

Extensive research on algal biochar as a bio-sorbent has been demonstrated to remove heavy metals and other pollutants [131]. Algal biochar has superior bio-sorption abilities. As a result, it is considered suitable for wastewater treatment applications such as eliminating different inorganic, ammonium-N, and organic contaminants from waste effluents [132]. For example, Cole employed biochar in 2017 to isolate dissolved phosphorous and nitrogen from municipal wastewater, while Jung used biochar to sift phosphate ions in 2016 [133]. Several traditional methods are available for removing heavy metals from water, such as chemical precipitation, solvent extraction, membrane filtration, ion exchange, electrochemical removal, and coagulation.

However, these methods have drawbacks, including limited efficiency, delicate working conditions, toxic sludge availability, high energy consumption, inadequate removal, and expensive disposal [134, 135]. Since adsorption tends to have the most significant impact on the transport, toxicity, and biological availability of heavy metals in aqueous environments (mainly at their trace concentrations) and is simple to use and affordable, it has been widely employed [136-138]. In the sorption of the binary components Cu^{2+} and Pb^{2+}, Kongsuwan et al. [139] studied the use of activated carbon produced from eucalyptus bark. Adsorption was found to be the primary mechanism for the uptake of both heavy metals, with the maximum adsorption capacities for Cu^{2+} and Pb^{2+} being 0.45 and 0.53 mmol/g, respectively. Božić et al. [140] used sawdust from beech, linden, and poplar trees as adsorbents to remove heavy metal ions from synthetic solutions. The maximum adsorption capacity (7 – 8 mg/g) was attained between a pH of 3.5 and 5.0. As a result, adsorption-based wastewater treatment presents a potentially effective way to combat water contamination. Many industries have found success in the effective removal of pollutants using adsorbent materials.

2.4.2. Factors affecting adsorption

Several factors influence the effectiveness of adsorption processes. These factors are outlined below. Understanding these factors is essential to optimize adsorption processes and create effective treatment plans.

2.4.2.1. Effect of pH

The pH of a solution significantly influences the efficiency of adsorption. The pH level impacts the ionization of adsorbates and their surface charge, affecting how well they interact [141]; and, this influences the effectiveness and the adsorbent's capacity. Moreover, the pH of the solution can modify both the adsorbent and the chemical composition of the solution. It also impacts the surface charge and ionization degree of the adsorbed ions [142, 143]. Cruz-Lopes et al. [144] found that the quantity of lead adsorbed onto soils increased as the pH increased. They proposed that this enhancement in adsorption resulted from a reduction in H^+ concentration and an elevation in negative charges due to the deprotonation of OH- groups. Changes in pH were recognized to exert different effects on adsorption, contingent upon the pollutant type and the functional groups on the adsorbent surface. For instance, prior research indicates that the elimination of oil from produced wastewater using castor oil and modified castor oil can be influenced by pH variations [145]. Adsorption is more effective at lower pH because as pH rises, more organic compounds are removed from produced wastewater, which increases competition with other ions for available adsorption sites. A solution's pH strongly influences the efficiency of adsorption processes. Surface charges can be managed to improve adsorption efficiency by understanding and maximizing the pH of the solution, which opens the door for more effective adsorption-based treatments and environmental remediation methods.

2.4.2.2. Effect of initial oil concentration

The oil concentration influences the overall adsorption efficiency, which also impacts the distribution of oil molecules in equilibrium and the available adsorption sites [146]. Understanding this relationship is essential for developing efficient oil removal strategies and improving adsorption-based treatment techniques. Since adsorption is a mass transfer phenomenon, the concentration of the pollutants is crucial because it affects the force that drives the contaminants out of the solution and onto the adsorption site. Investigating the effectiveness of coconut coir-activated carbon in cleaning up oil spills through adsorption, it was observed that raising the initial concentration of crude oil enhanced the adsorption capacity but reduced the percentage of crude oil removed [146]. This outcome stemmed from the presence of active sites on the surface of the adsorbent. A low initial crude oil concentration of 3888 mg/L and a heightened ratio of surface-active sites facilitated more significant interaction between natural oil molecules and the adsorbent, resulting in the occupation of more active sites on its surface. Consequently, this led to a substantial adsorption capacity of 971.925 mg/g and an impressive percentage removal of crude oil amounting to 99.99228%. Another study found that the percentage of oil removed decreased from 96% to 84.6% when the initial oil concentration decreased from 276 mg/L to 103 mg/L [128]. This trend can be attributed to the significance of external mass transfer in the process. As the initial concentration of oil increases, the adsorption of the pollutant accelerates onto the surface. However, Ewis et al. [147] observed a negative correlation between initial oil concentration and the amount of emulsified oil removed from produced water, with the amount of pollutant removed decreasing as initial oil concentration increased. The oil concentration at the beginning of the adsorption process profoundly influences its effectiveness, emphasizing the importance of optimizing initial conditions for efficient oil removal in environmental applications.

2.4.2.3. Effect of adsorbent dosage

The quantity of adsorbent used is critical in determining its capacity to adsorb a certain amount of substance under given operational conditions. Research findings indicate that there is a direct correlation between adsorption capacity and dosage [148, 149]. This suggests that as the dosage increases, the adsorption capacity also rises. This can be attributed to the expansion of the adsorbent's surface area and the availability of more sites for adsorption [150]. In their study of the crystal violet dye adsorption by Acacia nilotica sawdust-activated carbon, Gupta and Lataye [151] found that the percentage of dye removal increases as the adsorbent dosage increases up to 8 g/L. Moreover, the removal percentage increases only marginally when the adsorbent dosage is raised from 8 to 20 g/L. Beyond this point, dye removal stays relatively constant and is not influenced by further increases in the adsorbent dose. It has been reported that increasing the adsorbent dosage from 0.05 g to 0.1 g increased the percentage of oil removal from 18% to 28.4% [147]. Similar outcomes were attained by utilizing walnut shells to adsorb organic material [152], where an increase in dosage from 0.5 g to 3 g increased the oil recovery percentage from 39.6% to 62.3%. However, contradictory findings were reported from other studies, with their results indicating that the adsorbent dose increase led to a reduction in the adsorption capacity [153, 154]. This was attributed to the saturation of the adsorbent surface, the clustering of adsorbent particles at higher dosages, and the electrostatic repulsion between the adsorbate and the functional groups on the surface of the adsorbent [155].

2.4.2.4. Effect of temperature

In environmental remediation and separation approaches, the impact of temperature on adsorption processes is a crucial aspect to consider. Understanding the thermodynamics of the process and improving efficiency can benefit from looking at how temperature affects adsorption**.**

The adsorption process mainly depends on temperature since it alters the adsorption capacity of the adsorbent [156]. The degree of adsorption increases with temperature if the adsorption process is endothermic [157]. This might result in the molecules becoming more mobile and adsorption active sites as the temperature rises. Conversely, when the adsorption process is exothermic, an increase in temperature leads to a decrease in adsorption. This phenomenon occurs because as the temperature increases, the adsorption forces between the adsorbate species and the active sites on the adsorbent surface weaken, thereby reducing the extent of adsorption [158]. The research on the use of Imperata cylindrica for oil adsorption revealed that the adsorption capacity increased as the temperature increased from 20 to 60 °C [159]. Similarly, a rise in temperature from 20 °C to 70 °C led to an increase in the amount of lithium adsorbed, which went from 12.5 mg/g to 17 mg/g [160]. Additionally, crude oil adsorption capacity and the percentage removal increased in direct proportion to temperature [146]. This increase was explained by reinforcing the physical bond between the active sites of crude oil molecules and the adsorbent, which occurs as hydrogen bonds and van der Waals forces diminish at higher temperatures. Moreover, the decrease in solution viscosity and the increase in crude oil's solubility in water contributed to the heightened diffusion rate of crude oil molecules through the external boundary layer and the internal pores of the adsorbent particles as temperature increased [161, 162].

2.5. Adsorbents for wastewater treatment

Various adsorbents and their mechanisms have been extensively studied in the literature for wastewater treatment. These encompass a range of materials such as natural substances, industrial and agricultural residues, waste products, biomass materials, and more. When selecting an adsorbent for pollutant removal, crucial considerations include the concentration and nature of pollutants in the wastewater, the adsorbent's capacity for adsorption, and its effectiveness [163].

Adsorbents should also be easily regenerated, affordable, non-toxic, and readily available. Adsorbents for oily wastewater treatment are described below.

2.5.1. Natural adsorbents

Many naturally occurring substances have similar characteristics to those of an adsorbent. Although plentiful, these materials have demonstrated successful applications in removing various pollutants, such as heavy metal ions, organic compounds, and colorants from wastewater. Such materials include chitin, clay, zeolite, peat moss, coal, and wood [164]. Zeolites are structured crystalline aluminosilicates with microporous characteristics and a well-organized pore structure. These materials find widespread use in environmental protection endeavors, particularly in adsorbing volatile organic compounds and heavy metal ions. Their adaptability in pore size, notable hydrophobic properties, excellent thermal stability, and ease of surface modification contribute to their effectiveness in various environmental applications [165, 166]. It was found that zeolites typically exhibit an average specific surface area of 800 m^2/g, with a maximum of up to 1769 m^2/g. The average pore volume of zeolites is approximately 0.66 cm^3/g, reaching a maximum of 1.02 cm^3/g. Regarding adsorption capacity, the average saturated toluene adsorption on zeolites is around 137.2 mg/g, with a maximum capacity of up to 288.4 mg/g [167].

Chitin and chitosan, biopolymers used in fiber production, have gained notable recognition for their unique characteristics and decomposing ability. These fibers exhibit superior removal efficiency and strength compared to activated carbon, garnering considerable attention in various applications [168]. Chitin, a naturally sourced renewable substance, holds promise for multiple industrial applications, including its potential as an adsorbent in sectors such as wastewater treatment [169]. Chitosan has garnered significant interest as a potent biosorbent due to its cost-effectiveness compared to activated carbon. Its abundant amino and hydroxyl functional groups contribute to a robust adsorption capacity for various aquatic contaminants [170, 171]. This biopolymer presents an attractive alternative to current biomaterials due to its physicochemical attributes, chemical stability, heightened reactivity, remarkable chelation characteristics, and superior selectivity towards pollutants [172]. Natural chitosan has been subjected to numerous physical and chemical alterations to enhance its capacity to bind diverse contaminants. Various forms of chitosan, such as membranes, microspheres, gel beads, and films, have been produced and assessed for their effectiveness in treating wastewater. Previous studies extensively detail the structures of chitin and chitosan, and the diverse methods employed for their physical and chemical modifications [172-175].

The use of clay minerals as alternative inorganic adsorbents offers many benefits. The colloidal characteristics and negative charge layers enhance their ability to adsorb cations and organic compounds [176]. Clay-based adsorbents are a relatively new group recognized for their catalytic properties [177, 178]. Clay-based adsorbents offer versatility in adsorbing various contaminants, and various modification techniques can tailor them for selective sorption. These benefits encompass their widespread availability, ease of application, simple recoverability, cost-effectiveness, non-toxic nature, and suitability for a broad spectrum of contaminants [179]. Clay minerals, characterized by their significant surface area and robust sorption capacity, demonstrate excellent structural and chemical resilience when adsorbing organic and inorganic contaminants. The surface charge chemistry of clay directly influences the adsorption mechanism. Due to the mechanism of surface sorption, clay has received increased attention as an adsorbent for the treatment of different wastewater streams. Additionally, several clays, including bentonite [180], kaolinite [181], illite [182], sepiolite [183], montmorillonite [184], and pyrophyllite [185], are effective at removing pollutants. Several mechanisms, such as physical adsorption, micro-precipitation involving ion exchange at permanently charged sites, and the formation of complexes at edge sites with hydroxyl groups, along with chemisorption, have been documented for the sorption of metal ions by clay minerals [186, 187].

Wood is considered a non-renewable, inexpensive natural adsorbent that can be disposed of by burning [188]. Recently, there has been exploration into using wood across various energy storage domains, solar steam generation, and wastewater treatment. Wood, composed of cellulose microfibrils within a porous lignin matrix, capitalizes on its hierarchical and porous structure for these applications [189]. Wood was studied as an adsorbent for the removal of telon blue by Poots et al. [188] to develop a cost-effective adsorbent. The adsorbent was used after being sieved into various size ranges and investigated without pretreatment. The kinetics of the process was shown to be particle size dependent, with small particle sizes of 150 – 250 µm having the lowest kinetics (>3h) and big particle sizes of 710-1000 µm having the highest kinetics (>6h). A long contact period of 8 h, as well as a low adsorption capacity, were observed in this study. Additionally, the same wood adsorbent was employed to remove another dye (basic), astrazone blue [190]. However, it was shown that for this system, equilibrium adsorption required a shorter contact time of 2 h and had a greater adsorption capacity of 100.1 mgg^{-1} for particles between 150 and 250 µm.

2.5.2. Agricultural waste

Several investigations have shifted attention towards utilizing agricultural waste materials, including stone fruits, nuts and husks, peels, wood and forest residues, and plants, as cost-effective and eco-friendly biosorption materials for wastewater treatment. These materials are favored due to their unique chemical composition, widespread availability, renewable nature, and affordability [23, 191-193]. The primary constituents of these agricultural wastes consist of cellulose, hemicelluloses, and lignin. However, they may contain additional functional groups such as hydroxyl, aldehyde, carbonyl, carboxyl, phenolic, and ether. These functional groups can interact with pollutants present in wastewater through diverse specific binding mechanisms and interactions [194, 195]. They can serve as appealing alternatives to traditional adsorbents [196].

Nevertheless, compared to synthetic commercial adsorbents, raw agricultural wastes often have lower biosorption capabilities. Consequently, different pre-treatment methods have been utilized to augment the sorption properties of raw biomass, thereby enhancing their effectiveness and applicability for wastewater treatment [197]. These operations primarily consist of physical and chemical processes involving organic compounds, oxidizing agents, bases, organic and mineral acids, and organic compounds [198]. Chemical agents such as calcium hydroxide, sodium carbonate, sodium hydroxide, nitric acid, hydrochloric acid, sulfuric acid, tartaric acid, citric acid, formaldehyde, methanol, and hydrogen peroxide are commonly employed to enhance the pollutant adsorption capabilities of sorbents [199]. McKay et al. [200] studied the effectiveness of five low-cost adsorbents, including rice husk, bark, cotton, hair, and coal, for the adsorption of two cationic dyes (safranine and methylene blue). All the adsorbents under study, except for coal, had more excellent safranine monolayer adsorption capabilities than methylene blue.

In another study, barley straw treated with sodium hydroxide and the cationic surfactant hexadecyl pyridinium chloride monohydrate (CPC) was used to remove two anionic dyes from aqueous solution, Acid Blue (AB40) and Reactive Blue 4 (RB4) [201]. With a good removal % of AB40 and RB4, the CPC was seen to be firmly bonded to the surface of the straw. Although the desorption process was found to be generally ineffective, the adsorption of these dyes on modified straw was favorable in very acidic conditions. Numerous plant parts, including plant bark, coconut fiber, coconut shell, pine needles, neem leaf powder, and cactus leaves, have been tested for their ability to remove chromium and have demonstrated an effectiveness of more than 90% at the ideal pH level [202]. It was indicated that chromium may be removed from wastewater using natural and modified forms of sugarcane bagasse [166]. To effectively remove copper ions from wastewater, rice bran, rice straws, and soybean hulls are treated with citric acid [203].

2.5.3. Industrial waste

Industrial waste is one of the inexpensive adsorbents for removing heavy metals from wastewater [204]. It only needs a minimal amount of processing to boost its adsorptive ability. Industrial waste materials are affordable because they are widely accessible locally in huge quantities. The feasibility of employing various industrial by-products, including fly ash, blast furnace sludge, waste slurry, lignin, iron (III) hydroxide, and red mud, has been studied for the removal of heavy metals, organic compounds, and dyes from wastewater. The metal hydroxide sludge from industrial effluent from electroplating was used to create adsorbents for removing azo-reactive dyes [205, 206]. For azo reactive anionic dye, these adsorbents containing many metal hydroxides with positive charges had a maximum adsorption capacity of 48 – 62 mg/g. Fly ash is a byproduct of combustion primarily used to manufacture cement, bricks, and other building materials. Due to its high alumina and silica percentage and suitability for adsorption, fly ash is a cheap adsorbent [207]. Fly ash has been found to have a porous surface with tiny, irregularly shaped, glassy spherical particles. The features of fly ash have been altered to make it more adsorption-friendly [208]. Using fly ash from a heat and power plant and oxides with a SiO_2/Al_2O_3 oxide composition over 2.4, class "F" fly ash was generated [209]. The adsorbent exhibited remarkable performance and created a new substrate with high adsorption capacity for heavy metals in multi-cation wastewater treatment. Disposing of bagasse fly ash, a waste product from the sugar industry, poses a persistent challenge. Previously used primarily as a filler in construction materials, bagasse fly ash has recently been repurposed into an efficient adsorbent to remove harmful chemicals [210]. Bagasse has recently demonstrated its use in eliminating zinc and other metals from aqueous solutions [211].

2.5.4. Nano-adsorbents

Nano-adsorbents have been effectively developed via nanotechnology for wastewater treatment, which has become a rapidly expanding and fascinating field of research [212]. Nano-adsorbents possess diverse physical and chemical characteristics, encompassing high surface area, chemical reactivity, conductivity, catalytic activity, selectivity, and magnetic and optical properties. Because of the vast surface area, there are more active sites where different contaminants interact with nano-adsorbents. Due to these characteristics, they have more excellent adsorbent properties than their corresponding bulk materials [213-216]. In fixed bed columns, 16 metal oxide nanoparticles, including TiO_2, NiO, Fe_2O_3, and ZrO_2, were examined [217] for their ability to remove arsenic. All nanoparticles displayed a removal capacity of about 98% except ZrO_2. The Freundlich adsorption isotherm provided good agreement with the adsorption results. Some well-known nanomaterials employed in wastewater treatment include carbon nanotubes, ordered mesoporous carbon, graphene, carbon nanofibers, and titania nanotubes and their variations. Large surface areas cause a higher concentration of surface defects and make it easier for contaminants to interact with the surface [218].

Numerous carbon-based nanomaterials have been generated due to the rising need for nanotechnology [219]. Nanomaterials of carbon and graphene, like nanotubes, come in functionalized and non-functionalized varieties [220]. Two crucial advantages result from the alterations made to nanostructures made of carbon. Firstly, improvement in hydrophilicity promotes dispersion in an aqueous medium, suggesting that better distribution provides a larger surface area for exposure to contaminants or other undesirable species [221, 222]. The second factor is an increase in the electrostatic interactions between the adsorbent and the adsorbate, which increases adsorption capacity. If a negative charge functionalizes the surface, the electrostatic interactions are the primary mechanism that drives the adsorption of particularly positively charged species such as heavy metals [223]. Surface modification enhances the adsorption activity of carbon-based nanomaterials by amplifying the presence of organic functional groups [224]. The widely favored adsorption material is activated carbon, renowned for its outstanding physical and chemical properties, including a vast specific surface area, many functional groups, chemical stability, strong mechanical strength, and resilience against acids and alkalis [225, 226]. Activated carbon has an average surface area of 1404 m^2/g and a specific surface area ranging from 478 to 3167 m^2/g [167]. The range of the pore volume, which runs from 0.41 to 1.75 cm^3/g, is 0.72 cm^3/g on average. The average adsorption capacity for volatile organic compounds is 460.0 mg/g, ranging from 170.0 to 737.0 mg/g. Non-zerovalent iron was impregnated on activated carbon and utilized to adsorb the arsenic contaminant As (III) [227]. The nanocomposite removed roughly 1.997 mg/g in 2.0 mg/L of arsenic solution at a pH of 6.5. The authors suggested this adsorbent as a prime candidate for treating drinking water contaminated with arsenic [228]. The ability of coconut shell-activated carbon to remove the dye methylene blue with the help of magnetic particles was examined [229]. The uptake of methylene blue hampered the encapsulated activated carbon on regenerated cellulose beads and only reached complete adsorption after 90 min. The dye removal efficiency of granular coconut shell activated carbon obtained 99.7% within 2 min. This suggests that the dye took a lengthy time to enter the beads' interior [229].

Because of their unique one-dimensional structures, remarkable mechanical strength, superior electronic properties, and wide-ranging applications, carbon nanotubes have emerged as a captivating addition to the carbon family, attracting considerable research attention. They encompass single-walled and multi-walled varieties, distinguished by their number of layers. The exceptional thermal and chemical stability of carbon nanotubes has prompted their adoption as carriers for catalysts [230], in addition to the potential for creating improved composites [231] and nanoscale electrode devices [232]. Structurally, they are the perfect adsorption material due to their enormous specific surface areas and hollow and layered structures. The adsorption characteristics of carbon nanotubes for various toxic substances, including lead, cadmium, and 1,2-dichlorobenzene, were determined. The results indicate that carbon nanotubes are superb and effective adsorbents for eliminating these hazardous substances from water [195]. The adsorption of small molecules [233-235], heavy metal ions [236-238], radionuclides [239, 240], and organic compounds [241, 242] on various carbon nanotubes (CNTs) (single-walled or multiwalled, closed- or open-ended CNTs), has already been the subject of numerous experimental studies. From a theoretical and practical perspective, the research of CNT adsorption properties is significant because it may provide fresh insight into the adsorption mechanism in complex systems.

Effective adsorbents can be produced widely at a reasonable cost using functionalized graphene [243]. This arises from the two-dimensional layer structure of the materials, their expansive surface area, significant pore volume, and content of surface functional groups. Inorganic nanoparticles help prevent the adsorbent from aggregating. Research has shown that the equilibrium data were well suited to the Langmuir model, while the kinetic data followed a pseudo-second-order model [244]. Additionally, the graphene nanocomposite adsorbent of a mono-component system had a maximum Cd^{2+} adsorption capacity of 91.29 mg g^{-1}. Similar outcomes for the maximal adsorption capacity for cadmium biosorption were previously obtained [245].

2.5.5. Bio-sorbent

Growing interest and research into using inexpensive adsorbents have led to several successful applications of these affordable, naturally occurring, and easily accessible organic adsorbents in treating industrial effluents using adsorption processes [246]. Biosorbents offer numerous advantages, including affordability, high efficacy, reduced production of chemical or biological sludge, the capability for biosorbent regeneration, and the potential for metal recovery [247]. Bio-sorbents, as their name suggests, originate from biological origins. With specific functional groups on their surfaces, these materials are inclined to attract and bind contaminants [248]. Magnetic-activated carbon and magnetic biosorbents were created to remove lead, with adsorption capabilities ranging from 11.6 mg/g to 35.7 mg/g. Pb^{2+}, Cr^{6+}, and Cu^{2+} removal efficiencies on biosorbents modified with zero-valent iron reached 99.4%, 66.7%, and 99.1%, respectively, on zero-valent iron-modified biosorbents through complexation with -OH/-COOH functional groups or delocalized π electrons [212]. A potential technique for producing bio-sorbents with practical sorption capabilities has been shown in another work using modified walnut shells. High inorganic acid concentration modifications increase the sorption capability. These bio-sorbents can also be employed in the low wastewater demineralization method [249].

Table 2.3: Adsorption performances of different adsorbents for wastewater treatment

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Removal efficiency (%)	Optimal pH	References
Activated carbon	Crystal violet dye	84.11	85-90	10.0	[250]
multi-walled carbon nanotubes	Reactive Red M-2BE textile dye	95-352.1	-	2.0	[251]
Graphene	Cd	106.3	-	pH 6.0 ± 0.1	[252]
TiO_2 nanotubes/CNTs	Pb	192-588	-	-	[253]

Few-layered graphene oxide (FGO)	Pb(ii)	842-1850	-	7-8.1	[254]
Fe_3O_4 nanoparticles	Pd, Cd, Cu	369.0–523.6	98	7.0	[255]
Activated carbon	Pb^{2+}	294.1	-	-	[256]
Bentonite	Malachite Green	-	>90	9.0	[257]
Kaolin	Methylene Blue	52.76	-	6.0	[258]
Kaolinite	Methylene Blue	102.04	-	6.0-10.0	[259]
Montmorillonite	Methylene Blue	289.12	-	11.0	[260]
Natural bentonite	Diazo dye	74.5	>95	10.0	[261]
Open burnt clay	Congo Red	-	98	3.0	[262]
Fungal and bacterial biomass	VOCs	374-620	-	-	[263]
Modified lemon leaf	Cationic dye	36.10	70	5.0	[264]
***Citrus limetta* residue**	Fluoride	12.6	74-76.5	4.0	[265]
Modified biogas residue	Nitrate	64.12	>82	5.0-9.0	[266]
Waste-based bio-sorbent	Fluoxetine	21.86–233.5	-	7.0-9.0	[267]
Eggshell waste	Cu	142.86	93.17	6.0	[268]
Modified sawdust	Cr (VI)	8.84	100	2.0	[269]
Wheat straw	Cu^{2+}	7.05	-	5.0	[270]
Fly ash (geopolymer)	Anionic surfactant	714.3	-	2.0	[271]
Coal fly ash	Anionic surfactant	2.95	96	-	[272]
Chromium Leather waste	Anionic surfactant	423	>90	4.0-8.0	[273]

2.6. Oily wastewater treatment using adsorption.

A variety of treatment approaches, including physical methods (filtration, electrodialysis, flotation, and adsorption), chemical techniques (precipitation, chemical oxidation, and electrochemical technologies), and biological methods (activated sludge, aerated biological filters, microbial capacitive desalination, and microalgae-based treatment) have been used for oily wastewater treatment [274-277]. However, most of these techniques are either overly complicated, expensive, or ineffective since they are inefficient at removing smaller oil droplets and emulsions [278, 279]. The adsorptive methods have been utilized extensively because they have low production costs and good selectivity, are applicable in low concentrations, and may be employed in batch and continuous processes. Adsorbent materials can also be regenerated and used in subsequent adsorption cycles [280, 281]. Hence, in recent years, sorption has emerged as one of the most efficient methods for completely removing spilled oil under ambient conditions. Adsorption is frequently employed as a secondary removal step after a crude oil removal method, like skimming [282, 283]. However, the adsorbent parameters, such as surface area, pore size, pore diameter, and functional groups, considerably impact the method's effectiveness.

To remove PAHs from wastewater, some carbon-based nanomaterials have caught the interest of researchers. Specific properties of carbon-based materials, such as hydrophobicity, electrical conductivity, high surface area, mechanical resistance, and low production costs, make it easier to use them in adsorption techniques to treat effluents [284]. The removal of dibenzothiophene from petroleum distillates through activated carbon in a continuously packed bed column was explored [285]. In this study, activated carbon was used as an adsorbent in a continuous mode to desulfurize model diesel that only included dibenzothiophene. According to the findings, the adsorbent has an approximate 16 mg kg^{-1} adsorption capacity for adsorbate at a flow rate of 3 ml/min and a dosage of 2.0 g. Furthermore, the Langmuir isotherm model was an ideal fit for the adsorbent's adsorption behavior. Abdullahi et al. showed a simple method to generate hydrophobic graphene oxide (GO) films functionalized with alkylamines that can be used as sorbents to remove oil from water mixtures [286]. Through nucleophilic substitution and amidation processes, GO and three distinct alkylamines (hexylamine, dodecyl amine, and hexadecylamine) were combined to create the hydrophobic alkylamine-functionalized graphene oxide sorbents. The water contact angle of the top-performing C_{16}^{-}FGO surface, which has been functionalized with hexadecylamine, was 141.08±1.65°, demonstrating exceptional hydrophobicity. Additionally, the C_{16}^{-}FGO has shown great effectiveness in the separation of the oil-water mixture as well as excellent performance in oil adsorption. Its reusability was evaluated to demonstrate the applicability of the produced sorbent in more complicated situations. Most recently, a heat-localization device based on reduced GO and silver nanoparticles was presented by Wang's group for the adsorption of oil particles using a simple coating process [287]. The adapted sensor exhibited photothermal properties and hydrophobicity, resulting in a notable solar-steam evaporation efficiency of 86.8% and outstanding adsorption capacity for organic solvents and low-viscosity oils ranging from 54.0 to 123.0 g/g. The adsorbent decreased the oil's viscosity to achieve a high heavy crude oil adsorption capacity (68.0 g/g). Moreover, Zhuo and co-workers introduced a hierarchical nano-adsorbent composed of carbon nanotubes. They reduced GO to enhance the adsorption of heavy crude oil with the assistance of solar light heating [288]. The developed rough and oleophilic surface-based adsorbent reduced the oil diffusion resistance to speed up the adsorption of heavy crude oil via capillary force. Compared to other oil adsorbents previously reported, the proposed adsorbent provided an exceptional efficiency of heavy crude oil adsorption, up to 267 g $g^{-1,}$ within 10 min.

Different low-cost biowaste adsorbents such as tea waste [289, 290], palm tree leaves [291], corn silk [292], oil palm fruit [293], teff straw [294], rice husk [295], banana peels [296], rape straw [297], and mangosteen peels [298], have been used to remove different contaminants from wastewater. These adsorbents have attracted attention because of recent progress in modification methods, which create a large surface area and distinctive physicochemical and biological characteristics [299-301]. For instance, sugarcane bagasse and surplus biomass from rice straw were used as cost-effective adsorbents to successfully remove PAHs from oil industrial effluent [302]. The findings suggested a considerable interaction between bio-adsorbents and PAHs due to the non-spontaneous characteristics of the bio-adsorptive process, excellent affinity for the adsorbate, and endothermic nature. Barley straw, an agricultural byproduct, was chemically treated with a cationic surfactant known as hexadecylpyridinium chloride monohydrate (CPC) to remove emulsified canola oil from an aqueous solution [303]. The inclusion of CPC was found to render the surface of barley straw non-polar, thereby significantly enhancing the adsorption capacity of surfactant-modified barley straw for oil removal from water. The kinetic investigation showed that the equilibrium period was short, and the isotherm study showed that the Langmuir model adequately described the oil adsorption. The Langmuir isotherm revealed an adsorption capacity of 576.0±0.3 mg/g at 25 °C. Walnut shells possess distinctive qualities that render them a viable and eco-friendly option as an adsorbent material. Their accessibility, affordability, and impressive surface area make them well-suited for the filtration of contaminants in both water and air [304]. Due to their high surface area and porous structure, they are capable of adsorbing oil from wastewater. Recent studies have seen walnut shells undergo modification processes to enhance their adsorptive properties. A hydrophilic sulfonic acid group attached to the surface of walnut shells, creating a stable coating layer by chemically bonding it to the surface functional group, was developed [305]. This resulted in a decrease in micropore size, an augmentation of surface density, and an improvement in surface wettability, all while preserving its remarkable super-hydrophilic underwater oleophobic characteristics and compressive strength [305]. The results of this study revealed that the oil removal rate increased from 38.05% to 89.51% after the modification of the walnut shells. Wood sawdust offers an abundant supply and a systematic adsorbent suitable for various pollutants such as oil, heavy metals, and salts [306]. In recent research, activated carbon (AC) was produced by synthesizing different agricultural waste materials, such as bamboo and banana fibers, for oil spill treatment [307]. The study indicates that BANA-AC achieved a maximum oil adsorption capacity of 4.418 g/g with an activation ratio of 7:1 (H_3PO_4) and a surface area (SA) of 2,172.234 m^2/g. BAMB-AC (5:1 550 °C) exhibited the highest surface area at 2,760.447 m^2/g with a sorption capacity range of 3.3678 g/g. The findings suggest that further surface modifications of synthesized AC from various biomass sources could significantly enhance remediation efficiencies, given the correlation between SA and adsorption capacity. This research introduces a promising approach for addressing oil spills and potentially removing pharmaceuticals and heavy metals in wastewater treatment.

One technique used recently to treat wastewater is adsorption using clay. The substance has a large surface area, is cheap, and is abundant. Clay also exhibits significant mass transfer rates [308]. Clays have been subjected to physical and chemical alterations to produce materials for practical applications. Clay's properties can be altered through adsorption and intercalation of organic polymers. The modification process, known as pillarization, frequently involves intercalating cationic species to act as pillars, supporting the mineral layers and creating a porous material. This porous structure is advantageous for adsorbing organic molecules and other environmental uses [309]. One type of clay (kaolin) and one clay mineral (montmorillonite) were chosen and analyzed about transmembrane pressure and solution pH [310]. In addition, clay isotherms and adsorption rates were studied to understand the properties and behavior of the hybrid process. The findings revealed an 80% removal effectiveness for phenol and a 40 mg g^{-1} maximal adsorption capacity.

Adsorptive procedures are promoted as an easy, quick, and effective PAH remediation solution compared to other remediation technologies. For the removal of PAHs, a variety of adsorbents can be utilized, including activated carbon [311], organo-bentonite [312], zeolites [313], mesoporous materials based on silica [314], and nanomaterials based on graphene [315]. It is crucial to emphasize that research into adsorption's kinetics, equilibrium, and thermodynamics is required when creating an adsorbent material.

Table 2.4: Adsorption performances of various low-cost adsorbents for treating oily wastewater

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Treatment efficiency (%)	Optimal pH	References
Rice husk	Naphthalene, phenanthrene, pyrene	63.6, 50.4, and104.5	-	-	[316]
Biochar	Pyrene and benzo(a)pyrene	187.27 and 80.00	93.5 and 87.9	4.0	[317]
Bamboo powder	Petroleum ether	-	99.3	4.6	[318]
Bentonite	PAHs	-	88	7.5	[319]
Bentonite	Diesel oil	81.65	-	6.5	[320]
Iron Oxide/Bentonite	Diesel oil	54.04	67	6.5	[147]
Synthetic resins	Emulsified oil	11.86	>98	2.0-10.0	[321]
AC/Bentonite	Diesel oil	48	-	2.5-11.0	[322]
Montmorillonite	Dodecane	25.84	66.02	-	[323]
Zeolite	Diesel oil	600	-	-	[324]
Sawdust	Heavy crude oil	4100-6400	-	7.0	[325]
Peat	Diesel oil	9000-12000	99.21	-	[326]
Fly ash	Diesel oil	700-900	-	-	[327]

Raw *Posidonia oceanica* fiber	Crude oil	5300	99.98	7.45	[328]
Sawdust	Heavy crude oil	6400	95.5	7.0	[325]
Coconut coir-activated carbon	Crude oil	4860	-	6.0-7.0	[329]
Banana peel	Gas oil	5310	-	-	[330]
Wheat Straw	Crude oil	6910	-	7.7 ± 0.1	[331]
Saw Dust	Crude oil	4500-8500	99.8	-	[332]
Barley Straw	Crude oil	7000-12000	-	-	[333]
Sawdust	Motor oil-water	28.32	-	-	[334]
Nanosilica	Gasoline-water emulsion	-	99	-	[335]
Sepiolite	Crude oil	-	99	7.0	[336]
Bentonite	Crude oil	-	96	5.0	[337]
Date palm	Crude oil	1330-1425	-	-	[338]
Banana peel	Crude oil	194	~100	10.0	[339]
Pomegranate peel	Crude oil	555	92	9.5	[340]
Activated date-pit	Phenols from petroleum waste	88	78		[341]

Silica NPS	Oil saltwater	-	93	5.0	[342]
Alumina NPS	Oil saltwater	185.76	-	7.0	[343]

Chapter 3 Materials and Methods

3.1. Materials

3.1.1. Walnut shells (WS)

Ground WS is a durable, chemically inert, non-toxic, and biodegradable substance mainly utilized as an abrasive. The shell constitutes a significant portion of the nut, almost 50%. It has diverse applications, including as a component in cosmetics and dental goods, for polishing, and as a filtration medium [304]. Their availability as a renewable resource can be considered an extra benefit. The shell of the walnut fruit is a lignocellulosic agricultural byproduct consisting of cellulose (18%), hemicellulose (36%), and lignin (37%) [344]. The proportion of each component may vary slightly based on the walnut's source, plant genetics, the cultivation environment, and the processing circumstances of the fruit. The primary components of WS closely resemble those found in wood biomass, including lignin, cellulose, hemicellulose, and tannins, which can be extracted and utilized to produce various chemicals and materials [345].

WS is an efficient filtration medium for separating crude oil from water [346]. Currently, WS filtration processes generate water from oil fields, refinery effluent, direct spray, caster water from steel mills, quench water from ethylene plants, copper concentrate decant, and cooling water [347]. WS exhibits exceptional surface properties for coalescence and filtration, along with outstanding resistance to attrition. Research has been conducted to assess the efficacy of WS filters as a substitute for traditional sand filters in removing free oils and suspended particles [347]. WS-based adsorbents have been extensively investigated in various adsorption experiments, particularly for extracting heavy metal ions. Moreover, they have undergone thorough testing to remove organic substances, with methylene blue dye frequently employed as a benchmark representation [348]. In a typical example, Ashrafi et al. [351] eliminated green and Congo red dyes from an aqueous solution with WS modified with NaOH. The modified adsorbent exhibited a 2.3-fold increase in specific surface area. Also, Zhou et al. utilized a commercial activated carbon generated from WS to remove diazinon herbicides from aqueous solutions [349]. The activated carbon was subsequently treated with phosphoric acid to enhance adsorption efficiency [349]. Although research exists on using WS-based adsorbents as a substitute for traditional methods, the literature lacks comprehensive data regarding their oil sorption capability and recovery. This study would facilitate comparing and selecting a sorbent for a particular application. This work aims to assess the oil sorption capacity of the proposed WS-based adsorbent.

Table 3.1: Main materials

Name of material	Specification	Source
Conventional heavy crude oil	Ar	Natural Sciences and Engineering Research Council of Canada
Walnut shells	Ar	Interactivia, USA
Sodium hydroxide	Ar	Thermo Fisher Scientific, USA
Tetrabutylammonium bromide	98 +%	Thermo Fisher Scientific, USA
Tetrachloroethylene	≥ 99 %	Thermo Fisher Scientific, USA
Silica gel	Ar	Sigma Aldrich, USA
Sodium sulfate	99 %	Sigma Aldrich, USA
Xylene	Ar	Thermo Fisher Scientific, USA

Table 3.2: Main Apparatus

Name of instrument	Purpose	Manufacturer
Mikro-Bantam laboratory processing mill	Grinding adsorbent	Hosokawa Micron Powder Systems, USA
Planetary Ball Mill	Grinding adsorbent	IKA, USA
Scanning Electron Microscope (SEM)	Surface structure analysis	Hitachi, Japan
Furnace	Carbonization	Thermo Fisher Scientific, USA
Oven	Drying of materials	Thermo Fisher Scientific, USA
Electronic Balance	Mass measurements	Sartorius, Germany
Fourier transform infrared spectroscopy (FTIR)	Chemical properties analysis	Anton Paar, Canada
FTIR	Oil concentration measurement	PerkinElmer, UK
Homogenizer	Oil/water emulsion preparation	IKA, USA

3.2. Synthesis of WS/NaOH

The WS-modified with sodium hydroxide (NaOH) adsorbent was synthesized through a simple wet impregnation method. Initially, the raw WS was ground using a Mikro-Bantam laboratory processing mill. The resulting material was further milled using a Planetary Ball Mill Machine to obtain a fine, powder-like material. The ground material was then sieved using a laboratory sieve shaker to get the desired particle size of 425 µm.

Subsequently, 20 g of WS was dispersed into 300 mL of deionized (DI) water and stirred using a magnetic stirrer at 120° C and 200 rpm to ensure uniform suspension. Then, a 1 M NaOH solution was added dropwise to the mixture over 1 h using a pipette to ensure gradual and homogeneous mixing of the NaOH with the WS solution. The solution was left on the magnetic stirrer for 24 h at a constant temperature and rpm to achieve a gel-like material. Subsequently, this material was transferred into two 50 mL crucibles and dried in an oven for 24 h at a temperature of 115° C. The resulting material then underwent a carbonization process via thermal treatment. The materials were placed in a furnace at 550° C for 5 h. The obtained material was then allowed to cool at room temperature and kept in a 20 mL bottle.

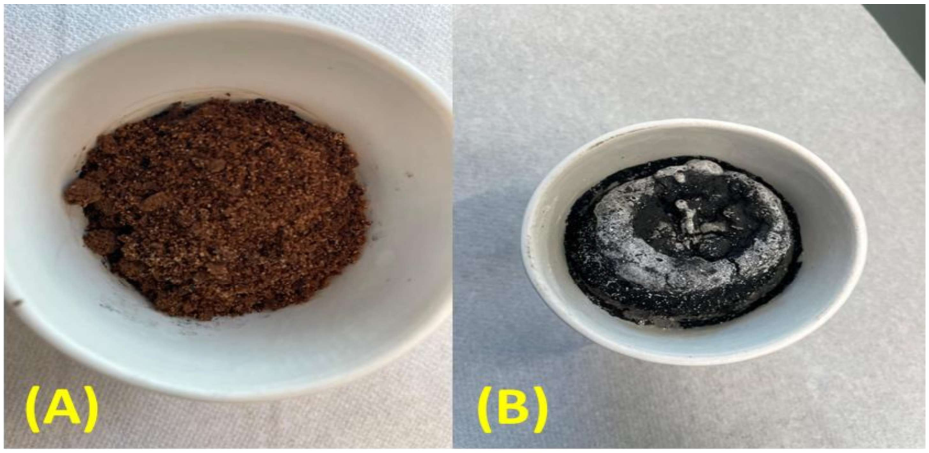


Figure 3.1: Images of (A) Walnut shells 24 h after the addition of NaOH via wet impregnation, and (B) Walnut shells/NaOH after carbonization for 5 h

3.3. Oil emulsion preparation

In this experiment, a 10 g sample of conventional crude oil was emulsified with 1 L of DI water. The emulsion was prepared using a high-speed homogenizer. The oil and water mixture was subjected to homogenization for 15-20 min at a controlled speed to ensure proper formation of the emulsion. Following homogenization, the emulsion was allowed to cool and settle at room temperature for 3 h to ensure phase stability. After this resting period, the emulsion was transferred into airtight containers and stored in a refrigerator at approximately 4°C to maintain the integrity of the emulsion for further analysis. To determine the known concentration of oil in the prepared emulsion, the standardized procedure by ASTM D7066 [350] was followed strictly. To evaluate the effect of salinity, different salt concentrations were added to the prepared oil/water emulsion.

Figure 3.2: Images of (A) prepared oil-water emulsion and (B) oil extraction step

3.4. Experimental design

A one-factor-at-a-time experimental design is mainly utilized when studying the outcome of one independent variable (an experimental factor) relative to the dependent variable [351]. In this case, all other experimental factors are held constant while one factor is changed to learn its impact on the dependent variable. A one-factor-at-a-time design was deemed desirable for this study for the following reasons:

1. *Simplicity.* Adsorption is a complex phenomenon. However, studying a single variable at a time makes it easier to understand the impact of a particular variable without confounding effects from other factors.
2. *Control over factors*. By maintaining all factors and changing only one factor, any observed changes certainly result from the studied factor. A one-factor-at-a-time design blocks interferences from other factors.

3. *Easy identification of optimal conditions*. With a one-factor-at-a-time experiment, it is easier to identify at which level each parameter performs best. This is the first step in optimizing experimental parameters and
4. When a single variable is altered, the data becomes more receptive to interpretation and statistical analysis. Trends can be observed about the influence of the independent variable on the dependent variable.

In this study, four independent variables, which were (1) IC, (2) AD, (3) RT, and (4) S, were studied at different levels to understand their impacts on the dependent variable (oil removal efficiency). The experiments were conducted in triplicate to ensure the reliability and consistency of results. The detailed experimental design with all parameters and their specifications are provided in Table 3.3. Adsorption isotherm and kinetic studies were conducted to evaluate the performance and mechanisms of the adsorption process.

Table 3.3: Experimental design details

Parameters	Levels	Runs
Adsorbent dosage (g/L)	1, 2, 3, 4, 5, 6	3
Initial oil concentration (mg/L)	200, 300, 400, 500	3
Reaction time (min)	10, 20, 30, 40, 50, 60	3
Salinity (g/L)	0, 15, 30	3

3.5. Material characterization and adsorption studies

The adsorbent materials (raw WS and WS/NaOH) were characterized to understand their structural and functional properties. Scanning electron microscopy (SEM) was employed to examine the surface morphology, providing insights into the texture, porosity, and structural features critical for adsorption. FTIR was utilized to identify functional groups present on the material's surface, which play a vital role in the interaction with oily contaminants. These characterization techniques ensured a comprehensive understanding of the adsorbent's properties and its potential for effective adsorption.

In the adsorption studies, a known amount of the adsorbent was added to a beaker containing 100 mL of oily wastewater with a predetermined initial concentration (IC) and salinity (S). The solution was placed on a magnetic stirrer and agitated for a specific duration to facilitate interaction between the adsorbent and the contaminants. After the adsorption process, samples were collected, and the final concentrations of the oily contaminants were measured to determine the adsorbent's efficiency. This setup enabled a controlled evaluation of adsorption performance under varied experimental conditions. The oil removal efficiencies and adsorption capacities were calculated with equations 1 and 2, respectively. The entire experimental procedure, including material preparation and batch adsorption studies, has been graphically presented in Figure 3.3.

$$R\,\% = \frac{(Co-Ce)}{Co} \times \mathbf{100} \qquad 1$$

$$q_{e=}\frac{Co-}{m} \times V \qquad 1$$

Where R = oil removal efficiency (%) Co = initial oil concentration (mg/L), Ce = concentration of oil at equilibrium (mg/L), q_e = adsorption capacity (mg/g), m = mass of adsorbent (g), and V = volume of solution (L).

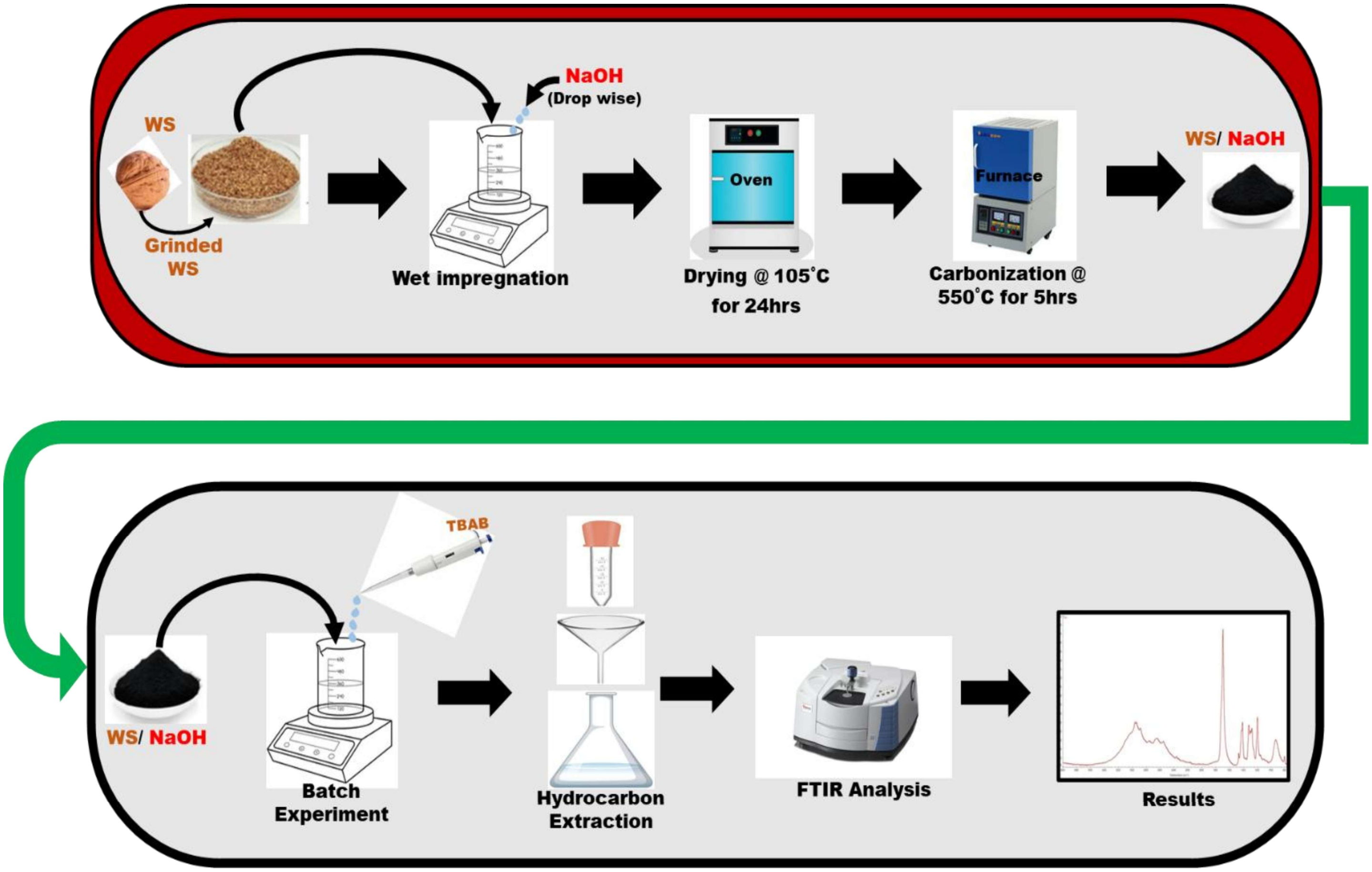


Figure 3.3: Preparation steps of raw walnut shells, Walnut shells/NaOH, batch adsorption studies, and sample analysis

Chapter 4 Results and Discussion

4.1. Characterization of WS/NaOH

The surface morphology of the adsorbents was analyzed by comparing the raw WS with the WS/NaOH sample, as illustrated in Figure 4.1, using SEM images. The SEM image of raw WS is shown in Figure 4.1 A. It reveals a coarse, porous, and heterogeneous surface typical of lingo-cellulosic biomass characterized by irregularly shaped tiny particles resulting from grinding, indicating potential for oil adsorption. The pores and fissures serve as active locations for oil entrapment. However, the efficacy of adsorption may be constrained in its unmodified form. Modifications to enhance the surface area and porosity can boost performance. Notwithstanding specific irregular characteristics, the shells exhibit favorable structural qualities as an adsorbent with potential enhancement. The SEM of WS/NaOH is shown in Figure 4.1 B. Unlike the raw WS, the SEM image of WS/NaOH displays a significantly more porous and rougher surface, characterized by an increase in micro-pores and surface area, which would enhance their adsorption capacity. The treatment disintegrates surface fibers and reveals supplementary pore structures, enhancing oil retention capacity. The modification additionally incorporates functional groups that enhance affinity for oil compounds, rendering WS more efficient as adsorbents for the remediation of oily wastewater.

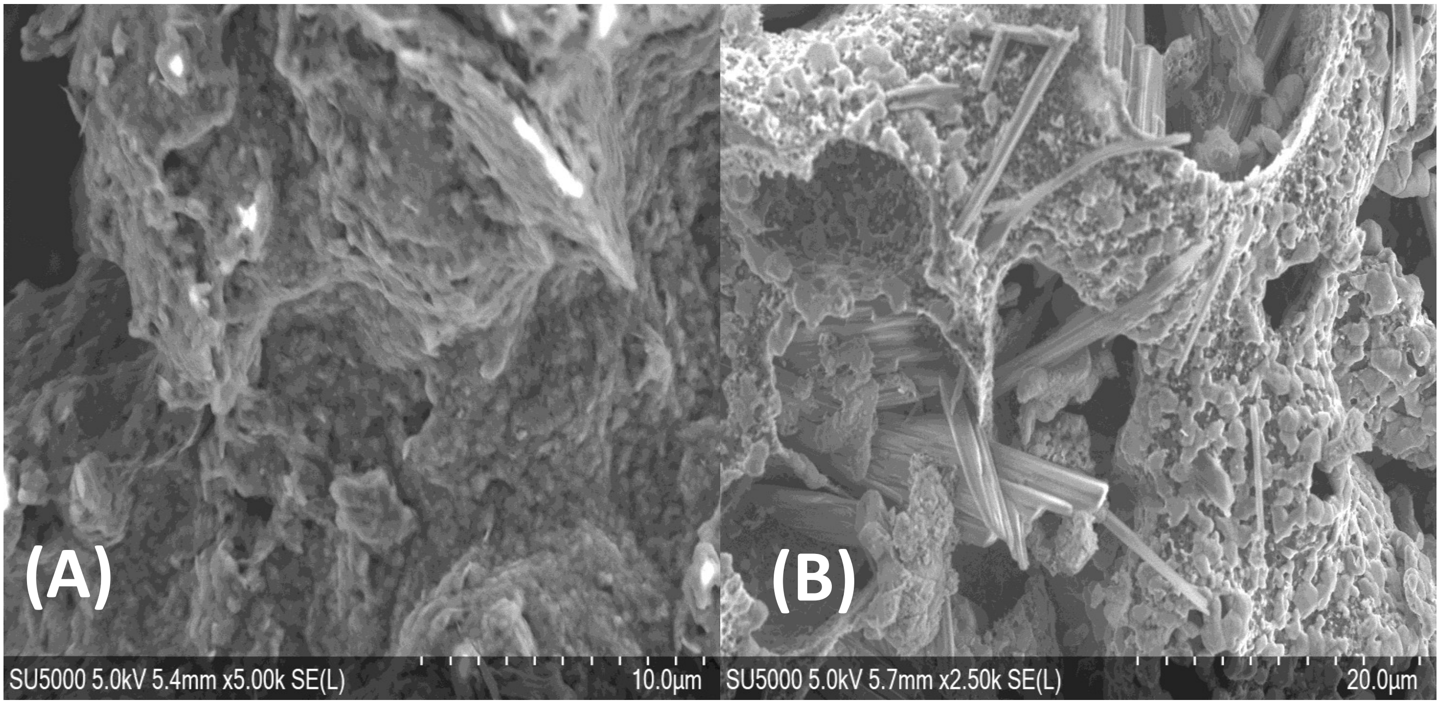


Figure 4.1: SEM images of raw walnut shells (A) and walnut shells/NaOH (B)

The surface chemistry of the sorbent, together with its porous shape, significantly influences adsorption processes. Consequently, the existence of functional groups was analyzed using FTIR. FTIR study of unmodified WS reveals functional groups that improve adsorption for oily wastewater treatment. The O-H groups (3200–3500 cm^{-1}) enhance the adsorption of polar contaminants via hydrogen bonding, whereas C-H groups (2800–3000 cm^{-1}) confer hydrophobic characteristics for non-polar compounds [352]. C=O groups (1700–1750 cm^{-1}) enhance interactions with polar molecules, while C-O groups (1000–1300 cm^{-1}) from cellulose provide functionality for binding ionic species. WS's hydrophilic and hydrophobic properties facilitate the adsorption of both polar and non-polar pollutants, rendering them suitable for wastewater treatment. On the other hand, the FTIR of WS/NaOH is presented in Figure 4.3. Preserved carbonyl groups observed in 1700–1750 cm^{-1} promote interactions with polar impurities. Still, the novel peak at 1422 cm^{-1} signifies augmented aliphatic C-H bending, improving hydrophobic characteristics for non-polar compounds. The peaks at 877.98 cm^{-1} and 700.87 cm^{-1} indicate the existence of aromatic structures, enhancing hydrophobicity. The peak at 500–650 cm^{-1} may signify metal-oxygen bonds, thus improving the adsorption of ionic pollutants [353]. Although hydroxyl groups decrease, the modified shells successfully expand their adsorption spectrum for oily pollutants.

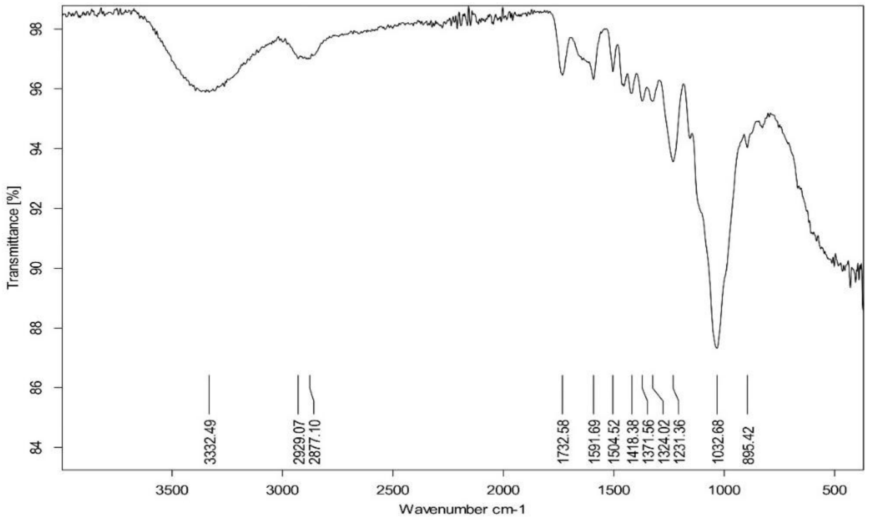


Figure 4.2: FT-IR spectra of raw walnut shells

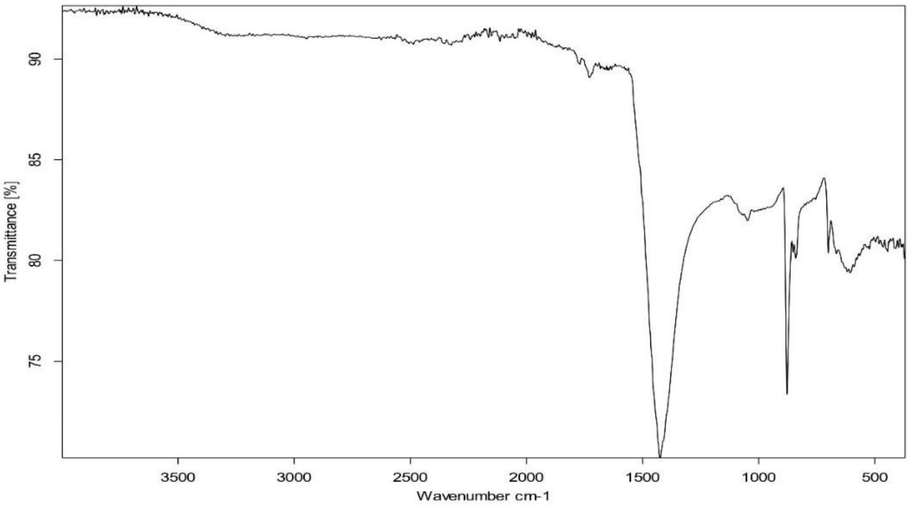


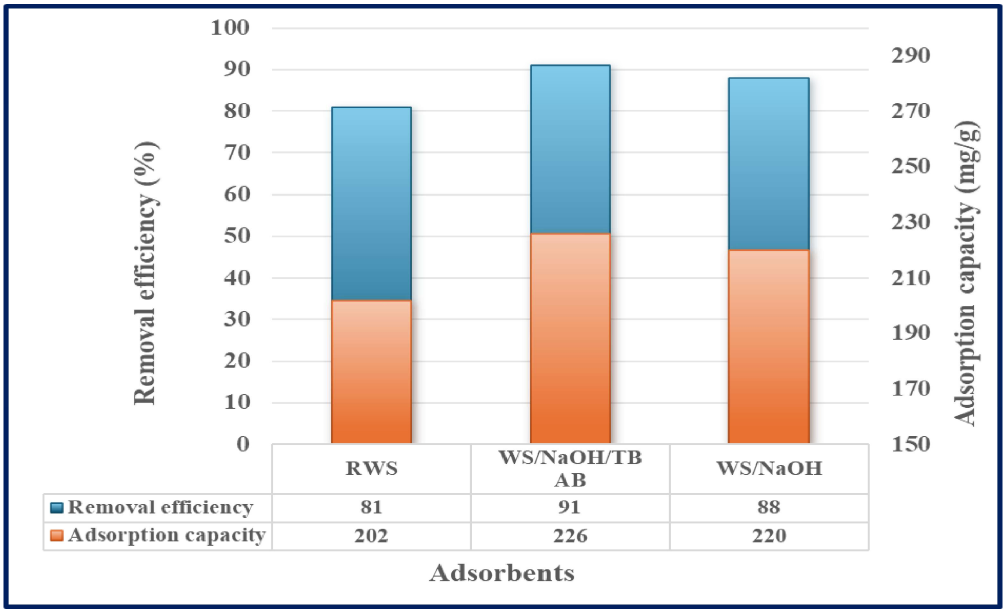
Figure 4.3: FT-IR spectra of Walnut shells/NaOH

4.2. Batch Adsorption Studies

All tests were conducted at ambient temperature in batch mode. In the preliminary batch experiment, 0.2 g of raw walnut shells (RWS) and WS/NaOH adsorbent were placed in separate beakers containing 100 mL of oil-water emulsion and continuously stirred at 200 rpm with a magnetic stirrer. The studies were conducted under various experimental conditions, including AD (2 g/L), RT (40 min), IC (500 mg/L), and S (3 g/L). The oil removal efficiency of the two adsorbents was assessed.

This study evaluated raw WS and WS/NaOH as adsorbents for oily wastewater treatment. The results indicated that WS/NaOH exhibited superior removal efficiency, achieving 88% compared to 81% for raw WS. Correspondingly, the adsorption capacity of WS/NaOH was 220 mg/g, higher than the 201 mg/g for the raw WS. The improved removal efficiency and adsorption capacity of the WS/NaOH can be attributed to several factors. The NaOH treatment enhances the surface of the shells by increasing the number of functional groups, such as hydroxyl and carboxyl, which provide more active sites for adsorption [348]. It also increases the porosity of the WS, allowing greater access to internal surfaces for oil molecules [354]. Additionally, the modification makes the surface more hydrophilic, facilitating better interaction with the oil and higher adsorption rates than RWS [355].

To improve the oil removal efficiency of the WS/NaOH, tetrabutylammonium bromide (TBAB) was introduced as a co-adsorbent at a concentration of 0.04 M. The slow addition of TBAB during the batch experiment resulted in a removal efficiency of 91% and an adsorption capacity of 226 mg/g, both showing significant improvements over the WS/NaOH alone. TBAB, which is a quaternary ammonium compound, enhances the surface charge of WS, promoting electrostatic attraction between the positively charged TBAB and negatively charged oil droplets [356]. Its hydrophobic nature also increases the interaction between the adsorbent and oil molecules. [357]. Additionally, TBAB helps disperse the oil molecules more effectively, increasing their contact with the adsorbent surface. These combined effects lead to the observed increase in efficiency and adsorption capacity.



	RWS	WS/NaOH/TBAB	WS/NaOH
🟦 Removal efficiency	81	91	88
🟧 Adsorption capacity	202	226	220

Figure 4.4: Oil removal efficiencies and adsorption capacities of raw walnut shells (RWS), walnut shells/NaOH, and raw walnut shells/NaOH/TBAB

4.3. Effect of experimental conditions on hydrocarbon adsorption

4.3.1. Effect of adsorbent dosage

This study determined the effect of the quantities of adsorbent used for dosages in the 1 – 6 g/L range for the WS/NaOH. The experimental conditions for this test were IC = 500 mg/L, RT = 40 min, and S = 30 g/L. As shown in Figure 4.6, oil removal increased gradually from 87 % to 89 %, 91 %, 93 %, and 94 % to 95 %. These results were expected, given that increased AD correlates with a rise in available adsorbent sites. These quantities attach additional ions to their surfaces, increasing removal efficiency. Comparable outcomes were documented utilizing various materials as adsorbents. [359].

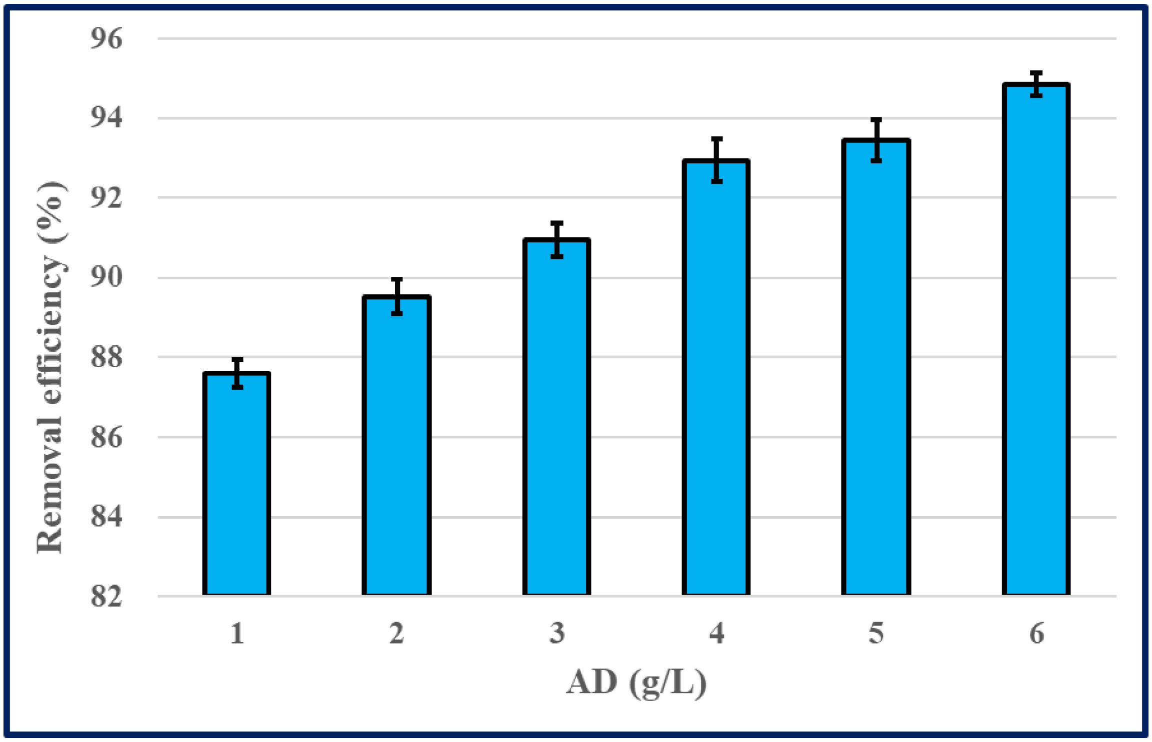


Figure 4.5: Effect of adsorbent dosage on the adsorption of oil from oil-water emulsion using the raw walnut shells/NaOH/TBAB

4.3.2. Effect of reaction time

The influence of RT on the performance of the WS/NaOH/TBAB was examined, as shown in Fig. 4.7. The experimental conditions for this test were AD = 6 g/L, IC = 500 mg/L, and S = 30 g/L. In the first 40 min, rapid adsorption was observed for the WS/NaOH/TBAB, with a removal efficiency of 88 %, 901 %, 93 %, and 95 % at RT 10, 20, 30, and 40, respectively. After approximately 58 min, the adsorption reached equilibrium. At 60 min, an efficiency of 96 % was achieved. Compared with the adsorption performance at 40 min, the removal efficiency did not increase significantly. On the whole, the adsorption process can be divided into two steps based on the adsorption rate (Fig. 4.7): rapid adsorption (first stage) and slow adsorption (second stage). In the first stage, the oil molecules are quickly adsorbed because of numerous adsorption sites on the WS/NaOH/TBAB surface. The slow adsorption rate in the second stage is due to the saturation of adsorption sites, reduced diffusion of oil molecules, and less favorable interactions as the surface becomes more covered.

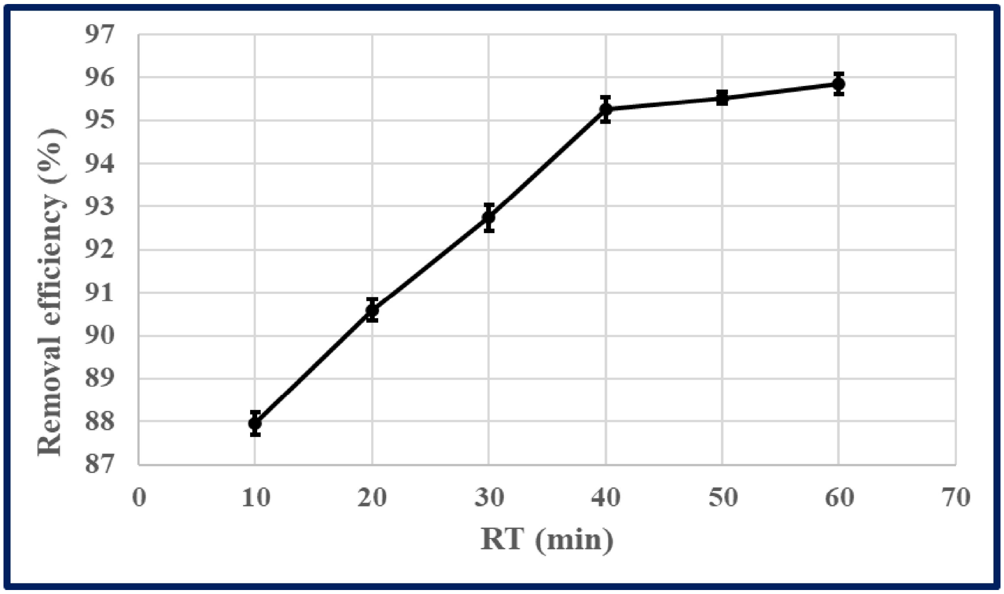


Figure 4.6: Effect of reaction time on the adsorption of oil from oil-water emulsion using the WS/NaOH/TBAB

4.3.3. Effect of initial oil concentration

To further probe the adsorption process, the effect of IC was investigated. The experimental conditions for this test were AD = 6 g/L, RT = 60 min, and S = 30 g/L. From Figure 4.7, the results revealed an increase in removal efficiency with higher IC, with removal rates of 91%, 93%, 94%, and 95% observed for concentrations of 200, 300, 400, and 500 mg/L, respectively. This trend suggests that the WS/NaOH/TBAB has a higher capacity to adsorb oils at increased concentrations. A possible explanation for this could be that higher oil concentrations provide more molecules for adsorption, allowing the adsorbent to more effectively remove oil from the emulsion. As the concentration increases, there are more interactions between the oil molecules and the adsorption sites, leading to higher removal efficiencies.

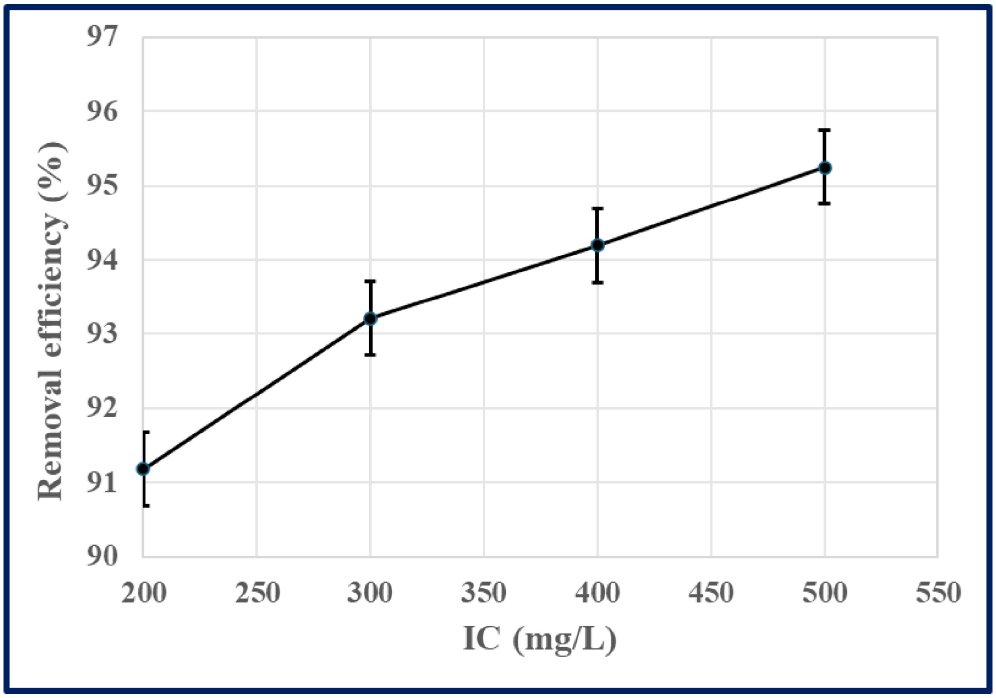


Figure 4.7: Effect of initial oil concentration on the adsorption of oil from oil-water emulsion using the Walnut shells/NaOH/TBAB

4.3.4. Effect of oil/water salinity concentration

The pre-prepared oil/water emulsion was evaluated by introducing different salt concentrations to examine the influence of salinity on its stability. Alterations in droplet coalescence, emulsion destabilization, and phase separation were examined to assess the influence of salinity on emulsion behavior. Regarding the influence of S, the results showed efficiencies of 86%, 93%, and 95% for S concentrations of 0, 15, and 30 g/L (Figure 4.8), representing control, moderate, and typical seawater concentrations, respectively. The initial lower removal efficiency at 0 g/L S (control) could be due to the absence of salts, which may reduce the stability of the oil-water emulsion and hinder oil adsorption [358]. However, the removal efficiency improves as S increases to moderate (15 g/L) and typical seawater levels (30 g/L). This could be explained by the role of S in enhancing emulsion stability, which facilitates better contact between the oil molecules and the adsorbent surface.

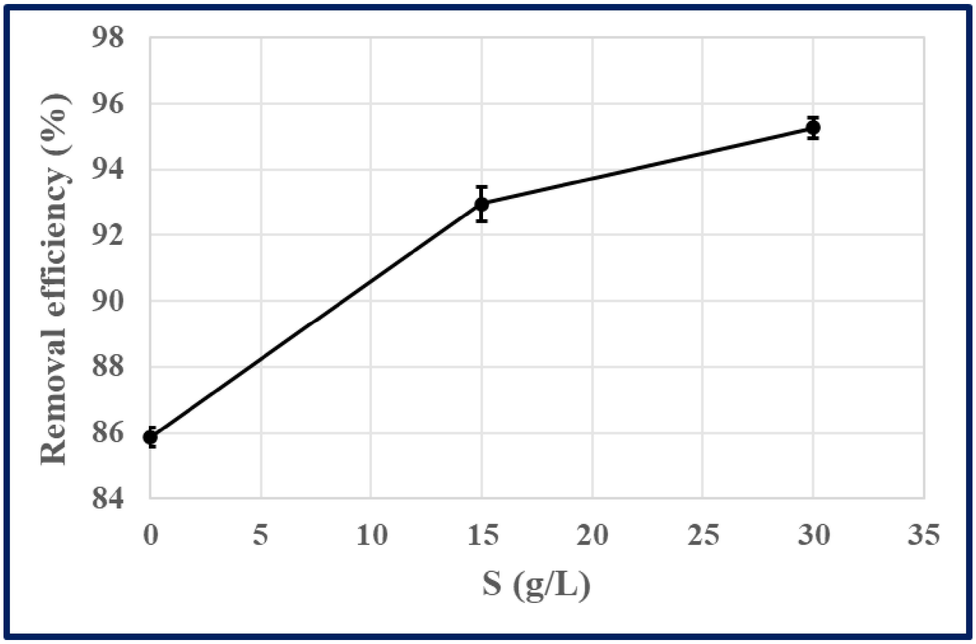


Figure 4.8: Effect of salinity concentration on the adsorption of oil from oil-water emulsion using the Walnut shells/NaOH/TBAB

4.4. Adsorption isotherm models

Under constant ambient conditions, the adsorption isotherm establishes a relationship between the total mass of adsorbate adsorbed per unit mass of sorbent. This mathematical formulation is employed to predict effective parameters that affect the adsorption process, together with a quantitative evaluation of adsorption behavior in adsorption systems. The Langmuir isotherm describes single-layer adsorption of uniformly adsorbed material with consistent energy across all adsorbent surfaces. In contrast, the Freundlich isotherm pertains to multilayer and heterogeneous adsorption on the adsorbent surface. Both are prominent models in solid-liquid adsorption [359]. Experimental studies on both isotherms were conducted at room temperature.

Based on the adsorbent dosages studied in Figure 4.5, adsorption isotherms studies for the WS/NaOH/TBAB adsorbent were expressed using Langmuir isotherm by plotting *1/qe* against 1/*Ce* (as shown in Fig. 4.9) and Freundlich isotherm by plotting *qe* against *Ce* (as shown in Fig. 4.10). The results in Figures 4.9 and 4.10 are correlated by the Langmuir and the Freundlich equations (see equations 3 and 4) with the resulting parameters listed in Table 4.1.

$$\frac{1}{q_e} = (\frac{1}{q_{max}} K_l)(\frac{1}{C_e}) + \frac{1}{q_{max}} \qquad 2$$

$$q_e = K_F C_e^{1/n} \qquad 3$$

Where K_l = Langmuir isotherm constant, C_e = oil concentration at equilibrium, q_{max} = maximum adsorption capacity, K_F = Freundlich constant, and n = Freundlich exponent.

Table 4.1: Adsorption isotherms constants for oil removal from oil-water emulsion

Langmuir			**Freundlich**		
K_l	**q_{max}**	**R^2**	**1/n**	**K_f**	**R^2**
0.00786	294.117	0.9171	0.2886	36	0.9695

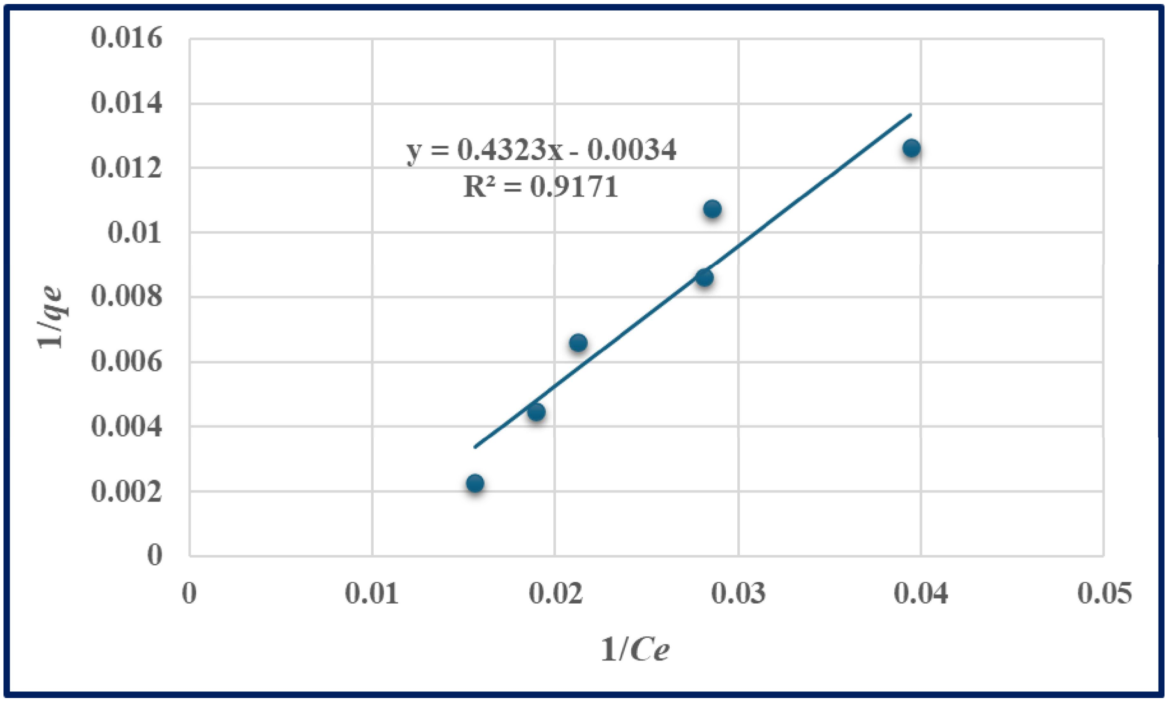


Figure 4.9: Langmuir isotherm adsorption of oil from oil-water emulsion

From the data results, it can be concluded that the Freundlich isotherm best fits the experimental data, as indicated by a higher R^2 value (0.9695) compared to the Langmuir isotherm ($R^2 = 0.9171$). This suggests that adsorption likely occurs on a heterogeneous surface, which aligns with the Freundlich model's assumption of multilayer adsorption on varied binding sites rather than the uniform monolayer adsorption assumed by the Langmuir model. Additionally, the

Freundlich parameter 1/n = 0.2886 suggests strong adsorption intensity, supporting that the WS/NaOH possesses a heterogeneous adsorption surface. [360].

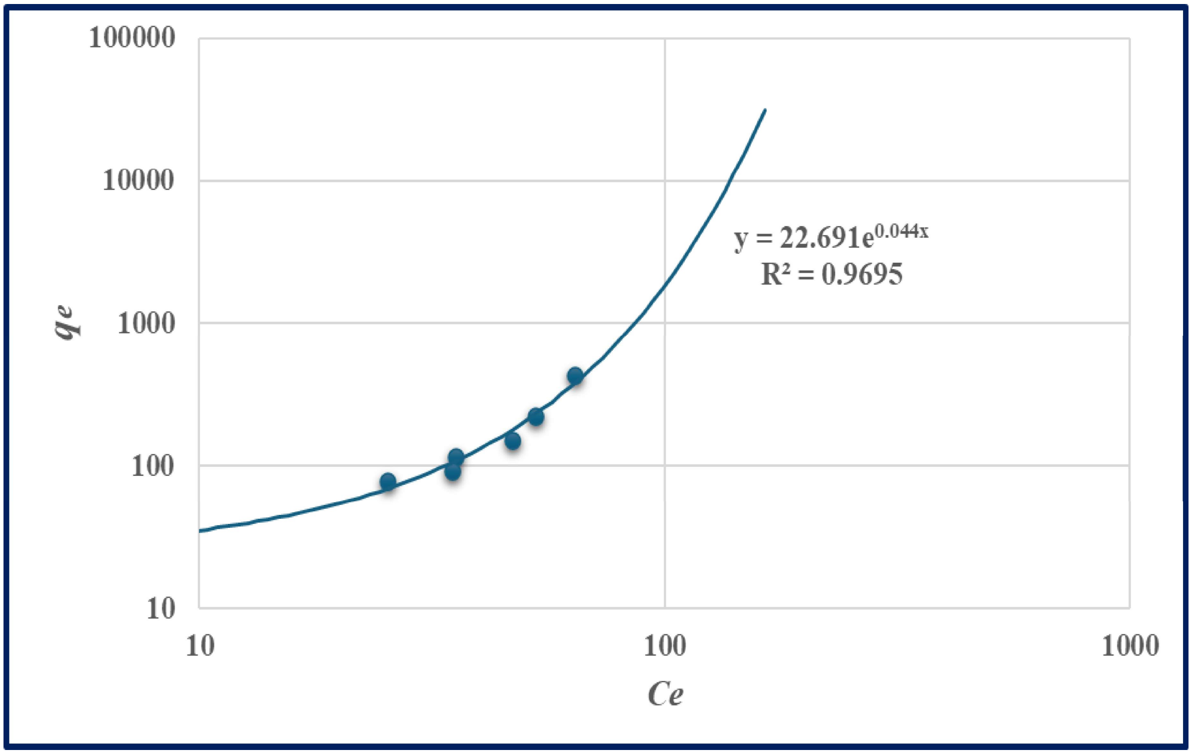


Figure 4.10: Freundlich isotherm adsorption of oil from oil-water emulsion

4.5. Adsorption kinetic studies

The adsorption kinetics typically indicate the physical characteristics of the adsorbent. These kinetic models, which include pseudo-first-order and pseudo-second-order, can project the adsorption rate, mechanism, rate-limiting step, and diffusion process. The pseudo-first-order model describes adsorption driven by physisorption, where the rate depends on the number of unoccupied sites, typically fitting fast initial adsorption. In contrast, the pseudo-second-order model assumes chemisorption, involving stronger chemical bonds and adsorption rates based on site availability, making it more accurate for equilibrium predictions.

Based on the effect of reaction time studied in Figure 4.6, adsorption kinetic studies for the WS/NaOH/TBAB adsorbent were expressed using pseudo-first-order by plotting ln (q_e-q_t) against time (as shown in Fig. 4.11) and pseudo-second-order by plotting t/q_t against time (as shown in Fig. 4.12). All studies were carried out at room temperature. The calculated kinetic parameters of pseudo-first and second-order models are given in Table 4.2 (using equations 5 and 6), and the corresponding values are shown in Figures 4.10 and 4.11, respectively. It can be visually seen that pseudo-second-order kinetics fits better with a higher R^2 of 0.9998 compared to that of pseudo-first order (0.95).

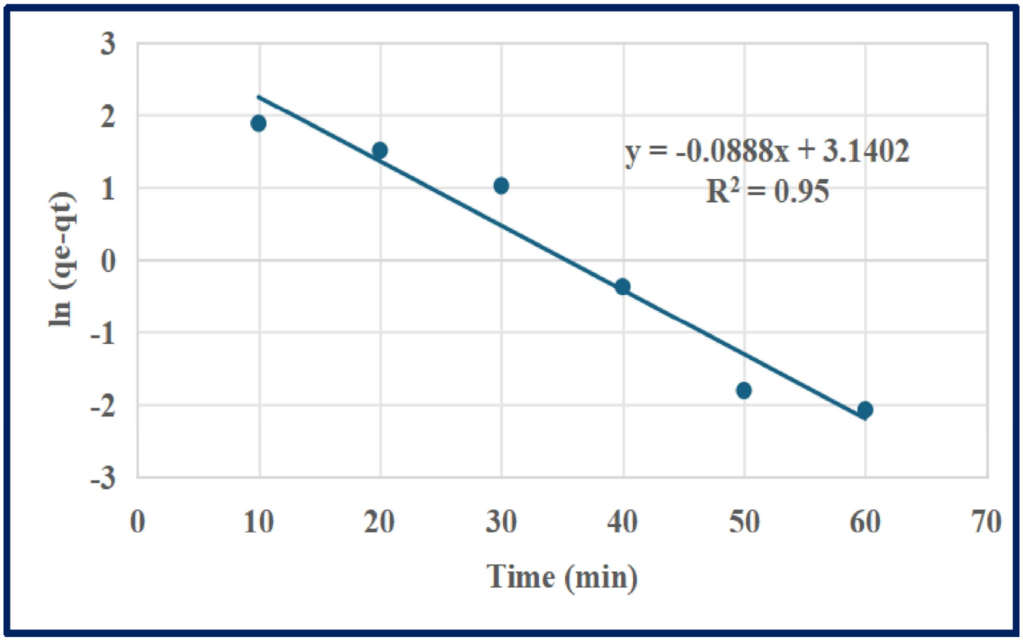


Figure 4.11: Pseudo first-order kinetic model for adsorption of oils in oil-water emulsion

$$ln(qe - qt) = ln\, qe - K_1 t \qquad 4$$

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{t}{qe} \qquad 5$$

Where q_e = amount adsorbed at equilibrium (mg/g), q_t = amount adsorbed at time t (mg/g), K_1= rate constant (min^{-1}), t = Time (min), and K_2 = rate constant (mg/g.min).

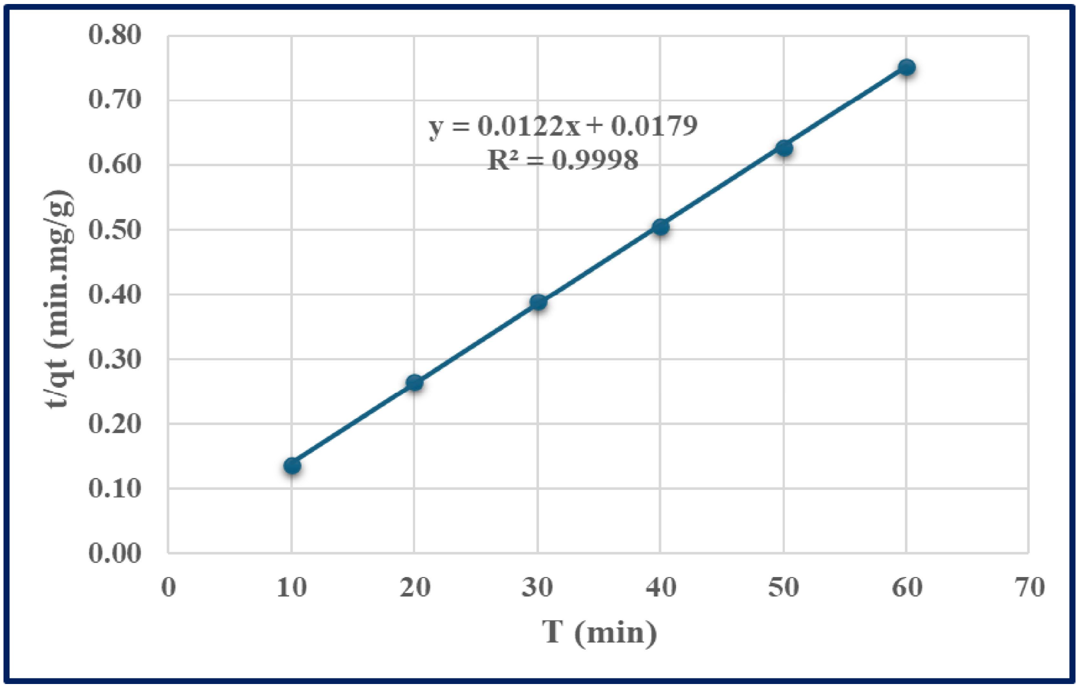


Figure 4.12: Pseudo second order kinetic model for adsorption of oil in oil-water emulsion

Table 4.2: Kinetic parameters for oil removal from oil-water emulsion

Pseudo first order			**Pseudo second order**		
K_l	**ln qe**	**R^2**	**qe**	**K_2**	**R^2**
0.8883	3.1402	0.95	81.9672	0.0083	0.9998

Table 4.3: Comparison of oil removal efficiency of the proposed WS/NaOH/TBAB with other natural adsorbents

Adsorbent	Adsorbate	Adsorbate Concentration (mg/L)	Removal efficiency (%)	Reference
Thermally modified orange peel	Crude oil	-	45	[361]
Pomegranate peel/n-hexane	Crude oil	300	92	[340]
Activated date pit	Petroleum waste	950	78	[341]
Sawdust	Crude oil	-	96	[362]
Biochar	Pyrene	-	88	[317]
WS//Na_2CO_3/$NaHSO_3$/Na_2SO_3	Crude oil	405	90	[363]
Animal bones/NaOH	Crude oil	1000	94	[364]
Anise residues/DI Water	Crude oil	1000	70	[364]
WS/NaOH/TBAB	Crude oil	500	96	This work

Chapter 5. Conclusion and Recommendations

5.1. Conclusion

The increasing occurrence of oil spills has driven research into efficient and sustainable oily wastewater treatment methods. Current efforts prioritize oil recovery from marine environments, and a polishing step to treat the residual oil prior to discharging the water back to the aquatic environment. Adsorption, particularly using natural materials, stands out as a simple, cost-effective, and eco-friendly solution, offering a sustainable approach to addressing the environmental impact of oil contamination. This study explored a cost-effective, eco-friendly technique for treating oily wastewater with WS-based adsorbent. To improve WS's surface properties, chemical composition, and adsorption potential, a synthesis mechanism via wet impregnation by the slow addition of NaOH and carbonization method under thermal treatment was employed to generate the proposed WS/NaOH adsorbent. The generated WS/NaOH displayed good potential for the adsorption of oily particles from oil-water emulsion with a removal efficiency and adsorption capacity of 88% and 220 mg/g, respectively. To further enhance the adsorption potential of the WS/NaOH, TBAB was introduced as a co-adsorbent during the batch test. The outcome revealed that the WS/NaOH/TBAB adsorbent is an excellent technique for the remediation of oil-water separation with an efficiency of 96% and an adsorption capacity of 226 mg/g. The surface morphologies and chemical compositions of the WS/NaOH were examined by SEM and FTIR, respectively. Adsorption isotherm and kinetic studies conducted in this research revealed that the Freundlich and Pseudo second-order models best represent the experimental results. The simplicity and economic viability of adsorption, particularly with eco-friendly adsorbents, make it an appealing solution. By targeting residual oil in emulsions post-primary recovery, adsorption helps protect aquatic ecosystems and aligns with the broader goal of sustainable environmental management. In the face of the intricate challenges posed by oil spills, the continual progress and application of adsorption technology presents a hopeful avenue for alleviating the severe impact of oily wastewater on our planet's fragile ecosystems.

5.2. Limitations of the study

This research was subject to several limitations. First, the modification method used to enhance the adsorption capacity is highly sensitive and thus requires much time and attention. Second, there are significant challenges in scaling up the batch experiment to real-world applications, where adsorbent efficiency may vary under continuous operation. Third, using highly toxic and flammable chemicals in the modification and PAHs extraction processes raises health and safety concerns that must be carefully addressed. Lastly, the study does not account for the impact of other environmental contaminants commonly found in wastewater, which may interfere with the adsorption process and reduce overall effectiveness.

5.3. Recommendations

Based on the results obtained from this thesis, it is imperative to explore the following research areas further to advance the development of eco-friendly and cost-effective adsorbents:

(i) Evaluating the effectiveness of adsorption in various organic and inorganic pollutants typically present in oily wastewater. Oily wastewater is intricate; investigating competitive adsorption helps elucidate the influence of other compounds on oil adsorption effectiveness, enhancing its relevance to real-world scenarios.

(ii) Performing experiments at various pH levels and temperatures to ascertain the influence of these variables on adsorption efficiency. In this case, actual oily wastewater's pH and temperature ranges must be considered.

(iii) The study’s outcome suggests a pathway for large-scale testing. Column adsorption experiments with WS-based adsorbents could be tested to simulate continuous flow conditions that mimic large-scale wastewater treatment. Batch experiments provide valuable insights; however, column studies will illustrate the adsorbent's performance in a realistic, scalable context, which is essential for practical application.

References

1. Awad, A.M., et al., *Adsorption of organic pollutants by nanomaterial-based adsorbents: An overview.* Journal of Molecular Liquids, 2020. **301**: p. 112335.
2. Ali, I., M. Asim, and T.A. Khan, *Low cost adsorbents for the removal of organic pollutants from wastewater.* Journal of Environmental Management, 2012. **113**: p. 170-183.
3. Cherubini, F., *The biorefinery concept: Using biomass instead of oil for producing energy and chemicals.* Energy Conversion and Management, 2010. **51**(7): p. 1412-1421.
4. Kujawinski, E.B., et al., *Fate of Dispersants Associated with the Deepwater Horizon Oil Spill.* Environmental Science & Technology, 2011. **45**(4): p. 1298-1306.
5. Thakur, C., et al., *Mechanistic Study and Multi-Response Optimization of the Electrochemical Treatment of Petroleum Refinery Wastewater.* Clean – Soil, Air, Water, 2018. **46**(3): p. 1700624.
6. Al-Futaisi, A., et al., *Assessment of alternative management techniques of tank bottom petroleum sludge in Oman.* Journal of Hazardous Materials, 2007. **141**(3): p. 557-564.
7. Hu, G., J. Li, and G. Zeng, *Recent development in the treatment of oily sludge from petroleum industry: A review.* Journal of Hazardous Materials, 2013. **261**: p. 470-490.
8. Varjani, S.J. and V.N. Upasani, *A new look on factors affecting microbial degradation of petroleum hydrocarbon pollutants.* International Biodeterioration & Biodegradation, 2017. **120**: p. 71-83.
9. Chen, J., et al., *Oil spills from global tankers: Status review and future governance.* Journal of Cleaner Production, 2019. **227**: p. 20-32.

10. Tayeb, A.M., et al., *Oil spill clean-up using combined sorbents: a comparative investigation and design aspects.* International Journal of Environmental Analytical Chemistry, 2020. **100**(3): p. 311-323.

11. Chuvilin, E.M., et al., *The use of permafrost for the storage of oil and oil products and the burial of toxic industrial wastes in the Arctic.* Polar Record, 2000. **36**(198): p. 211-214.

12. Jin, H., et al., *Stability of engineering foundations of oil pipelines in permafrost regions: A review.* Oil Gas Stor. Transp., 2006. **25**: p. 13-18.

13. Dunn, D., *US Energy Information Administration Monthly Energy Review*. 2016, August.

14. Purvis, A., *Ten largest oil spills in history.* Planet Watch. Time International, 1999. **153**(8): p. 12.

15. Fraser, G.S. and V. Racine, *An evaluation of oil spill responses for offshore oil production projects in Newfoundland and Labrador, Canada: Implications for seabird conservation.* Marine Pollution Bulletin, 2016. **107**(1): p. 36-45.

16. King, G.M., et al., *Microbial responses to the Deepwater Horizon oil spill: from coastal wetlands to the deep sea.* Ann Rev Mar Sci, 2015. **7**: p. 377-401.

17. Alavi, S.A. and S.R. Hashemi. *A Review on Diesel Fuel Desulfurization by Adsorption Process*. in *Proceedings of the International Conference on Chemical, Agricultural, and Biological Sciences, Antalya, Turkey*. 2014.

18. Xu, Q., et al., *Pore-scale modelling of the coupled thermal and reactive flow at the combustion front during crude oil in-situ combustion.* Chemical Engineering Journal, 2018. **350**: p. 776-790.

19. Zhu, H., et al., *A Robust and Cost-Effective Superhydrophobic Graphene Foam for Efficient Oil and Organic Solvent Recovery.* Small, 2015. **11**(39): p. 5222-5229.

20. Kang, S.M., et al., *One-Step Modification of Superhydrophobic Surfaces by a Mussel-Inspired Polymer Coating.* Angewandte Chemie International Edition, 2010. **49**(49): p. 9401-9404.

21. Xue, Z., et al., *Special wettable materials for oil/water separation.* Journal of Materials Chemistry A, 2014. **2**(8): p. 2445-2460.

22. Li, J., et al., *One-step fabrication of robust fabrics with both-faced superhydrophobicity for the separation and capture of oil from water.* Physical Chemistry Chemical Physics, 2015. **17**(9): p. 6451-6457.

23. De Gisi, S., et al., *Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review.* Sustainable Materials and Technologies, 2016. **9**: p. 10-40.

24. Medeiros, A.D.L.M.d., et al., *Oily Wastewater Treatment: Methods, Challenges, and Trends.* Processes, 2022. **10**(4): p. 743.

25. Tian, X., et al., *A comprehensive review on toxic petrochemical wastewater pretreatment and advanced treatment.* Journal of Cleaner Production, 2020. **245**: p. 118692.

26. Jasmine, J. and S. Mukherji, *Characterization of oily sludge from a refinery and biodegradability assessment using various hydrocarbon degrading strains and reconstituted consortia.* Journal of Environmental Management, 2015. **149**: p. 118-125.

27. Wake, H., *Oil refineries: a review of their ecological impacts on the aquatic environment.* Estuarine, Coastal and Shelf Science, 2005. **62**(1): p. 131-140.

28. Mrayyan, B. and M.N. Battikhi, *Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge.* Journal of Hazardous Materials, 2005. **120**(1-3): p. 127-134.

29. Saien, J. and H. Nejati, *Enhanced photocatalytic degradation of pollutants in petroleum refinery wastewater under mild conditions.* Journal of Hazardous Materials, 2007. **148**(1): p. 491-495.

30. Varjani, S.J., et al., *Polycyclic Aromatic Hydrocarbons from Petroleum Oil Industry Activities: Effect on Human Health and Their Biodegradation*, in *Waste Bioremediation*, S.J. Varjani, et al., Editors. 2018, Springer Singapore: Singapore. p. 185-199.

31. Perera, F.P., et al., *Prenatal Polycyclic Aromatic Hydrocarbon (PAH) Exposure and Child Behavior at Age 6–7 Years.* Environmental Health Perspectives, 2012. **120**(6): p. 921-926.

32. Zeng, Y., et al., *Feasibility investigation of oily wastewater treatment by combination of zinc and PAM in coagulation/flocculation.* Journal of Hazardous Materials, 2007. **147**(3): p. 991-996.

33. Dinçer, A.R., et al., *REMOVAL OF COD FROM OIL RECOVERY INDUSTRY WASTEWATER BY THE ADVANCED OXIDATION PROCESSES (AOP) BASED ON H2O2.* Global NEST Journal, 2008. **10**(1): p. 31-38.

34. Gasim, H.A., et al., *Optimization of Anaerobic Treatment of Petroleum Refinery Wastewater Using Artificial Neural Networks.* Research Journal of Applied Sciences, Engineering and Technology, 2013. **6**(11): p. 2077-2082.

35. Hasan, D.u.B., A.R. Abdul Aziz, and W.M.A.W. Daud, *Oxidative mineralisation of petroleum refinery effluent using Fenton-like process.* Chemical Engineering Research and Design, 2012. **90**(2): p. 298-307.

36. Saber, A., et al., *Optimization of Fenton-based treatment of petroleum refinery wastewater with scrap iron using response surface methodology.* Applied Water Science, 2014. **4**(3): p. 283-290.

37. Abdelwahab, O., N.K. Amin, and E.-S.Z. El-Ashtoukhy, *Electrochemical removal of phenol from oil refinery wastewater.* Journal of Hazardous Materials, 2009. **163**(2-3): p. 711-716.

38. Tony, M.A., P.J. Purcell, and Y. Zhao, *Oil refinery wastewater treatment using physicochemical, Fenton and Photo-Fenton oxidation processes.* J Environ Sci Health A Tox Hazard Subst Environ Eng, 2012. **47**(3): p. 435-40.

39. Demırcı, Ş., B. ErdoĞan, and R. Özcımder, *Wastewater treatment at the petroleum refinery, Kirikkale, Turkey using some coagulants and Turkish clays as coagulant aids.* Water Research, 1998. **32**(11): p. 3495-3499.

40. Akob, D.M., et al., *Wastewater Disposal from Unconventional Oil and Gas Development Degrades Stream Quality at a West Virginia Injection Facility.* Environmental Science & Technology, 2016. **50**(11): p. 5517-5525.

41. Seveso, D., et al., *The Mauritius Oil Spill: What's Next?* Pollutants, 2021. **1**(1): p. 18-28.

42. Poulton, S.W., et al., *The use of hydrous iron (III) oxides for the removal of hydrogen sulphide in aqueous systems.* Water Research, 2002. **36**(4): p. 825-834.

43. Attiogbe, F., M. Glover-Amengor, and K.T. Nyadziehe, *Correlating biochemical and chemical oxygen demand of effluents: a case study of selected industries in Kumasi, Ghana.* West African Journal of Applied Ecology, 2007. **11**(1): p. 155-164.

44. Jafarinejad, S., *Oil-Spill Response*, in *Petroleum Waste Treatment and Pollution Control*, S. Jafarinejad, Editor. 2017, Butterworth-Heinemann. p. 117-148.

45. An, H., et al., *Features and evolution of international crude oil trade relationships: A trading-based network analysis.* Energy, 2014. **74**: p. 254-259.

46. Goldman, R., et al., *Oil spill contamination probability in the southeastern Levantine basin.* Marine Pollution Bulletin, 2015. **91**(1): p. 347-356.

47. Brekke, C. and A.H.S. Solberg, *Oil spill detection by satellite remote sensing.* Remote Sensing of Environment, 2005. **95**(1): p. 1-13.

48. Kollo, M., J. Laanearu, and K. Tabri, *Hydraulic modelling of oil spill through submerged orifices in damaged ship hulls.* Ocean Engineering, 2017. **130**: p. 385-397.

49. Fragouli, D. and A. Athanassiou, *Oil spill recovery: Graphene heaters absorb faster.* Nat Nanotechnol, 2017. **12**(5): p. 406-407.

50. Saadoun, I.M.K., *Impact of Oil Spills on Marine Life*, in *Emerging Pollutants in the Environment*, L.L. Marcelo and S. Sonia, Editors. 2015, IntechOpen: Rijeka. p. Ch. 4.

51. Ahmad, T., K. Ahmad, and M. Alam, *Sustainable management of water treatment sludge through 3'R' concept.* Journal of Cleaner Production, 2016. **124**: p. 1-13.

52. Le, T.V., et al., *Performance of tiny microbubbles enhanced with "normal cyclone bubbles" in separation of fine oil-in-water emulsions.* Chemical Engineering Science, 2013. **94**: p. 1-6.

53. Hanafy, M. and H.I. Nabih, *Treatment of Oily Wastewater Using Dissolved Air Flotation Technique.* Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2007. **29**(2): p. 143-159.

54. Mysore, D., T. Viraraghavan, and Y.C. Jin, *Oil/water separation technology - A review.* Journal of Residuals Science and Technology, 2006. **3**: p. 5-14.

55. Xing, Y., et al., *Recent experimental advances for understanding bubble-particle attachment in flotation.* Advances in Colloid and Interface Science, 2017. **246**: p. 105-132.

56. Rubio, J., M.L. Souza, and R.W. Smith, *Overview of flotation as a wastewater treatment technique.* Minerals Engineering, 2002. **15**(3): p. 139-155.

57. Al-Shamrani, A.A., A. James, and H. Xiao, *Separation of oil from water by dissolved air flotation.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2002. **209**(1): p. 15-26.

58. Nieuwenhuis, E., et al., *Statistical modelling of Fat, Oil and Grease (FOG) deposits in wastewater pump sumps.* Water Research, 2018. **135**: p. 155-167.

59. Saththasivam, J., K. Loganathan, and S. Sarp, *An overview of oil–water separation using gas flotation systems.* Chemosphere, 2016. **144**: p. 671-680.

60. Cambiella, A., et al., *Centrifugal Separation Efficiency in the Treatment of Waste Emulsified Oils.* Chemical Engineering Research and Design, 2006. **84**(1): p. 69-76.

61. Li, W., et al., *Optimization of an oil recovery process from oily sludge using a combined technique of froth flotation and centrifugal treatment.* Journal of Cleaner Production, 2023. **400**: p. 136752.

62. Changmai, M., M. Pasawan, and M.K. Purkait, *Treatment of oily wastewater from drilling site using electrocoagulation followed by microfiltration.* Separation and Purification Technology, 2019. **210**: p. 463-472.

63. Cruz Viggi, C., et al., *The "Oil-Spill Snorkel": an innovative bioelectrochemical approach to accelerate hydrocarbons biodegradation in marine sediments.* Front Microbiol, 2015. **6**: p. 881.

64. Kayvani Fard, A., et al., *Enhancing oil removal from water using ferric oxide nanoparticles doped carbon nanotubes adsorbents.* Chemical Engineering Journal, 2016. **293**: p. 90-101.

65. Zhao, C., et al., *Application of coagulation/flocculation in oily wastewater treatment: A review.* Science of The Total Environment, 2021. **765**: p. 142795.

66. Lourenço, A.d.S., *Development of novel flocculants to treat oily waters using health-friendly processes*. 2018, 00500:: Universidade de Coimbra.

67. Daud, Z., et al., *Suspended Solid, Color, COD and Oil and Grease Removal from Biodiesel Wastewater by Coagulation and Flocculation Processes.* Procedia - Social and Behavioral Sciences, 2015. **195**: p. 2407-2411.

68. Abou-Taleb, E.M., M.S. Hellal, and K.H. Kamal, *Electro-oxidation of phenol in petroleum wastewater using a novel pilot-scale electrochemical cell with graphite and stainless-steel electrodes.* Water and Environment Journal, 2021. **35**(1): p. 259-268.

69. Bajracharya, S., et al., *Carbon dioxide reduction by mixed and pure cultures in microbial electrosynthesis using an assembly of graphite felt and stainless steel as a cathode.* Bioresource Technology, 2015. **195**: p. 14-24.

70. Ochando-Pulido, J.M., et al., *Physicochemical analysis and adequation of olive oil mill wastewater after advanced oxidation process for reclamation by pressure-driven membrane technology.* Science of The Total Environment, 2015. **503-504**: p. 113-121.

71. Santos, F.V., et al., *Photocatalysis as a tertiary treatment for petroleum refinery wastewaters.* Brazilian Journal of Chemical Engineering, 2006. **23**(4): p. 451-460.

72. Jamaly, S., A. Giwa, and S.W. Hasan, *Recent improvements in oily wastewater treatment: Progress, challenges, and future opportunities.* Journal of Environmental Sciences, 2015. **37**: p. 15-30.

73. Mohan, S.V., et al., *Microbial Electrochemical Technology: Emerging and Sustainable Platform*, in *Microbial Electrochemical Technology*, S.V. Mohan, S. Varjani, and A. Pandey, Editors. 2019, Elsevier. p. 3-18.

74. Ma, H. and B. Wang, *Electrochemical pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection.* Journal of Hazardous Materials, 2006. **132**(2-3): p. 237-243.

75. Council, N.R., *Oil Spill Dispersants: Efficacy and Effects*. 2005, Washington, DC: The National Academies Press. 396.

76. Cai, Q., et al., *A cross-comparison of biosurfactants as marine oil spill dispersants: Governing factors, synergetic effects and fates.* Journal of Hazardous Materials, 2021. **416**: p. 126122.

77. Zhu, Z., et al., *Fish Waste Based Lipopeptide Production and the Potential Application as a Bio-Dispersant for Oil Spill Control.* Frontiers in Bioengineering and Biotechnology, 2020. **8**.

78. Etkin, D.S., *Oil spill dispersants: from technology to policy*. 1999: Cutter Information.

79. Das, N. and P. Chandran, *Microbial degradation of petroleum hydrocarbon contaminants: an overview.* Biotechnol Res Int, 2011. **2011**: p. 941810.

80. Habibollahi, H. and A. Salehzadeh, *Isolation, Optimization, and Molecular Characterization of a Lipase Producing Bacterium from Oil Contaminated Soils.* Pollution, 2018. **4**(1): p. 119-128.

81. Lal, B. and S. Khanna, *Degradation of crude oil by Acinetobacter calcoaceticus and Alcaligenes odorans.* Journal of Applied Bacteriology, 1996. **81**(4): p. 355-362.

82. Amund, O.O. and N.G. Nwokoye. *Hydrocarbon Degradation Potentials of Yeast Isolates from a Polluted Lagoon*. 1993. Environmental Science, Biology.

83. Jones, D.M., et al., *The recognition of biodegraded petroleum-derived aromatic hydrocarbons in recent marine sediments.* Marine Pollution Bulletin, 1983. **14**(3): p. 103-108.

84. Perry, J.J., *Microbial metabolism of cyclic alkanes*, in *Petroleum Microbiology*, R.M. Atlas, Editor. 1984, Macmillan: New York, NY, USA. p. 61-98.

85. Chanthamalee, J., T. Wongchitphimon, and E. Luepromchai, *Treatment of Oily Bilge Water from Small Fishing Vessels by PUF-Immobilized Gordonia sp. JC11.* Water, Air, & Soil Pollution, 2013. **224**(7): p. 1601.

86. Ma, C., et al., *Study on Characteristics of Marine Petroleum-Degrading Strains and Their Bioremediation Utilization of Carbon Source Spectrum.* Journal of Bionanoscience, 2015. **9**(2): p. 127-134.

87. Srikanth, S., et al., *Long-term operation of electro-biocatalytic reactor for carbon dioxide transformation into organic molecules.* Bioresource Technology, 2018. **265**: p. 66-74.

88. Uma, V. and R. Gandhimathi, *Organic removal and synthesis of biopolymer from synthetic oily bilge water using the novel mixed bacterial consortium.* Bioresource Technology, 2019. **273**: p. 169-176.

89. Zimmerman, W.B., et al., *On the design and simulation of an airlift loop bioreactor with microbubble generation by fluidic oscillation.* Food and Bioproducts Processing, 2009. **87**(3): p. 215-227.

90. Zhang, J., et al., *An anaerobic reactor packed with a pair of Fe-graphite plate electrodes for bioaugmentation of azo dye wastewater treatment.* Biochemical Engineering Journal, 2012. **63**: p. 31-37.

91. Meng, F., et al., *Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material.* Water Research, 2009. **43**(6): p. 1489-1512.

92. Le-Clech, P., V. Chen, and T.A.G. Fane, *Fouling in membrane bioreactors used in wastewater treatment.* Journal of Membrane Science, 2006. **284**(1): p. 17-53.

93. Emadian, S.M., et al., *Treatment of a low-strength bilge water of Caspian Sea ships by HUASB technique.* Ecological Engineering, 2015. **82**: p. 272-275.

94. Cui, J., et al., *Preparation and application of zeolite/ceramic microfiltration membranes for treatment of oil contaminated water.* Journal of Membrane Science, 2008. **325**(1): p. 420-426.

95. Yang, T., Z.-F. Ma, and Q.-Y. Yang, *Formation and performance of Kaolin/MnO2 bi-layer composite dynamic membrane for oily wastewater treatment: Effect of solution conditions.* Desalination, 2011. **270**(1): p. 50-56.

96. Li, Y., et al., *A robust salt-tolerant superoleophobic alginate/graphene oxide aerogel for efficient oil/water separation in marine environments.* Scientific Reports, 2017. **7**(1): p. 46379.

97. Li, Y., et al., *A robust salt-tolerant superoleophobic aerogel inspired by seaweed for efficient oil–water separation in marine environments.* Physical Chemistry Chemical Physics, 2016. **18**(36): p. 25394-25400.

98. Nahui, F.N.B., et al., *Electroflotation of emulsified oil in industrial wastes evaluated with a full factorial design.* Brazilian Journal of Chemical Engineering, 2008. **25**(3): p. 435-442.

99. Chavalparit, O. and M. Ongwandee, *Optimizing electrocoagulation process for the treatment of biodiesel wastewater using response surface methodology.* Journal of Environmental Sciences, 2009. **21**(11): p. 1491-1496.

100. Srirangsan, A., M. Ongwandee, and C. Orathai, *Treatment of Biodiesel Wastewater by Electrocoagulation Process.* EnvironmentAsia, 2009. **2**: p. 15-19.

101. Körbahti, B.K. and K. Artut, *Electrochemical oil/water demulsification and purification of bilge water using Pt/Ir electrodes.* Desalination, 2010. **258**(1-3): p. 219-228.

102. Asselin, M., et al., *Organics removal in oily bilgewater by electrocoagulation process.* Journal of Hazardous Materials, 2008. **151**(2-3): p. 446-455.

103. Zhao, X., et al., *Oil field wastewater treatment in Biological Aerated Filter by immobilized microorganisms.* Process Biochemistry, 2006. **41**(7): p. 1475-1483.

104. Pendashteh, A.R., N. Chaibakhsh, and F.-R. Ahmadun, *Biological treatment of high salinity produced water by microbial consortia in a batch stirred tank reactor: Modelling and kinetics study.* Chemical Engineering Communications, 2018. **205**(3): p. 387-401.

105. Shariati, S.R.P., et al., *The effect of hydraulic retention time on the performance and fouling characteristics of membrane sequencing batch reactors used for the treatment of synthetic petroleum refinery wastewater.* Bioresource Technology, 2011. **102**(17): p. 7692-7699.

106. Campo, R., et al., *Characterization and Treatment Proposals of Shipboard Slop Wastewater Contaminated by Hydrocarbons.* Water, 2017. **9**(8): p. 581.

107. Azhdarpoor, A., B. Mortazavi, and G. Moussavi, *Oily wastewaters treatment using Pseudomonas sp. isolated from the compost fertilizer.* J. Environ Health Sci. Eng., 2014. **12**: p. 77.

108. Ghosh, S. and S. Chakraborty, *Influence of inoculum variation on formation and stability of aerobic granules in oily wastewater treatment.* Journal of Environmental Management, 2019. **248**: p. 109239.

109. Morgan-Sagastume, F., et al., *Anaerobic treatment of oil-contaminated wastewater with methane production using anaerobic moving bed biofilm reactors.* Water Research, 2019. **163**: p. 114851.

110. Jimenez-Espadafor, F., et al., *Supercritical Water Oxidation of Oily Wastes at Pilot Plant: Simulation for Energy Recovery.* Ind. Eng. Chem. Res., 2011. **50**(2): p. 775-784.

111. Guan, D., et al., *Effect of micro-electrolytic fillers on the oil removal efficiency in wastewater.* IOP Conference Series: Materials Science and Engineering, 2019. **490**(3): p. 032019.

112. Han, Y., et al., *Micro-electrolysis biological fluidized bed process for coking wastewater treatment.* Journal of Water Process Engineering, 2020. **38**: p. 101624.

113. Cai, Q., et al., *Oil-in-water emulsion breaking marine bacteria for demulsifying oily wastewater.* Water Research, 2019. **149**: p. 292-301.

114. Yang, Z., et al., *Application of biosurfactant surfactin as a pH-switchable biodemulsifier for efficient oil recovery from waste crude oil.* Chemosphere, 2020. **240**: p. 124946.

115. Gidudu, B. and E.M.N. Chirwa, *Biosurfactants as demulsification enhancers in bio-electrokinetic remediation of petroleum contaminated soil.* Process Safety and Environmental Protection, 2020. **143**: p. 332-339.

116. Nandi, B.K., et al., *Treatment of oily wastewater using low cost ceramic membrane: Comparative assessment of pore blocking and artificial neural network models.* Chemical Engineering Research and Design, 2010. **88**(7): p. 881-892.

117. Sarfaraz, M.V., et al., *Experimental investigation and modeling hybrid nano-porous membrane process for industrial oily wastewater treatment.* Chemical Engineering Research and Design, 2012. **90**(10): p. 1642-1651.

118. Lakherwal, D., *Adsorption of heavy metals: A review.* International Journal of Environmental Research and Development. , 2014. **4**(1): p. 41-48.

119. Tripathi, A. and M.R. Ranjan, *Heavy Metal Removal from Wastewater Using Low Cost Adsorbents.* Journal of Bioremediation & Biodegradation, 2015. **06**(06): p. 315.

120. Rashid, R., et al., *A state-of-the-art review on wastewater treatment techniques: the effectiveness of adsorption method.* Environmental Science and Pollution Research, 2021. **28**(8): p. 9050-9066.

121. Khalili, N.R., M. Pan, and G. Sandí, *Determination of fractal dimensions of solid carbons from gas and liquid phase adsorption isotherms.* Carbon, 2000. **38**(4): p. 573-588.

122. Wong, S., et al., *Effective removal of anionic textile dyes using adsorbent synthesized from coffee waste.* Scientific Reports, 2020. **10**(1): p. 2928.

123. Mishra, S.P., *Adsorption-desorption of heavy metal ions.* Current Science, 2014. **107**(4): p. 601-612.

124. Burakov, A.E., et al., *Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review.* Ecotoxicology and Environmental Safety, 2018. **148**: p. 702-712.

125. Schweich, D. and M. Sardin, *Adsorption, partition, ion exchange and chemical reaction in batch reactors or in columns — A review.* Journal of Hydrology, 1981. **50**: p. 1-33.

126. Radhika, R., et al., *Adsorption performance of packed bed column for the removal of perchlorate using modified activated carbon.* Process Safety and Environmental Protection, 2018. **117**: p. 350-362.

127. Slatni, I., et al., *Mesoporous silica synthesized from natural local kaolin as an effective adsorbent for removing of Acid Red 337 and its application in the treatment of real industrial*

textile effluent. Environmental Science and Pollution Research, 2020. **27**(31): p. 38422-38433.

128. Anil, I., et al., *Design of Crosslinked Hydrogels Comprising Poly(Vinylphosphonic Acid) and Bis[2-(Methacryloyloxy)Ethyl] Phosphate as an Efficient Adsorbent for Wastewater Dye Removal.* Nanomaterials, 2020. **10**(1): p. 131.
129. Wang, S., et al., *Removal of dyes from aqueous solution using fly ash and red mud.* Water Research, 2005. **39**(1): p. 129-138.
130. Shi, W., X. Xu, and G. Sun, *Chemically modified sunflower stalks as adsorbents for color removal from textile wastewater.* Journal of Applied Polymer Science, 1999. **71**(11): p. 1841-1850.
131. Davis, T.A., B. Volesky, and A. Mucci, *A review of the biochemistry of heavy metal biosorption by brown algae.* Water Research, 2003. **37**(18): p. 4311-4330.
132. Hina, K., *Application of biochar technologies to wastewater treatment: a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Soil Science, Massey University, Palmerston North, New Zealand*. 2013, Massey University.
133. Michalak, I., et al., *Biochar from A Freshwater Macroalga as A Potential Biosorbent for Wastewater Treatment.* Water, 2019. **11**(7): p. 1390.
134. Eccles, H., *Treatment of metal-contaminated wastes: why select a biological process?* Trends in Biotechnology, 1999. **17**(12): p. 462-465.
135. Barakat, M.A., *New trends in removing heavy metals from industrial wastewater.* Arabian Journal of Chemistry, 2011. **4**(4): p. 361-377.
136. Santhosh, C., et al., *Role of nanomaterials in water treatment applications: A review.* Chemical Engineering Journal, 2016. **306**: p. 1116-1137.

137. Leung, W.C., et al., *Removal and recovery of heavy metals by bacteria isolated from activated sludge treating industrial effluents and municipal wastewater.* Water Science and Technology, 2000. **41**(12): p. 233-240.

138. Coelho, G.F., et al., *Removal of metal ions Cd (II), Pb (II), and Cr (III) from water by the cashew nut shell Anacardium occidentale L.* Ecological Engineering, 2014. **73**: p. 514-525.

139. Kongsuwan, A., P. Patnukao, and P. Pavasant, *Binary component sorption of Cu(II) and Pb(II) with activated carbon from Eucalyptus camaldulensis Dehn bark.* Journal of Industrial and Engineering Chemistry, 2009. **15**(4): p. 465-470.

140. Božić, D., et al., *Adsorption of heavy metal ions by sawdust of deciduous trees.* Journal of Hazardous Materials, 2009. **171**(1-3): p. 684-692.

141. Forrester, J.V., et al., *Chapter 6 - General and ocular pharmacology*, in *The Eye (Fourth Edition)*, J.V. Forrester, et al., Editors. 2016, W.B. Saunders. p. 338-369.e1.

142. Yildirim, A., *Removal of the Anionic Dye Reactive Orange 16 by Chitosan/Tripolyphosphate/Mushroom.* Chemical Engineering & Technology, 2021. **44**(8): p. 1371-1381.

143. Gamoudi, S. and E. Srasra, *Adsorption of organic dyes by HDPy+-modified clay: Effect of molecular structure on the adsorption.* Journal of Molecular Structure, 2019. **1193**: p. 522-531.

144. Cruz-Lopes, L.P., et al., *Ideal pH for the adsorption of metal ions Cr6+, Ni2+, Pb2+ in aqueous solution with different adsorbent materials.* Open Agriculture, 2021. **6**(1): p. 115-123.

145. Hassan, A.A., et al., *CHEMICAL MODIFICATION OF CASTOR OIL AS ADSORBENT MATERIAL FOR OIL CONTENT REMOVAL FROM OILFIELD PRODUCED WATER.* Poll. Res., 2020. **39**(4): p. 892-900.

146. Ukpong, A.A., H.G. Rhoda, and I.O. Oboh, *Adsorption Studies of Oil Spill Clean-up Using Coconut Coir Activated Carbon (CCAC).* American Journal of Chemical Engineering, 2020. **8**(2): p. 36.

147. Ewis, D., et al., *Removal of Oil Content from Oil-Water Emulsions Using Iron Oxide/Bentonite Nano Adsorbents.* Journal of Water Process Engineering, 2020. **38**: p. 101583.

148. Saleh, A.J., et al., *ACTIVATED CARBON PREPARED FROM MORINGA HUSKS FOR TREATMENT OF OIL FIELD PRODUCED WATER.* Poll. Res. , 2020. **39**(2): p. 240-247.

149. Sulyman, M., J. Namiesnik, and A. Gierak, *Low-cost Adsorbents Derived from Agricultural By-products/Wastes for Enhancing Contaminant Uptakes from Wastewater: A Review.* Polish Journal of Environmental Studies, 2017. **26**(2): p. 479-510.

150. Larous, S. and A.-H. Meniai, *The Use of Sawdust as by Product Adsorbent of Organic Pollutant from Wastewater: Adsorption of Phenol.* Energy Procedia, 2012. **18**: p. 905-914.

151. Gupta, T.B. and D.H. Lataye, *Removal of crystal violet and methylene blue dyes using Acacia Nilotica sawdust activated carbon.* Indian Journal of Chemical Technology, 2019. **20**(1): p. 52-68.

152. Rashid, A.H., et al., *Treatment of oil content in oilfield produced water using chemically modified waste Sawdust as Biosorbent.* Eco. Env. & Cons., 2020. **26**(4): p. 1563-1571.

153. Mottaghi, H., et al., *Experimental investigation of crude oil removal from water using polymer adsorbent.* Journal of Water Process Engineering, 2021. **40**: p. 101959.

154. Adewoye, T.L., et al., *Optimization of the adsorption of total organic carbon from produced water using functionalized multi-walled carbon nanotubes.* Heliyon, 2021. **7**(1): p. e05866.
155. Khurshid, H., et al., *Adsorptive removal of COD from produced water using tea waste biochar.* Environmental Technology & Innovation, 2021. **23**: p. 101563.
156. Bulut, Y. and H. Aydın, *A kinetics and thermodynamics study of methylene blue adsorption on wheat shells.* Desalination, 2006. **194**(1-3): p. 259-267.
157. Aksu, Z., A.İ. Tatlı, and Ö. Tunç, *A comparative adsorption/biosorption study of Acid Blue 161: Effect of temperature on equilibrium and kinetic parameters.* Chemical Engineering Journal, 2008. **142**(1): p. 23-39.
158. Salleh, M.A.M., et al., *Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review.* Desalination, 2011. **280**(1): p. 1-13.
159. Hadi, H., K.M.M. Al-zobai, and M.J.A. Alatabe, *Oil Removal from Produced Water Using Imperata cylindrica as Low-Cost Adsorbent.* Current Appied Science and Technology, 2020. **20**(3): p. 494 - 511.
160. Seip, A., et al., *Lithium recovery from hydraulic fracturing flowback and produced water using a selective ion exchange sorbent.* Chemical Engineering Journal, 2021. **426**: p. 130713.
161. Ndifreke, W.E. and N. Pasaoglulari Aydinlik, *KOH modified Thevetia peruviana shell activated carbon for sorption of dimethoate from aqueous solution.* J Environ Sci Health B, 2019. **54**(1): p. 1-13.
162. Wang, S. and Z.H. Zhu, *Effects of acidic treatment of activated carbons on dye adsorption.* Dyes and Pigments, 2007. **75**(2): p. 306-314.
163. Fu, L., et al., *Adsorption behavior of organic pollutants on microplastics.* Ecotoxicology and Environmental Safety, 2021. **217**: p. 112207.

164. Qasem, N.A.A., R.H. Mohammed, and D.U. Lawal, *Removal of heavy metal ions from wastewater: a comprehensive and critical review.* npj Clean Water, 2021. **4**(1): p. 36.

165. Tidahy, H.L., et al., *Influence of the exchanged cation in Pd/BEA and Pd/FAU zeolites for catalytic oxidation of VOCs.* Applied Catalysis B: Environmental, 2007. **70**(1): p. 377-383.

166. Yousef, R.I., B. El-Eswed, and A.a.H. Al-Muhtaseb, *Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: Kinetics, mechanism, and thermodynamics studies.* Chemical Engineering Journal, 2011. **171**(3): p. 1143-1149.

167. Li, X., et al., *Adsorption materials for volatile organic compounds (VOCs) and the key factors for VOCs adsorption process: A review.* Separation and Purification Technology, 2020. **235**: p. 116213.

168. Yoshida, H., et al., *Breakthrough curve for adsorption of acid dye on crosslinked chitosan fiber*, in *Studies in Surface Science and Catalysis*. 1993, Elsevier. p. 767-774.

169. Agboh, O.C. and Y. Qin, *Chitin and Chitosan Fibers.* Polymers for Advanced Technologies, 1997. **8**(6): p. 355-365.

170. Varma, A.J., S.V. Deshpande, and J.F. Kennedy, *Metal complexation by chitosan and its derivatives: a review.* Carbohydrate Polymers, 2004. **55**(1): p. 77-93.

171. Gerente, C., et al., *Application of Chitosan for the Removal of Metals From Wastewaters by Adsorption—Mechanisms and Models Review.* Critical Reviews in Environmental Science and Technology, 2007. **37**(1): p. 41-127.

172. Crini, G. and P.-M. Badot, *Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature.* Progress in Polymer Science, 2008. **33**(4): p. 399-447.

173. Crini, G., *Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment.* Progress in Polymer Science, 2005. **30**(1): p. 38-70.

174. Ravi Kumar, M.N.V., *A review of chitin and chitosan applications.* Reactive and Functional Polymers, 2000. **46**(1): p. 1-27.

175. Miretzky, P. and A.F. Cirelli, *Hg(II) removal from water by chitosan and chitosan derivatives: A review.* Journal of Hazardous Materials, 2009. **167**(1-3): p. 10-23.

176. Abidi, N., et al., *Treatment of dye-containing effluent by natural clay.* Journal of Cleaner Production, 2015. **86**: p. 432-440.

177. Kim, D.-S. and D.-K. Lee, *Low-temperature catalytic aqueous phase oxidation of microcystin-LR with iron-doped TiO2 pillared clay catalysts.* Environmental Technology, 2021. **42**(22): p. 3546-3553.

178. Volzone, C., *Removal of metals by natural and modified clays*, in *Clay Surfaces: Fundamentals and Applications*, F. Wypych and K.G. Satyanarayana, Editors. 2004, Elsevier. p. 290-320.

179. Najafi, H., et al., *A comprehensive study on modified-pillared clays as an adsorbent in wastewater treatment processes.* Process Safety and Environmental Protection, 2021. **147**: p. 8-36.

180. Bereket, G., A.Z. Arog, and M.Z. Özel, *Removal of Pb(II), Cd(II), Cu(II), and Zn(II) from Aqueous Solutions by Adsorption on Bentonite.* Journal of Colloid and Interface Science, 1997. **187**(2): p. 338-343.

181. Jiang, M.-q., et al., *Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay.* Desalination, 2010. **252**(1-3): p. 33-39.

182. Echeverría, J.C., et al., *Simultaneous effect of pH, temperature, ionic strength, and initial concentration on the retention of lead on illite.* Applied Clay Science, 2005. **30**(2): p. 103-115.

183. Lazarević, S., et al., *Adsorption of Pb2+, Cd2+ and Sr2+ ions onto natural and acid-activated sepiolites.* Applied Clay Science, 2007. **37**(1-2): p. 47-57.

184. Ijagbemi, C.O., M.-H. Baek, and D.-S. Kim, *Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions.* Journal of Hazardous Materials, 2009. **166**(1): p. 538-546.

185. Gupta, N., et al., *Modeling the Adsorption Kinetics of Divalent Metal Ions onto Pyrophyllite Using the Integral Method.* Industrial & Engineering Chemistry Research, 2009. **48**(4): p. 2125-2128.

186. Kraepiel, A.M.L., K. Keller, and F.M.M. Morel, *A Model for Metal Adsorption on Montmorillonite.* Journal of Colloid and Interface Science, 1999. **210**(1): p. 43-54.

187. Bradbury, M.H. and B. Baeyens, *Modelling the sorption of Zn and Ni on Ca-montmorillonite.* Geochimica et Cosmochimica Acta, 1999. **63**(3-4): p. 325-336.

188. Poots, V.J.P., G. McKay, and J.J. Healy, *The removal of acid dye from effluent using natural adsorbents—I peat.* Water Research, 1976. **10**(12): p. 1061-1066.

189. Guan, H., Z. Cheng, and X. Wang, *Highly Compressible Wood Sponges with a Spring-like Lamellar Structure as Effective and Reusable Oil Absorbents.* ACS Nano, 2018. **12**(10): p. 10365-10373.

190. Poots, V.J.P., G. McKay, and J.J. Healy, *Removal of Basic Dye from Effluent Using Wood as an Adsorbe.* Journal of Water Pollution Control Federation, 1978. **50**: p. 926-935.

191. Yi, Z.-j., et al., *Removal of Pb(II) by adsorption onto Chinese walnut shell activated carbon.* Water Science and Technology, 2015. **72**(6): p. 983-989.

192. Saba, B., A.D. Christy, and M. Jabeen, *Kinetic and Enzymatic Decolorization of Industrial Dyes Utilizing Plant-Based Biosorbents: A Review.* Environmental Engineering Science, 2016. **33**(9): p. 601-614.

193. Janyasuthiwong, S., et al., *Copper, lead and zinc removal from metal-contaminated wastewater by adsorption onto agricultural wastes.* Environmental Technology, 2015. **36**(24): p. 3071-3083.

194. Karić, N., et al., *Bio-waste valorisation: Agricultural wastes as biosorbents for removal of (in)organic pollutants in wastewater treatment.* Chemical Engineering Journal Advances, 2022. **9**: p. 100239.

195. Ali, A. and K. Saeed, *Phenol removal from aqueous medium using chemically modified banana peels as low-cost adsorbent.* Desalination and Water Treatment, 2016. **57**(24): p. 11242-11254.

196. Singh, N.B., et al., *Water purification by using Adsorbents: A Review.* Environmental Technology & Innovation, 2018. **11**: p. 187-240.

197. Enaime, G., et al., *Biochar for Wastewater Treatment—Conversion Technologies and Applications.* Applied Sciences, 2020. **10**(10): p. 3492.

198. Ramrakhiani, L., S. Ghosh, and S. Majumdar, *Surface Modification of Naturally Available Biomass for Enhancement of Heavy Metal Removal Efficiency, Upscaling Prospects, and Management Aspects of Spent Biosorbents: A Review.* Applied Biochemistry and Biotechnology, 2016. **180**(1): p. 41-78.

199. Pokharel, A., A. Bishnu, and F. Aitazaz, *Biochar-Assisted Wastewater Treatment and Waste Valorization*, in *Applications of Biochar for Environmental Safety*, A.A. Ahmed and H.H.A. Mohammed, Editors. 2020, IntechOpen: Rijeka. p. Ch. 14.

200. McKay, G., J.F. Porter, and G.R. Prasad, *The Removal of Dye Colours from Aqueous Solutions by Adsorption on Low-cost Materials.* Water, Air, and Soil Pollution, 1999. **114**(3): p. 423-438.

201. Ibrahim, S., et al., *Adsorption of anionic dyes in aqueous solution using chemically modified barley straw.* Water Science and Technology, 2010. **62**(5): p. 1177-1182.

202. Dakiky, M., et al., *Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents.* Advances in Environmental Research, 2002. **6**(4): p. 533-540.

203. Ahmad Khan, N., S. Ibrahim, and P. Subramaniam, *Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents.* Malaysian Journal of Science, 2004. **23**(1): p. 43-51.

204. Ahmaruzzaman, M., *Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals.* Advances in Colloid and Interface Science, 2011. **166**(1-2): p. 36-59.

205. Netpradit, S., P. Thiravetyan, and S. Towprayoon, *Adsorption of three azo reactive dyes by metal hydroxide sludge: effect of temperature, pH, and electrolytes.* Journal of Colloid and Interface Science, 2004. **270**(2): p. 255-261.

206. Netpradit, S., P. Thiravetyan, and S. Towprayoon, *Evaluation of metal hydroxide sludge for reactive dye adsorption in a fixed-bed column system.* Water Research, 2004. **38**(1): p. 71-78.

207. Bhatnagar, A. and M. Sillanpää, *Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review.* Chemical Engineering Journal, 2010. **157**(2): p. 277-296.

208. Tiadi, N., A. Mohanty, and C.R. Mohanty, *Removal of chromium and lead from aqueous solution using industrial wastes: batch and column studies.* Desalination and Water Treatment 2018. **101**: p. 223-231.

209. Visa, M., L. Isac, and A. Duta, *Fly ash adsorbents for multi-cation wastewater treatment.* Applied Surface Science, 2012. **258**(17): p. 6345-6352.

210. Gupta, V.K. and I. Ali, *Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste.* Water Research, 2001. **35**(1): p. 33-40.

211. Gupta, V.K. and S. Sharma, *Removal of Zinc from Aqueous Solutions Using Bagasse Fly Ash − a Low Cost Adsorbent.* Industrial & Engineering Chemistry Research, 2003. **42**(25): p. 6619-6624.

212. Förstner, U. and G. Wittmann, *Heavy metals in the aquatic environment*. 1981, Berlin: Springer Verlag.

213. Hurt, R.H., M. Monthioux, and A. Kane, *Toxicology of carbon nanomaterials: Status, trends, and perspectives on the special issue.* Carbon, 2006. **44**(6): p. 1028-1033.

214. Lu, Y., et al., *Recent developments in bio-monitoring via advanced polymer nanocomposite-based wearable strain sensors.* Biosensors and Bioelectronics, 2019. **123**: p. 167-177.

215. Ilisz, I., et al., *Photocatalytic water treatment with different TiO2 nanoparticles and hydrophilic/hydrophobic layer silicate adsorbents.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2003. **230**(1): p. 89-97.

216. Kalfa, O.M., Ö. Yalçınkaya, and A.R. Türker, *Synthesis of nano B2O3/TiO2 composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium.* Journal of Hazardous Materials, 2009. **166**(1): p. 455-461.

217. Hristovski, K., A. Baumgardner, and P. Westerhoff, *Selecting metal oxide nanomaterials for arsenic removal in fixed bed columns: From nanopowders to aggregated nanoparticle media.* Journal of Hazardous Materials, 2007. **147**(1-2): p. 265-274.

218. Ali, M.E., et al., *Nanoadsorbents for wastewater treatment: next generation biotechnological solution.* International Journal of Environmental Science and Technology, 2020. **17**(9): p. 4095-4132.

219. Smith, S.C. and D.F. Rodrigues, *Carbon-based nanomaterials for removal of chemical and biological contaminants from water: A review of mechanisms and applications.* Carbon, 2015. **91**: p. 122-143.

220. Kuila, T., et al., *Chemical functionalization of graphene and its applications.* Progress in Materials Science, 2012. **57**(7): p. 1061-1105.

221. Saleh, N.B., L.D. Pfefferle, and M. Elimelech, *Aggregation Kinetics of Multiwalled Carbon Nanotubes in Aquatic Systems: Measurements and Environmental Implications.* Environmental Science & Technology, 2008. **42**(21): p. 7963-7969.

222. Ahmed, F., et al., *Antimicrobial Applications of Electroactive PVK-SWNT Nanocomposites.* Environmental Science & Technology, 2012. **46**(3): p. 1804-1810.

223. Wang, H., et al., *Adsorption characteristics and behaviors of graphene oxide for Zn(II) removal from aqueous solution.* Applied Surface Science, 2013. **279**: p. 432-440.

224. Upadhyayula, V.K.K., et al., *Application of carbon nanotube technology for removal of contaminants in drinking water: A review.* Science of The Total Environment, 2009. **408**(1): p. 1-13.

225. Hassan, M.F., et al., *Recent trends in activated carbon fibers production from various precursors and applications—A comparative review.* Journal of Analytical and Applied Pyrolysis, 2020. **145**: p. 104715.

226. Rakić, V., et al., *The adsorption of pharmaceutically active compounds from aqueous solutions onto activated carbons.* Journal of Hazardous Materials, 2015. **282**: p. 141-149.

227. Zhu, H.J., et al., *Removal of arsenite from drinking water by activated carbon supported nano zero-valent iron.* Huan Jing Ke Xue, 2009. **30**(6): p. 1644-1648.

228. Hu, J., I.M.C. Lo, and G. Chen, *Comparative study of various magnetic nanoparticles for Cr(VI) removal.* Separation and Purification Technology, 2007. **56**(3): p. 249-256.

229. Moosavi, S., S. Gan, and S. Zakaria, *FUNCTIONALIZED CELLULOSE BEADS WITH ACTIVATED CARBON Fe3O4/CoFe2O4 FOR CATIONIC DYE REMOVAL.* Cellulose Chemistry and Technology, 2019. **53**(7-8): p. 815-825.

230. Che, G., et al., *Carbon nanotubule membranes for electrochemical energy storage and production.* Nature, 1998. **393**(6683): p. 346-349.

231. Dalton, A.B., et al., *Super-tough carbon-nanotube fibres.* Nature, 2003. **423**(6941): p. 703.

232. Li, Y.H., et al., *Carbon nanotubes - the promising adsorbent in wastewater treatment.* Journal of Physics: Conference Series, 2007. **61**(1): p. 698.

233. Chen, C.-H. and C.-C. Huang, *Hydrogen adsorption in defective carbon nanotubes.* Separation and Purification Technology, 2009. **65**(3): p. 305-310.

234. Masenelli-Varlot, K., E. McRae, and N. Dupont-Pavlovsky, *Comparative adsorption of simple molecules on carbon nanotubes: Dependence of the adsorption properties on the nanotube morphology.* Applied Surface Science, 2002. **196**(1-4): p. 209-215.

235. Gaur, A. and M. Shim, *Substrate-enhanced O2 adsorption and complexity in the Raman G-band spectra of individual metallic carbon nanotubes.* Physical Review B, 2008. **78**(12): p. 125422.

236. Li, Y.-H., et al., *Lead adsorption on carbon nanotubes.* Chemical Physics Letters, 2002. **357**(3-4): p. 263-266.

237. Chen, C. and X. Wang, *Adsorption of Ni(II) from Aqueous Solution Using Oxidized Multiwall Carbon Nanotubes.* Industrial & Engineering Chemistry Research, 2006. **45**(26): p. 9144-9149.

238. Li, Y.-H., et al., *Competitive adsorption of Pb2+, Cu2+ and Cd2+ ions from aqueous solutions by multiwalled carbon nanotubes.* Carbon, 2003. **41**(14): p. 2787-2792.

239. Chen, C.L., X.K. Wang, and M. Nagatsu, *Europium Adsorption on Multiwall Carbon Nanotube/Iron Oxide Magnetic Composite in the Presence of Polyacrylic Acid.* Environmental Science & Technology, 2009. **43**(7): p. 2362-2367.

240. Chen, C., et al., *Surface complexation modeling of Sr(II) and Eu(III) adsorption onto oxidized multiwall carbon nanotubes.* Journal of Colloid and Interface Science, 2008. **323**(1): p. 33-41.

241. Goering, J. and U. Burghaus, *Adsorption Kinetics of Alcohols on Single-Wall Carbon Nanotubes: An Ultrahigh Vacuum Surface Chemistry Study.* The Journal of Physical Chemistry C, 2008. **112**(27): p. 10114-10124.

242. Hyung, H. and J.-H. Kim, *Natural Organic Matter (NOM) Adsorption to Multi-Walled Carbon Nanotubes: Effect of NOM Characteristics and Water Quality Parameters.* Environmental Science & Technology, 2008. **42**(12): p. 4416-4421.

243. Kemp, K.C., et al., *Environmental applications using graphene composites: water remediation and gas adsorption.* Nanoscale, 2013. **5**(8): p. 3149-3171.

244. Deng, J.-H., et al., *Simultaneous removal of Cd(II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent.* Chemical Engineering Journal, 2013. **226**: p. 189-200.

245. Loukidou, M.X., et al., *Diffusion kinetic study of cadmium(II) biosorption by Aeromonas caviae.* Journal of Chemical Technology & Biotechnology, 2004. **79**(7): p. 711-719.

246. Oboh, I., E. Aluyor, and T. Audu, *Biosorption of Heavy Metal Ions from Aqueous Solutions Using a Biomaterial.* Leonardo Journal of Sciences, 2009(14): p. 58-65.

247. Sud, D., G. Mahajan, and M.P. Kaur, *Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review.* Bioresource Technology, 2008. **99**(14): p. 6017-6027.

248. Chojnacka, K., *Biosorption and bioaccumulation – the prospects for practical applications.* Environment International, 2010. **36**(3): p. 299-307.

249. Halysh, V., et al., *Utilization of Modified Biosorbents Based on Walnut Shells in the Processes of Wastewater Treatment from Heavy Metal Ion.* Journal of Ecological Engineering, 2020. **21**(4): p. 128-133.

250. Sarabadan, M., H. Bashiri, and S.M. Mousavi, *Removal of crystal violet dye by an efficient and low cost adsorbent: Modeling, kinetic, equilibrium and thermodynamic studies.* Korean Journal of Chemical Engineering, 2019. **36**(10): p. 1575-1586.

251. Machado, F.M., et al., *Adsorption of Reactive Red M-2BE dye from water solutions by multi-walled carbon nanotubes and activated carbon.* Journal of Hazardous Materials, 2011. **192**(3): p. 1122-1131.

252. Zhao, G., et al., *Few-Layered Graphene Oxide Nanosheets As Superior Sorbents for Heavy Metal Ion Pollution Management.* Environmental Science & Technology, 2011. **45**(24): p. 10454-10462.

253. Sadegh, H., et al., *The role of nanomaterials as effective adsorbents and their applications in wastewater treatment.* Journal of Nanostructure in Chemistry, 2017. **7**(1): p. 1-14.

254. Zhao, G., et al., *Removal of Pb(ii) ions from aqueous solutions on few-layered graphene oxide nanosheets.* Dalton Transactions, 2011. **40**(41): p. 10945-10952.

255. Xin, X., et al., *Highly efficient removal of heavy metal ions by amine-functionalized mesoporous Fe3O4 nanoparticles.* Chemical Engineering Journal, 2012. **184**: p. 132-140.

256. Karnib, M., et al., *Heavy Metals Removal Using Activated Carbon, Silica and Silica Activated Carbon Composite.* Energy Procedia, 2014. **50**: p. 113-120.

257. Tahir, S.S. and N. Rauf, *Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay.* Chemosphere, 2006. **63**(11): p. 1842-1848.

258. Mouni, L., et al., *Removal of Methylene Blue from aqueous solutions by adsorption on Kaolin: Kinetic and equilibrium studies.* Applied Clay Science, 2018. **153**: p. 38-45.

259. Anoop Krishnan, K., et al., *Kinetic and Isotherm Modeling of Methylene Blue Adsorption onto Kaolinite Clay at the Solid-Liquid Interface.* Separation Science and Technology, 2015. **50**(8): p. 1147-1157.

260. Almeida, C.A.P., et al., *Removal of methylene blue from colored effluents by adsorption on montmorillonite clay.* Journal of Colloid and Interface Science, 2009. **332**(1): p. 46-53.

261. Toor, M. and B. Jin, *Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye.* Chemical Engineering Journal, 2012. **187**: p. 79-88.

262. Mumin, M.A., et al., *Potentiality of open burnt clay as an adsorbent for the removal of Congo red from aqueous solution.* International Journal of Environmental Science & Technology, 2007. **4**(4): p. 525-532.

263. Cheng, Z., et al., *Novel biosorbents synthesized from fungal and bacterial biomass and their applications in the adsorption of volatile organic compounds.* Bioresource Technology, 2020. **300**: p. 122705.

264. Putri, K.N.A., A. Keereerak, and W. Chinpa, *Novel cellulose-based biosorbent from lemongrass leaf combined with cellulose acetate for adsorption of crystal violet.* International Journal of Biological Macromolecules, 2020. **156**: p. 762-772.

265. Ibrahim, M., et al., *Adsorptive Removal of Fluoride from Aqueous Solution by Biogenic Iron Permeated Activated Carbon Derived from Sweet Lime Waste.* Acta Chim Slov, 2019. **66**(1): p. 123-136.

266. Pan, J., et al., *Modified biogas residues as an eco-friendly and easily-recoverable biosorbent for nitrate and phosphate removals from surface water.* Journal of Hazardous Materials, 2020. **382**: p. 121073.

267. Silva, B., et al., *Waste-based biosorbents as cost-effective alternatives to commercial adsorbents for the retention of fluoxetine from water.* Separation and Purification Technology, 2020. **235**: p. 116139.

268. Zheng, W., et al., *Adsorption of Cd(II) and Cu(II) from aqueous solution by carbonate hydroxylapatite derived from eggshell waste.* Journal of Hazardous Materials, 2007. **147**(1-2): p. 534-539.

269. Chakraborty, R., et al., *Adsorption of hazardous chromium (VI) ions from aqueous solutions using modified sawdust: kinetics, isotherm and thermodynamic modelling.* International Journal of Environmental Analytical Chemistry, 2021. **101**(7): p. 911-928.

270. Wu, Y., et al., *Adsorption of Copper Ions and Methylene Blue in a Single and Binary System on Wheat Straw.* Journal of Chemical & Engineering Data, 2009. **54**(12): p. 3229-3234.

271. Siyal, A.A., et al., *Fly ash based geopolymer for the adsorption of anionic surfactant from aqueous solution.* Journal of Cleaner Production, 2019. **229**: p. 232-243.

272. Zanoletti, A., et al., *Embodied energy as key parameter for sustainable materials selection: The case of reusing coal fly ash for removing anionic surfactants.* Journal of Cleaner Production, 2017. **141**: p. 230-236.

273. Mi-Na, Z., L. Xuepin, and S. Bi, *Adsorption of surfactants on chromium leather waste.* Journal of The Society of Leather Technologists and Chemists, 2006. **90**(1): p. 1-6.

274. Wang, J. and S. Wang, *Preparation, modification and environmental application of biochar: A review.* Journal of Cleaner Production, 2019. **227**: p. 1002-1022.

275. Piubeli, F., et al., *Enhanced reduction of COD and aromatics in petroleum-produced water using indigenous microorganisms and nutrient addition.* International Biodeterioration & Biodegradation, 2012. **68**: p. 78-84.

276. Zhao, S., et al., *Hardness, COD and turbidity removals from produced water by electrocoagulation pretreatment prior to Reverse Osmosis membranes.* Desalination, 2014. **344**: p. 454-462.

277. Ezechi, E.H., et al., *Boron removal from produced water using electrocoagulation.* Process Safety and Environmental Protection, 2014. **92**(6): p. 509-514.

278. Yuan, T., et al., *A Scalable Method toward Superhydrophilic and Underwater Superoleophobic PVDF Membranes for Effective Oil/Water Emulsion Separation.* ACS Applied Materials & Interfaces, 2015. **7**(27): p. 14896-14904.

279. Oshomogho, F.O., *COMPARATIVE STUDIES ON THE DEGRADABILITY OF ANTHRACENE AND PYRENE BY SYNTHETIC AND BIO-SURFACTANTS*, in *Chemical Engineering*. 2015, University of Benin.

280. Hoang, A.T., et al., *An absorption capacity investigation of new absorbent based on polyurethane foams and rice straw for oil spill cleanup.* Petroleum Science and Technology, 2018. **36**(5): p. 361-370.

281. Nasuhoglu, D., et al., *Removal of the antibiotic levofloxacin (LEVO) in water by ozonation and TiO2 photocatalysis.* Chemical Engineering Journal, 2012. **189-190**: p. 41-48.

282. Mirshahghassemi, S. and J.R. Lead, *Oil Recovery from Water under Environmentally Relevant Conditions Using Magnetic Nanoparticles.* Environmental Science & Technology, 2015. **49**(19): p. 11729-11736.

283. Khosravi, M. and S. Azizian, *Synthesis of a Novel Highly Oleophilic and Highly Hydrophobic Sponge for Rapid Oil Spill Cleanup.* ACS Applied Materials & Interfaces, 2015. **7**(45): p. 25326-25333.

284. Chen, W.-H. and J.-R. Huang, *Chapter 3 - Adsorption of organic including pharmaceutical and inorganic contaminants in water toward graphene-based materials*, in *Contaminants of Emerging Concern in Water and Wastewater*, A.J. Hernández-Maldonado and L. Blaney, Editors. 2020, Butterworth-Heinemann. p. 93-113.

285. Sadare, O.O., et al. *Removal of Sulfur (eg. DBT) from Petroleum Distillates using Activated Carbon in a Continuous Packed-bed Adsorption Column*. in *World Congress on Engineering and Computer Science*. 2018. San Francisco, USA.

286. Abdullahi, B.O., et al., *Facile fabrication of hydrophobic alkylamine intercalated graphene oxide as absorbent for highly effective oil-water separation.* Journal of Molecular Liquids, 2021. **325**: p. 115057.

287. Wang, K., et al., *Functional photothermal sponges for efficient solar steam generation and accelerated cleaning of viscous crude-oil spill.* Solar Energy Materials and Solar Cells, 2020. **204**: p. 110203.

288. Luo, Z., et al., *Photothermal hierarchical carbon nanotube/reduced graphene oxide microspherical aerogels with radially orientated microchannels for efficient cleanup of crude oil spills.* Journal of Colloid and Interface Science, 2020. **570**: p. 61-71.

289. Rajapaksha, A.U., et al., *Pyrolysis condition affected sulfamethazine sorption by tea waste biochars.* Bioresource Technology, 2014. **166**: p. 303-308.

290. Altare, C.R., et al., *Regeneration and long-term stability of surfactant-modified zeolite for removal of volatile organic compounds from produced water.* Microporous and Mesoporous Materials, 2007. **105**(3): p. 305-316.

291. Lee, X.J., et al., *Biochar potential evaluation of palm oil wastes through slow pyrolysis: Thermochemical characterization and pyrolytic kinetic studies.* Bioresource Technology, 2017. **236**: p. 155-163.

292. Asadpour, R., et al., *Acetylation of corn silk and its application for oil sorption.* Fibers and Polymers, 2015. **16**(9): p. 1830-1835.

293. Asadpour, R., et al., *Acetylation of oil palm empty fruit bunch fiber as an adsorbent for removal of crude oil.* Environmental Science and Pollution Research, 2016. **23**(12): p. 11740-11750.

294. Desta, M.B., *Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (Eragrostis tef) Agricultural Waste.* Journal of Thermodynamics, 2013. **2013**: p. 375830.

295. Vithanage, M., et al., *Kinetics, thermodynamics and mechanistic studies of carbofuran removal using biochars from tea waste and rice husks.* Chemosphere, 2016. **150**: p. 781-789.

296. Zhou, N., et al., *Effect of phosphoric acid on the surface properties and Pb(II) adsorption mechanisms of hydrochars prepared from fresh banana peels.* Journal of Cleaner Production, 2017. **165**: p. 221-230.

297. Gao, R., et al., *High-efficiency removal capacities and quantitative sorption mechanisms of Pb by oxidized rape straw biochars.* Science of The Total Environment, 2020. **699**: p. 134262.

298. Asma, N., et al., *Efficient removal of methylene blue dye using mangosteen peel waste: Kinetics, isotherms and artificial neural network (ANN) modeling.* Desalination and Water Treatment, 2017. **86**: p. 191-202.

299. Zhang, L., et al., *Efficient removal of Cr(VI) from water by the uniform fiber ball loaded with polypyrrole: Static adsorption, dynamic adsorption and mechanism studies.* Chemosphere, 2020. **248**: p. 126102.

300. Ahmed, M.B., et al., *Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater.* Bioresource Technology, 2016. **214**: p. 836-851.

301. Dada, A.O., et al., *Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn 2+ Unto Phosphoric Acid Modified Rice Husk.* IOSR Journal of Applied Chemistry, 2012. **3**: p. 38-45.

302. Younis, S.A., et al., *Kinetic, isotherm, and thermodynamic studies of polycyclic aromatic hydrocarbons biosorption from petroleum refinery wastewater using spent waste biomass.* Desalination and Water Treatment, 2015. **56**(11): p. 3013-3023.

303. Ibrahim, S., S. Wang, and H.M. Ang, *Removal of emulsified oil from oily wastewater using agricultural waste barley straw.* Biochemical Engineering Journal, 2010. **49**(1): p. 78-83.

304. Srinivasan, A. and T. Viraraghavan, *Removal of oil by walnut shell media.* Bioresource Technology, 2008. **99**(17): p. 8217-8220.

305. Yin, X., et al., *Modified walnut shell filter material for the enhanced removal of oil from oilfield wastewater.* Environmental Engineering Research, 2021. **26**(1): p. 190369-0.

306. Ajmal, M., et al., *Role of sawdust in the removal of copper(II) from industrial wastes.* Water Research, 1998. **32**(10): p. 3085-3091.

307. Ngofa, O., et al., *Activated Carbon from Bamboo and Banana Wood Fibers as Adsorbent Materials for the Removal of Oil Samples.* Biointerface Research in Applied Chemistry, 2022. **12**(2): p. 2701-2714.

308. Qu, F., L. Zhu, and K. Yang, *Adsorption behaviors of volatile organic compounds (VOCs) on porous clay heterostructures (PCH).* Journal of Hazardous Materials, 2009. **170**(1): p. 7-12.

309. Bergaya, F., B.K.G. Theng, and G. Lagaly, *Modified Clays and Clay Minerals*, in *Developments in Clay Science*. 2006, Elsevier. p. 261.

310. Lin, S.-H., R.-C. Hsiao, and R.-S. Juang, *Removal of soluble organics from water by a hybrid process of clay adsorption and membrane filtration.* Journal of Hazardous Materials, 2006. **135**(1): p. 134-140.

311. Rasheed, A., et al., *Analysis of sorption efficiency of activated carbon for removal of anthracene and pyrene for wastewater treatment.* Desalination and Water Treatment, 2016. **57**(1): p. 145-150.

312. Wu, Z. and L. Zhu, *Removal of polycyclic aromatic hydrocarbons and phenols from coking wastewater by simultaneously synthesized organobentonite in a one-step process.* Journal of Environmental Sciences, 2012. **24**(2): p. 248-253.

313. Wołowiec, M., et al., *Experimental Study on the Removal of VOCs and PAHs by Zeolites and Surfactant-Modified Zeolites.* Energy & Fuels, 2017. **31**(8): p. 8803-8812.

314. Yuan, P., et al., *Tailored Design of Differently Modified Mesoporous Materials To Deeply Understand the Adsorption Mechanism for Polycyclic Aromatic Hydrocarbons.* Langmuir, 2018. **34**(51): p. 15708-15718.

315. Song, T., et al., *Adsorption Behaviors of Polycyclic Aromatic Hydrocarbons and Oxygen Derivatives in Wastewater on N-Doped Reduced Graphene Oxide.* Separation and Purification Technology, 2021. **254**: p. 117565.

316. Yakout, S.M., A.A.M. Daifullah, and S.A. El-Reefy, *Adsorption of Naphthalene, Phenanthrene and Pyrene from Aqueous Solution Using Low-Cost Activated Carbon Derived from Agricultural Wastes.* Adsorption Science & Technology, 2013. **31**(4): p. 293-302.

317. Qiao, K., et al., *Preparation of biochar from Enteromorpha prolifera and its use for the removal of polycyclic aromatic hydrocarbons (PAHs) from aqueous solution.* Ecotoxicology and Environmental Safety, 2018. **149**: p. 80-87.

318. Wu, D., et al., *Waste to treasure: Superwetting foam enhanced by bamboo powder for sustainable on-demand oil-water separation.* Journal of Hazardous Materials, 2023. **441**: p. 129829.

319. Karaca, G., H.S. Baskaya, and Y. Tasdemir, *Removal of polycyclic aromatic hydrocarbons (PAHs) from inorganic clay mineral: Bentonite.* Environmental Science and Pollution Research, 2016. **23**(1): p. 242-252.

320. Ewis, D., et al., *Enhanced Removal of Diesel Oil Using New Magnetic Bentonite-Based Adsorbents Combined with Different Carbon Sources.* Water, Air, & Soil Pollution, 2022. **233**(6): p. 195.

321. Albatrni, H., et al., *Polymeric adsorbents for oil removal from water.* Chemosphere, 2019. **233**: p. 809-817.

322. Eman Abdelwahab, E., *Modified Activated Carbon and Bentonite Used to Adsorb Petroleum Hydrocarbons Emulsified in Aqueous Solution.* Am. J. Environ. Prot., 2013. **2**(6): p. 161-169.

323. Rotaru, A., et al., *Performances of clay aerogel polymer composites for oil spill sorption: Experimental design and modeling.* Separation and Purification Technology, 2014. **133**: p. 260-275.

324. Carmody, O., et al., *Adsorption of hydrocarbons on organo-clays—Implications for oil spill remediation.* Journal of Colloid and Interface Science, 2007. **305**(1): p. 17-24.

325. Annunciado, T.R., T.H.D. Sydenstricker, and S.C. Amico, *Experimental investigation of various vegetable fibers as sorbent materials for oil spills.* Marine Pollution Bulletin, 2005. **50**(11): p. 1340-1346.

326. Cojocaru, C., M. Macoveanu, and I. Cretescu, *Peat-based sorbents for the removal of oil spills from water surface: Application of artificial neural network modeling.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2011. **384**(1): p. 675-684.

327. Karakasi, O.K. and A. Moutsatsou, *Surface modification of high calcium fly ash for its application in oil spill clean up.* Fuel, 2010. **89**(12): p. 3966-3970.

328. Ben Jmaa, S. and A. Kallel, *Assessment of Performance of Posidona oceanica (L.) as Biosorbent for Crude Oil-Spill Cleanup in Seawater.* BioMed Research International, 2019. **2019**: p. 6029654.

329. Abel, U.A., G.R. Habor, and O.I. Oseribho, *Adsorption Studies of Oil Spill Clean-up Using Coconut Coir Activated Carbon (CCAC).* American Journal of Chemical Engineering, 2020. **8**(2): p. 36-47.

330. Alaa El-Din, G., et al., *Study on the use of banana peels for oil spill removal.* Alexandria Engineering Journal, 2018. **57**(3): p. 2061-2068.

331. Sidiras, D., et al., *Simulation of autohydrolysis effect on adsorptivity of wheat straw in the case of oil spill cleaning.* Chemical Engineering Research and Design, 2014. **92**(9): p. 1781-1791.

332. Galblaub, O.A., et al., *Oil spill cleanup of water surface by plant-based sorbents: Russian practices.* Process Safety and Environmental Protection, 2016. **101**: p. 88-92.

333. Husseien, M., et al., *Availability of barley straw application on oil spill clean up.* International Journal of Environmental Science & Technology, 2009. **6**(1): p. 123-130.

334. Soliman, E.M., S.A. Ahmed, and A.A. Fadl, *Adsorptive removal of oil spill from sea water surface using magnetic wood sawdust as a novel nano-composite synthesized via microwave approach.* Journal of Environmental Health Science and Engineering, 2020. **18**(1): p. 79-90.

335. Syed, S., M.I. Alhazzaa, and M. Asif, *Treatment of oily water using hydrophobic nano-silica.* Chemical Engineering Journal, 2011. **167**(1): p. 99-103.

336. Rytwo, G., A. Rettig, and Y. Gonen, *Organo-sepiolite particles for efficient pretreatment of organic wastewater: Application to winery effluents.* Applied Clay Science, 2011. **51**(3): p. 390-394.

337. Dewi, R., R. Sari, and Syafruddin, *The effect of the natural bentonite to reduce COD in palm oil mill effluent by using a hybrid adsorption-flotation method.* IOP Conference Series: Materials Science and Engineering, 2017. **210**(1): p. 012016.

338. Sueyoshi, M., et al., *Preparation and characterization of adsorbents for treatment of water associated with oil production.* Journal of Analytical and Applied Pyrolysis, 2012. **97**: p. 80-87.

339. El-Nafaty, U.A., I.M. Muhammad, and S. Abdulsalam, *Biosorption and Kinetic Studies on Oil Removal from Produced Water Using Banana Peel.* Civil and environmental research, 2013. **3**: p. 125-136.

340. Ibrahim, T.H., et al., *Produced water treatment using naturally abundant pomegranate peel.* Desalination and Water Treatment, 2016. **57**(15): p. 6693-6701.

341. El-Naas, M.H., S. Al-Zuhair, and M.A. Alhaija, *Reduction of COD in refinery wastewater through adsorption on date-pit activated carbon.* Journal of Hazardous Materials, 2010. **173**(1): p. 750-757.

342. Franco, C.A., et al., *Water Remediation Based on Oil Adsorption Using Nanosilicates Functionalized with a Petroleum Vacuum Residue.* Adsorption Science & Technology, 2014. **32**(2-3): p. 197-207.

343. Franco, C.A., N.N. Nassar, and F.B. Cortés, *Removal of oil from oil-in-saltwater emulsions by adsorption onto nano-alumina functionalized with petroleum vacuum residue.* Journal of Colloid and Interface Science, 2014. **433**: p. 58-67.

344. Altun, T. and E. Pehlivan, *Removal of Cr(VI) from aqueous solutions by modified walnut shells.* Food Chemistry, 2012. **132**(2): p. 693-700.

345. Jahanban-Esfahlan, A. and R. Amarowicz, *Walnut (Juglans regia L.) shell pyroligneous acid: chemical constituents and functional applications.* RSC Advances, 2018. **8**(40): p. 22376-22391.

346. Owens, N. and D. Lee. *The use of micro bubble flotation technology in secondary and tertiary produced water treatment—A technical comparison with other separation technologies*. in *Proceedings of the the TUV NEL, 5th Produced Water Workshop, Aberdeen, Scotland*. 2007.

347. Blumenschein, C., K.W. Severing, and E. Boyle, *Walnut shell filtration for oil and solids removal from steel mill recycle systems.* AISE Steel Technology, 2001. **78**: p. 33-37.

348. Albatrni, H., H. Qiblawey, and M.J. Al-Marri, *Walnut shell based adsorbents: A review study on preparation, mechanism, and application.* Journal of Water Process Engineering, 2022. **45**: p. 102527.

349. Bayat, M., A. Alighardashi, and A. Sadeghasadi, *Fixed-bed column and batch reactors performance in removal of diazinon pesticide from aqueous solutions by using walnut shell-modified activated carbon.* Environmental Technology & Innovation, 2018. **12**: p. 148-159.

350. Higgins, F.J.A.T., Danbury, CT, USA, *Environmentally friendly oil in water analysis by FTIR spectroscopy, based on ASTM D7678-11.* 2012.

351. Winer, B.J., *Design and analysis of single-factor experiments*, in *Statistical principles in experimental design.* 1962, McGraw-Hill Book Company: New York, NY, US. p. 46-104.

352. Kokab, T., et al., *Effective Removal of Cr(VI) from Wastewater Using Biochar Derived from Walnut Shell.* International Journal of Environmental Research and Public Health (IJERPH), 2021.

353. Li, X., et al., *Characterization and comparison of walnut shells-based activated carbons and their adsorptive properties.* Adsorption Science & Technology, 2020. **38**: p. 026361742094652.

354. Enache, A.-C., et al., *An Eco-Friendly Modification of a Walnut Shell Biosorbent for Increased Efficiency in Wastewater Treatment.* 2023. **15**(3): p. 2704.

355. Tobbi, O., et al., *Cost-effective walnut shell biosorbent for efficient Cr(VI) removal from water: Batch adsorption and optimization using RSM-BBD.* Desalination and Water Treatment, 2024. **320**: p. 100783.

356. Liang, D., et al., *Quaternary ammonium salts targeted regulate the surface charge distribution of activated carbon: A study of their binding modes and modification effects.* Environ Res, 2022. **214**(Pt 4): p. 114103.

357. Song, Y.S., Y.H. Choi, and D.H. Kim, *Microextraction in a tetrabutylammonium bromide/ammonium sulfate aqueous two-phase system and electrohydrodynamic generation of a micro-droplet.* J Chromatogr A, 2007. **1162**(2): p. 180-6.

358. Nyah, F., et al., *Comprehensive review on the role of salinity on oil recovery mechanisms during chemical flooding.* Journal of Molecular Liquids, 2024. **415**: p. 126308.

359. Babatunde, K.A., et al., *Adsorption of gases on heterogeneous shale surfaces: A review.* Journal of Petroleum Science and Engineering, 2022. **208**: p. 109466.

360. Li, S., et al., *Effective Modified Walnut Shell Adsorbent: Synthesis and Adsorption Behavior for Pb 2+ and Ni 2+ from Aqueous Solution.* Environmental Engineering Science, 2019. **36**.

361. El Gheriany, I.A., et al., *Oil spill sorption capacity of raw and thermally modified orange peel waste.* Alexandria Engineering Journal, 2020. **59**(2): p. 925-932.

362. Annunciado, T., T. Sydenstricker, and S.J.M.p.b. Amico, *Experimental investigation of various vegetable fibers as sorbent materials for oil spills.* 2005. **50**(11): p. 1340-1346.

363. Yin, X., et al., *Modified walnut shell filter material for the enhanced removal of oil from oilfield wastewater.* 2021. **26**(1).

364. Al-Najar, J.A., et al., *Cost-Effective Natural Adsorbents for Remediation of Oil-Contaminated Water.* 2023. **15**(6): p. 1186.

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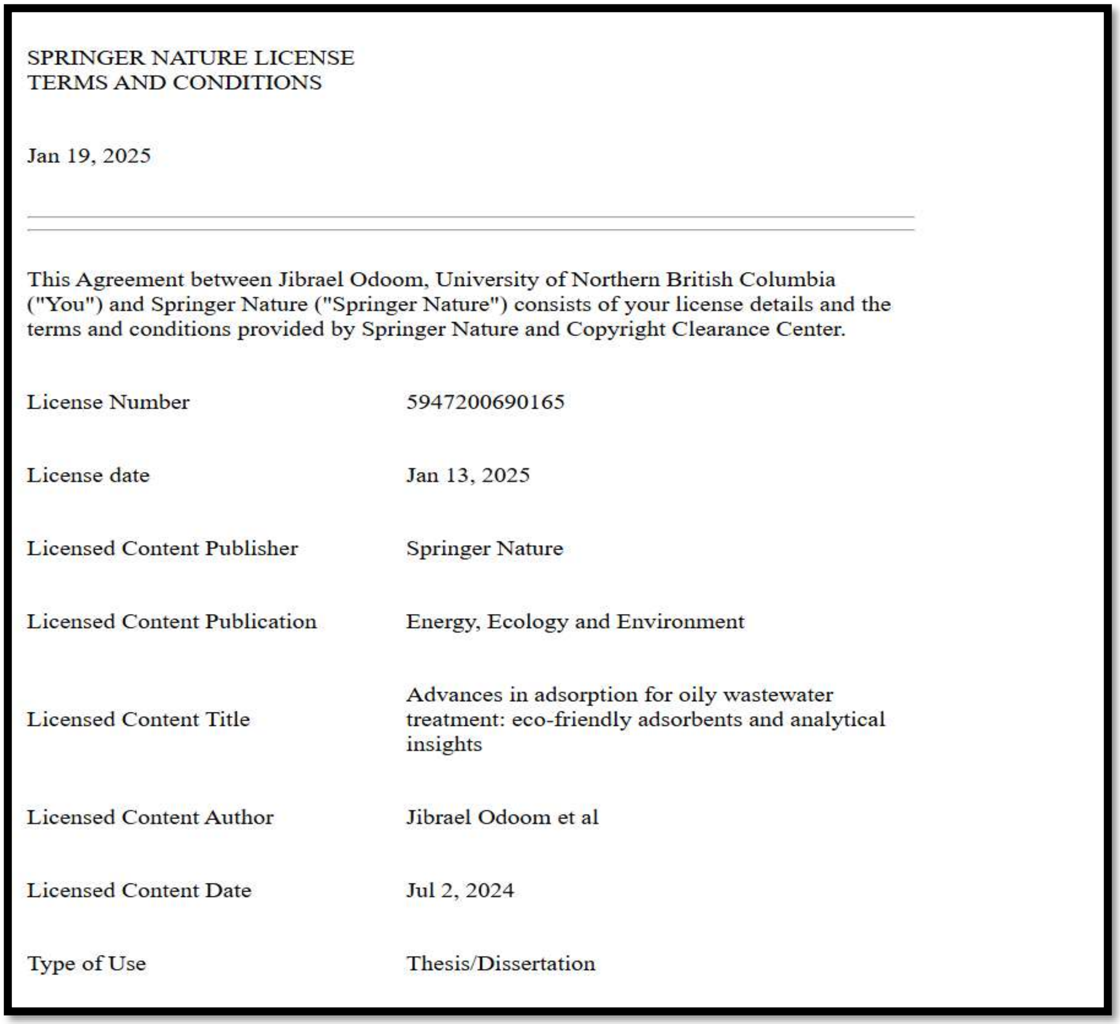

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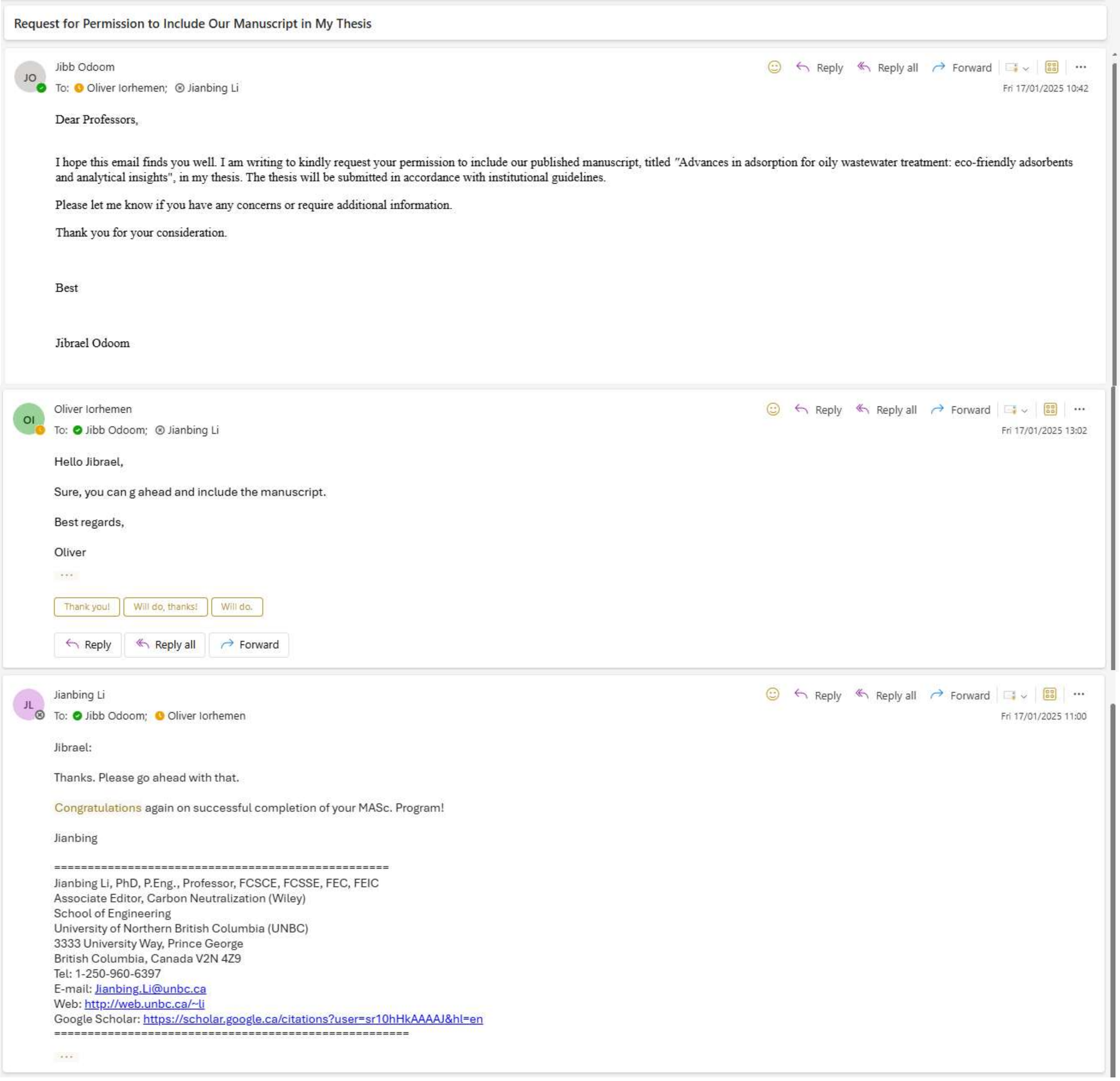

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Thanks. Please go ahead with that.

Congratulations again on successful completion of your MASc. Program!

Jianbing

==
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